lyzed disproportionation of O_2^- appears to be

$$\mathrm{Mn^{II}Q_2(H_2O)_2 + O_2^- \rightarrow Mn^{III}Q_2(O_2H)(H_2O) + OH^-} \quad (6)$$

$$\mathrm{Mn^{III}Q_2(O_2H)(H_2O) + O_2^- \xrightarrow{H_2O} Mn^{II}Q_2(H_2O)_2 + O_2 + HO_2^-} \quad (7)$$

secondary reactions

$$\mathrm{Mn^{II}Q_3^- + O_2^- \xrightarrow{H_2O} Mn^{III}Q_3(O_2H)^- + OH^-} \quad (8)$$

$$\mathrm{Mn^{III}Q_3(O_2H)^- + O_2^- \rightarrow Mn^{II}Q_3^- + O_2 + HO_2^-} \quad (9)$$

The most remarkable feature of this model is the apparent ability of a manganese(II) complex to reduce O_2^- to HO_2^-. Such a process, on the basis of the electrochemical peak potentials for the individual components, Figure 1, appears to be thermodynamically impossible. Apparently, eq 6 is favored as a result of the strong interaction of the product species, Mn^{III} and HO_2^- [14]

The apparent oxidation by O_2^- ion (generated from oxygen plus xanthine-xanthine oxidase or from illumination of spinach chloroplasts) of Mn(II) to Mn(III) in the presence of a pyrophosphate buffer system has been reported recently.[15] However, the authors conclude that the Mn(II)-pyrophosphate complex does not act as a disproportionation catalyst for O_2^- ions, and imply that the Mn(III)-pyrophosphate does not oxidize O_2^- ion but does oxidize H_2O_2. This is in sharp contrast to the results of the present study (eq 6-9).

Although the Fridovich mechanism (eq 1-4) invokes a third oxidation state for the enzyme to rationalize the kinetic results, there is another possible explanation. The slower catalytic state of the enzyme may simply be a different hydrolytic species.

Because protons catalyze the disproportionation of O_2^- ions and coordinated Me_2SO might serve as a proton source, the experiments of Figure 1 have been repeated in a pyridine solvent system. The results are qualitatively identical. Combination of 1 mM $Mn^{II}Q_2$ with 2 mM O_2^- immediately destroys all of the O_2^- and yields a solution that contains $Mn^{II}Q_2$, O_2, and H_2O_2 in amounts equivalent to 70-90% efficiency for eq 6-9.

Another possible interpretation of the results is that the $Mn^{II}Q_2$ complex acts as a Lewis acid to catalyze the disproportionation of O_2^- ions. However, when the experiment of Figure 1 is repeated with $Mg^{II}Q_2$ or $Zn^{II}Q_2$ substituted for $Mn^{II}Q_2$ the rate of decomposition for O_2^- is as slow as for Me_2SO solutions without added metal complexes (about 5-15% per hour). This supports the conclusion that $Mn^{II}Q_2$ acts as a redox catalyst.

The present study is being extended to determine what effects the ligands have on both the redox chemistry of the complexes and their ability to catalyze the decomposition of superoxide ion. In particular, ligands are being sought which will stabilize manganese(II) complexes toward nucleophilic displacement by OH^- ions and which will accelerate reaction 6. We also are trying to find a suitable buffer system to facilitate the formation of hydrogen peroxide and prevent the ultimate destruction of the catalyst. Such a system will make it possible to evaluate the kinetic parameters for the various reactions.

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(7) $Mn^{II}Q_3^-$ was prepared in situ in an electrochemical cell by the exhaustive controlled potential electrolysis of a 1 mM solution of $Mn^{III}Q_3 \cdot \frac{1}{2}H_2O \cdot CH_3OH$ in Me_2SO at -0.50 V vs. SCE.

