and the observed value is on the order of 10^{-2} sec^{-1}. Considering the drastic approximations, this agreement is excellent and substantiates the proposed explanation. Further supporting evidence is available in the fact that the 4-bromo-2,2-disubstituted-butylamine hydrobromides melt with dissociative decomposition in the range 170–195°, freely evolving hydrogen bromide with concomitant formation of the corresponding pyrrolidine hydrobromides. In fact, the isopropyl compound is so predisposed to cyclize that solutions of the pure bromoamine salt in carbon tetrachloride begin visibly to evolve hydrogen bromide at 50°. Rate studies of cyclization in 48% hydrobromic acid are planned for the future in order to throw additional light on this unexpected phenomenon.

Department of Chemistry
University of Southern California
Los Angeles 7, California

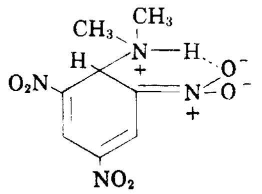
The Dimethylamine–1,3,5-Trinitrobenzene Complex in Dioxane

Mortimer M. Labes and Sidney D. Ross

Received April 27, 1956

Evidence has been presented[1] that 1,3,5-trinitrobenzene reacts with four molecules of dimethylamine in dioxane solution to form a colored 4:1 complex. The particular treatment used to test this hypothesis assumed that the only species present in the solution were dimethylamine, 1,3,5-trinitrobenzene, and the 4:1 complex. We find that the color produced by dimethylamine and 1,3,5-trinitrobenzene in dioxane is formed instantaneously and is stable with time at constant temperature. It, therefore, seems to us improbable that only a 4:1 complex is formed, particularly since this would necessitate a transition state involving five molecules. Moreover, if 1:1, 2:1, or 3:1 complexes are intermediates for formation of the 4:1 complex, then it seems to us inconsistent with both the chemical nature of the reagents involved and the principle of microscopic reversibility that none of these lower complexes persist at equilibrium. Accordingly, it is our present purpose to offer an alternate hypothesis which fits the available data equally well and which appears to us to be more probable.

Studies of the acidity of aromatic nitro compounds towards amines by Lewis and Seaborg[2] suggest a possible mode of interaction of dimethylamine and 1,3,5-trinitrobenzene. These authors suggest that the attachment of the amine to the nitro compound is *via* the direct addition of the base to one of the ring carbons that is not attached to a nitro group and *via* hydrogen bonding between the amine hydrogen and an oxygen of a nitro group. To illustrate, we have represented one of the contributing structures to the resonance state of the 1:1 complex in the formula below.



Since 1,3,5-trinitrobenzene has three nitro groups and three intervening ring carbon atoms, there are possibilities for forming three complexes, a 1:1, a 2:1, and a 3:1 complex.

For this type of interaction the three equilibria involved are

$$\begin{gathered} T + A \rightleftharpoons TA \\ TA + A \rightleftharpoons TA_2 \\ TA_2 + A \rightleftharpoons TA_3 \end{gathered}$$

where T is the trinitrobenzene and A is dimethylamine, and the three associated equilibrium constants are given by

$$K_1 = \frac{TA}{T{\cdot}A}$$

$$K_2 = \frac{TA_2}{A{\cdot}TA}$$

and

$$K_3 = \frac{TA_3}{A{\cdot}TA_2}$$

To relate these equilibrium constants to the spectroscopic data in a manageable form it is necessary to make some assumptions as to the relative amounts of the 1:1, the 2:1, and 3:1 complexes at equilibrium. The simplest assumption we can make is that the relative amounts of the three complexes are determined by purely statistical considerations; *i.e.*, $K_1 = 9\ K_3$ and $K_2 = 3\ K_3$. This assumption is probably justified, since all of the species involved are neutral molecules and no strong electrostatic forces are involved. Further, we assume that

$$A \cong Ao,$$

where A is the equilibrium concentration of amine and Ao is the initial concentration of the amine. This assumption is clearly permissible, since in all of the measurements the amine concentration is at least 200 times as great as the trinitrobenzene concentration. Finally, we assume that

$$TA_3\ \epsilon_{TA_3} \gg TA\ \epsilon_{TA} \text{ or } TA_2\ \epsilon_{TA_2},$$

where the ϵ's are extinction coefficients. This assumption is, we feel, a reasonable approximation based on the qualitative results reported by Lewis and Seaborg.[2]

The resulting equation, which relates the optical data and the equilibria is

---

(1) Foster, Hammick, and Wardley, *J. Chem. Soc.*, 3817 (1953).

(2) Lewis and Seaborg, *J. Am. Chem. Soc.*, **62**, 2122 (1940).

$$\frac{1}{9}\sqrt[3]{\frac{To}{d_c}} = \frac{1}{K_3\sqrt[3]{\epsilon_{TA_3}}}\left[\frac{1}{3Ao}\right] + \frac{1}{\sqrt[3]{\epsilon_{TA_3}}}$$

where $d_c = d_T - To\epsilon_T - Ao\epsilon_A$ and d_T is the total measured optical density in an absorption cell having a 1-cm. light path. To test this equation, we plot $\frac{1}{9}\sqrt[3]{\frac{To}{d_c}}$ *vs.* $\frac{1}{3Ao}$. The points should fall on a straight line with the slope equal to $\frac{1}{K_3\sqrt[3]{\epsilon_{TA_3}}}$ and the intercept equal to $\frac{1}{\sqrt[3]{\epsilon_{TA_3}}}$. Such a plot, using the data reported by Foster, Hammick, and Wardley,[1] is shown in Figure 1. As can be seen from the figure, the fit is all that can be expected and lends some support to our structural hypothesis.

