

# The Effect of Picric Acid and Pyridine on the Conductance of an Amine N-Oxide Picrate in *o*-Dichlorobenzene at 25°<sup>1a</sup>

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The conductance of tri-*n*-butylamine N-oxide picrate has been measured as a function of salt concentration in *o*-dichlorobenzene as solvent at 25°. The addition of picric acid results in a large depression in the conductance of the salt. The addition of pyridine results in large increases in the equivalent conductance of the salt. The results are interpreted in terms of acid-base dissociation of the salt to yield free amine N-oxide and picric acid and formation of a 1:1 complex between the cation from the salt and the amine N-oxide. Analysis of the results indicates that the amine N-oxide is a stronger base, toward picric acid, in this aprotic solvent than is the corresponding amine—just the reverse of the order observed in water.

The increases in the ion-pair dissociation of amine N-oxide picrates are greater than for amine picrates upon the addition of amines in nitrobenzene as solvent.<sup>2</sup> These results led us to investigate the conductance of tri-*n*-butylamine N-oxide picrate in *o*-dichlorobenzene (ODCB) as solvent, at 25° with and without added pyridine, as a parallel to a study<sup>3</sup> of amines and amine picrates in this lower dielectric solvent.

## Experimental

The picrate salt of tri-*n*-butylamine N-oxide (BOHPi) was prepared, following Witschonke and Kraus,<sup>2</sup> by stirring tri-*n*-butylamine with excess hydrogen peroxide in 95% ethanol at room temperature for 5 hr. The excess peroxide was decomposed with a platinum wire catalyst. The resulting solution, containing the N-oxide, was titrated with picric acid, using phenolphthalein as an external indicator. After five recrystallizations from 95% ethanol, the salt melted at 110.0–111.0°. A mixture melting point with tri-*n*-butylammonium picrate occurred at 94–95°. *Anal.* Calcd. for C<sub>18</sub>H<sub>30</sub>O<sub>8</sub>N<sub>4</sub>: C, 50.22; H, 7.02; O, 29.73; N, 13.02. Found: C, 50.27, 50.32; H, 7.18, 7.07; O, 29.86, 29.82; N, 13.11, 13.10.

Picric acid, recrystallized from ethanol, was supplied by R. E. Stamm. ODCB and pyridine were prepared as previously.<sup>3</sup> All solutions were made up by weight in a nitrogen-filled drybox.

Conductance cells and bridge have already been described.<sup>3</sup>

All measurements were carried out in an oil-filled thermostat at 25.00°.

The following physical constants of ODCB were used in subsequent calculations: dielectric constant, 10.06<sup>4</sup>; density, 1.3007 g./ml.<sup>5</sup>; and viscosity, 1.272 cp.<sup>6</sup>

(1) (a) This work has been supported in part by a grant from the U. S. Army Research Office, Durham; (b) Guy F. Lipscomb Fellow; 1962–1963.

(2) C. Witschonke and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 2472 (1947).

(3) E. K. Ralph, III, and W. R. Gilkerson, *ibid.*, **86**, 4783 (1964).

## Results

The equivalent conductances of tri-*n*-butylamine N-oxide picrate in ODCB and in ODCB-pyridine mixtures at 25° are shown in Table I. In each case, the solvent

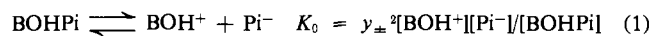
Table I. Tri-*n*-butylamine N-Oxide Picrate in *o*-Dichlorobenzene with Added Pyridine

