entropy change from reactants to the transition state becomes

$$\Delta S^{\circ\ddagger} \cong [\text{C-(C)(H)}_3] - [\text{C-(C)(H)}_2\text{(I)}] - 3.7 + R \ln 12 - S^{\circ}(\text{I,g,298}) \cong -30 \text{ cal mol}^{-1} \text{ K}^{-1} \quad [\langle \Delta C_{\text{p}}{}^{\circ} \rangle = 0] \quad (15)$$

This model should represent a very tight transition state[13] yet yields an *A* factor of $10^{9.0}$ l. mol^{-1} sec^{-1} at 500°K, a factor of 5 greater than observed. Thus, the trend toward lower *A* factors with sucessive methyl substitution, first indicated in the results for *trans*-2-butene and now confirmed in this work, must remain an anomaly until further work is done on related systems. It is interesting to note that, as is frequently the case, the decrease in the activation energy in these reactions is almost exactly compensated by this decrease in the *A* factors.

Finally, it is worthwhile to consider the dependence of our conclusions upon the estimation of E_{b} and E_{c}. Since, from thermochemistry[8]

$$DH^{\circ}_{298}(\text{DM-2B,C}_{\text{p}}\text{-H}) - DH^{\circ}_{298}(\text{DM-1B,C}_{\text{t}}\text{-H}) = 1.7 \text{ kcal mol}^{-1}$$

it would be very unlikely that $|E_{\text{b}} - E_{\text{c}}| > 2$ kcal mol^{-1} even if E_{b} and E_{c} should prove greater than the estimated 1 kcal mol^{-1}. As a result then, $k_{\text{b}}/(k_{\text{b}} + k_{\text{c}})$ and $k_{\text{c}}/(k_{\text{b}} + k_{\text{c}})$ will still be temperature independent and $E_{\text{a}} = E_1$ and $E_{\text{d}} = E_2$ as before. However, the bond dissociation energies would now be given by

$$DH^{\circ}_{298}(\text{DM-2B,C}_{\text{p}}\text{-H}) = 78.0 - (E_{\text{c}} - 1.0) \text{ kcal mol}^{-1}$$

and

$$DH^{\circ}_{298}(\text{DM-1B,C}_{\text{t}}\text{-H}) = 76.3 - (E_{\text{b}} - 1.0) \text{ kcal mol}^{-1}$$

They would become weaker!

Thus, while our quantitative results depend upon the estimation of E_{b} and E_{c}, the general conclusion that the allyl radical is stabilized by methyl substituents (and by about 3 kcal mol^{-1} per group) does not.

Kinetics of Competing Free Radical Reactions with Nitroaromatic Compounds

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Abstract: Rate constants for the competing reactions between alcohol donor free radicals and nitroaromatic compounds, and their relative efficiencies, have been measured by pulse radiolysis. The kinetics of formation of the nitroaromatic anion species are dependent upon the sum of the rate constants for both competing reactions and not upon the rate constant for radical oxidation alone. The rate constants for donor radical oxidation and adduct formation increase with increasing redox potential of the electron acceptor. Although α- and β-hydroxy radicals have similar reactivities, α-hydroxy radicals are oxidized preferentially whereas β-hydroxy radicals predominantly form adducts.

The high reactivity of free radicals with organic nitro compounds and other electron acceptors is well recognized. Electron-transfer oxidation by nitro compounds of $\cdot\text{CO}_2\text{H}$ or $\cdot\text{CO}_2^-$, α-hydroxy, and α-alkoxy radicals has been demonstrated by electron spin resonance studies.[1-4] Alkyl and β-hydroxy radicals and the radicals $\cdot$OH and $\cdot\text{NH}_2$, on the other hand, react readily by addition to the electron acceptor.[5-7] The rates of alkyl radical adduct formation,[5,6] like those of α-hydroxy radical oxidation,[3,8] increase with increasing redox potential of the electron acceptor. We have studied the kinetics of these competing donor free radical reactions with nitroaromatic compounds by direct observation of the reactive species, using the technique of pulse radiolysis.[9] The extent of donor radical oxidation is obtained from the yield of the transient radical anion of the nitro compound, and the rate constants for radical oxidation and adduct formation are determined from the rates of build-up of the nitroaromatic radical anion for different concentrations of nitro compound, according to the kinetic analysis described. These data are particularly important in the study of chemical and biological radiosensitization.[8,10,11] Electron-affinic compounds,[11] particularly nitroaromatic and nitroheterocyclic compounds, are believed to radiosensitive at low concentrations by

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secondary reactions involving radicals formed in the biological "target(s)."[8,10,11] Experiments of the type described in this paper enable us to study the kinetics of these competing reactions between simple chemical "target" radicals and nitroaromatic compounds as potential radiosensitizers.

