Basicity of Some Nitrilated Amines

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In the course of estimating the basicity of some amines with the Davidson Indicators[2] it was found that β-dimethylaminopropionitrile and β,β'-dicyanodiethylamine were in the pK_b range of 7 to 12. Since the common aliphatic amines have pK_b values between 3 and 4, these semiquantitative observations indicated the presence of a large inductive effect in nitrilated amines. In order to ascertain the magnitude of this effect a few compounds were prepared, and the pK_a values of their conjugate acids were measured.

The pK_a values of cyanamide, diethylcyanamide, alpha and beta substituted nitrilated amines at 29° are given in Table I. The magnitude of the inductive effect between the parent amine and a nitrilated derivative may be judged from the difference in their pK_a values. On the average the substitution of a cyano group for an N-hydrogen increases the pK_a value 9.0 units, for an alpha hydrogen 5.6 units, and for a β-hydrogen 3.2 units.

By the application of thermodynamic theory alone Langmuir[4] showed that the interaction of an electronegative group with a carboxyl group on a chain should fall off exponentially with distance. This follows from the standard free energy equation (1).

$$F = -RT \ln K_a \qquad (1)$$

Applying this equation to the ionization of acids it follows that the difference (λ) in the standard free energies of ionization of two acids is the difference in the work per mole of removing their ionizable protons. For the case of an unsubstituted acid and a derivative we obtain Equation 2.

$$\lambda = \Delta F° \text{ (parent)} - \Delta F° \text{ (derivative)} = \frac{RT \ln K \text{ (derivative)}}{K \text{ (parent)}} \qquad (2)$$

Equation 2 may be tested by investigating the constancy of the ratios of any two isomers which differ in having the constituent groups separated by a single carbon atom on a chain. In order to so utilize equation 2 for the direct calculation of λ ratios from pK values, it has been modified as given in Equation 3.

TABLE I

DISSOCIATION CONSTANTS (pK_a) OF SOME NITRILATED AMINES

Compound	Boiling Point,[a] °C. (Found)	Boiling Point,[a] °C. (Literature)	pK_a 29°C. (Found)	pK_a (Literature)
Cyanamide	45[b]	43[b,c]	1.1	
Diethyl cyanamide	186	186[d]	1.2	
Aminoacetonitrile	60/21 mm.	58[e]/15 mm.	5.3	
Dimethylaminoacetonitrile	136	137[f]	4.2	
Diethylaminoacetonitrile	84/30 mm.	71/24[g] mm.	4.5	
α-Aminoisobutyronitrile 2-Amino-2-cyanopropane	58/18 mm.	52/15[h] mm.	5.3	
β-Aminopropionitrile	89/23 mm.	89/23[i] mm.	7.7	
β-Isopropylaminopropionitrile	87/17 mm.	87/17[i] mm.	8.0	
β-Dimethylaminopropionitrile	172	172[i]	7.0	6.86 (30°)
β-Diethylaminopropionitrile	108/30 mm.	87/20[i] mm.	7.6	
β,β'-Dicyanodiethylamine	179/14 mm.	173/10[i] mm.	5.2	5.3 (25°)

[a] Boiling points are at atmospheric pressure unless otherwise indicated. [b] Melting point. [c] A. Franssen, *Bull. soc. chim. France*, (4), **43**, 185 (1928). [d] Cyanamide New Product Bulletin, **Coll. Vol. I**, American Cyanamid Co., New York, N. Y., 1949. [e] A. Klages, *J. prakt. Chem.* (2), **65**, 189 (1902). [f] J. Von Braun, *Ber.*, **40**, 3937 (1907). [g] A. Klages, *J. prakt. Chem.* (2), **65**, 193 (1902). [h] A. P. Snessarew, *J. Prakt. Chem.* (2), **89**, 364 (1914). [i] A. N. Kost, *Vestnik Moskov Univ., No. 2*, 141 (1947); *Chem. Abstr.* **42**, 3722 (1948). [j] Cyanamide New Product Bulletin, **Coll. Vol. II**, American Cyanamid Co., New York, N. Y., 1950.

The various attempts to combine thermodynamic and electrostatic theory toward a basic understanding of inductive effects is amply reviewed by Wheland.[3] These treatments, however, require assumptions of some predominant molecular conformation of the solute and its effect on the dielectric constant of the solvent.

$$\frac{\lambda_1}{\lambda_2} = \frac{2.303RT \log \dfrac{K \text{ (derivative 1)}}{K \text{ (parent)}}}{2.303RT \log \dfrac{K \text{ (derivative 2)}}{K \text{ (parent)}}} = \frac{pK \text{ (parent)} - pK \text{ (derivative 1)}}{pK \text{ (parent)} - pK \text{ (derivative 2)}} \qquad (3)$$

The λ ratios calculated from the data in Table I are given in Table II. In the later table the parent amines and their nitrilated derivatives are shown in horizontal apposition. Several assumptions were

(1) North American Aviation Corp., Los Angeles, Calif.

