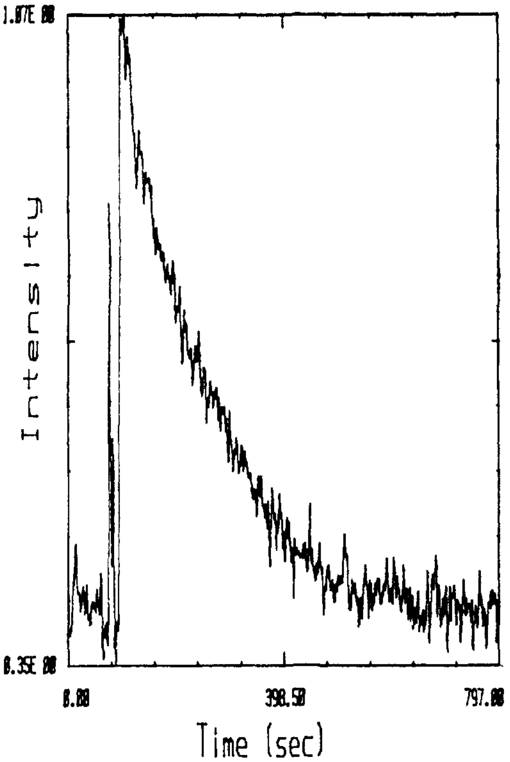

Figure 2. Near-infrared emission at 1278 nm as a function of time for the decomposition of triethylsilyl hydrotrioxide at −60 °C in CH_2Cl_2($t_{1/2}$ 150 s).

spectrometer.[6] Figure 1 shows the emission spectrum obtained which is as expected for $^1\Delta_g\ O_2 \rightarrow {}^3\Sigma_g\ O_2$ with a strong 0,0 peak at 1278 nm and a weak 0,1 peak at 1594 nm.[7] It is clear that these emissions originate from free $^1\Delta_g\ O_2$ molecules because of their wavelength and relative intensities, the latter being very similar to the gas-phase Franck–Condon factors.[7] The intensity of $^1\Delta_g\ O_2$ emission is one of the strongest observed to date from any chemical source.

The stability of the $^1\Delta_g\ O_2$ precursor, triethylsilyl hydrotrioxide, was measured by monitoring the decay in emission at 1278 nm with time. The value of $t_{1/2}$ obtained for the solution in methylene chloride at ca. −60 °C was 150 s (Figure 2). Parallel experiments performed with the same components in carbon disulfide solution at ca. −60 °C gave a $t_{1/2}$ of 10 s. The lifetime of $^1\Delta_g\ O_2$ in carbon disulfide solution is known to be considerably longer than in methylene chloride as solvent, but far less than in the gas phase.[8] Presumably carbon disulfide interacts less with $^1\Delta_g\ O_2$ than methylene chloride or benzene. It would appear that methylene chloride stabilizes the silyl hydrotrioxide, perhaps through hydrogen bonding, more than does carbon disulfide and that such stabilization results in the slower rate of decomposition observed in methylene chloride. The effect of more polar solvents (e.g., methanol) on the stability of the hydrotrioxide is of considerable interest in light of these results.

The above described experiments demonstrate the feasibility of a new approach to the chemical generation of singlet dioxygen from ozone which has both practical and mechanistic implications.[9]

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(6) (a) Khan, A. U. *J. Photochem.* **1984**, *25*, 327. (b) Khan, A. U.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6047.

(7) The apparent shift of 10 nm to longer wavelength for both 0,0 and 0,1 from values obtained in the gas phase may be due to uncompensated monochromoter–detector characteristics. Khan, A. U. In *Singlet O_2*; Fimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. I, p 39.

(8) (a) Foote, C. S.; Peterson, E. R.; Lee, K.-W. *J. Am. Chem. Soc.* **1972**, *94*, 1032. (b) *Singlet Molecular Oxygen, Benchmark Papers in Organic Chemistry*; Schaap, A. P., Ed.; Dowden, Hutchinson and Ross: Stroudsberg, PA, 1976; Vol. V.

