The structure of Sodium β-hyponitrite

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The substance formed by the action of NO gas on metallic sodium dissolved in liquid ammonia, $(NaNO)_x$, referred to occasionally in the past as sodium nitrosyl is shown to be $Na_2N_2O_2$ by correlation of new with older experimental evidence. It is named β-hyponitrite because it is not identical with Divers' hyponitrite. The infrared spectrum of the solid substance is rich in absorption bands. When dissolved in water part of the substance decomposes immediately. What remains exhibits a Raman spectrum identical whith that of sodium hyponitrite. Possible structures are discussed in view of all experimental evidence available. The latter suggests that β-hyponitrite is a mixture of *cis-* and *trans-* stereoïsomers.

The structure of the hyponitrite ion has recently been established fairly well (1). It is bent *trans*-centrosymmetric ‾O—N=N—O‾. Generally the hyponitrites referred to in the literature are the salts (and the corresponding acid) prepared by suitable reactions from sodium hyponitrite, the latter being obtained by reduction of an aqueous solution of $NaNO_2$ by sodium amalgam (2).

Another substance has long been known (3) to have the same stoichiometric composition $(NaNO)_x$. It is formed when NO gas reacts with metallic sodium dissolved in anhydrous liquid ammonia, and it is referred to by some investigators as sodium hyponitrite (4) and by others as sodium nitrosyl (5). Attempts to elucidate the structure of this substance have been made by means of its Debye Scherrer pattern (5) and magnetic susceptibility (6), but no conclusive information was obtained in either way.

We undertook a spectroscopic examination of the substance with the thought that this should throw some more light on the problem of its structure.

Experimental

The substance was prepared as reported in the literature (3,5,6). Metallic sodium dissolves in liquid ammonia to give a deep blue solution. This absorbs NO gas easily and is decolourised, a suspension of a white crystalline powder in liquid NH_3 being formed.

Nitric oxide was prepared by dropping sulphuric acid into a solution of KNO_2 and KI. The gas evolved was washed through conc. NaOH and stored over water. When needed it was conducted through two towers in series containing (a) $CaCl_2$ and (b) P_2O_5 before use.

Gaseous ammonia from a cylinder was passed through a tower full of pellets of NaOH and condensed in a small bottle where a piece of metallic sodium had been placed. Then it was left to evaporate and so purified it was condensed in the reaction vessel which was kept in a solid CO_2,—alcohol mixture. A freshly cut piece of metallic sodium, dried as well as possible with soft paper, was then introduced into the liquid ammonia (2—3 g of Na per 30 ml of solvent) and NO gas dried as explained in the preceding paragraph was conducted through the ammoniacal solution of sodium, which was gently shaken occasionally to facilitate the reaction.

All the manipulations were performed in a closed apparatus.

When the blue colour had disappeared the temperature was allowed to rise. After ammonia had evaporated the white powder left behind was submitted to vacuum to remove any traces of absorbed NH_3, and placed in a vac—H_2SO_4 dessicator.

The chemical properties of the substance were found to be as reported by previous investigators. It was highly hygroscopic and deliquescent. As soon as it came in contact with water some gas [N_2O (6)] was evolved. The solution gave by addition of silver nitrate a yellow precipitate (i. e. silver hyponitrite) but also some metallic silver appeared after a few minutes.

Vibrational spectrum

1. Raman. Attempts to obtain the Raman spectrum of the substance in the solid state were unsuccesful. The Raman spectrum of its aqueous solution was observed by using a truncated-cone cell which just filled the aperture-cone of the spectrograph and allowed escape of gas bubbles formed by the slow decomposition of the sample.

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The spectra were recorded on a Hilger E 612 spectrograph by using Kodak Oa-O fast plates.

Fig. 1 shows a microphotometer tracing of one of them. The strongest Raman frequency of hyponitrite anion, i. e. 1383. cm⁻¹ (1), was found
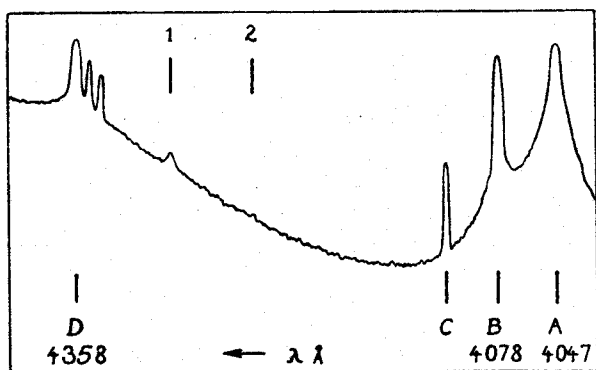

Fig. 1. Raman spectrum in aqueous solution. A,B,C,D, are mercury lines. 1: Raman , 1383 cm⁻¹(N₂O₂²⁻). 2: Raman , 1065 cm⁻¹(CO₃²⁻). Both excited by Hg λ 4047 Å.

in a number of spectra. No other Raman line was detectable apart from 1065 cm⁻¹ due to CO_3^{2-} which was formed during even a short exposure of the solid substance or its highly alkaline solution to the atmosphere. It is known (1) that the second in intensity Raman line of $N_2O_2^{2-}$ is too weak to appear in spectra like the one in Fig. 1.

