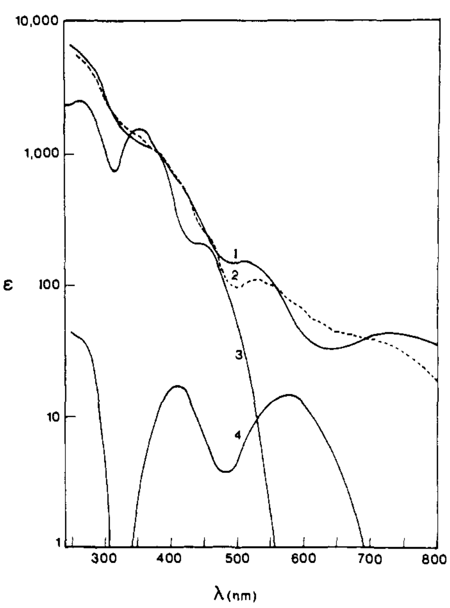


Figure 2. Spectra of chromium(VI), chromium(V), and chromium(III) in water at 25 °C: chromium(V) complex with 2-hydroxy-2-methylbutyric acid (1), chromium(V) complex with citric acid (2), chromium(VI) at the beginning (3) and chromium(III) at the end (4) of the oxidation of 2-hydroxy-2-methylbutyric acid by chromic acid under conditions given in Figure 1.

Scheme III

$$\mathrm{Cr(VI)} + 2\mathrm{HMBA} \rightarrow \mathrm{Cr(III)} + 2\mathrm{MEK} + \mathrm{CO_2} + \cdot\mathrm{CO_2H}$$

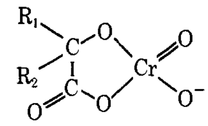
$$\mathrm{Cr(VI)} + \cdot\mathrm{CO_2H} \rightarrow \mathrm{Cr(V)} + \mathrm{CO_2}$$

The nature of the intermediates formed in the first phase of the reaction can be conveniently examined when the oxidation is interrupted by cooling the reaction mixture down to room temperature. At this point the color has changed from the original yellow to red-brown. The absorption spectra (corrected by subtracting the chromium(III) absorption), shown in Figure 2, together with the spectra of chromium(VI) and chromium(III) are in good agreement with the spectrum previously obtained for the chromium(V)-oxalic acid complex[8] and are completely different from the spectra of any known chromium(IV) compounds.[11,12] The conclusion that the intermediates are chromium(V) species is also consistent with the known extreme instability and reactivity of chromium(IV) in aqueous solutions.[13-18]

The solutions of the chromium(V) complexes are stable at room temperature for several hours, at 0 °C for about 1 day, and can be stored frozen at −20 °C for several weeks. Their stability can be extended considerably by careful deaeration. The solution obtained in the chromic acid oxidation of 2-hydroxy-2-methylbutyric acid has been further purified by passing it through a cation exchange column (Dowex 50W-X8) which did not affect the chromium(V) complex, but completely removed chromium(III). The chromium(III)-free solution was analyzed iodometrically (a) directly and (b) after oxidation to chromium(VI) by hydrogen peroxide in alkaline solution. The ratio of the I_3^- yields in procedures (a) and (b) were 1:1.52 providing additional proof that the complex is a chromium(V) compound.

While chromium(V) resembles in many respects chromium(VI),[8,19,20] its reactivity towards iodide ions is greater by a factor of more than 50 (for HMBA). This observation permitted the development of a method for the quantitative analysis of chromium(V)-chromium(VI) mixtures.[21]

Although insufficient information about the nature of the chromium(V) complexes is available at this time, the following structures appear plausible and are consistent with the need for two functional groups to stabilize the chromium(V) valence state. Kinetic data[21] suggest that the chromium(V) compound first produced is a 1:1 complex, although it is entirely possible that the stable complex contains an additional molecule of hydroxyacid. The negative charge is consistent with the observation that the complexes are not absorbed by a cation-exchange resin, but are retained by an anion-exchange column (Dowex 2-X8).



I, $R_1 = CH_3$; $R_2 = CH_2CH_3$

II, $R_1 = R_2 = CH_2CO_2H$

The second phase of the reaction in which chromium(V) is rapidly reduced to chromium(III) appears to involve a free radical chain reaction initiated by traces of oxygen and inhibited by chromium(VI).

