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The Relative Basicities of Tribenzylamine and Tribenzylamine Oxide in Benzene and Water. Preparation and Properties of Tribenzylamine Oxide[1]

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In continuation of studies of instantaneous reactions of organic bases with hydrogen acids in benzene, the equilibrium constant (0.13) for the *association* of tribenzylamine with the acidic indicator dye, bromophthalein magenta E (3′,3″,5′,5″-tetrabromophenolphthalein ethyl ester), in benzene at 25° was measured spectrophotometrically. This constant, when combined with earlier data, permits comparing the acidities of bromophthalein magenta E, picric acid and trinitro-*m*-cresol in benzene (in terms of reactivity with tribenzylamine) and also the basicities of tribenzylamine and several other basic compounds in benzene (in terms of reactivity with bromophthalein magenta E). The strengths of the bases in benzene were compared with their ionic dissociation constants in water. A slow change in spectral absorption was observed to occur in benzene solutions containing tribenzylamine and bromophthalein magenta E, and shown to be due to oxidation, by dissolved air, of part of the tribenzylamine to tribenzylamine oxide, which then combines with bromophthalein magenta E. As part of this study the new compound, tribenzylamine oxide, was prepared; its structure was established by microanalyses, titration with perchloric acid in glacial acetic acid, reduction to tribenzylamine, and the general similarity of its properties to those of other amine oxides; an approximate value (5×10^{-10}) for its ionic dissociation constant in water was obtained; and the constant ($\sim 4.8 \times 10^{5}$) for its association with bromophthalein magenta E in benzene at 25° was measured. The spectral absorption curve which is characteristic of salts of tertiary amine oxides with bromophthalein magenta E, when dissolved in benzene, is different from the absorption curve obtained for tertiary ammonium salts of the indicator; this difference, together with the widely different tendencies of tribenzylamine and tribenzylamine oxide to combine with bromophthalein magenta E, made possible the explanation of the slow change. Parallel differences were observed when picric acid or trinitro-*m*-cresol was substituted for bromophthalein magenta E. A summary of available data shows that amine oxides combine at least as readily as tertiary amines with hydrogen acids and other Lewis acids, but are, nevertheless, ionized to a uniformly low extent in water. A plausible explanation of this behavior is suggested by the characteristic differences in the spectral absorption of salts of tertiary amines with hydrogen acids (bromophthalein magenta E, picric acid or trinitro-*m*-cresol) in benzene solution and the spectral absorption of the corresponding salts of tertiary amine oxides. The general conclusions reached from spectrophotometric studies of *acid–base* reactions are in complete harmony with deductions of Kraus and co-workers from their studies of the conductance, dielectric constants and freezing point-lowering of *salts* of different types in various organic solvents. Earlier, Fuoss and co-workers observed that toluene solutions of tribenzylammonium picrate undergo puzzling changes in conductance, and, as a tentative explanation, proposed the hypothesis of a slow intramolecular proton shift. The results described in this paper indicate that the changes in conductance could have been caused by partial oxidation of tribenzylamine, present in the solution from the acid–base dissociation of its picrate.

Introduction

Previous work in this Laboratory[2,3] showed that tertiary aliphatic amines and some aryl derivatives of guanidine combine instantaneously with certain nitro or halogen derivatives of phenol in benzene according to the equation

$$\underset{\text{base}}{\mathrm{B}} + \underset{\text{acid}}{\mathrm{HA}} \rightleftharpoons \underset{\text{salt}}{\mathrm{BH^{+}\ldots A^{-}}} \qquad (1)$$

The phenolic acids in question are indicator dyes, so that their reactions with bases can be observed visually. By use of a spectrophotometer, the concentrations of acid, salt, and base present in various equilibrium mixtures can be determined, and from such data the association constant for a reaction is calculated. The magnitude of $K_{\text{assocn.}}$ for a reaction provides a measure of the reactivity of the base and also of the acid.[4]

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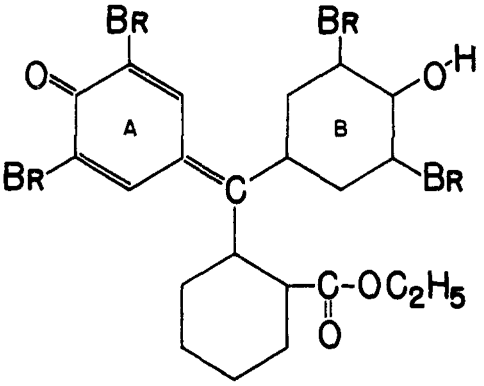
[1] Presented in part before the 122nd Meeting of the American Chemical Society, Atlantic City, September, 1952 (see Abstracts, 52–3 M). The investigation was partially supported by the Office of Naval Research. Article not copyrighted.

[2] M. M. Davis and P. J. Schuhmann, *J. Research Natl. Bur. Standards*, **39**, 221 (1947).

[3] M. M. Davis and E. A. McDonald, *ibid.*, **42**, 595 (1949).

[4] $K_{\text{assocn.}}$ (the equilibrium constant corresponding to equation 1) = [S]/[A][B]. The symbols [A], [B] and [S] refer to the *equilibrium* concentrations of acid, base and salt, respectively, expressed in moles/l.; C_a, C_b and C_s are the symbols used to represent the respective *initial* concentrations. Formation of the salt $BH^{+}\ldots A^{-}$ is regarded as resulting from a partial transfer of the proton from the acid HA to the base B (which is here assumed to belong to the class of neutral molecules that can be regarded as derivatives of ammonia). Obviously, the greater the affinity of the base for protons and the greater the readiness of the acid to release protons, the greater will be the tendency for $BH\ldots A^{-}$ to form. Therefore, the relative magnitudes of the equilibrium constants obtained for the combination of a series

The original purpose of this investigation was to measure the constant at 25° for the association of tribenzylamine with bromophthalein magenta E (I) in benzene. The constants for the association of tribenzylamine with picric acid and with trinitro-*m*-cresol in benzene being already known,[3] the measurement would thus permit a quantitative comparison of the strengths in benzene of the three phenolic acids. It would also make possible a comparison of the basicity of tribenzylamine with the basicities of several other organic bases whose reactivity with bromophthalein magenta E in benzene had previously been measured.[2,5,6]



Formula I. Bromophthalein magenta E.

In the absence of a base, bromophthalein magenta E gives a yellow solution in benzene, but the salts under discussion give a magenta solution.[7] When both the acid and the salt are present in a solution, the color is some tone of orange or red, depending on the relative amounts of the two substances. Tribenzylamine, when added in very large excess, was found to combine immediately with bromophthalein magenta E in benzene, but to only a very small extent, shown by a change from yellow to orange-yellow. Unexpectedly, reaction was found to continue slowly for a long time, even for several months. During this period the colors of mixtures gradually changed from orange-yellow to rose. The objective of the investigation was modified to include an explanation for the slow reaction, not merely because of its theoretical interest, but also because our problem of devising procedures for measuring acidity and basicity in solvents like benzene requires an understanding of the kinds of reactions that may take place.[8]

Some years ago, Brönsted[9] raised the question whether velocities of reaction would prove to be unequal for acid–base systems of different strengths. From structural considerations and their known behavior, tribenzylamine and bromophthalein magenta E would not be classed among the strongest bases and acids, and one possible explanation for the slow reaction was a slow rate of combination of tribenzylamine with bromophthalein magenta E.

A somewhat different possibility was suggested by studies of Fuoss and co-workers.[10] As an explanation for peculiar changes in the conductance of tribenzylammonium picrate in toluene with time, they suggested that establishment of an equilibrium mixture in solutions of amine picrates may involve the three reactions indicated by equations 2 to 4

$$R_3N + HPi \rightleftarrows R_3N{\cdot}HPi \tag{2}$$

$$R_3N{\cdot}HPi \rightleftarrows R_3NH^+{\cdot}Pi^- \tag{3}$$

$$R_3NH^+{\cdot}Pi^- \rightleftarrows R_3NH^+ + Pi^- \tag{4}$$

Equation 2 indicates the formation of an addition compound from the base R_3N and picric acid; equation 3 involves an intramolecular shift of the proton from the oxygen of picric acid toward the nitrogen of tribenzylamine, yielding an ion-pair; and 4 shows the separation of ion-pairs into free ions. It was suggested that 2 and 4 probably occur practically instantaneously, but that 3 takes place at a measurably slow rate.

However, in studies of the acid–base equilibrium of tribenzylammonium picrate in benzene, a very closely related system, neither Davis and McDonald[3] nor Maryott[11] observed evidence of a slow reaction. Furthermore, Witschonke and Kraus,[12] who measured both the ionic dissociation and the acid–base dissociation of pyridonium picrate in nitrobenzene, did not obtain evidence of an equilibrium corresponding to equation 3, although, they stated, the presence of a very small fraction of the solute as a "non-ionic molecular species" was not excluded.

Spectrophotometric and chemical studies reported in this paper established that the slow change in benzene solutions of tribenzylamine and bromophthalein magenta E involves oxidation of part of the tribenzylamine to tribenzylamine oxide. No data indicating a slow reaction of the base and acid[9] or a slow intramolecular shift of protons, converting molecules of an addition compound to ion-pairs and *vice versa*,[10] were obtained. To support the spectrophotometric evidence, tribenzylamine oxide was synthesized, its structure was established, and some of its properties were studied. The equilibrium constants for the association of bromophthalein magenta E with tribenzylamine and tribenzylamine oxide in benzene were measured spectrophotometrically. Not only are the association constants very different in magnitude, but the nature of the

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of bases with any given acid HA in benzene should provide a measure of the strengths of the bases. Moreover, the values of these association constants would be expected to parallel, at least roughly, the ionization constants of the bases in water, as these constants also measure the varying tendencies of the bases to acquire protons. Reasons for regarding the attraction of the cation of the salt $BH^+\ldots A^-$ to the anion as involving hydrogen bonding were discussed in refs. 2 and 3.

(5) M. M. Davis and H. B. Hetzer, *J. Research Natl. Bur. Standards*, **46**, 496 (1951).

(6) M. M. Davis and H. B. Hetzer, *ibid.*, **48**, 381 (1952).

(7) The "primary" reaction (equation 1) is succeeded by a "secondary" reaction, $BH^+\ldots A^-$ (magenta) + B (colorless) $\rightleftarrows$ $(BHB)^+A^-$ (blue), if a large excess of a base is added. See refs. 2, 5 and 6.

(8) Some striking differences in acid–base reactions in water and in organic solvents such as hydrocarbons have been pointed out in NBS Technical News Bulletin, **36**, 168 (1952), and in references cited there.

(9) J. N. Brönsted, *Ber.*, **61**, 2050 (1928), footnote 1.

(10) R. M. Fuoss, D. Edelson and B. I. Spinrad, THIS JOURNAL, **72**, 327 (1950). See also M. A. Elliott and R. M. Fuoss, *ibid.*, **61**, 294 (1939).

(11) A. A. Maryott, *J. Research Natl. Bur. Standards*, **41**, 7 (1948), measured the constant for the dissociation of tribenzylammonium picrate into tribenzylamine and picric acid in benzene from the variation of the dielectric constant with concentration. Davis and McDonald determined the constant for the opposite reaction—the association of tribenzylamine with picric acid—from spectrophotometric data. The results of the two methods are in excellent agreement.

