Ion Radicals. XXII. Reaction of Thianthrenium Perchlorate ($C_{12}H_8S_2^{\cdot +}\ ClO_4^-$) with Aromatics[1,2]

JUANA J. SILBER[3] AND HENRY J. SHINE*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

Received March 9, 1971

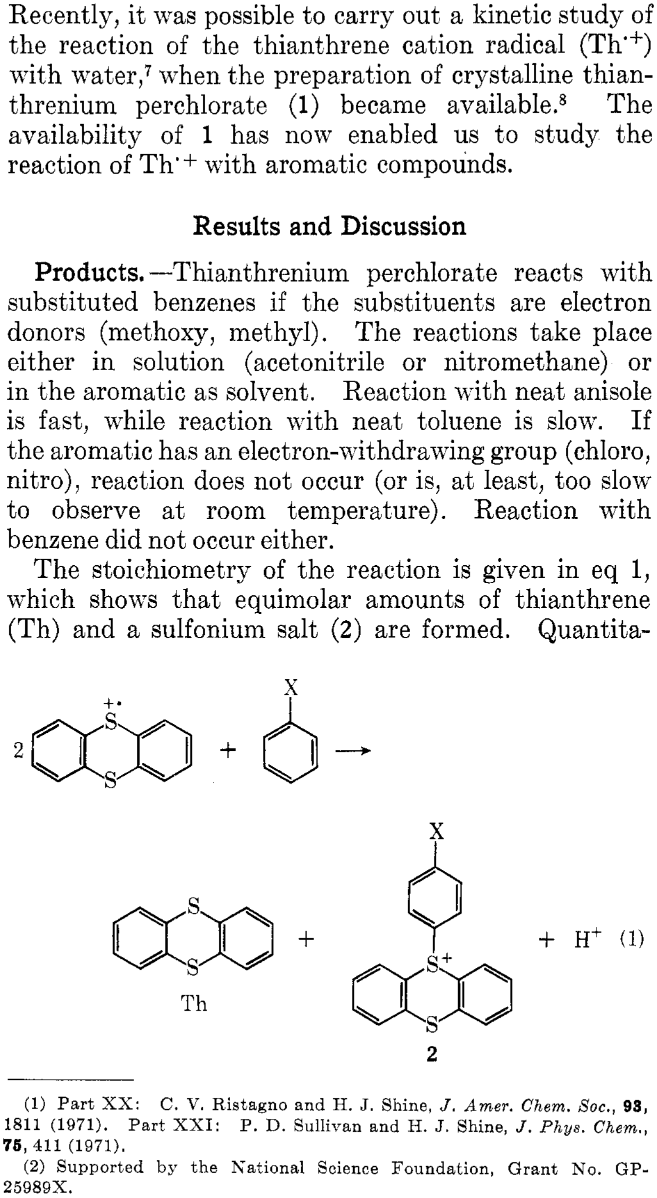
Thianthrenium perchlorate (1) reacts rapidly with C_6H_5X where X is methoxy and slowly where X is methyl. The product is a sulfonium perchlorate, $C_{12}H_8S_2C_6H_4X^+\ ClO_4^-$, in which the thianthrene unit is para to X. Kinetic studies with anisole show that reaction is second order in the thianthrene cation radical ($Th^{\cdot +}$). This is interpreted as showing that the reactive agent is the thianthrene dication (Th^{2+}), formed in low concentration in solution by disproportionation of the cation radical. Reaction of 1 with benzene, chlorobenzene, and nitrobenzene was too slow to observe. Reaction with *m*-xylene was slow and gave a sulfonium salt which could not be crystallized.

Few authentic reactions of organosulfur cation radicals (sulfinium ions) are known. Occasionally, cases are to be found in the literature in which sulfinium ion reactions are inferred from the behavior of organosulfur compounds at an anode[4] or in strong acid solutions.[5,6] Recently, it was possible to carry out a kinetic study of the reaction of the thianthrene cation radical ($Th^{\cdot +}$) with water,[7] when the preparation of crystalline thianthrenium perchlorate (1) became available.[8] The availability of 1 has now enabled us to study the reaction of $Th^{\cdot +}$ with aromatic compounds.