(8) $Mn_2^{III}OQ_4(HQ)_2 \cdot 2CH_3OH$ was prepared by the reaction of air with a saturated solution of $Mn^{II}Q_2 \cdot 2H_2O$ in 50% CH_3OH/H_2O. The black crystals were filtered, washed with H_2O and CH_3OH, and dried in vacuo at room temperature for 2 h. Anal. Calcd for $Mn_2C_{56}N_6H_{46}O_9$. Mn, 10.39; C, 63.64; N, 7.95; H, 4.38. Found: Mn, 10.14; C, 63.70; N, 7.76; H, 4.30. Magnetic susceptibility measurements indicate that Mn(III) compounds with this stoichiometry are high-spin d^4 systems in the solid state ($\mu_{\mathrm{eff}} = 5.02\ \mu_B$ by the Guoy method; spin-only value, 4.82 μ_B), but are diamagnetic in Me_2SO solutions ($\mu_{\mathrm{eff}} \simeq 0.0\ \mu_B$ by the NMR method).[9] Because all known Mn(III)–Me_2SO complexes also are high-spin,[10] solvent effects sufficient to cause spin pairing are unlikely. The observed diamagnetism implies strong antiferromagnetic coupling of the type that is observed for other μ-oxobridged binuclear Mn(III) and Mn(IV) complexes,[11] and that the molecular form of the complex in solution is $[(HQ)Mn^{III}Q_2–O–Mn^{III}Q_2(HQ)]$.

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(13) $Mn^{II}Q^+$ probably reacts with water to form $Mn^{II}Q(OH) + H^+$. Neither manganese compound is electrochemically active.

(14) Several unsuccessful attempts have been made to isolate a Mn(III)–(8-*quinolato)–peroxide complex. Combinations in Me_2SO with reaction stoichiometries of*

$$\mathrm{6Mn^{II}Q_2 + 2O_2 + 3H_2O \rightarrow Mn_2^{III}OQ_4(HQ)_2 + 2Mn^{III}Q_2(HO_2) + 2Mn^{II}Q(OH)}$$

$$\mathrm{Mn^{II}Q_2 + H_2O_2 \xrightarrow[CPE]{+0.25\ V} Mn^{III}Q_2(HO_2) + H^+ + e^-}$$

have been studied by cyclic voltammetry. Both solutions exhibit an additional cathodic peak at -0.75 V (besides the peak at -0.31 V for $Mn_2^{III}OQ_4(HQ_2)$) which has the characteristic shape of H_2O_2 reductions in Me_2SO (-1.3 V) and may result from the reduction of $Mn^{III}Q_2(HO_2)$.

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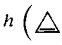
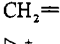
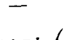
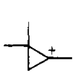
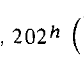
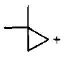
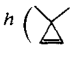
Heats of Formation of $C_3H_5^+$ Ions. Allyl, Vinyl, and Cyclopropyl Cations in Gas-Phase Proton-Transfer Reactions

Sir:

Allyl cation intermediates in solution have been known for many years,[1] but the possibility of vinyl and cyclopropyl cation intermediates has recently attracted much interest. Vinyl cations now appear to be genuine intermediates in solvolysis reactions and electrophilic additions to allenes and acetylenes in solution.[2] Up to now, however, there have been no cases in which simple cyclopropyl cations have been unambiguously demonstrated as intermediates in solvolysis reactions,[3,4] since ring opening to an allyl cation appears to be concurrent with loss of the leaving group.[5] Theoretical calculations of the $C_3H_5^+$ energy surface[6] indicate that the 2-propenyl cation is at 17 kcal/mol higher energy than the allyl cation and rearranges to the allyl cation with a 17 kcal/mol barrier, while the cyclopropyl cation is some 39 kcal/mol higher in energy than the allyl cation with little or no barrier to rearrangement.[6b,d] We report here experimental evidence on the heats of formation of $C_3H_5^+$ ions and related allyl, vinyl, and cyclopropyl cations.