(12) C. R. Witschonke and C. A. Kraus, THIS JOURNAL, **69**, 2472 (1947). See also W. F. K. Wynne-Jones, *J. Chem. Soc.*, 795 (1931).

change is not exactly the same for the two reactions. The results of the studies are presented in this paper, and their general bearing on aspects of acid–base behavior is discussed.

Results and Discussion

Spontaneous Oxidation of Tribenzylamine to Tribenzylamine Oxide.—Within an hour after the first measurements of the absorbance of mixtures of tribenzylamine and bromophthalein magenta E in benzene it was evident that the absorbance was gradually changing, and with some mixtures the change could easily be observed visually within a few days. In order to follow the changes occurring in solutions containing various proportions of the base and the acid, a portion of each solution was transferred to an absorption cell and the absorption curve was measured; this procedure was continued at appropriate intervals until all of the solution had been used.

In all cases of the combination of tertiary aliphatic amines with bromophthalein magenta E in benzene so far studied[2,5,6] the resulting magenta solution has been found to have a characteristic absorption band with λ_{max} near 540 mμ. This band intersects the absorption band for the unchanged indicator near 355 and 455 mμ. 1,3-Diphenylguanidine and 1,3-di-*o*-tolylguanidine also give rise to this absorption band upon their reaction with bromophthalein magenta E. If the slow reaction in benzene solutions containing tribenzylamine and bromophthalein magenta E had been producing this magenta salt, the absorption should have gradually increased, and continued to be greatest, at 540 mμ. However, although the absorption at 540 mμ increased, the position of the maximum soon shifted to around 520 mμ, and, although one of the isosbestic points (points of intersection with the curve for bromophthalein magenta E alone) was still near 355 mμ, the other isosbestic point shifted to 447 mμ. The new absorption curves, in fact, looked very similar to the curves that had been obtained[13] after the addition of an excess of solid trimethylamine oxide to a benzene solution of bromophthalein magenta E. The gradual change in the absorption of mixtures of bromophthalein magenta E and tribenzylamine in benzene was thus of the type that would be expected if tribenzylamine were undergoing slow oxidation to tribenzylamine oxide and the latter compound combined instantaneously with bromophthalein magenta E. This explanation was supported by the observation that the changes were not exactly reproducible for different solutions having the same content of the indicator and the base, but seemed to be affected by the amount of air dissolved in the benzene. The final proof needed was supplied by synthesizing tribenzylamine oxide and studying its reaction in benzene with bromophthalein magenta E, as described later in this paper.

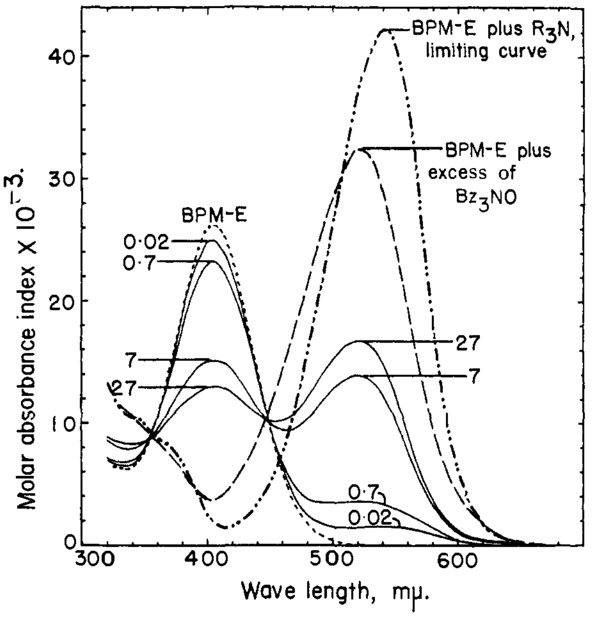

Fig. 1.—Change with time of absorption curves of benzene solutions initially 2.5 × 10^{-6} M with respect to bromophthalein magenta E and 0.25 M with respect to tribenzylamine. Numbers indicate the ages of the mixtures in days. BPM-E, absorption curve for bromophthalein magenta E without added base; BPM-E plus R_3N, limiting curve for reaction of bromophthalein magenta E with a base of the type R_3N (refs. 2, 5 and 6); BPM-E plus excess of Bz_3NO, curve for bromophthalein magenta E after addition of an excess of solid tribenzylamine oxide.

Examples of the changes in spectral absorption which were observed are presented in Figs. 1, 3 and 4. In Fig. 1 molar absorption curves are given for the following benzene solutions: bromophthalein magenta E (curve marked "BPM-E"); a solution initially 2.5 × 10^{-5} M with respect to bromophthalein magenta E and 0.25 M with respect to tribenzylamine, measured within 0.02 day (~35 minutes) after preparation; and the same solution after standing for various longer periods of time (0.7, 7 and 27 days). Figure 1 also shows the absorption curve which is obtained for tertiary ammonium salts of bromophthalein magenta E (curve marked "BPM-E plus R_3N")[14] and likewise the absorption curve obtained for the tribenzylamine oxide salt of bromophthalein magenta E (curve marked "BPM-E plus excess of Bz_3NO"). Although the curve obtained within 0.02 day shows only a little change from the curve for the indicator without any added base, a flat maximum near 540 mμ is apparent, and the system of curves consisting of this curve, the curve for the indicator without added base, and the curve for a tertiary ammonium salt of the indicator shows isosbestic points near 355 and 455 mμ. However, the curves which were obtained after the mixture of bromophthalein magenta E and tribenzylamine had been standing for 0.7 day or a longer period reveal a shift in the absorption maximum toward 520 mμ, and, together with the curve for bromophthalein magenta E alone and the curve for the tribenzylamine oxide salt of bromophthalein

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[13] Reference 2, p. 252, Fig. 22.

[14] See refs. 2, 5 and 6. The curve for a tertiary ammonium salt is obtained by constantly increasing the proportion of a tertiary amine in a solution having a fixed quantity of bromophthalein magenta E until the spectral absorption shows no further change (reaches a limit). The limiting curve shown in Fig. 1 was actually obtained (ref. 6) for a mixture of bromophthalein magenta E and di-*o*-tolylguanidine, and is thought to be the most accurately measured curve for salts of this class. The molar absorbance index at 540 mμ is ~42,300.

magenta E, form a system of curves having quite well-marked isosbestic points near 355 and 447 mμ.

Figure 2 shows the close similarity of the absorption curves obtained for benzene solutions of bromophthalein magenta E mixed with trimethylamine oxide[13] and with tribenzylamine oxide (both in excess). The two curves are believed to be slightly in error in the vicinity of 600 mμ, the spectral region in which secondary changes[7] caused by traces of water would be most apparent.

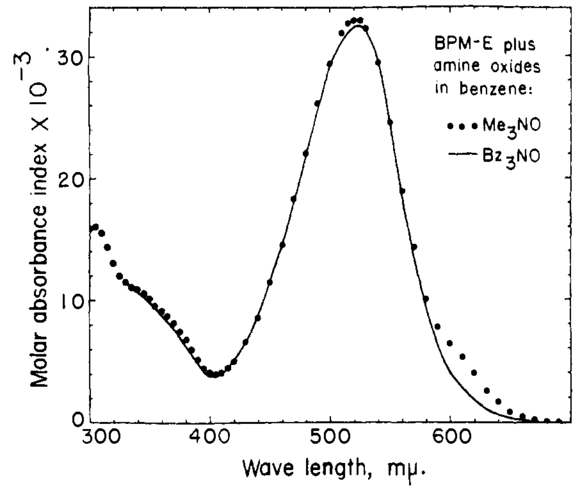

Fig. 2.—Absorption curves obtained after adding an excess of solid trimethylamine oxide (see note 13) or tribenzylamine oxide to bromophthalein magenta E in benzene.

Figures 3 and 4 indicate the progressive changes in the spectral absorption at 520 mμ that occurred in solutions containing various initial proportions (C_a and C_b) of the indicator and tribenzylamine. In Fig. 3 the data are for mixtures of four different initial compositions (indicated in the legend), while Fig. 4 shows the results of three separate experiments with mixtures having the same initial composition. When the solution was essentially air-free (curve 2a)[15] the first measured absorbance at 520 mμ was very small. When there was more opportunity for air to have entered the solution (curves 2b and 2c), the first value obtained for the absorbance at 520 mμ was greater, indicating that some conversion of tribenzylamine to tribenzylamine oxide had already occurred; such conversion was especially evident when the stock solution of tribenzylamine used in the experiment was already two weeks old (curve 2c).[16]

Although it is well recognized that amines undergo spontaneous oxidation in contact with air, the nature of the products is not fully known. We have found no indications in the literature that an amine oxide has hitherto been identified as a product of the oxidation of tertiary amines by air.[17] In our experiments the quantity of tribenzylamine oxidized to tribenzylamide oxide by air was actually very small, even though the presence of tribenzylamine oxide was easily detected because of its strong tendency to combine with bromophthalein magenta E in benzene and the slight tendency of tribenzylamine to combine with this indicator.[18] No tendency for tribenzylamine to undergo oxidation to tribenzylamine oxide while in the solid state was detected, but liquid tertiary amines, many of which are stronger bases than tribenzylamine, probably become contaminated with their oxides upon

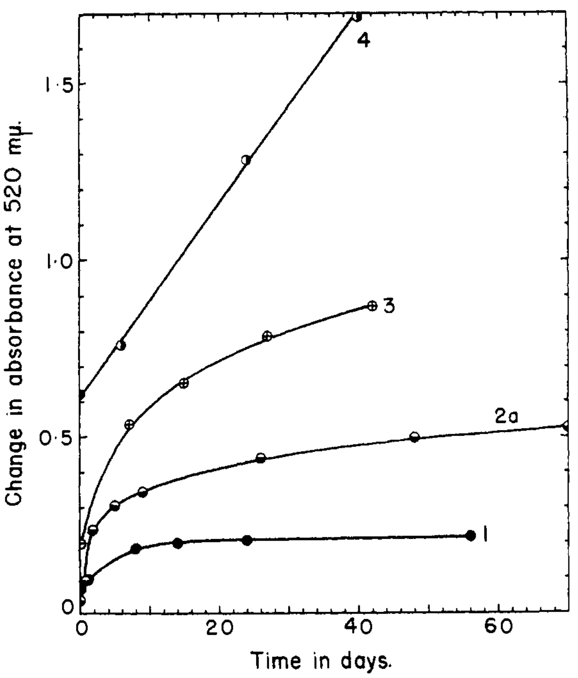

Fig. 3.—Change in absorbance at 520 mμ *vs.* time, of benzene solutions containing bromophthalein magenta E mixed with tribenzylamine; 1-cm. absorption cells. Initial molarity with respect to bromophthalein magenta E (C_a): 1, 10^{-5}; 2a, 2.5×10^{-5}; 3, 5.0×10^{-5}; 4, 5.0×10^{-4}. Initial molarity with respect to tribenzylamine (C_b): 1, 0.475; 2a and 4, 0.25; 3, 0.28.

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(15) Curve 2a was obtained with the solution that gave the curve marked "0.02" in Figs. 1 and 2. The solution was prepared using benzene from which air had been removed by boiling, and the first measurements of the absorbance were made as rapidly as possible.

