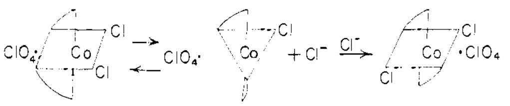


The chloride ion approaching the penta-coördinated intermediate would have to penetrate the field due to the perchlorate in order to form the *trans*-isomer. If these conditions existed in the alcohol solutions, it is possible to account for the lower rate of isomerization in the presence of perchlorates. Initially, k_2 would be expected to be significant compared to k_3 because of the repulsive nature of the perchlorate ions on the negative ions, which results in the shift of equilibrium II toward the *cis*-dichloro complex. As the reaction progresses, the value of k_3 apparently contributes to such a point that the rate of isomerization attains a constant value.

The introduction of water into the system would tend to break up the ion pairs, such that the rates of isomerization increase. Such appears to be the case in the lithium chloride systems due to the high degree of hydration of this salt. In ethanol and propanol systems containing both lithium chloride and sodium perchlorate, a trace of water has a large affect. It should be noted that the activity coefficients in the presence of relatively high concentrations of salt are quite different from those in which there are no added ions.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM WM. A. NOYES LABORATORY, UNIVERSITY OF ILLINOIS]

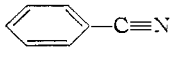
The Integrated Intensity of the Infrared C≡N Band of Benzonitriles in Various Solvents

BY THEODORE L. BROWN

RECEIVED AUGUST 9, 1957

The integrated intensity of the infrared C≡N band for a group of substituted benzonitriles in various solvents has been studied. The magnitude of the intensity for any one compound is strongly dependent on the solvent, but the relative magnitudes within the series are not. The intensity is greatest for compounds containing the most electron-releasing substituents, suggesting a similarity between the C≡N stretching vibration and electrophilic rate processes. From the intensity results a set of reactivity constants is determined and compared with rate data taken from the literature.

Numerous studies of the infrared intensity of an absorption band possessed in common by a series of related molecules have shown that the variations of intensity within the series can be correlated with other molecular properties. These correlations are particularly good when the absorption is one which can be assigned in large measure to a localized functional group vibration. Among the functional group absorptions which have been studied in this way are the carbonyl,[1] aliphatic and aromatic hydroxyl,[2,3] and aliphatic and aromatic cyanides.[4] From intensity studies which have been made of functional groups attached to the phenyl ring it is clear that substituents on the ring exert a pronounced effect on the magnitude of the intensity. The direction of intensity change for a particular substituent compared with another is dependent on the nature of the functional group which is absorbing. For example, the OH intensity of *p*-nitrophenol is much greater than that of phenol, whereas the C≡N intensity of *p*-nitrobenzonitrile is lower than that of the unsubstituted molecule. The absorption intensity, A, is related by a proportionality constant to $(\delta\mu/\delta Q)^2$, where μ is the dipole moment of the molecule and Q is the vibrational coördinate. For vibrations which consist largely of a stretching motion along one bond axis, Q can be considered as the bond distance, r. It is frequently possible to fix the sign of the term $\partial\mu/\partial r$ from chemical or structural arguments. For example, the ground state of benzonitrile can be represented as a mixture of structures I, II and III; in the charge-separated canonical forms the carbon–nitrogen bond order is only two. It is to be expected, then, that as this bond distance increases during a stretching motion, the importance of the charge-separated forms increases, so that $\partial\mu/\partial r$ is then positive. Electron-releasing groups attached to the ring should facilitate this process; larger values of intensity are indeed observed for the more electron-releasing groups.[4]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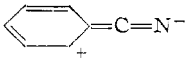
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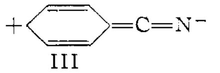
III

While it is easy to understand the intensity variations from a qualitative point of view, quantitative relationships with other molecular properties are more difficult to establish. Nevertheless such relationships have been found for a few cases.[1,3,4] From consideration of the intensity results for a number of *m*- and *p*-substituted benzonitriles, Thompson and Steel have obtained a linear relationship between log A and the Hammett σ-constant of the substituent for the intensities measured both in carbon tetrachloride and in chloroform.[4] The slopes of the lines were surprisingly different, however, in the two solvents. There is also some question as to the significance of the linear relationship which was obtained. Log A is not related from theory in a simple way to any other molecular properties, so that the use of this function would appear to be for reasons of utility only. Furthermore, there is considerable evidence that the use of the Hammett σ-values is inappro-

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(1) G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

(2) T. L. Brown and M. T. Rogers, This Journal, **79**, 577 (1957).

(3) T. L. Brown, *J. Phys. Chem.*, **61**, 820 (1957).

