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Progress Report

PULSE RADIOLYTIC STUDIES OF ELECTRON TRANSFER PROCESSES
AND APPLICATIONS TO SOLAR PHOTOCHEMISTRY

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SCOPE

The pulse radiolysis technique is applied to the study of electron transfer processes in a variety of chemical systems. Reactive intermediates are produced in solution by electron pulse irradiation and the kinetics of their reactions are followed by time resolved absorption spectrophotometry. Complementary experiments are carried out with excimer laser flash photolysis. These studies are concerned with mechanisms, kinetics, and thermodynamics of reactions of organic and inorganic radicals and unstable oxidation states of metal ions. Reactions are studied in both aqueous and non-aqueous solutions. The studies focus on the unique ability of pulse radiolysis to provide absolute rate constants for reactions of many inorganic radicals and organic peroxy radicals, species that are key intermediates in many chemical processes. A special concern of this work is the study of electron transfer reactions of metalloporphyrins, which permits evaluation of these molecules as intermediates in solar energy conversion. Metalloporphyrins react with free radicals via electron transfer, involving the ligand or the metal center, or via bonding to the metal, leading to a variety of chemical species whose behavior is also investigated.

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Electron transfer and other reactions of various short-lived intermediates have been studied by pulse radiolysis and, in certain cases, by laser flash photolysis. The highlights of our results during the past year are summarized below under two main sections: (a) metalloporphyrin electron transfer and associated reactions, and (b) solvent effects on reactions of inorganic radicals and organic peroxy radicals.

(a) Metalloporphyrin Electron Transfer and Associated Reactions

Metalloporphyrins are considered as efficient photosensitizers for solar energy conversion and storage due to their broad absorption spectra in the visible light range and to the rich redox chemistry of the various synthetic metalloporphyrins available. The rich redox and organometallic chemistry of some metalloporphyrins also led to their use as homogeneous catalysts in various reactions. The general aim of our studies is to understand the electron transfer reactions of various metalloporphyrins and their radicals in order to be able to apply them as photosensitizers, e.g. in the photochemical decomposition of water to hydrogen and oxygen, and as catalysts in various reactions.

In several metalloporphyrins, redox reactions involving the metal center may take place with nearly the same potential as those involving the porphyrin ligand; the actual mode of reaction, then, is critically dependent on minor changes in structure or medium. Since metalloporphyrins may catalyze

specific reactions via oxidized or reduced states of their metal centers, we have examined the initial products of one-electron reduction and oxidation of several metalloporphyrins (of Co, Ni, and Cr) by pulse radiolysis in various media and discovered their dependence on porphyrin structure, axial ligands, and medium. The most critical dependence was found for the reduction of chromium(III) porphyrins, where the pathway of the initial reduction was found to depend strongly on the electron affinity of the porphyrin ligand and on the electron donor properties of the axial ligands, L_1 and L_2 , which affect the electron density on the metal center.

If we classify the axial ligands as weak ($L_w = Cl^-$), intermediate ($L_i = ROH, RO^-, H_2O, OH^-$), and strong ($L_s = \text{pyridine, DMSO}$) electron donors, we find that Cr^{III} -tetraphenylporphyrin is reduced to $Cr^{II}P$ when the Cr center bears L_wL_i , but yields the $Cr^{III}P^{\cdot\cdot}$ when the Cr bears L_iL_i or L_wL_s . Pyrrole-substituted porphyrins, whose macrocyclic rings have lower electron affinities than tetraphenylporphyrin, are reduced on the π -system only when the Cr center bears L_iL_s or stronger ligands but form $Cr^{II}P$ with weaker ligands.