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Chemistry of Superoxide Ion. II. Reaction with Hydroperoxides[1]

Sir:

The elegant work of Fridovich and his group[2] has clearly demonstrated the damaging effects of superoxide ion ($O_2\cdot^-$) in biological systems. However, little work has yet appeared on the chemical reactions which superoxide can undergo with simple organic substrates.[1,3-11]

Both H_2O_2 and $O_2\cdot^-$ are formed in the reaction of xanthine oxidase with its substrates, and the system is destructive to organisms.[12] However, neither H_2O_2 nor $O_2\cdot^-$ alone is sufficient to account for the damage, and it has been hypothesized that OH·, a powerful oxidizing agent, is produced in the reaction of H_2O_2 and $O_2\cdot^-$.[12-14]

$$H_2O_2 + O_2\cdot^- \rightarrow OH\cdot + OH^- + O_2$$

As a model for this reaction, we have studied the reaction

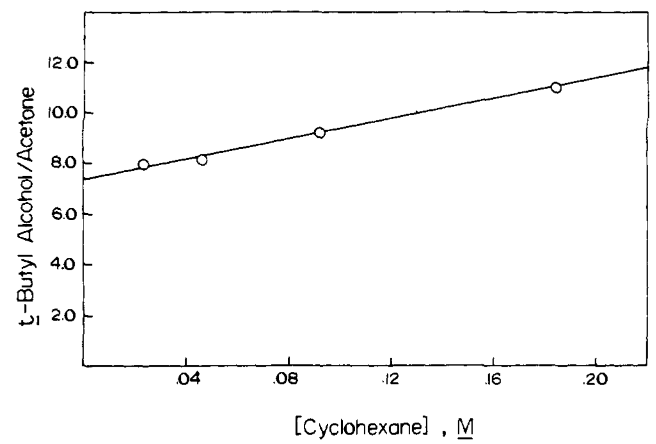

Figure 1. Alcohol/acetone ratio from the reaction of *tert*-butyl hydroperoxide with $(CH_3)_4N^+O_2\cdot^-$ in CH_3CN as a function of added cyclohexane.

between alkyl hydroperoxides and $O_2\cdot^-$ and report that alkoxy radicals are a major product of the reaction.

$$ROOH + O_2\cdot^- \rightarrow RO\cdot$$

The experiments were carried out using tetramethylammonium superoxide,[15] a reagent which is soluble in polar aprotic solvents (up to 0.05 M in CH_3CN) and provides a convenient, easily handled source of superoxide. In preliminary experiments, 0.01 M *tert*-butyl hydroperoxide in dry acetonitrile was rapidly added to an equivalent amount of solid $(CH_3)_4N^+O_2\cdot^-$.[16] The products (determined by GLC, internal standard) were acetone (0.001 M) and *tert*-butyl alcohol (0.009 M). When an identical experiment was carried out, except with 0.02 M *tert*-butyl hydroperoxide and half an equivalent of superoxide, the products were acetone (0.001 M), *tert*-butyl alcohol (0.009 M), and unreacted hydroperoxide (0.01 M). Thus the reaction is stoichiometric. No other products were detectable by GLC. Depending on the rate of addition, a pale pink to burgundy color developed; the solution again became colorless within 30 s after addition was complete.

The β-scission of alkoxy radicals (k_d) and hydrogen abstraction from solvent or added H donor (k_a) are well-established reactions.[17,18] The relative rates of the two processes provide a convenient diagnostic test for the presence of alkoxy radicals, in comparison with values determined in other reactions.[19]

$$R(CH_3)_2CO\cdot \xrightarrow{k_d} CH_3COCH_3 + R\cdot$$

$$R(CH_3)_2CO\cdot + R'H \xrightarrow{k_a} R(CH_3)_2COH + R'\cdot$$

If k_d and k_a are the only sources of acetone and *tert*-butyl alcohol, respectively, a plot of alcohol/acetone ratios against added R'H should yield a linear relationship with a slope of k_a/k_d. A comprehensive study of this type was originally done by Walling and Wagner,[20] with k_a/k_d ratios determined as a function of solvent and temperature using *tert*-butyl hypochlorite as a source of *tert*-butoxy radicals.

