icity constant now is B; of the twelve correlations where β was negative, only in one case is the value of B negative. In this case, correlation of K_{sp} values for precipitates of thallous ion, the value of B (-0.08) is probably not significantly discrepant since the experimental errors are large.

It is instructive to consider some more complicated donors using the above correlation of nucleophilic character with polarizability and basicity. The basicities to protons of the following oxyanions are known to fall in the order

$$CO_3^{=} > SO_4^{=} > NO_3^{-} > ClO_4^{-}$$

Their nucleophilic strengths fall in the same order, but specific numerical values are not at hand for the two extreme cases. Employing equation II, the known basicities and polarizabilities and also the assumption that the polarizability of only one oxygen is important, calculated E_n values were obtained for these oxyanion donors. The data are presented in Table II. It is apparent that the calculated values are low; it seems reasonable to conclude that the polarizability of the electrons on more than one atom is involved. Statistical factors may also be involved, of course.

TABLE II

CONSTANTS FOR OXYANION DONORS

Donor	H^a	$R_\infty{}^b$	E_n (calcd.)^c	E_n (obsd.)
ClO_4^-	−9.0	3.30	−0.73	<0.00
NO_3^-	0.4	3.67	.03	.29^a
$SO_4^=$	3.7	3.70	.24	.59^a
$CO_3^=$	12.1	4.05	.91	>1.1

[a] Data of ref. 3. [b] These values are the values of R_∞ for the whole ion divided by the number of oxygens in the ion. Data of ref. 4. [c] Calculated using equation II and the constants given in Table I.

The conclusion that the polarizability of more than the one atom at the reaction site is involved in nucleophilic character seems to be borne out by the E_n value for cyanide ion. The observed[5] E_n value is about 2.02; as the value obtained from the electrode potential data[3] is unquestionably high, the value from rate data[5] is used here. Using the values $H = 10.88$ and $R_\infty = 8.66$ along with equation II, the calculated value is 2.01 in good agreement with the observed value. The above value of R_∞ is, however, that for the whole cyanide ion; the necessity of using the total polarizability in this case is further evidence that the electrons on other than the reacting atom of the donor are involved in nucleophilic character.

Only one other case is sufficiently straight-forward to allow calculation. Employing $H = 11.22$ and $R_\infty = 5.61$, the E_n value for ammonia is calculated to be 1.36. This is lower than the E_n value of 1.84 which comes from electrode potential data; however, the latter value is undoubtedly too high.[3] Further data are certainly desirable for this case.

Acknowledgment.—The helpful comments and criticisms of Professor R. G. Pearson of Northwestern University and Professor L. B. Clapp of Brown University are appreciated.

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(5) M. F. Hawthorne, G. S. Hammond and B. M. Graybill, THIS JOURNAL, **77**, 486 (1955).

PROVIDENCE, R. I.

[JOINT CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

The Vibrational Spectrum and Structure of the Hyponitrite Ion

BY LESTER KUHN AND ELLIS R. LIPPINCOTT

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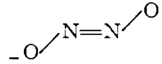
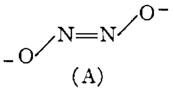
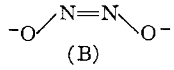
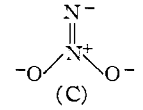
Infrared spectra are reported for sodium, silver and mercury hyponitrites, in the region from 400 to 4000 cm.$^{-1}$, along with Raman spectra for sodium hyponitrite in aqueous solution. The results are interpreted in terms of possible structures for the hyponitrite ion. It is concluded that this ion has the *trans* configuration  . An assignment is given of the observed frequencies to the normal modes of vibration for this ion.

Although salts of hyponitrous acid have been known for some time, there has been little definite information on the structure of the ion. Previous workers[1-4] have concluded that the hyponitrite ion has the *trans*-form of structure A. Alternative possible structures are the *cis*-form B and structure C.


(A)


(B)


(C)

Structure C is isoelectronic with carbonate and nitrate ions and would be expected to be stabilized by resonance, similar to that for the NO_3^- and $CO_3^=$ ions.

No previous spectroscopic studies have been reported for the salts of hyponitrous acid. We wish to report here infrared and Raman spectroscopic studies on sodium, silver and mercury salts of hyponitrous acid which furnish conclusive evidence that the hyponitrite ion has the *trans*-form (A).

Experimental

Sodium hyponitrite was made according to the method of Scott.[1] The product was dried over P_2O_5 *in vacuo*. The sodium salt was converted to the insoluble silver salt by reaction with silver nitrate, and was converted to the insoluble mercury salt by reaction with mercuric acetate, according to the method of Partington and Shah.[2]

The samples were mulled in Nujol and infrared spectra from 400 to 4000 cm.$^{-1}$ were taken with a Perkin-Elmer double beam spectrometer equipped with a rock salt and a

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(1) A. Scott, THIS JOURNAL, **49**, 987 (1927).