10°C		10A		10°C		10A	
+ 0.003107 M Py							
6.448	0.8758	66.03	2.021				
12.94	0.7411	73.95	1.958				
21.44	0.6497	82.58	1.892				
33.55	0.5762	92.48	1.836				
41.66	0.5437	102.8	1.783				
50.04	0.5172	112.0	1.742				
58.03	0.4971	121.3	1.706				
63.53	0.4852	130.2	1.674				
10°C		10A		10°C		10A	
+ 0.02087 M Py							
0.9408	7.297	1.891	7.065	5.151	9.138		
2.096	5.596	2.927	6.130	6.000	8.685		
3.793	4.637	3.992	5.550	6.940	8.282		
5.764	4.074	4.793	5.237	8.041	7.909		
7.444	3.775	5.418	5.041	9.212	7.585		
8.964	3.583	6.098	4.853	10.50	7.221		
				11.33	7.139		
				12.29	6.976		

specific conductance was subtracted from that of the solution to obtain the specific conductance of the salt. This correction was less than 1% in the most unfavorable case.

## Discussion

As can be seen from inspection of the results in Table I, tri-*n*-butylamine N-oxide picrate is a very weak electrolyte in ODCB, as is tri-*n*-butylammonium picrate.<sup>3</sup> For a weak electrolyte, dissociating according to



where  $\gamma_{\pm}$  is the mean ionic activity coefficient, assumed given by the Debye-Hückel limiting law, the conductance equation reduces to

$$\Lambda^2 C g^2 = \Lambda_0^2 K_0 \quad (2)$$

when  $\Lambda$  is much smaller than  $\Lambda_0$ . In eq. 1 and all subsequent equilibrium expressions, the activity coefficients of uncharged species will be taken to be unity, in the absence of more information. The factor  $g$  in eq. 2 is a known function<sup>7</sup> of  $\Lambda_0$ , the solvent dielectric con-

(4) P. H. Flaherty and K. H. Stern, *ibid.*, **80**, 1034 (1958).

(5) H. L. Curry and W. R. Gilkerson, *ibid.*, **79**, 4021 (1957).

(6) F. Accascina, E. L. Swarts, P. L. Mercier, and C. A. Kraus, *Proc. Natl. Acad. Sci. U. S.*, **39**, 917 (1953).

(7) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933).

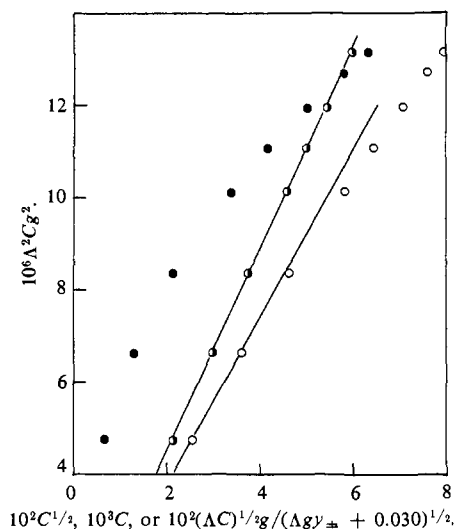
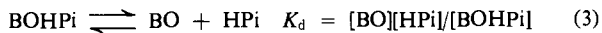


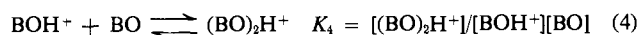
Figure 1. The conductance function of tri-*n*-butylamine N-oxide picrate in *o*-dichlorobenzene at 25°: open circles, vs.  $C^{1/2}$ ; closed circles, vs.  $C$ ; half-filled circles, vs. the function  $(\Delta C)^{1/2}g/(\Delta g y_{\pm} + 0.030)^{1/2}$ ; the origin was taken as a hold point for both straight lines.

stant, and the viscosity, correcting  $\Lambda$  for ion atmosphere effects, and including the Debye-Hückel value for  $y_{\pm}$ .  $\Lambda_0$  cannot be determined independently for such a weak electrolyte, so that we must estimate a value, 40, as a reasonable<sup>8</sup> one. The largest value of  $\Lambda$  observed in this study was 1.095, at a salt concentration of  $1.36 \times 10^{-4} M$ , or an ion concentration of the order of  $4 \times 10^{-6} M$ . At this concentration,  $g$  should still be valid as a correction factor,<sup>7</sup> and eq. 2 should hold for an equilibrium such as eq. 1.

