

CHIMIKA CHRONIKA

NEW SERIES

AN INTERNATIONAL EDITION
OF THE ASSOCIATION OF GREEK CHEMISTS



1/93

CMCRCZ 22(1), 3-64(1993)

ISSN 0366-693X

Volume 22, No 1 p.p. 3-64 January-March 1993

CHIMIKA CHRONIKA

NEW SERIES

AN INTERNATIONAL EDITION

Published by the Association of Greek Chemists (A.G.C.)
27 Kaningos str. Athens 106 82 Greece

Journals Managing Committee, A.G.C.:

A. Cosmatos, P.N. Dimotakis, D. Hadjigeorgiou-Giannakaki, M. Kazanis,
M. Petropoulou-Oschsenkühn

Editor-in-chief: P.N. Dimotakis

Editors: N. Alexandrou, A. Cosmatos, A. Evangelopoulos, M. Georgiadis,
N. Hadjiliadis, N. Hadjichristidis, M.I. Karayannis, N. Katsanos, J. Petropoulos, D. Tassios.

Foreign Advisors: P. Bontchev (Sofia), H. Işçi (Ankara), G.M. Milanovic (Belgrade), K.C. Nikolaou (Cyprus), E. Plasari (Tirana).

Correspondence, submission of papers, subscriptions, renewals and changes of address should be sent to Chimika Chronika-New Series, 27 Kaningos street, Athens 106 82, Greece. The Guide to Authors is published in the first issue of each volume, or sent by request. Subscriptions are taken by volume at 2000 drachmas for Corporations in Greece and 50 U.S. dollars to all other countries except Cyprus, where subscriptions are made on request.

Phototypesetted and Printed in Greece by EPTALOFOS S.A.

12, Ardittou Str. 116 36 ATHENS Tel. 9217.513

Υπεύθυνος σύμφωνα με το νόμο: Π. Ξυθάλης, Κάνιγγος 27, Αθήνα 106 82.

Responsible under law: P. Xythalis, 27 Kaningos St., Athens 106 82, Greece.

GUIDE TO AUTHORS

Since January 1, 1988, all contributions to *Chimika Chronika, New Series* are reproduced from camera-ready typescripts prepared by the authors.

Scope and Editorial Policies. — This International edition invites original contributions on research in all branches of chemistry and related sciences at the molecular level. Negative results will only be accepted when they can be considered to contribute significantly by the science. In the selection by the editors of manuscripts for publication, emphasis is placed on the quality and originality of the work.

Papers should be written in English. Authors need not be members of the Greek Chemists Association.

Manuscripts are classified as (normal length) *papers, short papers or notes, preliminary communications or letters, and reviews. A short paper* is a concise but complete description of a small, rounded off investigation or of a side part from the main line of investigation, which will not be included in a later paper. It is not a portion of work, that can be more suitably incorporated in a normal length paper, after the investigation has progressed further.

As *Notes* are characterized short papers on limited facets of an investigation e.g. describing a useful modification of an experimental technique or method, reporting additional data and eventually, more precise values for measurements already existing in the literature, and so on.

A *Preliminary Communication* is a brief report of work, which will be included in a later normal length paper. Criteria for its publication are first, when it is considered that the science would be advanced if results were made available as soon as possible to others working on the same subject and second, for the protection of priority for the author. Every effort is made in order to publish preliminary communications as soon as possible and it would help the editors if the author, in a covering letter, were to give his reasons for believing that publication is urgent: Although extensive references to the earlier literature are not usually needed, the most recent papers on the same subject should be referred to, and sufficient experimental details should be given so that those familiar with the subject can immediately repeat the experiments. In general, preliminary communications should be more than an abstract or a summary.

As *Letters* are characterized any other types of communications, previously included in the terms "letter to editor" or "communication to editor", but not fulfilling the criteria mentioned above for a preliminary communication or a note, or dealing with scientific criticism of published work in this (or other) journals.

Reviews should be fully comprehensive on a

narrow field of specialized research, expected to be interesting for a broad number of scientists: they are invited papers, otherwise submitted after contracting the editors.

Organization of Manuscripts. — Authors should submit *three copies* of the manuscript in double-spaced typing on the one side of pages of uniform size, with a margin 5 cm wide on the left; this applies also to summaries (english and greek), references and notes.

Every manuscript should begin with a *Cover Page* and attached to it on a separate sheet, the *Acknowledgments* and notice of grant support (if appropriate).

The cover page should contain the title, the name(s) of author(s) (first-name in full, middle, surname), the name and address of laboratory of research, the footnotes to the title and/or to an author's name (both made with asterisks), and the name and address of the recipient correspondence. It should also contain a Running Title, not exceeding 40 letters.

The purpose of this arrangement is to facilitate the reviewing procedure, which is based on a protective anonymity between reviewers and authors, closed in order to meet the requirements of a highly objective selection of papers to be published in this journal, and to increase the validity of criticisms. Cover page and acknowledgements are not sent to reviewers and accordingly, sentences in first person accompanied by literature references to earlier papers of the author(s) should be completely avoided in the text.

The next pages of the manuscript should be numbered in one consecutive series by the following sequence:

Page 1. — *Title* followed by a *summary* in English. The title should consist of carefully selected and properly presented key words which clearly identify the subjects considered in the paper. The *summary* should be as brief as possible but intelligible in itself, without reference to the paper, and containing sufficient information to serve as an *abstract*.

Every *summary* should end with up to ten *key words*, necessary to direct the attention of abstracting services and readers to subjects in the article that are not referred to in the title.

Page 2. — *Abbreviations and Terminology*, i.e. a list of all abbreviations and unusual terms used in the paper; it may include the systematic name of any compound, mentioned in the text by a shorter "trivial" or "common" name.

Page 3 and subsequent. — The text divided into sections and, if necessary, subsections. The first section of a normal-length paper is always an *Introduction* stating the reasons for performing the work, with brief reference to previous work on the subject; the background discussion should be restricted to pertinent material, avoiding an extensive review of prior work; and documentation of the literature should be selective rather than exhaustive, particularly if reviews can be cited.

The arrangement of the text after the introduction is left to the author(s). The order *Materials, Methods, Results and Discussion*, with headings, subheadings and sideheadings chosen by the author(s), is usually the most satisfactory. However, in lengthy papers (usually, of synthetic work) the manuscript may be organized so that the principal findings and conclusions are concisely presented in an initial section (Theoretical Part), with supporting data, experimental details, and supplementary discussion in a separate section (Experimental Part).

Photocopies of tables, figures, legends, footnotes etc should be pasted on the appropriate place, so that each page will be ready for reproduction. The size of letters chosen for the original should be legible after 20% reduction during reproduction.

Subsequent Pages — After the text pages separate sheets should be used for the following: a) greek summary; b) references and notes.

The *greek summary*, headed by a greek translation of the title, should be extensive and may refer to literature citations and to tables or figures of the paper, in order to give a brief but factual account of the contents and conclusions of the paper, and of its relevance; for this purpose, it may exceed half printed page. In its place, foreign authors may submit an extensive summary in english, which will be gladly translated into greek by care of the editors.

References and Notes, as already mentioned, should be brought together at the end of the paper in one consecutive series by order of citation in the text (not in alphabetical order). Authors should check whether every reference in the text appears in the list and *vice versa*. References to papers "in press" imply that the paper has been accepted for publication and, therefore, the name of the journal should be given. References to a "personal communication" (never "private") will be accepted only when the author

submits written permission of the worker concerned. References should be listed according to the following style:

For journal articles: Last name(s) of author(s) and initials: *Name of journal* (abbreviated according to Chemical Abstracts, Service Source Index (CASSIS) 1907-1984, *Volume number*, First page of article, Year in parentheses.

Example: I Smith, J.B. and Jones, A.B.: *J. Am. Chem. Soc.* 47, 115 (1945).

For books and monographs: Author's names as above: *Title of book*, (Number of edition), Page, Publisher, City, Year of edition.

Example: 2 Smith, J.B.: *Organic Chemistry*, (2d edition), p. 57, Wiley, London (1945).

For multi-author volumes (Articles in books): Authors' names as above: Name of editor(s): *Name of book* Volume number Part number, Page(s), Publisher, City, Year of edition.

Example: 3 Smith, J.B.: Jones, A.B.: *Organic Chemistry*, Vol. 5. Part A, p. 57 (or pp. 46-62), Elsevier, Amsterdam, 1953.

Manuscripts for short papers and preliminary communications should be organized on the same principles. Besides some minor modifications in their published form, they differ from a normal length paper in that the headings and subheadings in the text, as well as the summary preceding the text are omitted. In these cases, the first paragraph of the text may serve the purpose of an abstract, summing up very briefly the scope and the main findings and conclusions of the investigation. However, for reasons already mentioned, the text is always followed by a greek extensive summary.

After the paper is accepted for publication it is returned to the authors for the preparation of the final camera ready typescript. The authors are required to prepare the typescript on a special paper supplied by the Editing Committee according to enclosed instructions.

Page Charge and Reprints. A page charge of 4000 drachmas or 50 U.S. dollars assessed to cover in part the cost of publication, plus the cost of 50 reprints, which will be mailed to the recipient correspondence without any additional requirement. However, papers are accepted or rejected only on the basis of merit and the decision to publish a paper is made before the charge is assessed.

**MECHANISTIC STUDY OF THE RATE OF CONVERSION
OF 1 - AMINO - 3 - IMINO - HEPTAFLUOROCYCLOHEXENE
WITH WEAK ORGANIC ACIDS BY DYNAMIC NMR**

A. VALAVANIDIS

*Department of Chemistry, University of Athens, University Campus Zografou, 15771
Athens, Greece.*

(Received May 18, 1990)

SUMMARY

Dynamic Nuclear Magnetic Resonance (DNMR) techniques have been used to study the rate of conversion of 1-amino-3-iminoheptafluorocyclohexene in solutions of anisole. Benzoic acid and its derivatives were added in relatively small amounts in the solution for the measurements. ^{19}F n.m.r. line broadening techniques were applied to the spectra and a linear relationship between the rate of conversion and the strength of the acids (pKa) was established.

Key words: Dynamic n.m.r., kinetic and mechanistic data, fluorinated organic compounds

INTRODUCTION

Frequencies of observation in nuclear magnetic resonance are much lower than these in infrared and ultraviolet spectroscopic methods, so that we can separate two different conformations of a molecule by observing a splitting of the spectroscopic lines. This method of studying rates of conversion is called Dynamic Nuclear Magnetic Resonance (DNMR).

DNMR spectroscopy is suited for the study of intermolecular as well intramolecular chemical processes in which a magnetic nucleus exchanges its position with another of the same kind or migrates into a new magnetic environment. Intermolecular chemical processes amenable to DNMR investigation include proton jumps between acidic molecules of the same or different kinds, ligand exchanges involving inorganic complexes or organometallic compounds, the dissociation of covalent compounds into ions or the reverse process of ion recombination, and those exchange processes of particular importance for biochemistry in which a small substrate molecule or inorganic ion is in equilibrium between its free form in aqueous solution and its protein - bound state. ¹

The DNMR phenomena are a consequence of the Heisenberg Uncertainty Principle and when the mean lifetime of one conformation from the other differ substantially so that they can be observed as two different spectroscopic n.m.r. lines. But as the rate of conversion increases the two lines approach each other and, finally typical phenomena of exchange broadening and coalescence of n.m.r. lines occur. ²

Data analysis of the spectra can be performed by the Iterative Multisite Exchange NMR Programme (carried out by a mainframe computer) with which an estimated value of the rate constants is produced.

In this paper we investigate the rate of conversion of 1-amino-3-imino heptafluorocyclohexene in solutions of anisole, with the addition of increasing amounts of weak acids (benzoic acid and its derivatives), by ¹⁹F n.m.r. line broadening technique (DNMR). The aim of the project was to find the relationship between the rate of the reaction and the pKa of the acids used, and if possible the mechanistic explanation of the conversion (or interconversion).

EXPERIMENTAL

Preparation of 1 - amino - 3 - imino heptafluorocyclohexene (AIFC) ³

A slow stream of ammonia passed for 4 hrs through a solution of decafluorocyclohexene (b. p. 52 - 53 °C, prepared by fluorination of cyclohexene). Decafluorocyclohexene was tested for purity by ¹H n.m.r., i.r. and gas chromatography. 11 g of decafluorocyclohexene was added in 110 ml of dry ether and a stream of NH₃ was passed through the solution. After the end of the reaction water was added and the aqueous phase was washed with ether and the extracts were filtered and evaporated under reduced pressure to leave a yellow solid which can be sublimed and then recrystallised from CCl₄ to give approximately 6g of AIFC. The purity of AIFC was tested by ¹H and ¹⁹F n.m.r., i.r. spectroscopy and elemental analysis (M.W.: 236, C₆ H₃ F₇ N₂: theoretical : C, 30.5; H, 1.3; N, 11.9; F, 56.3 %. Found : C, 30.6; H, 1.2; N, 11.8; F, 56.2 %. The m.p. was 95 - 96 °C).

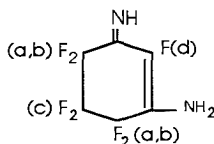
Dynamic ¹⁹F n.m.r. studies

Traces of HF were present as impurities in AIFC. Purification was performed by washing AIFC with K₂CO₃ solutions and then AIFC was dried under reduced pressure.

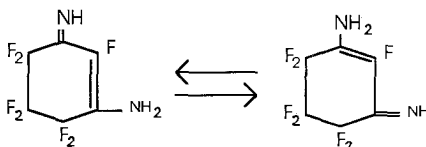
Samples of AIFC were weighed with accuracy up to the 5th decimal point (0.00001 g, 40 mg for standard kinetic studies). Samples of benzoic acid and its derivatives were weighed separately. The AIFC samples were transferred quantitatively with great care into the specimen tubes of the weighed acids. The mixing of the two reagents was performed few hours before the kinetic measurements. Usually 10 specimens were used for every kinetic

study with electronic parameters of the n.m.r. spectrometer remaining relatively steady throughout. Anisole, 0.50 ml, was added by a micropipette few minutes prior to the introducing the n.m.r. tube into the instrument. Measurements were taken at, approx. 32°C.

The ^{19}F n.m.r. spectrum of AIFC has four peaks for the fluorine atoms: (a) 116.5 ppm, (b) 121.84, (c) 134.5 and (d) 156.7 (the internal standard CFCl_3 has one peak at 106.3 ppm).



The two separate peaks at 116.5 and 121.84 ppm are the fluorine atoms near the groups -NH₂ and =NH. As the rate of conversion of the two groups increases with the addition of weak acids, the two peaks broadened and at some point coalesced into one broad peak. With excess addition of acid each original peak split into four peaks. All parameters of the spectra were used by the Iterative Multisite Exchange NMR Programme for the calculation of the rate constants.



The DNMR measurements were carried out by using a 100 MHz Varian XL - 100 spectrometer. Spectra were expanded in the area under investigation (between 116 and 121 ppm) and recorded under slow sweep conditions (R.F. attenuator 76 - 77 db, sweep width 500 - 1000 cps, sweep time 250 secs, lock signal ext. H₂O, temperature 32.3 - 32 °C).

Data analysis of the spectra by the Iterative Multisite Exchange NMR Programme (INMR) carried out by an ICL 1906A digital computer.

Rate constants were calculated by an INMR programme and executed in a few minutes by a mainframe computer (University of Birmingham). The inputs for the INMR programme were: experimental spectrum in digital form, site positions, relative intensities, linewidths, relative transition probabilities and an estimated value of the rate constant (expected). Also, the programme contained standard parameters which were calculated from the spectra of the two extreme conditions, i.e., one without acid and the other with excess acid (no change in spectrum) in 0.50 ml anisole. The two at extreme conditions spectra are shown below:

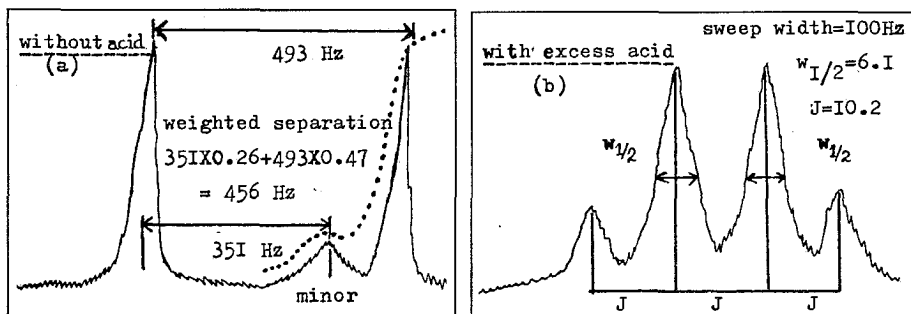


FIG. 1: (a) ^{19}F n.m.r. (expanded) of AIFC without acid. The n.m.r. spectrum gave a weighted separation of the two peaks: 456 Hz. (b) the ^{19}F n.m.r. (expanded) of AIFC with excess acid, sweep width: 100 Hz, gave four (4) peaks of the following characteristics: i. spin coupling, $J = 10.2$ Hz, ii. natural half height linewidth, $w_{1/2} = 6.1$ Hz, iii. peak separation = 456 Hz, and iv. number of sites = 8 (in the half of the spectrum we can see four peaks and another four in the other half of the spectrum).