Results and Discussion

Products.—Thianthrenium perchlorate reacts with substituted benzenes if the substituents are electron donors (methoxy, methyl). The reactions take place either in solution (acetonitrile or nitromethane) or in the aromatic as solvent. Reaction with neat anisole is fast, while reaction with neat toluene is slow. If the aromatic has an electron-withdrawing group (chloro, nitro), reaction does not occur (or is, at least, too slow to observe at room temperature). Reaction with benzene did not occur either.

The stoichiometry of the reaction is given in eq 1, which shows that equimolar amounts of thianthrene (Th) and a sulfonium salt (2) are formed. Quantitative results with anisole support this stoichiometry. That is, 100% of the anticipated thianthrene and 96% of the anticipated sulfonium salt were obtained.



The structure of the sulfonium salts is deduced from analogy with the literature (see below), nmr spectra, and elemental analysis. The compounds are crystalline solids, readily crystallizable from conventional solvents.

Compound 2 is a triarylsulfonium salt. Analogous salts are described in the literature as resulting from reaction of diaryl sulfoxides with aromatics in concentrated sulfuric acid,[9] in the presence of phosphorous pentoxide,[9] or aluminum chloride.[10] It is noted in these cases also that the aromatic must not carry an electron-withdrawing group. The conditions of McEwen's method (boiling with an excess of aluminum halide)[10] are such, however, that it is possible to prepare a phenylthianthrenonium salt from thianthrene 5-oxide and benzene (X = H)[11] by that method but not by direct reaction of 1 with benzene at room temperature. Reaction of 1 with *m*-xylene occurred very slowly and gave a product which we have not been able to crystallize.

Kinetics and Mechanism.—Mechanistic studies of the formation of triarylsulfonium salts in acid media have never been carried out to our knowledge. Certain diaryl sulfoxides give diarylsulfinium ions in strong acids.[12] The mechanism of formation of the sulfinium ions is not known but has been represented occasionally as the homolysis of the O-protonated sulfoxide (eq 2).[5,6,12,13] Schmidt[6,13] has proposed, therefore,

$$R_2S^+\text{—}OH \longrightarrow R_2S^{\cdot +} + \cdot OH \qquad (2)$$

that formation of a sulfonium ion (*e.g.*, 2) from a sulfoxide and an aromatic in strong acid involves reaction of the sulfinium ion (the cation radical) with the aromatic. Some insight into the mechanism of this type of substitution reaction could be obtained if the kinetic order in sulfinium ion were known. We have now been able to follow the kinetics of reaction of a sulfinium ion (*e.g.*, $Th^{\cdot +}$) with anisole and can set out a reasonable mechanism.

Kinetics were carried out by following the disappearance of $Th^{\cdot +}$ spectroscopically at 546 nm. An all-glass, evacuated, sealed apparatus was used. Two methods

---

[1] Part XX: C. V. Ristagno and H. J. Shine, *J. Amer. Chem. Soc.*, **93**, 1811 (1971). Part XXI: P. D. Sullivan and H. J. Shine, *J. Phys. Chem.*, **75**, 411 (1971).

[2] Supported by the National Science Foundation, Grant No. GP-25989X.

[3] Predoctoral Fellow.

[4] G. Cauquis, *Bull. Soc. Chim. Fr.*, 1618 (1968).

[5] H. J. Shine and L. Piette, *J. Amer. Chem. Soc.*, **84**, 4798 (1962).

[6] U. Schmidt, K. H. Kabitzke, and M. Markau, *Justus Liebigs Ann. Chem.*, **672**, 78 (1964).

[7] Y. Murata and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969).

[8] E. A. C. Lucken, *J. Chem. Soc.*, 4963 (1962).

[9] J. Goerdler in "Methoden der Organischen Chemie," Vol. IX, 4th ed, Houben-Weyl, Georg Thieme, Stuttgart, 1955, pp 184, 185.

[10] G. H. Wieland and W. E. McEwen, *J. Org. Chem.*, **33**, 2671 (1968).

[11] The chloride has been prepared by Dr. T. L. Vigo in the laboratories of the U. S. Department of Agriculture, New Orleans, La. We are indebted to Dr. Vigo for sending us details of the method.

[12] H. J. Shine, *Organosulfur Chem.*, 93 (1967).

[13] U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **3**, 602 (1964).