(2) D. Davidson, *J. Chem. Educ.*, **19**, 221 (1942).

(3) G. W. Wheland, *Advanced Organic Chemistry*, John Wiley & Sons, Inc., New York, N. Y., 1949, Chapter XI.

(4) I. Langmuir, *Chem. Revs.*, **6**, 467 (1929).

TABLE II
λ Values of Some Nitrilated Amines[a]

Parent Amine	N-Nitrilated Amine	α-Carbon Nitrilated Amine	$\dfrac{\lambda(N-C\equiv N)}{\lambda(\alpha C-C\equiv N)}$	β-Carbon Nitrilated Amine	$\dfrac{\lambda(\alpha C-C\equiv N)}{\lambda(\beta C-C\equiv N)}$
Methylamine 10.7	Methyl cyanamide[b] 1.2	Aminoaceto-nitrile 5.3	1.8		
Dimethylamine 10.7	Dimethyl cyanamide[b] 1.2				
Trimethylamine 9.9		Dimethylamino-acetonitrile 4.2	1.7		
Ethylamine 10.7	Ethyl cyanamide[b] 1.2				
				β-Aminopropioni-trile 7.7	1.8
Isopropylamine 10.7		2-Amino-2-cyano propane 5.3	1.8		
Diethylamine 11.1	Diethylcyanamide 1.2				
Triethylamine 10.8				β-Diethylamino-propionitrile 7.6	1.8
Methyldiethylamine 10.4		Diethylamino-acetonitrile 4.5	1.7		

[a] pK_a values are given below the name of the compound. Values other than those given in Table I were obtained from the Handbook of Chemistry and Physics, 31st ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1952–53, p. 1450.
[b] These assumed values are discussed in the text.

made in calculating these ratios because of a lack of data. These were the following:

(1) The monoalkylcyanamides have the same pK_a values as diethylcyanamide. Literature values are unavailable, and we found these derivatives to be difficult to prepare in a pure state because of rapid polymerization to the corresponding N-alkylmelamines. However, in view of the fact that cyanamide and diethylcyanamide differ by only 0.1 pK_a unit, this assumption is reasonable.

(2) Branched chain compounds have the same pK_a values as straight chain ones if the number of carbon atoms is unequal by one or two. This assumption is borne out by the fact that ethyl and isopropyl amines have about the same pK_a values as do aminoacetonitrile and α-aminoisobutyronitrile.

(3) The pK_a values of several parent amines were needed in making calculations on nitrilated tertiary amines. A secondary amine was necessary to obtain the pK_a difference between it and the corresponding cyanamide derivative, whereas a tertiary amine was required to calculate the pK_a difference between it and the alpha and beta substituted derivatives.

Despite the handicap of insufficient data, the λ ratios are constant at 1.8. It should be noted that the constancy of these ratios is independent of whether the nitrile group is on a nitrogen or carbon atom of the chain. Hence, one may conclude that

the transmission of electrostatic effects in these compounds is a property of single bonds. Using the ionization constants of chlorinated propionic and butyric acids, Langmuir showed the λ ratios for any two isomers with chlorine on adjacent carbon atoms to be constant and equal to 2.7. Langmuir assumed this value to be independent of the nature of the interacting groups, but a property of the chain only. It may well be that he was considering the interaction of uncharged groups, i.e., dipole-dipole effects, whereas in the nitrilated ammonium ions the interaction is charge-dipole. There should be a considerable difference in these interactions because the electrostatic field around a charge decreases as the first power of the distance whereas it falls off as the square of the distance around a dipole.

The difference in pK_a between triethylamine and diethylaminopropionitrile is 3.2 units, whereas the difference between diethylamine and β,β'-dicyano-diethylamine is 5.9 units. This result indicates that independent inductive effects in these compounds are approximately additive.

EXPERIMENTAL

The compounds used in this study were either redistilled commercial samples or were prepared by the reaction of glyconitrile, acetone cyanohydrin, and acrylonitrile with amines. Two examples are given as typical of the rest of the preparations. All compounds were distilled a few days

before the pK_a measurements were made. The fractions collected for pK_a measurements boiled over less than a 1° range.

Dimethylaminoacetonitrile. A commercial sample of glycolonitrile was cooled to 0° in a heavy walled flask and saturated with dimethylamine. The latter was generated by dropping a concentrated aqueous solution of the hydrochloride onto pellets of sodium hydroxide. After the flask was tightly stoppered, it was removed from the ice bath and allowed to warm up to room temperature. On standing for 4 to 6 hr. the reaction mixture was fractionally distilled. The product boiled at 135–136° at atmospheric pressure.

β-Aminopropionitrile. Four hundred milliliters of an ice cold 28% aqueous solution of ammonia and 100 ml. of ice cold acrylonitrile were mixed in a heavy walled liter flask. After the flask was securely stoppered, it was allowed to warm up and remain at room temperature for several days. It was then fractionally distilled under reduced pressure. The product boiled at 89°/23 mm. Aminoacetonitrile polymerizes quite rapidly so that it was titrated immediately after preparation.

