hot toluene. ^{1}H NMR (CD_2Cl_2): δ 7.5–7.3 (br, m). IR (KBr): 3040 w, 1585 m, 1485 s, 1450 m, 1380 vs, 1305 w, 1260 m, 1150 w, 1070 w, 1045 s, 1020 w, 1000 m, 910 s, 885 s, 870 s, 825 w, 795 s, 730 m, 690 s, 645 s, 610 m, 515 w, 485 w, 460 w, 415 w, 355 m cm^{-1}.

$Li[S_2CNC(CH_3)_2(CH_2)_3C(CH_3)_2]$. A 2.0-g (0.014 mol, dried over 4A sieves and deoxygenated) sample of tetramethylpiperidine and 20 mL of heptane were placed in a 100-mL Schlenk flask. The solution was cooled to 0 °C and 8.7 mL of BuLi (1.55 M in hexanes, 0.013 mol) was added dropwise. Approximately halfway through the addition a colorless precipitate was observed. After the addition the reaction was warmed to room temperature and stirred for 1 h. Next, a solution of 0.85 mL (1.08 g, 0.014 mol) of CS_2 in 10 mL of heptane was added over a 20-min period; the solution turned orange. After the solution was allowed to stand at room temperature, yellow crystals were deposited, which were filtered, washed with heptane, and dried under vacuum. Yield: 1.8 g, 60%.

$MoO_2[S_2CNC(CH_3)_2(CH_2)_3C(CH_3)_2]_2$. A 1.0-g (4.5-mmol) sample of $Li[S_2CNC(CH_3)_2(CH_2)_3C(CH_3)_2]$ was placed in a 50-mL flask fitted with a pressure-equalizing addition funnel containing 0.30 g (1.5 mmol) MoO_2Cl_2. To both the flask and the funnel were added 20 mL of ether, dissolving both reagents. The flask was cooled to 0 °C, and the MoO_2Cl_2 solution was added dropwise, with stirring. A purple solid precipitated during the addition and was isolated by filtration. This product was identified as $Mo_2O_3(R_2dtc)_4$ by its color and Mo–O absorption in the infrared spectrum at 940 cm^{-1}. Yield: 88%. This product was placed in 10 mL of toluene, and to it was added 0.06 g (6.0 mmol) of pyridine *N*-oxide in 10 mL of toluene. After the mixture was stirred overnight, the orange product was isolated by filtration and recrystallized from hot toluene. ^{1}H NMR ($CDCl_3$): δ 1.76 (s, 12 H), 1.55–1.95 (m, 6 H). IR (KBr): 2960 vs, 2760 m, 1587 m, 1460 m, 1380 vs, 1350 s, 1281 m, 1254 m, 1161 s, 1124 m, 1024 m, 986 m, 973 w, 904 s, 872 s, 803 m, 762 w, 601 w, 538 w.

Cyclic Voltammetry. Acetonitrile was purified by stirring over activated alumina, distilling first from a mixture of $KMnO_4$ (1 g/100 mL) and Li_2CO_3 (1 g/100 mL), and then twice from CaH_2. It was stored under nitrogen in a glass bulb fitted with a high-vacuum Teflon stopcock. Tetrabutylammonium hexafluorophosphate was recrystallized from hot H_2O/EtOH and then dried under vacuum overnight at 120 °C. Measurements were made with a Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a Model 176 current to voltage converter. The voltammograms were recorded on a Houston Omnigraphic Series 2000 X-Y recorder.

All measurements were made in a nitrogen-filled glovebox. In a typical procedure, the voltammetry cell was fit with a freshly polished glassy-carbon working electrode, and a platinum-wire counter electrode. The reference electrode consisted of a silver wire immersed in a solution of solvent and electrolyte, and was separated from the voltammetry cell by a porous glass disk. The cell was then charged with 15 mL of 0.1 M n-Bu_4NPF_6 in acetonitrile. Enough of the molybdenum complex under investigation was added to make a 1 mM solution. The cyclic voltammogram was then recorded. Next, a solution of ferrocene in acetonitrile was added such that the ferrocene concentration was 0.5 mM. The potential and electrochemical reversibility of the ferrocene/ferrocenium redox couple was recorded and used as an internal standard.[25]

The molybdenum complexes described in this report exhibit irreversible redox behavior. Thus, no detectable oxidation wave is observed during reverse anodic scans. This is a general observation for *cis*-dioxomolybdenum(VI) complexes.[17] As a result, we are able to report only the potential at the maximum cathodic current, E_{pc}. Topich[17] has shown that these values may be used to relate relative oxidizing strengths in place of the true Mo(VI)/Mo(V) potentials if the voltammograms are recorded under identical conditions.[26] All measurements were made at room temperature, and the scan rate was held constant at 100 mV/s.

Acknowledgment. The laboratory expertise and enthusiasm of Teresa Fortin is sincerely appreciated. Discussions with members of the Union Carbide Catalysis Skill Center and Professors B. L. Shaw, G. L. Geoffroy, F. A. Cotton, and T. J. Marks proved invaluable. I also thank Union Carbide Corp. for permission to publish these results.

---

(25) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2855–2857.

(26) For an explanation see: Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3034–3043.

Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Phosphine Basicities As Determined by Enthalpies of Protonation

Russell C. Bush and Robert J. Angelici*

Received August 6, 1987

Enthalpies of protonation (ΔH_{HP}'s) have been determined for 12 tertiary alkyl-, aryl-, and mixed alkylarylphosphines from the heats of the reactions $R_3P + CF_3SO_3H \rightarrow R_3PH^+CF_3SO_3^-$, in 1,2 dichloroethane, by use of titration calorimetry. The ΔH_{HP}'s range from −17.9 kcal mol^{-1} for $(p\text{-}ClC_6H_4)_3P$ to −36.6 kcal mol^{-1} for $(t\text{-}Bu)_3P$. An excellent correlation of the ΔH_{HP} values with reported pK_a's is observed. Comparisons with other basicity measures and correlations with Hammett σ_{para}, Taft σ^*, and Kabachnik σ^{ph} substituent parameters are also discussed.

