CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
SOUTHWESTERN COLLEGE, WINFIELD, KANSAS 67156

Protonic Basicity of Periodic Group Va Triaryls

BY ORLAND W. KOLLING AND ELIZABETH A. MAWDSLEY

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In complex formation the triarylphosphines, -arsines, and -stibines usually function as soft Lewis bases and are quite effective in substitution reactions on transition metal carbonyls and related π-bonded species. Available evidence on platinum complexes indicates no exact correlation exists between nucleophilic reactivity constants for these donors and ligand basicity toward the proton.[1] However, there is little quantitative information available on proton-exchange equilibria involving the periodic group Va triaryls, because of their low solubility in aqueous media and their extremely weak basicity in methanol. An indirect method based on titration data in nitromethane has been applied to alkyl- and arylphosphines.[2] Other studies have not dealt with the triaryls of all members of group Va in a single differentiating solvent, nor have the limited data been sufficiently precise to allow reliable comparisons.

As a nonleveling solvent toward strong and weak bases, anhydrous acetic acid is a suitable medium in which to detect small differences in basicity within a series of closely related proton acceptors. We have examined the extent of dissociation of the solvated bases in the equilibrium

$$R_3B \cdot HOAc \rightleftharpoons R_3BH^+ + OAc^-$$

by a comparative method similar to that reported earlier,[3] using sodium acetate as a reference base. Potentiometric measurements in acetic acid solutions of the bases were made with the glass and calomel electrode pair, and the altered form of the Nernst equation which was derived by Bruckenstein and Kolthoff[4] is that given by

$$E_B = E_{GC}^\circ + E_j + \frac{RT}{F} \ln K_s - \frac{RT}{2F} \ln K_B C_B \quad (1)$$

where E_{GC}° is the total standard potential of the cell, E_j the liquid junction potential for the reference electrode, and C_B is the stoichiometric concentration of the base having a dissociation constant K_B. Although eq 1 was originally developed for the chloranil indicator electrode, it has been shown that the empirical glass electrode functions in the same manner in base solutions in acetic acid media.[5] If the first three terms in eq 1 give an essentially constant contribution to E_B in moderately dilute solutions, one may restate the Nernst relationship as

$$E_B = Y + M(pK_B) - M \log C_B \quad (2)$$

Here, the theoretical slope (M) will be 0.0295 at 25° and, at a fixed C_B, it is expected that E_B will be a linear function of pK_B for a series of weak bases.

Experimental Section

Reagents.—Commercial glacial acetic acid was dehydrated with acetic anhydride following the method reported earlier.[6] The maximum water content of the solvent distillate (by Karl Fischer method) was 0.003%, and this increased by less than 0.001% during emf measurements.

The organic bases were Eastman White Label grade, and those having experimental melting points (corrected) differing by more than 0.5° from accepted literature values were recrystallized from distilled petroleum ether (bp 64–75°). Because of the low melting points of several of the bases and their tendency to turn slightly colored on moderate heating, the maximum temperature of the crystallizing solvent was kept in the 40–50° range. All bases were dried in a magnesium perchlorate desiccator and stored in the dark. The melting points of the purified solids are as follows: diphenylamine, 53°; triphenylamine, 126.3°; triphenylphosphine, 80°; tri-*o*-tolylphosphine, 125°; tri-*m*-tolylphosphine, 100°; tri-*p*-tolylphosphine, 147°; triphenylarsine, 60°; triphenylstibine, 53°; triphenylbismuthine, 78°.

Solutions of the aryl bases in anhydrous acetic acid were prepared determinately, and since it was observed that these tended to be unstable on prolonged standing, each was freshly made just prior to measurement. Stock solutions of the reference bases LiOAc, NaOAc, and KOAc in anhydrous acetic acid were standardized by titration with perchloric acid in the same solvent medium.

Procedure.—The Leeds and Northrup Model 7401 pH meter equipped with the glass and standard fiber junction calomel electrodes was used in all emf measurements. The electrodes were conditioned for 1 week in glacial acetic acid before use and stored in this solvent between measurements. When immersed in a base solution in anhydrous acetic acid, about 30 min was required before a stable potential was obtained. The temperature was 25–27°.

A fresh reference solution of sodium acetate having exactly the same stoichiometric concentration as the aryl base was prepared by dilution of a 0.10 M stock solution, and its emf was determined immediately before or after each series of measurements on a given aryl base.

The pK_B value was obtained graphically from a calibration plot of pK_B *vs.* emf for 0.0100 M bases. (The higher concentration level was necessary because the aryl bases are quite weak.) The empirical slope of the plot was established with 0.0100 M solutions of the ionic bases of periodic group Ia, urea, and 2,5-dichloroaniline. Calibration data obtained were: KOAc (pK_B = 6.10), 395 mV; NaOAc (6.58), 408; LiOAc (6.79), 413; 2,5-dichloroaniline (9.45), 479; urea (10.20), 498.[4] The experimental precision on these standards was ±1 mV for a minimum of nine measurements on each base, and that for all other bases was ±2 mV for six to nine results. (This is eqivalent to an uncertainty of ±0.11 in pK_B for the latter.)