The spectroscopic data of the frequencies of the 8 lines, their relative integrated intensity and the width of each line at half height (used as an effective T_2 , spin - spin relaxation time) can be arranged as 8 consecutive computer lines in the INMR.

The INMR programme is a FORTRAN language programme which can be executed in a few minutes by the ICL 1906A digital computer. The digitised spectrum contains more than 60 lines, which come in the end of the programme after the initial data and 8 lines containing the square transition probability matrix. The standard deviation must be less than 2 to have the "best fit" for the rate of the reaction. If not, improvements can be made by readjusting the line positions slightly of the X, Y points according to the graph of the spectrum. The graphs which are produced by the plotter of the computer give another picture of the calculated spectrum.

The INMR was programmed by Prof. W. B. Jennings (University of Birmingham) by extending to the general n - site case the iterative approach, originally devised by Jonas et al. ⁴ for the AB case in the programme SPECAB. INMR uses a subroutine MULTIS based on the classical equations of Anderson, Kubo and Sack as programmed by M. Saunders. ⁵ Practical aspects and difficulties for the computation and interpretation of the results are analysed elsewhere. ⁶

RESULTS AND DISCUSSION

Kinetic data for the (inter) conversion of AIFC at different amounts of benzoic acid and its derivatives were calculated by the Iterative Multisite Exchange NMR Programme (INMR). The amounts of benzoic acid and its derivatives were in the range of 2 - 9 mg. For the

case of insoluble acids in anisole only 2 - 3 measurements were performed. The mole fractions of the acids and the AIFC were calculated by assuming that the solution contained three components (including the mole fraction of anisole). The rate of (inter) conversion of AIFC were calculated in s^{-1} .

Experimental and "best fit" computer dynamic n.m.r. spectra of AIFC interconversion at 32.2 °C, in anisole, containing varying amounts of added benzoic acid are presented in Figure 2.

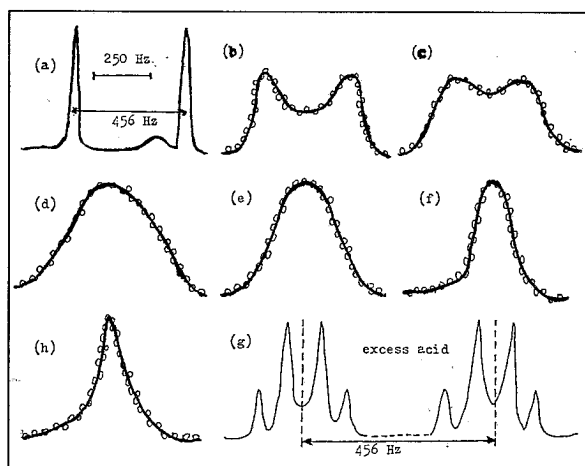


FIG. 2: ^{19}F high - resolution dynamic n.m.r. spectra of AIFC as a function of varying amounts of added benzoic acid. The observed spectra are represented by circles and the corresponding "best fit" theoretical line shapes by the solid lines. The amounts of added benzoic acid: (a) no acid, (b), 2.04 mg, (c) 2.5 mg, (d) 3.95 mg, (e) 4.98 mg, (f) 5.49 mg, (h) 6.03 mg, (g) excess acid (over 50 mg).

Kinetic data for varying amounts of weak organic acids in anisole are presented on Fig. 3. For the insoluble acids in anisole at higher concentrations only two measurements were achieved.

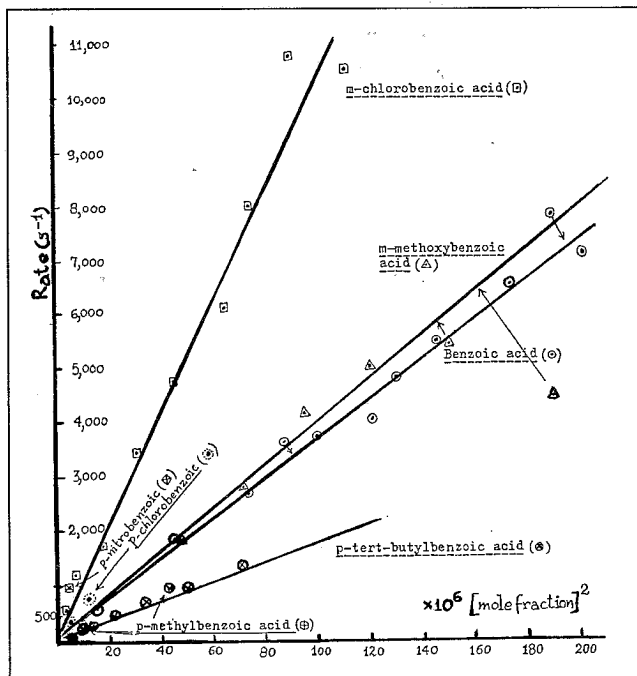


FIG. 3: Kinetic results : rates of reactions (s^{-1}) versus $(\text{mole fraction})^2$ of weak organic acids.

The results from the kinetic data of the various acids can be used to measure the correlation between the rates of interconversion of AIFC (s^{-1})/ $(\text{mole fraction})^2$ versus the ionization constants (K_a) of the acids (in water) as can be found in the CRC Handbook.⁷ The ionization constants represent a function of strength of the acids.

In Table I the various weak organic acids used, their pK_a and K_a (in water at 25°C) are presented in tabulated form. Note, that for the *p*-nitrobenzoic acid the K_a value is a calculated one. The slope for each case has been calculated from Fig. 3 as well as the intercept and the correlation.

TABLE I : Data of the least squares fit for $\text{rate}(\text{s}^{-1})$ versus $(\text{mole fractions})^2$ of the acids in 0.50 anisole (AIFC = 40 mg) at 32.2 °C.

organic acid	pKa	$K_a \times 10^5$	slope $\times 10^6$	intercept	r (correlation)
m - chlorobenzoic acid	3.82	15.1	99.62	387.97	0.9837
m - methoxybenzoic	4.1	8.1	36.77	208.15	0.9887
benzoic	4.19	6.4	34.62	261.5	0.97908
p - tert - butylbenzoic	4.39	4.0	19.65	121.1	0.99474
p - chlorobenzoic	3.98	10.4	~ 62 - 65	-	-
m - methylbenzoic	4.37	4.2	~ 22 - 25	-	-
p - nitrobenzoic	-	~ 15.3	~ 110 - 105	-	-

The slopes of the various kinetic data, which in effect are the $\text{rate}(\text{s}^{-1}) / (\text{mole fractions})^2 \times 10^6$ can be plotted versus the $K_a (\times 10^5)$ of the ionization constants of the weak organic acids. The plot is linear.

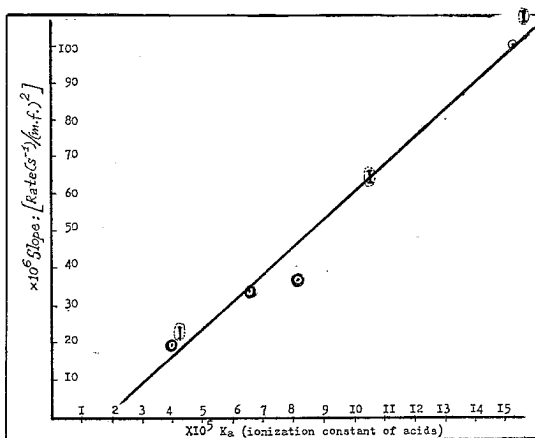


FIG. 4: Variation of slopes of the kinetic data $[\text{rate}/(\text{mole fractions})^2]$ versus ionization of added weak organic acids (K_a).

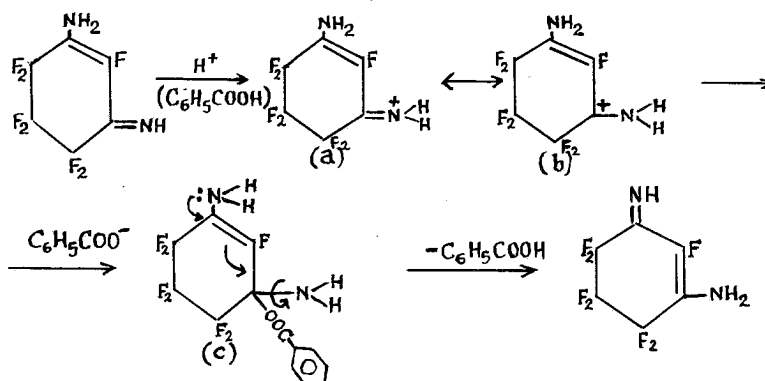
The rates of (inter) conversion of AIFC in anisole and in the presence of varying amounts of benzoic acids and its derivatives were studied effectively by ^{19}F n.m.r. at 32.2°C. In the majority of measurements the standard deviations were near 2 or under for the "best fit" theoretical line shapes produced by the INMR programme.

The rates (s^{-1}) of interconversion of AIFC were plotted versus the $(\text{mole fractions})^2$ of the acids giving a linear relationship. In the cases where experimental points were adequately a very good straight line was evident. The results are presented in Fig. 3.

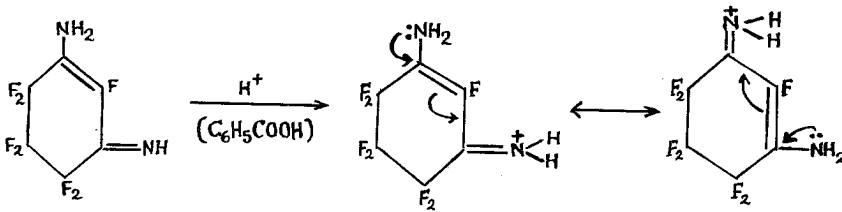
The slopes of these straight lines: rates/(mole fractions)² represent the "catalytic rate constants" for the various acids and can be interpreted by their strength (i.e. their ionization constants in the solution). In our case their ionization constant in water at 25 °C were used and a plot of the slopes versus the ionization constants, Fig. 4, gave a straight line, in agreement with our initial aim that the rate of interconversion is catalysed by the protonation of the imine group of the AIFC.

An overall rate of the interconversion of AIFC in anisole is very difficult to suggest at present. There are evident complications for the picture of the kinetic studies. Benzoic acid and its derivatives exist in monomeric and dimeric form. Measurements by i.r. spectroscopy (Perkin - Elmer 180 Grating IR) showed that the ratio of monomer : dimer was stable at various concentrations.

A mechanism of the "catalytic" interconversion of AIFC in the presence of weak acids is suggested below: the carboxylic acid may protonate the imine to generate the immonium ion (a). It has been suggested that rotation around the immonium double bond can be facilitated by this way.⁸ The rotational barrier in protonated imines is lowered by a contribution from the resonance canonical (b). The carboxylic acid might catalyse the imine isomerization by adding across the C = N bond to form the unstable intermediate (c). Release of the carboxylic acid from the unstable intermediate might transform the second imino group into an amino one with the shift of the double bond to the new position. The mechanism of geometrical isomerization about the carbon - nitrogen bond, whether the reaction proceeds by inversion at the nitrogen atom or by rotation has been investigated in recent years in many laboratories.⁹ We can assume that only a small fraction of imine appears to be protonated in the presence of equimolar amounts of benzoic acid.



Another suggestion is that the protonated form of AIFC is stabilized with resonance and further protonation can occur with excess carboxylic acid (benzoic acid and its derivatives) as shown below:



CONCLUSION

Despite its complications and experimental difficulties, Dynamic Nuclear Magnetic Resonance can be a useful tool for the study of intermolecular chemical processes. In our study we prove that the interconversion of AIFC can be studied effectively by the ^{19}F n.m.r. line broadening technique and that the rate of the reactions were relative to the carboxylic acid concentrations in anisole.

ΠΕΡΙΛΗΨΗ

Μηχανιστική μελέτη της ταχύτητας αλληλομετατροπής της 1-αμινο-3-ιμινο επιπυροκυκλοεξενίου με ασθενή οργανικά οξέα με τη μέθοδο DNMR.

Ο Δυναμικός πυρηνικός μαγνητικός συντονισμός (DNMR) χρησιμοποιήθηκε για τη μελέτη της σχετικής ταχύτητας αλληλομετατροπής της 1-Α-3-ΙΕ σε διαλύματα ανισόλης. Βενζοϊκό οξύ και παράγωγά του προστέθηκαν σε μικρές ποσότητες στα διαλύματα για τις μετρήσεις. Χρησιμοποιήθηκαν ^{19}F n.m.r. τεχνικές διαπλάτυσης των φασματικών γραμμών. Η σχέση μεταξύ της σχετικής ταχύτητας και της ισχύος των οξέων είναι γραμμική εξάρτηση.

ACKNOWLEDGEMENTS

I would like to thank Profs A. Pedler and W. B. Jennings of the Chemistry Dpt of the University of Birmingham for their help and advice during the experimental work. Especially many thanks to the technicians of the Chemistry Dpt and the Computer Dpt for their invaluable experimental expertise. My appreciation to Prof Jennings for supplying the Iterative Multisite Exchange NMR programme.

REFERENCES

1. Binsch, G. and Kessler, H. *Angewandte Chemie, Int*, edition, **19**, 411 (1980); Roberts J. D. *Pure Appl. Chem.*, **51**, 1037 (1979).
2. Becker, E. D. Exchange processes: Dynamic NMR. In: "High Resolution NMR: Theory and Chemical Applications". Academic Press, N. York, 1980, (2nd ed), pp. 240 - 247.
3. Robson, P. Roylance, J., Stephens, R., Tatlow, J. C. and Worthington, R. E. *J. Chem. Soc.*, 5748 (1964).
4. Jonas, J., Allerhand, A. and Gutowsky, H. S. *J. Chem. Phys.*, **42**, 3396 (1965).
5. Saunders, M. *Tetrahedron Let.*, 1699 (1963).
6. Chan, S. O. and Reeves, L. W. *J. Am. Chem. Soc.*, **95**, 670 (1973); Burton, J., Hotchkiss, J. C., Jennings, W. B. *J. Chem. Soc. Perking Trans.*, II, 1052 (1976).
7. Dissociation constants of organic acids. CRC Handbook, 61st edition, 1980 - 81, p. D - 164.
8. Jennings, W. B., Al - Showiman, S., Tolley, M. S. and Boyd D. R. *J. Chem. Soc., Perkin II*, 1535 (1975).
9. Swaddle, T. W., Doine, H., Kinrade, S. D., Sera, A., Asano, T. and Okada T. *J. Chem. Soc.*, **112**, 2378 (1990).

POLYMERIZATION OF Ph-C≡C-Ph USING MCl_x/AlCl₃ (M=Nb, Ta, Mo, W and x=5,6) AS CATALYST

M. G. SISKOS and G. KYRIAKAKOU.

Section of Organic Chemistry & Biochemistry, Department of Chemistry, University of Ioannina 45110, Greece.

(Received December 9, 1991)

SUMMARY

Diphenylacetylene (DPhA) was polymerized in high yields using MCl_x/AlCl₃ (M=Nb, Ta, Mo, W and x=5,6) as catalyst. In all cases, the polymers obtained were low molecular weight products, coloured and soluble in aromatic and chlorinated hydrocarbons. Their characterization was performed by IR, ¹H-NMR and UV-vis spectroscopy. The molecular weights were estimated by gel permeation chromatography (GPC). The thermal stability was investigated by thermal gravimetry analysis and the paramagnetism by ESR spectroscopy. It was found that the phenyl rings attached to the double bonds of the polyene chain are twisted.

Key words: Polymerization of Diphenylacetylene / IR, ¹H-NMR, UV-visible and ESR Spectroscopy / Polyene / Geometric Structure.

INTRODUCTION

The polymerization of a great number of monosubstituted acetylenes has been performed by using a wide range of catalysts and polymerization conditions^[1,2]. Among the catalysts the most common were homogeneous and heterogeneous Ziegler-Natta catalysts, transition metal complexes (Pd, W, Mo, Ni, Co, Fe etc), free radicals, cationic and anionic initiators.

The polymerization of disubstituted acetylenes, however, remains appreciably difficult, due to steric reasons. Consequently, a smaller number of related compounds have been polymerized, as compared with the monosubstituted ones. These include a variety of dialkyl, alkyl-aryl, diaryl and heteroatom-containing acetylenes. The above monomers can be polymerized by transition metal-based catalytic systems.

The polymerization of DPhA has been attempted so far by thermal^[3] and anionic initiators^[4]. In both cases polymers of low molecular weight have been obtained. Similar products have been obtained by exchange reactions between a conjugated carbonyl group and an olefinic double bond, using WCl_6 as catalyst^[5]. Insoluble polymers were afforded using metathesis catalysts^[6,7].

The purpose of the present work is to study the polymerization of DPhA by homogeneous catalysts such as $MCl_x/AlCl_3$ (1/12), where $M=Nb, Ta, Mo, W$ and $x=5,6$. The structure of the polymers obtained was examined by IR, 1H -NMR and UV-vis spectroscopy. The molecular weights were estimated by gel permeation chromatography. The paramagnetism was examined by ESR spectroscopy and thermal stability by thermal gravimetry analysis (TGA).