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Radical Cation Acidities in Dimethyl Sulfoxide Solution

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Radical cations have been implicated as intermediates in the oxidation of a wide variety of organic molecules, and proton loss from radical cations is a common route to the formation of radicals and products derived therefrom.[1] The acid–base equilibrium constants for the dissociation of radical cations have been measured or estimated in only a few instances, however.[1,2] In this paper we describe a potentially general method for estimating acidities of radical cations by combination of the pK_{HA} value of a given acid in Me_2SO solution with its oxidation potential, $E_{ox}(HA)$, and that of its conjugate base, $E_{ox}(A^-)$. The thermodynamic cycle involved[7] is shown in eq 1–4.

$$HA \rightleftarrows H^+ + A^- \qquad pK_{HA} \tag{1}$$

$$A^- \rightleftarrows A\cdot + e^- \qquad E_{ox}(A^-) \tag{2}$$

$$HA^{+}\cdot + e^- \rightleftarrows HA \qquad -E_{ox}(HA) \tag{3}$$

$$HA^{+}\cdot \rightleftarrows H^+ + A\cdot \tag{4}$$

The pK_{HA} values for phenothiazine and its 2-MeO, 2-Cl, and 2-CF_3 derivatives together with their oxidation potentials and those for their conjugate bases, all in Me_2SO solution, are summarized in Table I. Similar data for fluorene and its 2-MeO and 2,7-$(MeO)_2$ derivatives are also given, together with the $pK_{HA^{+}\cdot}$ constants for all seven of the corresponding radical cations.

The oxidation potentials for all four phenothiazines are reversible, indicating that loss of an electron in the oxidative step to form the radical cation is not followed by rapid loss of a proton to the solvent, as occurs with radical cation phenols.[12] The oxidation potentials for the conjugate bases of the phenothiazines are irreversible, suggesting that the radicals formed undergo rapid dimerization, or other reactions.[15]

The spin density in the phenothiazine radical cations **1** is

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(1) (a) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *12*, 115–278. (b) Hammerich, O.; Parker, V. D. *Ibid.* **1984**, *20*, 55–189. (c) Nelsen, S. F.; Parmelee, W. P.; Gobl, M.; Hiller, K.-O.; Veltwisch, D.; Amus, K.-D. *J. Am. Chem. Soc.* **1980**, *102*, 5606–5610.

(2) For example, in water, $pK_{HA^{+}\cdot}$ is −2 for $PhOH^{+}\cdot$, 4–5 for phenothiazine$^{+}\cdot$,[4] 6.5–7.5 for $Me_2NH^{+}\cdot$,[5] 7 for $PhNH_2^{+}\cdot$,[6] and −11 for $PhCH_3^{+}\cdot$ (calcd).[7]

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(10) We have observed that reversible $E_{ox}(HA)$ values in CH_3CN and Me_2SO differ by no more than 40 mV, in agreement with literature observations on solvation effects,[11] but the differences may be somewhat larger for irreversible $E_{ox}(HA)$ values.

(11) Svaan, M.; Parker, V. D. *Acta Chem. Scand., Ser B* **1984**, *B38*, 759–765.

(12) For example, in water 2,4,6-$(t\text{-}Bu)_3C_6H_2OH^{+}\cdot$ loses a proton during cyclic voltammetry, and the resulting radical is then oxidized further to the cation.[13] Radical cation formation from 3,6,7-trimethoxyfluoren-2-ol in CH_3CN has also been shown to be accompanied by deprotonation and cation formation.[14]

(13) Richards, J. A.; Whitson, P. E.; Evans, D. H. *J. Electroanal. Chem.* **1975**, *63*, 311–327. Evans, D. H. *Acc. Chem. Res.* **1977**, *10*, 313–319.

