other metal atom. This type of unsymmetrical bonding of $CH_3N(PF_2)_2$ to a pair of bonded metal atoms must be contrasted with the more usual symmetrical bonding exhibited by the other three $CH_3N(PF_2)_2$ ligands in $[CH_3N(PF_2)_2]_4Fe_2CO$ (I, L = CO) where all phosphorus–nitrogen bonds in the ligands are retained and each phosphorus atom donates a single electron pair to a single metal atom. Such unsymmetrical bonding of one $CH_3N(PF_2)_2$ ligand is required in $[CH_3N(PF_2)_2]_4Fe_2CO$ to give each iron atom the favored rare gas electronic configuration without requiring an iron–iron dative bond.

The single carbonyl group in $[CH_3N(PF_2)_2]_4Fe_2CO$ (I, L = CO) has the expected reactivity toward photochemical replacement by trivalent phosphorus ligands to give $[CH_3N(PF_2)_2]_4Fe_2PR_3$ derivatives (I, L = PR_3) which are the first known compounds where a pair of bonded iron atoms is surrounded by nine phosphorus atoms, i.e., a formal although not a structural analogue of $Fe_2(CO)_9$. For example, ultraviolet irradiation of $[CH_3N(PF_2)_2]_4Fe_2CO$ with triphenylphosphine or trimethyl phosphite in diethyl ether followed by chromatography on Florisil gives the corresponding solid $[CH_3N(PF_2)_2]_4Fe_2PR_3$ (R = OCH_3 and C_6H_5) derivatives[6] where apparently the unusual structure I is retained.

References and Notes

(1) R. B. King and J. Gimeno, *J. Chem. Soc., Chem. Commun.*, 142 (1977).
(2) M. G. Newton, R. B. King, M. Chang, N. S. Pantaleo, and J. Gimeno, *J. Chem. Soc., Chem. Commun.*, 531 (1977).
(3) R. B. King and J. Gimeno, unpublished results, 1977.
(4) J. F. Nixon, *J. Chem. Soc. A*, 2689 (1968).
(5) A. A. Hock and O. S. Mills, *Proc. Chem. Soc.*, 223 (1958); *Acta Crystallogr.*, **14**, 139 (1961).
(6) These compounds were characterized by correct C, H, and N analyses and ^{1}H NMR spectra.
(7) University of Georgia Graduate Fellow, 1976–1978.
(8) Departmento de Quimica Inorganica, Universidad de Zaragoza, Spain.
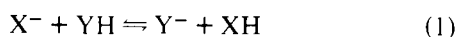
M. G. Newton, R. B. King,* M. Chang,[7] J. Gimeno[8]

*Department of Chemistry, University of Georgia
Athens, Georgia 30602*

Figure 1. The observed variation of ion signals recorded upon the addition of CH_3OH into a H_2O–He plasma in which unhydrated and hydrated hydroxide ions are initially present. P = 0.379 Torr, T = 294 K, L = 85 cm, $\bar{v}$ = 8.4 × 10^3 cm s^{-1}.

Figure 2. The shift in the position of equilibrium for the proton transfer between CH_3OH and OH^- as a function of the extent of solvation at 296 ± 2 K.
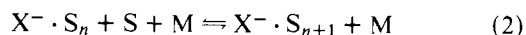
Bridging the Gap between the Gas Phase and Solution: Transition in the Relative Acidity of Water and Methanol at 296 ± 2 K

Sir:

For the past half decade the application of a variety of gas-phase experimental techniques to the measurement of rate and equilibrium constants for proton-transfer ion–molecule reactions of the type

$$X^- + YH \rightleftharpoons Y^- + XH \qquad (1)$$

has provided much quantitative information about their intrinsic kinetics and energetics.[1,2] Furthermore, ion–solvent interactions have been examined extensively through gas-phase equilibrium measurements of the stepwise solvation of ions by three-body ion association reactions of the type

$$X^- \cdot S_n + S + M \rightleftharpoons X^- \cdot S_{n+1} + M \qquad (2)$$

where S represents the solvent molecule and M is a stabilizing third body.[3] Such studies have proven to be extremely valuable for the elucidation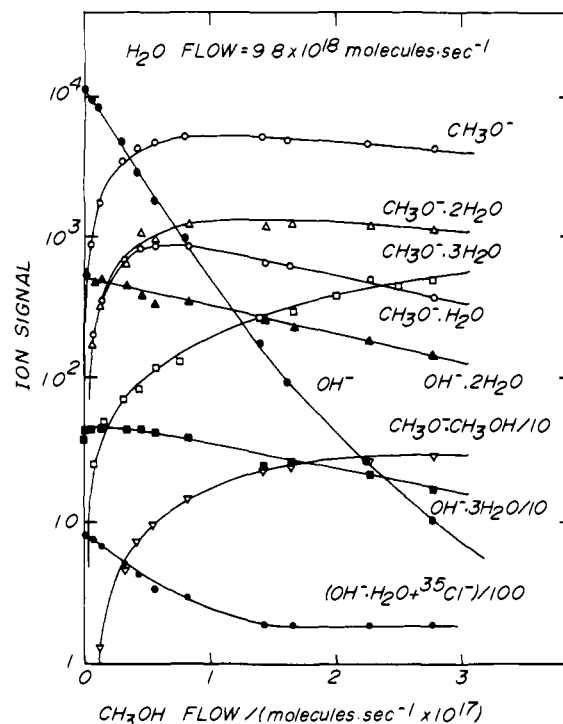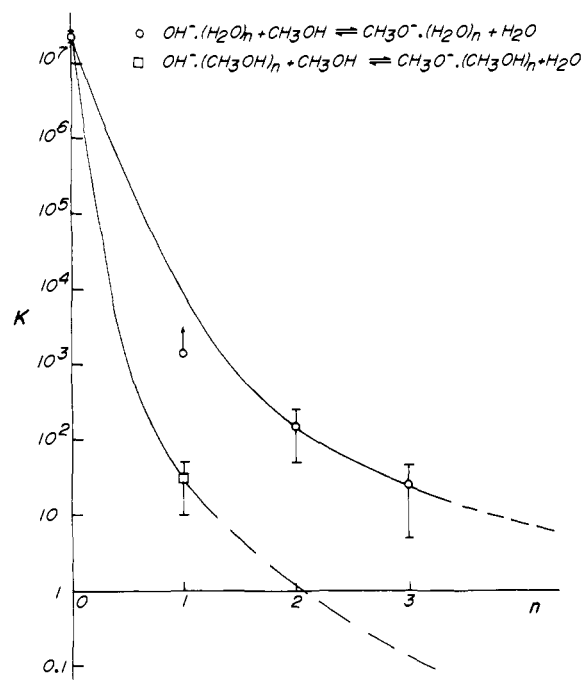 of the influence of intrinsic molecular parameters and ion–solvent interactions on proton-transfer kinetics and energetics and thus for the evolution of a unified model for acid–base chemistry.[4] We report here gas-phase equilibrium measurements for solvated proton-transfer reactions of the type
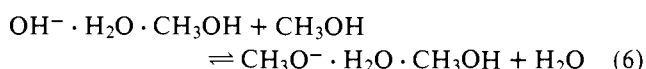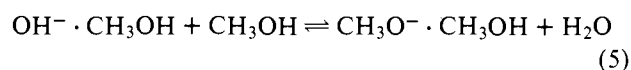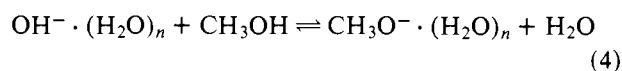
$$X^- \cdot S_n + YH \rightleftharpoons Y^- \cdot S_n + XH \qquad (3)$$

