[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Infrared Spectra of the Salts of the Dinitrososulfite Ion (Nitrosohydroxylaminesulfonates)

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The infrared spectra of the sodium, potassium and ammonium salts of the dinitrososulfite ion are reported. Differences in the spectra of these three salts are interpreted. It is also concluded that the N–N bond in this ion has considerably more single bond character in it than previously proposed.

The synthesis of several materials containing the dinitrososulfite ion can be accomplished by passing nitric oxide into a basic solution containing sulfite ion.[1,2] The reactions that the dinitrososulfites undergo are very complex and, as a result, attempts to deduce a structure from the chemical behavior led to conflicting results.[2–5] A single crystal, X-ray diffraction investigation was undertaken and the structures of the potassium, ammonium and thallium salts were determined.[6] An accurate determination of the bond orders could not be ascertained from these studies and recently there have been attempts[7,8] to explain the electronic structure of the dinitrososulfites from chemical behavior. Evans and Gergeley[9] have also proposed a structure based upon a molecular orbital system of bonding throughout the N_2O_2 group. The infrared spectra were obtained in order to gain additional information concerning the structures of these salts.

An X-ray study of the sodium salt was not undertaken by Cox, *et al.* Difficulties were encountered[5] in attempts to prepare single crystals of this salt because of its much greater solubility. In view of this surprising solubility, the infrared spectrum of the sodium salt also was studied in order to obtain evidence concerning its structure.

Experimental

The sodium and potassium salts were prepared by methods described by Weitz and Achterberg.[2] The ammonium salt was prepared by a metathesis reaction based on the insolubility of ammonium dinitrososulfite relative to the sodium salt. In this procedure excess ammonium chloride and ammonium hydroxide are added to the reactants used to prepare the sodium salt. The crude ammonium salt precipitates out as the reaction proceeds. The salt is purified by methods previously described.[2] The potassium salt can also be prepared by a similar type reaction. The purity of the salts employed in this study are indicated by the following analyses: Calcd. for $K_2SO_3N_2O_2$: N, 12.83; K, 35.84. Found: N, 12.74; K, 35.67. Calcd. for $Na_2SO_3N_2O_2$: N, 15.01; Na, 24.73. Found: N, 14.38; Na, 24.73. Calcd. for $(NH_4)_2SO_3N_2O_2$: N, 31.82. Found: N, 31.80.

Nujol mulls of the compounds were examined using a Perkin-Elmer model 21 infrared spectrometer with sodium chloride optics. The potassium salt was also examined in perfluorokerosene mull.

Results

Table I contains the results, obtained from the infrared study. Tentative assignments have been listed. Although the tentative assignments have been designated as originating within a particular bond, it should be pointed out that the group frequency vibrations in the 1300–650 region are not completely localized within the bond designated. There is only limited information available to support the assignment of the bond at 925 cm.$^{-1}$. Fortunately the doubtful assignment does not seriously affect the conclusions that can be drawn regarding the structure of these salts.

TABLE I

INFRARED BANDS AND TENTATIVE ASSIGNMENTS[a]

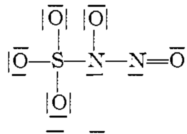
$K_2SO_3 \cdot 2NO$	$(NH_4)_2$-$SO_3 \cdot 2NO$	$Na_2SO_3 \cdot 2NO$	Assignments and lit. ref.
	3250 i,s		NH stretch[10]
	3110 i,m		
	1435 i,m		NH_4^+ bending mode[10]
1322 i,s	1330 i,s	1345 med,m	NO stretch[12]
1265–85 i,m	1282 i,m	1280 i,m	S–O stretch[11]
1230 i,s	1202 med,s	1240 i,s	N–O stretch[12]
1130 i,s	1132 i,s	1147 i,s	N–N stretch[12]
1055 i,s	1057 i,s	1060 i,s	S–O stretch[11]
922 i,s	925 i,s	934 i,s	(S–N–N) vibration[b]
625 med,br	625 med,br	625 i,br	S–O bending mode[11]

[a] The first symbol listed refers to the bond intensity: i, intense; med, medium intensity; wk, weak. The second symbol refers to band width: s, sharp, m, medium, br, broad. [b] Very little information is available on this type of linkage. This bond does not occur in compounds that contain only one nitrogen on the sulfur.[11,13] It does occur both in the compounds reported above and in hydrazinosulfuric acid.[13] The parentheses indicate this assignment is questionable and requires further investigation.