EXPERIMENTAL

Materials: Diphenylacetylene was purchased from Fluka and recrystallized from ethanol, m.p 59-60°C. WCl_6 (Fluka), $MoCl_5$ (Aldrich) and $AlCl_3$ (Fluka) were purified by sublimation before use. $NbCl_5$ and $TaCl_5$ were purchased from Merck and were used as received. Polymerization solvents, chlorobenzene (Chl) and toluene (Tol), were washed with dilute sulfuric acid, aqueous sodium hydroxide solution, water, dried over calcium chloride overnight, refluxed over CaH_2 and finally distilled under argon.

Measurements: Gas chromatographic analysis were carried out on a Perkin-Elmer model 8310 B gas chromatograph with a SE 30, 10 % Chromosorb, 60/80 mesh, 2m column. Infrared (IR) spectra were recorded on a Perkin-Elmer 783 spectrophotometer as KBr pellets. 1H -NMR spectra were obtained on a Varian EM-390 spectrometer using CCl_4 as solvent and tetramethylsilane as internal standard. UV-vis spectra were run on a Perkin-Elmer model-15 Lambda spectrophotometer in CH_2Cl_2 solutions.

The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Varian 5000 liquid chromatograph, containing a series of 3 columns (LC-1, LC-301 and 500 A^o Ultrastyrigel), detected using a UV-50 Varian instrument at 254 nm, previously calibrated with a series of narrow molecular weight distribution polystyrene standards. Methylene chloride at a flow rate of 1 ml/min was used as eluent.

Thermogravimetric analysis (TGA) was conducted with a Chyo Balance Corporation RDA3 thermal analyzer at a heating rate of 10°C/min under nitrogen.

The ESR spectra were recorded on a Varian E109 specrometer at room temperature. The g values were estimated using 1,1-diphenyl-2-picrylhydrazyl (DPPH) as reference.

Polymerization of Diphenylacetylene: The reactions were carried out in Schlenk glassware under dry deoxygenated argon. To the flask were added 79 mg (0.2 mmol) of WCl_6 and 0.320 g (2.40 mmol) of $AlCl_3$ which was flushed with argon for 15 min and injected with 9.0 ml of dry chlorobenzene through a septum, followed by 1 ml of dry heptane (internal standard for gas chromatographic measurements). The dark red mixture was stirred for 24 hours at 30°C (for $AlCl_3$ dissolution) before adding 1.78 g (10 mmol) of DPhA. After 30 minutes, the reaction mixture turned from dark red to black and gradually became green and viscous. After 24 hours, the polymer was precipitated by adding the above mixture into a large amount of acidified methanol (to remove the catalyst residue) and purified by reprecipitating from benzene solution into an excess of methanol. The yield was determined by gravimetry.

RESULTS AND DISCUSSION

Polymerization of DPhA by $MCl_x/AlCl_3$

The results of DPhA polymerization are shown in Table I. We conclude that $AlCl_3$ combined with Nb, Ta, Mo and W chlorides forms highly active catalytic systems with yields of polymer approaching 90 %. The $AlCl_3$ alone was found inactive as catalyst and the metal chlorides give only oligomers which are soluble in methanol^[6,7].

Table I: Polymerization of DPhA by $MCl_x/AlCl_3$ catalysts

No	Catalyst	[DPhA]/[M]	T °C	Solvent	Conversion %	Yield %
1	$WCl_6/AlCl_3$	100/1	0	Chl	52	35
2	$WCl_6/AlCl_3$	100/1	30	Chl	85	68
3	$WCl_6/AlCl_3$	100/2	30	Chl	100	85
4	$MoCl_5/AlCl_3$	100/2	30	Chl	100	87
5	$TaCl_5/AlCl_3$	100/2	30	Chl	100	75
6	$NbCl_5/AlCl_3$	100/2	30	Chl	100	81
7	$WCl_6/AlCl_3$	100/2	30	Tol	95	10
8	$TaCl_5/AlCl_3$	100/2	30	Tol	91	6

[DPhA]=1 mol/l, [A]= 12×10^{-2} mol/l, [M]=Concentration of metal chloride, [M]/[A]=1/12, Solution volume 10ml, Reaction time 24 hours.

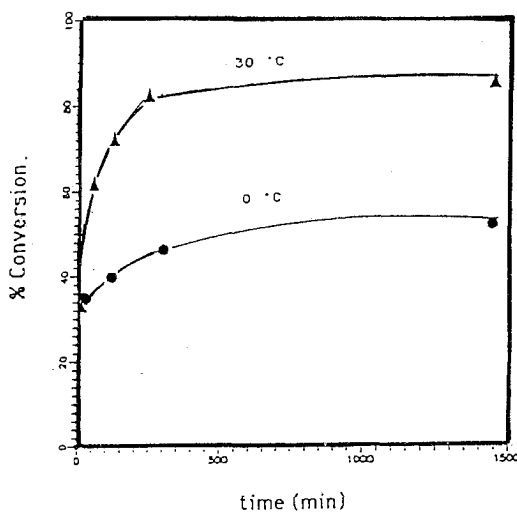


FIG. 1. Time-conversion curves for the polymerization of DPhA with $WCl_6/AlCl_3$ (1/12) in chlorobenzene at 0 and 30°C.

Table I shows that the polymer yield is increasing if temperature and concentration of transition metal are increasing. A temperature increase from 0 to 30°C results in the doubling of yield and % conversion of monomer at the initial stages of polymerization. The time-conversion curves are represented in Figure 1. They show high initial polymerization rate which gradually decreases to a constant value. This suggests that the concentration of the active species responsible for the polymerization diminishes.

Changing the metal chloride does not effect the polymer yield or the kinetics of the reaction (exp. 3,4,5,6).

The yield shows a strong dependence on the nature of solvent, CHl vs Tol. However, the % conversion of monomer remains at the same level. This difference is rather attributed to the fact that in toluene the formation of oligomer products is dominant. The latter occurs because side termination reactions from the polymerization are favoured in this solvent.

Polymer Characterization

The polymers formed via the aforementioned reactions are all coloured and soluble in aromatic and chlorinated hydrocarbons (benzene, toluene, $CHCl_3$, CCl_4 etc).

A common characteristic of these polymers is their low molecular weight, something which is anticipated due to the stereochemical inhibition between the two phenyl rings. Table II shows the number (M_n) and weight-average (M_w) molecular weights and their polydispersity (I). Particularly important is the difference noticed when the transitional metal is changed. In the case of $NbCl_5$ and $MoCl_5$ the M_n and polydispersity factor are doubled, as compared with the other metals.

TABLE II: Influence of metal on PDPHA molecular weight

No	Catalytic system	T °C	M_w	M_n	$I = M_w/M_n$
1	$WCl_6/AlCl_3$	0	810	645	1.26
2	$WCl_6/AlCl_3$	30	1530	1060	1.45
3	$TaCl_5/AlCl_3$	30	1530	1080	1.42
4	$MoCl_5/AlCl_3$	30	4610	1920	2.40
5	$NbCl_5/AlCl_3$	30	5780	2130	2.72

$[M] = 2 \times 10^{-2}$ mol/l, $[M]/[Al] = 1/12$, $[DPhA]/[M] = 100/2$, Reaction time 24 hours

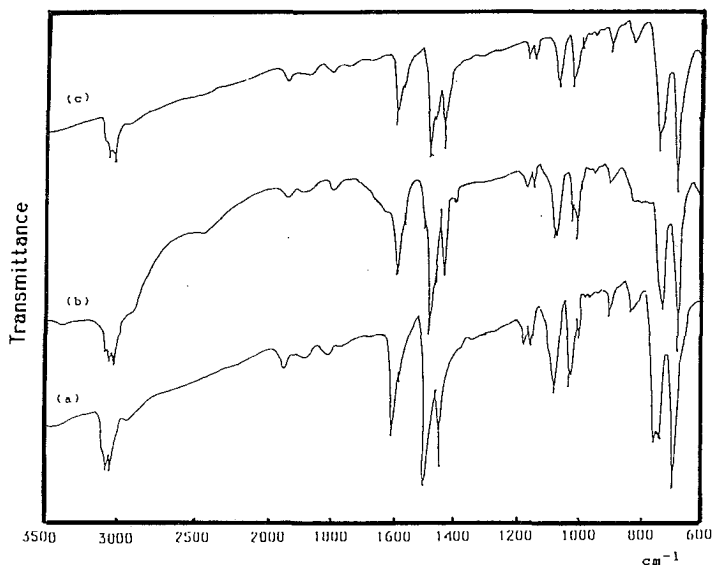


FIG.2. IR spectra of PDPHA with a) $WCl_6/AlCl_3$, 30°C, b) $MoCl_5/AlCl_3$, 30°C, c) $WCl_6/AlCl_3$, 0°C.

The IR spectra, Figure 2, of different PDPHA are virtually identical to each other showing strong absorption bands at 3070 and 3035 cm^{-1} , as well as less strong at 3090 and 3015 cm^{-1} ; these are rather attributed to the stretching vibrations of $=\text{C-H}$ bonds. The aromatic ring double bonds, $-\text{C}=\text{C}-$, absorb at 1605 , 1580 , 1498 and 1450 cm^{-1} . The absorbances at 1180 , 1160 , 1085 , 1035 cm^{-1} are attributed to C-H in-plane deformations of the aromatic ring. The out-of-plane deformations appear at 915 and 760 cm^{-1} . The absorption at 695 cm^{-1} is characteristic of the C-H out-of-plane deformations of monosubstituted benzene rings.

The $^1\text{H-NMR}$ spectra of the DPhA polymers show a strong absorption signal in the range $6.3\text{--}7.3\text{ ppm}$ with the center at 7 ppm .

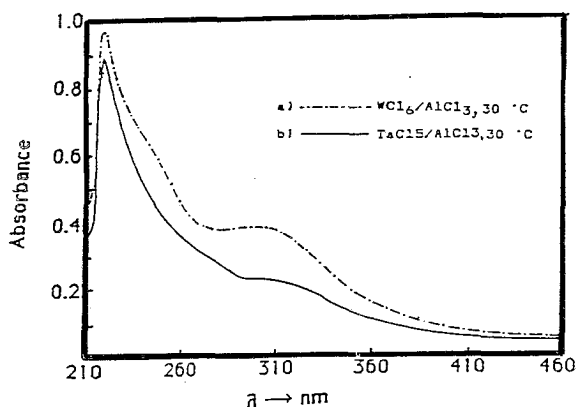


FIG.3a. UV-vis spectra of PDPHA with a) $\text{WCl}_6/\text{AlCl}_3$, 30°C , b) $\text{TaCl}_5/\text{AlCl}_3$, 30°C ,

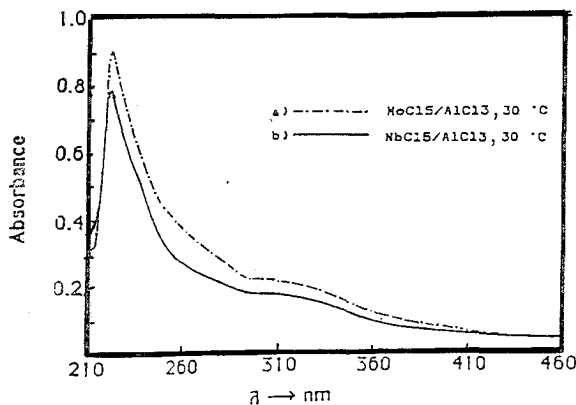


FIG.3b. UV-vis spectra of PDPHA with a) $\text{MoCl}_5/\text{AlCl}_3$, 30°C , b) $\text{NbCl}_5/\text{AlCl}_3$, 30°C ,

The UV-vis spectra of polymers, Figures 3a and 3b, in CH_2Cl_2 solutions exhibit a maximum absorption band at 228 nm ($\epsilon \approx 12000\text{-}15000$ per monomer unit), a shoulder at 310 nm, and a monotonic decrease in absorption until 460 nm. The maximum absorption band at 228 nm is attributed to $\pi\text{-}\pi^*$ transitions of aromatic rings. The partial overlapping between the π orbitals of the conjugate system of double bonds of polymer chain and the aromatic ring, accounts for extended absorption till 460 nm. A particular interesting fact is that even with having molecular weights (M_w) three or four times larger than the polymers obtained with other catalysts, the absorption is weaker after 260 nm in comparison with lower molecular weight polymers. This is due to rather smaller overlap of π -orbitals of the aromatic rings with the π -conjugate system of double bonds of the main chain. The above observations lead to the conclusion that phenyl groups are not at the same plane, but twisted with dihedral angle between the rings increasing as the molecular weight increases. A decrease in absorption is also observed between $\text{-(PhC=CH)}_n\text{-}$ and $\text{-(PhC=CCH}_3\text{)}_n\text{-}$ even when the molecular weight of the latter is higher^[8]. It seems that the introduction of a CH_3 group reduces the overlap between phenyl group orbitals and those of the polymer chain.

The thermal stability of the polymers was studied thermogravimetrically (TGA and DTG) under a atmosphere of nitrogen. Figure 4 shows representative thermographs. The curves show that the polymers are stable within the range 100 to 300°C while the percentage weight reduction is proportional to the molecular weight.

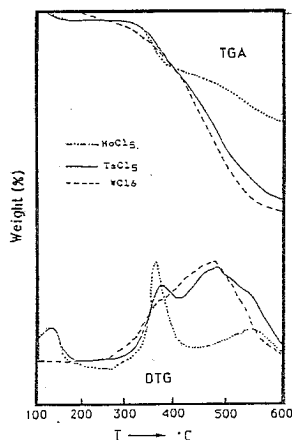


FIG. 4. TGA and DTG spectra of PDPPhA with
a) $\text{WCl}_6/\text{AlCl}_3$, 30°C b) $\text{TaCl}_5/\text{AlCl}_3$, 30°C
c) $\text{MoCl}_5/\text{AlCl}_3$, 30°C.

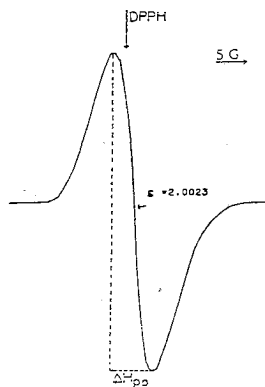


FIG. 5. ESR spectrum of PDPPhA
 $\text{MoCl}_5/\text{AlCl}_3$, 30°C

The polymer paramagnetism and polyene structure have been proved by ESR spectroscopy. The spectra, Figure 5, consist of a symmetrical single line without hyperfine structure and a peak-to-peak width in the range 7.0-7.7 Gauss. The g values were found between 2.0019-2.0025. Similar values have been found for PDPPhA obtained from different catalytic systems^[3-7].

From the above, we conclude that the polymer structure is likely the shown in Figure 6. The phenyl rings have trans configuration and they are out of plane with respect to the polyene chain and at the same time twisted. The absence of a broad absorption in the region 1630-1570 cm^{-1} of the IR spectra and the decrease of absorption seen in the UV-vis spectra as a function of the molecular weight also point to the aforementioned conclusion.

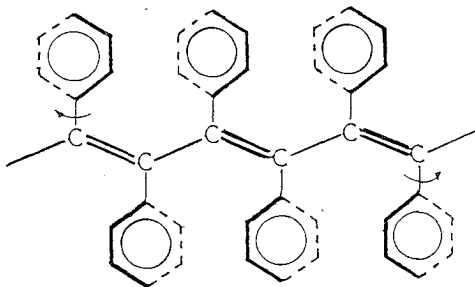
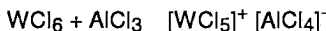


FIG. 6. PDPPhA structure

Preliminary studies of the already mentioned catalytic systems with a group of monosubstituted acetylenes showed that these systems were very active. The polymer characteristics indicate that the active centre has ionic character. There is also an equilibration between catalyst and co-catalyst and this agrees with observations of other researchers^[9,10].



Further investigations on the DPhA polymerization, the activity of catalyst systems against other acetylenic compounds and the elucidation of the reaction mechanism are in progress.

Acknowledgement

The authors would like to thank one of the referees for stylistic improvement and the Research Committee of the University of Ioannina for financial support.

ΠΟΛΥΜΕΡΙΣΜΟΣ ΤΟΥ $\text{PhC}\equiv\text{CPh}$ ΜΕ ΚΑΤΑΛΥΤΕΣ ΣΥΣΤΗΜΑΤΑ ΤΟΥ ΤΥΠΟΥ $\text{MCl}_x/\text{AlCl}_3$ ($\text{M} = \text{Nb}, \text{Ta}, \text{Mo}, \text{W}$ και $x = 5,6$).**ΠΕΡΙΛΗΨΗ**

Το διφαινυλοακετυλένιο (DPhA) πολυμερίσθηκε σε υψηλές αποδόσεις χρησιμοποιώντας καταλυτικά συστήματα του τύπου $\text{MCl}_x/\text{AlCl}_3$ ($\text{M} = \text{Nb}, \text{Ta}, \text{Mo}, \text{W}$ και $x = 5,6$). Σε όλες τις περιπτώσεις τα προκύπτοντα πολυμερή ήταν χαμηλού μοριακού βάρους, έγχρωμα και διαλυτά σε αρωματικούς και χλωριωμένους υδρογονάνθρακες. Ο χαρακτηρισμός τους έγινε με φασματοσκοπίες IR, $^1\text{H-NMR}$, UV-ορατού και ο προσδιορισμός των μοριακών βαρών με χρωματογραφία πηκτής (GPC). Η θερμική σταθερότητα εξετάστηκε θερμοσταθμικά και η παραμαγνητικότητα τους με φασματοσκοπία ESR. Βρέθηκε ότι οι φαινυλομάδες δεν είναι συνεπίπεδες με τους διπλούς δεσμούς της αλυσίδας του πολυμερούς.