(4) H. W. Thompson and G. Steel, *Trans. Faraday Soc.*, **52**, 1451 (1956).

priate in this case. It has been shown that for electrophilic substitution reactions the Hammett equation does not apply when the usual values for σ-constants are employed[5,6]; in these cases the transition state is strongly electron-demanding as far as the phenyl ring is concerned, and the rates are abnormally high for substituent groups such as *p*-methoxy and *p*-amino. From this point of view the $\mathrm{C{\equiv}N}$ stretching vibration can be looked upon as an electron-demanding process; that is, the vibrationally excited state is electron-demanding, as far as the phenyl ring is concerned, with respect to the ground state. It follows that a comparison of the $\mathrm{C{\equiv}N}$ intensities with rate data for benzonitriles cannot be justified unless the reactions studied are electrophilic in nature; those chosen by Thompson and Steel are nucleophilic.[4] In this paper an attempt has been made to find a more satisfactory quantitative relationship between the intensity of the $\mathrm{C{\equiv}N}$ bond and other properties characteristic of the aromatic group to which it is attached. In addition the effect of the solvent has been more thoroughly studied.

Experimental

Materials.—All of the nitriles employed were Eastman Kodak Co. white label materials, except for the *p*-amino compound which was Eastman practical grade. All of the compounds were purified by repeated recrystallizations, followed usually by vacuum sublimation.

Carbon tetrachloride, chloroform and pyridine were reagent grade materials which were dried with anhydrous magnesium sulfate prior to use. Hexane and tetrachloroethylene were commercial solvents which were carefully fractionated through a packed column and then dried with magnesium sulfate. The mixed pyridine–carbon tetrachloride solvent was made up to contain 10% pyridine *by volume*.

Procedure.—The general procedure has been described elsewhere.[2] In the present study a Perkin-Elmer model 112 spectrometer with lithium fluoride optics was employed. Using tables supplied by the manufacturer, a spectral slit width of 1.8 cm.$^{-1}$ was calculated from the value of mechanical slit width, 0.150 mm., employed. The integration interval was 50 cm.$^{-1}$. The values reported are those obtained directly from the integration; no wing corrections were employed.

Results.—The results of the intensity measurements on eight benzonitriles are shown in Table I. With the exception of the *p*-amino compound, all of the half intensity widths, $\Delta\nu_{1/2}$, for the compounds in hexane, tetrachloroethylene and carbon tetrachloride were 6.0–7.0 cm.$^{-1}$. For the pyridine–carbon tetrachloride mixed solvent, $\Delta\nu_{1/2}$ was in the range 6.5–7.5 cm.$^{-1}$, and in chloroform, 10.5–12 cm.$^{-1}$. $\Delta\nu_{1/2}$ for the *p*-amino compound was larger because the band shape was not symmetrical. This may have been due to impurity, although every attempt was made to obtain a pure material. Comparison with the data of Thompson and Steel shows numerous disagreements.[7] The values for the compounds in carbon tetrachloride are larger in the present study. The agreement for the compounds in chloroform seems somewhat better; the data of Sensi and Gallo[8] are in good agreement with the present results when the approximate nature of their method is considered. The present values are reproducible to within 0.01 intensity unit.

TABLE I

THE INTEGRATED INTENSITY (IN UNITS OF 1×10^4 MOLE^{-1} LITER CM.$^{-2}$) OF THE $\mathrm{C{\equiv}N}$ BAND OF SOME SUBSTITUTED BENZONITRILE IN A VARIETY OF SOLVENTS

Compound	Hexane	Tetra-chloro-ethylene	Carbon tetra-chloride	10% pyridine in CCl_4	Chloro-form
p-Amino	. .	. .	0.82	1.08	1.43
p-Methoxy	0.34	0.41	.44	0.50	0.76
p-Methyl	.21	.26	.28	.32	.48
m-Methyl	.15	.18	.20	.26	.35
H	.15	.19	.20	.28	.35
p-Fluoro	.15	.18	.20	.24	.37
p-Chloro	.14	.18	.20	.25	.36
p-Nitro	. .	. .	. .	.11	.15

Discussion

It is clear from the data in Table I that the solvent has a pronounced effect on the $\mathrm{C{\equiv}N}$ intensity of any one compound. It is also clear, however, that the relative intensities throughout the series are essentially unchanged. This is a rather important point, since it means that a study of intramolecular effects can be pursued in any one of a variety of solvents with the same result. The large increase in intensity for the compounds in chloroform as compared with the other solvents presumably is due to hydrogen bonding to the nitrile.[4] The increased intensities in the mixed solvent containing pyridine may be due to interaction of the lone pair electrons of the pyridine nitrogen with the positive centers in the solute molecules. It is quite possible, however, that simple dipole–dipole interactions are responsible. At any rate, the variations in intensity for the compounds in this mixed solvent do not appear to be quite as regular as for the other solvents. Since with this exception the relative order of intensities in the series is not dependent on the solvent, the data for chloroform solutions will be used in the discussion which follows.