The product  $\Lambda^2 C g^2$  should be constant if no ion triples or higher aggregates are present. If both possible ion triples become significant, then  $\Lambda C^{1/2} g$  should increase linearly with  $C$ . If only one ion triple is important<sup>3,9</sup> then  $\Lambda^2 C g^2$  should increase linearly with  $C$ . Neither is the case here. The quantity  $\Lambda^2 C g^2$  appears in Figure 1 for the salt in pure ODCB, plotted vs. both  $C$  and  $C^{1/2}$ . The latter dependency seems to give a better fit. The clue to the cause of this unexpected behavior is furnished by the variation of the conductance of a  $4.011 \times 10^{-4} M$  solution of the amine oxide picrate as a function of added picric acid (Figure 2). The equivalent conductance drops sharply, upon the addition of less than  $0.5 \times 10^{-4} M$  picric acid, and then levels off at a much lower value of  $\Lambda$  after the addition of more picric acid. If acid-base dissociation is occurring (eq. 3) in addition to eq. 1, then<sup>10,11</sup> addi-



tion of picric acid should result in an increase in conductivity. However, both the decrease in conductance with added free acid and the  $C^{1/2}$  dependency of the quantity  $\Lambda^2 C g^2$  for the salt can be explained if, in addition to eq. 1 and 3, complex formation between the amine oxide, BO, and the cation,  $\text{BOH}^+$ , is postulated (eq. 4). This is not unreasonable at the outset, since



(8) See ref. 3 for the approach used in arriving at this estimate.

(9) C. B. Wooster, *J. Am. Chem. Soc.*, **59**, 377 (1937).

(10) M. A. Elliott and R. M. Fuoss, *ibid.*, **61**, 294 (1939).

(11) E. G. Taylor and C. A. Kraus, *ibid.*, **69**, 1731 (1947).

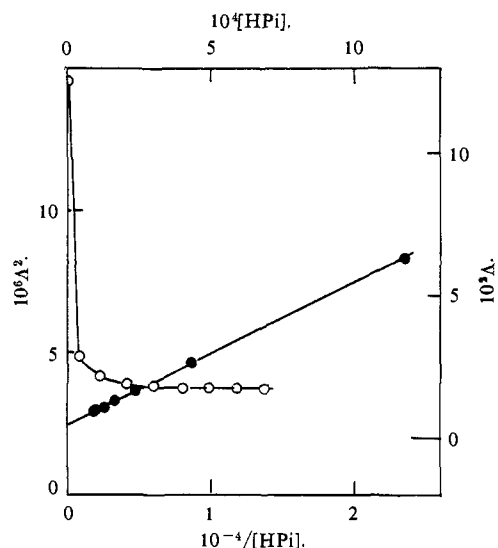


Figure 2. Effect of added HPI on the conductance of tri-*n*-butylamine N-oxide picrate in *o*-dichlorobenzene at 25°: open circles; right-hand ordinate, upper abscissa; closed circles, left-hand ordinate, lower abscissa.