Introduction

A casual examination of the current literature of transition-metal complexes is all that is required to gauge the importance of phosphines as ligands in organometallic and coordination chemistry. The ability of phosphines to bind to transition metals is usually described in terms of steric and electronic properties. Quantitative determination of these binding characteristics has been the aim of a number of studies,[1] leading to parameters such as Tolman's cone angles (θ) and ν(CO) values (for the A_1 vibration in $Ni(CO)_3PR_3$) for describing steric and electronic effects, respectively, of phosphorus ligands. These parameters have often been employed to understand reactions involving phosphines.[1c,d,2] Attempts to further dissect electronic effects have led to the development of a method for quantitatively analyzing reactions in terms of the σ-bonding, π-bonding, and steric properties of phosphines.[3] Application of this method to data for ligand-dependent substitutions and reactions of phosphine-containing complexes has shown that, although π-bonding is important in some cases,[3b] most of the data can be explained in terms of steric

---

(1) (a) Strohmeier, W.; Müller, F.-J. *Chem. Ber.* **1967**, *100*, 2812. (b) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953. (c) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956. (d) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(2) (a) Burke, N. E.; Singhal, A.; Hintz, M. J.; Leg, J. A.; Hui, H.; Smith, L. R.; Blake, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 74. (b) Schenkluhn, H.; Scheidt, W.; Weimann, B.; Zähres, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 401. (c) Nolan, S. P.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *290*, 365. (d) See references cited in ref 3a.

(3) (a) Golovin, M. N.; Rahman, Md. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981. (b) Rahman, Md. M.; Hong, Y. L.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650.

properties and σ-bonding alone.[3a]

In view of the importance of phosphine σ-bonding in determining reactivity, a reliable measure of σ-bonding ability is critical to the interpretation of reactivity data. Values of ΔG or ΔH for reactions of phosphines with protonic or Lewis acids are the most obvious choices for such a measure. Free energies and enthalpies of phosphine adduct formation with group 13 Lewis acids (BH_3, BF_3, BMe_3, and $GaMe_3$, among others) have been measured,[4] as have reaction enthalpies (and some free energies) with mercury dihalides[5] and silver salts.[6] Gas-phase proton affinities have also been determined for a few phosphines;[7] the results in some cases contrast sharply with what is observed in solution studies.[7d]

The basicities of phosphines toward protonic acids in solution are the most commonly encountered measures of σ-bonding ability in metal complexes. A few pK_a's have been evaluated for phosphines in aqueous EtOH,[8] but the most systematic investigation was that reported by Streuli for potentiometric measurements in polar aprotic media.[9] The pK_a's (referenced to aqueous solution) were estimated from the potential, measured with a glass electrode, at half-neutralization in titrations of the phosphines in CH_3NO_2 with 0.1 N HCl. The basicities determined in this manner are consistent with the expectations for substituent effects from organic chemistry, i.e., higher pK_a's for phosphines with more electron-donating alkyl groups than with aryl groups, and a correlation was noted between the pK_a's and Taft's σ^* substituent parameters[10] (designed to gauge electronic effects of substituents bound to carbon). These pK_a's, and others similarly determined,[11] are the basis for many mechanistic proposals in organo–transition-metal chemistry.

Our particular interest in measures of phosphine basicity stems from a desire to study how phosphines contribute to the basicities of transition metals in complexes. Numerous phosphine complexes are known to undergo protonation at the metal center;[12,13] one would expect the basicity in a series of $M'PR_3$ (M' = a particular metal–ligands fragment; PR_3 = various phosphines) complexes to vary linearly with the basicity of PR_3. In order to make correlations of phosphine basicity with metal–phosphine complex basicity as direct as possible, a system for measuring the basicities of phosphines in a reliable way, which would also be suitable for metal complexes, was desired. The development of such a system and its application to phosphine basicity measurement are the subject of the present study.

The basicity measure employed is the protonation enthalpy (ΔH_{HP}) of a phosphine, as determined by calorimetric titration with CF_3SO_3H in 1,2-dichloroethane (eq 1). This acid/solvent

$$R_3P + CF_3SO_3H \xrightarrow[\text{DCE}]{} [R_3PH^+CF_3SO_3^-];\quad \Delta H_{HP} \qquad (1)$$

system gives rapid and complete protonation even of weakly basic phosphines. The ΔH_{HP} values for 12 tertiary phosphines are reported, and comparisons of the results with other measures of basicity are discussed.

Experimental Section

Purification of Reagents. Inert gases employed in this study were dried by using the following procedures. Argon used in solvent distillation was dried by passage through a 45-cm column of $CaSO_4$, while Ar used to maintain an inert atmosphere in the calorimeter reaction vessel was dried with a 20-cm column of 4A molecular sieves and a −78 °C trap; both the $CaSO_4$ and molecular sieves were dried at 350 °C for 12 h under vacuum. Nitrogen was passed through a 40-cm column of activated $CaSO_4$ and then through a liquid-N_2 trap.

The solvent 1,2-dichloroethane (DCE) was purified by the procedure outlined by Perrin, Armarego, and Perrin,[14] by washing with concentrated H_2SO_4, 5% NaOH, and then distilled H_2O. The solvent was predried over $MgSO_4$, stored in amber bottles over molecular sieves for at least 12 h, and then distilled from P_2O_5 under Ar immediately before use.

Trifluoromethanesulfonic acid (Aldrich) was fractionally distilled under N_2 at ambient pressure. Trifluoroacetic acid was refluxed over, and then fractionally distilled from, P_2O_5 under N_2 after the method of Perrin et al.[14] The acids were distilled (typically 4–8 mL) directly into a graduated reservoir (similar to Kontes Model K-288630), which allowed for delivery of a known volume of acid with minimal exposure to the atmosphere during preparation of acid solutions.

Triphenylphosphine was recrystallized twice from hexanes and then from EtOH by dissolving in the hot solvent, filtering, and allowing the filtrate to cool to 0 °C; the crystals were then stored under N_2. A solution of tricyclohexylphosphine in hexanes was filtered and evaporated to dryness in a flow of N_2; alternatively, it was purified by preparing and recrystallizing the CS_2 adduct and then regenerating the phosphine.[15] The phosphines Et_3P and $MePh_2P$ (Aldrich) were distilled prior to use, and Me_3P was generated by heating $Me_3P{\cdot}AgI$ (Aldrich) under vacuum. The remaining phosphines, (p-$ClC_6H_4)_3P$, (p-$FC_6H_4)_3P$, (p-$MeOC_6H_4)_3P$, (t-$Bu)_3P$ (Strem), (p-$MeC_6H_4)_3P$, (o-$MeC_6H_4)_3P$ (Pressure Chemical), and Me_2PhP (Aldrich), were used as received.

1,3-Diphenylguanidine ($(PhNH)_2CNH$, hereafter referred to as DPG) was available as a primary standard from GFS Chemicals. The compound was dried in an oven at 110 °C for 3–6 h and then stored in a desiccator over P_2O_5.