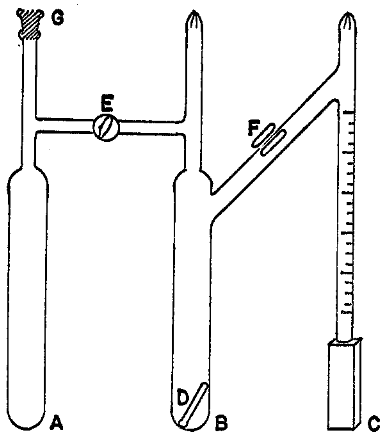


Figure 1.

of obtaining rate data were used. In the first, plots of $1/A$ against time were linear and indicated that reaction was second order in $\mathrm{Th}^{\cdot+}$. Log plots for the first-order reactions were definitely not linear.

The reaction that is second order in $\mathrm{Th}^{\cdot+}$ is most simply interpreted as involving an initial disproportionation step (eq 3),[7] and a reaction of a dication (Th^{2+}) with anisole (eq 4). By assuming that eq 3 represents

$$2\mathrm{Th}^{\cdot+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Th} + \mathrm{Th}^{2+} \tag{3}$$

$$\mathrm{Th}^{2+} + \mathrm{ArH} \xrightarrow{k_3} \mathrm{ThAr}^{+} + \mathrm{H}^{+} \tag{4}$$

rapidly achieved equilibrium, eq 5 can be written in which K is the equilibrium constant. Integration gives eq 6 and expressing cation radical concentrations as absorbances, A, leads to eq 7. In these equations, C

$$\mathrm{d}(\mathrm{Th}^{\cdot+})/\mathrm{d}t = k_3K[\mathrm{Th}^{\cdot+}]^2[\mathrm{ArH}]/[\mathrm{Th}] \tag{5}$$

$$1/[\mathrm{Th}^{\cdot+}] = k_3KCt + 1/[\mathrm{Th}^{\cdot+}]_0 \tag{6}$$

$$1/A_t = k_3KCt/\epsilon d + 1/A_0 \tag{7}$$

is $[\mathrm{ArH}]/[\mathrm{Th}]$, ϵ is the extinction coefficient of $\mathrm{Th}^{\cdot+}$ at 546 nm ($9.3 \times 10^3\ M^{-1}\ \mathrm{cm}^{-1}$), and d is the cell length. Since both [ArH] and the [Th] change during reaction, the term C must be kept constant during a run to simplify kinetic work, and this was achieved by using an excess of ArH and an excess of Th. The term C, therefore, represents $[\mathrm{ArH}]_0/[\mathrm{Th}]_0$ in our usage.

The addition of an excess of Th at the start of a run served not only to maintain C as a constant but also to slow down the disappearance of $\mathrm{Th}^{\cdot+}$. Without added Th, the reaction of $\mathrm{Th}^{\cdot+}$ with anisole was too fast to follow. This in itself is support for the reaction sequence proposed in eq 3 and 4.

By plotting $1/A$ against time, the slope $k_3KC/\epsilon d$ was obtained, and from this the apparent rate constant $k_{\mathrm{app}} = k_3K$. Values of k_{app} are given in Tables I and II, for the solvents acetonitrile and nitromethane. The values are reasonably constant with the exception of runs 4–6 and therefore support the application of eq 3–7 to this reaction. Runs 4–6 show high values of k_{app}. These runs were characterized by serious experimental problems. The high initial concentration of $\mathrm{Th}^{\cdot+}$ in them caused reaction to be very fast with a half-life comparable with the time of mixing of reactants. The recording of A *vs.* time could begin, therefore, only after at least one half-life, and there is considerable uncertainty about the real time of commencing reaction. The data we present for these runs, however, are compatible with a kinetic order in $\mathrm{Th}^{\cdot+}$ close to two rather than equal to one.

TABLE I

KINETIC DATA FOR REACTION OF THIANTHRENIUM PERCHLORATE (1) WITH ANISOLE (ArH) IN ACETONITRILE

Run	$10^4[\mathbf{1}]_0$, M	$10^3[\mathrm{Th}]_0$, M	$10^3[\mathrm{ArH}]_0$, M	k_{app}[a]	Correlation[b] coefficient
1	1.98	1.69	6.52	2.16	0.9998
2	2.25	1.47	7.44	2.21	0.9998
3	1.51	1.48	6.71	2.96	0.9993

[a] $k_{\mathrm{app}} = k_3K$ in $M^{-1}\ \mathrm{sec}^{-1}$. Values of slope obtained by least-squares treatment. [b] Correlation coefficient for the plot $1/A$ *vs.* t.