To determine whether *tert*-butoxy radicals are generated from the reaction of superoxide with *tert*-butyl hydroperoxide, a similar study was carried out. All experiments were done at room temperature (23 °C) in dry acetonitrile (refluxed and distilled over P_2O_5). A series of solutions of *tert*-butyl hydroperoxide (0.01 M) containing various amounts of cyclohexane (R'H) was prepared and added dropwise, with stirring, to flasks containing an amount of solid $(CH_3)_4N^+O_2\cdot^-$ equivalent to the hydroperoxide. After addition of internal standard (toluene), the acetone and *tert*-butyl alcohol were determined by GLC.[21] The alcohol/acetone ratios are plotted as a function of cyclohexane concentration (Figure 1). The value of (k_a/k_d) determined from this plot is $19.6 \pm 0.6\ M^{-1}$, in good agreement with the value of Walling and Wagner[20] for *tert*-butoxy radicals generated from *tert*-butyl hypochlorite in CH_3CN at 25 °C ($19.8\ M^{-1}$).

It was also shown by Walling and Padwa[22] that changing the structure of the alkyl groups attached to the alkoxy radical drastically alters the product ratios, with β-scission becoming more favorable with increasing stabilization of R·.[18,22] Thus k_a/k_d changed from 50 to 0.5 as R was changed from CH_3 to C_2H_5 (for hypochlorites in CCl_4, 40 °C, R'H = cyclohexane).[22] These conditions could not be duplicated because the superoxide is not soluble in CCl_4. However, qualitatively similar behavior is observed. Thus reaction of *tert*-amyl hydroperoxide in CH_3CN (23 °C, no added H donor) as described above gave an alcohol/acetone ratio of 0.5, compared to 7.4 for *tert*-butyl hydroperoxide.

These results support the contention that alkoxy radicals are generated in the reaction of $O_2\cdot^-$ with hydroperoxides. Extrapolation to the H_2O_2 system would suggest that $O_2\cdot^-$ should react with hydrogen peroxide to give hydroxyl radicals.

Hydroperoxides might also react with $O_2\cdot^-$ to give $\cdot OH + RO^-$ instead of $RO\cdot + OH^-$. However, the latter reaction is more favorable from electronegativity arguments, and the k_a/k_d value determined in Figure 1 should have been much higher if an appreciable fraction of the other reaction was occurring.

Either reaction predicts O_2 production equivalent to the hydroperoxide consumed. In initial experiments with potassium superoxide, we did find an equivalent of O_2 evolved based on hydroperoxide, but the reaction was found to produce no color during addition of reactants. However, using the much more soluble $(CH_3)_4N^+O_2\cdot^-$, 60% or less of O_2 was evolved (depending on addition rate), but a colored intermediate was formed as discussed earlier. (Probably the O_2 is consumed by radicals formed by reaction of *tert*-butoxy radicals with solvent, as well as with $CH_3\cdot$ formed).

An alternative reaction between $O_2\cdot^-$ and *tert*-butyl hydroperoxide to give *tert*-butylperoxy radical and H_2O_2 could also generate *tert*-butoxy radicals by the reaction shown below. However, some (3-5%) di-*tert*-butyl peroxide should have been formed from cage recombination if this reaction was taking place,[23] and none (detection limit 0.05%) was found in any of the experiments, although it is easily detected gas chromatographically, and is much less reactive to superoxide than the hydroperoxide.[24]

$$(CH_3)_3COOH \xrightarrow[R\cdot]{} (CH_3)_3COO\cdot$$

$$2(CH_3)_3COO\cdot \rightarrow (2x)(CH_3)_3CO\cdot + (1 - x)(CH_3)_3COOC(CH_3)_3 + O_2$$

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(24) As a control, 0.01 M *tert*-butyl hydroperoxide, and 0.005 M di-*tert*-butyl peroxide in 50 ml of CH_3CN was added to 0.5 mmol of solid tetramethylammonium superoxide; the products were 0.009 M *tert*-butyl alcohol, 0.001 M acetone, and 0.005 M di-*tert*-butyl peroxide. Also, a similar reaction without hydroperoxide gave peroxide and only a trace of alcohol after 30 min.