REFERENCES

1. H.W. Gibson, " *Substituted Polyacetylenes* ", in Handbook of Conducting Polymers, Dekker, New York and Basel, 1986, pp. 405-436.
2. M.G. Chauser, Y.M. Rodionov, V.M. Misin, and M.I. Cherkashin, *Russ. Chem. Rev.*, **45**, 348 (1976).
3. P.P. Kisilitsa, M.I. Cherkashin, and A.A. Berlin, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1959 (1967).
4. V.M. Misin, P.P. Kisilitsa, N.I. Bolondyeva, and M.I. Cherkashin, *Vysokomol. Soedin. Ser. A*, **18**, 1726 (1976).
5. a) I. Schopov and L. Mladenova, *Macromol. Chem. Rapid Commun.*, **6**, 659 (1985).
b) C. Jossifov and I. Schopov, *Macrom. Chem.*, **192**, 863 (1991).
6. T. Masuda, H. Kawai, T. Ohtori and T. Higashimura, *Polymer J.* **11**, 813 (1979).
7. A. Niki, T. Masuda and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 1553 (1987).
8. N. Sasaki, T. Masuda and T. Higashimura, *Macromolecules*, **9**, 664 (1976).
9. P. R. Marshal and B. J. Ridcewell, *Eur. Polym. J.*, **5**, **29** (1969).
10. C. M. C. De Figueiredo and A. De Souza Gomes, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2845 (1979).

REACTION OF PPh_2Cl , PBu_3 OR PPh_3 WITH AROYLHYDRAZINES

DIMITRIOS A. HARISTOS

Department of General and Inorganic Chemistry, Aristotle University, 54006 Thessaloniki - G R E E C E.

(Received January , 1992)

SUMMARY

The reaction of $C_6H_5-C(O)NHNH_2$, 2, and its *m*- CH_3O , 3, and *p*- Cl , 4, derivatives with PPh_2Cl , 5, in dry solvents C_6H_6 or $CHCl_3$ or THF or CH_3CN at 0-4 °C was studied. The major products were 2.HCl or 3.HCl or 4.HCl respectively, also $Ph_2P(O)OH$, 8, and an oily residue. Increase in polarity of the solvent yielded an increase in 2.HCl or 3.HCl or 4.HCl. The reaction of 2, with PBu_3 , 6, or PPh_3 , 7, was studied at reflux. Nucleophilic attack of 6 or 7 probably occurs at imine N or carbonyl O resulting the formation of phosphinoyl and oily or resinous product. In all cases oxidation of trivalent phosphorus was observed in spite of the generally known reductive character of aroylhydrazines.

Keywords: aroylhydrazine, phosphine, diphenylphosphinic acid, phosphinoyl.

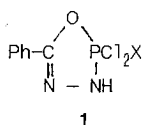
Abbreviations: THF=tetrahydrofuran; TLC=thin layer chromatography; CC=column chromatography; IR=infrared (m=medium, br=broad band).

INTRODUCTION

Bidentate phosphines are common ligands in organometallic and coordination chemistry. Thus it is of interest the possibility to obtain ligands containing both the "soft" σ -donor phosphorus and the "hard" ligating sites of imine N and carbonyl O. Some of these ligands possess a P-N-N linkage¹. It was also postulated that PR_3 (R=alkyl, Ph) reacting with a great variety of oxygen containing organic compounds caused reduction in most cases with the formation of $R_3P=O^{2-4}$. At the investigation of phosphorus substituents on the reactivity it was observed

that PBu_3 was more effective than PPh_3 . Tervalent phosphorus compounds are also known as convenient reagents with conjugated dienes as those containing the group (with aromatic carbon atoms) $-\text{C}(\text{O})-\text{C}=\text{NH}-$ to which e.g. PPh_3 was postulated to react with both carbonyl O and imine N thus forming five-membered phosphorus containing heterocycles¹⁰⁻¹².

The initial attempts to react benzoylhydrazine with PCl_3 or PCl_5 have led either to a phosphorus containing unstable product¹³ or to a final mixture of PhCHCl_2 and PhCCl_3 ¹⁴. In the latter case there has not been identified any phosphorus containing intermediate compound. This has been, however, achieved in the reaction of benzoylhydrazine with PCl_5 or PhPCl_4 and the product was oxaphosphadiazoline, 1 :



(X=Cl or Ph).

Spirocyclic phosphoranes which contained the ring of 1 were also obtained by reacting benzoylhydrazine with $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ ¹⁶. Simple product containing P-N bond which preserves the structure of benzoylhydrazine was that of $p\text{-R-C}_6\text{H}_4\text{-C}(\text{O})\text{NHNH-PPh}_3\text{Br}$ ¹⁷ which was obtained by reacting the corresponding aroylhydrazine with Ph_3PBr_2 in the presence of Et_3N .

The present paper is an investigation of the reaction between (i) the benzoylhydrazine $\text{C}_6\text{H}_5\text{-C}(\text{O})\text{NHNH}_2$, 2, and its $m\text{-CH}_3\text{O}$, 3, and $p\text{-Cl}$, 4, derivatives with chlorodiphenylphosphine PPh_2Cl , 5, under N_2 or He in several solvents of various polarity and (ii) 2 with tributylphosphine PBu_3 , 6, or triphenylphosphine PPh_3 , 7, under N_2 in C_6H_6 .

EXPERIMENTAL

Reagents

The reagents 2, 3 and 4 were prepared from the corresponding aromatic acids according to known methods¹⁸ and they were recrystallised from $\text{H}_2\text{O}/\text{EtOH}$ 50%. 5, 6 and 7 were of Merck for synthesis. C_6H_6 , CHCl_3 , THF and CH_3CN used as solvents were of analytical purity and they were further

purified and dried according to the provided methods. Merck silica gel 60 was used for TLC and CC.

Instruments

Infrared spectra were recorded in the 4000–250 cm^{-1} region in KBr pellets or in nujol mull on a Perkin-Elmer 467 spectrophotometer. The determination of C, H, N was performed on a Perkin-Elmer 240 elemental analyser. The apparatus used to carry out the reaction was consisted of a three neck round bottom flask kept into ice, joined with a bottle of inert gas and adapted to a separating funnel and to a condenser. Next to the condenser was connected a CaCl_2 tube.

General procedure

The general procedure was based on that of the preparation of the hydrazinophosphines¹⁹. The major products were separated by distillation, crystallization or chromatography.

i. Accurately weighted amounts of 2 or 3 or 4 were dissolved into the chosen solvent in the round bottom flask under continuous stirring. Then the calculated ml of 5, dissolved in the same solvent, were added dropwise by the separating funnel. The mixture of the reactants was kept under continuous bubbling of either He or N_2 purified from O_2 by passing through alkaline solution of pyrogallol and then through CaCl_2 tube. The inert gas was gone out through the condenser. During the reaction there was special care to maintain strictly anhydrous conditions. The addition of 5 was completed in 30–40min under stirring which was further continued for 6–8h. At that time the temperature was kept below 4 °C. Then the flask was left for 24h at room temperature and, where necessary, was kept in a refrigerator. The precipitate was filtered in a Gooch No 4 and the filtrate was selected in a tube with glass stopper. The filtration was carried out in a sealed glove box under N_2 . After having been washed with small amounts of cold solvent, the precipitate was identified as 2.HCl or 3.HCl or 4.HCl. The filtrate, free of solvent by distillation in vacuum, gave a yellow or light yellow oily product from which there were isolated mainly diphenylphosphinic acid $\text{Ph}_2\text{P}(\text{O})\text{OH}$, **8**, and besides 2.HCl

or 3.HCl or 4.HCl in small amounts, usually after addition of petroleum ether. Identification of 2.HCl or 3.HCl or 4.HCl and 8 was based on elemental analysis, m.p. and IR spectra^{20a-c,21a}. The m.p. of 2.HCl, 3.HCl and 4.HCl are 180-2, 196-7.5 and 248-9 °C respectively and they were checked against the synthesized ones. The oily residue of the filtrate, treated by means of TLC revealed the presence of unreacted e and at least two unidentified substances. The attempts to isolate them were performed by means of CC. The first fractions contained 8, the next fractions contained 2 (or 3 or d correspondingly) and the last ones gave small amounts of a gluey product with a rancid odor. Decomposition occurs upon distillation even at reduced pressures and no way was found to effect isolation and/or purification.

ii. Accurately weighted amounts of 2 were dissolved in dry C_6H_6 in the round bottom flask of the previously described apparatus, under continuous stirring and bubbling of N_2 . Then the calculated amounts of 6 or 7 dissolved also in dry C_6H_6 , were added dropwise at room temperature. The addition of 6 or 7 was completed in 15-20min. The solution was kept under stirring for 6-8h at room temperature for 24h and then was kept overnight in a refrigerator. After distillation of the solvent, there was obtained a mixture of a white solid and a yellow-brown oily product. The mixture, after having been treated with absolute EtOH and dry Et_2O , gave $Bu_3P=O$, 9, or $Ph_3P=O$, 10, and small amounts of unreacted 2. 10 was identified by its m.p. and IR spectrum^{21b,22a,23}. As 9 was characterised a highly hygroscopic compound m.p. 55- 62 °C (lit. m.p. of 9 is 68-69 °C)^{22b} which showed the following main IR assignments: $1460m,br\ cm^{-1}$ attributed to $\nu(CH_3)$ and $\nu(CH_2)$ and $1240-1160m,br\ cm^{-1}$ possibly attributed to the free or bonded $\nu(P=O)$ ^{23,24a}. The oily residue of the reaction of 2 with 6 or 7, treated by means of TLC revealed the presence of two major compounds whereas the application of CC gave 9 or 10, also 2 and a brown gluey product. The IR spectra of the last product in nujol mull showed a broad and strong absorption band near $1125\ cm^{-1}$ which could be related to a possible presence of tetracoordinate phosphorus^{25,25}. The IR spectrum of the corresponding product of the reaction of 2 and 6, in nujol mull, showed also the bands near $3400-3150m,br\ cm^{-1}$ due mainly to $\nu(N-H)$, the bands at $1620m$ and $1460m,br\ cm^{-1}$ attributed to $\nu(CH_3)$ and $\nu(CH_2)$ and the

band at 1340 cm^{-1} which could be attributed to the group $\text{P}=\text{N}-\text{C}-\text{O}^{24b}$ although a strong band at 1345 cm^{-1} occurs also in 2^{20b} and thus could be attributed to the presence of unreacted 2. This band however was not clearly assigned in the IR spectrum of the analogous product of the reaction of 2 and 7.

At the addition of 7 on 2 a white muddling was initially observed which was gradually disappeared by further stirring. Centrifugation proceedings to isolate the muddling were failed because it was gradually converted into an oily yellowish product which gave 10 in poor yield.

Chromatography

TLC: They were developed separately the precipitate, the initial filtrate (free of solvent) as well as pure (synthesized) samples of 2.HCl or 3.HCl or 4.HCl in solvent mixture $\text{MeOH}/\text{CHCl}_3$ 1:4 and 1:6 v/v.

CC: The filtrate, free of solvent, was dissolved in pure CHCl_3 or in $\text{CHCl}_3/\text{C}_6\text{H}_6$ 75/25 or 50/50 % v/v and then was flowed through the column. Fractions of 40 ml were collected and investigated.

Reaction treatments

7.48g (55mmol) of 2 dissolved in 120ml of dry solvent (C_6H_6 or CHCl_3 or THF or CH_3CN) are treated with 6.06g (27.5mmol) of 5 dissolved in 20ml of the corresponding solvent and give b.HCl (yields 35–40 %, increasing with the polarity of the solvent), also 8 and oily residue.

7.48g (55mmol) of 2 dissolved in 120ml of dry solvent (CHCl_3 or THF) are treated with 12.12g (55mmol) of 5 dissolved in 20ml of the corresponding solvent and give 2.HCl (yields 42 and 46% respectively), also 8 and oily residue.

4.15g (25mmol) of 3 dissolved in 120ml of dry solvent (CHCl_3 or THF) are treated with 5.51g (25mmol) of 5 dissolved in 20ml of the corresponding solvent and give 3.HCl (yields 46 and 50% respectively), also 8 and oily product.

4.26g (25mmol) of 4 dissolved in 120ml of dry solvent (CHCl_3 or THF) are treated with 5.51g (25mmol) of 5 dissolved in 20ml of the

corresponding solvent and give 4.HCl (yields 38 and 43 % respectively), also 8 and oily product.

3.4g (25mmol) of 2 dissolved in 120ml of dry C_6H_6 , are treated with 5.05g of 6 dissolved in 20ml of C_6H_6 and produce 9 (yields 30-40 %) and oily or resinous product.

3.4g (25mmol) of 2 dissolved in 120ml of dry C_6H_6 , are treated with 6.55g of 7 dissolved in 20ml of C_6H_6 and produce 10 (yields under 20 %) and oily or resinous product.

RESULTS AND DISCUSSION

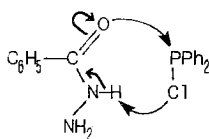
i. The main products of the reaction of 2 or 3 or 4 with 5 were correspondingly 2.HCl, 3.HCl or 4.HCl and, further, 8 and an oily residue. The higher yield of 3.HCl over 2.HCl and 4.HCl could be considered as evidence for the electrophilic character of 5. The yields in 8 at initial molar ratio 1:1 of 2 or 3 or 4:5 seem to be slightly exceeding the half compared with those of 2.HCl or 3.HCl or 4.HCl but they could not be determined with a satisfactory precision. Increase in yields were also observed with the increase in polarity of the solvent. This could be attributed to a facile elimination of the imine hydrogen as cation enhancing thus the nucleophilicity of 2 or 3 or 4 upon $\overset{+}{P}Ph_2$ whereas 2.HCl or 3.HCl or 4.HCl become inert to further reaction with 5. This affords an evidence that the reaction site of the aroylhydrazines with 5 has been protonated or it is affected by the protonated site and becomes positively charged or, at least, less electrophilic.

ii. The major reaction products of 2 with 6 or with 7 were respectively 9 or 10 and an unstable oily mixture some IR assignments of which, in nujol mull, could be attributed to phosphorus compounds. In the case of equimolecular initial quantities the different yields in 9 or 10 could not be considered as a distinction due to the different nucleophilic reactivity between 6 or 7 but, in part, could be attributed to the steric effect which is stronger in 7. This point is enhanced by the appearance

of the white muddling at the reaction of 2 and 6 which might be attributed to the formation of a relatively stable adduct of 6 with 2. Thus the reaction seems to be affected by the different inductive effect between β u and Ph and besides by a steric effect which affects the reactivity of mainly the PPh_3 on the reaction site of 2. Nevertheless it is well established the fact that phosphines have a strong tendency to donate the $3s^2$ electrons in these nucleophilic reactions, owing to the relatively low ionization potential²⁷. The reaction, however, under the experimental conditions is not kinetically controlled. Besides, deoxygenation of 2 or 3 or 4 is expected to give tertiary phosphinoxides the first stage of the reaction usually involved carbonyl addition^{28,29}.

Reaction Mechanism

i. The reaction of 2 (also 3 or 4) with 5 it is believed to occur in two main steps: first the labile and more acidic imine hydrogen of 2 is eliminated by the chlorine atom of 5 and then the carbonyl oxygen attacks the phosphorus atom which formally positively charged, is highly electrophilic (scheme 1)

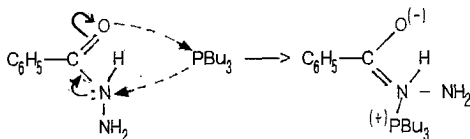


Scheme 1

The produced HCl is binded by another molecule of 2. Oxidation of trivalent phosphorus to pentavalent proceeds possibly on elimination of the carbonyl oxygen^{30,31}. Any attempt to isolate aroylhydrazine derivatives containing P-N bonds or certain aroylhydrazine reduction products was unsuccessful.

ii. The reaction of 6 or 7 with 2 proceeds by a mechanism which probably involves attack on the imine N or the carbonyl O including the formation of an adduct. Thus on treating 6 with 2, attack may occur preferentially at imine N whereas the bulkier 7 is possibly directly linked to the carbonyl O. The possible adduct formation could be related to the

initially appeared white muddling at the addition of 6 on 2 and shows a trend of stabilization of the quaternary phosphonium containing adduct (scheme 2).



Scheme (2)

CONCLUSIONS

The reaction of 2 (also 3 or 4) with 5 is probably an oxidative action of the aroylhydrazines upon the tervalent phosphorus as a consequence of the nucleophilic attack of the carbonyl oxygen atom on the positively charged phosphorus site. The reaction of 2 with 6 or 7 proceeds possibly via the nucleophilic attack of the tervalent phosphorus initially at the imine N or the carbonyl O resulting finally in the conversion of the starting phosphines to the corresponding phosphinoyl oxides. In spite of the adequately reported reductive character of the aroylhydrazines only oxidation products of the tervalent phosphorus of the starting phosphines were obtained while among the reaction products, under the present experimental conditions, it was not able to obtain derivatives containing the P-N-N linkage.