TABLE II

KINETIC DATA FOR REACTION OF THIANTHRENIUM PERCHLORATE (1) WITH ANISOLE (ArH) IN NITROMETHANE

Run	$10^5[\mathbf{1}]_0$, M	$10^4[\mathrm{Th}]_0$, M	$10^3[\mathrm{ArH}]_0$, M	k_{app}[a]	Correlation[b] coefficient
4	342	202	10.8	36.36	0.9997
5	240	194	8.66	36.10	0.9999
6	148	141	81.8	29.90	0.9992
7	25.7	26.9	11.4	8.98	0.9993
8	18.3	25.6	11.6	5.73	0.9997
9	20.2	23.9	12.0	6.28	0.9999
10	19.0	21.7	10.8	3.70	0.9996
11	13.8	24.0	7.44	5.99	0.9997
12	2.29	3.28	1.63	5.68	0.9980
13	1.41	7.78	1.13	3.81	0.9989

[a] $k_{\mathrm{app}} = k_3K$ in $M^{-1}\ \mathrm{sec}^{-1}$. Values of slope obtained by least-squares treatment. [b] Correlation coefficient for the plot $1/A$ *vs.* t.

The kinetic order in $\mathrm{Th}^{\cdot+}$ was also obtained by measuring initial rates.[14] Spectrophotometer plots of absorbance at 546 nm against time were extrapolated to zero time, and the tangent to each plot at zero time was drawn. At zero time, the initial rate of reaction, v_0, is given by eq 8, in which n is the order in $\mathrm{Th}^{\cdot+}$.

$$v_0 = dA_0/dt = k_3KCA_0^{\,n}/\epsilon d \tag{8}$$

TABLE III

INITIAL RATE DATA FOR REACTION OF THIANTHRENIUM PERCHLORATE (1) WITH ANISOLE (ArH) IN NITROMETHANE

Run	$10^5[\mathbf{1}]_0$, M	C[a]	v_0, min^{-1}	v_0/C
4	342	0.536	11.850	22.100
5	240	0.446	6.040	13.540
6	148	5.76	12.030	2.088
7	25.7	4.24	0.1560	0.0360
8	18.3	4.53	0.0436	0.0097
9	20.2	5.02	0.0738	0.0147
10	19.0	4.97	0.0325	0.0063
11	13.8	3.10	0.0178	0.0056
12	2.29	4.98	0.0013	0.000261
13	1.41	14.6	0.00075	0.000051

[a] $C = [\mathrm{ArH}]_0/[\mathrm{Th}]_0$.

Values of v_0 are given in Table III for runs in which $[\mathbf{1}]_0$ was varied over 240-fold. Simple inspection of Table III shows that a tenfold increase in $[\mathbf{1}]_0$ gave almost a 100-fold increase in v_0/C (*e.g.*, runs 11 and 13, 7 and 12). These results are consistent with a reaction which is second order in $\mathrm{Th}^{\cdot+}$. A 100-fold increase in

---

(14) M. Letort, *Bull. Soc. Chim. Fr.*, **9**, 1 (1942).

$[1]_0$ should cause a 10,000-fold increase in v_0/C. The data in Table III show about 40,000-fold (runs 6 and 13) or 50,000-fold (runs 5 and 12) increases. In view of the experimental problems with runs 4–6, these data are not thought to be seriously in error.

A plot of log v_0/C against log A_0 according to eq 9 has

$$\log v_0/C = \log k'_{\text{app}} + n \log A_0 \tag{9}$$

a slope n and intercept $k'_{\text{app}} = k_3KC/\epsilon d$. Ideally, k'_{app} and k_{app} should be the same. Our results are given in Table IV. Those for runs 7–13 express, we believe, the true description of the reaction, since these runs were not so susceptible to the experimental error of the faster ones, runs 4–8. Inclusion of runs 4–6 in the calculations gives a value of n somewhat higher than 2. The discrepancy is not serious in our attempt to distinguish between reactions which are first and second order in $Th^{\cdot +}$.