(2) J. Partington and C. Shah, *J. Chem. Soc.*, 2595 (1932).

(3) Yost and Russel, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, p. 57.

(4) A. Hantzsch, *Ber.*, **66**, 1566 (1933).

KBr prism. The sodium salt was also run as a mull in perfluorokerosene.

Raman spectra of aqueous solutions of $Na_2N_2O_2$ were obtained photographically on a Hilger 612 spectrograph,[5] by standard methods using both 4358 and 4047 Å. Hg excitation, with the appropriate optical filters. After dissolving solid $Na_2N_2O_2$ in distilled water the solutions (approximately 1 *M*) were filtered into the Raman tubes through a Corning ultrafine sintered-glass bacteriological filter. Satisfactory spectra were obtained using one to two hours exposure times. A slight continuum appeared on the plates with the longest exposures. The infrared and Raman data are summarized in Table I.

TABLE I

INFRARED AND RAMAN SPECTRA[a] OF SALTS OF HYPONITROUS ACID (CM.$^{-1}$)

$Na_2N_2O_2$ Infrared	$Na_2N_2O_2$ Raman	$Ag_2N_2O_2$ Infrared	$Hg_2N_2O_2$ Infrared	Assignment
	1392			N=N stretching
1090 mw		1075 mw		
1035 s		1058 s	1138 s	Antisym N–O stretching
	958 m			Sym N–O stretching
885 w				
629 m		571 s	618 s	NNO bending
492 w		422 w	418 w	ONNO distortion

[a] s, strong; m, medium; mw, medium weak; w, weak.

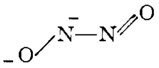
Discussion

The structures A, B and C may be classified as having C_{2h}, C_{2v} and C_{2v} symmetries, respectively. The selection rules for these point groups are well known. The *trans* C_{2h} structure predicts three Raman active (3 A_g species) and three infrared active fundamentals (1 A_u and 2 B_u, respectively). No coincidences between infrared and Raman fundamentals are predicted for the *trans* form. The C_{2v} symmetry predicts for the *cis* structure, B, the appearance of six Raman active and five infrared active fundamentals while for structure C all six fundamentals are predicted in both the Raman and infrared spectrum. For both C_{2v} structures all of the infrared active fundamentals are predicted to appear in the Raman spectrum.

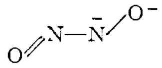
An examination of the data presented in Table I shows the presence of only two Raman lines and two or three infrared bands with sufficient intensity to be interpreted as fundamentals. Although the Raman and infrared spectra of $Na_2N_2O_2$ were obtained in different physical states the observed frequencies are so far apart that there is little doubt that there are no coincidences between Raman and infrared frequencies. These observations indicate strongly that the $N_2O_2^{=}$ ion has the *trans* C_{2h} configuration. The failure to observe a third Raman frequency is attributed to its low intensity along with the limited exposure times used, due to an appearance of a continuum on the plates. The rather sharp, weak or medium infrared bands at 885 and 1090 cm.$^{-1}$ in $Na_2N_2O_2$ and 1075 cm.$^{-1}$ in $Ag_2N_2O_2$ are unexplained but probably are due to the effect of crystal forces.

Additional evidence against structure C is furnished by a comparison with the vibrational spectra of the NO_3^- and $CO_3^{=}$ ions. Since all three ions are isoelectronic their spectra should be similar[6–8] except for the effects of symmetry, and one would expect a very strong infrared band near 1400 cm.$^{-1}$ where none is observed. In the Raman spectrum the intensity of the 956 cm.$^{-1}$ Raman line should be considerably greater than the 1392 cm.$^{-1}$ lines whereas the reverse situation is observed.

The observed fundamental frequencies are readily assigned to the modes of vibration for the *trans* structure (see Table I). It is surprising that the N=N frequency occurs at the low frequency of 1392 cm.$^{-1}$ since its value in azomethane[9] is 1576 cm.$^{-1}$. We interpret the low value of this frequency as being due to resonance best illustrated by the structures



and



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[5] The Raman studies were carried out in the Department of Chemistry, Kansas State College, Manhattan, Kansas.

[6] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

[7] N. Emberidos, *Z. Physik*, **65**, 266 (1935).

[8] W. Gerlach, *Anal. Phys.*, **5**, 196 (1930).

[9] W. West and R. B. Killingsworth, *J. Chem. Phys.*, **6**, 1 (1938)