Table I. Equilibrium Constants at 296 ± 2 K

Reaction			K^a
$OH^- + CH_3OH$	$\rightleftharpoons$	$CH_3O^- + H_2O$	$(2.2 \pm 0.4) \times 10^7$ [b]
$OH^- \cdot H_2O + CH_3OH$	$\rightleftharpoons$	$CH_3O^- \cdot H_2O + H_2O$	$>1.3 \times 10^3$ [c]
$OH^- \cdot (H_2O)_2 + CH_3OH$	$\rightleftharpoons$	$CH_3O^- \cdot (H_2O)_2 + H_2O$	$(1.5 \pm 1.0) \times 10^2$
$OH^- \cdot (H_2O)_3 + CH_3OH$	$\rightleftharpoons$	$CH_3O^- \cdot (H_2O)_3 + H_2O$	25 ± 20
$OH^- \cdot CH_3OH + CH_3OH$	$\rightleftharpoons$	$CH_3O^- \cdot CH_3OH + H_2O$	30 ± 20
$OH^- \cdot H_2O \cdot CH_3OH + CH_3OH$	$\rightleftharpoons$	$CH_3O^- \cdot H_2O \cdot CH_3OH + H_2O$	30 ± 15

[a] Each value represents the average of a series of measurements together with its estimated total accuracy.[8] [b] Calculated from the absolute standard free energies of deprotonation for H_2O and CH_3OH which were determined to be 384.3 ± 0.15 and 374.4 ± 2.2 kcal mol^{-1}, respectively, from the electron affinities of OH and CH_3O reported by H. Hotop, T. A. Patterson, and W. C. Lineberger, *J. Chem. Phys.*, **60**, 1806 (1974), and K. J. Reed and J. I. Brauman, *J. Am. Chem. Soc.*, **97**, 1625 (1975), and appropriate support data found in the JANAF Thermochemical Tables, 2nd ed, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **37** (1971), and 1974 Supplement, *J. Phys. Chem. Ref. Data*, **3** (1974), and reported by H. E. O'Neal and S. W. Benson in "Free Radicals", J. K. Kochi, Ed., Wiley, New York, N.Y., 1973. [c] Only a lower limit could be obtained in this case. The attainment of equilibrium could not be monitored owing to the low initial $OH^- \cdot H_2O$ signal and the apparently large value of K.

which have remained largely inaccessible.[5] When coupled with corresponding measurements for the "nude" reaction ($n = 0$), viz., reaction 1, and solvation reactions of type 2, such measurements provide important additional insights for the extrapolation of intrinsic gas-phase behavior to that in the condensed phase. Specifically, we have been able to follow the transition in the relative acidity of H_2O and CH_3OH which occurs between the gas-phase and solution through measurements of the solvated proton-transfer equilibria

$$OH^- \cdot (H_2O)_n + CH_3OH \rightleftharpoons CH_3O^- \cdot (H_2O)_n + H_2O \tag{4}$$

$$OH^- \cdot CH_3OH + CH_3OH \rightleftharpoons CH_3O^- \cdot CH_3OH + H_2O \tag{5}$$

$$OH^- \cdot H_2O \cdot CH_3OH + CH_3OH$$
$$\rightleftharpoons CH_3O^- \cdot H_2O \cdot CH_3OH + H_2O \tag{6}$$

where $n = 1-3$, and by comparison with analogous information available for water–methanol solutions.[6]

The measurements were carried out using the flowing afterglow technique.[7] Hydroxide ions (~ 10 ppb) were generated by electron impact on H_2O upstream in a flowing helium plasma at total pressures in the range 0.1–0.5 Torr. The hydroxide ions were hydrated by reactions of type 2 and thermalized by collision in the He bath during the ~ 10 ms available prior to reaction downstream. Partial water vapor pressures were in the range 0.0005–2 mTorr. The approach to equilibrium for reactions 4–6 was monitored mass spectrometrically as a function of addition of CH_3OH into the reaction region up to partial pressures of ~ 0.01 mTorr. The observations recorded in one such experiment are shown in Figure 1. Equilibrium between a given pair of ions was assumed to be established when their ion signal ratio became independent of CH_3OH addition. The data was analyzed to yield equilibrium constants in our usual manner.[7,8] The results are summarized in Table I.