In Fig. 1 is graphed the intensity of the $\mathrm{C{\equiv}N}$ stretch for each compound *vs.* the Hammett σ-constant.[9] It is quite clear that the plot is not linear; use of log A instead of A does not change the shape of the graph by much. It is interesting to note that a very similarly shaped curve was obtained by Kuivila and Hendrickson[5] for a plot of their rate data for brominolysis of phenylboronic acids *vs.* the Hammett σ-constants. This suggests that the infrared data can be correlated with reactivities in electrophilic processes. A set of reactivity constants, R, can be obtained from the infrared results, using the expression

$$R = -1.39(A/A_{\mathrm{H}} - 1)$$

The average values of A/A_{H} for all of the solvents except the pyridine–carbon tetrachloride mixture were employed. The value of the constant, -1.39, was chosen so that the value of R for the *p*-nitro group would be the same as the Hammett σ-value. The values of R obtained from use of this equation are listed in Table II. It is of interest to compare the values obtained for R with rate data for electrophilic processes. In Figs. 2 and 3 are shown the plots of log rate data *vs.* R for two reactions

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(5) H. G. Kuivila and A. R. Hendrickson, THIS JOURNAL, **74**, 5068 (1952).

(6) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

(7) Professor Thompson has kindly supplied the author with data from a paper to be published in *Trans. Faraday Soc.*, in which the intensities of substituted benzonitriles in a variety of solvents are reported. The agreement of the present results with these data is generally very good.

(8) (a) P. Sensi and G. Gallo, *Gazz. chim. ital.*, **85**, 235 (1955); (b) *Ann. chim.* (*Rome*), **46**, 816 (1956).

(9) H. H. Jaffé, *Chem. Revs.*, **53**, 222 (1953).

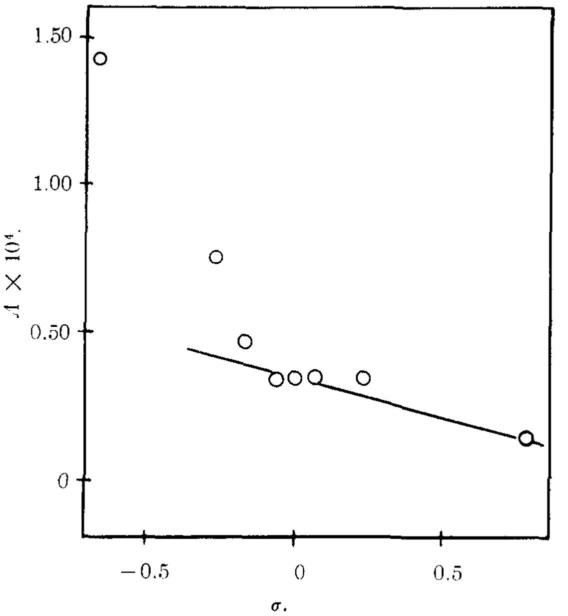

Fig. 1.—Intensity of the C≡N band *vs.* the Hammett σ-constant for substituted benzonitriles.

which are clearly facilitated by electron release[5,10]; the relations are quite linear over a wide range of substituents. For the majority of electrophilic reactions the relationship is non-linear, however, the rates for groups such as *p*-amino and *p*-methoxy being slower than would be predicted from the *R* constants. It will be seen that there is a resemblance between the reactivity constants *R* and values of substituent constants. In Table II the Hammett substituent constants and the electrophilic substituent constants, σ^+, determined by Okamoto and Brown[11] are shown for comparison.

TABLE II

REACTIVITY CONSTANTS, *R*, FOR ELECTRON-DEMANDING PROCESSES, DERIVED FROM INFRARED INTENSITIES OF BENZONITRILES, AND A COMPARISON WITH THE HAMMETT AND σ^+-VALUES

Substituent	*R*	σ^9	σ^{+11}
p-Nitro	+0.78	+0.78	+0.78
m-Nitro[a]	+ .69	+ .71	+ .66
m-Chloro[a]	+ .38	+ .37	+ .37
p-Chloro	+ .04	+ .23	+ .11
m-Methyl	+ .03	− .07	− .07
H	.00	.00	.00
p-Fluoro	− .01	+ .06	− .07
m-Hydroxy[a]	− .49	.00	....
m-Amino[a]	− .50	− .16	....
p-Methyl	− .53	− .17	− .31
p-Methoxy	−1.67	− .27	− .76
p-Hydroxy[a]	−2.24	− .36	....
p-Amino	−4.31	− .66	....

