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CHIMIKA CHRONIKA, *NEW SERIES*

CONTENTS

September 1975 Volume 4, Number 3

Chimika Chronika, New Series, 4, 75-79 (1975)

PARAMAGNETIC CENTERS IN X-RAY IRRADIATED $ZnSO_4(NH_4)_2SO_4 \cdot 6H_2O$ SINGLE CRYSTALS

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(Received February 11, 1975)

Summary

Analysis of the electron spin resonance spectra of X-ray irradiated single crystals of $ZNSO_4(NH_4)_2SO_4 \cdot 6H_2O$ shows that paramagnetic centers of F type are formed around the radical $NH_{3\pm}$. Isotropic hyperfine splittings are found equal to 64.26 MHz for the nitrogen and 68.48 MHz for the hydrogen.

Introduction

It is well known that X-ray irradiation produces paramagnetic defects in single crystals. It has been shown[1] that in crystals of NH_4ClO_4 paramagnetic defects are produced which can be identified as the radical $NH_{3\pm}$. In this paper the analysis of the paramagnetic defects produced by the X-ray irradiation of $ZnSO_4(NH_4)_2SO_4 \cdot 6H_2O$ single crystals is presented.

Experimental

Single crystals were grown from aqueous solution[2] of $ZnSO_4 \cdot 7H_2O$ and $(NH_4)_2SO_4$. The saturated aqueous solution which had originally a temperature of 40°C was cooled gradually to the room temperature at the rate of 0.5°C degrees/hour. The crystals were irradiated for 3 hours at room temperature with a copper target X-ray tube operating at 34 KV and 18 mA. Crystals were 5 cm from the window of the tube.

Tutton salt $ZnSO_4(NH_4)_2 \cdot 6H_2O$ is monoclinic containing four nitrogen atoms and four sulphur atoms in the unit cell. Every Zn atom is surrounded by six aqueous molecules. Cell dimensions are $a_o = 9.223$ A°, $b_o = 12.50$A°, $c_o = 6.237$A° and the angle $B = 106°52'$. The space group is $C_{5_{2h}}$ $(P_{2_{1/a}})$.[3,4]

The E.S.R. spectra were taken with an X band spectrometer in a TE_{011} cylindrical cavity and 100 KHz field modulation.

Results

E.S.R. spectra were taken at room temperature from the planes of the axes a,b,c.* There are two types of spectra which are 200 gauss and 2,500 gauss wide about the center field 3,371 gauss.

The 200 gauss wide spectrum from the ac* plane ($c^* = c\sin\beta$) consists of a strong line, Q, at 3,371 gauss which is isotropic in the rotation of the field and twelve

anisotropic lines in four groups of three lines. The relative intensity of the groups is 1:3:3:1. The center of gravity of the lines is isotropic in the rotation of the field and coincides with the Q line. Fig. 2a and 2b shows the angular variation of the hyperfine splittings when the magnetic field lies in the ac* plane.

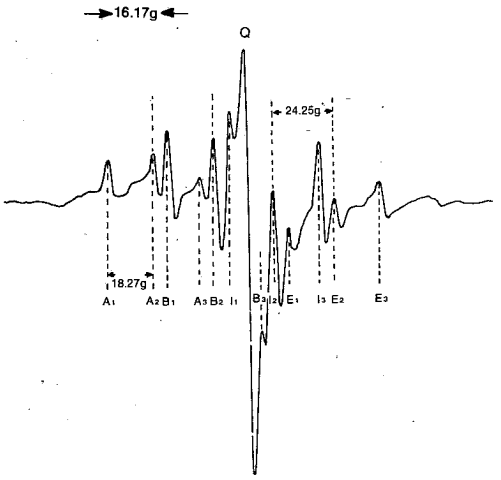

FIG. 1. *E.P.R. Spectrum of irradiated* $ZnSO^{4}(NH_4)_2SO_4 \cdot 6H_2O$ *Single crystal.*

The 200 gauss wide spectra of the ab and c*b planes consist of a group of six anisotropic lines and of one isotropic line, Q, in 3,371 ±0.5 gauss. The variation of the hyperfine splittings is shown in Fig. 3 and 4 when the magnetic field lies in the ab and c*b planes respectively.

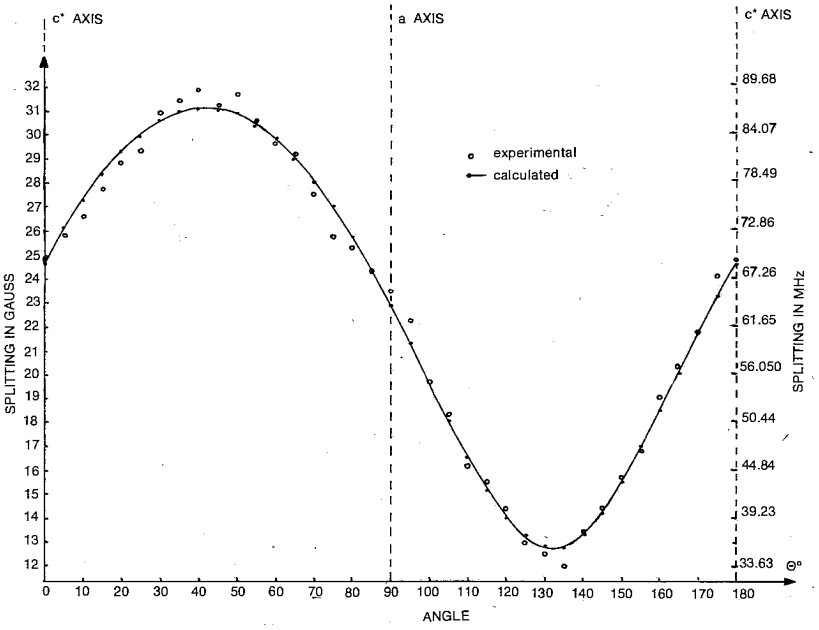

FIG. 2 a . *Angular variation of the hyperfine splitting* A_N *of the* $NH_3 \pm$ *defect when magnetic field lies on the ac* plane.*

The 2,500 gauss wide spectra taken on the three planes ac*, ab, c*b consist of many weak lines strongly anisotropic. The measurement of the crystal conductivity with a R, C Boonton 74C bridge at room temperature showed that it remained constant after irradiation. The crystal conductivity was found $10^{-8}\ \Omega^{-1}\ cm^{-1}$ at 8 KHz and $10^{-10}\ \Omega^{-1}$ at 200 KHz.

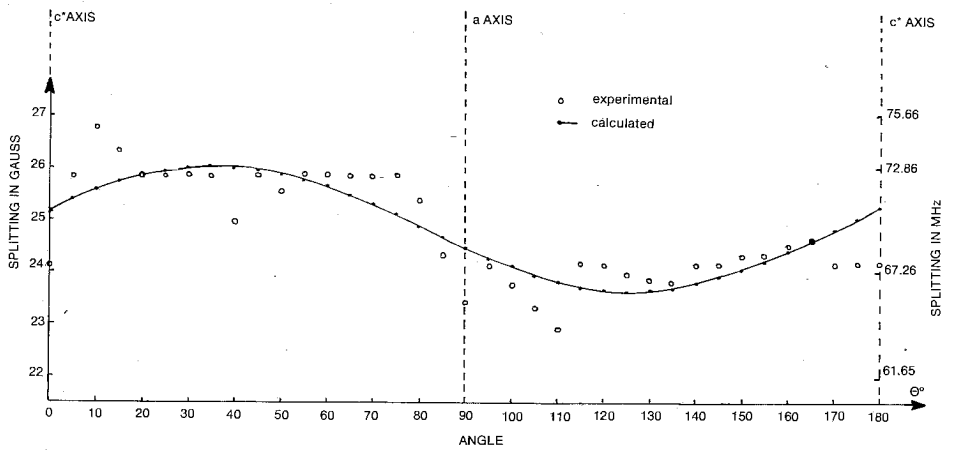

FIG. 2b. *Angular variation of the hyperfine splitting A_H of the $N_{H3\pm}$ defect when magnetic field lies on the ac* plane.*

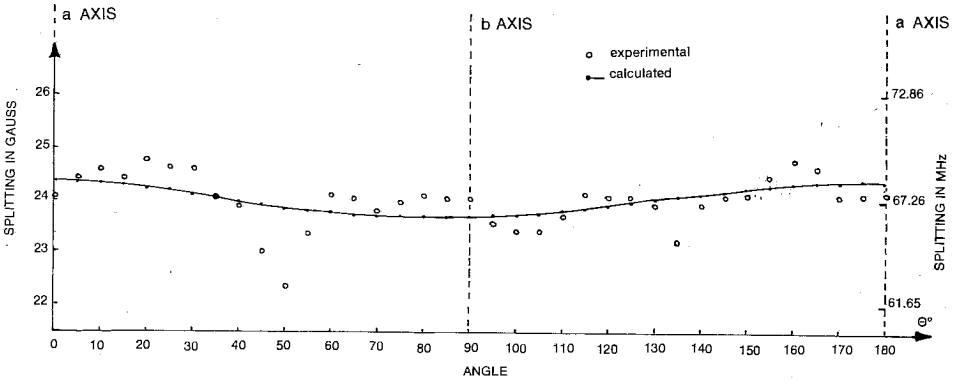

FIG. 3. *Angular variation of the hyperfine splitting A_N of the $NH_{3\pm}$ defect when magnetic field lies on the ab plane.*

Analysis

Analysis of the 200 gauss wide spectra showed that their center of gravity is on the Q line which coincides with the line of D.P.P.H. This means that the Q line and the lines of the group have the same isotropic g factor equal to 2.0033.

The small value of the crystal conductivity in combination to the isotropic g factor leads to the conclusion that the paramagnetic centers are of F type.

The spectrum of Fig. 1 can be decomposed into an equally spaced triplet of quarters. Each quarter has relative intensities of 1:3:3:1 as illustrated in Fig. 5. This spectrum arises if the unpaired electron in the defect interacts with one nucleus of spin 1 (as nitrogen) and three equivalent nuclei of spin 1/2 (as hydrogen).

In Table I the components of the hyperfine splitting tensors their normalized eigenvectors and their direction are given.