Figure 2 displays the observed variation in the position of equilibrium for the proton transfer between CH_3OH and OH^- as a function of solvation by either water or methanol molecules. The magnitude of the equilibrium constant decreases dramatically upon solvation by one molecule, viz., by $\sim 10^3$ in the case of H_2O and by $\sim 10^6$ in the case of CH_3OH, and continues to drop, but at a decreased rate, for higher solvent molecule additions. This means that water becomes increasingly more acidic than methanol upon solvation and more so for excess methanol than excess water. This trend implies a higher solvent (H_2O and CH_3OH) affinity for OH^- than for CH_3O^- and more so for CH_3OH than H_2O. Apparently solvation by more than approximately two methanol molecules actually results in a reversal of the relative acidity of H_2O and

CH_3OH. The extrapolation in Figure 2, albeit crude, implies a value of $K \simeq 1$ for reaction 5 with $n = 2$. As expected, the mixed solvated reaction 6 has an equilibrium constant, $K = 30 \pm 20$, intermediate between that for excess methanol, viz., reaction 5 with $n = 2$, and that for excess water, viz., reaction 4 with $n = 2$ for which $K = (1.5 \pm 1.0) \times 10^2$. Equilibrium studies for the proton transfer between CH_3OH and OH^- in solution have been reported by Unmack.[9] Her calculations, based on conductivity, solubility, and electrochemical potential measurements and the dissociation constants of H_2O and CH_3OH, indicate an equilibrium constant slightly >1 and <1 in excess water and methanol, respectively, consistent with expectations based on our gas-phase measurements if ion–solvent interactions predominate in determining the position of equilibrium in solution.

When combined with standard free energies of hydration for OH^- determined previously by Kebarle and co-workers[10,11] through equilibrium measurements for reactions of type 2, the standard free-energy changes dictated by our measurements of K_4 provide standard free energies of hydration for CH_3O^-. At this time, however, only limiting values can be deduced as only a lower limit for K_4 ($n = 1$) could be obtained in the present study. We are in the process of constructing a temperature-variable flowing afterglow system which should allow us to overcome this deficiency as larger amounts of hydrated hydroxide ions will become available for chemical manipulation at lower temperatures. We should also then be able to extend the extrapolation of the influence of solvent to higher hydrates as well as other ion–solvent equilibria.

References and Notes

(1) P. Kebarle, "Interactions Between Ions and Molecules", P. Ausloos, Ed., Plenum Press, New York, N.Y., 1974, pp 459–487.
(2) D. K. Bohme, in ref 1, pp 487–504.
(3) P. Kebarle, "Modern Aspects of Electrochemistry", Vol. 9, B. E. Conway and J. O. M. Bockris, Ed., Plenum Press, New York, N.Y., 1974, pp 1–46.
(4) E. M. Arnett, *Acc. Chem. Res.*, **6**, 40 (1973).
(5) The first step in the transition in the relative acidity of CH_3OH and C_2H_5OH has been reported by R. T. McIver, J. A. Scott, and J. M. Riveros, *J. Am. Chem. Soc.*, **95**, 2706 (1973). We have been able to confirm their results using our flowing afterglow technique as will be reported in a future paper.
(6) The molecular formulae of the solvated ions have been written to express explicitly the nature of the solvent; viz., we have artificially distinguished between $X^- \cdot YH$ and $Y^- \cdot XH$, e.g., $OH^- \cdot CH_3OH$ and $CH_3O^- \cdot H_2O$. This convention facilitates the comparison of unsolvated and solvated proton transfer and is not meant to imply a difference in structure or energy as the proton is actually shared by both X^- and Y^- nor is it meant to imply a specific reaction mechanism (reactions 5 and 6 may be viewed to proceed by solvent exchange rather than proton transfer).
(7) D. K. Bohme, R. S. Hemsworth, H. W. Rundle, and H. I. Schiff, *J. Chem. Phys.*, **58**, 3504 (1973).
(8) G. I. Mackay, R. S. Hemsworth, and D. K. Bohme, *Can. J. Chem.*, **54**, 1624 (1976).