ΠΕΡΙΛΗΨΗ

Αντίδραση της PPh_2Cl , PBU_3 ή PPh_3 με αροϋλοϋδραζίνες

Επειδή οι διδραστικές φωσφίνες έχουν μεγάλο ενδιαφέρον στη χημεία των οργανομεταλλικών ενώσεων και των ενώσεων συναρμογής, έγινε προσπάθεια να συντεθούν ligands τα οποία να περιέχουν το P ως "μαλακό" δότη και το ιμινικό N ή το καρβονυλικό O ως "σκληρό" δότη. Για το σκοπό αυτό μελετάται:

i. Η αντίδραση της βενζοϋλοϋδραζίνης $\text{C}_6\text{H}_5\text{-C(O)NHNH}_2$, **2**, και των m- CH_3O , **3**, και p-Cl, **4**, παραγώγων αυτής με χλωροδιφαινοϋλοφωσφίνη PPh_2Cl , **5**, σε ξηρούς διαλύτες C_6H_6 ή CHCl_3 ή THF ή CH_3CN σε 0-4 °C και σε ατμόσφαιρα N_2 ή He. Τα προϊόντα της αντίδρασης είναι **2.HCl** ή **3.HCl** ή **4.HCl** και επίσης διφαινοϋλοφωσφινικό οξύ $\text{Ph}_2\text{P(O)OH}$, **8**, ενώ παραμένει ένα ελαιώδες υπόλειμμα το οποίο

κατά την ανάλυση με TLC έδειξε την ύπαρξη **5** το οποίο δεν έχει αντιδράσει και τουλάχιστον δύο ακόμη κύριων συστατικών. Έγινε προσπάθεια να απομονωθούν τα συστατικά αυτά με CC και απομονώθηκαν το **8** και επίσης **2** ή **3** ή **4** ενώ απέμεινε ένα ιξώδες υπόλειμμα δρμείας οσμής μη ταυτοποιηθέν.

ii. Η αντίδραση της **2** με τριβουτυλοφωσφίνη PBu₃, **6**, ή τριφαινυλοφωσφίνη PPh₃, **7**, σε ξηρό C₆H₆ με κάθετο ψυκτήρα σε ατμόσφαιρα N₂. Τα προϊόντα της αντίδρασης είναι το τριβουτυλοφωσφινόξειδιο Bu₃P=O, **9**, ή το τριφαινυλοφωσφινόξειδιο Ph₃P=O, **10**, επίσης **2** που δεν αντέδρασε και ένα κιτρινοκαστανόχρουν ελαιώδες υπόλειμμα το οποίο με TLC έδειξε την παρουσία δύο τουλάχιστον κύριων προϊόντων. Με την εφαρμογή της CC ελήφθησαν **9** ή **10**, επίσης **2** και ένα καστανόχρουν ιξώδες προϊόν. Ορισμένες ταινίες του φάσματος IR του προϊόντος αυτού μπορούν να αποδοθούν στην παρουσία συναρμοσμένου φωσφόρου ή στην ομάδα P=N-C-O.

Μηχανισμός της αντίδρασης

Κατά την αντίδραση της **2** (επίσης **3** ή **4**) με το **5** αρχικά πιστεύεται ότι αποσπάται, ως πιο όξινο, το ιμινικό H με το άτομο Cl του **5** το δε καρβονυλικό O προσβάλλει το ισχυρώς ηλεκτρονιόφιλο ⁺PPh₂ (scheme 1). Η οξειδωση του τρισθενούς φωσφώρου σε πεντασθενή γίνεται πιθανώς με απόσπαση καρβονυλικού O. Η προσπάθεια απομόνωσης ενώσεων που να περιέχουν δεσμό P-N ή προϊόντων αναγωγής της αρούλουδραζίνης, δεν έδωσε αποτέλεσμα.

Κατά την επίδραση της **6** ή της **7** επί της **2**, η προσβολή γίνεται είτε στο ιμινικό N με πιθανό σχηματισμό ενός adduct (scheme 2), είτε στο καρβονυλικό O. Η **6** πιστεύεται ότι προσβάλλει αρχικά το ιμινικό N ενώ η ογκωδέστερη και λιγώτερο δραστική **7** προσβάλλει μάλλον απ' ευθείας το καρβονυλικό O. Ο σχηματισμός του adduct μπορεί να συσχετισθεί με το αρχικά εμφανιζόμενο λευκό θόλωμα κατά την προσθήκη της **6** στη **2** αυτό δε πιθανώς δείχνει μια τάση για σταθεροποίηση του περιέχοντος το τεταρτοταγές φωσφώνιο adduct.

Συμπέρασμα

Κατά την επίδραση των φωσφινών **5** ή **6** ή **7** σε αρούλουδραζίνες λαμβάνει χώρα γενικά οξειδωση του P(III) σε P(V) παρά την ευρύτητα γνωστή συμπεριφορά των αρούλουδραζινών ως αναγωγικών ενώσεων ενώ μεταξύ των προϊόντων της αντίδρασης, υπό τις παρούσες πειραματικές συνθήκες, δεν κατέστη δυνατό να ληφθούν ενώσεις που να περιέχουν την ομάδα P-N-N.

REFERENCES

1. Majoral J.P., Badri M., Caminade A.M., Delmas M. and Gaset A., *Inorg. Chem.*, **27**, 3873 (1988).
2. Horner L. and Jurgeleit W., *Ann.*, **591**, 138 (1955).
3. Shabarov Yu.S., Mochalov S.S., Fedorov A.N. and Kalaschnikov V.V., *Khim. Geterotsikl. Soedin* (9), 1195 (1975); *C.A.* **84**, 30946g (1976).
4. Corrie J.E.T., Kirby G.W. and Sharma R.P., *J. Chem. Commun.* **22**, 915 (1975).
5. Lindblom L. and Samuelson D., *Acta Chem. Scand., Ser. B.* **B31**(10), 907 (1977).
6. Wolkoff P., *Can. J. Chem.* **53**, 1333 (1975).
7. Corrie J.E.T., Kirby G.W. and Sharma R.P., *J. Chem. Soc. Perkin Trans 1*(7), 1571 (1982).
8. Bhattacharjya A., Chattopadhyay P., Bhaumik M. and Pakrashi S.C., *J. Chem. Research (S)*, 228 (1989).
9. Amoo-Neizer E.H., Ray S.K., Shaw R.A. and Smith B.C., *J. Chem. Soc.* 4296 (1962).
10. Stegmann H.B., Stocker F. and Bauer G., *Liebigs Ann. Chem.*, **755**, 17, (1972).
11. Stegmann H.B., Haller R. and Scheffler K., *Chem. Ber.*, **110**, 3817 (1977).
12. Speier G., Tyeklar Z. Fulop V. and Parkanyi L., *Chem. Ber.*, **121**, 1685 (1988).
13. Schmidt H., Meyer G., Domagk G., *Farbenfabriken Bayer Akt.-Ges. Ger.*, 961,346 (1957); *C.A.* **53**, 13182c (1959).
14. Mikhailov V.S., Matyusheva G.I., Derkach G.I. and Yagupol'skii L.M., *Zh. Org. Khim.*, **6**, 149 (1970); *C.A.* **72**, 90373n (1970). Yagupol'skii L.M., Mikhailov V.S. and Matyusheva G.I., *ibid.*, **6**, 1648 (1970); *C.A.* **73**, 109124g (1970).
15. Yagupol'skii L.M., Mikhailov V.S. and Matyusheva G.I., *Zh. Org. Khim.*, **11**, 1574 (1975); *C.A.* **83**, 193183g (1975).
16. Schmidtpeter A. and Luber J., *Chem. Ber.*, **110** (3), 112 (1977).
17. Hitachi Ltd JPN Kokai Tokkyo JP 58 88, 371; *C.A.* **99**, 139973g (1983).
18. Beilstein, *Handbuch der Organischen Chemie*, **9**, 319, Verlag Springer, Berlin.
19. Nielson R.P. and Sisler H.H., *Inorg. Chem.*, **2**, 753 (1963).
20. (a) Beilstein, **9**, 341, (b) Manoussakis G.E., Haristos D.A. and Youri C.E., *Chim. Chron., New Series*, **1**, 182 (1972), (c) Haristos D.A., *Chim. Chron., New Series*, **12**, 129 (1983).
21. (a) Pouchert C.J., *The Aldrich Library of Infrared Spectra*, Aldrich Chem. Co. Inc. USA 1970, p. 872F, (b) *ibid* p. 873c.
22. (a) Edmundson R.S., *Organophosphorus Compounds*. Chapman and Hal Ltd. G. Britain 1982, p. 836, (b) *ibid*. p. 795.
23. Bellamy L.J., *The infrared Spectra of Complex Molecules*. J. Wiley and Co, G. Britain (1964), p. 795.
24. (a) Pretsch-Clerc-Seidi-Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*. Editors Boschke F.L., Fresenius W., Huber J.F.K., Pungor E., Rechnitz, Simon W. and West Th.S., Springer-Verlag, Berlin (1983), p.1245, (b) *ibid*. p. 1235.
25. Buckler A.S., *J. Am.Chem. Soc.*, **84**, 3093 (1962).
26. Nielsen R.P., Vincent J.F. and Sisler H.H., *Inorg. Chem.*, **2**, 760 (1963).

27. DiStefano G., Innorta G., Pignataro S. and Foffani A., *J. Organomet. Chem.*, **14**, 165 (1968).
28. Hudson R.F., *Structure and Mechanism in Organo-Phosphorus Chemistry*, Academic Press, G. Britain (1965).
29. McNeily S.T. and Miller J.A., *J. Chem. Soc. (C)* 3007 (1971).
30. Ainscough E.W., Peterson L.K. and Sabourin D.E., *Can. J. Chem.*, **47**, 3405 (1969).
31. Sosnovsky G., Zaret E.H. and Schmit K.D., *J. Org. Chem.*, **35**, 33 (1970).

ACKNOWLEDGEMENTS

The author is most grateful to Ass. Professor E. G. Bakalbassis for his assistance in the early stages of the work as well as for helpful discussions.

Many thanks are also due to the Laboratory Assistant Mrs Efi Pavlidou for the elemental analyses.

ELECTRON IMPACT MASS SPECTRA OF SOME ETHOXYCARBONYL HYDRAZONES, SEMI-CARBAZONES, AND SULPHONYLHYDRAZONES OF *o*-HDROXYARYLKETONES

ANTIGONI KOTALI

Laboratory of Organic Chemistry, College of Engineering, University of Thessaloniki, Thessaloniki GR-54006, Greece

(Received April 4, 1992)

SUMMARY

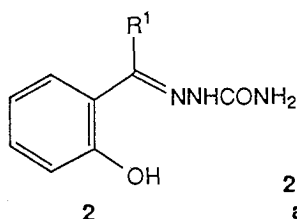
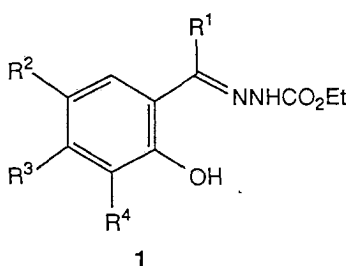
The electron impact mass spectra of some ethoxycarbonyl hydrazones, semicarbazones and sulphonylhydrazones of *o*-hydroxyarylketones are reported. The molecular ion appears in all cases with relative intensity 14-100%. In addition to the main fragmentation sequences which involve cleavage of N-N and N-CO bonds, each class of molecules show characteristic fragmentation pattern. Thus, for ethoxycarbonyl hydrazones characteristic peaks appear at values corresponding to the $|M-O|^{+}$, $|M-OH|^{+}$ and $|M-EtOH|^{+}$ ions, whereas for semicarbazones to the $|M-NCNH_2|^{+}$ and $|M-NHCO|^{+}$. No *ortho*-effect was observed for semicarbazones and sulphonylhydrazones.

Key Words : Ethoxycarbonyl Hydrazones, Semicarbazones, Sulphonylhydrazones, *o*-Hydroxyarylketones, Mass Spectra.

INTRODUCTION

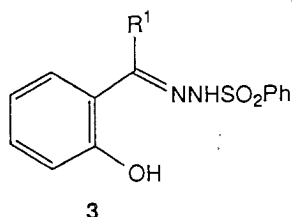
Recently we reported¹ the synthesis of ethoxycarbonyl hydrazones 1 along with their conversion to ethyl *o*-acylbenzoates, by treatment with lead tetraacetate.

The synthetic importance of the above reaction as well as its interesting mechanism² stimulated us to study the mass spectra of 1 and of the related systems 2 and 3.



2-3	R ¹
a	Me
b	Et
c	H

	R ¹	R ²	R ³	R ⁴
1	R	R ²	R ³	R ⁴
a	Me	H	H	H
b	Me	Br	H	Br
c	Me	H	OMe	H
d	Et	H	H	H
e	Ph	Me	H	H
f	Ph	H	OMe	H
g	H	H	H	H



RESULTS AND DISCUSSION

The results are discussed in terms of three main divisions representing the three classes of the molecules examined: (i) ethoxycarbonyl hydrazones 1, (ii) semicarbazones 2, and (iii) sulphonylhydrazones 3.

The spectra of compounds 1-3 are recorded in Table 1. Representative examples of the main fragmentation pathways of each class are delineated in Schemes 1, 2 and 3, respectively.

(i) **Ethoxycarbonyl hydrazones 1.** Each showed a prominent peak corresponding to the molecular ion with relative intensity 62-100%, in contrast to the weak molecular ions previously reported for some methoxycarbonyl hydrazones.³

The main fragmentation sequences involve cleavage of the N-N and N-CO bonds giving rise to the ions a and b at m/z 134 and 149, respectively. A similar pattern has been observed in the arylhydrazones of acetophenone and benzaldehyde⁴ as well as in the carbonyl hydrazones of *o*-hydroxyaryl ketones.⁵ However, in methoxycarbonyl hydrazones of

aliphatic compounds no fragments due to the scission of the -NH-CO-bond were observed.³ Fragment b subsequently leads to ions c and d. Further decomposition of a and d is according to the data reported in the literature for 1,2-benzisoxazole and indazole.⁶

A second pathway involves the loss of an oxygen from the molecular ion to give the ion 1 at m/z 206.

A third fragmentation route proceeds via a loss of a OH radical from the molecular ion to give the prominent ion e at m/z 205. A similar fragmentation has been also observed in the mass spectra of phenyl- and 2,4-dinitrophenyl-hydrazone derivatives,⁷ but not in those of aroyl hydrazones of o-hydroxyl arylketones, where the $[M-OH]^+$ ion appeared only once.⁵

A fourth fragmentation route involves loss of an EtOH molecule from the molecular ion to give an ion at m/z 176. Two heterocyclic isomeric structures the 1,3,4-benzoxadiazepinone-2 g or the 1,3,4-oxadiazolone-2 f, could explain the resulting fragments. Using MOPAC program (version 4.00 with the Hamiltonian and precise keyword) the final heat of formation was found to be 0.49177 Kcal for g, and 10.13192 Kcal for f. In addition it is known that 1,3,4-oxadiazepines have been prepared by photochemical reaction of 1,3,4-oxadiazoles.⁸

No such fragmentation of an EtOH molecule from the molecular ion has been observed for the methoxycarbonyl hydrazones.³ Subsequently, loss of a molecule of diazomethane or carbon dioxide from either f or g gives rise to the ions i and h, respectively. Fragments i and a, which both appeared at m/z 134, have different elemental analysis. The diazirine h could be assigned for the fragment at m/z 132. The elimination of CO_2 is according to the reported data for 2-substituted 1,3,4-oxadiazoles.⁹ However, no data are available for the mass spectra of 1,3,4-benzoxadiazepinones-2.