(16) All of the containers used in our experiments, including the absorption cells, were provided with ground glass stoppers, and solutions were directly exposed to the atmosphere only briefly during their preparation and transfer. However, A. Tian, in studying the "spontaneous ventilation of vessels" (*Ann. faculté sci. Marseille*, **19**, 157 (1948)), found that appreciable interchange of gases between the interior of stoppered vessels and the external atmosphere can occur, the interchange being greater for vessels provided with ground glass stoppers than for those having cork stoppers.

(17) Upon oxidation with potassium permanganate in acetone, tribenzylamine was found to give a 20% yield of N,N-dibenzylbenzamide (J. Forrest, S. H. Tucker and M. Whalley, *J. Chem. Soc.*, 303 (1951)). However, the action of ozone on tribenzylamine was reported to yield benzoic acid, with evidence of benzaldehyde as an intermediate product (W. Strecker and M. Baltes, *Ber.*, **54**, 2693 (1921)); in parallel experiments, conversion of trimethylamine, triethylamine and tri-*n*-propylamine to the corresponding amine oxides was observed. D. F. Evans, *J. Chem. Soc.*, 345 (1953), recently reported evidence that combination with molecular oxygen may be the initial stage in the oxidation of aromatic substances such as phenols and amines. A study of the mechanism of the oxidation of tribenzylamine by air when dissolved in benzene is beyond the scope of our investigations, and we do not know whether the active oxidizing agent is molecular oxygen, ozone or some peroxide.

(18) It was calculated that, in one mixture of 2.5×10^{-5} *M* bromophthalein magenta E and 0.25 *M* tribenzylamine, 1.36×10^{-5} *M* tribenzylamine oxide was present after the solution had been standing for 27 days; for a different solution of the same initial composition it was calculated that 1.44×10^{-5} *M* tribenzylamine oxide was present at the end of 26 days. Perfect agreement of the results of the two experiments was not expected, because no effort was made to make all the conditions of the experiments identical (such as the proportions of the volumetric flasks and the amount of air space within the flasks).

very slight contact with air. The evidence for rapid conversion of tertiary amines to amine oxides by air has an obvious bearing, of course, on their use as antioxidants and corrosion inhibitors.

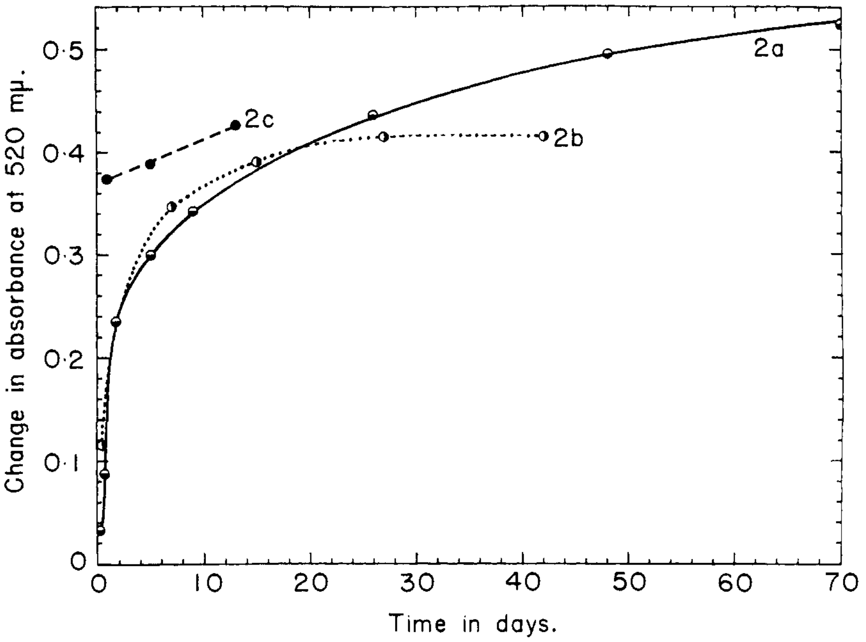

Fig. 4.—Change in absorbance at 520 mμ *vs.* time, of benzene solutions initially 2.5×10^{-5} *M* with respect to bromophthalein magenta E and 0.25 *M* with respect to tribenzylamine; 1-cm. absorption cells: 2a, benzene practically air-free at start; 2b, benzene not air-free although solutions were prepared just before mixing; 2c, tribenzylamine solution 2 weeks old at time of mixing.

Preparation and Properties of Tribenzylamine Oxide.—In order to determine beyond question the nature of the slow change in benzene containing bromophthalein magenta E and tribenzylamine, tribenzylamine oxide was prepared and its properties were studied. No record of its previous preparation was found although preparation of the isomeric compound, O,N,N-tribenzylhydroxylamine, was reported many years ago.[19]

The accepted procedure for the preparation of a tertiary amine oxide is reaction of the amine with hydrogen peroxide or an organic peracid. Tribenzylamine oxide was prepared by treatment of tribenzylamine with hydrogen peroxide and also by treatment with perbenzoic acid, but in the latter case it was not isolated. Preliminary trials indicated that treatment of a suspension of tribenzylamine in water (in which solvent the amine is nearly insoluble) with hydrogen peroxide would not yield satisfactory results; acetone and methanol were also tried as solvents, but it was concluded that acetic acid was more satisfactory. It also appeared that the more concentrated the hydrogen peroxide, the better. In the final preparation the tribenzylamine was dissolved in glacial acetic acid and twice the calculated quantity of 30% aqueous hydrogen peroxide was added, the volume of acetic acid used being just sufficient to prevent precipitation of the amine when the aqueous solution of hydrogen peroxide was added. When the solution was diluted with water after 24 hours, tribenzylamine oxide precipitated. The crude product, which contained a little unreacted tribenzylamine, was 46% of the calculated yield. The product was thoroughly washed with water to remove acetic acid and hydrogen peroxide, and, after air-drying, it was extracted with cold benzene to remove the other most likely impurity, tribenzylamine.[20]

Whenever the tribenzylamine oxide was warmed with any solvent, the odor of benzaldehyde became evident, and the removal of most of the loosely bound water and benzene was therefore accomplished by leaving the product in a vacuum oven at room temperature for long periods, during which the composition of the product was tested periodically by dissolving portions in glacial acetic acid and titrating them with standard 0.1 *N* perchloric acid in acetic acid.[21] In such a manner the purity of one sample was raised in stages from 76.4 to 99.5% (as computed from the quantity of perchloric acid required). It did not seem practicable to increase the purity further. On the assumption that the sole remaining impurity was water, this tribenzylamine oxide would contain less than 10 mole % of water. Microanalyses for all four elements (C, H, N, O), and likewise spectrophotometric measurements, gave full support to this assumption.

A 0.1-g. sample of tribenzylamine oxide upon treatment with zinc dust in acid solution yielded over 0.06 g. of tribenzylamine, shown by melting point and mixed-melting point determinations. This test, the method of preparation, the results of microanalyses and titrations, and the resemblance of the properties of our product to the properties of other amine oxides, leave no doubt as to its identity.

The thermal decomposition of tertiary amine oxides has been studied by various investigators, with somewhat conflicting conclusions. It appears that the structure of the amine oxide determines the course of thermal decomposition. The studies most pertinent to this investigation are those of the thermal decomposition of benzyldialkylamine

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[19] F. Walder, *Ber.*, **19**, 1626 (1886), described it as short, prismatic crystals, m.p. 119° (from ether); R. Behrend and K. Leuchs, *Ann.*, **257**, 203 (1890), claimed that it is a liquid which decomposes on distillation *in vacuo*.

[20] Tests of very small portions of the reaction mixture with a little bromophthalein magenta E in benzene, after neutralization, were useful in judging when appreciable oxidation of tribenzylamine had taken place; when this had occurred, the test solution turned a decided rose color. In a later preparation the yield was increased by extending the time of reaction to three days and by reducing the quantity of water used in precipitating and washing the product. See also Experimental section.

[21] W. Seaman and E. Allen, *Anal. Chem.*, **23**, 592 (1951). Both the glass-calomel electrode system and crystal violet were satisfactory for locating the end-point.

oxides, performed by Cope and co-workers.[22] Benzyldimethylamine oxide, prepared as a concentrated sirup, rearranged on distillation at reduced pressure to give a 61% yield of O-benzyl-N,N-dimethylhydroxylamine.[22a] Benzyldiethylamine oxide, prepared and treated in a comparable manner, rearranged in part into O-benzyl-N,N-diethylhydroxylamine, but several other products also were formed as the result of an elimination reaction.[22b] This elimination reaction was observed only for tertiary amine oxides having hydrogen atoms on a carbon beta to the nitrogen atom,[22b] and behavior resembling that of benzyldimethylamine oxide is therefore more likely to occur for tribenzylamine oxide, particularly since the benzyl group seems to migrate easily from nitrogen to oxygen.[22b] Further rearrangement, accompanied by scission, could yield benzaldehyde and dibenzylamine; we did not detect the latter compound, but probably only very slight decomposition of tribenzylamine oxide occurred at room temperature. Our interest was in preventing decomposition, rather than in determining the nature of thermal decomposition products and, as a precautionary measure, samples of the solid were kept in a refrigerator when not in use.

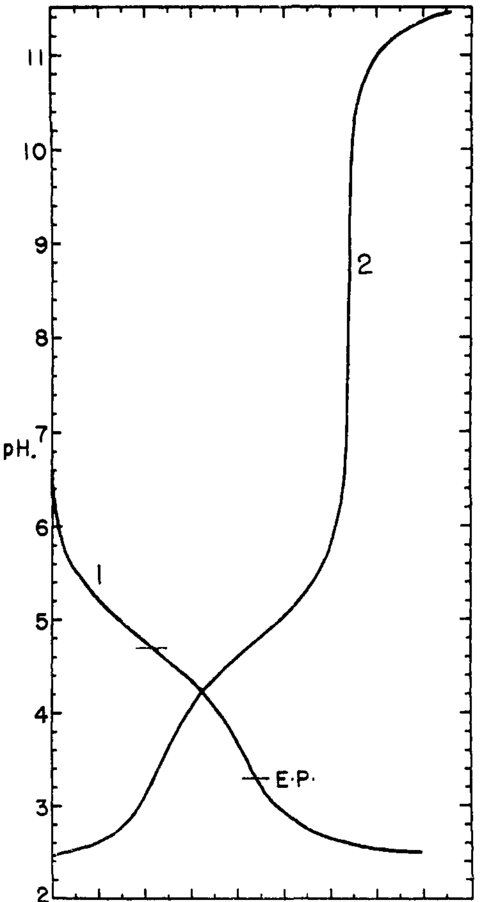

Fig. 5.—(1) Titration of 0.2739 g. of tribenzylamine oxide (99.2% pure) with 0.1019 N HCl; initial solution contained 10 ml. of EtOH and 90 ml. of water; (2) back titration with 0.1121 N NaOH; E.P., calculated end-point.