Preparation and Standardization of Acid Solutions. A volume of acid (CF_3SO_3H or CF_3CO_2H) corresponding to approximately 10 mmol was added directly to 100 mL of freshly distilled DCE with use of the graduated acid reservoir. After mixing, 50 mL of solution was transferred via Teflon cannula to a titration buret under N_2. The acid solution was then standardized by titration against a DCE solution of DPG (~1.5 mmol) in air, using bromophenol blue as indicator.[16] This procedure generally gave concentrations reproducible to ±0.2%.

Apparatus. The protonation enthalpies were measured with a Tronac Model 458 isoperibol calorimeter equipped with a motor-driven (4 rpm) buret for delivery of titrant. A 50-mL silvered Dewar flask was used as the reaction vessel. Thermistor output was recorded with an Apple II+ computer using the ADALAB instrument interface card (Interactive Microwave, Inc.). Operation of the system was checked by measuring the heat of protonation of tris(hydroxymethyl)aminomethane (THAM) with aqueous HCl. Our value of -11.2 ± 0.3 kcal mol^{-1} is in good agreement with the literature value of -11.33 kcal mol^{-1}.[17]

Experimental Procedure. Glassware was dried in an oven at 140 °C for at least 4 h and allowed to cool in a desiccator over P_2O_5. The Dewar flask and buret plunger were also stored in a P_2O_5-dried desiccator for at least 12 h before a sequence of runs; the Dewar flask was returned to the desiccator between runs.

In a typical experiment, a solution of CF_3SO_3H in DCE (generally near 0.1 M) was loaded into the calorimeter buret (2-mL capacity) with use of a Teflon tube. The empty Dewar flask was then attached to the calorimeter's insert assembly, and the insert was lowered into the 25.0 °C bath. The reaction vessel was flushed with Ar for 20–40 min. A 5-mL aliquot of a freshly prepared solution of the phosphine in DCE (approximately 0.033 M) was injected into the reaction vessel via syringe,

---

(4) (a) Stone, F. G. A. *Chem. Rev.* **1958**, *58*, 101. (b) Graham, W. A. G.; Stone, F. G. A. *J. Inorg. Nucl. Chem.* **1956**, *3*, 164.

(5) (a) Farhangi, Y.; Graddon, D. P. *Aust. J. Chem.* **1973**, *26*, 983. (b) Gallagher, M. J.; Graddon, D. P.; Sheikh, A. R. *Aust. J. Chem.* **1976**, *29*, 759.

(6) Hultên, F.; Persson, I. *Inorg. Chim. Acta* **1987**, *128*, 43.

(7) (a) Holtz, D.; Beauchamp, J. L.; Euler, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 7045. (b) McDaniel, D. H.; Coffman, N. B.; Strong, J. M. *J. Am. Chem. Soc.* **1970**, *92*, 6697. (c) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 6252. (d) Ikuta, S.; Kebarle, P.; Bancroft, G. M.; Chan, T.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 5899. (e) Ikuta, S.; Kebarle, P. *Can. J. Chem.* **1983**, *61*, 97.

(8) (a) Davies, W. C.; Addis, H. W. *J. Chem. Soc.* **1937**, 1622. (b) Goetz, H.; Sidhu, A. *Justus Liebigs Ann. Chem.* **1965**, *682*, 71.

(9) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985.

(10) Henderson, W. A.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791.

(11) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716.

(12) (a) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231. (b) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (c) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927.

(13) For a few examples, see: (a) Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653. (b) Laing, K. R.; Roper, W. R. *J. Chem. Soc., A* **1969**, 1889. (c) Collman, J. P.; Vastine, F. D.; Roper, W. R. *J. Am. Chem. Soc.* **1968**, *90*, 2282. (d) Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 2653. (e) Arabi, M. S.; Mathieu, R.; Poilblanc, R. *J. Organomet. Chem.* **1976**, *104*, 323. (f) Werner, R.; Werner, H. *Chem. Ber.* **1982**, *115*, 3781. (g) Werner, H.; Gotzig, J. *Organometallics* **1986**, *5*, 1337. (h) Hommeltoft, S. I.; Baird, M. C. *Organometallics* **1986**, *5*, 190.

(14) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.

(15) Isslieb, K.; Brack, A. *Z. Anorg. Allg. Chem.* **1954**, *277*, 258.

(16) Huber, W. *Titrations in Nonaqueous Solvents*; Academic: New York, 1967.

(17) Eatough, D. J.; Christensen, J. J.; Izatt, R. M. *Experiments in Thermometric and Titration Calorimetry*; Brigham Young University Press: Provo, UT, 1974.

Table I. ΔH_{HP} and pK_a(aq) Values for Tertiary Phosphines

	PR_3	$-\Delta H_{HP}$, kcal mol^{-1} [a]	pK_a
1	$(p\text{-}ClC_6H_4)_3P$	17.9 (0.2)[b]	1.03[c]
2	$(p\text{-}FC_6H_4)_3P$	19.6 (0.2)	1.97[c]
3	Ph_3P	21.2 (0.1)	2.73[d]
4	$(o\text{-}MeC_6H_4)_3P$	22.6 (0.2)	3.08[c]
5	$(p\text{-}MeC_6H_4)_3P$	23.2 (0.3)	3.84[c]
6	$(p\text{-}MeOC_6H_4)_3P$	24.1 (0.2)	4.57[c]
7	$MePh_2P$	24.7 (0.0)	4.59[e]
8	Me_2PhP	28.4 (0.2)	6.50[d]
9	Me_3P	31.6 (0.2)	8.65[d]
10	$(c\text{-}C_6H_{11})_3P$	33.2 (0.4)	9.70[d]
11	Et_3P	33.7 (0.3)	8.69[d]
12	$(t\text{-}Bu)_3P$	36.6 (0.3)	11.4[c]

[a] For protonation with CF_3SO_3H in DCE solvent at 25.0 °C. [b] Numbers in parentheses are average deviations. [c] Reference 11. [d] Reference 9. [e] Reference 3a.

followed by 45 mL of DCE. The phosphine was kept in slight excess (approximately 10%) of the total amount of acid to be added. The temperature of the reaction vessel contents was adjusted to give a voltage reading below the set point of 0.00 mV (25.0 °C) by electrical heating with the calibration heater or cooling with a flow of Ar. The starting point of each experiment was chosen so that the midpoint of the titration curve would coincide as nearly as possible with the thermistor set point. This minimizes errors due to differences in titrant/titrate temperatures during an experiment. Each run consists of an initial heat capacity determination, titration, and final heat capacity determination, each preceded by a base line acquisition period. Heat capacities were evaluated by resistance heating. Titrations were generally set for 3–3.5 min at a buret delivery rate of 0.398 ± 0.001 mL min^{-1}. Tronac specifications list a typical instrument sensitivity of 35 mV $°C^{-1}$. The recorded voltages for the experiments generally spanned about 15 mV, so the overall temperature change during each run was approximately 0.4 °C, and the temperature change during titration was less than 0.2 °C.