Finally, a fifth pathway involves loss of an ethyl carbazate radical from the molecular ion to give the ion k at m/z 119. It is proposed that an isomerization to the quinonoid ion j takes place prior to decomposition. In the mass spectra of aroyl hydrazones of o-hydroxy arylketones fragment k has not been observed.⁵

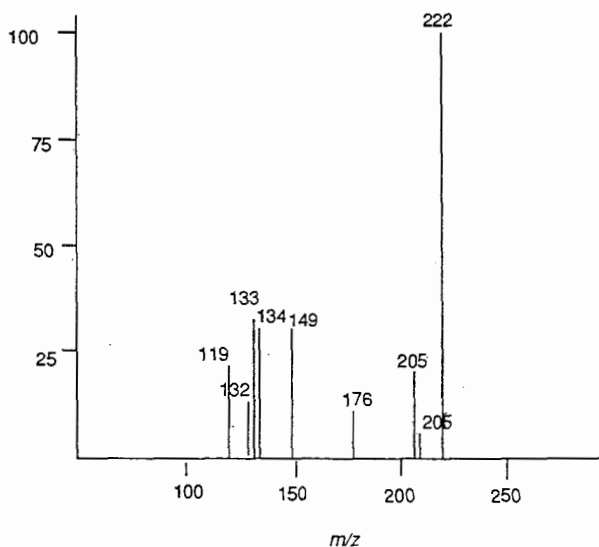


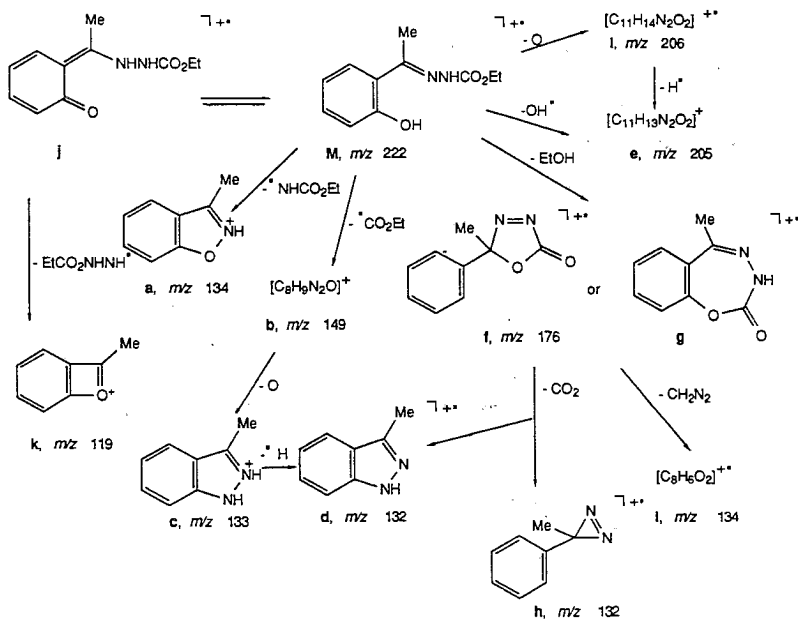
FIG. 1. Mass spectrum of ethoxycarbonyl hydrazone of 2-hydroxyacetophenone (1a)

TABLE I. Fragment Ions in the Mass Spectra of Hydrazones 1-3

Compound	Fragment Ions (m/z) and Relative Abundances (%)
1a	222(100) ^a M ⁺ , 206(4), 205(32), 176(11), 149(32), 134(30), 133(32), 132(12), 119(22)
1b	380(100) M ⁺ , 364(2), 363(17), 334(46), 307(26), 292(25), 291(45), 290(29), 277(14)
1c	252(100) M ⁺ , 236(2), 235(22), 206(16), 179(14), 164(15), 163(17), 162(2), 149(31)
1d	236(100) M ⁺ , 220(3), 219(28), 190(8), 163(26), 148(70), 147(13), 146(63), 133(34)
1e	298(96) M ⁺ , 282(12), 281(72), 252(23), 225(46), 210(28), 209(45), 208(35), 195(100)
1f	314(62) M ⁺ , 298(3), 297(23), 268(1), 241(28), 226(28), 225(17), 211(100)
1g	208(88) M ⁺ , 191(2), 162(14), 135(22), 120(66), 119(100), 105(21)
2a	193(83) M ⁺ , 177(4), 151(2), 150(11), 149(30), 148(3), 134(22), 119(23)
2b	207(100) M ⁺ , 191(3), 165(2), 164(21), 163(26), 162(3), 148(19), 133(16)
2c	179(90) M ⁺ , 163(3), 137(2), 136(9), 135(20), 134(13), 120(15), 105(100)
3a	290(14) M ⁺ , 157(6), 149(100), 133(29), 119(18)
3b	304(47) M ⁺ , 163(100), 157(59), 147(33), 133(28)
3c	276(36) M ⁺ , 157(1), 135(44), 119(1), 105(100)

^a Numbers in parentheses indicate percentage relative abundances.

^b Abundance of the most intense isotopic peak.

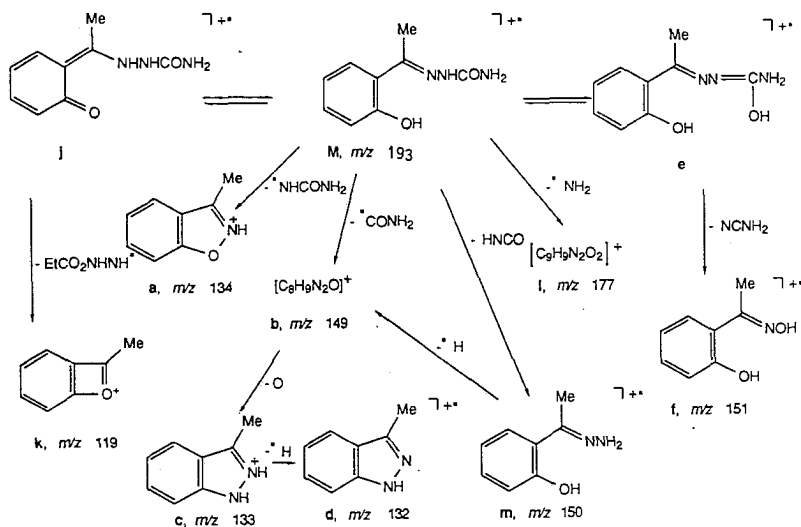


SCHEME 1. Proposed pathways for the fragmentation of ethoxycarbonyl hydrazone of 2-hydroxyacetophenone (1a)

(ii) Semicarbazones 2. Semicarbazones 2 give molecular ion with intensity 83-100%. Some of their main fragmentation pathways are similar to those above suggested for the ethoxycarbonyl hydrazones. Therefore, the ions, a, b, c, d and k, that appear at m/z 149, 134, 133, 132 and 119 respectively, are common for both 1a and 2a (Schemes 1 and 2). However, no ortho-effect was observed; and therefore, no peak at m/z 176 derived from the molecular ion by loss of a OH radical. No loss of oxygen was observed, contrary to the ethoxycarbonyl hydrazones.

An alternative fragmentation pathway involves loss of a molecule of cyanamide from the molecular ion to give rise to the ion at m/z 151. The structure of oxime f could explain the resulting fragments.

A keto-enol isomerization is proposed prior the fragmentation, similar to the carbonyl hydrazones of hydroxy arylketones.⁵



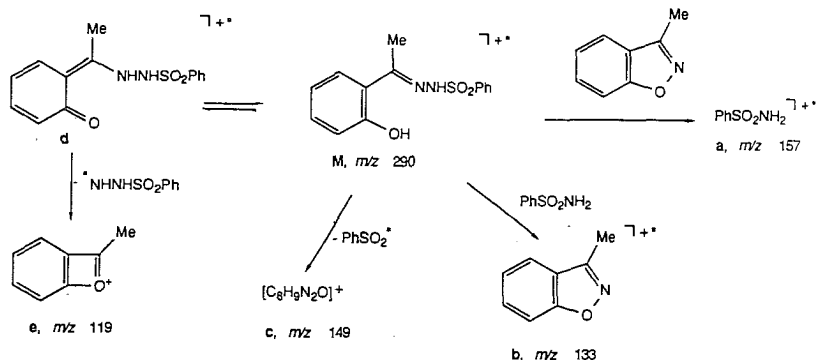
SCHEME 2. Proposed pathways for the fragmentation of semicarbazone of 2-hydroxyacetophenone (2a)

Finally, loss of a molecule of isocyanate leads to the formation of ion m. Similar pattern has been observed in the mass spectra of aliphatic semicarbazones.¹⁰ No ion corresponding to the precursor carbonyl compound was observed, contrary to the aliphatic semicarbazones.¹⁰

(iii) Sulphonylhydrazones 3. The electron impact mass spectra of sulphonylhydrazones 3 are simple. The main fragmentations resemble those discussed above and involve scission of the $=\text{N}-\text{NH}-$ and $-\text{NH}-\text{S}-$ bonds giving rise to the ions a, b and c at m/z 157, 133 and 149 respectively. However, no elimination of OH or O radicals from the molecular ion was observed. In addition, no elimination of N_2 as well as CH_3CN from c was observed, in contrast with the previously reported

extrusion of these fragments in the spectrum of phenylsulphonyl hydrazone of acetophenone.¹¹

Finally, the formation of ion e at m/z 119 could be explained by the isomerization shown in Scheme 3, as suggested for the ethoxycarbonyl hydrazones.



SCHEME 3. Proposed pathways for the fragmentation of phenylsulphonyl hydrazone of 2-hydroxyacetophenone (3a)

EXPERIMENTAL

Hydrazones 1 and 2 were prepared according to published methods.^{1,12,13} Most of them are known compounds with the exception of 1b, 1e and 2b which were characterized by their nmr spectra (Table 2) and gave satisfactory elemental analysis.

Hydrazones 3 were prepared according to the following general procedure: To a solution of the corresponding carbonyl compound (0.01 mol) in ethanol (20 ml) phenylsulphonyl hydrazide (0.01 mol) was added. The mixture was stirred at room temperature 24 hrs. The solid precipitated was filtered and dried. Hydrazones 3 gave satisfactory elemental analysis without further purification. Their nmr data are shown in Table 2.

TABLE II. Preparation and NMR Data of the Novel Hydrazones 1-3

Comp.	M.p. (lit. m.p.) [°C]	Yield (%)	¹ H NMR δDMSO/TMS	¹³ C NMR DMSO/TMS
1b	240-41	65	1.3 (t, 3H, J=7), 2.3 (s, 3H), 3.38 (s, 1H), 4.25 (q, 2H, J=7), 7.62- 7.9 (m, 2H), (s, 1H), 14.1 (s, 1H)	13.4, 14.4, 109.4, 111.6, 121.9, 129.5, 129.6, 135.0, 153.9, 154.2
1e	218	73	1.2 (t, 3H, J=7), 2.25 (s, 3H), 4.14 (q, 2H, J=7), 6.8 (s, 1H), 7.0 (d, 1H, J=8), 7.2 (d, 1H, J=8), 7.35 (m, 3H), 7.5 (m, 2H), 8.6 (s, 1H), 9.76 (s, 1H)	14.5, 20.0, 60.9, 116.4, 118.2, 120.8, 128.25, 128.4, 128.5, 129.0, 129.6, 131.6, 137.4, 149.3, 153.2
2b	210-11	86	1.15 (t, 3H, J=7), 2.76 (q, 2H, J=7), 3.48 (s, 1H), 6.35 (s, 2H), 6.88-7.5 (m, 4H), 10.0 (s, 1H)	10.5, 19.0, 117.2, 118.5, 119.0, 127.3, 130.0, 152.8, 155.2, 158.9
3a	154-55	89	2.38 (s, 3H), 6.9-8.0 (m, 9H), 11.2 (s, 1H), 11.7 (s, 1H)	14.6, 117.0, 118.9, 119.5, 127.4, 128.6, 129.5, 131.4, 133.5, 138.4, 157.6, 158.7
3b	156-57	90	0.9 (t, 3H, J=7), 2.7 (q, 2H, J=7), 6.7-8.82 (m, 9H), 11.1 (s, 1H), 11.6 (s, 1H)	11.3, 20.6, 117.7, 118.5, 119.5, 127.7, 128.8, 129.9, 131.8, 133.9, 138.8, 158.6, 163.1
3c	166	95	6.75-7.82 (m, 9H), 8.08 (s, 1H), 10.1 (s, 1H), 11.45 (s, 1H)	116.3, 119.1, 119.5, 127.2, 129.3, 131.5, 133.2, 138.8, 146.4, 156.6

Low- and high-resolution mass spectra were recorder of Finnigan MAT 4500 and AEI MS-30 spectrometers, respectively, with a 70 eV ionization energy and source temperatures in the range 150-300°C. All samples were introduced into the ion source through a direct insertion probe.

ΠΕΡΙΛΗΨΗ

Φασματα μαζών ηλεκτρονικού ιονισμού καρβονυλοϋδραζονών.

Στην εργασία αυτή μελετώνται τα φάσματα μαζών ηλεκτρονικού ιονισμού μιας σειράς αιθοξυκαρβονυλοϋδραζονών, σεμικαρβαζονών και σουλφονυλοϋδραζονών ο-υδροξυαρυλο κετονών. Το μοριακό ιόν εμφανίζεται σε όλες τις περιπτώσεις με σχετική ένταση 14-100%. Οι κύριες διαδικασίες θραυσματοποίησης περιλαμβάνουν θραύση των δεσμών N-N και N-CO. Χαρακτηριστικές εναλλακτικές θραυσματοποιήσεις παρατηρούνται παράλληλα σε κάθε τάξη ενώσεων. Οι αιθοξυκαρβονυλοϋδραζόνες εμφανίζουν θραύσματα σε τιμές που αντιστοιχούν στα ιόντα $[M-O]^+$, $[M-OH]^+$ και $[M-EtOH]^+$; ενώ οι σεμικαρβαζόνες στα ιόντα $[M-NCNH_2]^+$ και $[M-NHCO]^+$. Οι σεμικαρβαζόνες και σουλφονυλοϋδραζόνες δεν έδωσαν θραυσματοποίηση που χαρακτηρίζει την ο-υποκιτάσταση.

REFERENCES

1. Katritzky A.R. and Kotali A., *Tetrahedron Lett.*, **31**, 6781 (1990).
2. Katritzky A.R., Harris P.A. and Kotali A., *J. Org. Chem.*, **56**, 5049 (1991).
3. MacLeod J.K., Becher D. and Djerassi C., *J. Org. Chem.*, **31**, 4050 (1966).
4. Kingstone D.G.I., Tannenbaum H.P., Dimmock J.R., Baker G.B. and Taylor W.G., *J. Chem. Soc. (C)*, 2574 (1970).
5. Kotali A., and Vassiliou A., *Org. Mass Spectrom.*, **25**, 291 (1990).
6. Katritzky A.R., "Comprehensive Heterocyclic Chemistry", Vol. 5, p. 203 and Vol. 6 p. 7, Pergamon Press (1984).
7. Calbe J., Kagal S.A. and MacLeod J.K., *Org. Mass Spectrom.*, **6**, 301 (1972).
8. De K., Tashiro M. and Tsuge O., *J. Org. Chem.*, **42**, 1496 (1977).
9. Murato K., Yatsumani T. and Iwasaki S., *Helv. Chim. Acta*, **63**, 588 (1990).
10. Budzikiewicz H., Djerassi C. and Williams D.H., "Mass Spectrometry of Organic Compounds", p. 376, Holden-Day Inc. San Fransisco (1964).
11. Becher D., Sample S.D. and Djerassi C., *Chem. Ber.*, 2284 (1966).
12. Bhati A., Jonstone R.A.W. and Millard B.J., *J. Chem. Soc. (B)*, 358 (1966).
13. Beilstein, "Handbuch der Organische Chemie", **8**, 51, 534; I, 521, Spring Verlag.

MODIFICATION OF THE CLASSIFICATION OF THE ELEMENTS.

III. MOLECULAR SHIELDING CONSTANTS OF NUCLEAR CHARGE.

Ana Medved

Department of General and Inorganic Chemistry, Faculty of
Chemical Engineering and Technology, University of Zagreb.

(Received November 24, 1992)

SUMMARY

The application of molecular shielding constants is interpreted by calculating the absorption maxima in the spectrum of iodine. The principle of shielded nuclear charge is requesting a regular sequence of orbitals, i.e. the valence electrons of iodine in the *f*-orbital, whereby iodine becomes an inner transition element. In such a way, a complete accordance of the measured and calculated values of the absorption maxima resulted.

KEYWORDS

Calculation of absorption maxima in the spectrum of iodine, by the use of molecular shielding constants.

INTRODUCTION

The principle of shielding constants of nuclear charge was introduced by J.C. SLATER¹. He has determined the atomic shielding coefficients which are valid for the effective nuclear charge of atoms. Thereby the frequency rule of BOHR became applicable for polyelectronic atoms as well, but he did not mention in his work the possibility to apply such a principle for molecules, neither did he determine the molecular shielding coefficients.

In this work it is shown how ingeniously SLATER's principle solves the problem of a subatomic electrical field, giving a basis for the extension upon molecules and complex ions as well, an extension requesting a modified equation and shielding coefficients supplemented with additional values for electrons forming the covalent bond or coordinative bonds in hybridized orbitals respectively.

THEORY, MEASUREMENTS OF SPECTRA AND CALCULATIONS.

A solution of I_2 appeared as an example appropriate for the presentation of the applicability and utility of the preceding principles.

The first diagram is showing the absorption maxima viz. transmission minima in the spectrum of iodine. Literature data are completely accordant with the measured values in the spectrum, occurring at the following wave lengths:

$$\lambda = 288 \text{ nm}$$

$$\lambda = 350 \text{ nm}$$

$$\lambda = 465 \text{ nm}$$

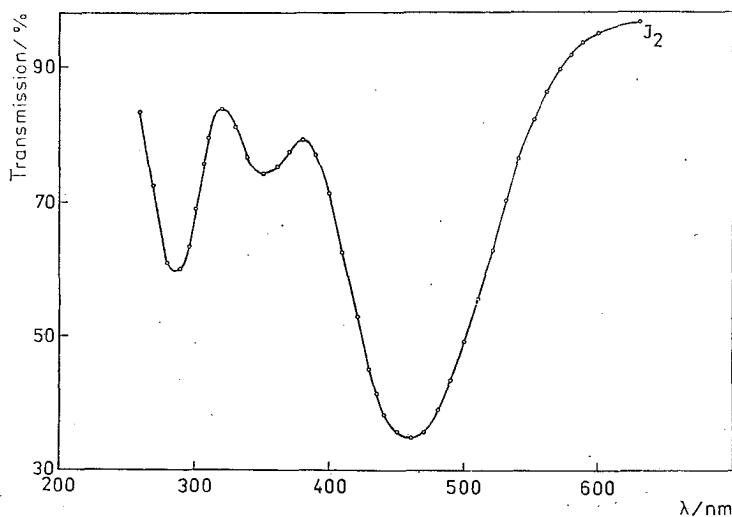


Figure 1.