TABLE IV

KINETIC ORDER (n) AND RATE CONSTANT OBTAINED FROM INITIAL RATE DATA (TABLE III)

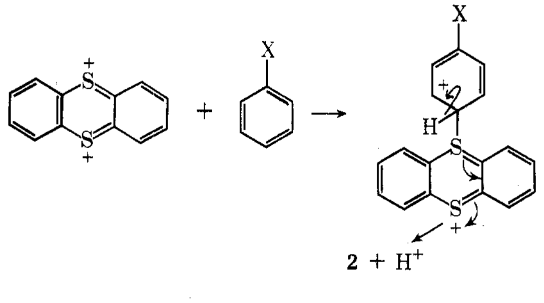
Runs	n^a	k'_{app}, M^{-1} sec^{-1b}	Correlation coefficient
4–13	2.35 ± 0.4	4.00	0.991
4–6	2.43 ± 0.1	4.86	0.929
7–13	1.98 ± 0.2	3.86	0.987

[a] n = slope in plot of log v_0/C *vs.* log A_0. [b] k'_{app} obtained from the intercept of same plot. Slope and intercept are calculated by least-squares treatment.

Finally, the intercept value of k'_{app} is considered to be in acceptable agreement with values of k_{app} obtained by the integrated rate method (Table II).

The rate expressions of eq 3–9 include the assumption that eq 3 represents an equilibrium. Similar expressions can be developed, without affecting the end result, for the assumption that Th^{2+} is at a steady-state concentration.

Our kinetic results and interpretation call for electrophilic substitution by Th^{2+} in the aromatic (eq 10).



(10)

The substitution reactions are slow, indicating that the concentration of dication (eq 4, 5) must be quite low. The equilibrium constant (eq 3) calculated from oxidation potentials is approximately 10^{-7}.[15] The effect of substituents is in accord with a cationic reaction rather than a radical reaction, and it is probable that the earlier synthetic methods[9,10] follow the cationic path (eq 4).

We have set out above what we consider to be the simplest interpretation of our results. Another series of steps may be written (eq 11–13) which also suits the stoichiometry of the substitution (eq 1). Equations 11 and 12 are entirely analogous to simple electrophilic

$$\text{Th}^{\cdot +} + \text{ArH} \underset{k_5}{\overset{k_4}{\rightleftarrows}} \text{ThArH}^{\cdot +} \tag{11}$$

$$\text{ThArH}^{\cdot +} \underset{k_7}{\overset{k_6}{\rightleftarrows}} \text{ThAr}\cdot + \text{H}^+ \tag{12}$$

$$\text{ThAr}\cdot + \text{Th}^{\cdot} + \underset{k_9}{\overset{k_8}{\rightleftarrows}} \text{ThAr}^+ + \text{Th} \tag{13}$$

substitution. In order for second-order kinetics in $Th^{\cdot +}$ to prevail, the substitution step (k_4) would have to be faster than the electron-transfer step (k_8), a requirement about which we have intuitive doubt. Furthermore, while second-order kinetics requires the electron-transfer step (k_8) to be rate determining, retardation by added thianthrene (Th) requires that step to be reversible. Simple second-order kinetics might be observed, then, if k_9 was very small. Our feeling is that these restrictions make the validity of this series of steps questionable.

Experimental Section

Thianthrenium perchlorate (**1**) was prepared essentially as described earlier.[7] Only quantities of the order of 50–100 mg were prepared at a time. The solid **1** was filtered through glass fiber paper under a stream of nitrogen, washed with dry carbon tetrachloride, dried under vacuum, and used without long delay.

Warning! Although used without trouble for over 12 months, $Th^{\cdot +}ClO_4^-$ has proved to be extremely hazardous. A freshly made batch of 1–2 g exploded violently after being dried by suction and when being transferred to a petri dish from the sintered-glass filter. Explosion may have been initiated by the friction of transfer or by rubbing with a glass rod.