The thermistor output voltages were recorded at the rate of 1 s^{-1}. The voltage/time data were stored on diskette for each run. The data were then analyzed by linear regression for each segment of the experiment: calculated slopes (corrected for base line heat effects) and intersection points were used to determine heat capacities and total reaction heat, by using the general method outlined by Eatough et al.[17] The reaction enthalpies were corrected for the heat of dilution of the acid solution with DCE, resulting in the values of ΔH_{HP}. Four experimental runs were used to determine ΔH_{HP} for all phosphines except Ph_3P (five runs), $(t\text{-}Bu)_3P$ (five runs), and $(c\text{-}C_6H_{11})_3P$ (three runs).

Measurement of the heat of dilution was complicated by interference from protonation of traces of H_2O in the titration vessel. This interference could not be completely eliminated but was minimized by rinsing the Dewar flask with anhydrous Et_2O, flushing with Ar for 10 min, and then leaving the Dewar flask in a P_2O_5-dried desiccator for 4 h. This procedure allowed determination of the dilution heat by extrapolation of the data from the final one-third of the titration segment, giving a value of −0.32 kcal mol^{-1}.

In some ΔH_{HP} runs, a slight depression of reaction heat was noted at the beginning of the titration segment. This randomly observed depression was most likely due to traces of H_2O in the titrant delivery tube, which converted some of the CF_3SO_3H in the first titrant portion to the weaker acid, $(H_3O)(O_3SCF_3)$. In these instances, the first one-third of the titration data were neglected in the ΔH_{HP} calculation.

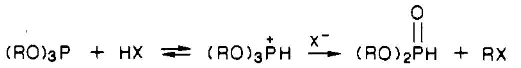
Results

The enthalpies of protonation, with average deviation error limits, determined for 12 common phosphine ligands are listed in Table I. Titration curves of the phosphines exhibited no evidence of incomplete reaction. Neat CF_3SO_3H is one of the strongest acids known,[18] and the titration behavior observed in this study indicates that a 0.1 M solution of CF_3SO_3H in DCE is a strongly acidic medium as well, completely protonating even the weak base $(p\text{-}ClC_6H_4)_3P$ (pK_a = 1.03). The ΔH_{HP} values have been corrected for the heat of dilution of the acid solution, which was found to be −0.32 kcal mol^{-1} for a 0.1011 M solution. As the range of acid concentrations varied only from 0.0951 to 0.1148 M, we consider a correction of 0.3 kcal mol^{-1} valid for all of the experimental runs with CF_3SO_3H in DCE.

Our reference base for the evaluation of the solvent/acid system was DPG (pK_a = 10.1),[19] and its protonation enthalpy with CF_3SO_3H was found to be −37.2 ± 0.4 kcal mol^{-1}. To compare the strength of CF_3SO_3H and CF_3CO_2H, the protonation enthalpies of DPG and Et_3P were also determined with the latter acid. The values obtained (corrected for the heat of dilution of 0.1 M CF_3CO_2H, 0.3 kcal mol^{-1}) were −23.5 ± 0.3 kcal mol^{-1} for DPG and −12.9 ± 0.1 kcal mol^{-1} for Et_3P, both substantially lower (>10 kcal mol^{-1}) than the ΔH values with the stronger acid CF_3SO_3H.

For some of the compounds studied, there was evidence of heat contributions from other reactions. The experimental data for $(t\text{-}Bu)_3P$ showed a roughly 2-fold increase in slope for the base line preceding and following titration, when compared to runs for the other phosphines in Table I. This could be attributed to oxidation of the extremely air-sensitive $(t\text{-}Bu)_3P$ by adventitious oxygen and would be expected to contribute to the overall heat of reaction. However, since the side reaction proceeded to the same extent before and after titration, the heat of this reaction was subtracted from the ΔH_{HP} value by the normal base line correction. This, coupled with the observation that the increase in base line slope is only 3% of the titration slope, leads us to conclude that the ΔH_{HP} for $(t\text{-}Bu)_3P$ is reliable.

For other compounds where side reactions were evident, ΔH_{HP} measurements were not judged to be as reliable. The phosphine $(p\text{-}Me_2NC_6H_4)_3P$ did not exhibit clean protonation; a highly exothermic secondary reaction was apparent after addition of the acid, making estimation of ΔH_{HP} impossible. The data for the phosphite $(i\text{-}PrO)_3P$ revealed an endothermic process after titration. Calculation of ΔH_{HP} in the normal manner gives a value of −23.6 kcal mol^{-1}, a reasonable value based on the reported pK_a of 4.08[3b] (see Discussion for relation of ΔH_{HP} to pK_a). However, the observed decrease in base line slope amounts to 12% of the titration slope, so the actual ΔH_{HP} could be 2–3 kcal mol^{-1} more exothermic. The reverse behavior is noted for $(MeO)_3P$, which exhibits an exothermic secondary process occurring after addition of acid. Analysis of the base line slopes suggests that the actual ΔH_{HP} could be 2–3 kcal mol^{-1} less exothermic than the measured value of −21.3 kcal mol^{-1}. Side reactions in the protonation of alkyl phosphites are well-known, with acids reacting to give dialkyl phosphonates as shown in eq 2.[20] We suspect that the complications noted for $(i\text{-}PrO)_3P$ and $(MeO)_3P$ arise from this type of reaction.



$$(RO)_3P + HX \rightleftharpoons (RO)_3\overset{+}{P}H \xrightarrow{X^-} (RO)_2\overset{O}{\overset{\|}{P}}H + RX \qquad (2)$$

The phosphite $(PhO)_3P$ exhibits different behavior, with normal base line slopes but an exothermic jump at the beginning of the titration, occurring to a different degree in three runs. We suspect that, as in the dilution studies, H_2O in the titrate causes the deviations. Analysis of the second half of the titration data gives a consistent value of ΔH_{HP} = −7.25 ± 0.08; however, as some other reaction may be causing the deviation, this value was not considered definitive.

Discussion

Interpretation of ΔH_{HP} Values. Although the heat of protonation (ΔH_{HP}) of phosphines has been discussed in terms of the reaction shown in eq 1, one needs to consider the possibility that other processes (such as the reactions in eq 3–5) may contribute

$$2CF_3SO_3H \overset{K_3}{\rightleftharpoons} (CF_3SO_3H)_2 \qquad (3)$$

$$(CF_3SO_3H)_2 \overset{K_4}{\rightleftharpoons} CF_3SO_3H_2^+ + CF_3SO_3^- \qquad (4)$$

$$[R_3PH^+CF_3SO_3^-] \overset{K_5}{\rightleftharpoons} R_3PH^+ + CF_3SO_3^- \qquad (5)$$

---

(18) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69.