Metalloporphyrins reduced at the metal center often react with carbon-centered radicals to form metal-carbon bonds, which are important intermediates in various reactions. We have

studied the reactions of alkyl ($\cdot\text{CH}_3$, $\cdot\text{C}_2\text{H}_5$, $\cdot\text{C}_4\text{H}_9$, $\cdot\text{CH}_2\text{CO}_2^-$, $\cdot\text{CH}(\text{CO}_2^-)_2$, $\cdot\text{CH}_2\text{CN}$) and fluoroalkyl ($\cdot\text{CF}_3$, $\cdot\text{CF}_2\text{Cl}$) radicals with Ni-, Fe-, and Mn-porphyrins (P) by radiolytic techniques in various solvents. All the radicals (R) react with $\text{Fe}^{\text{II}}\text{P}$ to form $\text{R-Fe}^{\text{III}}\text{P}$ with stable Fe-C bond. These products are oxidized by O_2 to $\text{Fe}^{\text{III}}\text{P}$. Although $\text{Ni}^{\text{I}}\text{P}$ and $\text{Ni}^{\text{II}}\text{P}$ also react rapidly with the radicals to form Ni-C bonds, only the reactions of fluoroalkyl radicals with $\text{Ni}^{\text{I}}\text{P}$ yield stable products. Reactions of alkyl radicals with $\text{Ni}^{\text{I}}\text{P}$ result in unstable $\text{R-Ni}^{\text{II}}\text{P}$ products ($t_{1/2}$ several seconds) that eventually yield $\text{Ni}^{\text{II}}\text{P}$. Reactions of alkyl radicals with $\text{Ni}^{\text{II}}\text{P}$ are reversible and the short lived $\text{R-Ni}^{\text{III}}\text{P}$ products ($t_{1/2} \sim \text{ms}$) disappear through radical reactions, with recovery of $\text{Ni}^{\text{II}}\text{P}$. Alkyl radicals react rapidly with $\text{Mn}^{\text{II}}\text{P}$, probably via addition to the metal, but the adduct gives $\text{Mn}^{\text{III}}\text{P}$ immediately. $\cdot\text{CF}_3$ radicals also react with $\text{Mn}^{\text{III}}\text{P}$ by addition to C=C bonds of the porphyrin ligand.

In the case of chromium mesoporphyrin-IX (MSP), both the Cr^{II} and the Cr^{III} states react rapidly with carbon-centered radicals to form relatively stable Cr-C bonds. The products of these reactions are formulated as $\text{R-Cr}^{\text{III}}\text{MSP}$ and $\text{R-Cr}^{\text{IV}}\text{MSP}$, respectively. Whereas $\text{Cr}^{\text{II}}\text{MSP}$ is oxidized by O_2 very rapidly to $\text{Cr}^{\text{III}}\text{MSP}$, $\text{R-Cr}^{\text{III}}\text{MSP}$ is oxidized more slowly to give the same product, $\text{Cr}^{\text{III}}\text{MSP}$, and $\text{R-Cr}^{\text{IV}}\text{MSP}$ is oxidized very slowly to give a product oxidized on the porphyrin ring. The observed stability of $\text{R-Cr}^{\text{IV}}\text{MSP}$ is in contrast with the reported very short lifetime of other R-Cr^{IV} species.

Certain alkyl-metalloporphyrins have been found to undergo alkyl transfer from the metal to the pyrrolic nitrogen upon oxidation, and the reverse process upon reduction. To unravel the mechanism of this unique alkyl transfer process, we have examined this reaction with several water soluble metalloporphyrins. N-Methyl-tetrakis(4-sulfonatophenyl)-porphinato-Co(II), -Ni(II), and -Cu(II) [$M^{II}(N-Me)TSP\bar{P}$] have been prepared and their reduction in aqueous solutions has been studied by radiolytic methods. In all cases, one-electron reduction was found to take place on the ligand to form transient π -radical anions, [$M^{II}(N-Me)TSP\bar{P}$] $\cdot^-$. These species were found to undergo two competing reactions, (a) disproportionation and protonation to yield the two-electron reduced phlorin anions, $M^{II}(N-Me)TSP\bar{P}H^-$, a process that is favored at high radical concentration, or (b) migration of the methyl group from the pyrrolic nitrogen to the metal center to form metal-carbon bonds, $MeM^{III}TSP\bar{P}$. Both pathways were observed with the Co and Ni derivatives, and their contributions depended on the experimental conditions. Moreover, the Ni derivative produced $MeNi^{III}TSP\bar{P}$ which was unstable and gave $Ni^{II}TSP\bar{P}$ and methyl radicals. Independent experiments on the reaction of methyl radicals with $Ni^{II}TSP\bar{P}$ indicated an equilibrium process, in agreement with the results discussed above. In the case of the Cu complex, on the other hand, only disproportionation of the radical anion was observed and no evidence was found for methyl group transfer.