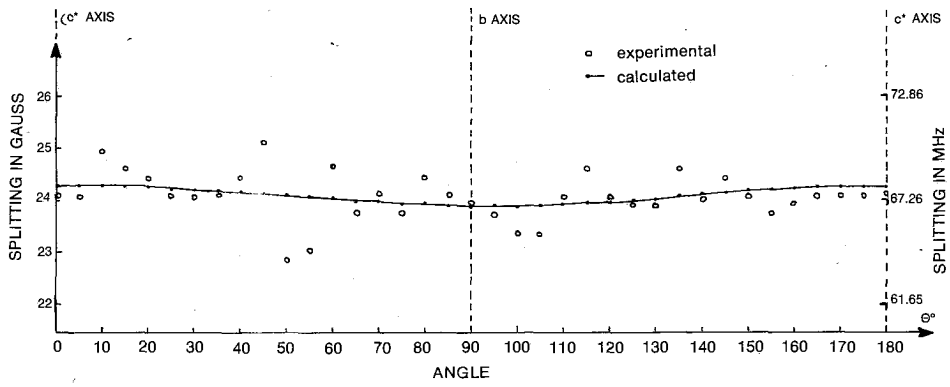

FIG. 4. *Angular variation of the hyperfine splitting AN of the $NH_{3\pm}$ defect when magnetic field lies on the bc* plane.*

From the crystal structure analysis it was found that: a) in the crystal cell there are two directions along which pairs of atoms of sulphur and nitrogen lie in their closest distance and b) these directions intersect c axis at an angle of 33°84′ and they are vertical to the b axis.

TABLE I.

Eigenvalues of the A^2 tensor	Normalized eigenvectors	Direction	Components of The AN tensor Gauss (MHz)
$(A^2)_{XX}$ 990.651	0.689-0.0009 0.725	46°.450 90°.051 43°.531	$(A_N)_{XX}$31.474 (88.204)
$(A^2)_{YY}$ 178.654	-0.724-0.006 0.689	136°.470 90°.344 46°.450	$(A_N)_{YY}$13.366 (37.457)
$(A^2)_{ZZ}$ 575.046	-0.004 0.999 0.005	90°.230 2°. 562 89°.713	$(A_N)_{ZZ}$23.980 (67.203)
Eigenvalues of A^2 tensor	Normalized eigenvectors	Direction	Components of the AH tensor Gauss (MHz)
$(A^2)_{XX}$ 662.189	0.654-0.002 0.756	49°.156 90°.114 40°.887	$(A_H)_{XX}$25.733 (72.116)
$(A^2)_{YY}$ 556.726	-0.748-0.145 0.648	138°.417 98°.337 49°.609	$(A_H)_{YY}$23.595 (66.124)
$(A^2)_{ZZ}$ 575.298	-0.072 0.994 0.08	94°.128 6°.278 85°.411	$(A_H)_{ZZ}$23.985 (67.172)

It is obvious that this direction is strongly related to the direction of the weakest component of the hyperfine splitting tensors.

Thus it was concluded that the paramagnetic defect is the radical $NH_{3\pm}$.

Isotropic hyperfine splitting constant for the radical $NH_{3\pm}$ was calculated.

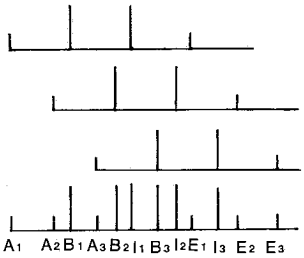

FIG. 5. *Synthesis of the $NH_{3\pm}$ spectrum from a triplet of quarters.*

$a_N = 64.26 \pm 0.4$ MHz for the nitrogen and
$a_H = 68.48 \pm 0.4$ MHz for the hydrogen.

It is probable[5] that the 2,500 gauss wide group of lines comes from the ^{33}S of the radical SO_4 due to the fact that in the spectrum there are groups of four lines which can be produced by the interaction of a single electron with a nucleus of spin 3/2.

Περίληψις

Παραμαγνητικὰ κέντρα εἰς κρυστάλλους $ZnSO_4(NH_4)_2 \cdot 6H_2O$ ἀκτινοβοληθέντας δι' ἀκτίνων X.

Ἡ ἀνάλυσις φασμάτων συντονισμοῦ ἠλεκτρονικῆς στροφορμῆς ληφθέντων ἐκ μονοκρυστάλλων $ZnSO_4(NH_4)_2SO_4 \cdot 6H_2O$ ἀκτινοβοληθέντων δι' ἀκτίνων X δεικνύει τὴν δημιουργίαν παραμαγνητικῶν κέντρων τύπου F πέριξ τῆς ρίζης $NH_{3\pm}$. Διακρίνομεν δύο φάσματα εὔρους 200 gauss (ἰσχυρὸν) καὶ 2500 gauss (ἀσθενές). Τὸ πρῶτον φάσμα ἀποτελεῖται ἐκ μιᾶς λίαν ἰσχυρᾶς ἰσοτρόπου κεντρικῆς γραμμῆς καὶ δώδεκα ἀνισοτρόπων γραμμῶν, ἐνῶ τὸ δεύτερον φάσμα ἀποτελεῖται ἀπὸ πληθώραν ἀσθενῶν γραμμῶν.

Ὁ παράγων g τῆς κεντρικῆς ἰσχυρᾶς φασματικῆς γραμμῆς ὡς καὶ ὁ παράγων g τῆς πρώτης ὁμάδος τῶν φασματικῶν γραμμῶν εὑρέθησαν ἰσότροποι καὶ ἔχοντες τιμὴν ἴσην περίπου μὲ τὴν τιμὴν τοῦ παράγοντος g τοῦ ἠλεκτρονίου. Ὁ προσδιορισμὸς τῶν τανυστῶν ὑπερλέπτου ὑφῆς, τῆς θέσεως καὶ τοῦ προσανατολισμοῦ αὐτῶν, ἐν συνδυασμῷ μὲ τὴν μορφὴν τῶν λαμβανομένων φασμάτων (πλῆθος γραμμῶν καὶ σχετικὴ ἔντασις αὐτῶν), ὁδηγοῦν εἰς τὸ συμπέρασμα ὅτι τὰ παραμαγνητικὰ κέντρα συνδέονται μὲ τὴν ρίζαν $NH_{3\pm}$, ἐνῶ ἡ εὐρυτέρα ὁμὰς τῶν φασματικῶν γραμμῶν προέρχεται πιθανὸν ἀπὸ τὸ ^{33}S τῆς ρίζης $^{-}SO_4$.

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ISOLATION AND PARTIAL CHARACTERIZATION OF MILK GANGLIOSIDES.*

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(Received July 5, 1975)

Summary

Milk and Collostrum were shown to contain gangliosides in the form of proeteolipid-type complexes. Collostrum gangliosides were isolated in preparative scale and fractionated via DEAE-cellulose and silicic acid column chromatography and purified by dialysis.

The structural units of the isolated ganglioside fractions were identified by chromatography and by specific spectrophotometric assays, after acid hydrolysis. Their molecular rations were found similar to the monosialo-gangliosides of brain.

Key words: Gangliosides, milk, collostrum, proteolipids, red-protein, mucolipids, sialic acid.
Abbreviations: NANA: N-acetyl-Neuraminic acid TLC: Thin layer Chromatography.

Introduction

Gangliosides, the main species of mucolipids, are normal constituents of a variety of animal tissues such as brain,[1] neural membranes, eye lens,[2] blood serum, kidneys, adrenals and intestines.[3]

The hydrophobic part of the gangliosides' molecule is a ceramidyl group (N-acetyl-sphingosine), combined to a hydrophilic oligosaccharide chain characterized by the presence of sialic acid and N-acetyl-hexosamine. In most cases, gangliosides occur in free form but there is also some experimental evidence indicating their occurence in complex forms with proteins.[4,5,6,7,8]

Described in this paper is a study on the isolation and partial characterization of milk gangliosides. During this study it was revealed that the gangliosides of milk exist mainly in the form of proteolipid-type complexes in which, as described elsewhere,[9] the protein residue is a fraction of the so-called "red protein" of milk.[10]

Experimental Procedures

Analytical Methods

Hexosamine and sialic acid were determined according to Svennerholm.[11,12] Hexose was determined as previously described.[13] Nitrogen was assayed by nesslerization,[14] using a modified Nessler reagent.[15]

* This work was taken in part from the doctoral dissertation of C.A. Demopoulos, School of Natural Sciences (Chemistry Section), University of Athens, Athens, Greece.

Sphingosine and fatty acids were identified by T.L.C. on silica gel G, after acid hydrolysis of the lipid samples in 6N HCl (1 hr reflux) and repeated extraction with chloroform. The plates were developed in chloroform-methanol-water, 100:42:6 (v/v/v) and the spots were visualized by exposure to iodine vapors or by spraying with ninhydrin for sphingosine.

Preparative thin-layer chromatographic isolation of gangliosides' fractions was carried out on silica gel G plates 1,0 mm thick. The plates were developed in n-propanol-water, 7:3 (v/v). Localization of bands (after development) was effected by observing the characteristic colors of red-protein fractions under U.V. light. After scrapping out the major part of the absorbent, the position of gangliosides' bands were assured by spraying a thin lane left on the plate with resorcinol spray reagent.[12]

Recovery of gangliosides from the corresponding sections of the absorbent was effected by mixing with an equal quantity of Celite 545, transferring the mixture to a small chromatographic column (id. 0,9 mm) and eluting with 25 ml chloroform-methanol, 1:2 (v/v).

Isolation of Gangliosides from Whole-milk Powder

Cow's whole-milk powder (300 g) was triturated with 900 ml acetone and kept for 30 min under continuous stirring at room temperature. The acetone extract was separated by decantation after centrifugation at 6000 rpm for 10 min, taken to dryness *in vacuo,* and re-dissolved in 50 ml of choroform-methanol, 2:1 (v/v).

The dry defatted residue of acetone extraction was treated with 2 liters of chloroform-methanol, 1:2 (v/v) at 40° C for 60 min. under continuous stirring. Chloroform was then added to a final chloroform-to-methanol ratio of 2:1 (v/v) and after thorough mixing, the soluble fraction was separated by decantation after centrifugation, as above. The residue was re-extracted with 900 ml of chloroform-methanol, 1:2 (v/v). The combined choloform-methanol extracts were taken to dryness *in vacuo* and re-dissolved in 20 ml of chloroform-methanol, 2:1 (v/v).