Results and Discussion

Even though the proportionality between E_B and $\ln C_B$ has been verified experimentally for solutions of bases in glacial and anhydrous acetic acids, the exact theoretical slope of 0.0295 for $\Delta E_B/\Delta \log C_B$ at 25° is not always found.[4] Published data for ionic acetates

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confirmed a slope of 0.030 for the periodic group Ia acetates used as reference standards in the present study.[3,7] Since our comparative method for evaluating pK_B must assume the same slope applies to all bases used, the function of emf *vs.* dilution was determined for the N, P, Sb, and Bi proton acceptors. The linear slopes listed in Table I were obtained for the concentration range of 0.010 to 0.0010 M and are sufficiently close to the theoretical value to justify the assumption of its constancy.

TABLE I

BASICITY CONSTANTS (pK_B) AND RELATED DATA FOR BASES IN ANHYDROUS ACETIC ACID AT 25–27°

Base	Slope $\Delta E_B/\Delta \log C_B$	E_B (for $C_B = 0.010$ M), mV	pK_B (exptl)
NaOAc	0.030	408	6.58
Diphenylamine	0.031	486	9.72
Triphenylamine	0.030	473	9.20
Triphenylarsine	...	508	10.60
Triphenylbismuthine	0.032	463	8.81
Triphenylphosphine	0.029	457	8.57
Triphenylstibine	0.030	462	8.76
Tri-*o*-tolylphosphine	...	475	9.28
Tri-*m*-tolylphosphine	...	438	7.79
Tri-*p*-tolylphosphine	...	438	7.79

In contrast to the dilution–emf change, the value of M in the pK_B term of eq 2 has not been evaluated in earlier studies. For the chloranil indicator electrode, the emf–concentration data for selected bases investigated by Bruckenstein and Kolthoff[4] were used to construct log C_B *vs.* E_B plots in order to find the value of E_B at 0.01 M. The corresponding graph of E_B (at 0.01 M) *vs.* pK_B is shown in Figure 1 (curve B), and an experimental slope of 0.0347 was found. The emf's for the same bases at the identical concentration were determined with the glass electrode, and the linear plot in Figure 1 (curve A) gives an M value of 0.0390. It is not unusual to find abnormal coefficients for Nernst equation terms in applying the glass electrode to nonaqueous solvents having low dielectric constants. Cheng and Howald[8] recently reported a slope larger than theoretical in anhydrous acetic acid, and in the extensive titration studies on bases in aprotic solvents Hall[9] consistently obtained slopes much greater than predicted.

The empirical slope of 0.0390 for $\Delta E_B/\Delta pK_B$ was used to find the pK_B values for the nine group Va aryl bases listed in Table I. The observed order of decreasing dissociation of the triphenyl derivatives in anhydrous acetic acid is: $(C_6H_5)_3P > (C_6H_5)_3Sb \sim (C_6H_5)_3Bi > (C_6H_5)_3N > (C_6H_5)_3As$. Although there is no exact correspondence between the pK_B value and the formal charge on the central atom (Sanderson's computation[10]), it is noteworthy that the first three bases in the sequence have close-lying constants and similar positive formal charges. By contrast, the triaryl N and As bases having negative formal charges on the central atom are significantly less ionized. The extent of dissociation in anhydrous acetic acid for the perchlorates of the oxo bases of these elements show the same sequence: phosphine oxide > amine oxide > arsine oxide.[11] Therefore, it would appear that the electronic structural energy differences between the elements serving as the central atom in the aryl derivatives are more important than solvation energy differences in the series, or else both the electronic energy and solvation energy differences show somewhat similar qualitative trends.

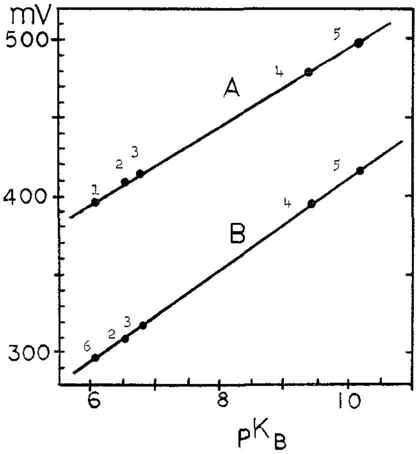

Figure 1.—Plots testing eq 2 at the base concentration of 0.01 M: curve A, glass electrode; curve B, saturated chloranil electrode. The bases are (1) KOAc, (2) NaOAc, (3) LiOAc, (4) 2,4-dichloroaniline, (5) urea, and (6) pyridine.

It will be noted that the *m*- and *p*-tolylphosphines have identical basicity constants and have a greater degree of ionization than triphenylphosphine. On the other hand, the larger pK_B for the *o*-tolyl derivative is indicative of a pronounced steric effect upon the ionization process. A similar steric hindrance in the *o*-tolylphosphorus donor is operative in the CO displacement reaction on $[RMn(CO)_5]$ in benzene solution.[12]

The position of the broad uv band for the complex *cis*-$Mn(CO)_4LBr$ in tetrachloroethane solution has a dependence upon the ligand L,[13] and the spectrochemical series decreases with L as follows: $CO > (C_6H_5)_3P > (C_6H_5)_3As > (C_6H_5)_3Sb >> (C_6H_5)_3N$ (too weak a nucleophile to complex). A parallel sequence is found for decreasing rate of the S_N1 reaction of *cis*-$Mn(CO)_4Br_2^-$ with L: $(C_6H_5)_3P > (C_6H_5)_3As > (C_6H_5)_3Sb$.[13] With the exception of the position of As, these are in the same relative order as that noted above for the triaryls as proton acceptors.

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