Preparation of *p*-Anisylthianthrenonium Perchlorate (2a).—To a solution of 117 mg (0.372 mmol) of **1** in *ca.* 10 ml of dry nitromethane was added a sufficient excess of anisole. The solution was stirred until the color of the cation radical had disappeared and was extracted with portions of cyclohexane until tlc of the nitromethane solution no longer showed the presence of thianthrene. The combined cyclohexane solutions which contained both thianthrene and the excess of anisole were evaporated to dryness under reduced pressure. The residue was dissolved in acetonitrile and analyzed spectroscopically (256 nm) for thianthrene, giving 40 mg (100%). The nitromethane solution was treated similarly giving 77 mg (96%) of **2a**. Compound **2a** was recrystallized from aqueous methanol and had mp 164–165°.

Anal. Calcd for $C_{19}H_{15}ClO_5S_2$: C, 53.86; H, 3.54; Cl, 8.37; S, 15.15. Found: C, 53.76; H, 3.82; Cl, 8.43; S, 15.44.

Compound **2a** is white and crystalline, soluble in methanol, acetone, and acetonitrile, and insoluble in cyclohexane and carbon tetrachloride. Its ultraviolet spectrum in acetonitrile had maxima at 310 nm (ϵ 5.36 × 10^3) and 247 (1.60 × 10^4). The nmr spectrum (in dimethyl sulfoxide using TMS as an external standard) had δ 1.9 (s, 3, methoxy group), 7 (m, 4, anisyl ring protons), 7.8 (m, 6, positions 2, 3, 4, 6, 7, 8 of thianthrenonium ring), 8.3 (m, 2, positions 1, 9 of thianthrenonium ring). A similar preparation starting with 109 mg (0.342 mmol) of **1** gave 36.9 mg (100%) of thianthrene.

Preparation of *p*-Tolylthianthrenonium Perchlorate (2b).—The same procedure was used but not carried out quantitatively. Reaction in this case took almost 1 month for completion. The product had mp 208–209° (aqueous methanol).

Anal. Calcd for $C_{19}H_{15}ClO_4S_2$: C, 56.02; H, 3.68; Cl, 8.71; S, 15.76. Found: C, 55.85; H, 3.66; Cl, 8.40; S, 15.90.

Compound **2b** had solubility characteristics similar to those of **2a**. The ultraviolet spectrum in acetonitrile had maxima at 310 nm (ϵ 6.53 × 10^3) and 227 (3.20 × 10^4). The nmr spectrum had δ 0.5 (s, 3, methyl group), 7.1 (m, 4, tolyl ring protons), 7.8 (m, 6, positions 2, 3, 4, 6, 7, 8 of thianthrenonium ring), 8.3 (m, 2, positions 1, 9 of thianthrenonium ring).

---

[15] We thank Dr. L. S. Marcoux for this information.

Preparation of Phenylthianthrenonium Chloride (2c).[11]—To a solution of 1.97 g of thianthrene 5-oxide in 100 ml of benzene was added 11.2 g of aluminum chloride. The solution turned dark purple immediately. During 24 hr of boiling the color gradually turned dark brown. The solution was cooled and poured onto a mixture of 100 g of ice and 10 ml of concentrated hydrochloric acid, extracted with benzene until the benzene layer was colorless, and then extracted with chloroform to give 963 mg of **2c**, mp 252–253° (benzene–methanol). The ultraviolet spectrum had maxima at 310 nm (ϵ 7.54 $\times 10^3$) and 225 (3.16×10^4).

Kinetics of Reaction of 1 with Anisole.—The apparatus in Figure 1 was used. An aliquot of a stock solution of thianthrene was introduced into B, and an aliquot of a stock solution of **1** was introduced into C. A sealed capillary (D) containing a known amount of anisole was placed in B. The chambers B and C were sealed by torch, the solvent was pumped out of B and C, and stopcock E was closed. Dried solvent was distilled into A which contained Linde Molecular Sieve 3A $^1/_{16}$. The solvent was then degassed by the freeze–thaw technique. After opening stopcock E, solvent was distilled into B, the stopcock was closed, and the apparatus was removed from the vacuum line at G. The capillary was then crushed by the magnet F, after which the solution was poured from B into C, and shaken well to dissolve the **1**. The volume was measured and the cell was placed in the spectrophotometer for absorbance measurements at 546 nm.

Kinetic measurements were made with both nitromethane and acetonitrile as solvent. Acetonitrile itself reacts very slowly with **1**, whereas nitromethane solutions are stable indefinitely.

Registry No.—**1**, 21299-20-7; **2a**, 30882-98-5; **2b**, 30882-99-6; **2c**, 30953-02-7.