This latter observation of the radical anion of $Cu^{II}-(N-$

Me)TSPP is in line with various reports suggesting that Cu^{II} -porphyrins are reduced on the ligand. Other reports, however, suggested reduction of the metal to give a Cu^{I} -porphyrin. In an attempt to resolve this discrepancy, we have studied the reduction of water-soluble Cu^{II} -porphyrins in neutral and alkaline solutions. The transient species produced by one-electron transfer processes were identified as the π -radical anions, based on their broad absorption spectra at 600-800 nm, and the two-electron reduction products were either Cu^{II} -phlorins or Cu^{II} -chlorins, depending on pH and on porphyrin structure. Reduction in acidic solution, however, often led to demetallation of these otherwise stable complexes. The pH at which demetallation became apparent was dependent on porphyrin structure and was <4 for TSPP, <3 for TAP [tetrakis(trimethylaminophenyl)porphyrin], and <1.4 for TMPyP [tetrakis(N-methyl-4-pyridyl)porphyrin]. Under these conditions, pulse radiolytic reduction gave the spectra of the products of protonation of Cu^{I} -porphyrin. It is concluded that the π -radical anions of Cu^{II} -porphyrins have some Cu^{I} character, which in acidic solutions results in protonation and demetallation due to the large ionic radius of Cu^{I} . The rate constant of protonation was measured to be 5×10^7 for $(\text{Cu}^{\text{II}}\text{TSPP})^{\cdot -}$ and $8 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ for $(\text{Cu}^{\text{II}}\text{TAP})^{\cdot -}$.

Following the above studies on metal-carbon bonding to form alkyl-metalloporphyrins, we are examining the possibility of reacting these products with either CO_2 or $\text{CO}_2^{\cdot -}$ to produce a new carbon-carbon bond between the alkyl group and one of these

reactants. Because insertion of CO_2 may be inhibited by the rigid structure of the alkyl-metalloporphyrin, we are also considering the use of other alkyl-metal complexes to examine the feasibility and mechanisms of such reactions.

(b) Solvent Effects on Reactions of Inorganic radicals and Organic Peroxyl Radicals

Electron transfer reactions of inorganic radicals and organic peroxy radicals can be conveniently studied by pulse radiolysis. They have been studied because of the importance of these radicals as intermediates in radiation chemistry and biology and in many chemical systems, the potential use of these radicals as probes for other systems, and the expectation that a better knowledge of their chemistry will lead to an improved theoretical understanding of electron transfer and other reactions.

In recent years we have studied the redox behavior of a wide variety of inorganic radicals ($\text{SO}_2^{\cdot\cdot}$, $\cdot\text{SO}_3^-$, $\text{SO}_4^{\cdot\cdot}$, $\text{SO}_5^{\cdot\cdot}$, $\text{ClO}^\cdot$, $\text{ClO}_2^\cdot$, $\text{BrO}_2^\cdot$, $\text{NO}_2^\cdot$, $\text{NO}_3^\cdot$, $\text{N}_3^\cdot$, $\cdot\text{PHO}_2^-$, $\cdot\text{PO}_3\text{H}^-$ and $\cdot\text{PO}_3^{2-}$, $\text{CO}_3^{\cdot\cdot}$, $\text{Cl}_2^{\cdot\cdot}$, $(\text{SCN})_2^{\cdot\cdot}$, and others) towards organic and inorganic compounds and utilized them for determination of redox potentials of several organic and inorganic radicals. All of the above studies have been carried out at room temperature. Recently, to achieve a more detailed characterization of the mechanisms of electron transfer reactions of inorganic radicals we have studied the temperature effects on rate constants for a number of these

reactions. We found activation energies ranging from -10 to 40 kJ mol⁻¹ and pre-exponential factors also varying considerably, from 10⁶ to 10¹⁴. The results suggested that although the reactions of the inorganic radicals with substitution-inert metal complexes (Fe(CN)₆⁴⁻, Mo(CN)₈⁴⁻, and W(CN)₈⁴⁻) take place by outer-sphere electron transfer, many reactions of these radicals with organic compounds and with simple anions probably occur via an inner-sphere mechanism. To shed light on the mechanisms of these reactions, we have studied solvent effects on their rate constants.