2. Infrared. The solid substance was mixed with KBr and pressed into a disc. This was used to obtain the infrared spectrum, on a Hilger D 209 spectrometer (Fig. 2). Two strong absorption bands at 1024 and 1272 cm⁻¹ are attributed to the spectrum of the substance investigated. Also some weaker ones at about 870, 910, 1800 cm⁻¹ etc. Several other weak bands may be due to
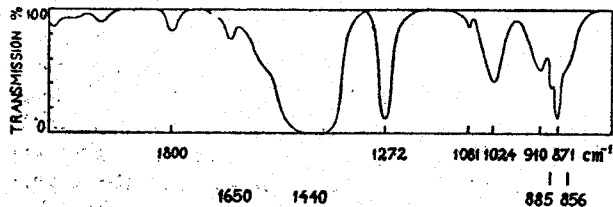

Fig. 2. Infrared spectrum in KBr disc.

impurities, e. g. the one at 1650 cm⁻¹ to traces of ammonia. The strong absorption at 1440 cm⁻¹ together with two weaker ones at 885 and 856 cm⁻¹ are known to be due to carbonate whose presence as impurity is almost inevitable.

Discussion

The many vibration bands in the infrared spectrum eliminate the possibility of the sub-

stance having the simple structure NaNO. The spectrum of this should consist of one fundamental corresponding to the vibration of the diatomic species NO⁻. Besides, this ion is isoelectronic with the oxygen molecule, and would be expected to be paramagnetic, whereas Frazer and Long (6) have found the substance diamagnetic.

Hence there can be little doubt that $N_2O_2^{2-}$, is the anion of the substance in question, which however, is not identical with anhydrous sodium hyponitrite for the following reasons:

. a) The two substances react differently with water. Anhydrous sodium hyponitrite does not show instantaneous decomposition but it only starts decomposing slowly. If this substance is dissolved in water, a part of it decomposes immediately. The rest is then identical with hyponitrite, as shown by its Raman spectrum and the silver hyponitrite reaction.

b) It is hygroscopic and deliquescent. In this it differs again from sodium hyponitrite.

c) The infrared spectrum of this substance is not the same as that of sodium hyponitrite, although the characteristic hyponitrite bands are also present.

d) According to Zintl and Harder (5) the Debye-Scherrer patterns of the two substances are different.

Thus the substance prepared by passing nitric oxide into a solution of sodium in liquid ammonia should no longer be called sodium nitrosyl or hyponitrite. We suggest it be known as β—hyponitrite, and we refer to it in this way in what follows.

Structure. In assigning a structure to the $N_2O_2^{2-}$ in β—hyponitrite the experimental data listed above must be accommodated. It will be seen that this can be best fulfilled if β—hyponitrite is viewed as a mixture of *cis* and *trans* stereoïsomers (I and II).

$$N = N \quad\quad N = N$$

I   II
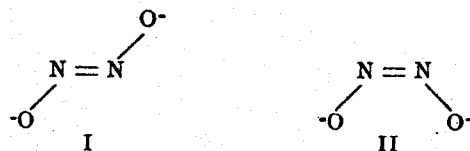
Divers' sodium hyponitrite has been shown (1) to have structure I. The strong absorption band at 1024 cm⁻¹ in the spectrum of β—hyponitrite coïncides with the only strong infrared active vibration of the hyponitrite ion (I), which has been reported (1) to be 1020 cm⁻¹ and assigned to N-O asymmetric stretching. Furthermore the strong Raman line of species I [1383 cm⁻¹ (1)] is also found in the Raman spectrum of β—hyponitrite in solution. The presence of hyponitrite (I) in this solution is also shown by the yellow silver hyponitrite reaction. These suggest that

a part of β—hyponitrite is indeed identical with Divers' hyponitrite i. e. it has the *trans* structure I.

At the same time the data (a) and (c) clearly indicate the presence of one more species, which is apparently far less stable in solution. Thus its spectrum is observed in the solid β—hyponitrite (infrared) but not in solution (Raman).

To assign a structure to this unstable constituent the method of preparation of β—hyponitrite must be considered. The spectroscopic measurements of Smith, Keller and Johnston (7) on liquid nitric oxide are also relevant. Condensed nitric oxide seems to consist mainly of N_2O_2. When diluted in solvents at low temperatures it partly dissociates into NO. According to these authors, N_2O_2 is most likely a bent ONNO molecule without a centre of symmetry, i. e. with a *cis* or staggered (intermediate between *cis* and *trans*) structure. Thus it seems possible for an anion like II to be formed from N_2O_2 dissolved in liquid ammonia.