Gangliosides were isolated from the final chloroform-methanol solutions of all the extraction steps described above by washing them with 0,2 volumes of 0,9% NaCl and a second washing with theoretical upper-phase (chloroform-methanol 1-0,9% NaCl, 3:48:47), according to Folch *et al.*[16,17] The remaing chloroform layers (after washing) were found free of NANA, indicating absence of gangliosides and, therefore, their quantitative recovery in the saline washings.

The aqueous-methanolic extracts were taken to dryness *in vacuo,* redissolved in 10 ml of chloroform-methanol 2:1 (v/v) and dialyzed [18] overnight against running water through a seamless cellulose tubing. The dialyzed residues were taken to dryness *in vacuo* and redissolved in a small volume of chloroform-methanol. Gangliosides were identified by T.L.C. and assayed by sialic acid determination.

Isolation of Gangliosides from Collostrum

Goat collostrum (660 g), taken within 2 hours after the delivery of the animal, was extracted successively (at room temperature) with methanol (600 ml) and acetone (600 ml) in order to remove water and fat. The residue was then extracted with methanol and chloroform by the method described by Kanfer[19] for lyophilised brain tissue with the omission of the barium salt precipitation and with some minor modifications, as depicted in the flow diagram of Fig. 1. As shown in the diagram (Fig. 1), during flash evaporation of the dialyzed ganglioside fraction (precipitate), it was colored red and kept the color after dissolution in chloroform-methanol, 2:1 (v/v).

Neuraminic acid assay on all fractions so obtained indicated that gangliosides

were quantitatively recovered in the final "precipitate" (Fig. 1). The yield was 6 mg of ganglioside per 100 g of collostrum.

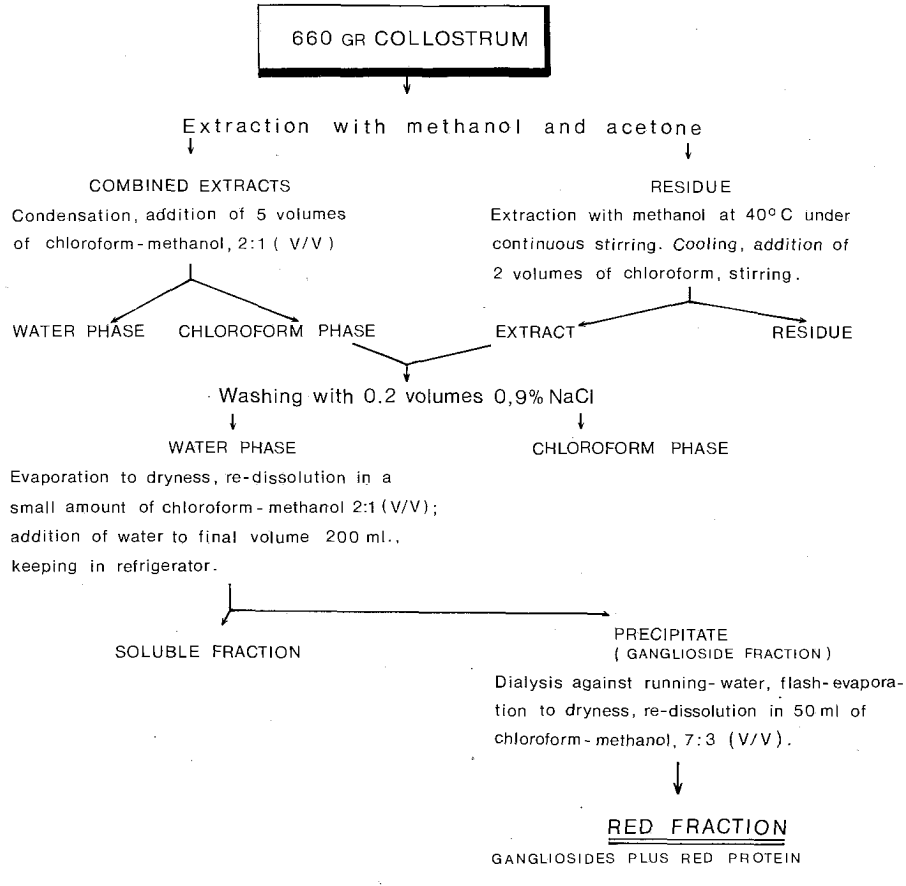

FIG. 1. *Flow diagram of the isolation of gangliosides from Collostrum.*

Fractionation by DEAE-cellulose acetate column chromatography

DEAE-cellulose was washed in a Büchner funnel (covered with some sheets of filter paper) by passage of 3 bed volumes each of 1N HCl, water and 1N KOH in three cycles, according to Rouser *et al.*[20] It was then dried by passage of methanol followed by vacuum dessication over dry KOH overnight.

The dried DEAE-cellulose was then converted to the acetate form by grinding (mortar and pestle) with glacial acetic acid to a homogeneous mass and kept overnight covered with glacial acetic acid.

Packing of the columns was effected by transferring the above slurry in small portions to the column through which were passed 3 bed volumes of glacial acetic acid, 6 volumes of methanol (to elute excess of acetic acid), 3 bed volumes of chloroform-methanol, 1:1 (v/v) and finally 3 bed volumes of chloroform.

Monitoring of the columns was effected by passing the eluate through an autographic U.V. - photometer (Uvicord, LKB) connected with a fraction collector. The samples were applied to the columns dissolved in a small volume of chloroform-methanol, 7:3 (v/v) and elution was continued, according to the scheme devised by Rouser *et al*[21] for fractionating brain gangliosides i.e., by passage of 7 bed volumes of chloroform-methanol, 7:3 (fraction A); 5 bed volumes of methanol (fraction B); 3 bed volumes of glacial acetic acid (fraction C); and 1 bed volume of methanol-water, 2:1 (fraction D).

Results and Discussion

Preliminary isolation of gangliosides from whole - milk powder, by appropriate modifications of Folch's procedure as described in the experimental part, proved definitely their presence in milk, according to previous indications.[21] They were identified by sialic acid and hexosamine assays and by T.L.C. However these preliminary experiments showed that the ganglioside content of milk is very low, i.e. of the order of 1-2 mg per 100 g of milk powder.

A better source of milk gangliosides was therefore highly desirable in order to facilitate further structural studies. As such, collostrum was expected to give a much better yield, on the basis of literature date[23] reporting an almost 10-fold concentration of sialic acid. Indeed, working with fresh goat collostrum, our prediction was proven real.

Following Kanfer's procedure[19] modified as described in the experimental part (see also flow diagram, Fig. 1), a better yield of gangliosides was obtained. However, even after crystallization and dialysis, the ganglioside fraction of collostrum was obtained in admixture with high amounts of protein, and flash evaporation of the dialysis product gave a red residue, which kept its reddish colour after dissolving it in chloroform-methanol. As already mentioned, strong evidence reported elsewhere[9] suggested that the protein material of the resulting "red fraction" (Fig. 1) is identical with the protein of milk, described by Groves.[10]

The presence of gangliosides in the red fraction isolated from collostrum as mentioned above, was proven by T.L.C. -identification of sphingosine and fatty acids after vigorous acid hydrolysis, whereas fatty acids, cerebrosides, sphingomyelin or other phospholipids were not identified prior to the vigorous acid hydrolysis or after mild saponification.

DEAE-cellulose column chromatographic fractionation was then carried out for the purpose of separating gangliosides from protein for further structural studies. The fractionation scheme was similar to the one devised by Rouser *et al*[21] for the fractionation of brain gangliosides based on elution with organic solvents. In addition, the column was monitored by passing the eluates through a Uvicord photometer (LKB) designed for protein fractionation. Fractions of 10 ml were collected using a fraction collector. One protein fraction was obtained with each of the 4 eluting solvents applied, named as fractions A, B, C and D.

According to literature data[21] and to our preliminary tests of this column chromatographic method (using a brain gangliosides preparation), gangliosides were expected in fraction C. In contrast, fractions B, C and D were found sialic-acid free.

All the sialic acid content of the red fraction applied to the column was eluted in fraction A, together with a small portion of red protein, while the major portion of the red protein, non-bound to sialic acid, was eluted in fraction D.

By sialic acid determination on each of the fractions eluted from the column, it was found that the sialic-acid content of each tube was proportional to the density

of the protein content of the tube. In addition T.L.C, separation of each tube's contents showed that the intensity of the ganglioside bands was proportional to the sialic acid-content of the respective tube.

As shown in Fig. 2, two ganglioside fractions were identified by T.L.C. of fraction A: band I which contained most of red protein and band II with a much lower mobility. Bands I and II were scraped-off the plates in preparative T.L.C. experiments and were found to contain both sphingosine and fatty acids, liberated only after vigorous acid hydrolysis. Also, both of them were found to contain hexose, hexosamine and sialic acid in the same molar ratios, namely 3:1:1.

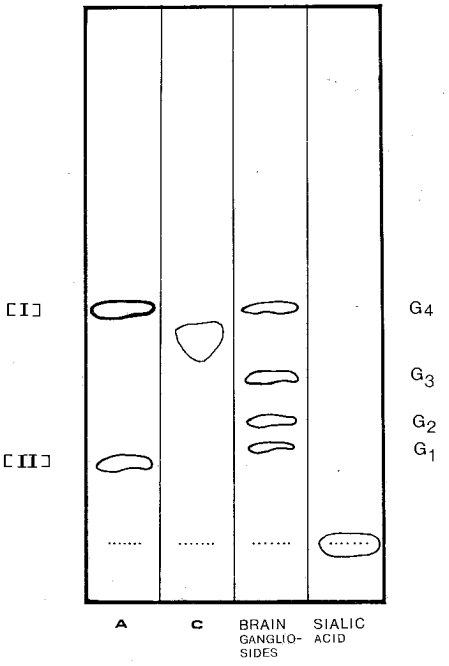

FIG. 2. *T.L.C. of fraction A, fraction C, brain gangliosides and sialic acid.* Solvent: n-propanol-water 7:3 (v/v). Spray: resorcinol reagent.

Finally, attempts to purify the gangliosides of fraction A by silicic acid chromatography showed that this tratment causes extensive degradation of the sialic acid of milk gangliosides, since in the fractions eluted from the silicic acid column, the number of resorcinol positive spots, after T.L.C., was increased to 5 with simultaneous low recovery of total sialic acid appied to the column.