In recent years we have studied also the electron transfer reactions of peroxy radicals with metalloporphyrins and with various organic reductants. We have investigated how substituents on the peroxy radical and on the substrate affect the rate constants of these reactions. Several reactions of peroxy radicals were investigated in several solvent mixtures and as a function of temperature as well. Again, wide variations were found in the temperature effects; activation energies ranging from 1 to 30 kJ mol⁻¹ and pre-exponential factors ranging from 10⁷ to 10¹⁴. Electron transfer from the organic reductants to the chlorinated methylperoxy radicals was suggested to take place via an inner sphere mechanism.

Recently, we have undertaken a more detailed study of solvent effects on rate constants of electron transfer reactions of inorganic and peroxy radicals. For peroxy radicals we chose CCl₃O₂[·] as the main probe because it is readily produced by

radiolysis of aerated solutions of CCl_4 in practically any solvent or solvent mixture. For inorganic radicals, however, the radiolytic production is restricted to aqueous solutions and few other solvents. To overcome this limitation, we utilized laser flash photolysis to produce either $\text{SO}_4^{\cdot\cdot}$ radicals from persulfate or $\text{NO}_3^{\cdot}$ radicals from ceric ammonium nitrate in various solvents. We then studied the solvent effects on reactions of these radicals and on reactions of other inorganic radicals produced from these in the presence of other additives, such as $\text{Cl}^{\cdot}$.

In this manner, rate constants for several reactions of inorganic radicals with inorganic anions in aqueous and aqueous/acetonitrile solutions have been measured. The reactions studied were (1) $\text{Cl}_2^{\cdot\cdot} + \text{N}_3^-$, (2) $\text{Br}_2^{\cdot\cdot} + \text{N}_3^-$, (3) $\text{Cl}_2^{\cdot\cdot} + \text{SCN}^-$, (4) $\text{Br}_2^{\cdot\cdot} + \text{SCN}^-$, (5) $\text{SO}_4^{\cdot\cdot} + \text{Cl}^-$, (6) $\text{SO}_4^{\cdot\cdot} + \text{CO}_3^{2-}$, (7) $\text{N}_3^{\cdot} + \text{I}^-$. The rate constants ranged from 10^6 to $10^9 \text{ L mol}^{-1}\text{s}^{-1}$. The Arrhenius activation energies (E_a) varied from 2 to 12 kJ mol^{-1} for the first 4 reactions, were higher for reaction 6, and negative for reaction 5. The pre-exponential factors (A) also varied considerably, from 10^5 to 10^{14} . The values of k_{298} decreased in most cases by more than an order of magnitude upon increasing the acetonitrile (ACN) fraction from 0 to 70%. For most reactions, this decrease in k_{298} was due to changes in $\log A$ with little regularity in the small changes observed in E_a . For reaction 7, k_{298} was practically unchanged due to compensating effects of the changes in E_a and $\log A$ with ACN mole fraction, giving an isokinetic relationship. An isokinetic relationship was also

observed in the case of reaction 6; E_a and $\log A$ change in parallel while changing ACN mole fraction. Reaction 3 was also studied in water/t-butanol and water/acetic acid mixtures. Linear correlation was found between $\log k$ and the dielectric constant of the medium for water/ACN and water/t-BuOH but the lines for the two solvent mixtures had different slopes, suggesting specific solvation effects in addition to the primary solvent polarity effects. With water/acetic acid, k decreased and then increased upon addition of acetic acid, possibly due to dimer formation in acetic acid, which plays a role only at low water content.