The infrared spectrum of structure II is expected to consist of five fundamentals. The observed absorption bands in the infrared spectrum of β—hyponitrite (apart from the one at 1024cm⁻¹) may be attributed to the *cis* isomer (II), but it is difficult to assign each one to a particular mode of vibration. Three of the fundamentals are stretching vibrations i. e. symmetric N=N and N—O (both species A_1) and asymmetric N—O (species B_1) all expected in the region 1000—1400 cm⁻¹ by analogy with the hyponitrite spectrum. 1272 cm⁻¹ appears a little lower than the N=N and higher than the N—O stretching vibration frequencies of hyponitrite. In the latter 1020 and 1115 cm⁻¹ have been assigned (1) to N—O and 1383 cm⁻¹ to N=N stretchings. Howe-

IIa   III
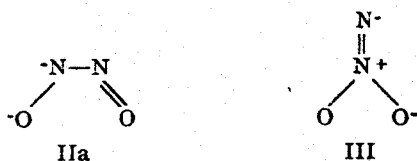
ver there is a possibility of resonance between II and forms like IIa which would lower the order of the N=N bond and increase that of the N—O bond. Thus 1272 cm⁻¹ could be due to one of the stretching modes mentioned.

The possibility of the structure III can not be eliminated by the spectroscopic evidence but it is difficult to see how a species like III could be formed from either NO gas or N_2O_2.

Finally the hypothesis that β—hyponitrite consists entirely of the *cis* isomer can also be excluded, because it would leave unexplainable why a part of this species should decompose rapidly in water while the rest of it isomerizes to the *trans* isomer.

ΠΕΡΙΛΗΨΙΣ

'Η σύνταξις τοῦ β-ὑπονιτρώδους νατρίου.

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Μεταλλικὸν νάτριον διαλύεται εὐκόλως ἐντὸς ὑγροποιηθείσης ἀπολύτως ξηρᾶς ἀμμωνίας. Τὸ διάλυμα εἶναι βαθέως κυανοῦν. 'Εὰν δι' αὐτοῦ διαβιβασθῆ καθαρὸν καὶ ξηρὸν NO, σχηματίζεται μία λευκὴ κρυσταλλικὴ κόνις τῆς ὁποίας ἡ σύστασις, $(NaNO)_x$, εἶναι γνωστὴ ἀπὸ μακροῦ (3), ἡ σύνταξις δὲ αὐτῆς ὑπετίθετο ὅτι ἦτο NaNO, ἐπειδὴ διαφέρει οὐσιωδῶς τοῦ ἀνύδρου ὑπονιτρώδους νατρίου $Na_2N_2O_2$. 'Εν τούτοις ἡ ὑπόθεσις ὅτι ἡ οὐσία περιέχει τὸ ἀνιὸν NO⁻ δὲν ἠδύνατο νὰ εὐσταθήσῃ ἀφ' ὅτου αὕτη εὑρέθη διαμαγνητικὴ (6).

Πρὸς διευκρίνισιν τῆς συντάξεως τῆς οὐσίας ταύτης ἐμελετήθη τὸ φάσμα δονήσεως αὐτῆς ἐν στερεᾷ καταστάσει (ὑπέρυθρον) καὶ ἐν διαλύσει (Raman). 'Εὰν ἡ οὐσία ἦτο NaNO τὸ φάσμα ἀπορροφήσεως εἰς τὸ ὑπέρυθρον ἔπρεπε νὰ ἀποτελῆται ἀπὸ μίαν μόνον περιοχὴν ἀπορροφήσεως. 'Εν τούτοις τὸ φάσμα ἐμφανίζεται κατὰ πολὺ πλουσιώτερον καὶ ἑπομένως ἡ οὐσία ἀποδεικνύεται ὅτι εἶναι $Na_2N_2O_2$. 'Επειδὴ ὅμως αὕτη διαφέρει τοῦ κατὰ Divers ὑπονιτρώδους νατρίου προτείνεται ὅπως αὕτη ἀναφέρεται ἐφεξῆς ὡς β-ὑπονιτρῶδες νάτριον. 'Οσον ἀφορᾷ δὲ εἰς τὴν σύνταξιν τοῦ β-ὑπονιτρώδους νατρίου συσχέτισις ὅλων τῶν διατιθεμένων πειραματικῶν δεδομένων ὁδηγεῖ εἰς τὸ συμπέρασμα ὅτι τοῦτο εἶναι ἐν μῖγμα *trans* καὶ *cis* στερεοϊσομερῶν (I καὶ II).

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