These last results are comparable to those of Huang[24] in his study of butter milk gangliosides after silicic acid column fractionation. Huang's ganglioside mixture eluted from the column was separated by T.L.C. into five components of which the fastest and slowest moving spots (20% and 50% of total) were identified as monosialo - and disialo-hematosides respectively. In contrast, we found positively hexosamine and hexose in the molar ratio of 1:3 in both corresponding spots (after silicic acid column fractionation), together with a much lower NANA concentration. Keeping in mind the well-known ability of certain gangliosides with respect of losses of sialic acid during silicic acid fractionation[25,26] and the different source of ganglioside and methodology used by Huang, our present data indicate pisitively the following:

1. Gangliosides occur in collostrum and whole-milk in the form of proteolipids, i.e. strong complexes with a specific fraction of red protein.

2. Ganglioside-protein complexes of this type show different thin-layer chromatographic mobilities compared to those of the corresponding free ganglioside.

3. The main species of milk gangliosides is monosialo-ganglioside, although evidence from Huang's experiments [24] suggests that disialo-fractions are also present in the proteolipid complexes.

Acknowledgments

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Περίληψις

Ἀπομόνωσις καὶ μερικὸς χαρακτηρισμὸς τῶν γαγγλιοζιτῶν τοῦ γάλακτος

Ἀπεδείχθη ἡ παρουσία γαγγλιοζιτῶν εἰς τὸ γάλα, οἱ ὁποῖοι ἀπεμονώθησαν τόσον ἐκ γάλακτος ὅσον καὶ — εἰς παρασκευαστικὴν κλίμακα — ἐκ πρωτογάλακτος, μὲ τὴν χρῆσιν καταλλήλως τροποποιηθείσης πρὸς τοῦτο ἠπίας μεθόδου (Σχ. 1).

Ἡ ποσότης τῶν ἀπαντώντων εἰς τὸ πρωτόγαλα γαγγλιοζιτῶν εὑρέθη 6mg/100g.

Διεπιστώθη ὅτι οἱ γαγγλιοζῖται τοῦ γάλακτος ἀπαντοῦν φυσικῶς ἐντὸς αὐτοῦ ὑπὸ μορφὴν συμπλόκων μετὰ πρωτεϊνῶν, τῶν ὁποίων ἡ σταθερότης εἶναι ἀνάλογος ἐκείνης τῶν πρωτεολιποειδῶν.

Τὸ ἀπομονωθὲν κλάσμα τῶν γαγγλιοζιτῶν ἐκ τοῦ πρωτογάλακτος ὑπεβλήθη εἰς καθαρισμὸν διὰ διαπιδύσεως καὶ κλασματώσεως εἰς στήλας DEAE — κυτταρίνης καὶ πυριτικοῦ ὀξέως. Εἰς τὰ κατ' αὐτὸν τὸν τρόπον ἀπομονωθέντα κλάσματα γαγγλιοζιτῶν, κατόπιν ὑδρολύσεως ἀπεδείχθη χρωματογραφικῶς καὶ χρωματομετρικῶς (διὰ χαρακτηριστικῶν φωτομετρικῶν μεθόδων προσδιορισμοῦ) ἡ παρουσία σφιγγοσίνης, λιπαρῶν ὀξέων, γαλακτόζης, γλυκόζης, ἐξοζαμίνης καὶ νευραμινικοῦ ὀξέος. Ἐκ τῶν ληφθέντων ἀναλυτικῶν στοιχείων προκύπτει ὅτι αἱ μοριακαὶ ἀναλογίαι ἐξόζης: ἐξοζαμίνης: νευραμινικοῦ ὀξέος εἶναι ὅμοιαι μὲ ἐκείνας τῶν μονοσιαλο-γαγγλιοζιτῶν τοῦ ἐγκεφάλου.

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Short Papers

ΜΕΛΕΤΗ ΤΩΝ ΦΑΣΜΑΤΩΝ ΜΑΖΗΣ ΤΩΝ 1 - ΚΥΑΝΟ - 2 - ΝΙΤΡΩΔΟ - ΕΝΩΣΕΩΝ

ΒΑΣΙΛΕΙΟΣ Π. ΠΑΠΑΓΕΩΡΓΙΟΥ
Ἐργαστήριον Ὀργανικῆς Χημείας τῆς Πολυτεχνικῆς Σχολῆς τοῦ Ἀριστοτελείου Πανεπιστημίου Θεσσαλονίκης.
(Ἐλήφθη τὴν 7 Ἰουνίου 1975)

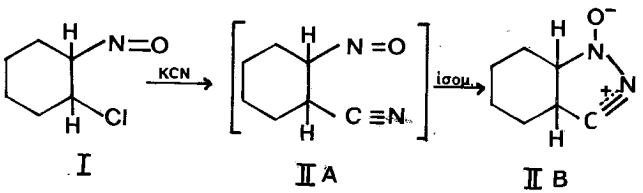
Περίληψις

Σκοπὸς τῆς παρούσης ἐργασίας εἶναι ἡ μελέτη τῶν φασμάτων μάζης τῶν 1-κυανο-2-νιτρωδο-ενώσεων καὶ εἰδικώτερον ἡ ἀνεύρεσις νέων δεδομένων, πρὸς ἐπιβεβαίωσιν τῆς ἀλληλεπιδράσεως τῆς κυανο- καὶ νιτρωδο-ομάδος ὑπὸ σχηματισμὸν ἑτεροκυκλικῶν δακτυλίων. Πρὸς τούτοις μελετῶνται τὰ φάσματα μάζης μερικῶν νέων ἐνώσεων διὰ τὰς ὁποίας τὰ φασματοσκοπικὰ δεδομένα συνηγοροῦν ὑπὲρ τῆς πυραζολικῆς δομῆς αὐτῶν, ἥτις εἶναι ἀποτέλεσμα ἰσομερειώσεως τῶν ἀντιστοίχων 1-κυανο-2-νιτρωδο-ενώσεων.

Συντμήσεις: NMR. = nuclear magnetic resonance, IR. = infrared, i = ἔντασις, μA = μικρο-ampère, E = τάσις, MeOH = μεθανόλη, M^+ = μοριακὸν ἰόν, GKE = κεκορεσμένον ἠλεκτρόδιον καλομέλανος, M = συγκέντρωσις εἰς mol/lit, m/e = μᾶζα/φορτίον ἰοντικοῦ θραύσματος.

Ἀποτελέσματα - Συζήτησις

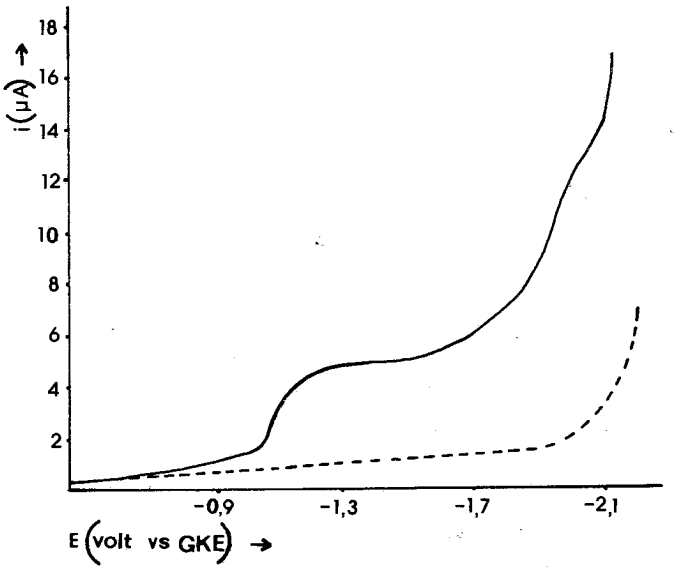
Ὡς ἤδη εἶναι γνωστὸν[1] ἡ μελέτη τῶν φασμάτων UV-Vis, IR καὶ NMR τοῦ προϊόντος IIB, τῆς ἐπιδράσεως κυανιούχου καλίου ἐπὶ 1-χλωρο-2-νιτρωδο-



κυκλο-εξανίου, δὲν ἀνταποκρίνεται εἰς τὸ κυανο-νιτρωδο-παράγωγον τοῦ τύπου IIA. Ἐπίσης κατὰ τὴν πολαρογραφικὴν μελέτην τῆς ἐν λόγῳ ἑνώσεως δὲν ἐλήφθη κῦμα ἀναγωγῆς ὡς συνέβη διὰ τὴν ἕνωσιν I (Διάγραμμα 1).

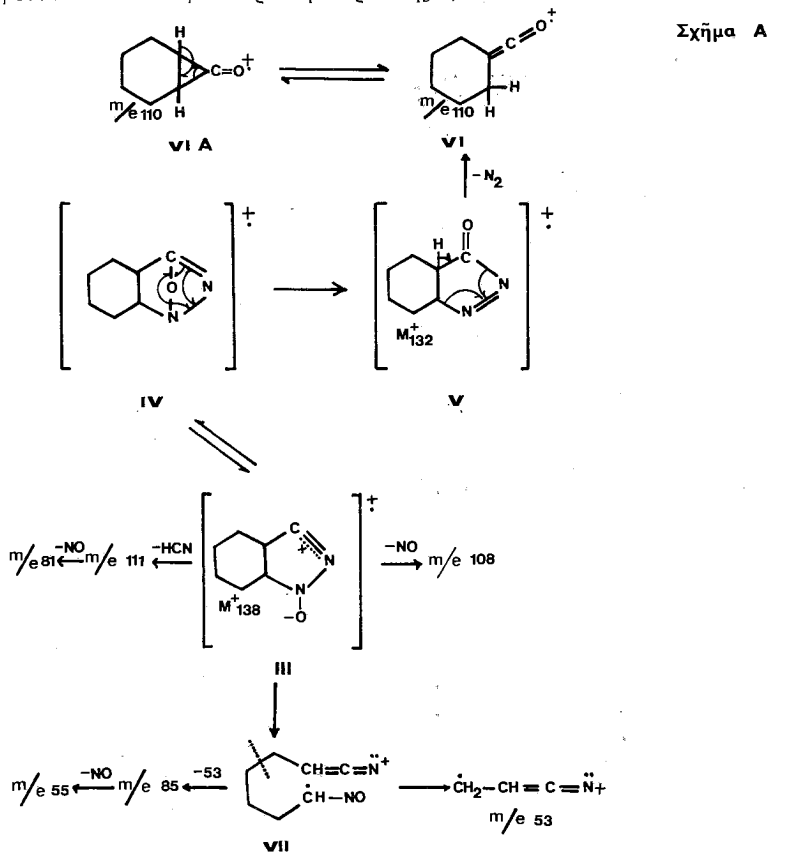
Ἡ μελέτη τοῦ φάσματος μάζης τῆς ἐν λόγῳ ἑνώσεως ἐπιβεβαιοῖ τὴν ὕπαρξιν πυραζολικοῦ δακτυλίου, ὡς ἐμφαίνεται ἐκ τοῦ τρόπου διασπάσεως ταύτης.