Table I. Thermodynamic Data for $C_3H_5^+$ Ions and Related Allyl, Vinyl, and Cyclopropyl Cations[a]

	$\Delta H_f^\circ(R^+)$	$\Delta H_f^\circ(R^+)$calcd	D(RH)	IP(R·)	HA(R⁺)	PA(olefin)[b]
$CH_2{=}CH{-}CH_2^+$	226[c]	(226)[d]	88[e]	188[c]	258	—
$CH_2{=}\overset{+}{C}{-}CH_3$	237	243[d]	104[f]	180	266	174 ($CH_3C{\equiv}CH$, $CH_2{=}C{=}CH_2$)
	238	265[d]	100[e]	178	259	194[h] ()
$CH_3\overset{+}{C}HCH_3$	192[g]	—	95[e]	174[g]	250	181 ($CH_3CH{=}CH_2$)
$(CH_3)_3C^+$	169[g]	—	92[e]	160[g]	233	194 ($Me_2C{=}CH_2$)
$CH_2{=}C(CH_3)CH_2^+$	211[c]	(211)[i]	85[f,c]	182[c]	248	—
	222[j]	230[i]	97[f]	171	249	203[h] (), 197[h] ()
	198[k]	—	97[f]	168	246	211[h] (), 202[h] ()
	217	—	100[f]	170	251	200[h] ()

[a] All values in kcal/mol. [b] PA scale based on equilibrium and double resonance data; ref 7. [c] Reference 9. Error limits: ±2–4 kcal/mol. [d] Calculated from STO-6-31G* basis set values (ref 6b) adjusted so that the allyl cation value (218 kcal/mol) fits the experimental value. [e] D. M. Golden and S. W. Benson, *Chem. Rev.*, 69, 125 (1969); D. M. Golden, A. S. Rodgers, and S. W. Benson, *J. Am. Chem. Soc.*, 88, 3196 (1966). Error limits ca. ±2 kcal/mol. [f] Estimated from values from footnote *e*. Error limits: ca. ±3 kcal/mol. [g] Reference 11. [h] Proton affinities determined by double resonance; error limits ca. ±3 kcal/mol. [i] Calculated from STO-3G basis set (ref 6c). [j] Calculated from PA's, error ±3 kcal/mol. From the bromide affinity (158 ± 3 kcal/mol) of 1-methylcyclopropyl cation, ΔH_f° = 220 ± 3 kcal/mol. [k] Calculated from PA's, error ±3 kcal/mol.

The gas-phase protonation of propyne by H_3S^+ has been found to be reversible, and the equilibrium constant has been measured by equilibrium ion cyclotron resonance techniques.[7]

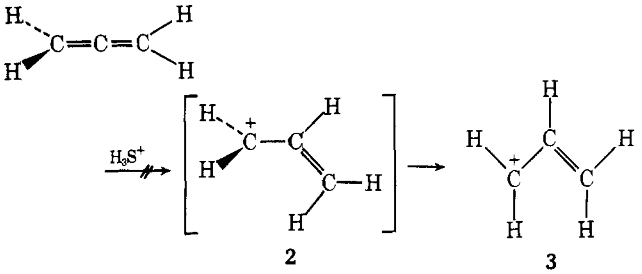
$$CH_3C{\equiv}CH + H_3S^+ \rightleftharpoons CH_3C^+{=}CH_2 + H_2S$$

$$\Delta G^0 = -2.1 \pm 0.1 \text{ kcal/mol}$$

$$CH_2{=}C{=}CH_2 + H_3S^+ \longrightarrow \underset{\mathbf{1}}{CH_3C^+{=}CH_2} + H_2S$$