Basicities of the Individual Amino Groups in ω-Dimethylamino Alkyl Amines[1a]

JACK HINE,[1b] FRANCIS A. VIA, AND JAMES H. JENSEN

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received February 19, 1971

The relative basicities of the two different amino groups in the compounds $Me_2N(CH_2)_nNH_2$ where n is 2–5 have been determined by nmr measurements of the chemical shifts of the methyl protons in aqueous solutions containing various amounts of added acid. The primary amino groups were 1.6–3.7 times as basic as the tertiary amino groups. The fact that the chemical shifts of the methyl protons of $Me_2N(CH_2)_2NMe_2$ and $Me_2N(CH_2)_3NMe_2$, which were used as reference compounds, were linear functions of the number of equivalents of protons added was taken as evidence against a cyclic hydrogen-bonded structure for the monoprotonated forms of these diamines. The observed relative basicities were combined with overall basicities determined by potentiometric titration to obtain the absolute basicities of the various individual amino groups in water at 35°.

In several cases polyamines, sometimes acting through their monoprotonated forms, have been found to give internal catalysis of various kinds of reactions.[2-4] For a quantitative understanding of such reactions it is desirable to know the basicities of the individual nitrogen atoms of such polyamines. Potentiometric, conductometric, and other standard methods of determining basicity constants, which yield directly only overall values, may be used for this purpose with symmetrical polyamines and are relatively satisfactory if various amino groups differ enough in basicity. However, with simple ω-dimethylamino alkyl amines, where the amino groups are of comparable basicity, it is not obvious how to partition the observed total basicity into that contributed by each of the two different basic centers. We have therefore made proton magnetic resonance measurements, somewhat like those used by Loewenstein and Roberts to determine the relative acidities of the different carboxy groups in citric acid.[5] The results have also shed light on the question of whether the monoprotonated forms of such diamines are stabilized by internal hydrogen bonding.

Results

When the chemical shifts of the methyl protons of compounds of the type $Me_2N(CH_2)_nNH_2$ (where n is 2, 3, 4, and 5) were measured in aqueous solution in the presence of increasing amounts of acid, the downfield shift that accompanied the addition of the first equivalent of acid was less than that which accompanied the addition of the second equivalent. Figure 1 illustrates this for the case of 3-dimethylaminopropylamine. (The experimental points deviate from the idealized line constructed from the initial and final slopes because of overlapping mono- and diprotonation of the amine.) Since the tertiary amino group is thus more affected by the second protonation, it follows that the first protonation takes place largely at the primary amino group. To treat the data quantitatively, let us define f_m as the fraction of the diamine that is monoprotonated, f_d as the fraction diprotonated, f_t as the fraction of monoprotonated diamine that is protonated at the tertiary position, δ_d as the downfield chemical shift of the methyl protons of the diprotonated diamine, δ_t as the shift of the methyl protons of the diamine monoprotonated at the tertiary position, and δ_p as the shift of the methyl protons of the primary-monoprotonated diamine (all chemical shifts relative to that of the methyl group of the unprotonated diamine). It may be shown that if the various differently protonated forms of the diamine are in rapid equilibrium with each other the observed chemical shift of the methyl protons may be expressed as shown in eq 1. The values of

$$\delta_{obsd} - f_d\delta_d = f_m[f_t(\delta_t - \delta_p) + \delta_p] \qquad (1)$$

---

[1] (a) This investigation was supported in part by Public Health Service Grants AM 06829-MCB and AM 10378 from the National Institute of Arthritis and Metabolic Diseases. Abstracted largely from the Ph.D dissertation of F. A. Via, The Ohio State University, 1970. (b) To whom communications should be addressed at The Ohio State University.

[2] J. Hine, F. E. Rogers, and R. E. Notari, *J. Amer. Chem. Soc.*, **90**, 3279 (1968).

[3] W. P. Jencks and K. Salvesen, *Chem. Commun.*, 548 (1970).

[4] J. Hine, M. S. Cholod, and J. H. Jensen, *J. Amer. Chem. Soc.*, **93**, 2321 (1971).

[5] A. Loewenstein and J. D. Roberts, *ibid.*, **82**, 2705 (1960); *cf.* R. B. Martin, *J. Phys. Chem.*, **65**, 2053 (1961).