it appears<sup>2,3</sup> that the weak base pyridine forms a stable complex,  $(\text{Py})_2\text{H}^+$ , with pyridinium ion in both nitrobenzene and ODCB. The formation of the complex results in increased conductance owing to mass action. In the following derivation, we shall assume that  $\Lambda_0$  for the hypothetical salt,  $(\text{BO})_2\text{HPi}$ , is the same as that for  $\text{BOHPi}$ . We cannot justify this assumption directly in the present system, since the electrolyte is so weak in ODCB that we are unable to obtain independent values of  $\Lambda_0$  (apparent) by extrapolation to infinite dilution. However, Kraus and Witschonke<sup>2</sup> were able to obtain separate values of  $\Lambda_0$  (apparent) and  $K$ , the ion-pair dissociation constant, for pyridinium picrate,  $\text{PyHPi}$ , as a function of added pyridine concentration in nitrobenzene as solvent at 25°. We assume<sup>2,3</sup> the increase in conductance in the presence of added pyridine to be due to the formation of the complex  $(\text{Py})_2\text{H}^+$  by a reaction analogous to eq. 4. Applying eq. 9 of ref. 3 to the nitrobenzene data, we calculate that  $\Lambda_0$  for the hypothetical salt  $(\text{Py})_2\text{HPi}$  is 33.3, while that for the uncomplexed salt is<sup>2</sup> 34.8. Thus, the addition of a pyridine molecule to pyridinium ion resulted in a 4.5% decrease in the limiting equivalent conductance for the salt. In our case here, even a 10% decrease in  $\Lambda_0$  for the amine oxide complex salt,  $(\text{BO})_2\text{HPi}$ , compared to that for the uncomplexed salt,  $(\text{BO})\text{HPi}$ , will not seriously affect the validity of the following argument. Let  $\Lambda'$  represent the equivalent conductance corrected for ion atmosphere effects:  $\Lambda' = \Lambda/(1 - S\sqrt{\Lambda C}/\Lambda_0^{1/2})$ , after Fuoss and Kraus,<sup>7</sup> where  $S$  is Onsager's<sup>12</sup> limiting slope. Then utilizing eq. 1 and 4

$$\begin{aligned} C\Lambda'/\Lambda_0 &= [\text{BOH}^+] + [(\text{BO})_2\text{H}^+] = \\ &[\text{BOH}^+](1 + K_4[\text{BO}]) = [\text{Pi}^-] \end{aligned}$$

Multiplying through by  $\Lambda'/\Lambda_0$  and rearranging, we obtain

$$C\Lambda'^2 = [\text{BOH}^+][\text{Pi}^-]\Lambda_0^2(1 + K_4[\text{BO}])/C$$

and since  $K_0/y_{\pm}^2 = [\text{BOH}^+][\text{Pi}^-]/C$ , when the degree

(12) L. Onsager, *Physik. Z.*, **28**, 277 (1927).

of dissociation is small, we get

$$\Lambda'^2 C y_{\pm}^2 = \Lambda^2 C g^2 = K_0 \Lambda_0^2 (1 + K_4 [\text{BO}]) \quad (5)$$

where  $g$  is the Fuoss function already mentioned.<sup>7</sup>

Equation 5 is most readily applied to the conductance of the amine oxide picrate in the presence of added picric acid. In this case, from eq. 3,  $[\text{BO}] = K_d C / [\text{HPi}]$ , and at the resulting small ion concentrations,  $g^2 = 1.00$ . Equation 5 then becomes

$$\Lambda^2 C = K_0 \Lambda_0^2 (1 + K_4 K_d C / [\text{HPi}])$$

A plot of  $\Lambda^2$  vs.  $1/[\text{HPi}]$  yields a straight line (Figure 2, closed circles). From the intercept and the salt concentration  $C$ , we calculate that  $\Lambda_0^2 K_0$  is  $1.00 \times 10^{-7}$ , so that with the choice of  $\Lambda_0$  as 40,  $K_0$  is  $6.2 \times 10^{-11}$ . This latter value is roughly one-fourth of the ion-pair dissociation constant for tri-*n*-butylammonium picrate<sup>3</sup> ( $2.86 \times 10^{-10}$ ) and almost twice the value ( $3.5 \times 10^{-11}$ ) for pyridinium picrate,<sup>3</sup> both in ODCB at 25°. From the slope and the intercept of the straight line in Figure 2, we obtain the result that  $K_4 K_d = 0.25$ .