(19) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965.

(20) (a) Weiss, R.; Vande Griend, L. J.; Verkade, J. G. *J. Org. Chem.* **1979**, *44*, 1860. (b) Olah, G. A.; McFarland, C. W. *J. Org. Chem.* **1971**, *36*, 1374.

to ΔH_{HP}. Equations 3 and 4 describe the dimerization and autoprotolysis of CF_3SO_3H, and eq 5 describes the dissociation of phosphonium triflate ion pairs. Thermodynamic data for these reactions in DCE have not been reported. However, estimates of their contributions to ΔH_{HP} can be made from data on related systems.

The reactions shown in eq 3 and 4 have been studied by means of conductivity measurements in CH_2Cl_2.[21] The overall equilibrium constant, K_3K_4, was found to be 9×10^{-8} at -15 °C. The authors estimate K_3 to be between 1 and 0.01, so K_4 should be no larger than 10^{-5}. Assuming similar values for K_3 and K_4 in DCE, only dimerization need be considered at the total acid concentrations typical of the ΔH_{HP} runs. It is perhaps more instructive at this point to consider the dimerization of CF_3CO_2H (eq 6), for which thermodynamic data in DCE are known (K_6 =

$$2CF_3CO_2H \overset{K_6}{\rightleftharpoons} (CF_3CO_2H)_2; \quad \Delta H_6 \qquad (6)$$

1.5 l mol^{-1}; $\Delta H_6 = -7$ kcal mol^{-1}).[22] At a total acid concentration of 3×10^{-3} M (a typical value after dilution of the original 0.1 M solution in the ΔH_{HP} studies), the concentration of $(CF_3CO_2H)_2$ is 2.2×10^{-5} M. The heat required to dissociate this quantity of dimer is 0.05 kcal mol^{-1}. From the estimated K_3 noted above, the concentration of $(CF_3SO_3H)_2$ can be assumed to be near or less than that determined for $(CF_3CO_2H)_2$. From studies of carboxylic acid association in aprotic solvents, there is a rough correlation of less exothermic association enthalpies with increasing acidity.[23] The association enthalpy of CF_3SO_3H would thus be expected to be less than that of CF_3CO_2H, and the heat associated with dimer dissociation in 3×10^{-3} M CF_3SO_3H in DCE should be less than 0.05 kcal mol^{-1}. This contribution is less than 0.2% of most ΔH_{HP} values and, therefore, is negligible, according to these estimates.

The enthalpy contribution of the ion-pair dissociation (eq 5) can be estimated from data available for $[(n\text{-}Bu)_4N](ClO_4)$ in DCE (eq 7) with $K_7 = 6.41 \times 10^3$ l mol^{-1}[24] and $\Delta H_7 = 1.3$ kcal

$$Bu_4N^+ + ClO_4^- \overset{K_7}{\rightleftharpoons} [Bu_4N^+ClO_4^-]; \quad \Delta H_7 \qquad (7)$$

mol^{-1} (calculated from data of Abraham et al.).[25] At a total salt concentration of 3×10^{-3} M (approximately the final concentration in the ΔH_{HP} experiments), 20% of the salt is dissociated, and the heat evolved in this process is -0.26 kcal mol^{-1}. The $(n\text{-}Bu)_4N^+$ ion should be similar in size to most of the phosphonium ions produced in this study, and there is evidence that R_3PH^+ species do not form strong hydrogen bonds[26] ($CF_3SO_3^-$ is likewise a poor hydrogen-bond acceptor[27]), so the heat contribution due to ion-pair dissociation in the present study should be of comparable magnitude to -0.26 kcal mol^{-1}. In addition, the total heat of solution of $[(n\text{-}Bu)_4N](ClO_4)$ at 2.5×10^{-3} M in DCE is only -0.45 kcal mol^{-1}.[25] If ΔH_{soln} were comparably small for the phosphonium triflates in eq 1, the heat contributions from all solvent interactions with the product salt would be less than 2% of the ΔH_{HP} values.

Thus, the measured ΔH_{HP} values predominantly represent the heat evolved when R_3P reacts with monomeric CF_3SO_3H to form the $R_3PH^+CF_3SO_3^-$ ion pair, with only minor contributions from acid dimerization and ion-pair dissociation.

General Trends in ΔH_{HP}. As expected, the ΔH_{HP} values in Table I become more exothermic as electron-donating substituents are substituted on phosphorus; thus, the trialkylphosphines give ΔH_{HP}'s approximately 10 kcal mol^{-1} more negative than those of the triarylphosphines. The series $Me_xPh_{3-x}P$ shows a very consistent increase in basicity as methyl replaces phenyl, with differences of 3.2, 3.7, and 3.5 kcal mol^{-1} noted between the respective pairs Me_3P–Me_2PhP, Me_2PhP–$MePh_2P$, and $MePh_2P$–Ph_3P. The change on substitution thus appears to be additive, and, unless steric properties (such as C–P–C angles) vary regularly through this series, the ΔH_{HP} differences should be due to electronic rather than steric factors (the cone angles do not show regular variation, with differences of 4, 14, and 9°, respectively, for the above pairs, suggesting that the ΔH_{HP} differences in the $Me_xPh_{3-x}P$ series are indeed not due to steric effects).

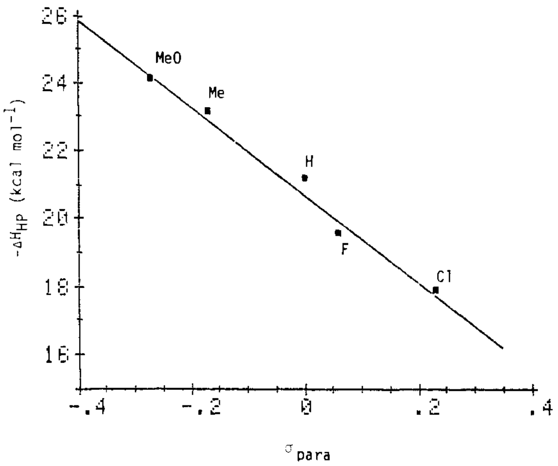


Figure 1. Plot of $-\Delta H_{HP}$ (at 25.0 °C in DCE) vs. Hammett σ_{para} parameters for the series $(p\text{-}XC_6H_4)_3P$.