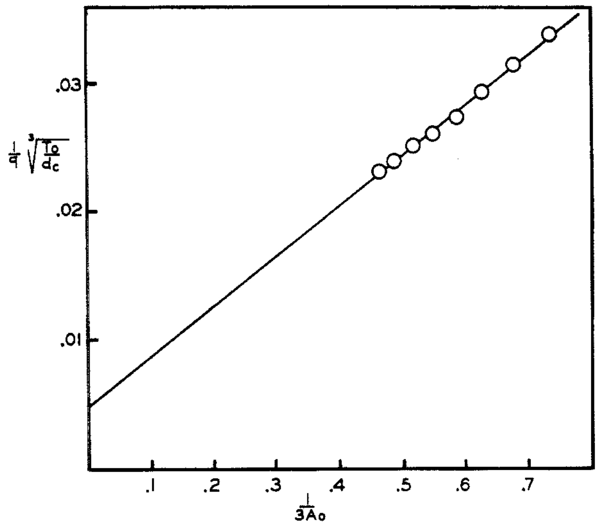


FIG. 1.—A PLOT OF $1/9\sqrt[3]{\frac{To}{d_c}}$ *vs.* $\frac{1}{3Ao}$ WHICH TESTS THE FIT OF THE DATA TO THE PROPOSED HYPOTHESIS OF 3:1 COMPLEXING CO-EXISTING WITH 1:1 AND 2:1 COMPLEXING.

In a similar way and making similar assumptions, it is possible to derive an expression for the case where the complexes present are 2:1 and 1:1.[3] However, when the data are plotted for this case a curve rather than a straight line is obtained. The possibility of simple 1:1 complexing has been adequately eliminated by Foster, Hammick, and Wardley.[1] We have not considered the possibility of a 4:1 complex coexisting with the 1:1, 2:1, and 3:1 complexes, since our structural hypothesis cannot accommodate the fourth amine molecule.

Finally, a dioxane solution which is 0.101 *M* in 1,3,5-trinitrobenzene and 0.043 *M* in dimethylamine shows appreciable color formation at 25° (d_c's of about 0.06 from 390 to 440 mμ). At the same temperature, a solution which was 0.021 *M* in trinitromesitylene and 0.043 *M* in dimethylamine showed no additional color formation (d_c's = 0). Similar observations have been reported by Lewis and Seaborg[2] for solutions in petroleum ether. We consider this to be evidence for the proposed hypothesis, since the anticipated effect of the methyl groups in trinitromesitylene is to inhibit resonance of the nitro groups with the ring and prevent formation of the postulated complexes.

RESEARCH LABORATORIES
SPRAGUE ELECTRIC CO.
NORTH ADAMS, MASSACHUSETTS

---

[3] The final equation for this case is

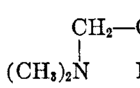
$$\sqrt{\frac{To}{d_c}} = \frac{1}{K_2\sqrt{\epsilon_{TA_2}}}\,\frac{1}{2\,Ao} + \frac{1}{\sqrt{\epsilon_{TA_2}}}$$

Amines. I. N,N,N′,N′-Tetramethyl-1,2-propanediamine and Its Characterization

ROSS W. MOSHIER AND LEONARD SPIALTER

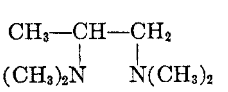
Received April 16, 1956

The methylation of ethylenediamine to the N,N,N′,N′-tetramethyl derivative, I, was first reported by Eschweiler[1] to result from the action of excess formaldehyde on the primary diamine. Subsequently, the Clarke modification, where formic acid is used as the reductant, was introduced[2] in the methylation of 1,4-butanediamine and certain monoamines. Wide application of this method of N-methylation to the synthesis of poly-tertiary amines has been hindered by the unavailability of the starting polyamines. It was, therefore, surprising to find that N,N,N′,N′-tetramethyl-1,2-propanediamine (II) had not been previously reported although 1,2-propanediamine is a common commercial chemical,[3] as is also 1,2-dichloropropane,[3] an intermediate for the alternative preparative route *via* condensation with dimethylamine. This latter reaction has been used for the synthesis from 1,3-dichloropropane of the isomeric N,N,N′,N′-tetramethyl-1,3-propanediamine (III) and for the preparation of compound I.[4]



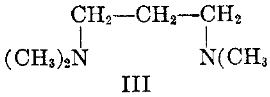
$(CH_3)_2N{-}CH_2{-}CH_2{-}N(CH_3)_2$

I



$CH_3{-}CH(N(CH_3)_2){-}CH_2{-}N(CH_3)_2$

II



$(CH_3)_2N{-}CH_2{-}CH_2{-}CH_2{-}N(CH_3)_2$

III

---

[1] W. Eschweiler, *Ber.*, **38**, 880 (1905).

[2] H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *J. Am. Chem. Soc.*, **55**, 4571 (1933).

[3] This compound, ethylenediamine and various polyethylenepolyamines are prepared and marketed by Carbide and Carbon Chemicals Corporation, 30 E. 42nd Street, New York 17, N. Y.

[4] (a) L. Knorr and P. Roth, *Ber.*, **39**, 1420 (1906); (b) M. Freund and H. Michaels, *Ber.*, **30**, 1374 (1897); (c) G. F. Grail, L. E. Tenenbaum, A. V. Tolstoouhov, C. J. Duca, J. F. Reinhard, F. E. Anderson, and J. V. Scudi, *J. Am. Chem. Soc.*, **74**, 1313 (1952); (d) I. G. Farbenindustrie A-G, French Patent 802,105 (1936).