$$\Delta G^0_{app} = -2.0 \pm 0.1 \text{ kcal/mol}$$

From the known proton affinity (PA) of H_2S of 172 kcal/mol,[8] the PA of propyne is 174 kcal/mol, and the heat of formation of the 2-propenyl cation, **1**, formed is 237 kcal/mol. The analogous reaction with allene has a choice of protonating on the terminal carbon to give the vinyl cation, **1**, or protonating on the central carbon to give the allyl cation **3**. The heat of formation of the allyl cation **3** is known to be 226 kcal/mol,[9] 11 kcal/mol more stable than **1**, but the proton affinity of allene is found by double resonance and apparent proton-transfer equilibrium experiments[10] to be ca. 174 kcal/mol, indicating that the vinyl cation **1** is formed rather than the allyl cation, **3**. The 2-propenyl cation structure for the ion formed from protonation of allene was confirmed by observing that this ion readily transfers a proton to methanol. The allyl cation formed from fragmentation of allyl chloride does not readily transfer protons to bases even stronger than methanol (PA = 183 kcal/mol). Protonation of allene in solution[2f] likewise gives a vinyl rather than an allyl cation, presumably because direct protonation to give the twisted allyl cation **2** is unfavorable energetically.[6b] A concerted protonation and CH_2 rotation to directly give the stable cation **3** apparently has a high enough barrier that formation of the vinyl cation **1** is preferred. Furthermore, since the ion formed from protonation of allene can reversibly proton transfer to H_2S and methanol, it is clear that it does not rapidly rearrange to the allyl cation **3** subsequent to its formation by proton transfer, as expected from the large calculated barrier for the rearrangement of **1** to **3**.[6b]



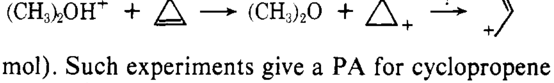
2 **3**

The heat of formation of **1** is about as expected from theoretical calculations relative to allyl cation (Table I).[6b] The calculated hydride affinity, HA(R⁺), for the 2-propenyl cation in the overall reaction (1) indicates that it requires 16 kcal/mol

$$CH_3CH{=}CH_2 \xrightarrow{D(R-H)} CH_3C{=}CH_2 + H \xrightarrow{IP(R\cdot)\,+\,EA(H\cdot)} CH_3\overset{+}{C}{=}CH_2 + H^- \quad (1)$$

more energy for formation by hydride abstraction than the 2-propyl cation.[11] This change in HA(R⁺) stems from changes in the bond dissociation energies and ionization potentials in eq 1. Although the bond dissociation energies of vinyl C–H bonds are subject to some uncertainty,[12] the D(R–H) and IP(R·) data in Table I indicate that about half of the 16 kcal/mol destabilizing effect in vinyl cations results from a high vinyl C–H bond energy and the remainder results from the IP's of vinyl radicals.[13]

Using ion cyclotron double resonance techniques, we find that cyclopropene forms a $C_3H_5^+$ ion by proton transfer from dimethyloxonium ion, reaction 2 ($PA(Me_2O)$ = 190 kcal/mol), but not from diethyloxonium ion ($PA(Et_2O)$ = 198 kcal/mol). Such experiments give a PA for cyclopropene of 194 ± 3 kcal/mol, suggesting that the $C_3H_5^+$ ion formed has a heat of formation of 238 kcal/mol. This value is not consistent with the heat of formation of allyl cation,[9] and suggests that a cyclopropyl cation might have been formed. The reaction (2) is not readily reversible and equilibrium proton transfer is not observable,[14] but the suggested heat of formation of the $C_3H_5^+$ ion formed was confirmed as 240 ± 8 kcal/mol by studying bromide transfer reactions[15] from cyclopropyl bromide to ethyl cation and 2-propyl cation.



(2)

If the cyclopropyl cation, indeed, has a heat of formation of ca. 238 kcal/mol, this would be much lower than predicted by molecular orbital calculations. The derived HA for cyclopropyl cation is 9 ± 3 kcal/mol higher, however, than that of 2-propyl cation, in rough accord with the 12 kcal/mol I-strain of introducing an sp^2 center in a three-membered ring.[5a,16] Should the heat of formation of the cyclopropyl cation be as high as indicated from MO calculations (Table I), a large (ca. 25 kcal/mol) destabilizing effect in addition to the simple I-strain effect would be required. Our results indicate clearly that the allyl cation is not readily formed by protonation and concomitant opening of the cyclopropyl ring. Concerted protonation and rearrangement to an allyl cation could, however, explain our results if this process had an energy barrier such that it could only occur at an observable rate when the protonating species has ca. 12 kcal/mol more energy than needed to form an allyl cation. In that case, the transition state might still resemble the cyclopropyl cation in structure and energy, and the apparent PA would at least give a lower limit on $\Delta H_f°(\Delta^+)$. While the structure of the $C_3H_5^+$ ion formed from cyclopropene is not yet certain; the ion formed from allene appears not to be the allyl cation as indicated earlier. In both cases, a significant barrier to a process involving protonation with concomitant rearrangement to the allyl cation must exist.