In view of the thermal instability of tertiary amine oxides, it was not surprising to find that a sharp and reproducible melting point for tribenzylamine oxide could not be obtained. The solid always showed signs of softening before the main portion began to melt, it never resolidified after melting, and the temperature range in which most of the melting occurred was higher when the capillary tube containing the sample was not placed in the bath until the melting region was being approached. To illustrate, for the product presumed to be the purest (99.5%), the melting range 120.7–121.9° was found when a sample was heated continuously from room temperature, while the melting range 122.3–123° was found when the sample was placed in the bath when the temperature of the latter had risen to ~75°. All of the melting points obtained for different specimens of tribenzylamine oxide were in the same general region, however, indicating a melting point (or temperature of rearrangement) about 30° higher than the melting point of tribenzylamine.[23]

In addition to a difference in the melting point, tribenzylamine oxide differs from tribenzylamine in being much less soluble in benzene and more soluble in water. A further difference is in the solubility of the perchlorate in glacial acetic acid. For example, when approximately 0.001 mole of the base was dissolved in 30 ml. of glacial acetic acid and titrated with 0.1 N perchloric acid in acetic acid, about 10 ml. of the perchloric acid solution being used to reach the end-point, a precipitate formed during the titration in the case of tribenzylamine, but not in the case of tribenzylamine oxide.[21,24]

Goldschmidt and Salcher[25] estimated an ionization constant not exceeding 4×10^{-9} for *tribenzylamine* in water. We obtained the approximate value 5×10^{-10} at ~22° for the ionization constant of *tribenzylamine oxide* in water by dissolving two samples in "carbon dioxide-free" water with the aid of a little ethanol and titrating the solutions potentiometrically with 0.1018 N hydrochloric acid. Although the titration curves did not show a sharp change in slope at the end-point, in both cases a change occurred in the expected region. The end-point was taken as being the calculated end-point, and pK_b was computed from the pH value of the solution when one-half of the calculated quantity of acid had been added. The titration curve for one of the samples is shown in Fig. 5 (curve 1); the calculated end-point was 8.80 ml. Curve 2 of Fig. 5 is for the back titration of this solution with 0.1121 N sodium hydroxide.

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[22] (a) A. C. Cope and P. H. Towle, THIS JOURNAL, **71**, 3423 (1949); (b) A. C. Cope, T. T. Foster and P. H. Towle, *ibid.*, **71**, 3929 (1949).

[23] The highest melting range observed (124.5–125.7°) was found for a sample which was believed to contain only water as an impurity, and which titration in acetic acid indicated to be 77.7% pure. This suggests that hydration protects the amine oxide from thermal rearrangement and decomposition (see ref. 22a). However, tribenzylamine oxide does not appear to form a highly stable hydrate, in contrast to trimethylamine oxide, which combines avidly with two molecules of water.

[24] The titration curves (e.m.f. *vs.* volume of acid) found for acetic acid solutions of 1,3-dicyclohexylguanidine, 1,3-diphenylguanidine, tribenzylamine oxide and triethylamine were practically identical except for slight vertical displacements.

[25] H. Goldschmidt and R. M. Salcher, *Z. physik. Chem.*, **29**, 89 (1899).

TABLE I

IONIC DISSOCIATION CONSTANTS OF AMINES AND AMINE OXIDES IN WATER

Formula	$K_b \times 10^{10}$	Formula	$K_b \times 10^{10}$
$(CH_3)_3NO$	3.0[a]; 4[b]	$(CH_3)_3N$	631,000[d]
$(C_2H_5)_3NO$	9.1[a]	$(C_2H_5)_3N$	5.500.000[e]
$(C_6H_5CH_2)_3NO$	5[c]	$(C_6H_5CH_2)_3N$	40[f]
$C_6H_5N(O)(CH_3)_2$	1.1[a]	$C_6H_5N(CH_3)_2$	11[g]
$C_6H_5N(O)(C_2H_5)_2$	2.3[a]	$C_6H_5N(C_2H_5)_2$	360[g]
o-$CH_3C_6H_4N(O)(CH_3)_2$	4.1[a]	o-$CH_3C_6H_4N(CH_3)_2$	72[g]
p-$CH_3C_6H_4N(O)(CH_3)_2$	1.4[a]	p-$CH_3C_6H_4N(CH_3)_2$	32[g]

[a] P. Nylén, *Tids. Kjemi Bergvesen*, **18**, 48 (1938); t = 20°, quinhydrone electrode. [b] T. D. Stewart and S. Maeser, THIS JOURNAL, **46**, 2583 (1924); t = 20°; colorimetric determination of extent of hydrolysis of halides. [c] This paper; $t \cong 22°$, potentiometric titration (glass-calomel) with 0.1 N HCl. [d] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A177**, 499 (1941); t = 25°. [e] N. F. Hall, THIS JOURNAL, **52**, 5115 (1930); t = 25°. [f] H. Goldschmidt and R. M. Salcher, *Z. physik. Chem.*, **29**, 89 (1899); t = 25°, extent of hydrolysis of salt. [g] N. F. Hall and M. R. Sprinkle, THIS JOURNAL, **54**, 3469 (1932); t = 25°, potentiometric (hydrogen–calomel).

Aqueous ionization constants for only a few tertiary amine oxides are recorded in the literature. Table I gives the ionization constants for seven tertiary amine oxides and also for the corresponding tertiary amines. While the values of K_b found for the amine oxides are all about the same, ranging from 1.1×10^{-10} to 9.1×10^{-10}, K_b for a tertiary amine is in all cases larger than K_b for the related amine oxide, and its value varies considerably with the structure of the amine. The close similarity of K_b for tribenzylamine oxide to the values for other amine oxides constitutes still further proof of its structure.

As shown in Fig. 6, the spectral absorption of tribenzylamine oxide in ethanol is greater than that of tribenzylamine.[26] For tribenzylamine oxide there are absorption bands near 258, 263.5 and 269.5 mμ and a less distinct band near 252 mμ. Tribenzylamine shows an absorption band near 259 mμ, a less distinct band near 252.5 mμ, and evidence of other bands near 247.5, 264 and 269 mμ. The absorption bands for tribenzylamine in ethanol are not in the same positions as the bands obtained by Purvis for tribenzylamine dissolved in ether[27]; it seems likely that studies of the effects of different solvents on the absorption spectra of tribenzylamine and tribenzylamine oxide would throw light on the extent of interaction, for example, through hydrogen bonding.

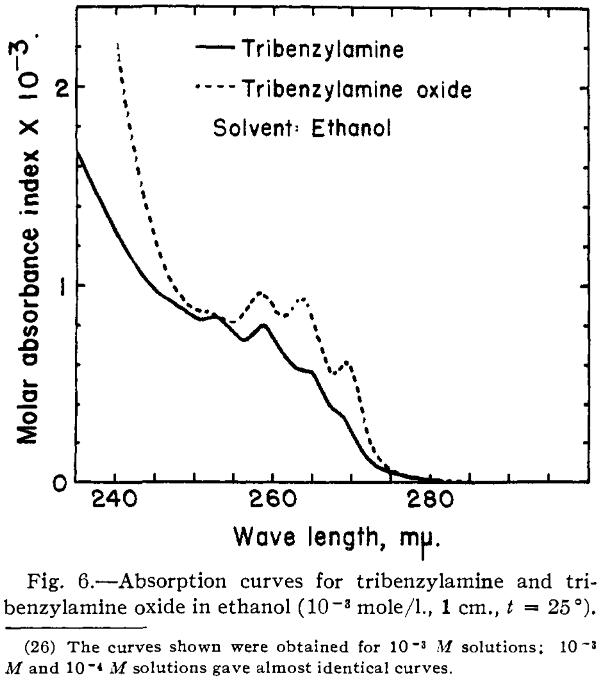

Fig. 6.—Absorption curves for tribenzylamine and tribenzylamine oxide in ethanol (10^{-3} mole/l., 1 cm., t = 25°).

Association of Tribenzylamine Oxide with Bromophthalein Magenta E in Benzene.[4]—In

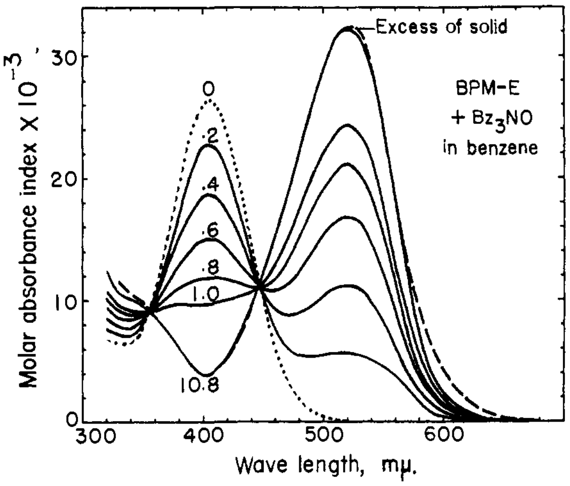

Fig. 7.—Change in the spectral absorption of bromophthalein magenta E (initially 2.5×10^{-5} M) in benzene upon addition of various amounts of tribenzylamine oxide: O, bromophthalein magenta E without added base; the numbers indicate the initial quantities of tribenzylamine oxide, expressed as molar equivalents of bromophthalein magenta E.

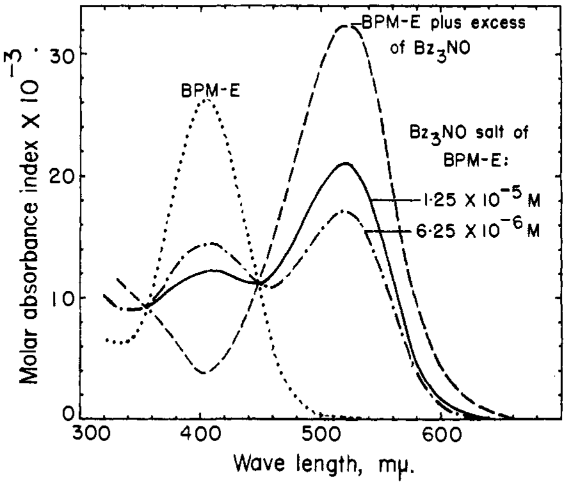

Fig. 8.—Change in the absorption curve of the tribenzylamine oxide salt of bromophthalein magenta E in benzene upon dilution from 1.25×10^{-5} M to 6.25×10^{-6} M. BPM-E, bromophthalein magenta E in benzene; BPM-E plus excess of Bz_3NO, curve after addition of an excess of solid tribenzylamine oxide.

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[26] The curves shown were obtained for 10^{-3} M solutions; 10^{-3} M and 10^{-4} M solutions gave almost identical curves.

[27] J. E. Purvis, *J. Chem. Soc.*, **105**, 1372 (1914); see Fig. 2, p. 1374. Purvis's figure shows three absorption bands which seem to be located near 263, 267 and 270 mμ.

measuring spectrophotometrically the constant for the association of tribenzylamine oxide with bromophthalein magenta E in benzene the usual method of obtaining the "limiting curve" for the reaction[14] was not very practicable because of the rather limited solubility of tribenzylamine oxide in benzene. Instead, an excess of the solid base was added to a benzene solution of bromophthalein magenta E (2.5 $\times 10^{-5}$ M), the mixture was shaken mechanically for about an hour, and the absorption curve was measured after filtration or, equally satisfactorily, after all visible suspended particles had settled. After additional periods of shaking, always with an excess of the solid base present, the only measurable change in the absorption curve was a progressive increase in the absorbance at wave lengths shorter than 370 mμ. These increases were interpreted as signifying continued solution of tribenzylamine oxide in excess of the quantity required to produce the limiting curve. The first curve was therefore regarded as the closest approximation to the correct limiting curve; this curve, which was shown in Fig. 1, is also shown in Figs. 7 and 8.[28]

The association constant was calculated from two kinds of data[5]: (1) The changes in the absorption produced by varying the quantity (C_b) of tribenzylamine oxide mixed with a fixed quantity of bromophthalein magenta E (the final concentration C_a, of which was always 2.5 $\times$ 10^{-5} M) and (2) the changes in the absorption of stock solutions of the tribenzylamine oxide salt of bromophthalein magenta E produced by dilution. Typical data of the two varieties are presented, respectively, in Figs. 7 and 8. Both sets of curves show two well-marked isosbestic points, near 355 and 447 mμ. The pronounced tendency for tribenzylamine oxide to combine with bromophthalein magenta E is evident from Fig. 7, which shows that the extent of combination is appreciable in a solution of the indicator as dilute as 2.5 $\times$ 10^{-5} M, even when the concentration of the base is still less than that of the indicator, and that conversion of the indicator to its amine oxide salt is essentially complete when the concentration of the amine oxide is only about 3 $\times$ 10^{-4} M.[29]

The absorption data for 520 mμ and also for 405 mμ were used in calculation of the association constant. Table II summarizes results obtained for the reaction of bromophthalein magenta E with tribenzylamine oxide. The average of the values obtained from data at 520 mμ is 4.8 $\times$ 10^5, and the average from data at 405 mμ is 4.5 $\times$ 10^5; the value obtained for 520 mμ is believed to be the better one, because the increments measured were larger and no allowance had to be made for the absorption of unreacted bromophthalein magenta E. From data for the salt, a value of the same order of magnitude, 4 $\times$ 10^5, was obtained.