Rate constants have been measured in several aqueous/organic solvent mixtures also for the addition reaction of $\text{Cl}_2^{\cdot\cdot}$ radicals with unsaturated alcohols and an alkene. The activation energies were relatively low ($1\text{--}10 \text{ kJ mol}^{-1}$) and the pre-exponential factors varied over the range $\log A = 7.9$ to 9.4 . The rate constants decreased (by up to a factor of 30) upon increasing the fraction of organic solvent and $\log k$ correlated linearly with the dielectric constant for a given water/organic solvent system, but the lines for the different solvent systems had different slopes. A better correlation of $\log k$ was found with a combination of the solvatochromic factor, $E_T(30)$, and the hydrogen-bond donor acidity factor, α . This suggests that the rate of reaction is influenced by the solvent polarity and also by specific solvation of the ionic reactant and product.

Rate constants have been measured for the reactions of the

sulfate radical, $\text{SO}_4^{\cdot\cdot}$, with alkanes, alkenes, alcohols, ethers, and amines in 95% acetonitrile solution. The rate constants were in the range of $10^6 \text{ L mol}^{-1}\text{s}^{-1}$ for the abstraction reactions and $10^7 - 10^9 \text{ L mol}^{-1}\text{s}^{-1}$ for the addition and electron transfer reactions. These values are 20 to 80 times lower than those measured in aqueous solutions. Furthermore, the rate constants for the reactions of $\text{SO}_4^{\cdot\cdot}$ with the primary alcohols increase with the number of carbon atoms and then level off, in contrast to the behavior observed in aqueous solution, where the rate constant increases more sharply for the larger alcohols. In other words, the reactions in ACN exhibit a normal behavior where the rate constant per added carbon decreases with chain length. For the reactions in water, however, the rate constant per added carbon increases with the chain length of the alcohol. We suggest that this greater reactivity of the longer alcohols in water is associated with the hydrophobic end of the alcohols which are very poorly solvated. Attack of a $\text{SO}_4^{\cdot\cdot}$ radical on any of the alcohols leads to a transition state which is better solvated than the parent alcohol; for the larger alcohols, however, the difference is greater.

Comparison of rate constants in water and ACN was also done for the reactions of the nitrate radical, $\text{NO}_3^{\cdot}$, with a number of alkanes, alkenes, and arenes. The rate constants measured in ACN solutions were significantly greater than the values for aqueous solutions (and those measured in 60% acetic acid were slightly greater than those measured in water). These trends in rate

constants are opposite to those reported for the $\text{SO}_4^{\cdot -}$ radicals, where the values were higher in aqueous than in ACN solutions. The reactivity of $\text{NO}_3^{\cdot}$ radicals in aqueous solutions is lower than that of $\text{SO}_4^{\cdot -}$ by a factor in the range of 25-55, in contrast with the case of ACN solutions, where the reactivity of $\text{NO}_3^{\cdot}$ is higher than that of $\text{SO}_4^{\cdot -}$ for all compounds examined. This reversal of trends in the reactivities of $\text{NO}_3^{\cdot}$ and $\text{SO}_4^{\cdot -}$ radicals may be due to differences in the solvation of these radicals and of the transition states of their reaction. In ACN solutions, where solvation is by dipolar interaction, $\text{NO}_3^{\cdot}$ is expected to be much less solvated than $\text{SO}_4^{\cdot -}$ because it is uncharged and symmetric and because the N-O bonds are less polar than the S-O bonds. In the transition state, however, $\text{NO}_3^{\cdot}$ loses its symmetry and becomes more polar and thus is probably much better solvated by ACN. This effect provides a strong driving force for the reaction. For $\text{SO}_4^{\cdot -}$, on the other hand, it may be assumed that both the radical and the transition state are somewhat similarly solvated and thus there is no large driving force for the reaction caused by solvation. This effect, which enhances the reactivity of $\text{NO}_3^{\cdot}$ as compared with that of $\text{SO}_4^{\cdot -}$, has only a minor contribution in aqueous solutions where solvation by hydrogen bonding probably predominates and thus both radicals may be similarly solvated.

Thus, all inorganic radicals examined, except for $\text{NO}_3^{\cdot}$, react more rapidly in aqueous than in organic solvents. Organic peroxy radicals also were found to react generally more rapidly

in water than in organic solvents. Recently, we have measured the rate constants for the reactions of $\text{CCl}_3\text{O}_2^\cdot$ radicals with chlorpromazine [2-chloro-10-(3-dimethylaminopropyl)phenothiazine hydrochloride] (ClPz) and trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) by pulse radiolysis in 16 different solvents. The rate constants were found to vary with solvent between 10^7 and $10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. We attempted to correlate these variations with the different solvent parameters available in the literature.