(9) A. Unmack, *Z. Phys. Chem.*, **133**, 45 (1928).
(10) M. Arshadi and P. Kebarle, *J. Phys. Chem.*, **74**, 1483 (1970).
(11) J. D. Payzant, R. Yamdagni, and P. Kebarle, *Can. J. Chem.*, **49**, 3308 (1971).

Gervase I. Mackay, Diethard K. Bohme*

Department of Chemistry, York University
Downsview, Ontario, Canada
Received September 20, 1977

## Base-Induced Generation of Superoxide Ion and Hydroxyl Radical from Hydrogen Peroxide

Sir:

Substantial yields of superoxide ion, $O_2^-\cdot$, are obtained when tetraalkylammonium hydroxide is added to hydrogen peroxide in pyridine. Superoxide ion has been identified by its ESR spectrum at 77 K, which is identical with the previously reported spectra,[1] and by cyclic voltammetry (see Figure 1a).[2]

Table I summarizes the results for a series of reactions in which varying amounts of tetra-n-propylammonium hydroxide (TPAOH) have been added to hydrogen peroxide in pyridine. The initial yield approaches 0.5 mol of $O_2^-\cdot$/mol of H_2O_2. The superoxide ion subsequently disappears over a period of 1–2 h and oxygen is evolved.

To measure both the concentration of $O_2^-\cdot$ and the amount of evolved O_2 from the base-induced decomposition of H_2O_2, several reactions have been carried out in a sealed cell (with negligible headspace) that contained 50 mL of 0.1 M tetra-n-propylammonium perchlorate (TPAP) in pyridine (initially bubbled with argon to remove dissolved oxygen). In a typical reaction, 0.08 mmol of H_2O_2 (8 μL of 30% aqueous H_2O_2) is combined with 0.03 mmol of TPAOH (25 μL of 25% aqueous TPAOH). (The concentration of water in the final reaction mixture is ~0.05 M.) The formation of superoxide ion is complete in <30 s with a yield of 0.011 mmol of $O_2^-\cdot$ (0.22 mM) and ~0.02 mmol of O_2 (0.4 mM). Other possible products have not been identified. Figure 1b illustrates the cyclic voltammetry of the mixture of $O_2^-\cdot$ and O_2. (The peak above the axis is due to O_2 and the peak below the axis represents $O_2^-\cdot$.)

When 50-fold larger concentrations of H_2O_2 and TPAOH are combined, $O_2^-\cdot$ is not obtained,[3] but a stoichiometric amount of O_2 is produced, based on the reaction

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2 \qquad (1)$$
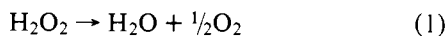
We also have carried out the reaction of H_2O_2 and TPAOH in the presence of the spin trap, phenyl-N-*tert*-butylnitrone (PBN). The ESR spectrum in acetonitrile at room temperature for a reaction mixture of 3 M pyridine, 1 M PBN, 0.01 M H_2O_2, 0.005 M TPAOH, and 0.25 M H_2O exhibits three doublets of approximately equal intensity with splittings of 15.2 ± 0.2 and 2.8 ± 0.2 G. This is consistent with the previously reported ESR spectrum[4] of the PBN adduct with $\cdot OH$,[1] but the possibility that the spectrum corresponds to the PBN adduct with $HO_2\cdot$ cannot be excluded. (The approximately equal relative intensities of the three doublets and the fact that the solution is basic argue in favor of the $\cdot OH$ adduct.)