The spectrum registered in a saturated water solution of I_2 .

The necessity of a modified classification of elements is gaining emphasis by calculations involving shielding constants which are requesting a parallelism between the regular sequence of quantum numbers and the sequence of filling the orbitals with electrons. It is often observed in the literature the condition essential for the scientific progress i.e. to correct or modify certain

theories or classifications² (p. 1115), f.i. for the clear understanding of the bond in the triiodide I₃ ion, the iodine must not be classified as a halogen element with a 5s² 5p⁵ configuration. By the sequence of orbitals accordant with the theory of SLATER 1s, 2sp, 3sp, 3d, 4sp, 4d, 4f, 5sp, 5d, 5f, 5g, the element iodine is classified as an f-orbital element, and based upon such a configuration its spectrum can be calculated.

The next figure displays a scheme of possible electron transitions in the iodine molecule. Four of such electron transitions are denoted with the corresponding wave lengths in the spectrum.

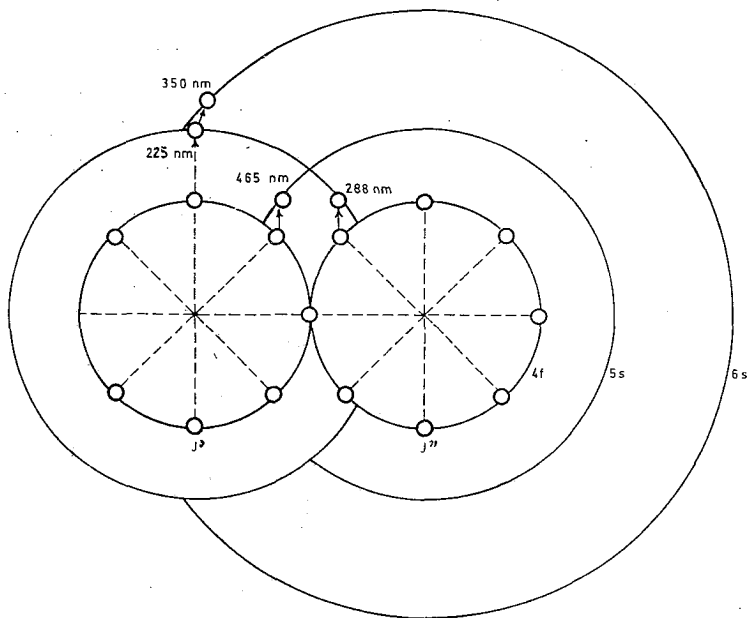


Figure 2.

The scheme of electron transition in the I₂ molecule.

The maxima of absorption were calculated by the frequency rule of BOHR:

$$h \cdot \nu = E' - E''$$

The effective nuclear charge and the corrected quantum number n* were determined after SLATER:

$$h \cdot \nu = 13,6 \cdot \left\{ \left[\frac{(Z-s)'}{n'} \right]^2 - \left[\frac{(Z-s)''}{n''} \right]^2 \right\} \quad \text{a)}$$

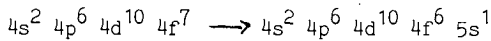
The second formula was devised for the application upon molecules:

$$h \cdot \nu = 13,6 \cdot (Z-s)''^2 \cdot \left\{ \frac{1}{n',2} - \frac{1}{n''^2} \right\} \quad \text{b)}$$

Such a formula contains the unchanged principal quantum numbers and the effective nuclear charge of the atom into which the electron is promoted. The formula is valid for interatomic transitions of electrons in a molecule and is accordant also with the FRANCK-CONDON principle stated for molecular spectra³.

The formula a) is valid for excitation spectra within the atoms. Its application is shown beneath, along with the measured value, registered in a diluted solution of a covalent compound CaI_2 .

1. Interatomic transition in a covalently bonded iodine atom



The effective nuclear charge (Z-s) was calculated by deminishing the atomic number with the shielding coefficient \underline{s} :

		(Z-s)
1s	53 - 0,3 =	52,70
2s2p	53 - 7 · 0,35 - 2 · 0,85 =	48,85
3s3p	53 - 7 · 0,35 - 8 · 0,85 =	41,75
3d	53 - 9 · 0,35 - 18 · 1,0 =	31,85
4s4p	53 - 7 · 0,35 - 18 · 0,85 - 10 · 1,0 =	25,25
4d	53 - 9 · 0,35 - 36 · 1,0 =	13,85
4f	53 - 6 · 0,35 - 46 · 1,0 =	4,90
5f	53 - 23 · 0,85 - 28 · 1,0 - 0,80 =	4,65

The coefficients $[(Z-s)/n^*]^2$ in the frequency rule of BOHR have been calculated with corrected quantum numbers n^* after SLATER in accordance with equation a) :

1s	$(52,7)^2$	2777,29
2s2p	$(48,85/2)^2$	596,34
3s3p	$(41,75/3)^2$	193,67
3d	$(31,85/3)^2$	112,71
4s4p	$(25,25/3,7)^2$	46,57
4d	$(13,85/3,7)^2$	14,01
4f	$(4,90/3,7)^2$	1,7529
5f	$(4,65/4)^2$	1,3502
		<u>0,40</u>

By inserting in the frequency rule of BOHR:

$$h \cdot \nu = 13,6 \cdot 0,40 = 5,48 \text{ eV}$$

$$\lambda = 2,25 \cdot 10^{-7} \text{ m}^{-1} = 225 \text{ nm (measured 225 nm)}$$

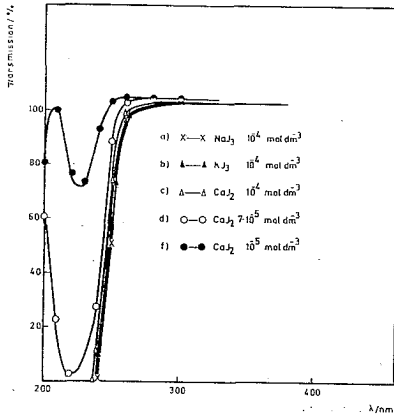
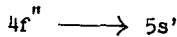


Figure 3.

The spectrum registered in a water solution of CaI_2

2. Interatomic electronic transition in the I_2 molecule



From figure 2. it is discernable that the composition of the surface layer corresponds to 7 electrons in the $4f'$ orbital of the left atom, above which the electron from the right atom is promoted. Accordingly:

$$5s' \quad 53 - 2 - 8 - 18 - 25 \cdot 0,85 = \quad (Z-s) \quad 3,75$$

ANA MEDVED

The wave number must be calculated by the application of the original quantum numbers in the frequency rule:

$$\frac{1}{\lambda} = 1,097 \cdot 10^7 \cdot (Z-s)^2 \cdot \left[\frac{1}{n^2} - \frac{1}{n'^2} \right]$$

$$\frac{1}{\lambda} = 1,097 \cdot 10^7 \cdot (3,75)^2 \cdot \left[\frac{1}{16} - \frac{1}{25} \right]$$

$$\frac{1}{\lambda} = 1,097 \cdot 10^7 \cdot 14,06 \cdot 0,0225$$

$$\lambda = 288 \text{ nm (measured 287 nm)}$$

3. Interatomic transition in the higher level



After the transfer of the electron from the 4f'' orbital, into the 5s' orbital of the left atom, the promotion into the 6s'' orbital of the right atom can occur. By using 6 electrons as the number of electrons in the righthand 4f'' orbital, the calculated wave length is in agreement with the measured maximum, whereas the covalent electron and the 7th electron are reckoned as belonging to the left atom in such a moment.

The effective nuclear charge is calculated, accordingly, with 24 electrons in the surface layer:

$$6s'' \quad 53 - 2 - 8 - 18 - 24 \cdot 0,85 = \begin{matrix} (Z-s) \\ 4,6 \end{matrix}$$

Inserting this in the formula b) derived previously, results in a calculated wave length agreeing with the experimental value of the second maximum (Figure 1.)

$$\frac{1}{\lambda} = 1,097 \cdot 10^7 \cdot (4,6)^2 \cdot \left[\frac{1}{25} - \frac{1}{36} \right]$$

$$\frac{1}{\lambda} = 1,097 \cdot 10^7 \cdot 21,16 \cdot 0,123 = 0,285 \cdot 10^7 \text{ m}^{-1}$$

$$\lambda = 350 \text{ nm (measured 350 nm)}$$

MODIFICATION OF CLASSIFICATION OF THE ELEMENTS

4. Interatomic electronic transition



The absorption at 465 nm is effected by a transition of electrons from the 4f' orbital of the left atom into the 5s'' orbital of the neighboring atom in the iodine molecule. In the moment of the electron transition, there are 26 electrons underneath the 5s'' orbital, participating in the shielding of the nuclear charge:

$$5s'' \quad 53 - 2 - 8 - 25 \cdot 0,85 - 0,8 = \quad (Z-S) \quad 2,95$$

The shielding constant for the covalent electron is quantized with a coefficient 0,8.

$$\frac{1}{\lambda} = 1,097 \cdot 10^7 \cdot (2,95)^2 \cdot \left\{ \frac{1}{16} - \frac{1}{25} \right\}$$

$$\frac{1}{\lambda} = 1,097 \cdot 10^7 \cdot 8,70 \cdot 0,0225 = 0,215 \cdot 10^7 \text{ m}^{-1}$$

$$\lambda = 465 \text{ nm (measured 465 nm)}$$

The exact correspondence of the calculated and measured wavelengths of the absorption maxima in the spectrum of iodine is convincingly indicating the necessity of classifying I₂ as an inner transition element. The theoretical impass, mentioned in BAILLAR² in connection with the configuration of the triiodide ion, is removed thereby.

Particular attention deserves the shielding coefficient of the electron obtained by the covalent bond. The determination of its value relies upon identical principles which were applied by SLATER for the atomic shielding constants, namely the attainment of the most acceptable value accordant with the experimental values.

Consequently, whether the shielding coefficients are reliable it can be shown by a further test f.i. by calculating the absorption maxima in the violet solutions of iodine. Might the theory guide and the measurement of the wave length enable the comparison.

The scheme on figure 2. is indicating which of the remaining electron transitions is possible. It is the transition from the 5th energy level of the left atom into the 6th layer on the right:



The estimation of the nuclear charge was done by including as shielding electrons 24 electrons below and in addition an electron obtained by the covalent bond:

$$6s' \quad 53 - 2 - 8 - 18 - 24 \cdot 0,85 - 0,8 = \quad 3,80$$

$$\frac{1}{\lambda} = 1,097 \cdot 10^7 (3,80)^2 \cdot \left\{ \frac{1}{25} - \frac{1}{36} \right\}$$

$$\frac{1}{\lambda} = 1,097 \cdot 10^7 \cdot 14,44 \cdot 0,0123 = 0,195 \cdot 10^7 \text{ m}^{-1}$$

$$\lambda = 513 \text{ nm (measured 512 nm)}$$

The spectroscopically measured value in the solution of iodine in CHCl_3 is remarkable consistent with the theory.

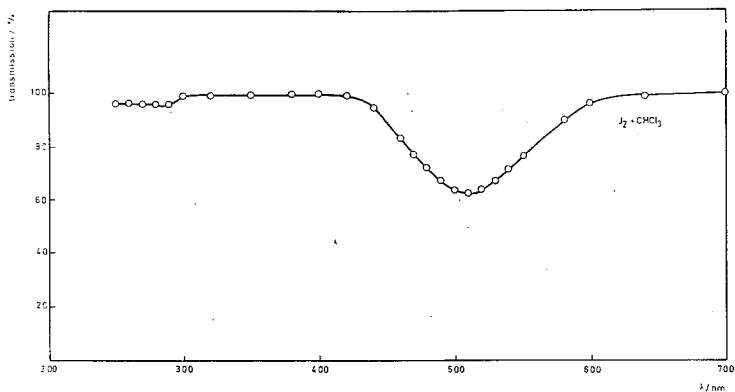
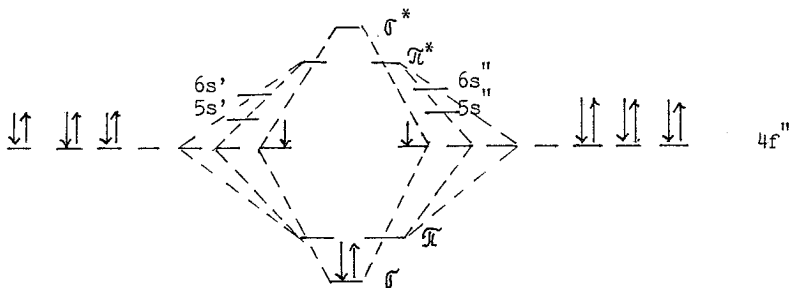


Figure 4.

The spectrum registered in a solution of I_2 in CHCl_3

The scheme shown in Figure 2. is indispensable for the correct assignment of the maxima in the spectrum of iodine, but the preceding principles and the bonding in the I_2 molecule are gaining clarity by the MO diagram containing 7 electrons in the f -orbitals. Whereas the conventional classification does not comply completely with the properties of iodine, the f -orbital insertion is in accord with all experimentally established properties of such element.



The electrons forming the covalent bond are not participating in the electron transitions, instead the transitions are effected by nonbonding electrons.

The calculations are revealing that the nonbonding electrons are paired, which means that the rule of HUND is not valid for large atoms. Such founding is in BAILAR² (p.1558) explained by stereochemical arguments.

The spectra of iodine have been studied extensively^{4,5,6,7,8,9} but the conventional sp-orbital MO diagram is in discord with the spectroscopic data, and several properties of iodine can not be interpreted as long as iodine is regarded as a halogen element. In contrast, the f -orbital approach shown in this work has established accordance between the experimental values and the theory.

ΠΕΡΙΛΗΨΗ

Μετατροπές στην ταξινόμηση των στοιχείων.Μοριακές σταθερές προασπίσεως πυρηνικού φορτίου.

Η εφαρμογή των μοριακών σταθερών προάσπισης ερμηνεύεται με υπολογισμό των μεγίστων απορρόφησης στο φάσμα του ιωδίου.Η αρχή της προάσπισης του πυρηνικού φορτίου απαιτεί μία κανονική ακολουθία τροχιακών, ήτοι των ηλεκτρονίων σθένους του ιωδίου εις το f - τροχιακό, όπου το ιώδιο γίνεται ένα εσωτερικό στοιχείο μετάπτωσης.Κατ'αυτόν τον τρόπο προέκυψε πλήρης συμφωνία μεταξύ μετρήσεων και τιμών που υπολογίσθηκαν για τη μέγιστη απορρόφησης.

REFERENCES

1. J. C. SLATER: "Atomic Shielding Constants", Phys. Rev. A. Chem. Soc. 36, (1930), 57.
2. J. C. BAILAR et al.: "Comprehensive Inorganic Chemistry" Edited by Pergamon Press, Oxford, 1975, Vol. 2.
3. G. HERZBERG: "Molecular Spectra and Molecular Structure" Edited by Van Nostrand Comp. Princeton, 1957.
4. A. MEDVED: "A Modification of the Classification of the Elements. II. The Bonding in KI_3 and NaI_3 " Chim. Chron. 19, (1990).183-194.
5. H. ISCI and W. R. MASON: Inorg. Chem. 24, (1985) 271.
6. J. A. COXON: "Molecular Spectroscopy", Vol. 1. Chem Soc. Special. Periodical Report, (1973) 177.
7. W. P. TASHER: Mol. Phys. 33, (1977), 511.
8. N. N. GREENWOOD and A. EARNSHAW: "Chemistry of the Elements" Pergamon Press, Oxford, 1986.
9. GMELIN'S HANDBUCH DER ANORGANISCHEN CHEMIE: Jod, (1933), Verlag Chemie, Weinheim.

SHORT PAPER

Chimika Chronika, New Series, 22, 55-63 (1993)

NEPHELOMETRIC DETERMINATION OF THE TETRABUTYLAMMONIUM CATION

GERASIMOS M. TSIVGOULIS, DIONYSIOS S. ANAGNOSTOPOULOS and PANAYIOTIS V. IOANNOU*

Department of Chemistry, University of Patras, Patras, Greece

(Received October 24, 1991)

Key words: Nephelometry; tetrabutylammonium determination; sodium tetrphenylborate; clathrate hydrates.

INTRODUCTION

To investigate the phase diagram of $\text{Bu}_4\text{NOH}/\text{H}_3\text{AsO}_3/\text{H}_2\text{O}^1$ by the Schreinemakers' method we needed a sensitive method to determine the tetrabutylammonium cation in the presence of As(III). Existing methods for the determination of this cation use potentiometric titrations,²⁻⁴ liquid chromatography with indirect photometric detection⁵ but the majority of the methods are based on ion pair formation with bromophenol blue or bromothymol blue,² anthracene-2-sulfonate,⁶ bis(maleonitriledithiolato)nickelate(II),⁷ $\text{Fe}(\text{SCN})_m^{n-}$,⁸ and methyl orange⁹ followed by extraction and photometric^{2,7-9} or fluorimetric⁶ determination.