Οὕτως ἐκ τοῦ μοριακοῦ ἰόντος M^+ (Σχῆμα A), θεωρουμένου ὡς προϊόντος πολικῆς πυραζολικῆς συντάξεως (III), εἶναι δυνατὸν νὰ σχηματισθῇ τὸ δεσμικὸν ταυτομερὲς IV, τὸ ὁποῖον ἐν συνεχείᾳ μετατρέπεται εἰς τὸ ἰὸν V, ἐκ τοῦ ὁποίου εὐκόλως λαμβάνει χώραν ἀπόσπασις N_2 ὑπὸ σχηματισμὸν τοῦ πρωτεύοντος ἰόντος VI (m/e 110), ὁ σχηματισμὸς τοῦ ὁποίου μόνον διὰ τῆς ὁδοῦ ταύτης εἶναι δυνατὸν νὰ δικαιολογηθῇ.



ΔΙΑΓΡ. 1. *Πολαρογραφικὴ καμπύλη ἐντάσεως-τάσεως τῶν σωμάτων Π[Β] (----) καὶ Ι (—) εἰς μεθανολικὸν διάλυμα.* Φέρων ἠλεκτρολύτης 0,1 Μ LiCl.

Σχῆμα Α



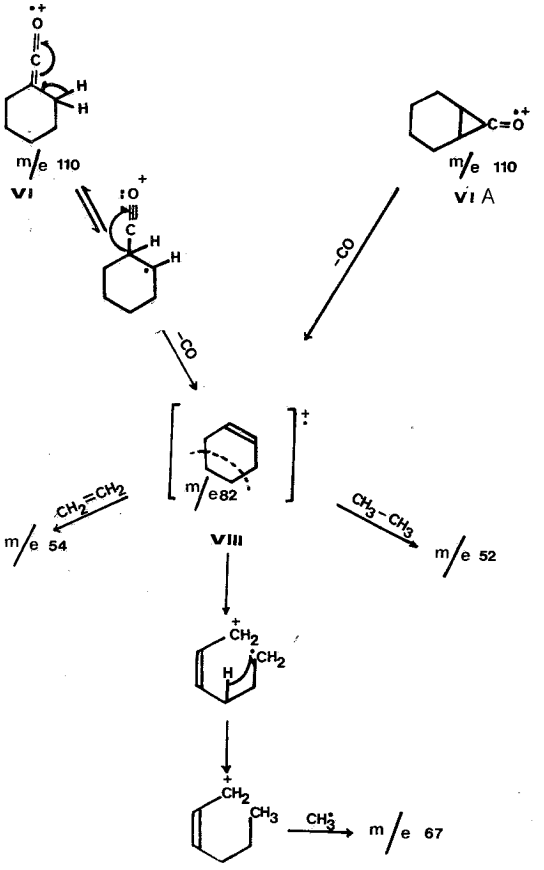
Τὸ ἰὸν VI δι' ἀποβολῆς ἐν συνεχείᾳ τῆς ὁμάδος CO μετατρέπεται εἰς τὴν κατιονικὴν ρίζαν τοῦ κυκλοεξενίου VIII, ἥτις περαιτέρω ὑπὸ διάνοιξιν τοῦ κυκλοεξενικοῦ δακτυλίου διασπᾶται,[2] ὡς δεικνύεται εἰς τὸ σχῆμα B.

Σημειωτέον ὅτι διὰ τὸ ἰὸν VI εἶναι δυναταὶ δύο δεσμικῶς ταυτομερεῖς μορφαὶ τῶν τύπων VI καὶ VI [A]. Ἐκ τοῦ μοριακοῦ ἰόντος III (Σχῆμα *A*) ὑπὸ ἀπόσπασιν ἑνὸς μορίου HCN σχηματίζεται τὸ ἰὸν m/e 111, ἐκ τοῦ ὁποίου δι' ἀποσπάσεως τῆς ὁμάδος NO προκύπτει καὶ πάλιν ἡ κατιονικὴ ρίζα τοῦ κυκλοεξενίου. Ἀναλόγως δι' ἁπλῆς ἀποσπάσεως τῆς ὁμάδος NO σχηματίζεται τὸ ἰὸν m/e 108.

Τὸ μοριακὸν ἰὸν εἶναι δυνατὸν διὰ διανοίξεως τοῦ πυραζολικοῦ δακτυλίου νὰ μετατραπῇ εἰς τὸ ἀνοικτῆς συντάξεως κυανο-νιτρωδο-παράγωγον, τὸ ὁποῖον περαιτέρω διὰ διανοίξεως τοῦ κυκλοεξανικοῦ δακτυλίου[3] μετατρέπεται εἰς τὴν κατιονικὴν ρίζαν VII. Ἐξ αὐτῆς κατόπιν διὰ διαφόρων διασπάσεων εἶναι δυνατὸν νὰ προκύψουν τὰ ἰόντα m/e 85 καὶ m/e 55 καθὼς καὶ τὸ ἰὸν m/e 53.

Πρέπει νὰ τονισθῇ ὅτι ὁ σχηματισμὸς τοῦ ἰόντος VII θὰ ἠδύνατο νὰ ἐξηγηθῇ καλύτερον, ἐὰν ἐγένετο δεκτὴ ἡ ἀνοικτὴ σύνταξις τοῦ κυανο-νιτρωδο-παραγώγου. Δεδομένου ὅμως ὅτι ἐκ τῆς συντάξεως ταύτης δὲν εἶναι δυνατὸν νὰ

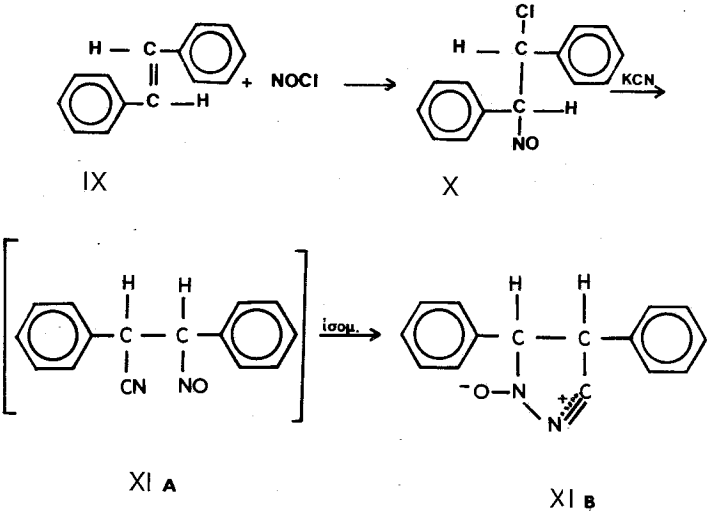
Σχῆμα B



δικαιολογηθῇ ἀπόσπασις N_2, διὰ τοῦτο θεωροῦμεν τὴν ἀνοικτὴν σύνταξιν ὡς μὴ ἀρχικῶς ὑπάρχουσαν ἀλλὰ ὡς σχηματιζομένην κατόπιν διὰ διανοίξεως τοῦ πυραζολικοῦ δακτυλίου.

Ἐν συμπεράσματι ἀναφέρομεν, ὅτι ὁ τρόπος διασπάσεως τῆς ὑπὸ ἐξέτασιν ἑνώσεως ἐντὸς τοῦ φασματογράφου μαζῶν εὑρίσκεται ἐν συμφωνίᾳ μὲ τὴν προτεινομένην διπολικὴν πυραζολικὴν σύνταξιν.

Τὸ ἑπόμενον μελετηθὲν σῶμα ἦτο τὸ προϊὸν ἐπιδράσεως κυανιούχου καλίου ἐπὶ τοῦ 1-χλωρο-2-νιτρωδο-1,2-διφαινυλο-αιθανίου. Διὰ τὸ σῶμα τοῦτο ὁ μοριακὸς τῦπος $C_{15}H_{12}N_2O$ δὲν ἀνταποκρίνεται εἰς τὸ ἀναμενόμενον κυανο-νιτρωδο-παράγωγον τοῦ τύπου XI [A]. Τοῦτο προέκυψεν ἐκ τῆς μελέτης[1] τῶν φασμάτων UV-Vis, IR καὶ NMR.

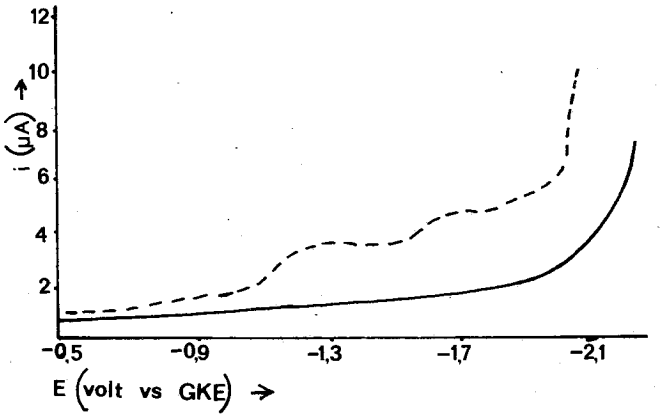


Ἐπίσης κατὰ τὴν πολαρογραφικὴν μελέτην τοῦ σώματος δὲν ἐλήφθη κῦμα ἀναγωγῆς ὡς συνέβη διὰ τὴν ἔνωσιν X (Διάγραμμα 2).

Τὸ φάσμα μάζης τῆς ἑνώσεως XI [B] ἐμφανίζει εἰς γενικὰς γραμμὰς τὸν αὐτὸν τρόπον διασπάσεως μὲ τὸ προαναφερθὲν φάσμα τῆς ἑνώσεως II [B], ὡς δεικνύεται εἰς τὸ σχῆμα Γ.