In the absence of added picric acid, the situation becomes more complex. Now, using eq. 3 and 4

$$[\text{HPi}] = [\text{BO}] + [(\text{BO})_2\text{H}^+] = \frac{[\text{BO}](1 + K_0 K_4 C / [\text{Pi}^-] y_{\pm}^2)}$$

or

$$[\text{HPi}] = [\text{BO}](1 + K_0 K_4 \Lambda_0 / \Lambda' y_{\pm}^2)$$

Substituting this result into the equilibrium expression (eq. 3) we find

$$[\text{BO}] = K_d^{1/2} C^{1/2} / (1 + \Lambda_0 K_0 K_4 / \Lambda' y_{\pm}^2)^{1/2}$$

so that now eq. 5 becomes

$$\Lambda^2 C g^2 = K_0 \Lambda_0^2 \{ 1 + K_4 K_d^{1/2} (\Lambda C)^{1/2} g / (\Lambda' y_{\pm}^2 + \Lambda_0 K_0 K_4)^{1/2} \} \quad (6)$$

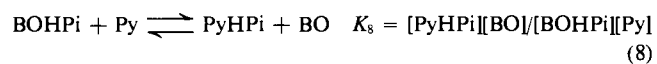
If the term  $\Lambda_0 K_0 K_4$  in the denominator of the right-hand side of eq. 6 were small enough, linear  $C^{1/2}$  dependency would be obtained. It is apparent from the curvature in this plot in Figure 1, that the latter term cannot be neglected. An approximate value for  $\Lambda_0 K_0 K_4$  is obtained in the following manner: define  $R = \Lambda^2 C g^2 / \Lambda_0^2 K_0$ , where the denominator in the right-hand side is taken to be  $1.00 \times 10^{-7}$ , the result obtained in the presence of added picric acid. Now, after rearrangement, we obtain

$$\Lambda g y_{\pm} + \Lambda_0 K_0 K_4 = K_4^2 K_d \Lambda C g^2 / (R - 1)^2 \quad (7)$$

From the intercept of a plot of  $\Lambda g y_{\pm}$  vs.  $\Lambda C g^2 / (R - 1)^2$ , we obtained a value of 0.030 for  $\Lambda_0 K_0 K_4$ . The slope corresponded to  $K_4^2 K_d = 5.2 \times 10^6$ . Now having a value of the correction term  $\Lambda_0 K_0 K_4$  in the denominator of eq. 6, a plot of this last equation as  $\Lambda^2 C g^2$  vs.  $(\Lambda C)^{1/2} g / (\Lambda g y_{\pm} + 0.030)^{1/2}$  appears also in Figure 1 (half-filled circles). The slope of this plot yields a value of the product  $K_4 K_d^{1/2} = 2.2 \times 10^3$ . This compares well with the value  $2.3 \times 10^3$ , obtained using eq. 7. From the added picric acid result,  $K_4 K_d = 0.25$ , and the foregoing result, we finally obtain the individual values for the two equilibrium constants:  $K_4 = 1.9 \times 10^7$  and  $K_d = 1.3 \times 10^{-8}$ .

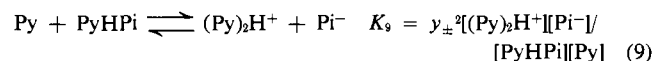
The greatly increased conductances of the amine oxide picrate salt solutions in the presence of pyridine

are not immediately evident from inspection of Table I. Qualitatively, the ratio  $\Lambda^2 C$  (in presence of pyridine) /  $\Lambda^2 C$  (in absence of pyridine) is roughly proportional to the ratio of the effective ion-pair dissociation constants in the two media, respectively. These ratios are of the order of 100. This could be due to one, or a combination, of several factors: (a) exchange, to form pyridinium picrate (eq. 8), which we already know<sup>3</sup> is much more highly dissociated in the presence of added pyridine; (b) exchange (eq. 8) with the resulting



free amine oxide complexing further with the protonated amine oxide from the original salt (eq. 4); (c) complex formation by the pyridine with one or more of the types of amine oxide cations already present in the solutions.