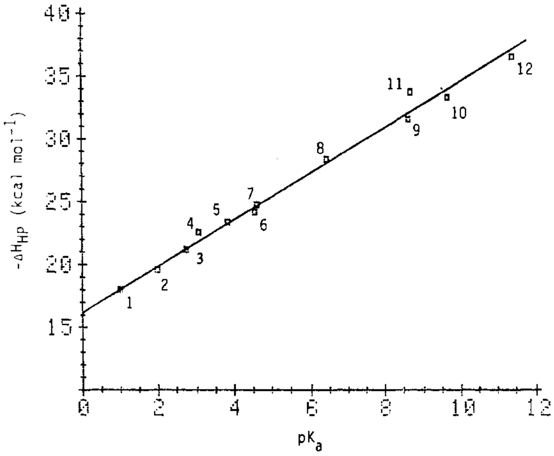


Figure 2. Plot of $-\Delta H_{HP}$ in DCE vs. pK_a's from ΔHNP measurements in CH_3NO_2. Numbers refer to Table I.

Consistent differences in ΔH_{HP} are also noted in the isosteric series $(p\text{-}XC_6H_4)_3P$ (X = Cl, F, H, Me, MeO) (Table I). The ΔH_{HP} values give an excellent correlation with Hammett σ_{para} substituent parameters (r, the correlation coefficient, is 0.992),[28] with $-\Delta H_{HP}$ decreasing in the order X = MeO > Me > H > F > Cl (Figure 1).

Comparison of ΔH_{HP} with Other Protonic Basicity Measures. The ΔH_{HP} values show a strong linear correlation with the reported pK_a's (from the half-neutralization potentials, ΔHNP's, in CH_3NO_2 noted previously), as seen in the plot of $-\Delta H_{HP}$ vs pK_a (Figure 2). Linear least-squares regression gives eq 8 as the best

$$-\Delta H_{HP} = 1.82pK_a + 16.3 \quad (\text{kcal mol}^{-1}) \qquad (8)$$

fit for the data ($r = 0.994$). The most significant deviation from the correlation is observed for Et_3P ($pK_a = 8.69$), whose ΔH_{HP} value of -33.7 kcal mol^{-1}) indicates a difference of 1.6 kcal mol^{-1}

---

(21) Chmelir, M.; Cardona, N.; Schulz, G. V. *Makromol. Chem.* **1977**, *178*, 169.

(22) Milne, J. B. In *The Chemistry of Nonaqueous Solvents*; Lagowski, J. J., Ed.; Academic: New York, 1978; Vol. VB, p 1.

(23) Davis, M. M. "Acid-Base Behavior in Aprotic Solvents"; NBS Monograph 105; U.S. Government Printing Office: Washington, DC, 1968; p 31.

(24) Abraham, M. H.; Danil de Namor, A. F. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 955.

(25) Abraham, M. H.; Danil de Namor, A. F.; Schulz, R. A. *J. Solution Chem.* **1976**, *5*, 529.

(26) Arnett, E. M.; Wolf, J. F. *J. Am. Chem. Soc.* **1973**, *95*, 978.

(27) Leucks, M.; Zundel, G. *Can. J. Chem.* **1980**, *58*, 311.

(28) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981.

Table II. Gas-Phase Proton Affinities and Solution ΔH_{HP}'s for the Series $Me_xPh_{3-x}P$

R_3P	PA, kcal mol^{-1} [a]	$-\Delta H_{HP}$, kcal mol^{-1} [b]	R_3P	PA, kcal mol^{-1} [a]	$-\Delta H_{HP}$, kcal mol^{-1} [b]
Ph_3P	226.7	21.2	Me_2PhP	226.0	28.4
$MePh_2P$	226.7	24.7	Me_3P	223.5	31.6

[a] Reference 7d. Estimated errors are ±0.2 kcal mol^{-1} except for Ph_3P, where the error is >±0.2 kcal mol^{-1}. [b] This work. In DCE solvent at 25.0 °C.

(more exothermic) from the best fit line. The origin of this deviation is not entirely clear; however, it is possible that the original pK_a value for this phosphine is slightly in error. Streuli measured the pK_a's of several phosphines by extrapolation of data from titrations in aqueous MeOH,[9] and these were compared to values obtained from the ΔHNP method. The differences in pK_a were 0.2 pK unit or less for the tertiary phosphines studied, except for Et_3P, where the pK_a from the aqueous MeOH data was 9.10 (a difference of 0.41). This higher pK_a value is in better accord with the ΔH_{HP} value.

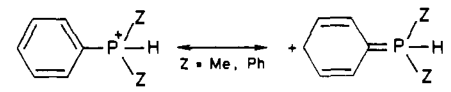
Considering the vastly different properties of the solvents employed in the ΔH_{HP} and pK_a determinations, it is perhaps surprising that the values correlate so well. Other linear ΔH–ΔG relationships have been noted for protonation enthalpies of amines and pyridines in organic solvents with aqueous pK_a's.[29] In Arnett's study of amine protonation in FSO_3H and H_2SO_4,[29b] the conditions leading to such relationships are discussed. In these protonations, free energy changes ($\Delta\Delta G$) for a series of compounds in one solvent (CH_3NO_2) may be proportional to enthalpy changes ($\Delta\Delta H$) in another (DCE), provided $\Delta\Delta G_{CH_3NO_2}$ is proportional to $\Delta\Delta G_{DCE}$ and $\Delta\Delta S_{DCE}$ is either proportional to $\Delta\Delta H_{DCE}$ or equal to 0. However, from the available data, it is not possible to say which condition is satisfied for the correlation between ΔH_{HP} and pK_a.

Arnett's calorimetric studies of N-donor molecules in neat FSO_3H have been extended to cover O-, S-, and a few P-donor bases,[26,30] with a linear correlation (r = 0.986) observed between ΔH_i (defined as the difference between ΔH of solution in FSO_3H and ΔH of solution in an inert solvent, such as CCl_4) and aqueous pK_a's for over 50 bases (eq 9). The similarity of the slopes for