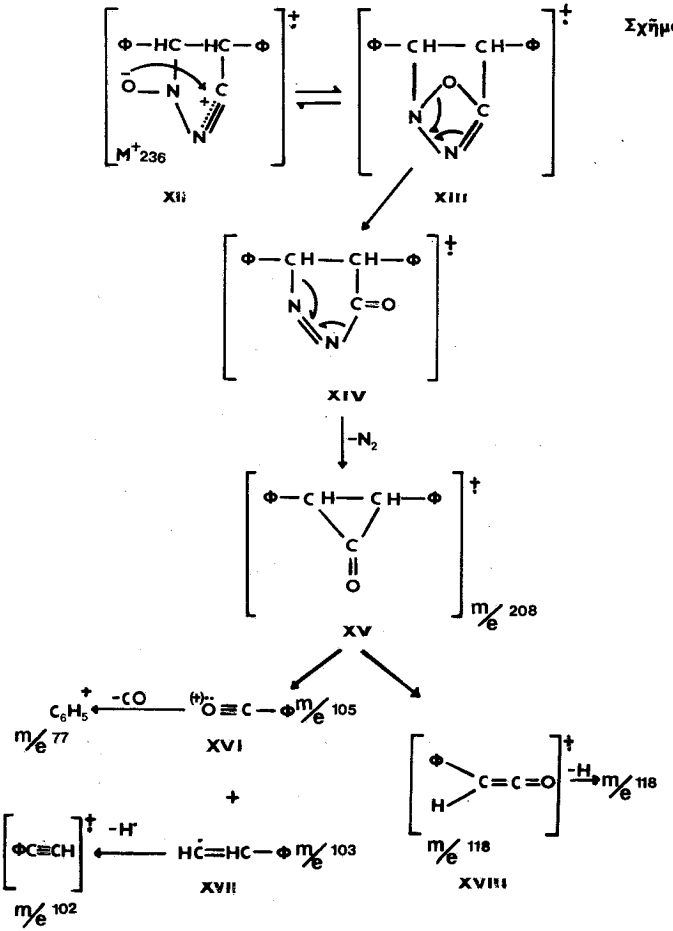
Ἀρχικῶς ἐκ τοῦ μοριακοῦ ἰόντος M^+ (XII) λαμβάνει χώραν ἀπόσπασις N_2 ὑπὸ σχηματισμὸν τοῦ βασικῆς σημασίας ἰόντος M-28 μὲ m/e 208 XV. Ὁ σχηματισμὸς τοῦ ἰόντος τούτου ἐξηγεῖται, μόνον ἐὰν θεωρήσωμεν τὴν κυανο-νιτρωδο-ενωσιν ὑπὸ τὴν μορφὴν τοῦ διπολικοῦ πυραζολικοῦ δακτυλίου XII. Ἡ ἀπόσπασις τοῦ N_2 δεχόμεθα ὅτι γίνεται ἀπὸ τὴν πυραζολόνην-5 XIV, ἥτις σχηματίζεται ἐκ τοῦ μοριακοῦ ἰόντος XII, ὑπὸ τὸν σχηματισμὸν τοῦ κετοκυκλο-προπανικοῦ προϊόντος XV. Ἡ ἀπόσπασις αὕτη τοῦ N_2 ἐπιβεβαιοῦται ἐκ τῆς παρουσίας μεταστάθοῦς κορυφῆς m* εἰς 183,4 μονάδας μάζης ($m^* = 208^2/236 = 183,3$). Διὰ διασπάσεως τοῦ ἰόντος XV ὑπὸ μετάθεσιν τοῦ ἑνὸς φαινυλίου εἶναι δυνατὸν νὰ σχηματισθῇ τὸ ἰὸν XVI μὲ m/e 105 ὡς καὶ τὸ XVII μὲ m/e 103. Τὸ ἰὸν τοῦ βενζοϋλίου δι' ἀποβολῆς τοῦ CO σχηματίζει τὸ ἰὸν τοῦ φαινυλίου m/e 77, ἡ διάσπασις δὲ αὕτη ἐπιβεβαιοῦται διὰ τῆς μεταστάθοῦς κορυφῆς m* εἰς 56,5 μονάδας μάζης ($m^* = 77^2/105 = 56,4$).

Ἐκ τῆς κατιονικῆς ρίζης M-28 (XV) δι' ἀποσπάσεως 89 μονάδων μάζης προκύπτει ἡ κατιονικὴ ρίζα XVIII μὲ m/e 118.



ΔΙΑΓΡ. 2. *Πολαρογραφικὴ καμπύλη ἐντάσεως-τάσεως τῶν σωμάτων XI[B] (—) καὶ X (----) εἰς μεθανολικὸν διάλυμα.* Φέρων ἠλεκτρολύτης 0,1 M LiCl.

Σχῆμα Γ



Ὁ τρόπος οὗτος διασπάσεως δικαιολογεῖ τὰς περισσοτέρας ἐκ τῶν ἐμφανιζομένων κορυφῶν εἰς τὸ φάσμα μάζης καὶ εὑρίσκεται ἐν συμφωνίᾳ μὲ ὅλα τὰ προαναφερθέντα[1] πειραματικὰ καὶ φασματοσκοπικὰ δεδομένα, τὰ ὁποῖα συνηγοροῦν ὑπὲρ τῆς παραδοχῆς τῆς πυραζολικῆς συντάξεως XI (B).

ΠΙΝΑΞ I: *Φάσμα μάζης τοῦ σώματος II(B)*

138 (23),	111 (27),	110 (15),	109 (50),	108 (7,7),	106 (62),
94 (73),	85 (46),	82 (88),	81 (58),	80 (78),	77 (88),
70 (88),	67 (46),	66 (58),	55 (48),	54 (36),	53 (100),
52 (96),	39 (96).				

Οἱ ἀριθμοὶ πρὸ τῶν παρενθέσεων ἀντιπροσωπεύουν τιμὰς μάζης/φορτίου τῶν ἰοντικῶν θραυσμάτων, αἱ τιμαὶ δὲ ἐντὸς τῶν παρενθέσεων τὰς σχετικὰς ἐντάσεις αὐτῶν.

ΠΙΝΑΞ II. *Φάσμα μάζης τοῦ σώματος XI [B]*

236 (75),	*235 (17),*	*208 (20,1),*	*165 (18,1),*	*119 (18,5),*	*118 (20,8),*
105 (100),	*103 (6),*	*102 (1,31),*	*90 (19,2),*	*89 (49,4),*	*77 (70,19).*
m 183,3 (236→208), 56,4 (105→77).*					

Οἱ ἀριθμοὶ πρὸ τῶν παρενθέσεων ἀντιπροσωπεύουν τιμὰς μάζης/φορτίου τῶν ἰοντικῶν θραυσμάτων, αἱ τιμαὶ δὲ ἐντὸς παρενθέσεων τὰς σχετικὰς ἐντάσεις αὐτῶν.
m* = Μεταστάθὴς κορυφή.

Εὐχαριστῶ θερμῶς τοὺς Καθηγητὰς κ.Ν.Ἀλεξάνδρου καὶ Δ. Γιαννακουδάκην διὰ τὴν εὐγενικὴν διάθεσιν τῶν ὀργάνων καὶ τὴν προσωπικήν των συμβολὴν εἰς τὴν ἐκπόνησιν τῆς παρούσης ἐργασίας.

Ἐπίσης, θεωρῶ ὑποχρέωσίν μου νὰ εὐχαριστήσω τὸν συνάδελφον Ἐπιμελητὴν τοῦ Ἐργαστηρίου Ὀργανικῆς Χημείας τοῦ Πανεπιστημίου Θεσσαλονίκης κ. Ε. Μικρομάστοραν διὰ τὴν σημαντικὴν βοήθειάν του.

Abstract

The mass spectra of 1-cyano-2-nitroso-cycloexane and 1-cyano-2-nitroso-1,2-diphenyl-ethane has been recorded and interpreted to elucidate their structures. They all showed abundant molecular ions.

In addition to other spectroscopic data the results provide more evidence for the interaction of cyano and nitroso-groups indicating as more possible a polar pyrasolic structure for these compounds.

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3 ibid. p. 107, 116.

OXIDATION VON CYCLOHEXEN MIT PALLADIUM (II) CHLORID LÖSUNGEN

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Laboratorium für Organische Chemie der Universität Athen
(Erhalten am 26 Juni, 1975)

Zusammenfassung

Bei der Oxidation von Cyclohexen in wässrigen Pd (II) - und Cu (II) - Lösungen entsteht Cyclohexanon und Cyclohexanol.

Der Prozess besteht aus der folgenden Stuffen:
1) Bildung während der Reaktion eines (Pd) - Cyclohexen - Komplexes. 2) Hydrolyse des Komplexes und Entstehung von Cyclohexanon und Cyclohexanol. 3) Wiederoxidation von Pd(0) zu Pd (II) mit Cu (II) - Salzen. 4) Oxidation des entstehenden Cu (I) - Salzes mit Sauerstoff. Auf Grund dieser theoretischen und experimentellen Daten ist eine Reihe von optimalen Versuche ausgeführt. In der vorliegender Arbeit werden solche Versuche beschrieben.

Einleitung

Cyclohexanon und Cyclohexanol haben in neuerer Zeit als Zwischenprodukte zunehmend an Bedeutung gewonnen. Cyclohexanol wird als Lösungsmittel vielseitig angewandt, auserdem ist es eine Basisprodukt zur Herstellung von Adipinsäure, Cyclohexanon (für Perlon) und Estern (Weichmachern).

Cyclohexanon ist ein wichtiges Zwischenprodukt für ε-Caprolactam den Ausgangsmaterial für Perlon (Polyamide). Seine Methylderivate werden öfters als Lösungsmittel verwandt. Ferner dient Cyclohexanol, in Mischung mit leichten Kohlenwasserstoffen, zum Entparaffinieren von Schmierölen. In der Textilindustrie wird es ähnlich wie Cyclohexanon den Mercerisierlaugen zugesetzt.

Oxidation von Cyclohexen mit Palladiumchlorid

Hafner und Jira [1] beobachteten, dass bei der Oxidation von Cyclohexen mit $PdCl_2$ als Katalysator, Cyclohexanon neben geringen Mengen von Cyclohexanol entsteht, dessen Bildung durch Hydrolyse von Cyclohexen in stark Saurer Lösung zu erklären ist. Neuere Untersuchungen[2] ergaben dass die Cyclohexanolbildung auf Kosten von Cyclohexanon ansteigen kann, wenn man die Reaktionsbedingungen varriert.[3] Über die Oxidation von Olefinen mit Hilfe von Palladiumchloridverbindungen ist vor einiger Jahren berichtet.[4]

Die Umsetung von Cyclohexen mit Palladiumchlorid verläuft in stöchiometrischer Reaktion gemäss (Gl.1). Dabei wird metallisches Palladium ausgeschieden.