Discussion

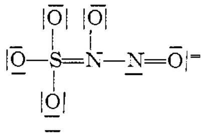
The following structures are possible for the dinitrososulfite ion. (Resonance forms for the $-SO_3$ group are not included.)

(I)



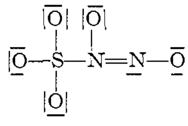
$[O_3S{-}N(O){-}N{=}O]^-$

(II)



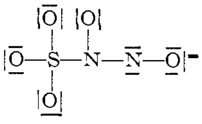
$[O_3S{=}N(O){-}N{=}O]^-$

(III)



$[O_3S{-}N(O){=}N{-}O]^-$

(IV)



$[O_3S{-}N(O){-}N{-}O]^-$

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(1) J. Pelouze, *Ann. Pharm.*, **15**, 240 (1835).

(2) E. Weitz and F. Achterberg, *Ber.*, **66B**, 1718 (1933).

(3) F. Raschig, *Ann.*, **241**, 232 (1887).

(4) E. Divers and T. Haga, *J. Chem. Soc.*, **67**, 452 (1895); **69**, 1610 (1896).

(5) A. Hantzsch, *Ber.*, **27**, 3264 (1894).

(6) E. G. Cox, G. A. Jeffrey and H. P. Stadler, *J. Chem. Soc.*, 1783 (1949); *Nature*, **162**, 770 (1948); G. A. Jeffrey and H. P. Stadler, *J. Chem. Soc.*, 1467 (1951).

(7) M. Goehring and R. Otto, *Z. anorg. allgem. Chem.*, **280**, 143 (1955).

(8) E. Degener and F. Seel, *ibid.*, **285**, 129 (1956).

(9) M. G. Evans and J. Gergeley, *Nature*, **162**, 771 (1948).

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 285.

(11) H. J. Hofmann and K. R. Andress, *Naturwissenschaften*, **41**, 94 (1954).

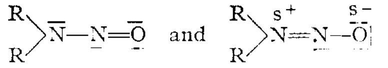
(12) R. N. Haszeldine and J. Jander, *J. Chem. Soc.*, 691 (1954), Errata, *ibid.*, 4778 (1954); R. N. Haszeldine and B. J. H. Mattinson, *ibid.*, 4172 (1955).

(13) S. West, Ph.D. Thesis, University of Illinois, 1955.

The actual structure undoubtedly is a resonance hybrid consisting of most of these forms. From the X-ray study it was concluded that structure III is of greatest significance in contributing to the final structure and in other publications[7] structure III was the only one indicated.

The absence of absorption in the 1500 cm.$^{-1}$ region indicates that the N–N bond has a considerable amount of single bond character in it. This would indicate that other structures (I or I and II) are quite significant in determining the final state of the molecule. The Raman and infrared spectra of hyponitrite ion have been reported[14] and absorption at 1392 cm.$^{-1}$ was attributed to the N–N bond. The authors interpreted this as indication of a considerable amount of single bond character in the N–N bond. Using similar arguments these studies indicate that the N–N bond in the dinitrososulfite ion has more single bond character than the N–N bond in hyponitrite for the spectra of the potassium salt in perfluorokerosene shows the absence of absorption up to 1322 cm.$^{-1}$.