$$-\Delta H_i = 1.77pK_a + 28.1 \quad (\text{kcal mol}^{-1}) \qquad (9)$$

eq 8 and 9 is perhaps fortuitous, but a comparison of the intercepts clearly shows that neat FSO_3H is a stronger protonating medium than CF_3SO_3H in DCE. This increased strength is also evident in the ΔH_i values of the two tertiary phosphines, Ph_3P[29b] and Me_3P,[26] included in Arnett's studies. The ΔH_i values for Ph_3P and Me_3P are −28.7 and −44.6 kcal mol^{-1}, respectively (compare with ΔH_{HP} = −21.2 kcal mol^{-1} for Ph_3P and ΔH_{HP} = −31.6 kcal mol^{-1} for Me_3P (Table I)). The difference in ΔH_i for Ph_3P and Me_3P (15.9 kcal mol^{-1}) suggests that the slope of a $-\Delta H_i$ vs pK_a plot for phosphines will be different (larger) from the value of 1.77 observed for other bases (eq 9). Arnett[30] has noted that particular classes of compounds would probably show deviations from eq 9 if more data were available; this appears to be true for the tertiary phosphines. A similar variation in basicity relationships between types of bases is noted in the comparison of protonation enthalpies in CF_3CO_2H/DCE with ΔH_{HP} values in CF_3SO_3H/DCE. The enthalpies obtained in this study (in kcal mol^{-1}) are −33.7 (CF_3SO_3H) and −12.9 (CF_3CO_2H) for Et_3P and −37.2 (CF_3SO_3H) and −23.5 (CF_3CO_2H) for $(PhNH)_2CNH$ (DPG). The difference between enthalpies measured with the two acids (14.1 kcal mol^{-1} for DPG, 20.8 kcal mol^{-1} for Et_3P) shows a sizable change in acid strength on going from CF_3SO_3H to CF_3CO_2H. These differences also indicate that the relationship between protonation enthalpies measured with CF_3SO_3H and CF_3CO_2H will not be the same for N- and P-donor bases.

Scheme I



As noted in the Introduction, basicity trends of phosphines in the gas phase are, in some cases, in contrast to trends observed in solution. Table II lists gas-phase proton affinities and ΔH_{HP} values (from Table I) for Ph_3P, $MePh_2P$, Me_2PhP, and Me_3P. The gas-phase proton affinities do not follow the same trend as the $-\Delta H_{HP}$ and pK_a values; in fact, Me_3P exhibits the lowest proton affinity. The gas-phase basicities also run counter to the results of several reactivity studies of phosphine complexes, where data are successfully analyzed by using the solution basicities as a measure of σ-bonding ability.[3] One of the arguments made in explaining the gas-phase proton affinity order was that phenyl-substituted phosphonium ions could be stabilized by aryl π to phosphorus d donation, as depicted in Scheme I.[7d,e] However, there is no conclusive evidence for such a π-bonding interaction. As mentioned above, the correlation of ΔH_{HP} with σ_{para} is excellent; but a poor correlation (r = 0.887) is found between ΔH_{HP} and σ^+ parameters[28] (these measure the effect of resonance donor substituents in direct conjugation with the reaction center, as would be the case in Scheme I). This indicates that the phenyl ring π system does not interact significantly with the phosphorus d orbitals in the phosphonium ion. A similar conclusion was reached in a photoelectron spectroscopy study of para-substituted triarylphosphines.[31] In light of these results, a reevaluation of the factors leading to the reversal of the solution basicity order for the series $Me_xPh_{3-x}P$ in the gas phase may be warranted.

Correlations of ΔH_{HP} with Taft σ^* and Kabachnik σ^{ph} Parameters. The pK_a's of phosphines were originally shown to be linearly related to Taft's σ^* parameters,[32] with a different line (of approximately equal slope) for tertiary, secondary, and primary phosphines.[10] A set of substituent parameters was later developed specifically for groups bound to phosphorus.[33] These constants, denoted σ^{ph}, were applied to the phosphine pK_a data, giving a linear correlation for all three phosphine classes on the same line, with a higher correlation coefficient. As the σ^{ph} parameters could have useful predictive value if they are truly superior to σ^* for substituents bound to phosphorus, correlations with ΔH_{HP} values were tested for both sets of parameters. The results are given in eq 10 and 11. For the tertiary phosphines examined σ^{ph} gives no

$$-\Delta H_{HP} = -5.83\textstyle\sum\sigma^* + 31.1 \quad (\text{kcal mol}^{-1}) \qquad (10)$$
$$(r = 0.966,\ 8 \text{ data points})$$

$$-\Delta H_{HP} = -5.44\textstyle\sum\sigma^{ph} + 13.4 \quad (\text{kcal mol}^{-1}) \qquad (11)$$
$$(r = 0.961,\ 11 \text{ data points})$$

better fit than σ^*. In fact, the data in the σ^{ph} correlation show somewhat random deviations, but only one point (for $(p\text{-}MeOC_6H_4)_3P$) in the σ^* correlation is significantly out of line. Thus, for tertiary phosphines such as those used in the present study, σ^{ph} does not appear to offer better predictive ability than σ^*.

Correlation of ΔH_{HP} with ΔH of $R_3P{\cdot}HgCl_2$ Adduct Formation. Enthalpies for the reactions of phosphines with Lewis acids may serve as measures of phosphine σ-donor ability. The stepwise reactions (eq 12 and 13) of phosphines with mercury dihalides

$$R_3P + HgX_2 \rightleftarrows (R_3P)HgX_2; \quad \Delta H_{12} \qquad (12)$$

$$R_3P + (R_3P)HgX_2 \rightleftarrows (R_3P)_2HgX_2; \quad \Delta H_{13} \qquad (13)$$

in benzene solution have been studied by calorimetry.[5] Heats of the respective reactions are plotted vs ΔH_{HP} in Figure 3. For ΔH_{12} vs ΔH_{HP}, linear regression shows a fair correlation (r =

---

(29) (a) Mead, T. E. *J. Phys. Chem.* **1962**, *66*, 2149. (b) Arnett, E. M.; Quirk, R. P.; Burke, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 1260.

(30) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875.

(31) Weiner, M. A.; Lattman, M.; Grim, S. O. *J. Org. Chem.* **1975**, *40*, 1292.

(32) Taft, R. W. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956, p 556.

(33) Kabachnik, M. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1969**, *38*, 795.

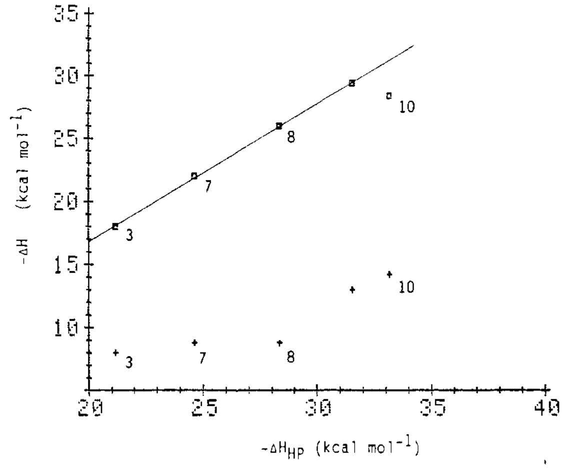


Figure 3. Plot of $-\Delta H_{12}$ (squares) for reaction of R_3P with $HgCl_2$ in C_6H_6 and $-\Delta H_{13}$ (crosses) for reaction of R_3P with $(R_3P)HgCl_2$ in C_6H_6 vs. $-\Delta H_{HP}$ for R_3P. Numbers refer to Table I; points not numbered are for $(n\text{-Bu})_3P$.