Um dies erneut verwendet zu können, muss das Palladiummetall wieder zum Chlorid oxidiert werden, was am besten durch Kupfer (II) chlorid geschieht (Gl.2). Das dabei entfallende Kupfer (I) chlorid, wird durch Sauerstoff oder Luft wiederoxidiert (Gl. 3) sodass letzlich die Oxidation des Cyclohexens zu Cyclohexanon und Cyclohexanol als katalytische Reaktion mit Sauerstoff verläuft.[5,6,7]

1)  $+ PdCl_2 + H_2O \longrightarrow$  $+ Pd + HCl$

2) $Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$

3) $2CuCl + \frac{1}{2}O_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$

---

4)  $+ \frac{1}{2}O_2 \xrightarrow{PdCl_2,\ CuCl_2}$  oder 

Die Reaktion führt über einen Palladium - Cyclohexen - Komplex der als zweikernige Verbindung ist.[8]

Die Untersuchungen der Reaktion des Cyclohexens mit Palladiumchlorid in wässriger Lösung unter Zusatz verschiedener Agenzien und Bedingungen, haben zu einem Verständnis der Vorgänge geführt, die sich am Komplex abspielen. Die Komplexbildung und Komplexhydrolyse bei der Reaktion, laufen im wässriger System meist nebeneinander ab. Sie ist eine Gleichgewichtsreaktion, Das in wässriger Lösung etwa als $[PdCl_2(OH)H_2O]H$ vorliegendes Palladiumchlorid absorbiert Olefine z. B. nach.:

5) $[PdCl_2(OH)H_2O]^- + Olefin \rightleftharpoons [PdCl_2(OH)Olefin]^- + H_2O$

Wird die Reaktion in Gegenwart von Komplexbildner ausgeführt, die eine grössere Affinität zum Palladium als Hydroxyl oder Wasser haben, so treten diese an deren Stelle und erschweren den Austausch mit dem Olefin (z. B. Cl^-),[9] d.h. sie verschieben das Komplexbildungsgleichgewicht in Richtung der Dissoziation z.B.

6) $[PdCl_4]^- + Olefin \rightleftharpoons [PdCl_3 \cdot Olefin]^- — Cl^-$

Der weiterer Schritt der Gesamtreaktion ist die Komplexhydrolyse zur Carbonylverbindung:

7) $[PdCl_3 \cdot Olefin]^- + H_2O \longrightarrow Carbonyl + Pd + 3Cl^- + 2H^+$

Der Verlauf der Olefinoxidation bei verschiedenen Temperaturen ermöglicht qualitative Ausagen darüber welche die Geschwindigkeit der Gesamtreaktion bestimmen. Bei tieferer Temperaturen Cyclohexen wird sehr rasch absorbiert, bis die Gleichgewichtskonzentration an Olefinkomplex gemäss Gl.6 erreicht ist. (Abb. 1).

Erhöht man die Temperatur, so verschiebt sich das Bildungsgleichgewicht nach links (Gl.6), d.h. die Gleichgewichtskonzentration an Cyclohexenkomplex und damit auch die Cyclohexenaufnahme wird erniedrigt.

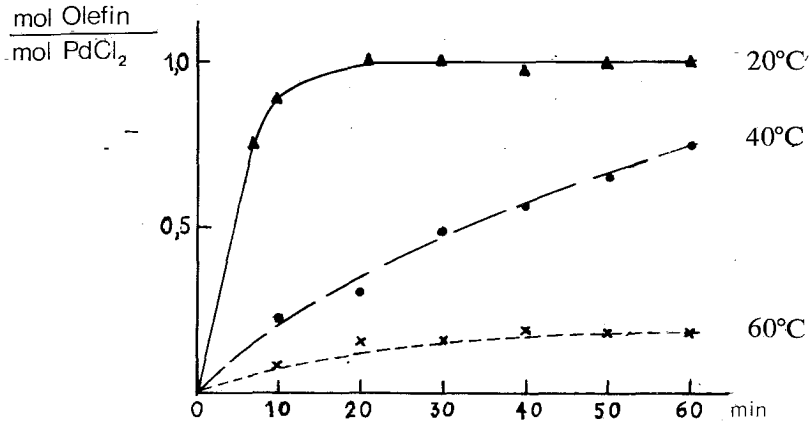


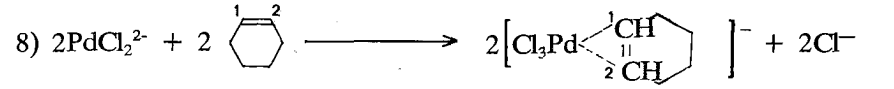
ABB. 1. *Cyclohexen - Aufnahme in 0,1 m $PdCl_2$ - Lösung*

Mechanismus der Reaktion

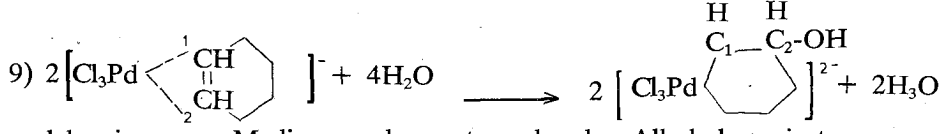
Wie schon erwähnt ist,[1] die Entstehung von Cyclohexanol bei der Oxidation des Cyclohexens bei höheren Säurekonzentrationen ist gering, und als eine Hydrolyse des Olefins[1] verantwortlich wird. Trotzdem, unter bestimmten Bedingungen die Ausbeuten an Cyclohexanol sind höher als an Cyclohexanon, sodass die Ausbildung an Cyclohexanol, als Produkt einer katalytischen Reaktion zu erklären ist.

Die Ausbildung von Cyclohexanol auf Kosten des Cyclohexanons, ist auf eine Acidolyse des hydratisierten π-Komplexes von C_6H_{10}-$PdCl_2$ zu verdanken, welche unter besonderen Bedingungen, Ihre Reaktionsgeschwindigkeit sehr grösser als die Zersetzungsgeschwindigkeit zu Carbonylverbindung ist. Als Nebenprodukte sind Essigester, halogeniertes Cyclohexanol, chlorierte Produkte des Cyclohexens sowie das Epoxyd des Cyclohexens zu bekommen. Das letzte ist öfters in grösseren Ausbeuten zu entstehen.

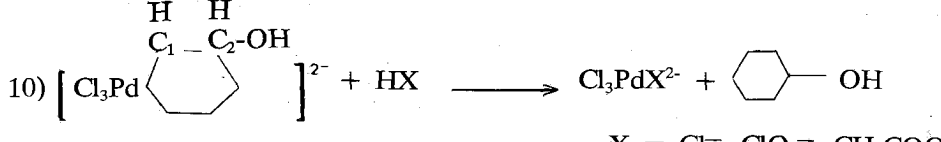
Der Ablauf der Reaktion besteht darin, dass das π-Elektronenpaar des Cyclohexens ganz an das Pd übergeht, wenn gleichzeitig ein Hydridion von C-2 in die entstehende Oktett-Lücke am C-1 überspringen kann.



der nächste Schritt ist die Entstehung eines Hydroxykomplexes

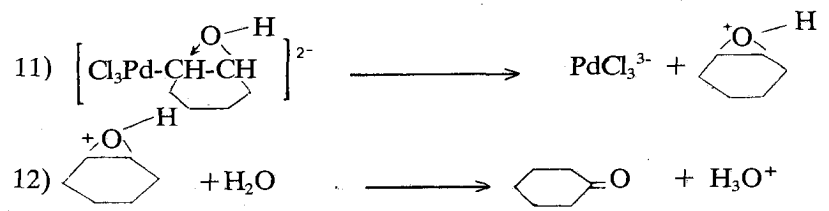


welcher in sauren Medium zu dem entsprechenden Alkohol reagiert



X = Cl^-, ClO_4^-, CH_3COO^-

Je nach der Reaktionsbedingungen, läuft eine parallele Reaktion zu dem entsprechenden Keton:[10]



Diese Hypothese über den Mechanismus der Komplexhydrolyse und derparallelität der Reaktion hat eine schöne Stütze. Erstens: Ausgehend aus Cyclohexanol Bzw. aus Cyclohexanon und unter der selben Bedingungen, fanden wir keinen Cyclohexanon Bzw. Cyclohexanol entsprechend. Zweitens: durch direkter Hydrolyse des Cyclohexen. $PdCl_2$ — Komplexes, erhielten wir grösseren Mengen an Cyclohexanol auf Kosten des Cyclohexanons.

Diskussion der Ergebnisse

Die Versuche wurden nach einem faktoriellen Versuchsplan ausgeführt, wobei die Variablen (pH, Säureart, Konzentrationen an $PdCl_2$ und $CuCl_2$, Temperatur) einzeln oder gleichzeitig nach einem bestimmten Schema geändert werden. Die Auswertung der Messergebnisse erfolgte mit Hilfe einer Varianzanalyse.[11] Nach unserem Versuchsplan wurden mit 4 Faktoren auf je 2 Ebenen das Molekülverhältnis Cyclohexanol / Cyclohexanon und die Ausbeute an Cyclohexanol als Zielgrössen behandelt.

Von allem durchgeführten Versuche wurde bewiesen, dass das Verhältnis Cyclohexanol / Cyclohexanon nicht aus der Temperaturänderung beeinflusst wird. Wie aus der Abb. 2 zu ersehen ist, der beste Temperaturbereich für die Durchführung der Reaktion liegt zwischen 40°-50°. Eine Erhöhung der Temperatur hat als Ziel, eine Erhöhung der Cyclohexanolausbeute.