TABLE II

EXPERIMENTAL DATA AND ASSOCIATION CONSTANT FOR THE PRIMARY REACTION OF BROMOPHTHALEIN MAGENTA E WITH TRIBENZYLAMINE OXIDE IN BENZENE AT 25°

$C_b \times 10^5$,[a] mole/l.	ΔA_s[b]	$K_{\text{assocn.}} \times 10^{-5}$[c]	$K_{\text{assocn.}} \times 10^{-5}$[d]
	Experiment 1		
0.498	0.1401	3.2*	2.3*
.995	.2781	3.8*	3.6*
1.492	.4176	5.2	4.2
1.990	.5232	4.8	4.5
2.488	.6065	4.8	4.3
	Experiment 2		
1.244	0.3520	4.8	4.3
1.741	.4711	4.8	4.5
2.239	.5709	5.0	4.7
2.736	.6319	4.5	4.6
2.985	.6609	4.6	4.7
Excess	.8108[e]		
Av.[f]		4.8	4.5

[a] C_a = 2.5 $\times$ 10^{-5} mole/l., cell length = 1 cm. [b] ΔA_s is the change in absorbance equivalent to the measured change in transmittance at 520 mμ; four decimal places were retained to avoid computational errors. [c] Based on measurements at 520 mμ. [d] Based on measurements at 405 mμ. [e] Limiting value. [f] The values marked with an asterisk were omitted in the computation of the average.

When Fig. 1 is compared with Figs. 7 and 8 the resemblance of the absorption curves obtained for solutions in which conversion of tribenzylamine to tribenzylamine oxide was suspected and the systems of curves obtained for solutions *known* to contain tribenzylamine oxide is very striking. Not only are the shape and position of the absorption band of the salt similar for the two kinds of mixtures, but the locations of the two isosbestic points, both as to wave length and as to molar absorbance index, are practically identical. Thus all the clues obtained in these studies point to the same explanation for the spontaneous slow changes in benzene solutions of tribenzylamine and bromophthalein magenta E, namely, gradual oxidation of part of the tribenzylamine to tribenzylamine oxide, through the agency of dissolved air.

Association of Tribenzylamine with Bromophthalein Magenta E in Benzene.—When a little

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(28) The value found for the molar absorbance index in the region of greatest absorbance (520 to 525 mμ) was 32,400. The purest sample of tribenzylamine oxide (99.5% by titration) was used in all the spectrophotometric measurements, and a correction was applied for the amount of impurity, which was assumed to be water and to be without effect on the reaction. The concentration of water would have been less than 2.5 $\times$ 10^{-6} M except in the mixtures prepared by adding solid tribenzylamine oxide to a solution of bromophthalein magenta E; in these solutions a slightly higher concentration of water was possible.

(29) Because of the thermal instability of tribenzylamine oxide heating was never employed to effect solution of tribenzylamine oxide or its salt with bromophthalein magenta E, and after preparation the solutions were used with the least possible delay. Some of the benzene solutions of tribenzylamine oxide had a slight odor of benzaldehyde after standing for a day, and solutions of bromophthalein magenta E mixed with tribenzylamine oxide very gradually faded from rose toward yellow, indicating a gradual loss of amine oxide. This change was expedited by heating or by exposing a solution to strong sunlight (in which case the change was believed to be caused by the heating rather than by visible or ultraviolet radiation). The effect of heat was found useful in establishing the correctness of the assumed composition (see equation 1) of the salt. For example, 200 ml. of a supposedly 1.25 $\times$ 10^{-5} M solution of the salt in benzene was prepared and a 25-ml. portion of this was heated for 20 minutes, during which it was concentrated to about 1/4 of the original volume, and then rediluted to 25 ml.; at wave lengths longer than ~350 mμ the absorption curve of the final solution was the same as that of 1.25 $\times$ 10^{-5} M bromophthalein magenta E in benzene. The disappearance of part of the tribenzylamine oxide could have been due to its reaction with glass (see refs. 2, 5 and 6). Measurements made with the tribenzylamine oxide salt of bromophthalein magenta E are thought to be less accurate than those made with mixtures of the indicator and base because more time was consumed in bringing about solution of the salt and diluting the stock solutions to various other concentrations.

bromophthalein magenta E dissolved in benzene was added to solid tribenzylamine, the yellow solution acquired a slightly pink tinge, which disappeared on heating but returned on cooling. The same effect was observed even after the benzene had been boiled to remove any dissolved air and the tribenzylamine had been kept near 100° for 1/2 hour to destroy any tribenzylamine oxide. Furthermore, as already mentioned in the discussion of Fig. 1, the spectral absorption of a solution of bromophthalein magenta E and tribenzylamine in benzene, when measured very promptly after preparation, showed indications of an absorption band of the type to be expected for a tertiary ammonium salt of bromophthalein magenta E. At first it seemed doubtful whether the small tendency for tribenzylamine and bromophthalein magenta E to combine in benzene could be measured accurately. However, by using benzene that had been freshly refluxed or boiled long enough to remove any dissolved air, avoiding subsequent exposure of the solutions to air, and performing the experiments as quickly as possible, values for $K_{\text{assocn.}}$ ranging from 0.12 to 0.15, with the average value 0.13, were calculated from data obtained at 540 mμ for six independently prepared solutions of widely varying compositions (see Table III, Series 2).[30] By contrast, values of $K_{\text{assocn.}}$ ranging from 0.14 to 0.46 were calculated from an earlier series of measurements that was made before recognition of the need for removing all air and for speed in making measurements (Table III, Series 1); these requirements were evidently met accidentally in the last experiment of this series.[31]

TABLE III

EXPERIMENTAL DATA AND ASSOCIATION CONSTANT FOR THE PRIMARY REACTION OF BROMOPHTHALEIN MAGENTA E WITH TRIBENZYLAMINE IN BENZENE AT 25°

C_a, mole/l.	C_b, mole/l.	Cell length, cm.	ΔA_s[a]	Limiting ΔA_s[b]	$K_{\text{assocn.}}$
		Series 1[c]			
0.00001	0.475	1.0	0.0649	0.4230	0.38
.000025	.25	0.5	.0549	0.5288	.46
.00005	.28	.5	.0972	1.058	.36
.0005	.25	.25	.1840	5.288	.14
		Series 2[d]			
0.000025	0.25	1.0	0.0388	1.058	0.15
.0001	.0625	1.0	.0329	4.230	.13
.0004	.016	1.0	.0338	16.92	.13
.0004	.0625	1.0	.1292	16.92	.12
.0008	.01	1.0	.0407	33.84	.12
.0016	.004	1.0	.0365	67.68	.13
				Av.[e]	.13

[a] ΔA_s is the change in absorbance equivalent to the measured change in transmittance at 540 mμ; four decimal places were retained in order to avoid computational errors. [b] Obtained by multiplying C_a by the factor (42,300 × cell length); this factor is based on the limiting value (0.5287 for 0.5-cm. cell) obtained in measurements of the reaction of 2.5×10^{-5} *M* bromophthalein magenta E with di-*o*-tolylguanidine in benzene (ref. 6). [c] Benzene not air-free. [d] Benzene essentially air-free. [e] Average of the values in series 2.

Comparative Strengths of Some Acids and Bases in Benzene.—At this point it is convenient to make the comparisons which were the original purpose of this investigation. The constants found[3] for the association of tribenzylamine with trinitro-*m*-cresol and picric acid in benzene are, respectively, 448 and 1580; thus the numerical values of *K* for the association of the three phenolic acids with tribenzylamine in benzene are consistent with the relative acidic strengths that would be expected from their chemical structures. A graphical way of comparing the differences in the reactivities of the three acids is presented in Fig. 9, which also shows how well the association reactions conform to the postulated equation 1 and the degree of precision attained in the measurements. If the reaction conforms closely to equation 1, the points obtained for a particular reaction must fall on a straight line with the slope −1 when log [S]/[A] is plotted against −log [B] as in Fig. 9, and log $K_{\text{assocn.}}$ will then be the value of the intercept of the diagonal on the abscissa for log [S]/[A] = 0.[4,32] The values for $K_{\text{assocn.}}$ increase

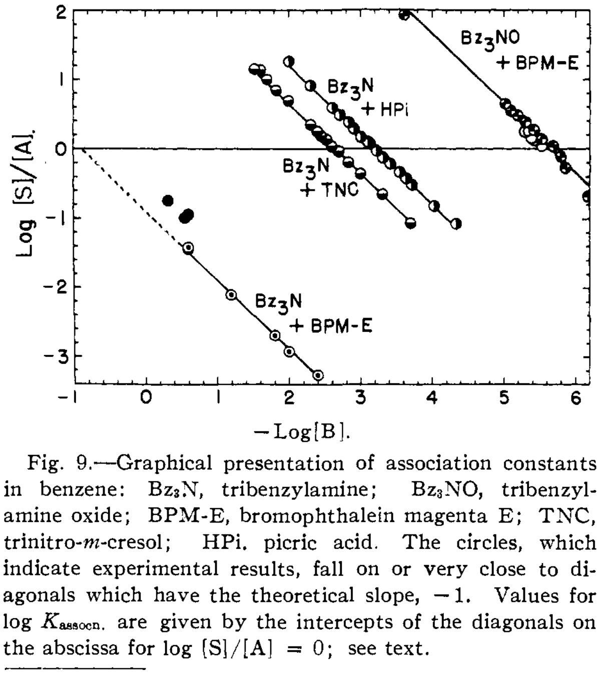

Fig. 9.—Graphical presentation of association constants in benzene: Bz_3N, tribenzylamine; Bz_3NO, tribenzylamine oxide; BPM-E, bromophthalein magenta E; TNC, trinitro-*m*-cresol; HPi, picric acid. The circles, which indicate experimental results, fall on or very close to diagonals which have the theoretical slope, −1. Values for log $K_{\text{assocn.}}$ are given by the intercepts of the diagonals on the abscissa for log [S]/[A] = 0; see text.

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[30] We are very much indebted to W. Stanley Clabaugh, who prepared and donated to us some porous gold "antibumpers." These were invaluable, because of their inertness and compactness, when some of the stock solutions of the indicator and the base were being concentrated so as to insure the removal of dissolved air.