[a] Intensity data from Sensi and Gallo, ref. 8.

It is interesting to note that the strongly electron-demanding character of the C≡N stretching leads to an appreciable deviation from the usual behavior for the *m*-hydroxy and *m*-amino groups.

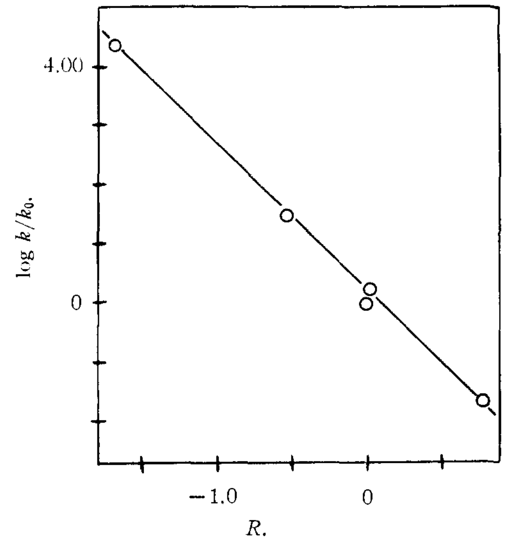

Fig. 2.—Solvolysis of benzyl tosylates in aqueous acetone.

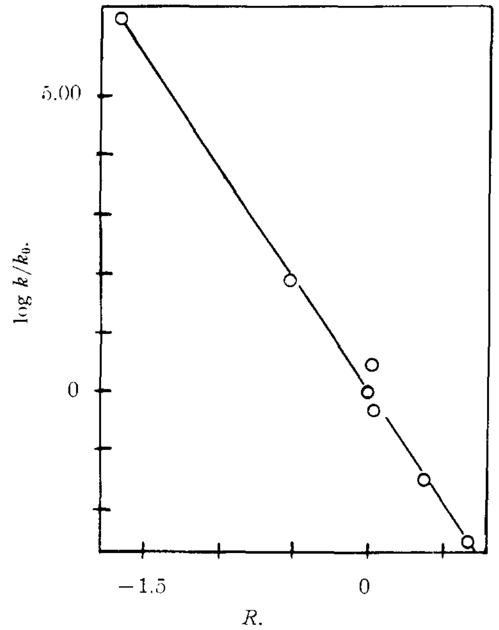

Fig. 3.—Brominolysis of phenylboronic acids in 20% acetic acid.

Because of the large resonance interaction of these groups with the ring a relatively high electron density develops at the positions *ortho* to the cyanide group, and is presumably relayed by induction to the electron-demanding site. This effect has been observed and explained by Brown and co-workers in studying the solvolysis rates of halodimethylcarbinyl chlorides.[12]

It will be noted that in Table II the *R* values for *m*- and *p*-nitro, *m*-chloro substituents and hydrogen retain essentially the Hammett σ-values. The *p*-methyl group shows a rather large negative value, especially when compared with the *m*-methyl group. It would appear that this is the result of hyperconjugative electron-release; however, this question is the subject of controversy at

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(10) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

(11) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(12) H. C. Brown, Y. Okamoto and G. Ham, THIS JOURNAL, **79**, 1906 (1957).

the present,[13] and more detailed intensity studies of p-alkyl substituted derivatives are under way in an effort to clarify the problem.

Summary

Studies of infrared absorption intensity of the C≡N intensity in a series of substituted benzonitrile solutions have permitted the following conclusions: (a) The C≡N intensity is strongly dependent on the properties of the solvent. (b) The relative order of intensities for a series of benzonitriles is essentially unaffected by a change in solvent when the solvent is non-polar or only slightly polar. (c) The intensity for a substituted benzonitrile can be related to a reactivity constant for the substituent. When these constants are compared with rate data taken from the literature it is found that a linear relationship is obeyed in a few cases for electrophilic rate processes.

Acknowledgment.—Thanks are due to Dr. H. G. Drickamer for his coöperation in the use of the infrared instrument, and to Dr. J. C. Martin for helpful discussion.