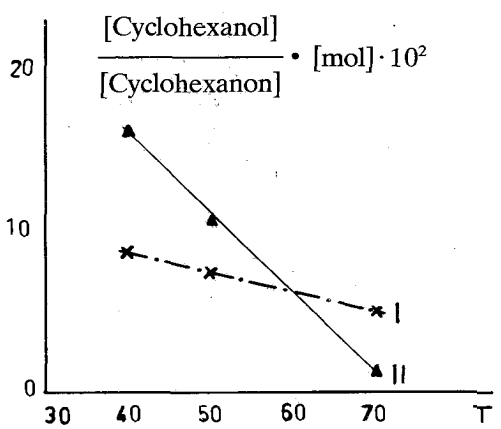


ABB. 2. *Änderung des Verhältnisses Cyclohexanol / Cyclohexanon durch Änderung der Temperatur.* I) $PdCl_2$=0,5m $CuCl_2$=1m HCl=0,1m II) $PdCl_2$=0,5m $CuCl_2$=1m HCl=0,5m

Im Bezug der Einfluss von $CuCl_2$ - Konzentrationen auf dem Verhältnis Cyclohexanol / Cyclohexanon, haben wir überaschend gute Ergebnisse gehabt. (Abb. 3)

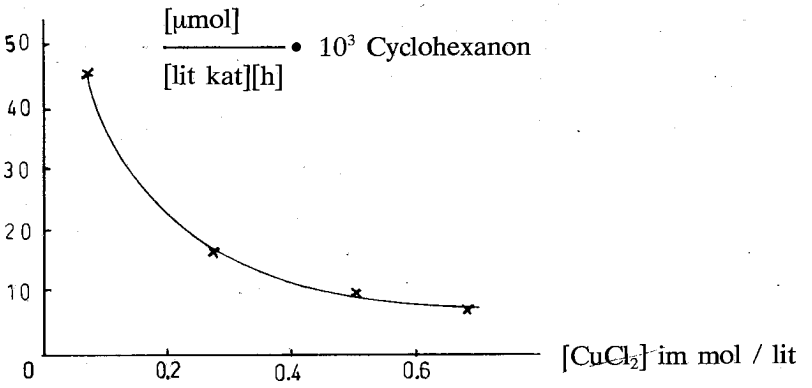


ABB. 3. *Einfluss von $CuCl_2$ - Konzentrationen bei 0,1m $PdCl_2$, 0,1m HCl, T=30°C*

Wie aus der Abb 3 zu sehen ist, mit zunehmender $CuCl_2$ - Konzentration, die Ausbeute an Cyclohexanon fällt ab. Der Einfluss von $HClO_4$ - und HCl - Konzentrationen geben ebenfalls gute Ergebnisse im Bezung der Ausbeute an Cyclohexanol. Das beste Verhältnis Cyclohexanol / Cyclohexanon erhalten wir durch variieren der CH_3COOH - Konzentration. Bei eine durchgeführte Reihe von ergänzenden Versuche, mit Konstante $PdCl_2$ - und Säurekonzentrationen zwischen 0,1-0,75m, ist eine Zunahme des Verhältnisses Cyclohexanol / Cyclohexanon mit gleichzeitiger Zunahme der Cyclohexanolausbeute zu beobachten Abb. 4

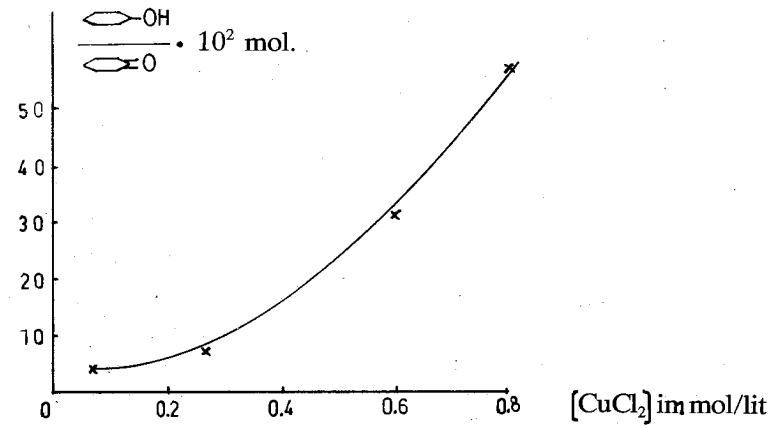


ABB 4. *Einfluss bei geänderten $CuCl_2$ - Konzentrationen und 0,1m $PdCl_2$, 0,1m HCl, T=40°C*

Auserdem eine Reihe von Versuchen welche ohne $PdCl_2$ - und vartierten $CuCl_2$ - Konzentrationen zwischen 0.1-0,25m durchgeführt wurden, geben auch gute Ergebnisse.

Davon ist zu ersehen das der $CuCl_2$ eine Hauptrolle spielt und wirkt auch katalytisch ein.

Um einen besseren Auskunft über die Einwirkung von Säureart und $PdCl_2$ - konzentration zu haben, sind Versuche mit HCl, $HClO_4$ und CH_3COOH durchgeführt worden. Eine Erhöhung seiner Konzentrationen sowie Versuche mit gleichzeitiger Änderung der $CuCl_2$ - und HCl-konzentration zwischen 0,1 - 0,8m hat befriedigende Ressultate gezeigt.

Für Versuche mit $HClO_4$, eine Erhöhung der Säurekonzentration und zwar bei gleichzeitiger Erhöhung der $CuCl_2$ - Konzentration hat positive Ergebnisse gezeigt.

Merkwürdig ist, dass bei der Erhöhung von CH_3COOH - Konzentration, ist eine Abnahme des Verhältnisses Cyclohexanol / Cyclohexanon zu beobachten.

Davon ist zu verstehen, dass die Säureeinwirkung für den HCl und $HClO_4$ Fall einen positiven und für CH_3COOH einen negativen Einfluss hat.

Eine Erhöhung der $PdCl_2$ - Konzentration mit HCl als Säureart zeigt negative Ergebnisse, während, eine gleichzeitige Erhöhung von $PdCl_2$ - Konzentration und Temperatur einen positiven Ergebnisse als Ziel hat.

Eine Erhöhung der $PdCl_2$ - Konzentration mit $HClO_4$ als Säureart, zeigt positive Ergebnisse im gegensatz zu der gleichzeitiger Erhöhung von $HClO_4$ - und $PdCl_2$ - Konzentration, welche negative Ergebnisse zeigt. Das selbe gilt für eine gleichzeitige Erhöhung von $CuCl_2$ - und $PdCl_2$ - Konzentration.

Experimenteler Teil

Alle Versuche wurden bei normalen Druck durchgeführt, in einem von uns hergestellten Gefäss, mit Vibrator, Rückflusskühler und Tropftrichter für das Zutropfen des Cyclohexens. Die Proben von 100 cm^3 der wässrigen Katalysatorlösung, enthielten wechselnde Konzentrationen an $PdCl_2$, $CuCl_2$, Essigsäure, HCl oder $HClO_4$. Es wurden FLUKA - Substanzen der Reinheit "purissimum" verwendet. $PdCl_2$ 99% ig. In der Reaktionslösung wurden 10ml Cyclohexen mit 3Nl/h Sauerstoff umgesetzt. Die Versuchsdauer betrug 2 h. Nach Beendigung eines jeden Versuches wurden die Reaktionsprodukte mit Äther Extrahiert und gaschromatographisch bestimmt.

Abstract

Oxidation of cyclohexene by the salts of palladium (II)

Cyclohexene is oxidized to cyclohexanone and cyclohexanol in the presence of aqueous solution of the salts of copper (II) and palladium (II). The process consists of the following stages:

1) Formation of a complex of cyclohexene whith the palladium salt. 2) Conversion of the complex and hydrolysis with the separation of cyclohexanone and cyclohexanol. 3) Oxidation of the palladium (0), formed in the previous stage, by the copper (II) salt. 4) Oxidation of the copper (I) its salt formed in stage 3 with oxygen to give the corresponding copper (II) salt.

On the basis of theoretical and experimental data a series of optimum parameters are proposed, to accelerate the catalytic process. Some experiments are described and are found to be most suitable for the process.

Περίληψις

Ὀξείδωσις τοῦ κυκλοεξενίου ὑπὸ ἁλάτων παλλαδίου (II)

Κατὰ τὴν ὀξείδωσιν τοῦ κυκλοεξενίου, παρουσία ὑδατικῶν διαλυμάτων ἁλάτων Pd (II) καὶ Cu(II), σχηματίζεται κυκλοεξανόνη καὶ κυκλοεξανόλη. Ἡ μέθοδος αὕτη χωρεῖ μέσῳ τῶν ἀκολούθων βαθμίδων:

1) Σχηματισμὸς κατὰ τὴν ἀντίδρασιν ἑνὸς συμπλόκου Pd-κυκλοεξενίου.
2) Μετατροπὴ τοῦ συμπλόκου καὶ ὑδρόλυσις αὐτοῦ πρὸς σχηματισμὸν κυκλοεξανόλης καὶ κυκλοεξανόνης.
3) Ὀξείδωσις τοῦ Pd(0) πρὸς Pd(II) παρουσίᾳ Cu(II) - ἁλάτων.
4) Ὀξείδωσις τοῦ σχηματιζομένου Cu(I) μὲ ὀξυγόνον πρὸς ἐπανασχηματισμὸν τῶν ἀντιστοίχων Cu(II) - ἁλάτων.

Βάσει τῶν θεωρητικῶν καὶ πειραματικῶν δεδομένων προτείνεται μία σειρὰ ἐκ χαρακτηριστικῶν παραμέτρων, αἵτινες περιγράφονται εἰς τὴν παροῦσαν ἐργασίαν.

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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).

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

Tables should be typed on separate sheets numbered with Roman numerals, and provided with a descriptive title, making clear the kind of results presented in the table and the experimental technique(s) used. A legend describing the way the particular experiment(s) was carried out, should be given below the title. (It is usually preferable to give such details here instead of in the text). The units in which the results are expressed may be given either in the legend, or in the columns' headings. In general, the title together with the legend and the column headings should make a table intelligible without reference to the text. Vetrical lines are not used to separate columns. Lines or columns largely empty should be avoided; details referring to one or two isolated items (e.g. an abnormal feature of a single experiments) should be given as footnotes to the table, indicated by superscript lowercase letters or asterisks. Considerable thought should be given to the layout of tables (and figures) so that the significance of the results can be most readily and quickly grasped by the reader. It is surprising sometimes how much easier is to understand the results presented in a table if it is turned through 90°.

Legends to figures should not be written on the figures but should be typewritten, each on a separate sheet attached to the corresponding figure. The legend should begin with the number of figure in Arabic numerals, and provided with a descriptive title and experimental details, as for tables.

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