[31] Because of the slight tendency for tribenzylamine to combine with bromophthalein magenta E in benzene, it was clearly impossible to obtain the limiting curve for this reaction experimentally, and the limiting value measured experimentally for the reaction of other bases with bromophthalein magenta E in benzene (see footnote 14) was used in calculating the association constant. This procedure was justified by the highly consistent values thus obtained, as well as by the conformity of the absorption curves for solutions containing only tribenzylamine and bromophthalein magenta E to the expected pattern (see, for example, Fig. 1, curve "0.02"). Some observations of A. A. Maryott, *J. Research Natl. Bur. Standards*, **41**, 1, 7 (1948), provide additional justification. He found that the dipole moment of tribenzylammonium picrate in benzene is practically the same as the dipole moments of the picrates of more strongly basic amines and concluded that "although tribenzylamine is a substantially weaker base than the trialkylamines, the proton transfer from acid to base appears to be equally complete in the two cases."

[32] See refs. 2, 3, 5 and 6. The values shown in Fig. 9 were calculated for the wave length thought to give the most reliable results, that is, near $\lambda_{\max}$ for the salt.

from left to right. In the reaction of tribenzylamine (Bz_3N) with bromophthalein magenta E (BPM-E) the solid circles are from series 1 of Table III and the other circles are from series 2. In the reaction of tribenzylamine oxide (Bz_3NO) with bromophthalein magenta E the open circles indicate the results obtained by diluting stock solutions of the tribenzylamine oxide salt of bromophthalein magenta E, and the remaining circles represent the two independent experiments (Table II) in which tribenzylamine oxide was added to bromophthalein magenta E.

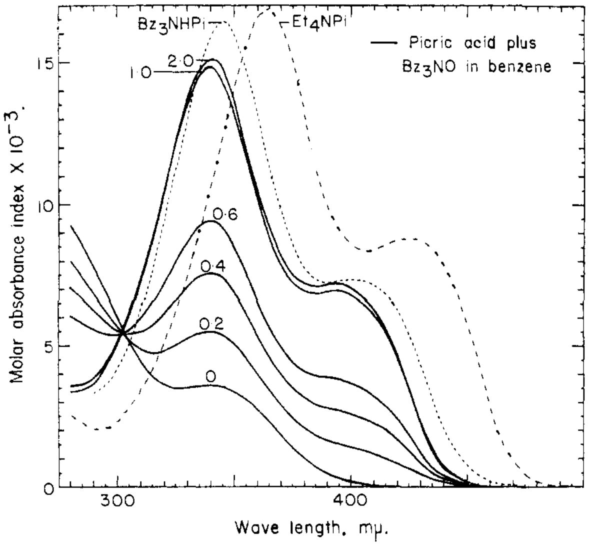

Fig. 10.—Change in the spectral absorption of picric acid (5.0×10^{-5} *M*) in benzene upon addition of various amounts of tribenzylamine oxide: O, picric acid without added base; the numbers indicate the various quantities of tribenzylamine oxide, expressed as molar equivalents of picric acid; note isosbestic point near 302 mμ; ...., limiting curve for tribenzylammonium picrate in benzene; ----, limiting curve for tetraethylammonium picrate in benzene.

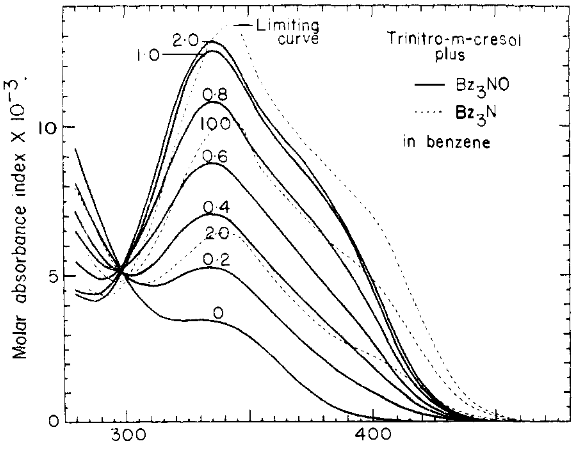

Fig. 11.—Change in the spectral absorption of trinitro-*m*-cresol (5.0×10^{-5} *M*) in benzene upon addition of various amounts of tribenzylamine oxide (solid lines) or tribenzylamine (dotted lines): O, trinitro-*m*-cresol without added base; the numbers indicate the various quantities of tribenzylamine oxide or tribenzylamine, expressed as molar equivalents of trinitro-*m*-cresol. For trinitro-*m*-cresol with tribenzylamine oxide, there is an isosbestic point near 298 mμ; with tribenzylamine, the isosbestic point is near 302 mμ.

Tribenzylamine is much the weakest of the compounds whose basic strengths in benzene we have measured in terms of their association with bromophthalein magenta E. For 1,2,3-triphenylguanidine, di-*n*-butylamine, triethylamine, piperidine, 1,3-diphenylguanidine and 1,3-di-*o*-tolylguanidine the values found were, respectively: 5.25×10^2, 1.55×10^4, 2.3×10^4, 1.2×10^5, 2.2×10^5, 1.1×10^6. It is interesting to note that tribenzylamine oxide combines with bromophthalein magenta E in benzene more readily than all of these bases except di-*o*-tolylguanidine.

Reaction of Tribenzylamine Oxide with Picric Acid and with Trinitro-*m*-cresol in Benzene. Possible Isomerism of Addition Compounds.—At the time the constants for the association of tribenzylamine with picric acid and with trinitro-*m*-cresol in benzene were measured,[3] the tendency for tribenzylamine to be oxidized by air to tribenzylamine oxide had not been discovered. Nearly all of the tribenzylamine oxide prepared for this investigation was used in the experiments with bromophthalein magenta E, but there was sufficient to determine the approximate extent of its reactivity with picric acid and trinitro-*m*-cresol, as well as the nature of the absorption curves of benzene solutions of its salts with these two acids.

Figures 10 and 11, respectively, show that dilute (5.0×10^{-5} *M*) picric acid and trinitro-*m*-cresol both combine very readily with tribenzylamine oxide in benzene. This high reactivity is indicated by the extensive changes in the absorption spectra of the acids produced by the addition of tribenzylamine oxide in amounts ranging from as little as 0.2 to 1.0 mole per mole of the acid, and by the small effect of increasing the concentration of the base from 1.0 mole to 2.0 moles per mole of the acid. Figure 11 also shows that tribenzylamine combines much less readily with trinitro-*m*-cresol than does tribenzylamine oxide.[33]

From comparing Figs. 7, 10 and 11 one would judge that tribenzylamine oxide combines at least as readily with picric acid and with trinitro-*m*-cresol as with bromophthalein magenta E in benzene; actually, the two nitrophenols would be expected to combine with tribenzylamine oxide even more readily than bromophthalein magenta E because of their greater acidity. The question arises as to whether the association constants reported earlier[3] for the reaction of tribenzylamine with picric acid and trinitro-*m*-cresol in benzene could have been seriously in error. The tendency of benzene solutions of these nitrophenols, especially picric acid, to absorb atmospheric moisture, shown by the gradually acquired yellow tinge of originally colorless solutions, introduces a problem in accurate measurements that was avoided in our experiments by always using freshly prepared solutions

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[33] The limiting curve for the reaction of trinitro-*m*-cresol with tribenzylamine in benzene is a calculated curve (see ref. 3), but it is almost exactly the same as the limiting curve found experimentally for the reaction of trinitro-*m*-cresol with di-*o*-tolylguanidine in benzene (M. M. Davis and E. A. McDonald, unpublished data).

and working rapidly. Both acids, as well as tribenzylamine, dissolve so easily in benzene that solutions can be prepared very quickly. Considering, then, the little time available for tribenzylamine oxide to have formed, the much greater reactivity of picric acid and trinitro-*m*-cresol with tribenzylamine, as compared with bromophthalein magenta E, and the fact that changes in the absorbance were not detected during the spectrophotometric measurements, it seems unlikely that amine oxide-formation introduced any measurable errors.

However, amine oxide-formation does offer a possible explanation, at least in part, for the baffling changes (in most circumstances, decreases) in the conductance of tribenzylammonium picrate in toluene with time and variations in temperature which were observed by Fuoss and co-workers and thought to be due perhaps to slow intramolecular proton shifts.[10] In their experiments an undesirable effect of dissolved air could not have been foreseen, and toluene was pumped from the storage flask into various other vessels by dry air pressure. It is reasonable to assume that the tendency for tribenzylamine to combine with picric acid is about the same in benzene and toluene, which would mean that the content of tribenzylamine in the 3×10^{-3} *M* solution of "tribenzylammonium picrate" in toluene discussed in ref. 10 would be $\sim 1.3 \times 10^{-3}$ mole/l.[34] On the further reasonable assumption that the oxidation of tribenzylamine to tribenzylamine oxide is likely to occur to about the same extent in benzene and toluene, it is quite conceivable that sufficient tribenzylamine oxide was formed during some of the conductance experiments (which involved checks of the initial measurements after periods of many hours) to cause measurable changes in the conductance.

The effect that conversion of tribenzylamine to tribenzylamine oxide could have on the conductance is apparent from investigations of Kraus and co-workers.[12,35] They have found that, in general, in non-basic solvents such as ethylene chloride and nitrobenzene, partially substituted ammonium salts (*e.g.*, mono-, di- and trialkylammonium picrates) have ionic dissociation constants only about one-thousandth as large as those of the corresponding completely substituted ammonium salts (*e.g.*, tetraalkylammonium picrates); the dissociation constants of the picrates of amine oxides are still smaller by about one-tenth. Thus, any expected change in the conductance of toluene solutions of tribenzylammonium picrate as a result of amine oxide-formation would be in the same direction as the changes actually observed.[10] Our discovery of the formation of tribenzylamine oxide in benzene solutions of tribenzylamine and bromophthalein magenta E was reported briefly by letter to Professor Fuoss, together with the suggestion that amine oxide-formation, rather than a slow proton shift, might have been the cause of the drifts in conductance observed in his laboratory. In reply Professor Fuoss stated that a slow intramolecular proton shift had never seemed to him to be a satisfactory explanation of the drift in the conductance of tribenzylammonium picrate, and that he believed our suggestion to offer the correct explanation.

The question whether electromeric forms of partially substituted ammonium salts, interconvertible by measurably slow proton shifts, exist is one of theoretical importance. Further experimental work may establish the existence of such isomers, but at present it would appear that in cases where experimental work has suggested their existence alternative explanations can be found.

The Relative Basicities of Amines and Amine Oxides. Further Discussion.—Tertiary amine oxides are known to form salts very readily with *hydrogen* acids, and it has been shown in this paper that tribenzylamine oxide has a high affinity for the comparatively weak acid bromophthalein magenta E in benzene solution. There is also evidence that tertiary amine oxides have a very high affinity for acids of the *Lewis* class. Thus, Burg observed that anhydrous trimethylamine oxide combines so vigorously with sulfur dioxide that in order to prevent charring the temperature must be kept at −80° or below during the reaction; he also concluded that trimethylamine oxide attracts sulfur dioxide more strongly than does trimethylamine.[36a,37] In addition, Burg and Bickerton found that trimethylamine oxide forms a very stable compound with boron trifluoride and appears to form stable compounds with silicon tetrachloride and phosphorus trichloride.[36b] Nevertheless, it is clear from Table I that tertiary amine oxides are only weak bases according to the usual criterion of basic strength—the magnitude of the ionization constant in water. For the amine oxides listed in the table, which includes both aliphatic and aromatic compounds, the ionization constants in water are uniformly of the order of 10^{-10}.[38] This ionization behavior is in marked contrast to the behavior of the tertiary amines listed in Table I, the ionization constants of which are all greater than the constants of the corresponding amine oxides and also vary over a far wider range.