The tentative assignments have been made for N–O and N–N absorption by considering the bond types to be similar to those in the dialkyl nitrosamines.[12] The following assignments have been reported for N–O and N–N vibrations in these compounds[12]: two vibrations for N–O stretch: 1315–1165 and 1265^{-1} cm.$^{-1}$; the N–N vibration between 1135–1190 cm.$^{-1}$. The structures of the nitrosamines were regarded as a hybrid of the forms



Absorptions from N=O do not occur at higher frequencies because of this resonance.

It should be kept in mind that in this study the spectra were obtained on Nujol mulls of the solid dinitrososulfites. It would be most desirable to check these measurements with Raman data on these compounds in solution to evaluate further the above assignments.

The spectra of the potassium, ammonium and sodium salts are all similar enough to indicate that the structure of the sodium salt is similar to that of the potassium and ammonium salt. With the exception of the NH_4^+ vibrations and the absorption at 1230 cm.$^{-1}$, the spectra of the potassium and ammonium salts are very much alike. The difference in the N–O vibration at 1230 cm.$^{-1}$ can be attributed to effects caused by hydrogen bonding in the ammonium salt. The existence of hydrogen bonding is further substantiated by the splitting of the N–H stretching vibration in the 3200 cm.$^{-1}$ region.

The shifts observed in the infrared spectra of the sodium salt compared to the other salts is interesting in view of the larger solubility of the sodium salt. The shifts probably arise from differences in crystal stability resulting from either anion–anion contact or from a different kind of crystal lattice in the case of the sodium salt.

URBANA, ILL.

[14] L. Kuhn and E. L. Lippincott, THIS JOURNAL, **78**, 1820 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF DUKE UNIVERSITY]

Near Ultraviolet Absorption Spectra of the Pyridine Monocarboxylic Acids in Water and Ethanol Solutions[1,2]

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The near ultraviolet absorption spectra of picolinic, nicotinic and isonicotinic acids (2-, 3- and 4-pyridinecarboxylic acids) have been measured in 95% ethanol and distilled water solutions, and for isonicotinic acid, also for several mixtures of these two solvents. Changes in the spectra which occur when the solvent is changed from ethanol to water have been interpreted to show that the pyridine monocarboxylic acids exist primarily in the neutral, undissociated form in ethanol, and in the anion and zwitterion forms in water.[4] The spectra of the several species are discussed with regard to rather limited theoretical information concerning the effects of a carboxyl substituent on the spectrum of benzene or pyridine.

Introduction

Recently the near ultraviolet absorption spectra of the three pyridine monocarboxylic acids in aqueous solution have been reported in a number of papers,[5–7] the spectra having been observed in order to determine the acid and base dissociation constants of these substances. In each of these papers the possible zwitterion forms of the molecules were considered unimportant for an interpretation of the observed spectra. However, Jaffé[8] has discussed the tautometric equilibria of a number of substituted pyridines and their 1-oxides in aqueous solution and has concluded that nico-

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[1] Based on a portion of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, 1952.

[2] This investigation was assisted by the ONR under Contract N6ori-107, T. O. I., with Duke University.

[3] Shell Oil Company Fellow in Physics, 1950–1951.

[4] For external reasons, the publication of this paper was much delayed. Before finally sending it off, a recent article by R. W. Green and H. K. Tong on "The Constitution of the Pyridine Monocarboxylic Acids in their Isoelectric Forms" (THIS JOURNAL, **78**, 4896 (1956)) has come to our attention, in which these authors came to the same conclusions about the species of these acids in aqueous solutions as are presented in this paper. However, since our approach to this problem came more from the spectroscopic side, this paper contains additional spectroscopic information which supplements the paper by Green and Tong.

[5] E. B. Hughes, H. H. G. Jellinek and B. A. Ambrose, *J. Phys. Colloid Chem.*, **53**, 414 (1949).

[6] R. F. Evans, E. F. G. Herington and W. Kynaston, *Trans. Faraday Soc.*, **49**, 1284 (1953).

[7] H. H. G. Jellinek and J. R. Urwin, *J. Phys. Chem.*, **58**, 548 (1954).

[8] H. H. Jaffé, THIS JOURNAL, **77**, 4445 (1955).