[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

# Polarizability, Basicity and Nucleophilic Character

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The nucleophilic strengths of some uncomplicated donors have been related to their polarizabilities and basicities. A double scale equation of the type used previously for donor reactivity correlations has been employed. Some consequences of this relation are discussed.

It has been felt for some time that the nucleophilic strength of a donor particle is probably related to the polarizability of the particle, but the relationship has never been characterized.[1] This paper deals with a relation of the nucleophilic constants to the corresponding polarizabilities and basicities.

Swain and Scott[2] set up their scale of nucleophilic strengths of donor particles with data from relative rates of displacements on methyl bromide. Edwards[3] obtained a similar set of nucleophilic strengths, the $E_n$ values, from electrode potentials and proposed the correlation equation

$$\log (K/K_0) = \alpha E_n + \beta H \qquad \text{(I)}$$

where $K/K_0$ is a relative (to water) rate or equilibrium constant, $E_n$ and $H$ are the nucleophilic and basic constants for the donors, and $\alpha$ and $\beta$ are the corresponding substrate constants.

If the assumption is made that the $E_n$ values do depend on polarizabilities, it can be shown that one relationship between polarizabilities and nucleophilicities can be obtained from a double-scale equation of the type of equation I. Thus, it becomes possible in principle to calculate rates and equilibrium constants for many donor reactions. For the donor particle, one needs only the $pK_a$ of its conjugate acid and the polarizability of the reaction site of the donor; for each substrate, the two corresponding constants are needed.

In Table I, data for seven uncomplicated donors are presented. It appears that the nucleophilic constants ($E_n$) of the donors are dependent both on their polarizabilities[4] (given as molar refraction $R_\infty$) and on their basicities to protons ($H = pK_a + 1.74$). Using the data of Table I and the method of least squares, the values of $a$ and $b$ in equation II

$$E_n = aP + bH \qquad \text{(II)}$$

where

$$P \equiv \log (R_\infty/R_{H_2O})$$

have been obtained. They are 3.60 and 0.0624, respectively. Calculated values of $E_n$ (using these constants) are placed in the last column of Table I. In spite of the marked variance in the orders of $H$ and $R_\infty$ (and also the estimated natures of some of the values), the order of $E_n$ values is maintained. Moreover, the agreement between calculated and observed values is strikingly good, for the largest deviation is only 0.06 $E_n$ unit.

TABLE I

POLARIZABILITIES, BASICITIES AND NUCLEOPHILIC STRENGTHS

| Donor | $E_n$ (obsd.)[a] | $H$[a] | $R_\infty$[b] | $P$ | $E_n$ (calcd.)[c] |
|---|---|---|---|---|---|
| $F^-$ | −0.27 | 4.9 | 2.6 | −0.150 | −0.23 |
| $H_2O$ | 0.00 | 0.0 | 3.67 | .00 | 0.00 |
| $Cl^-$ | 1.24 | (−3.0) | 9.0 | .389 | 1.21 |
| $Br^-$ | 1.51 | (−6.0) | 12.7 | .539 | 1.57 |
| $OH^-$ | 1.65 | 17.5 | 5.1 | .143 | 1.60 |
| $I^-$ | 2.06 | (−9.0) | 19.2 | .718 | 2.02 |
| $S^=$ | 3.08 | 14.7 | 15.0 | .611 | 3.11 |

[a] Data from ref. 3. [b] Data from ref. 4. [c] Calculated using $a = 3.60$ and $b = 0.0624$.

Equation II can be rearranged, in order to graphically demonstrate the relationship between nucleophilic strength and polarizability, by dividing through by $H$. The resulting equation

$$\frac{E_n}{H} = a\left(\frac{P}{H}\right) + b \qquad \text{(III)}$$

predicts that a plot of $E_n/H$ against $P/H$ should give a straight line, and this prediction is borne out well by the data of Table I. (It should be noted, however, that this linear equation can be used only for presentation of data and should never be used for calculations since it does not weight $H$ and $P$ equally.)

These data do not constitute proof for the validity of the assumption that the nucleophilic character of a particle is traceable to its polarizability and to its basicity. There is no doubt, however, that the calculated $E_n$ values closely parallel the experimental values obtained from electrode potential data and that the use of this assumption and of equation II has led to encouraging results.

It is noteworthy that this relation can resolve a somewhat disconcerting result of the previous work[3]; for some of the correlations, a negative value of $\beta$ in equation I was found. In order to explain such negative values of $\beta$, it was necessary to assume that $E_n$ values still included a sizable basicity contribution. Happily, the positive value of $b$ found in this work is strong evidence that nucleophilic character does depend on basicity. Quantitatively, the agreement is also encouraging. If equation II is substituted into equation I, a new double-scale equation

$$\log (K/K_0) = AP + BH \qquad \text{(IV)}$$

where $A = \alpha a$ and $B = \beta + \alpha b$, for correlation of rates and equilibria is obtained. The substrate bas-

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(1) *Cf.* A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 201.

(2) C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

(3) J. O. Edwards, *ibid.*, **76**, 1540 (1954).

(4) (a) N. Bauer and K. Fajans in "Physical Methods of Organic Chemistry," A. Weissberger, 2nd Ed., Vol. I, Part II, Interscience Pub., New York, N. Y., 1949, p. 1141–1240; (b) Landolt-Börnstein, "Zahlenwerte und Funktion," Verlag-Springer, Berlin, 1950; 6. Aufgabe, I. Band, I. Teil, p. 399; III. Teil, II, p. 509–517; (c) J. A. A. Ketelaar, "Chemical Constitution," Elsevier Pub. Co., Inc., Houston, 1953, p. 90; (d) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 119–125.

icity constant now is $B$; of the twelve correlations where $\beta$ 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 $R_\infty$ 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 $R_\infty$ 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.

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

# The Vibrational Spectrum and Structure of the Hyponitrite Ion

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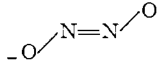
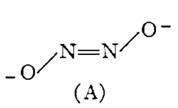
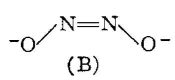
Infrared spectra are reported for sodium, silver and mercury hyponitrites, in the region from 400 to 4000 cm.$^{-1}$, along with Raman spectra for sodium hyponitrite in aqueous solution. The results are interpreted in terms of possible structures for the hyponitrite ion. It is concluded that this ion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

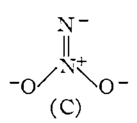
Although salts of hyponitrous acid have been known for some time, there has been little definite information on the structure of the ion. Previous workers[1-4] have concluded that the hyponitrite ion has the *trans*-form of structure A. Alternative possible structures are the *cis*-form B and structure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