Experimental Section

The experimental details of the nanosecond pulse radiolysis experiments to detect transient absorbing species by kinetic spectrophotometry have been described previously.[9] The radical species were generated in aqueous samples contained in a 1-cm path quartz cell by 50-nsec pulses of 3-MeV electrons delivering doses in the range 0.5 to 5 krad/pulse and characterized by their transient absorption spectra. The dose per pulse was monitored with a Faraday cup mounted behind the cell and the monitor was calibrated using the thiocyanate method.[12] The calculation of yields of nitroaromatic anions and alcohol radical oxidation efficiencies were based on the generally accepted values for the radiation chemical yields of the primary species in aqueous solutions: $G(e_{aq}^-) = 2.7$, $G(OH) = 2.8$, and $G(H) = 0.6$ (G = number of species formed per 100 eV of absorbed energy). To study radical oxidation reactions, hydrated electrons were converted to hydroxyl radicals as the principal reactive species by bubbling N_2O through the solutions in a multisample degassing unit, prior to irradiation. Direct electron attachment was studied in deoxygenated solutions containing 0.5 *M* *tert*-BuOH to scavenge OH. Fresh samples were admitted after each pulse. All solutions were prepared using triple distilled water. Nitrobenzene (Aldrich) was distilled, *p*-nitroacetophenone (Aldrich) was recrystallized from ligroin, and *anti*-5-nitro-2-furaldoxime (Aldrich) was used without purification.

Results and Discussion

All the donor free radicals ($\cdot RH$, $\cdot ROH$) formed by OH attack in the absence of nitroaromatic electron acceptor (NA) were shown to have negligible transient absorption above 300 nm. In aqueous N_2O saturated solutions at neutral pH, containing excess donor (RH_2, R) and from 10 to 100 × 10^{-6} *M* nitrobenzene, *p*-nitroacetophenone, or *anti*-5-nitro-2-furaldoxime, the competing reactions 3a and 3b of donor free radicals with each nitroaromatic electron acceptor were studied by monitoring the rate of formation of the transient nitroaromatic radical anion absorption (NA^-) as a function of [NA].

$$OH + RH_2 \longrightarrow \cdot RH + H_2O \qquad (1)$$

$$OH + R \longrightarrow \cdot ROH \qquad (2)$$

$$\cdot RH(\cdot ROH) + NA \xrightarrow{k_{ox}} RH^+(ROH^+) + NA^{-\cdot} \qquad (3a)$$

$$\cdot RH(\cdot ROH) + NA \xrightarrow{k_{add}} \cdot RHNA(\cdot ROHNA) \qquad (3b)$$

In all cases, the build-up of NA^- was exponential and first order in [NA]. The NA^- absorption spectra under these conditions agree closely with those obtained by direct e_{aq}^- attachment,[8,10] indicating that any adducts formed probably contribute negligible absorption in the wavelength range of observation. Spectral measurements of NA^- absorptions were made at the maxima: 400 nm for nitrobenzene (NB), 360 and 550 nm for *p*-nitroacetophenone (PNAP), and 395 nm for *anti*-5-nitro-2-furaldoxime (NF).

From a consideration of the following differential equations describing the rates of formation and decay of NA^- and $\cdot RH(\cdot ROH)$, respectively, a fact emerges which has not been fully appreciated in the literature.[13] Equation C shows that the "observed" rate of build-up of NA^-, $d[NA^-]/dt$, depends upon the sum of the rate constants $k_{ox} + k_{add}$ rather than upon the rate constant k_{ox} for oxidation alone, except where this reaction predominates. Since NA is in excess, $[NA] \simeq [NA]_0$

$$\frac{-d[\cdot RH]}{dt} = \frac{d[NA^-]}{dt} + \frac{d[\cdot RHNA]}{dt} =$$

$$(k_{ox} + k_{add})[NA]_0[\cdot RH] = \frac{k_{ox} + k_{add}}{k_{ox}}\frac{d[NA^-]}{dt} \qquad (A)$$

which, upon integration from time 0 to *t*, gives

$$[\cdot RH]_0 - [RH] = (k_{ox} + k_{add})/k_{ox}[NA^-] \qquad (B)$$

$$\therefore \frac{d[NA^-]}{dt} = k_{ox}[NA]_0[\cdot RH] =$$

$$-(k_{ox} + k_{add})[NA]_0[NA^-] + k_{ox}[NA]_0[\cdot RH]_0 \qquad (C)$$

$$\text{oxidation efficiency} = [k_{ox}/(k_{ox} + k_{add})]100\% \qquad (D)$$

The rate constant for oxidation is obtained experimentally by multiplying the "observed" rate constant ($k_{ox} + k_{add}$) obtained from the kinetics for build-up of NA^- by the oxidation efficiency. The rate constant for adduct formation is then the difference between the experimentally measured rate constant ($k_{ox} + k_{add}$) and the true calculated rate constant (k_{ox}) for NA^- formation.