(14) Nilsson, A.; Palmquist, U.; Roulân, A.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 3540–3541.

(15) There is evidence that the $E_{ox}(A^-)$ values obtained provide a good measure of relative e_T^- ability, however, since they give an excellent correlation with the rate constants for single electron transfer to the 1,1-dinitrocyclohexane electron acceptor.[16]

(16) Bausch, M. J. Ph.D. Dissertation, Northwestern University, Evanston, IL, Nov, 1984.

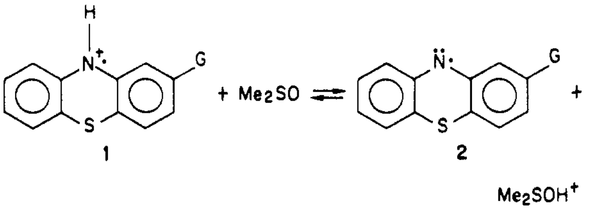
0002-7863/86/1508-2473$01.50/0

Table I. Equilibrium Acidities of Radical Cations Derived from Phenothiazine (Pz-H) and Fluorene (FlH_2), as Estimated from Acidity and Oxidation Potential Data (eq 1-4) in Me_2SO Solution at 25 °C.

HA	pK_{HA}	$E_{ox}(A^-)^e$	$E_{ox}(HA)$	$pK{\cdot}_{HA}{}^{+j}$
Pz-H	22.7^a	−0.107	$+0.985^f$	4.3^k
2-MeO-Pz-H	22.5^b	−0.119	$+0.943^f$	4.6
2-Cl-Pz-H	20.8^a	+0.038	$+1.042^f$	3.9
2-F_3C-Pz-H	20.65^c	+0.058	$+1.084^f$	3.4
FlH_2	22.6^a	−0.194	$+2.1^g$	−16
2-MeO-FlH_2	22.75^d	−0.189	$+1.8^h$	−11
2,7-$(MeO)_2FlH_2$	22.95^d	−0.195	$+1.53^{f,i}$	−6

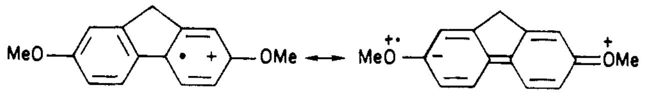
[a] Reference 8. [b] Measured by A. H. Clemens. [c] Present work. [d] Reference 9. [e] Irreversible oxidation potentials equal to the peak oxidation current measured by cyclic voltammetry using Pt and Ag/AgI working electrodes in Me_2SO solution with 0.1 M tetraethylammonium tetrafluoroborate electrolyte at a sweep rate of 100 mV/s (reproducible to <±10 mV); reversible ferrocene–ferrocinium redox couple at $E_{1/2}$ = 0.875 was used as a standard. [f] Reversible; the E_{ox} value is equal to one-half the sum of the voltages at peak oxidative and reductive currents. [g] Measured in CH_3CN; E_p for a shoulder preceding a wide irreversible wave with an E_p maximum at 2.4–2.5 V.[10] [h] Measured in CH_3CN; E_p for a narrow irreversible wave.[10] [i] Reversible in CH_3CN, but irreversible in Me_2SO.[10] [j] $pK{\cdot}_{HA}{}^+ = pK_{HA} + [E_{ox}(A^-) - E_{ox}(HA)] \times 23/1.37$. These values are estimated to have an accuracy of ±2 pK units, based on the assumption that E_{ox} values are accurate to ±0.1 V. The value for fluorene itself is less certain. [k] Alkaitas[4] reports 4–5 in H_2O.