URBANA, ILLINOIS

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[13] W. M. Schubert, J. Robins and J. L. Haun, THIS JOURNAL, **79**, 910 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Application of a Theory of Irreversible Polarographic Waves to the Reduction of Nitroalkanes in Non-aqueous Solvents[1]

BY ARTHUR F. FINDEIS, JR., AND THOS. DE VRIES

RECEIVED MARCH 11, 1957

A treatment of irreversible polarographic waves controlled by diffusion and rate of reaction is applied to the reduction of nitromethane and 2-methyl-2-nitropropane in methanol, ethanol, isopropyl alcohol and t-butyl alcohol. Data are given for αn_α values of the reduction and for the heterogeneous rate constants at zero applied voltage.

A satisfactory theory has been available for the interpretation of polarographic currents controlled by rate of reaction and by diffusion.[2] The application of the appropriate equations to the current–potential curves obtained for the irreversible reduction of organic compounds gives the constant for the rate controlled electrochemical reduction as it depends on the applied potential. It also furnishes the value of the transfer coefficient, α, the fraction of the electrode potential which favors the cathodic reaction process.

In this investigation the reduction of nitro compounds was studied to determine the effect of their structure and the properties of the solvent on the reduction process. Nitromethane and 2-methyl-2-nitropropane were reduced at a dropping mercury electrode in methanol, ethanol and isopropyl alcohol with 0.3 M lithium chloride as supporting electrolyte, and in t-butyl alcohol with 0.3 M lithium perchlorate as the supporting electrolyte. The calculations were based on the use of equations developed by Koutecky[2c] in which he included a term to correct for the movement of the growing mercury drop toward the diffusing species. Heterogeneous rate constants, $k_{\mathrm{f,h}}$, were calculated with the equation $\lambda = k_{\mathrm{f,h}}t^{1/2}/D^{1/2}$, where λ values are a function of i/i_{d}, based on maximum currents, D is the diffusion coefficient of the reducible species and t is the drop time.

When the electrode process is the rate-determining step, the relation between the rate constant and the applied potential, E, is $k_{\mathrm{f,h}} = k^0_{\mathrm{f,h}}\ \exp(-\alpha\, n_\alpha\, FE/RT)$, where n_α is the number of electrons involved in the rate-determining step and α is the transfer coefficient. Thus log k–E plots give $\alpha\, n_\alpha$ values.

Experimental

All current–voltage curves were obtained using a Leeds and Northrup Electrochemograph, Type E, with no damping of the recorder since maximum currents were desired for the calculations. The validity of the technique was checked by using a more elaborate set up in which a cathode ray oscilloscope was used to determine the true value of the instantaneous current.

The cells were made such that nitrogen could be passed through or over the solution as desired. A presaturator was used in series with the cell when the solutions were degassed with nitrogen passed through a vanadous sulfate solution.[3] All measurements were made at a thermostatically controlled temperature of 25 ± 0.2°.

The capillary had $m^{2/3}t^{1/6}$ values of 2.50 methanol, 2.15 in ethanol, 2.27 in isopropyl alcohol and 2.19 in t-butyl alcohol. The corresponding values of t were 2.77, 2.83, 2.51 and 3.14 seconds. These values were determined at voltages corresponding to the beginning of the plateau of the wave. A silver–silver chloride electrode was used as a reference electrode in all solvents except the t-butyl alcohol in which lithium chloride was not soluble enough to give a low cell resistance. In this case a mercury pool was used with 0.3 M lithium perchlorate as the supporting electrolyte. The cell resistances, measured at the instant of drop fall with a Serfass Conductivity Bridge were as follows: methanol, 500 ohms, ethanol, 950 ohms, isopropyl alcohol, 5,000 ohms and t-butyl alcohol, 10,000 ohms.

All of the solvents used were stored over Drierite although it was observed that addition of water up to 1% did not affect the current voltage curves to any measurable extent. Lithium chloride was dried at 110° before use. Lithium perchlorate, anhydrous, was prepared from perchloric acid and lithium carbonate. Ethyl cellulose, viscosity 7.2 seconds, or Triton X-100 (Rohm and Haas Co.) were used as maxima suppressors at a concentration of 0.0025% in the final solution.

After preliminary difficulties it was found that the capillary must be scrupulously clean before each determination to obtain reproducible results. The polarograms obtained with the higher molecular weight alcohols were in general

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[1] Presented at 131st National Meeting of the American Chemical Society, Miami, Florida, April, 1957.

[2] (a) P. Delahay, THIS JOURNAL, **73**, 4944 (1951); **75**, 1430 (1953); (b) P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951); (c) J. Koutecky, *Collection Czechoslov. Chem. Commun.*, **18**, 597 (1953).

[3] (a) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948); (b) A. F. Findeis, Jr., and Thos. De Vries, *ibid.*, **28**, 209 (1956).