Table I lists the oxidation efficiencies and the rate constants for radical oxidation and adduct formation for various alcohol radicals. The α-hydroxy radicals formed predominantly[14,15] in 1-propanol and 1-butanol are oxidized with a high efficiency by all three nitroaromatic electron acceptors, the rate constants for oxidation increasing with the redox potential of the acceptor. For the alcohols with an unsaturated >C=C< double bond, OH attack leads to a β-hydroxy radical adduct which is not readily oxidized by electron acceptors, including nitro compounds.[15] However, these radicals are still reactive, presumably forming adducts with the nitroaromatic compounds. Consequently, although the true rate constant for oxidation is low, the "observed" build-up of NA^- is very fast owing to the competing donor radical–acceptor re-

Table I. Oxidation Efficiencies and Rate Constants for Donor Radical Oxidation and Adduct Formation

Donor	Acceptor	Oxidation efficiency, %	Obsd	k, 10^9 M^{-1} sec^{-1}, oxidation	Adduct formation
1-Propanol	NB	60	1.0	0.6	0.4
	PNAP	45	2.4	1.1	1.3
	NF	52	3.2	1.6	1.6
1-Butanol	NB	31	1.1	0.3	0.8
	PNAP	24	2.2	0.6	1.6
	NF	32	3.4	1.1	2.3
Crotyl alcohol	NB	8	~1	~0.1	~0.9
	PNAP	9	2.0	0.2	1.8
	NF	10	2.4	0.2	2.2
Allyl alcohol	NB	5	~1.5	~0.1	~1.4
	PNAP	3	2.7	0.1	2.6
	NF	3	5.1	0.15	5.0

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actions. This competition is reflected by the low yield of NA^- measurable (as given by the low-oxidation efficiency). Again, the calculated rate constants for adduct formation increase with increasing nitro compound redox potential (NB < PNAP < NF).

The α-hydroxy radicals, formed by H abstraction, dissociate to form R^- at the $pK_a \sim 10$.[16] The same species R^- generated in alkaline solution by e_{aq}^- attachment to R have previously been shown to undergo rapid electron-transfer oxidation to restore R, and the rate constants are similar to those shown in Table I.[17] The RH^+ species formed by electron-transfer oxidation of $\cdot RH$, at neutral pH, will also rapidly dissociate to give a stable molecule R. For crotyl and allyl alcohols, deprotonation of $\cdot ROH$ and ROH^+ does not produce a stable species, and this may, in part, explain the low-oxidation efficiencies observed. Such specificities for reactions of biochemical free radicals with nitroaromatic compounds and other electron-affinic agents are now being studied by pulse radiolysis in an effort to explain the relative biological efficiencies of different cellular radiosensitizers.

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Electron Paramagnetic Resonance Studies of Equilibrium and Kinetics of Solvation and Ion Pair Structure. Solvation of Fluorenone Ketyls by Alcohol

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Abstract: Solvation of alkali metal ketyls of fluorenone by various alcohols was investigated. The effects of solvation on the alkali metal splittings and carbonyl ^{13}C splittings were carefully investigated. The observed changes of splittings were explained in terms of the solvation processes involving three solvated species. The possible structures of the solvated ion pairs were suggested from the values of splittings to best fit the experimental values. The line broadening due to the modulation of isotropic hyperfine splittings by solvation processes was investigated in several systems. The rates of formation of the solvated complexes and the lifetimes of the solvated complexes are estimated in sodium fluorenone in *i*-PrOH–THF mixtures.

Radical ions prepared by the alkali metal reduction of aromatic molecules form ion pairs in various organic solvents.[1] Since the structures and reactivities of ion pairs are strongly affected by solvation processes,[2-4] it is desirable to know the details of the solvation processes in order to understand the behavior of ion pairs in a variety of solutions. Epr is suited to investigating the microscopic details of the solvation processes, but most of the previous solvation studies of radical anions were limited to the dissociated free ions.[5-10] Furthermore, no data on the rates of formation and dissociation of solvated complexes were obtained in the previous studies. Accordingly, we have attempted to investigate the process of solvation of both cations and anions. The process of cation solvation by polar solvents such as DMF was described in detail in a previous paper.[4] In the present paper we discuss the solvation of ion paired anions by various alcohols.

Many radical anions are unstable in solutions containing protic solvents such as alcohol. However, we found that many ketyls are stable in the mixtures of alcohol and ether. Ketyls form alcohol solvated complexes through hydrogen bonding to the carbonyl oxygen atom. Since the cation is situated in the neighborhood of the carbonyl oxygen, solvation by alcohol can change the ion pair structure. The structural changes of ion pairs should be reflected in changes of the alkali metal splittings as well as the proton and the carbonyl ^{13}C splittings.

In this work we chose fluorenone ketyls and investigated the solvation of various alcohols to ion paired fluorenones. The solvation of free fluorenone anion by alcohol in DMF solution was studied previously by Luckhurst and Orgel.[7] Here we attempt to elucidate the detailed steps of the solvation processes and the structures of the solvated ion pairs and to study the kinetics of the solvation and desolvation processes.[11]

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