distributed between nitrogen and sulfur,[17] and the positive charge can be delocalized to the 2-substituent by resonance. The major effect of the 2-substituents on equilibrium 5 will be exerted on **1**, since remote substituent effects on radicals are small.[18] The decrease in acidity caused by the 2-MeO substituent and the increase caused by the 2-Cl and 2-CF_3 substituents is in line with their electron-donor and -acceptor effects, respectively. The $pK_{HA^{+\cdot}}$ for phenothiazine in Me_2SO is expected to be within one unit of that in water, as observed,[4] by analogy with the small difference in relative acidities of amine conjugate acids in these solvents.[19]



(5)

The high acidity found for the three fluorene radical cations in Table I is consistent with the high acidity reported for toluene[7] and for polymethylbenzene[20] radical cations. Also, the oxidation potential of 2,7-dimethoxyfluorene has been shown to be reversible when F_3CCO_2H is added to the CH_2Cl_2 solvent, suggesting that the irreversible behavior in its absence is associated with loss of a proton to the solvent.[21] The stronger acid-weakening effect of a methoxyl substituent on a radical cation C–H acid than on a radical cation N–H acid (Table I) is understandable since delocalization of the positive charge provides strong stabilization of the high-energy radical cation C–H acid formed by e_T^- from the π system (e.g., **3a**,**b**). Since the pK_{HA} and $E_{ox}(A^-)$ values for the three fluorenes differ but little (Table I), the acid-weakening MeO effects are caused almost entirely by differences in the $E_{ox}(HA)$ values.[22] (The $\Delta pK_{HA^{+\cdot}}$ values calculated by method I of Nicholas and Arnold,[7] assuming a BDE value of 80 ± 5 kcal/mol for fluorene,[23,24] are −14, −9, and −5.) In contrast, the acid-weakening effect of the MeO substituent in 2-methoxy phenothiazine is relatively small because the radical cation N–H acid is formed by transfer of an electron from nitrogen (**1**). Note that the (reversible) $E_{ox}(HA)$ for 2-methoxyphenothiazine is 0.59 eV more negative than the (reversible) $E_{ox}(HA)$ of 2,7-dimethoxyfluorene (in CH_3CN).[10] In Me_2SO, the latter $E_{ox}(HA)$ becomes irreversible, because the radical cation is deprotonated by the more basic solvent. Extension of this method to additional radical cation C–H and N–H acids, as well as to O–H and S–H acids, is in progress.



3a 3b

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New Isomeric Tetranuclear Cluster Anions $Mo_4Cl_{12}^{3-}$: Fragments of the $(Mo_6Cl_8)Cl_6^{2-}$ Octahedral Cluster Anion

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The paucity of known tetranuclear molybdenum clusters has prompted investigations which have begun to yield a rich and interesting chemistry. The first tetranuclear molybdenum clusters isolated were the ternary solid-state compounds $Mo_4S_4Br_4$[1] and MMo_4S_8[2] (M = Al, Ga), utilizing high-temperature preparations. Solid-state tetranuclear clusters were also found in the oxide compounds $M_xMo_8O_{16}$ (M = K, x = 2; M = Ba, x = 1.14).[3] Discrete molecular clusters are also exemplified by several recent discoveries. Thermal decomposition of $Mo(CO)_4I_3^-$ in chlorobenzene[4] and reaction between HI and $Mo_2(O_2CCH_3)_4$ in methanol[5] produced the butterfly cluster $Mo_4I_{11}^{2-}$. Rational synthetic pathways began to emerge with the addition of two quadruply bonded dimeric units to form $Mo_4X_8L_4$ compounds (X = Cl, Br, I; L = PR_3, RCN, MeOH, THF).[6] Similarly, the molecules $Mo_4(O\text{-}i\text{-}Pr)_8X_4$ (X = Cl, Br), formed by the coupling of two triply bonded dimeric molecules, were shown to adopt different geometric configurations depending on which halide was present.[7] More recently, the first discrete tetrahedral clusters, $Mo_4S_4(CN)_{12}^{8-}$[8,9] and $Mo_4S_4(S_2CNR_2)_6$,[10] have been isolated.

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