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(34) The molar concentration of tribenzylamine present in this solution was calculated by applying the results of spectrophotometric measurements at 25° (ref. 3) and dielectric constant measurements at 30° and 40° (ref. 11) of the equilibrium between tribenzylammonium picrate and its component acid and base in benzene.

(35) (a) C. A. Kraus, *J. Phys. Chem.*, **43**, 231 (1939); (b) C. A. Kraus, *Science*, **90**, 281 (1939); (c) E. G. Taylor and C. A. Kraus, THIS JOURNAL, **69**, 1731 (1947); (d) D. S. Burgess and C. A. Kraus, *ibid.*, **70**, 706 (1948); (e) C. A. Kraus, *Ann. N. Y. Acad. Sci.*, **51**, 789 (1949).

(36) (a) A. B. Burg, THIS JOURNAL, **65**, 1629 (1943). See also H. Z. Lecher and W. B. Hardy, *ibid.*, **70**, 3789 (1948); (b) A. B. Burg and J. H. Bickerton, *ibid.*, **67**, 2261 (1945).

(37) The generally accepted structure, $R_3N^+{-}O^-$, of tertiary amine oxides furnishes a ready explanation for a more pronounced tendency to attract electrophilic compounds than that shown by tertiary amines, but it is now obvious from the work of H. C. Brown and his students that the effective basicity of tertiary amines is greatly dependent on their steric requirements as well as on the steric requirements of any acid with which they are brought in contact (see, *e.g.*, *Science*, **103**, 385 (1946)). The importance of the steric requirements of tertiary amines is also apparent from studies of J. A. Moede and C. Curran, who measured the stabilities of addition compounds of sulfur dioxide with some amines when dissolved in aprotic solvents; as expected, the stabilities of the addition compounds formed with trimethylamine, triethylamine and tri-*n*-butylamine decrease in the order named (THIS JOURNAL, **71**, 852 (1949)).

(38) The aqueous ionization constants of the amine oxides are thus approximately the same as that of aniline, for which $K_b \cong 4.2 \times 10^{-10}$ at 25° (see N. F. Hall and M. R. Sprinkle, THIS JOURNAL, **54**, 3469 (1932)). [Note, however, that from conductance measurements A. Hantzsch and W. Graf (*Ber.*, **38**, 2154 (1905)) concluded that the extent of hydrolysis of salts of trimethylamine oxide (*e.g.*, the chloride and the iodide) is less than that of aniline hydrochloride.]

In Fig. 12 a comparison has been made of the relative strengths of tribenzylamine oxide and seven other bases in benzene (expressed as the values of log K for association with bromophthalein magenta E) and the corresponding strengths in water (expressed as log K_{dissocn}). The figure bears out the expectation[4,6] that there should be a general parallelism in the relative values for the association constants in benzene and the ionic dissociation constants in water, so far as the seven bases in which nitrogen is the electron donor are concerned; for five of these bases the parallelism is fairly close.[37,39] However, the point for tribenzylamine oxide is remote from the diagonal near or along which the other points are grouped, because the ionization constant in water is much too small for the parallelism to hold. What is the explanation for the extremely small ionization constants of tribenzylamine oxide and other amine oxides in water?

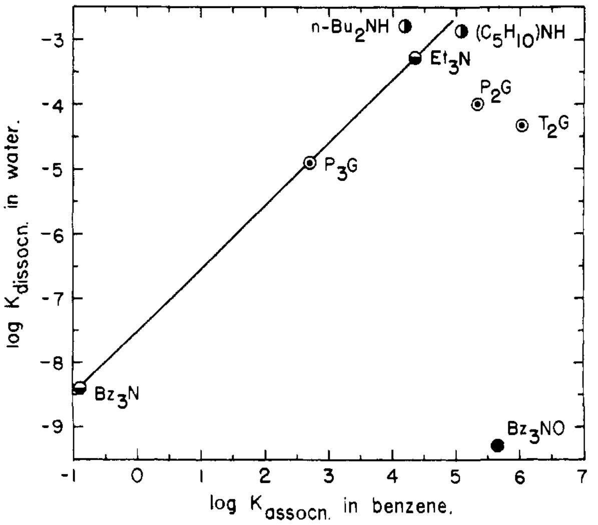

Fig. 12.—Comparative strengths of bases as measured by association with bromophthalein magenta E in benzene and by ionic dissociation constants in water: Bz_3N, tribenzylamine; P_3G, 1,2,3-triphenylguanidine; Et_3N, triethylamine; P_2G, 1,3-diphenylguanidine; T_2G, 1,3-di-*o*-tolylguanidine; Bz_3NO, tribenzylamine oxide; *n*-Bu_2NH, di-*n*-butylamine; $(C_5H_{10})NH$, piperidine.

A comparison of the absorption spectra of salts of tertiary amines and those of amine oxides in benzene solution furnishes a clue to this puzzling behavior. In earlier discussion we mentioned without comment that the oxides of trimethylamine and tribenzylamine differ from tertiary amines such as triethylamine, in the characteristic absorption curves obtained for their salts in benzene solution. Two differences in the absorption curves of the two classes of salts are easily detected in Fig. 1—the position of $\lambda_{\max}$ and the magnitude of the molar absorbance index at $\lambda_{\max}$. In the absorption curve for trialkylammonium salts of bromophthalein magenta E $\lambda_{\max}$ is 15 to 20 mμ nearer the infrared region than $\lambda_{\max}$ for the salts of bromophthalein magenta E with trimethyl- and tribenzylamine oxide, and the molar absorbance index at $\lambda_{\max}$ is more than 30% greater.[14,28] In the case of quaternary ammonium salts of bromophthalein magenta E the absorption is shifted even further toward the infrared region, and the molar absorbance index at $\lambda_{\max}$ is much greater still.[40] The different colors of benzene solutions of the three types of salts of bromophthalein magenta E were described in an earlier publication, and an explanation along the following lines was presented.[2] (a) **Quaternary Ammonium Salts, $R_4N^+A^-$ (Blue).**—When the phenolic proton of bromophthalein magenta E is replaced by a quaternary ammonium group, resonance involving groups A and B (see formula I) and the methane carbon atom occurs, the electrons of the anion becoming so loosely bound as to make possible the absorption of light of lower energy (near 600 mμ). (b) **Tertiary Ammonium Salts, $R_3NH^+ \ldots A^-$ (Magenta).** "The existence of a proton in place of one of the alkyl groups of the quaternary ammonium salt permits a closer approach of the positive and negative ions to each other, with a consequent increase in the coulombic force. However, the change in behavior that accompanies this modification in structure is undoubtedly due in part to the formation of a hydrogen bridge between the nitrogen of the base and the oxygen of the indicator acid. . ." (c) **Trimethylamine Oxide Salt, $(CH_3)_3NOH^+ \ldots A^-$ (Rose).**—"Degeneracy of the resonance structures of the anion of bromophthalein magenta appears to be less complete in the salt formed by combination of the indicator with trimethylamine oxide than in the salts formed by its combination with trialkylamines, indicating that the proton of the indicator acid undergoes a smaller displacement toward the oxygen of trimethylamine oxide than toward the nitrogen of (trialkylamines). . . ."

The absorption spectra of benzene solutions of picric acid (colorless) and various types of picrates (different tones of yellow) show differences paralleling those found for bromophthalein magenta E and its salts, and the differences can be accounted for in a similar way. However, the differences in color are too small in this case to be fully appreciated without measuring and comparing the absorption curves. In Fig. 10 it is clearly evident that in benzene solution picric acid and its salts with tribenzylamine oxide, tribenzylamine and tetraethylammonium hydroxide are distinctly differ-

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(39) The values found for $K_{\text{assocn.}}$ in benzene were given earlier in this paper; those for triethylamine, di-*n*-butylamine and piperidine are provisional (ref. 2), but are believed to be approximately correct. The values used for $K_{\text{dissocn.}}$ in water are the ones listed in Table I of this paper and Tables II and III of ref. 2. It will be observed that the "nitrogen" bases comprise two trialkylamines, two dialkylamines and three aryl derivatives of guanidine. The fact that tribenzylamine is one of the bases for which parallelism in the strengths in water and benzene seems to be close is an additional reason for confidence in the values cited here for its $K_{\text{assocn.}}$ in benzene and $K_{\text{dissocn.}}$ in water. For the five bases which were the first to be investigated, namely, the five bases indicated in the upper right corner of Fig. 12, there is a seemingly *inverse* correlation of the strengths in water and benzene (see ref. 2, Fig. 18 and related discussion). However, there are reasons why the aqueous dissociation constants of bases cannot, in all cases, be expected to parallel exactly other scales of basic reactivity; for a discussion of such reasons and suggested explanations for anomalies in the relative strengths of triethylamine, diphenylguanidine and ditolylguanidine in benzene and water, see ref. 6. The meagerness of the data in Fig. 12 illustrates how badly additional studies of the comparative strengths of bases in benzene are needed.

(40) See ref. 2, Figs 21 and 22 and related discussion.

ent in spectral absorption.[41] Measurements using trinitro-*m*-cresol as the acid (see Fig. 11) were less extensive, but they again indicate that the electrons in the anion are more loosely bound in the tribenzylamine oxide salt than in the acid, though less loosely than in the tribenzylammonium salt, and the differences are again consistent with the assumption that the proton of an acid is less displaced toward the oxygen of an amine oxide than toward the nitrogen of an amine.

The explanation adopted for the differences in the absorption spectra of various classes of salts accounts for the exceptionally low ionization constants of amine oxides in water (Table I), as well as for the very slight tendency for the picrates of amine oxides to ionize in nitrobenzene.[12,35] Such observations are only to be expected if the proton of the acid (*e.g.*, water, picric acid) remains more strongly attached to the anion (hydroxyl, picrate) when the acid combines with an amine oxide than is the case when the acid combines with an amine. It is very important, however, to note that in pyridine, the dielectric constant of which (~12) is much lower than that of nitrobenzene (~35), salts of both amines and amine oxides are highly ionized. A summary of Kraus's conclusions from conductance data for numerous quaternary ammonium and partly substituted ammonium salts is best expressed in his words: "Any negative ion tends to interact with an active proton attached to a positive ion. The extent to which such interaction may influence the properties of the resulting solution will depend upon the nature of the solvent molecules themselves. When a partially substituted ammonium salt is dissolved in a solvent medium the molecules of which have no affinity for the proton, interaction takes place between the negative ion and the proton of the positive ion. In other words, there is formed what is commonly known as a hydrogen bond, the energy of rupture of which may be much higher than the energy necessary to overcome the Coulombic forces acting between the ions. When, on the other hand, the same substance is dissolved in a solvent which has a marked affinity for the proton . . . the electrolyte behaves normally and in solution will be as strong as any normal electrolyte having ions of the same size. . . . Taking into account the difference in the behavior of ammonium salts in pyridine and in nitrobenzene or ethylene chloride, it seems clear that the low value of the dissociation constants in the latter solvents is due to interaction between the negative ion and the proton of the positive ion. The absence of such interaction in the case of pyridine solutions is doubtless due to the fact that, because of the relatively high affinity of the pyridine molecule for the proton, the interaction of the proton of the positive ion takes place with a pyridine molecule rather than with a negative ion. . . ."[35a] "The hydrogen of the OH group in the trimethylhydroxyammonium ion is very active and, in the absence of basic molecules, as in nitrobenzene, it bonds with the negative ion to yield a very weak electrolyte. If basic molecules are added to such a solution, they interact with the active hydrogen of the ion and the solute behaves like a stronger electrolyte; the stronger the added base, the more marked is this effect. . . ."[35e] Such conclusions reached by Kraus and his collaborators, who, for the most part, have been concerned with the behavior of various types of salts in non-aqueous solvents, as measured by conductance, dielectric constants and freezing point-lowering, are fully supported by the studies in this Laboratory of acid–base reactions in organic solvents (notably benzene), as measured by changes in spectral absorption in the ultraviolet and visible regions.[4-6,42] From such studies as these it seems obvious that the term "ion-pair" as applied to the molecules of incompletely substituted ammonium salts is a misnomer. The term "hydrogen-bonded ion-pair" would be more accurate.