The equilibrium constant  $K_8$  is given by the ratio  $K_{d1}/K_{d2}$ , where  $K_{d1}$  is the acid-base dissociation constant for the amine oxide picrate, and  $K_{d2}$  is the acid-base dissociation constant for pyridinium picrate. The latter has recently<sup>13</sup> been determined spectrophotometrically in this laboratory to be  $5.8 \times 10^{-5}$  in ODCB at 25°.  $K_8$  is thus  $2.2 \times 10^{-4}$  in this system. From this last value and the equilibrium constant,<sup>3</sup>  $K_9 = 6.6 \times 10^{-7}$  for the reaction 9, it can be shown that, with any reasonable choice (between 40 and 50) of  $\Lambda_0$  for



pyridinium picrate, reaction 9, and thus factor a above, cannot account for more than 10% of the observed increase in conductance of the amine oxide picrate in the presence of added pyridine.

Considering factor b, let us make the following approximations initially: that  $[\text{BOH}^+]$  is small compared to  $[(\text{BO})_2\text{H}^+]$  at finite salt concentrations (this is so in the absence of pyridine!), that the latter cation is the only one of importance in the pyridine solutions, and that the acid-base dissociation of the amine oxide picrate is almost completely repressed. Then,  $[\text{PyHPi}] = [(\text{BO})_2\text{H}^+] + [\text{BO}]$ , and  $[(\text{BO})_2\text{H}^+] \simeq [\text{Pi}^-] \simeq \Lambda' C / \Lambda_0$ , so that after substituting these relations into eq. 8 and using eq. 1 and 4, we obtain, after rearrangement, eq. 10. We already know from above

$$\Lambda^2 C g^2 = \Lambda_0^2 K_0 K_4 K_8^{1/2} [\text{Py}]^{1/2} (\Lambda C g y_{\pm})^{1/2} / (\Lambda g y_{\pm} + \Lambda_0 K_0 K_4)^{1/2} \quad (10)$$

that  $\Lambda_0 K_0 K_4 \simeq 0.030$ , so that dropping this term in comparison to the first in the denominator of the RHS of eq. 10 will only result in an error in slope of some 5% or less. With this last approximation, eq. 10 becomes

$$\Lambda^2 C g^2 \simeq \Lambda_0^2 K_0 K_4 K_8^{1/2} [\text{Py}]^{1/2} C^{1/2} \quad (11)$$

Plots of  $\Lambda^2 C g^2$  vs.  $C^{1/2}$  for the salt in solvent made up of various concentrations of added pyridine appear in Figure 3. Each set (in a solvent of constant pyridine concentration) appears to fit a straight line reasonably well. The slopes  $S$  and intercepts  $I$  (as  $C^{1/2}$  goes to zero) were obtained from Figure 3. From eq. 11, the slope  $S$  should be given by the product,  $\Lambda_0^2 K_0 K_4 K_8^{1/2} [\text{Py}]^{1/2}$ . In Figure 4,  $S$  is plotted vs.  $[\text{Py}]^{1/2}$ . The slope of the straight line drawn through the points is  $3.1 \times 10^{-2}$ . The value calculated from prior values for  $\Lambda_0^2 K_0$ ,

(13) W. R. Gilkerson and J. B. Ezell, to be submitted for publication.

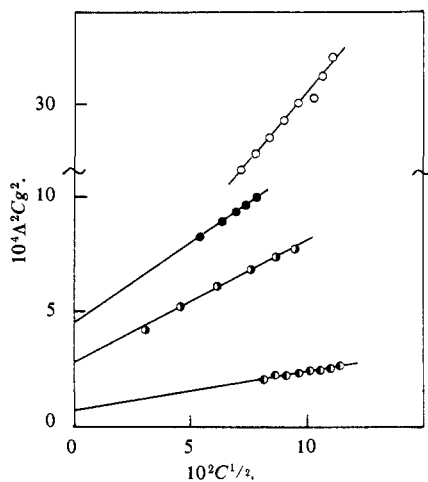


Figure 3. The conductance function vs.  $C^{1/2}$  for tri-*n*-butylamine N-oxide in *o*-dichlorobenzene at 25° in the presence of added pyridine: open circles, 0.1573 *M* Py; closed circles, 0.0356 *M* Py; right-half-filled circles, 0.0209 *M* Py; left-half-filled circles, 0.00311 *M* Py.

