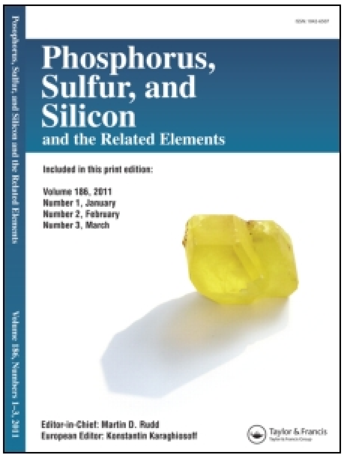

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THE EFFECT OF CHARGE DISPERSAL ON PHOSPHINE BASICITIES AND REACTIVITIES

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Abstract The effect of solvent charge dispersal on the reversal of gas phase and aqueous basicities and reactivities of trimethyl- and substituted triphenylphosphines will be discussed.

INTRODUCTION

The opposing aqueous and gas phase trends in trimethyl- and triphenylphosphine basicities have both been suggested to be fundamental predictors of phosphine ligand reactivity in organometallic and coordination chemistry. [1,2,3]

Phosphine ligand reactivities have been analyzed in terms of σ- bonding, π-bonding, and steric properties. σ-bonding ability in metal complexes has most commonly been estimated from basicities toward protonic acids in solution. As shown in Table 1 aqueous basicity and reactivity order seemingly follows the electronegativity order of the alkyl and aryl substitutents. The basicities in the gas phase are however reversed.

TABLE I Aqueous and Gas Phase Basicities and Reactivities

	PA[a] kcal/ mole	UV photo[b] electron spectra,eV	pKa[c] kcal/ mole	- ΔH_{HP}[d] kcal/mole	-ΔH[e] kcal/mole
Ph_3P	226.7	7.80	2.73	21.2	19.5
$MePh_2P$	226.7	8.28	4.57	24.7	22.1
Me_2PhP	226.0	8.32	6.50	28.4	25.0
Me_3P	223.5	8.62	8.65	31.6	26.2

a) Ref.4 ; b) Ref. 1; c) Ref. 5; d) enthalpies of protonation determined from heats of reaction with trifluoroacetic acid (Ref. 2); e) enthalpies of platinum - ligand bond formation in trans-$(CH_3Pt[P(CH_3)_2C_6H_5]_2L)^+(PF_6)^-$ complexes (Ref. 6).

A major contributing factor for the high triphenylphosphine basicity in the gas phase has been suggested to be the transfer of electrons from aryl π to phosphorus d orbitals . No evidence for such an effect on solution acidities has been reported. Basicities of 4-substituted aryl phosphines, for instance, show a high correlation with σ and not with σ^+.[2]

DISCUSSION

This seeming contradiction can be understood in terms of a solvent attenuation of reactivity parameters associated with substituent field/inductive (F), resonance (R), and polarizability (σ) effects as expressed in equation (1).[7]

$$-\partial\Delta G^{o} = \sigma_F\rho_F + \sigma_R\rho_R + \sigma_\alpha\rho_\alpha \qquad (1)$$

Dispersal of charge from the reaction center through solvation will attenuate the polarizability effect to nearly negligible in most solution studies. It is generally observed that substituent polarizability is the primary contributor to high gas phase basicities. This is indeed the case for phosphine systems in this study. The observed reversal in the aqueous and gas phase basicities of trimethyl- and triphenyl phosphine (equation 2) can be attributed directly to the greater polarizability of the phenyl substituent than the methyl.

$$(CH_3)_3P + (C_6H_5)_3PH^+ \rightleftarrows (CH_3)_3PH^+ + (C_6H_5)_3P \qquad (2)$$

$$\Delta G^\circ(aq) = -6.5 \text{ kcal/mol}$$

$$\Delta G^\circ(g) = +5.3 \text{ kcal/mol}$$

A dual substituent parameter analysis of a series of tertiary phosphines including Me_3-, Me_2Ph-, $MePh_2$-, Ph_3-, Et_3-, and $(n\text{-}Pr)_2Me$-, indicates that the aqueous basicities can be predicted from the gaseous basicities after correcting for the polarizability contributions (equation (3)).

$$PX_3 + Me_3PH^+ \rightleftarrows PX_3H^+ + Me_3P \qquad (3)$$

$$\partial\Delta G^\circ_{(aq)} = 0.0\ (\pm 0.6) + 0.6\ (\pm 0.2)\Delta G^\circ_{(g)} - 8.3\ (\pm .8)\ \Sigma\sigma_\alpha$$

$$R = .9875$$

$$SD = .7 \text{ kcal/mol}$$

Remote substituents in the gas phase, such as in 4-substituted triphenylphosphines, show very little dependence on polarizability effects (equations 4 and 5). Substituents in aqueous phase included Cl-, F-, H-,Me-,MeO-[2]; substituents in the gas phase included CF_3-, F-, H-, Me-, MeO- (Me and MeO- were estimated)[8].

$$\partial\Delta G^{\circ}_{(aq)} = -0.4(\pm 0.4) + 13.3(\pm 1.4)\sigma_F + 14.3(\pm 1.9)\sigma_R \quad (4)$$

$$R = .990$$

$$SD = .7 \text{ kcal/mol}$$

$$\partial\Delta G^{\circ}_{(g)} = -0.4(\pm 1.0) + 25.6(\pm 2.7)\sigma_F + 28.3(\pm 3.2)\sigma_R \quad (5)$$

$$R = .996$$

$$SD = .9 \text{ kcal/mol}$$

The inductive and resonance effects in the gas phase are enhanced by a factor of two due to the higher concentration of charge at the reaction center. There seems to be no greater enhancement of the resonance effect which might be expected if there were significant transfer from aryl $\underline{\pi}$ to phosphorous $\underline{d}$ orbitals. However, the effect of a strong electron donor such as the MeO- group might be weakened due to the existence of the three phenyl rings. There is therefore no direct evidence against the transfer of electrons from the aryl $\underline{\pi}$ to the phenyl $\underline{d}$ orbitals either in the gas phase or in aqueous studies which has been used to explain the greater substituent effects on phosphine vs amine basicities.[4]

Theoretical calculations on the STO-3G* level indicate that the $(CH_3)_3P$ monohydrate is more basic than $(CH_3)_3P$ by 10.0 kcal/mole, whereas the $(C_6H_5)P$ monohydrate, where the charge is delocalized into the phenyl rings, is expected to be 6.1 kcal/mole more basic. This is a partial indication of the reversal observed experimentally. In contrast, the more highly solvated $(CH_3)_3N$ is calculated to be 23 kcal/mole more basic.[9] Specific solvation in the phosphine system is expected to be weak since R_3P is a poor H-bond acceptor and R_3PH^+ is probably a poor H-bond donor; however, calculated charge distributions indicate twice as much charge dispersal into the monohydrate in the trimethyl vs. the triphenyl system (+0.177 vs. + 0.067).

There is therefore no seeming contradiction in the reversal of the aqueous vs. gas phase basicities of trimethyl vs. triphenyl phosphines when the polarizability effect is taken into consideration. As a measure of the σ-bonding ability in predicting reactivity in organometallic and coordination chemistry, the basicities as determined in solution will be the better predictors of reactivity in dipolar H-bond acceptor solvents, where the charge dispersal will be similar.

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