The PA's of substituted cyclopropenes give derived $\Delta H_f°$ and HA data (Table I) that show reasonable methyl group effects for an interpretation based on cyclopropyl cation formation. The 1-methylcyclopropyl cation[17] has an apparent heat of formation 11 kcal/mol higher than the methallyl cation, and its HA is 11 kcal/mol higher than the unstrained *tert*-butyl cation.[18] Similarly, the 1,2,2-trimethylcyclopropyl cation and the 3,3-dimethylcyclopropyl cation give heats of formation that are respectively 19 and 27 kcal/mol higher than those of corresponding rearranged allyl cations.[18] Thus, in all of the cases studied, either cyclopropyl cations are formed in the initial proton transfer, or the proton transfer must occur with 11–27 kcal/mol barriers to allyl cation formation in the proton transfer step.

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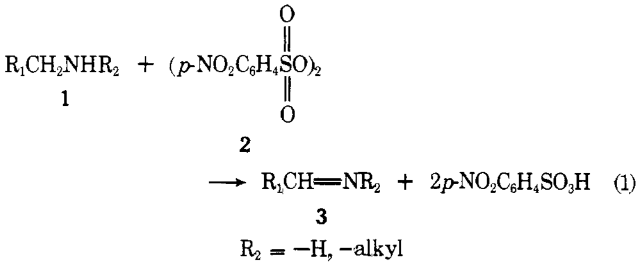
The Oxidation of Amines with Sulfonyl Peroxides

Sir:

Oxidative deamination can be achieved by a variety of methods including indirect routes[1,2] as well as direct oxidation of the amine function.[1] Metal containing oxidants such as $Pb(OAc)_4$,[3a] MnO_2,[3b] NiO_2,[3c] and Ag_2CO_3[3d] or peroxidic reagents such as hydroperoxides,[4a] acylperoxides,[4b] and sodium persulfate[4c] can be used to oxidize the amine group. Oxidative deamination with these reagents is characterized by competing oxidation processes that depend on both the amine type (primary and secondary) as well as the oxidizing agent which combine to produce a reaction that is often unpredictable and inefficient. Complex mixtures of oxidized products often result. We wish to report that both primary and secondary amines **1** can be oxidized with *p*-nitrobenzenesulfonyl peroxide (*p*-NBSP) **2** to the corresponding imine **3** (eq 1). The described oxidation is the initial report of the reactions



$$\underset{\mathbf{1}}{\mathrm{R_1CH_2NHR_2}} + \underset{\mathbf{2}}{(p\text{-}\mathrm{NO_2C_6H_4}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{O})_2} \longrightarrow \underset{\mathbf{3}}{\mathrm{R_1CH{=}NR_2}} + 2p\text{-}\mathrm{NO_2C_6H_4SO_3H} \quad (1)$$

$$\mathrm{R_2} = -\mathrm{H}, -\text{alkyl}$$

of sulfonyl peroxides with compounds other than π-electron donors and is a further characterization of the general electrophilic behavior of these peroxdes.[6] The reaction proceeds efficiently with respect to the peroxide and does not exhibit the multiple pathways often present in other amine oxidations. Hydrolysis of the imine **3** completes the oxidative deamination in fair to excellent overall yields with respect to the oxidizing agent (Table I).

Oxidations were carried out as follows: To a −78 °C solution of *p*-NBSP[6a] (0.6 g, 1.5 mmol) in ethyl acetate (30 ml) under nitrogen was added a solution of the amine (4.5 mmol for secondary amines, 6.0 mmol for primary amines) in ethyl acetate (3 ml). The amine solution was prepared under nitrogen and added by syringe. After vigorous stirring (2 h) at −78 °C, the ethyl acetate was removed on a rotary evaporator and 2 N HCl (40 ml) was added to the pasty residue. The mixture was immersed in a bath preheated to 150 °C and distilled until 15 ml of water had been collected. The distillate was treated with saturated sodium bicarbonate (20 ml) and extracted with