Measurements of pK_a values. The amine solutions titrated were between 0.05 and 0.10 molar. Hydrochloric acid (0.183M) was used as the titrant. The equivalence point was taken at the maximum $\dfrac{d(pH)}{d(ml)}$ from the titration curves. Activity coefficients were taken at unity so that the $pK_a = pH$ at half neutralization. The pH measurements were made with a Beckmann pH meter, industrial model, using glass and saturated calomel electrodes at 29 ± 1°. A conservative estimate of the total error involved in these measurements is 0.1 pK_a unit in the cases of cyanamide and diethylcyanamide. For the other compounds it is closer to 0.05 pK_a unit.

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## Chlorination of 1,1-Difluoro-2,2-dichloroethane

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Henne and Ladd[1] reported that photochemical chlorination of 1,1-dichloro-2,2-difluoroethane (I) at room temperature yields, as the only monochlorination product, 1,1-difluoro-2,2,2-trichloroethane (II). Since the other possible monochlorina-

$$CHF_2CHCl_2 + Cl_2 \xrightarrow{h\nu} CHF_2CCl_3$$
$$\text{I} \qquad\qquad\qquad\qquad \text{II}$$
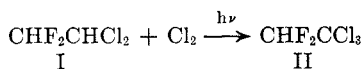
tion product, 1,1-difluoro-1,2,2-trichloroethane (III), and II should have nearly identical boiling points, Henne and Ladd[1] characterized their prod-
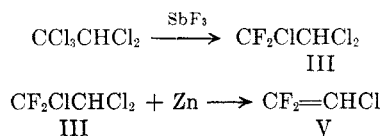
(1) A. L. Henne and E. C. Ladd, *J. Am. Chem. Soc.*, **58**, 402 (1936).

uct by dehalogenation with zinc, wherefrom only 1-fluoro-2,2-dichloroethylene (IV) (b.p. 35°) was isolated.

$$CHF_2CCl_3 + Zn \longrightarrow CHF{=}CCl_2$$
$$\text{II} \qquad\qquad\qquad\qquad \text{IV}$$
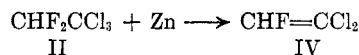
The photochemical chlorination of spectroscopically pure I, prepared by the method of Swarts,[2] was recently carried out in this laboratory using a procedure similar to that of Henne and Ladd.[1] The chlorination apparatus described by Muskat and Northrup[3] was used wherein the reaction mixture was heated under reflux (60–70°) and the chlorine was introduced into the vapor between the reflux condenser and the reflux boiler. A General Electric Photoflood No. RFL2 was used as the light source.

The monochlorination product (b.p. 72°) was separated by distillation and subjected to mass spectrometric and infrared analyses. The mass spectrum of pure III, prepared after Henne and Ladd[1] by fluorination of pentachloroethane with antimony trifluoride, was available. Henne and Ladd established the structure of III by zinc dehalogenation, which gave 2-chloro-1,1-difluoroethylene (V) (b.p. −17°). A quantitative com-

$$CCl_3CHCl_2 \xrightarrow{SbF_3} CF_2ClCHCl_2$$
$$\qquad\qquad\qquad\qquad\qquad \text{III}$$

$$CF_2ClCHCl_2 + Zn \longrightarrow CF_2{=}CHCl$$
$$\text{III} \qquad\qquad\qquad\qquad \text{V}$$

parison of the spectrum of pure III with that of the monochlorination product of I revealed that the latter contained 56 mole % III.[4] The remainder was assumed to be II, as there was no evidence for the presence of I or 1,1-difluoro-1,2,2,2-tetrachloroethane (VI). Thus, approximately equivalent amounts of the two isomers were produced and the reactivities of the two hydrogens of I were approximately equal at the reaction temperature (60–70°). These results will necessitate a slight modification of the theory advanced by Hauptschein and Bigelow.[6]

The mass spectrometric analysis was carried out at a high potential so that considerable bond rupture occurred. Table I gives a comparison of the major peaks in the mass spectra of pure I, III, and VI with the monochlorination product of I. The strong peaks of the mixture at m/e = 83, 85, and 87 are due to III, whereas those at m/e = 51, 117, 119, 133, and 135 are due to II. The peaks at m/e

(2) F. Swarts, *Chem. Zent.*, I, 13 (1903).

(3) I. E. Muskat and H. E. Northrup, *J. Am. Chem. Soc.*, **52**, 4043 (1930).

(4) A discussion of the factors involved and the methods of quantitative analysis by mass spectrometer has been given by Barnard.[5]

(5) G. P. Barnard, *Modern Mass Spectrometry*, The Institute of Physics, London, 1953, chapter 7.

(6) M. Hauptschein and L. A. Bigelow, *J. Am. Chem. Soc.*, **73**, 5591 (1951).