Efforts have been made to identify the reaction products that result from the combination of $\cdot OH$ and pyridine, but without success. The reaction mixtures are pale yellow and exhibit a weak absorption band with a λ_{max} at 313 nm.

The addition of base to hydrogen peroxide in acetonitrile yields O_2, but there is no evidence of $O_2^-\cdot$ (see Figure 1c). The maximum yield of oxygen is obtained when the ratio of base to hydrogen peroxide is low (e.g., 0.1 mol of OH^-/mol of
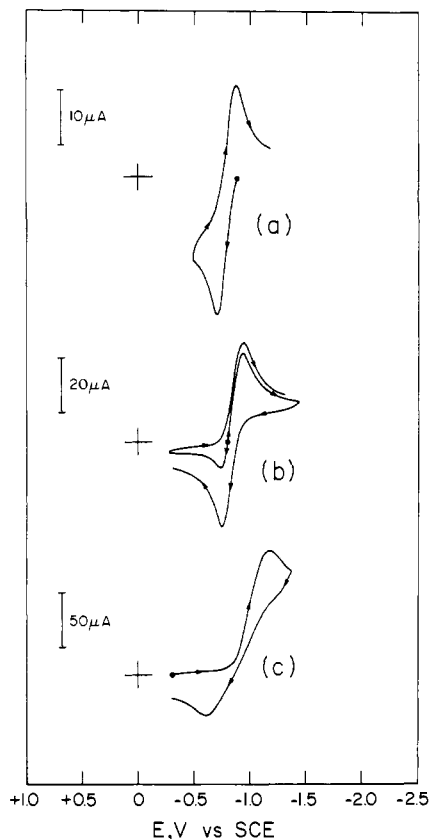
Figure 1. Cyclic voltammograms of the reaction products from the combination of H_2O_2 and TPAOH. All solutions contain 0.1 M TPAP; scan rate, 0.1 V/s at a platinum electrode (area, 0.23 cm²): (a) 2 mM H_2O_2 + 7.5 mM TPAOH in pyridine (argon bubbled to remove O_2); (b) 1.6 mM H_2O_2 + 0.62 mM TPAOH in pyridine, sealed cell; (c) 2 mM H_2O_2 + 0.24 mM TPAOH in acetonitrile, sealed cell.

Table I. Concentrations[a] of $O_2^-\cdot$ That Result from the Reaction of 2 mM Hydrogen Peroxide[b] with Varying Concentrations of TPAOH[c] in 0.1 M TPAP-Pyridine (Saturated with Argon)

[TPAOH], mM	[$O_2^-\cdot$], mM	Yield, mmol of $O_2^-\cdot$/ mmol of H_2O_2
0	0	0
0.25	0.08	0.04
0.50	0.23	0.12
1.0	0.58	0.29
2.0	0.89	0.44
4.0	1.08	0.54

[a] Extrapolated to the time of mixing. $O_2^-\cdot$ concentrations were determined by cyclic voltammetry with 0.1 M TPAP as the supporting electrolyte.[2] [b] Added as 30% aqueous H_2O_2. [c] Added as 25% aqueous TPAOH.

H_2O_2). At higher concentrations of OH^-, a secondary reaction slowly consumes the O_2 that is produced; this is presumed to be the base-catalyzed reaction of O_2 with acetonitrile. When 3 M pyridine is present in the H_2O_2–acetonitrile solution, addition of base results in the transient formation of $O_2^-\cdot$ (detected by cyclic voltammetry), but it disappears in 2–5 min.

The addition of base to H_2O_2 in water results in the slow base-catalyzed disproportionation of H_2O_2 to water and oxygen.[5] A reaction that contains 0.1 M PBN, 0.02 M H_2O_2, 0.01 M TPAOH, and 0.1 mM Na_2EDTA in water, when allowed to stand overnight, exhibits a weak three-line ESR spectrum.[6]

Based on the present results and other evidence that $O_2^-\cdot$ can be produced by reaction of base with hydrogen peroxide,