$K_4$ , and  $K_8$ , is  $2.8 \times 10^{-2}$ . The agreement is quite good, in view of the approximations involved in eq. 11. Thus we can account for the increase in  $\Delta^2 C$  as the salt concentration increases in the presence of added pyridine.

It is apparent from the increase in the intercepts  $I$  with increasing pyridine concentration, that some interaction with pyridine itself is occurring. A plot of  $I$  vs.  $[\text{Py}]$  also appears in Figure 4. The data points all fall on a straight line of slope  $1.2 \times 10^{-2}$ . This indicates to us that the following reaction is principally responsible for the increase in intercept with pyridine concentration.



In this case,<sup>3</sup> as  $C$  goes to zero,  $(\Delta^2 C_g^2) = \Delta_0^2 K_0 \cdot (1 + K_L[\text{Py}])$ , and from the slope of the plot in Figure 4 we obtain  $K_L = 1.2 \times 10^5$ .

We believe the most important outcome of this investigation is a determination of the acid-base dissociation constant of tri-*n*-butylamine N-oxide picrate in ODCB at 25° to be  $1.3 \times 10^{-8}$ . This result is surprisingly small when compared to that for the corresponding amine picrate,<sup>3</sup>  $9 \times 10^{-8}$ . Based on these two results, we conclude that in ODCB, the N-oxide is a

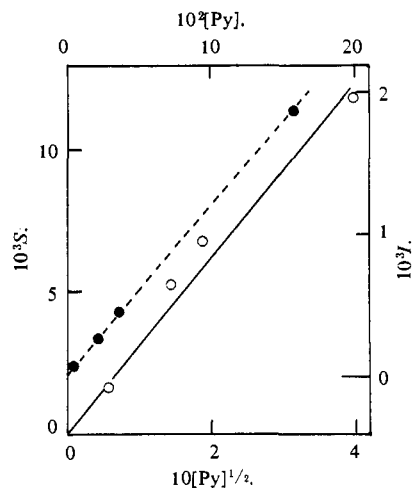
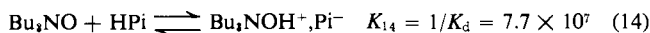
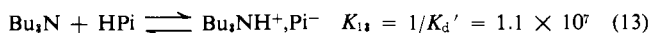
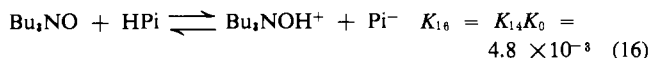
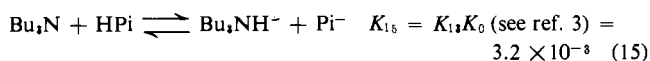


Figure 4. Slopes,  $S$ , of the straight lines in Figure 3 vs.  $[\text{Py}]^{1/2}$ : open circles, left-hand ordinate, lower abscissa. The intercepts,  $I$ , Figure 3, vs.  $[\text{Py}]$ , closed circles, right-hand ordinate, upper abscissa.

somewhat stronger base than the amine, whether one considers eq. 13 and 14 as the measure of base strength,



or, as Pearson<sup>14</sup> has suggested, eq. 15 and 16. In



aqueous solutions, oxides of tertiary aliphatic amines are 6 p*K* units less basic than their corresponding amines.<sup>15a,b</sup> The contrasting behavior in the two solvents, water and ODCB, we suspect, is due to more extensive solvation of the oxide by water, as compared to the amine. We are in the process of seeking other confirmatory measures of the enhanced basicity of amine oxides in aprotic solvents.

(14) R. G. Pearson and D. C. Vogelsong, *J. Am. Chem. Soc.*, **80**, 1038 (1958).

(15) (a) P. Nylén, *Z. anorg. allgem. Chem.*, **246**, 227 (1941); (b) E. M. Arnett, in "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, New York, N. Y., 1963, p. 274.