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Classical and Nonclassical Structures of the Vinyl Cation. An Accurate Computational Determination of Their Relative Stabilities and Optimum Rearrangement Path

Sir:

Vinyl cations are known[1] to play an important role as highly reactive intermediates in many organic reactions. Since they can have two possible structures, a classical linear one (Figure 1a) and a nonclassical bridged one (Figure 1b), a knowledge of the relative stabilities of both forms and the activation barrier between them is needed for a better understanding of their chemistry. In the absence of experimental data, these properties have to be deduced from theoretical calculations done on the parent system $C_2H_3^+$. The ab initio calculations reported in this communication, which include an accurate evaluation of correlation effects through extensive configuration interaction (CI), lead to the following chemical predictions after a critical estimation of all errors which can arise from defects in the calculations. (i) The two structures, both corresponding to minima in the potential energy surface, have the same energy to within 1-2 kcal/mol, the bridged structure probably having the lower energy. (ii) Molecular conformations along the lowest energy path for rearrangement from linear to bridged structures are planar. (iii) The barrier to rearrangement is small, less than 1-3 kcal/mol.

Previous calculations have addressed the question of the relative stabilities of the two structures, but have not given a definitive answer: semiempirical methods are known to strongly overestimate the stabilities of the nonclassical ions,[2,3] ab initio self consistent field (SCF) calculations[4,5] do not include correlation effects, and the independent-electron-pair approximation used in the CI approach of Zurawski et al.[6] lacks the so-called additivity corrections.[7] There have been no previous predictions of the rearrangement path. In our calculations, two levels of wave functions were computed for each nuclear conformation, (i) an SCF wave function for the dominant closed shell configuration in which occupied orbitals are expanded in a contracted Gaussian basis of "double-ζ plus polarization" quality, and (ii) a CI wave function, obtained by diagonalizing the Hamiltonian in an n-particle space spanned by the SCF configuration and all configurations derivable from it by single and double electron excitation into the unoccupied SCF orbitals. Energy differences between the SCF and CI wave functions give the correlation corrections to the potential energy surface. The calculations will be fully described elsewhere.[8,9]

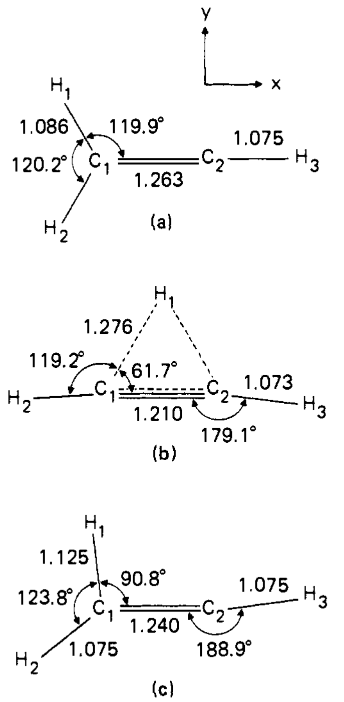

Figure 1. Optimized geometries for the vinyl cation: (a) classical (C_{2v}); (b) bridged (C_{2v}); (c) intermediate α = 90.8°. Internuclear distances are in Å.

SCF energies of the linear and bridged structures have been minimized with respect to all geometrical parameters, whose optimum values are shown in Figures 1a and 1b. We have determined computationally that these minimum energy structures are planar C_{2v}. Three points on the reaction path were chosen to give equal increments in the angle $H_1C_1C_2$ (Figure 1) between the linear and bridged structures. Having fixed this angle, α, the SCF energies were minimized with respect to variation of all the remaining geometrical parameters. Figure 1c shows the optimized conformation when angle α is halfway between its linear and bridged values (α = 90.8°). All points on the minimum energy reaction path, presented in Figure 2, have been shown computationally to be planar. We have determined that during the migration of H_1 (Figure 1) along the reaction coordinate, the atom H_3 moves trans to H_2, with angle $C_1C_2H_3$ equal to 188.9° when α = 90.8°, and then back through the linear position to a final $C_1C_2H_3$ angle of 179.1°. This emphasizes the necessity of geometrical optimization; assumed interpolations using only the linear and bridged geometries can result in errors of several kilocalories per mole in the energy along the reaction path. It is noteworthy that the $H_2C_1C_2H_3$ conformation in the bridged structure has a geometry very close to that of acetylene; π-protonation of acetylene causes very little distortion.

Figure 2 shows the reaction path computed with CI wave