0.977) for the five phosphines (ΔH_{HP} for $(n\text{-Bu})_3P$ estimated from eq 8), but $(c\text{-}C_6H_{11})_3P$ (point number 10) is obviously out of line. The correlation with the point for $(c\text{-}C_6H_{11})_3P$ removed is practically perfect ($r = 1.000$). The deviation of $(c\text{-}C_6H_{11})_3P$ can be attributed to specific steric hindrance ($\theta = 170°$ for this phosphine)[1d] to adduct formation. (There may also be some contribution from a repulsive π-interaction between $(c\text{-}C_6H_{11})_3P$, which can act as a π-donor,[3] and the filled d orbitals of $HgCl_2$). The values of ΔH_{13} are not correlated well with ΔH_{HP}'s ($r = 0.910$). For this reaction, steric effects would be expected to be more important; this, coupled with the now variable electronic properties of the acceptor, $(R_3P)HgCl_2$, eliminates any expectation of a linear correlation with ΔH_{HP}.

Conclusion

The present study demonstrates that protonation enthalpies (ΔH_{HP}'s, determined by calorimetric titration with CF_3SO_3H in DCE) are valid and consistent measures of phosphine basicity and are directly related to the electron-donating ability of phosphines in other solution media. The protonation reactions are highly exothermic ($-\Delta H_{HP} \geq 18$ kcal mol^{-1}) for the phosphines studied; thus, errors due to secondary reactions (such as acid dimerization or ion-pair dissociation) are not significant. The method described also offers the ability to measure basicity for a wide range of base strengths under the same conditions. The ΔH_{HP} values should prove to be extremely useful tools for investigations of reactivity in transition-metal chemistry; such studies aimed at determining the relationship between phosphine and metal-phosphine complex basicity are in progress in our laboratories.

Acknowledgment. This research was supported by the National Science Foundation (Grant No. CHE-8401844). Additional support in the form of a graduate fellowship (to R.C.B.) from The Procter and Gamble Co. is gratefully acknowledged. Special thanks are extended to John Sowa for invaluable assistance in developing some of the experimental procedures used in this study. We also thank Dr. Dale Wurster of the University of Iowa, College of Pharmacy, for helpful advice on calorimetry.

Registry No. $(p\text{-ClC}_6H_4)_3P$, 1159-54-2; $(p\text{-FC}_6H_4)_3P$, 18437-78-0; Ph_3P, 603-35-0; $(o\text{-MeC}_6H_4)_3P$, 6163-58-2; $(p\text{-MeC}_6H_4)_3P$, 1038-95-5; $(p\text{-MeOC}_6H_4)_3P$, 855-38-9; $MePh_2P$, 1486-28-8; Me_2PhP, 672-66-2; Me_3P, 594-09-2; $(c\text{-}C_6H_{11})_3P$, 2622-14-2; Et_3P, 554-70-1; $(t\text{-Bu})_3P$, 13716-12-6.

Contribution from the Department of Chemistry, University of Houston—University Park, Houston, Texas 77004,
Laboratoire de Synthèse et d'Electrosynthèse Organométallique, Associé au CNRS (UA 33), Faculté des Sciences "Gabriel",
Université de Dijon, 21100 Dijon, France, and Faculté des Sciences de Rabat,
Laboratoire de Chimie Physique Générale, Université Mohammed V, Rabat, Morocco

Electrochemical and Spectral Characterization of the Monomer-Dimer Equilibrium Involving (*meso*-Tetrakis(1-methylpyridinium-4-yl)porphinato)nickel(II) in Dimethylformamide

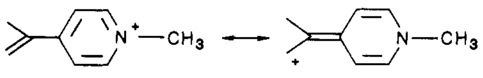
K. M. Kadish,*[1a] D. Sazou,[1a] Y. M. Liu,[1a] A. Saoiabi,[1b] M. Ferhat,[1b] and R. Guilard[1c]

Received June 30, 1987

The electrochemistry of $(TMPyP)Ni(ClO_4)_4$ (where TMPyP is the dianion of *meso*-tetrakis(1-methylpyridinium-4-yl)porphyrin) was characterized in DMF by polarography, cyclic voltammetry, spectroelectrochemistry, and ESR spectroscopy. The neutral and reduced $(TMPyP)Ni(ClO_4)_4$ exist in a monomer-dimer equilibrium in DMF, and this equilibrium results in the presence of four two-electron reductions. The dimerization was also characterized by electronic absorption and NMR spectroscopy. At concentrations of porphyrin close to 10^{-6} M the monomeric and dimeric forms of the complex exist in essentially equal amounts, but at polarographic concentrations the dimeric form prevails in solution. A dimerization constant was calculated from cyclic voltammetric measurements and was of the same order of magnitude as observed for dimerization of other TMPyP complexes in aqueous media.

Introduction

The free base porphyrin $[(TMPyP)H_2]^{4+}$ (where TMPyP is the dianion of (*meso*-tetrakis(1-methylpyridinium-4-yl)porphyrin) and its metal derivatives have potential therapeutic use because of their ability to react with DNA.[2-7] These "water soluble" *meso*-tetrakis(1-methylpyridinium-4-yl)porphyrins play an important role as photosensitizers and as labels for DNA and other biological cells. The diamagnetic $[(TMPyP)H_2]^{4+}$ complex has a positive charge on the pyridinium nitrogen atoms, which is delocalized over the porphyrin ring via resonance structures of the type[8]



---

(1) (a) University of Houston. (b) Université Mohammed V. (c) Université de Dijon.

(2) Fiel, R. J.; Howard, J. C.; Mark, E. H.; Datta Gupta, N. *Nucleic Acids Res.* **1979**, *6*, 3093.

(3) Fiel, R. J.; Munson, B. R. *Nucleic Acids Res.* **1980**, *8*, 283J.

(4) Pasternack, R. F.; Gibbs, E. J.; Villafranca, J. J. *Biochemistry* **1983**, *22*, 2406.

(5) Pasternack, R. R.; Gibbs, E. J.; Villafranca, J. J. *Biochemistry* **1983**, *22*, 5409.

(6) Banville, D. L.; Marzilli, L. G.; Wilson, W. D. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 148.

(7) Blom, N.; Odo, J.; Nakamoto, K.; Strommen, D. P. *J. Phys. Chem.* **1986**, *90*, 2847.