Sodium tetraphenylborate is a precipitation reagent for large cations, including tetrabutylammonium.³ We found that this reagent is also suitable for the nephelometric determination of the tetrabutylammonium cation.

EXPERIMENTAL

Apparatus . A Hach model 2100 A turbidimeter and a WTW micro-processor pHmeter model pH 95 were used.

Reagents . All reagents were of analytical-reagent grade. Te-

trabutylammonium hydrogen sulfate was prepared by neutralizing aqueous tetrabutylammonium hydroxide with sulfuric acid and recrystallizing twice from acetone, m.p. 171-2°C (literature¹⁰ m.p. 172.5°C). Triply distilled water, pH 5.7 ± 0.5, was used for the preparation of all solutions.

Tetrabutylammonium hydrogen sulfate. A 75.0 μM solution was prepared by dissolving 0.0255 g of the compound in 1L of water in a volumetric flask.

Sodium tetrphenylborate. A 4.38 mM aqueous solution was used. *Sulfuric acid.* 5M and 5 mM aqueous solutions were prepared from concentrated sulfuric acid.

Sodium hydroxide solution. 10 M and 10mM aqueous solutions were used.

Aqueous salt solutions. 7.5 mM and 0.75 mM aqueous solutions were used for interference studies.

Procedure. A typical procedure is as follows: To a 50 ml conical flask 19.70 ml water is added followed by 2.00 ml tetrabutylammonium hydrogen sulfate solution and swirled for mixing. Sodium tetrphenylborate solution (3.30 ml) is added on the surface of the solution in a circular manner, the flask is swirled gently for 2-3 s and then is left undisturbed for 30 min (unless the effect of time on the turbidity was studied) till the measurement.

The pH adjustment or the addition of solution for interference studies was always done before the addition of sodium tetrphenylborate solution.

The final volume, 25.0 ml, of the sample was transferred to the instrument's cell for measurement. All samples were kept at room temperature (23 ± 1°C). Duplicate samples were always run except for the calibration curve for which they were run in quintuple.

Statistical analyses. The analytical characteristics of the method were evaluated according to Miller and Miller.¹¹

RESULTS AND DISCUSSION

The concentration of the two combining ions and the stability of the suspension with time. At three concentrations of Bu_4N^+ (3, 9 and 15 μM) the effects of BPh_4^- concentration (from 59 up to 1170 μM) and time (from 10 min after mixing up to 120 min) were studied. The results are shown in Figure 1. At 3 μM Bu_4N^+ the suspensions give more consistent readings (NTU, Nephe-

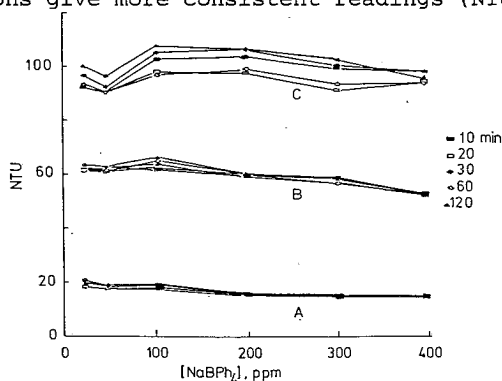


FIG.1. Effect of the reagent (NaBPh_4) concentration and time on the magnitude and stability of the turbidity. [Bu_4NHSO_4]: A 3, B 9, and C 15 μM . ■ 10, □ 20, ◆ 30, ◇ 60, and ▲ 120 min after mixing.

lometric Turbidity Unit) both with respect to excess of BPh_4^- and to time. Increasing the concentration of Bu_4N^+ causes a slight decrease of the readings at higher BPh_4^- concentrations, but they are fairly stable with time. At 15 μM Bu_4N^+ the readings are not stable with respect to both variables. We therefore have chosen a final concentration of NaBPh_4 200 p.p.m. (585 μM) for all our measurements and 30 min waiting time after mixing.

Effect of pH. The effect of pH on the turbidity was studied at constant NaBPh_4 concentration (585 μM) and three different Bu_4NHSO_4 concentrations. Results are shown in Figure 2. Sulfuric acid and sodium hydroxide were used for pH ad-

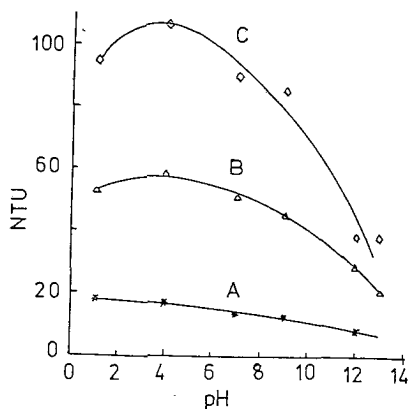


FIG.2. Effect of pH on the turbidity. $[\text{NaBPh}_4]: 585 \mu\text{M}$, $[\text{Bu}_4\text{NHSO}_4]$: A 3, B 9, and C 15 μM .

justment. The suspensions were stable up to 90 min after mixing. Figure 2 reveals that there is a pH-dependence and there is a maximum at pH 3-5. However the turbidity of CsBPh_4 is independent on pH changes.¹²

Interference. It is well known that Bu_4N^+ and BPh_4^- give insoluble salts in water with large anions, e.g. I_3^- ¹⁰ and large cations, e.g. K^+ , NH_4^+ , Rb^+ , Cs^+ , Cu(I) , Hg(I) , Ag^+ , Tl(I) ^{12,13} respectively. We therefore studied the effect of some anions and cations, which are likely to be encountered in practice, on the turbidity of Bu_4NBPh_4 . Because methanolic solutions of tetrabutylammonium hydroxide are commercially available, we also studied the effect of methanol on the turbidity. The results are shown in Table I. The interfering species of Table I interfere negatively compared to controls. The negative interference may not totally be associated to pH, because the pH of the solutions of

the hydrolyzable ions were in the range 5-6.5, while that of the controls, before the addition of the sodium tetraphenylborate solution were 5.7-6.3 (the pH after the addition of the reagent cannot be measured because precipitation takes place). Therefore the negative interference can probably be attributed to the number and size of the particles produced under these conditions. Methanol interferes by solubilizing the tetrabutylammonium tetraphenylborate salt.

TABLE I. Effect of different species on the turbidity of tetrabutylammonium hydrogen sulfate ($9 \mu\text{M}$) in the presence of sodium tetraphenylborate ($585 \mu\text{M}$). The interfering compounds affect the turbidity negatively.

Species	interference		
	mole Bu_4N^+ per mole species		
	1:100	1:10	1:1
Ions			
HSO_4^-	No		
Cl^-	No		
Br^-	Yes	Yes	No
I^-	Yes	Yes	Yes
H_2PO_4^-	Yes	Yes	No
H_3AsO_3^*	No	No	No
H_3AsO_4^*	Yes	No	No
Na^+	No		
K^+	Yes	Yes	Yes
NH_4^+	Yes	No	No
Solvent**	1% v/v	0.1% v/v	0.01% v/v
CH_3OH	Yes	No	No

* pH adjusted at 5.0

** volume of solvent in water

TABLE II. Turbidity of tetrabutylammonium hydrogen sulfate standards, at sodium tetraphenylborate concentration of 585 μM . The equation for the calibration graph is $y = 6.41 \cdot 10^6 x - 1.24$ and its correlation coefficient is $r = 0.9989$

Sample	Final concentration of Bu_4NHSO_4 , μM	NTU	Standard deviation
1	0	0.5	0.4
2	3.0	16.2	0.3
3	6.0	35.7	0.6
4	9.0	57.5	2.2
5	12.0	77.0	0.8
6	13.5	84.5	0.4

Analytical characteristics. Table II shows the NTU readings of standard solutions of Bu_4NHSO_4 pH 5.7-6.3 in the presence of constant concentration (585 μM) of NaBPh_4 and the equation of the calibration graph obtained. Linearity covers the range 3-13.5 μM , but data (not included) show that the linear part covers the range 0.3-30 μM Bu_4NHSO_4 . At higher concentrations the line curves to the x axis.

From the calibration graph the precision and accuracy of the method were evaluated: the coefficient of variation is 4.2% for the entire range (3-13.5 μM Bu_4NHSO_4), and the percentage error is -9.3% at 3 μM , -4.0 at 6 and +1.8 at 9 and 12 μM Bu_4NHSO_4 . The limit of detection from the graph¹¹ and from blanks (three times the standard deviation of the mean of 5 blanks) was 1 μM when working in the range 3-13.5 μM .

Applicability of the method. The method has been applied to the determination of the Bu_4N^+ in the system $\text{Bu}_4\text{NOH}/\text{H}_3\text{AsO}_3/\text{H}_2\text{O}$ by the Schreinemakers' wet residue method. The calibration

graph obtained at pH 9 in the range 5-24 μM Bu_4N^+ had $r = 0.9987$, and it was the same in the presence of arsenite. Eight replicates of titrated aqueous tetrabutylammonium hydroxide of $10.3 \pm 0.2 \mu\text{M}$ gave by the turbidimetric method $\bar{x} \pm \text{SD}$ $10.2 \pm 0.1 \mu\text{M}$. The results obtained showed that clathrate hydrates of the type $\text{Bu}_4\text{NOH} \cdot (21.1 \pm 1.5) \text{H}_2\text{O}$ and $\text{Bu}_4\text{NOH} \cdot (8.5 \pm 1.5) \text{H}_2\text{O}$ were formed.¹ The method should be applicable to other systems provided the effect of possible interfering species can be eliminated or evaluated.

CONCLUSIONS

The nephelometric determination of the Bu_4N^+ by BPh_4^- is simple, precise and accurate. It only requires dilution of the sample and adherence to the protocol for the generation of the suspension. Large cations and anions interfere at various degrees. The calibration graph and the measurements of the unknown solutions should be done under the same conditions.

ΠΕΡΙΛΗΨΗ

Νεφελομετρική μέθοδος προσδιορισμού του Bu_4N^+

Αναπτύχθηκε μία απλή νεφελομετρική μέθοδος προσδιορισμού του κατιόντος τετραβουτυλαμμωνίου με τετραφαινυλοβορικό ανιόν. Απαιτεί μόνο αραιώση του δείγματος και προσοχή στον τρόπο δημιουργίας του εναιωρήματος. Στην περιοχή 3-13,5 μM Bu_4NHSO_4 ο συντελεστής μεταβλητότητας ήταν 4,2%, το επί τοις εκατό σφάλμα ήταν +1,8% σε συγκέντρωση Bu_4NHSO_4 9 μM , και το όριο ανιχνεύσεως ήταν 1 μM Bu_4N^+ . Μεγάλα ανιόντα και κατιόντα παρεμποδίζουν τον προσδιορισμό. Η καμπύλη αναφοράς και οι μετρήσεις των αγνώστων πρέπει να γίνονται κάτω από τις ίδιες συνθήκες.

ACKNOWLEDGEMENTS

The financial support by the General Secretariat of Research and Technology, Ministry of Industry, Energy and Technology is gratefully acknowledged.

REFERENCES

1. Tsivgoulis, G.M., and Ioannou, P.V., *Chimika Chronika*, New Series, 1991, 20, 59.
2. Siggia, S., and Hanna, J.G., "Quantitative Organic Analysis via Functional Groups", 4th Edition, Wiley-Interscience, N.York, 1979, pp 688-693.
3. Bermudez, G., Blanco, H.L., and Vargas, N., *Rev.Colomb. Quim.*, 1982, 11, 33; *Chem.Abst.*, 1983, 98, 142895t.
4. Gur'er, I.A., and Drofa, M.I., *Zh.Anal.Khim.*, 1983, 38, 1659; *Chem.Abst.*, 1984, 100, 16974g.
5. Larson, J.R., and Pfeiffer, C.D., *Anal.Chem.*, 1983, 55, 393.
6. Westerlund, D., and Borg, K.O., *Acta Pharm.Suecica*, 1970, 7, 267; *Chem.Abst.*, 1970, 73, 69913z.
7. Sadanobu, I., and Sasaki, M., *Kitami Kogyo Daigaku Kendyn Hokoku*, 1981, 12, 221; *Chem.Abst.*, 1981, 95, 108157g.
8. Mendez, J.H., Perez, C.G., Sanz, M.J.C., and Melchor, A.B., *Quim. Anal. (Barcelona)*, 1984, 3, 129; *Chem.Abst.*, 1985, 103, 31798r.
9. Simon, M.B., Cózar, A. De E., and Díez, L.M.P., *Analyst*, 1990, 115, 337.
10. Brändström, A., "Preparative Ion Pair Extraction", *Apotekarsocieteten*, Stockholm, 1976, p.141.
11. Miller, J.C., and Miller, J.N., "Statistics for Analytical Chemistry", Ellis Horwood, Chichester, U.K., 1984, Chap.4.
12. Sahoo, P., Parida, F.C., Sivasubramanian, K., and Mukunda Rao, S.R., *Analyst*, 1990, 115, 1129.

13. Kolthoff, I.M., Sandell, E.B., Meehan, E.J., and Bruckenstein, S., "Quantitative Chemical Analysis", 4th Edition, Mackillan, London, 1969, p.276.

CONTENTS

Mechanistic study of the rate of conversion of 1-amino-3-imino-heptafluorocyclohexene with weak organic acids by dynamic NMR <i>by A.Valavanidis</i>	3
Polymerization of Ph-C≡C-Ph using MCl _x /AlCl ₃ (M=Nb,Ta,Mo,W and x=5,6) as catalyst <i>by M.G.Siskos, G.Kyriakakou</i>	13
Reaction of PPh ₂ Cl, PBu ₃ or PPh ₃ with aroylhydrazines <i>by D.A.Haristos</i>	23
Electron impact mass spectra of some ethoxycarbonyl hydrazones, semicarbazones, and sulphonylhydrazones of o- hydroxyarylketones <i>by A.Kotali</i>	35
Modification of the classification of the elements.III.Molecular shielding constants of nuclear charge <i>by Ana Medved</i>	45
Short Paper	
Nephelometric determination of the tetrabutylammonium cation <i>by G.M.Tsivgoulis, D.S.Anagnostopoulos, P.V.Ioannou</i>	55

*This year visit
Macedonia*

Macedonia

For 4,000 years* steeped in the history of Greece

Statue of Aristotle, Stagira.



Aristotle, the tutor of Alexander the Great, was born in Stagira in Macedonia in 384 BC. Together with Plato, he is regarded as one of the greatest philosophers the world has known. Aristotle was a true academic, concerned with Physics, Astronomy, Rhetoric, Literature, Political Science and History. His teachings laid the foundation for modern scientific thought.

The White Tower of Thessaloniki.



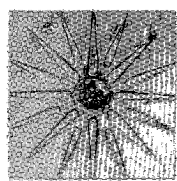
Thessaloniki, the heart of Macedonia, is a modern city with 1,000,000 inhabitants. It is strategically located at the crossroads of Europe with Asia. Having spread the Word at Philippi, the Apostle Paul continued his teachings in Thessaloniki. Its important monuments from antiquity and byzantium up to the present, provide testimony to the role that the city has played as the second capital of Hellenism.

The Bust of Alexander the Great, Acropolis Museum, Athens.



Alexander was born in 356 BC in Pella, Macedonia, established by his father Philip II, as the centre of Hellenism. Nurtured on the thoughts of his tutor, Aristotle, he rose to fame as a brilliant military leader. He influenced the course of history, rightfully earning his title as Alexander the Great. In 335 BC he became Commander in Chief of all the Greeks. By the time of his death in 323 BC he had created an enormous empire, stretching from the shores of the Adriatic to India, and from the Caucasus Mountains to Egypt. He spread the Greek spirit far and wide among nations who worshipped him as a god.

Symbol of the Greek Macedonian Dynasty from the tomb of Philip II, Archaeological Museum, Thessaloniki.



This 16 pointed star of Vergina was uncovered during the archaeological excavations at Vergina. This symbol of the Greek Macedonian Dynasty decorated the golden tomb of Philip II. The Star of Vergina, extracted from the soil of Macedonia, has since become the symbol of Hellenism.

The Olympian Aphrodite (3rd Century BC) Museum of Dion.



This statue of Aphrodite came to light during archaeological digs at the ancient sacred city of Dion. Dion, at the foot of Mt Olympus, was the most important spiritual site for the Northern Greeks, playing the same role in their lives as that of the oracle at Delphi.

4,000 years:* Post-Mycenaean ceramic relics found in Assiros and Mycenaean swords found in Grevena date back 4,000 years, evidence of Macedonia's role at the vortex of Greek history. Even in mythology Macedonia, mythical founder of the Macedonian race, is the son of Aeolus (god of the winds). Throughout the years Macedonia contributed to the fountain of knowledge of the Ancient Greeks. In the 5th century BC Demokritos, father of Atomic Theory, lived and worked in Avdira.

St Dimitrios, detail of 7th Century Mosaic, Church of St. Dimitrios, Thessaloniki.



St Dimitrios, Protector of the city of Thessaloniki, was martyred in 305 AD defending Christianity. He is regarded as the Patron Saint of Thessaloniki and its saviour during difficult moments.



Come to Greece and visit Macedonia

G R E E C E
Chosen by the Gods