Studies such as those discussed in this paper have a very general bearing on concepts of acidity and basicity, as has been pointed out elsewhere.[5,6,43] In addition, a better knowledge and understanding of the comparative behavior of amines and amine oxides has biochemical importance. It is well known, for example, that trimethylamine oxide is a constituent of the nitrogenous extractives of the muscle and entrails of most kinds of seafish and crustacea, notably dogfish and shrimp.[44a] The growth of certain types of bacteria was found to be retarded on the addition of 1% of trimethylamine oxide to agar culture media. The presence of trimethylamine oxide is perhaps the reason that marine fish keep better than fresh-water fish, which appear to contain only traces of trimethylamine oxide.[44b] Geneserine (the N-oxide of physostigmine) and trilupine (the di-N-oxide of *d*-lupanine) are said to be the only natural alkaloid N-oxides so far discovered,[45] but numerous alkaloid N-oxides have been prepared in the laboratory, notably by M. and

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(41) The curve for tetraethylammonium picrate is from studies by M. M. Davis, E. A. McDonald and P. J. Schuhmann, not yet published, of the spectral absorption of picric acid and trinitro-*m*-cresol and a number of their salts in benzene, cyclohexane and water. Practically identical absorption curves were found for the tetraalkylammonium picrates studied (tetraethyl-, tetra-*n*-propyl- and tetra-*n*-butyl-). The marked differences found for picric acid and different types of picrates in a hydrocarbon solvent disappear completely when water is the solvent. Studies of trinitro-*m*-cresol and its salts, although less complete, gave analogous results. See also H. von Halban and B. Szigeti, *Helv. Chim. Acta*, **20**, 746 (1937).

(42) This emphasis on the role of hydrogen bonding in the ionization of incompletely substituted ammonium salts has recently received new justification from studies of hydrogen bonding in crystals. According to J. Donohue, *J. Phys. Chem.*, **56**, 502 (1952), examination of the structures of a large number of organic crystals "reveals the rather remarkable fact that only in very exceptional cases does a hydrogen atom bonded to nitrogen or oxygen occupy a position such that hydrogen bond formation is impossible." In harmony with this statement, R. C. Lord and R. E. Merrifield, *J. Chem. Phys.*, **21**, 166 (1953), have reported that "the infrared absorption spectra of tertiary amine hydrohalides show features which indicate the presence of strong N^+–$H...X^-$ bonds in these salts." They also state that the characteristics of the infrared absorption bands "are incompatible with a simple electrostatic model of the hydrogen bond and . . . a quantum-mechanical model is undoubtedly required."

(43) In connection with the discussion in refs. 5 and 6, see also W. H. Rodebush and R. H. Ewart, THIS JOURNAL, **54**, 419 (1932); S. W. Pennycuick, *J. Phys. Chem.*, **32**, 1681 (1928).

(44) (a) O. A. Ronold and F. Jakobsen, *J. Soc. Chem. Ind.* (*London*), **66**, 160 (1947); (b) C. H. Castell, *J. Fisheries Research Board Can.*, **6**, 491 (1946), through *C. A.*, **41**, 815 (1947).

(45) L. Small, "Organic Chemistry, An Advanced Treatise," H. Gilman, Editor, Vol. II, 2nd edition, John Wilev and Sons, Inc., New York, N. Y., 1943, ch. 15, p. 1234.

M. Polonovski,[46] who suggested for them the general name "genalkaloids." Reports that genalkaloids resemble the corresponding alkaloids in pharmacological effects but are less toxic have stimulated investigations in the laboratories of several continents.

In the near future we hope to investigate the nature of the absorption band of bromophthalein magenta E when dissolved in a hindered alcohol, *e.g.*, heptadecanol (3,9-diethyltridecanol-6) and tetradecanol (7-ethyl-2-methylundecanol-4). Dilute solutions of bromophthalein magenta E in these two alcohols were found to have a magenta color rather than the blue color observed for solutions in unhindered alcohols like ethanol.[2] It was suggested that the proton of bromophthalein magenta E can become bridged to the oxygen of a hindered alcohol, but that complete solvation of the proton (which we believe requires two molecules of alcohol[5,6]) is prevented by steric factors. It will be interesting to discover whether hindered alcohols produce a characteristic absorption band and, if so, how closely this band resembles the characteristic absorption bands produced by the reactions of tertiary amines and amine oxides with bromophthalein magenta E in benzene.

Experimental

Apparatus.—(1) Spectral absorption was measured with a Beckman Model DU quartz photoelectric spectrophotometer, the temperature being maintained at 25.0 ± 0.1° by the use of a thermostated air-bath constructed at the National Bureau of Standards.[6] The absorption cells were glass-stoppered cells of variable lengths (usually 1 cm.) also constructed at the Bureau.[2] The "molar absorbance index" (molecular extinction coefficient) has its usual significance.[2] (2) Melting points were determined by the capillary-tube method, using an electrically heated high-boiling silicone oil and an A. S. T. M. thermometer for 3-inch immersion; as the silicone expanded during heating, the thermometer was gradually raised so as to maintain constant immersion. (3) A Precision-Shell Single Titrometer was used in potentiometric titrations.

Materials.—A high grade of **benzene** was dried over Drierite and then distilled, thus removing water and a light-absorbing impurity; in some experiments the benzene was refluxed or partly boiled away, in order to ensure the removal of dissolved air. **Bromophthalein magenta E** (3',3'',5',5''-tetrabromophenolphthalein ethyl ester) was some of the material prepared and purified for earlier measurements.[2,5,6] **Tribenzylamine** of the highest commercial grade was recrystallized once or twice from 95% ethanol and dried in a vacuum oven at room temperature; m.p. 92.8-93.2°. **Picric acid** and **trinitro-*m*-cresol** were commercial materials of high grade purified as described previously.[3]

Tribenzylamine Oxide.—(1) A solution of 14.4 g. (0.05 mole) of tribenzylamine (high commercial grade once recrystallized from 95% ethanol)[47] in 50 ml. of glacial acetic acid was stirred magnetically with 11.2 g. (~0.1 mole) of 30% hydrogen peroxide at 20 to 25° for about 24 hours. Crushed ice (450 g.) was added, and then chilled sodium hydroxide (40 g. of NaOH in 100 ml. of water) was added gradually while stirring. The snowy precipitate was filtered with the aid of suction and washed thoroughly with chilled water to remove any inorganic materials, including hydrogen peroxide. Tribenzylamine oxide appears to be appreciably soluble in water, and a large amount was probably lost during the washing. The crude product weighed 7 g. (46% yield) after drying at room temperature in a vacuum oven equipped with a Varsol-Dry Ice trap; m.p., 109.3-112.5°. A small amount of unreacted tribenzylamine was removed by extraction with benzene, after which the residue was kept under constant evacuation at room temperature for several days. The final product (m.p. 122.3-123.0°), when titrated with standard 0.1 *N* perchloric acid in glacial acetic acid, appeared to contain 0.5% of inert impurity, probably water.

Anal.[48] Calcd. for $C_{21}H_{21}NO$: C, 83.1; H, 7.0; N, 4.6; O, 5.3. Found: C, 82.7; H, 7.3; N, 4.6; O, 6.0. Calcd. on the assumption of 0.5% content of water: C, 82.7; H, 7.0; N, 4.6; O, 5.7.

In the preparation of solutions for absorption measurements the tribenzylamine oxide was assumed to contain 0.5% of water and appropriate corrections were made in the quantities used.

Reduction of Tribenzylamine Oxide to Tribenzylamine.—Tribenzylamine oxide (0.100 g.) was dissolved in 50% methanol (~20 ml.) which was also 0.05 *M* with respect to hydrochloric acid; 1 ml. of glacial acetic acid and an excess of zinc dust were added. After 5 days at 25 to 30°, during which small additional quantities of zinc dust and hydrochloric acid were added, the mixture was filtered and the filter was washed several times with a little methanol. The combined filtrate and washings were made alkaline by the addition of 10% sodium hydroxide. The precipitate which formed was filtered and washed thoroughly. The residue on the filter was allowed to dry in the air, then benzene was added and the solution was collected in a tared beaker; after evaporation of the benzene the residue (0.063 g.) had m.p. 89.3-90.8°; mixed m.p. with tribenzylamine, 91.3-92.1°. The m.p. of the residue was 92.0-92.7° after a recrystallization from 95% ethanol.

(2) Tribenzylamine oxide was also prepared by adding tribenzylamine (0.025 mole) to a slight excess of perbenzoic acid[49] dissolved in about 40 ml. of benzene. After about 15 minutes the benzene solution was extracted with 10% aqueous sodium carbonate. The aqueous extract was slightly acidified with hydrochloric acid and extracted with benzene (to remove any benzoic or perbenzoic acid) and finally shaken with moist, freshly precipitated silver oxide, then filtered. When the filtrate was shaken with an alcoholic solution of bromophthalein magenta E or its potassium salt the **tribenzylamine oxide salt of bromophthalein magenta E** separated in minute green plates having a metallic luster. The salt was filtered, air-dried, washed with benzene by decantation, and "dried" in a vacuum oven at room temperature. Its composition was checked by heating a benzene solution of known concentration until the rose color changed permanently to yellow, replacing the benzene lost by evaporation, and measuring the spectral absorption; at wave lengths longer than ~350 mμ this was the same as that found for a benzene solution of bromophthalein magenta E of equivalent molarity.

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[46] See *Bull. soc. chim.*, [4], **39**, 1147 (1926), and subsequent papers published during a period of about 10 years, mostly in the same journal.

[47] Recrystallization removed some impurity which gave an orange tinge to the reaction mixture; the impurity did not visibly contaminate the tribenzylamine oxide, however.

[48] For the microanalyses we are indebted to Rolf A. Paulson, according to whom the results for oxygen, with the apparatus used, may be in error by ±10% if the compound contains as much as 5% of oxygen.

[49] Prepared according to the directions of G. Braun ("Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 2nd edition, 1941, p. 431) except that the perbenzoic acid was extracted into benzene instead of into chloroform. The benzoyl peroxide used in the preparation was purified according to the procedure of K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).