For trolox, the best fit with a single parameter was obtained with Hildebrand's solubility parameter, either as δ_H ($R^2 = 0.53$) or δ_H^2 ($R^2 = 0.59$); all other parameters gave much lower R^2 values. A plot of $\log k$ vs. δ_H^2 shows that the main points deviating from the line are those for triethylamine, pyridine, CCl_4 , ether, and formamide. Excluding CCl_4 , these solvents are basic in nature, especially those that deviate the most, TEA and pyridine. This reinforces our previous conclusion that the contribution of solvent basicity should also be considered. Indeed, addition of a second parameter for the basicity improved the correlation tremendously. Combination of δ_H^2 with the pK_a values of the solvent molecules (when used as solutes in water or in acetonitrile, and excluding CCl_4 for which there is no value for pK_a) improved the correlation tremendously. The coefficients of the correlation of $\log k(\text{trolox})$ with δ_H^2 and pK_a

$$\log k = C_0 + C_1\delta_H^2 + C_2\text{pK}_a$$

are: $C_0 = 6.79 \pm 0.16$, $C_1 = (8.0 \pm 0.8) \times 10^{-4}$, $C_2 = 0.051 \pm 0.007$, $R^2 = 0.922$, when the pK_a values in ACN are used; and $C_0 = 7.04 \pm 0.18$, $C_1 = (8.3 \pm 0.9) \times 10^{-4}$, $C_2 = 0.065 \pm 0.011$, $R^2 = 0.903$, when the pK_a values in water are taken. The addition of third parameters did not improve the correlation further.

For the reaction of $\text{CCl}_3\text{O}_2\cdot$ with ClPz we found a poor correlation of $\log k$ with the dielectric constant ϵ ($R^2 = 0.47$), a somewhat improved correlation with Reichard's solvent polarity parameter, $E_T(30)$ ($R^2 = 0.75$), and the best fit with Hildebrand's solubility parameter, δ_H ($R^2 = 0.84$) or δ_H^2 ($R^2 = 0.81$). Other single parameters gave poor fits. Combining δ_H or δ_H^2 with any other parameter, showed only a marginal increase in the values of R^2 and there was no improvement in the fit when the pK_a values for the solvents were included in the correlation.

There is a clear difference, then, between the effect of solvent on the two reactants, trolox and ClPz. The measured rate constants for both were found to depend on the solubility parameter, δ_H , but only the trolox rate constants depended on solvent basicity. The solubility parameter, δ_H , is defined as the square root of the cohesive energy density, the energy required for breaking the bonds between the molecules in the solvent. It is derived from the latent heat of vaporization for the solvent: $\delta_H = [(\Delta H_v - RT)/V_M]^{1/2}$, where ΔH_v is the molar heat of vaporization at zero pressure and V_M is the molar volume. δ_H^2 , which has the units of pressure, has been called the cavity term or the cavity effect and was suggested to be a measure of the

work necessary to separate the solvent molecules and create a suitably sized cavity for the solute. The requirements for an increase or decrease in the space available while going from reactants to the transition state for a reactions should be essentially independent of solvent. The relation of the rate constant to δ_H or δ_H^2 , then, could be an indication of this requirement, with a positive coefficient indicating that less space is required for the transition state, while a negative coefficient indicates that the transition state occupies more space.

High values of δ_H result from strong solvent-solvent interactions, typically in the form of hydrogen bonding and dipole interactions. This ability of the solvent molecules to form intermolecular bonds indicates the possibility of solvent-solute interactions. An alternative explanation of the positive effect of δ_H on electron transfer reactions is that the transition state will be usually more polar than the reactants and hence will be more solvated in high- δ_H solvents. This will be especially true for O-centered radicals due to hydrogen bonding in the transition state.

The reaction of $\text{CCl}_3\text{O}_2\cdot$ with trolox was found to correlate also with the solvent basicity. The removal of a proton can accelerate the formation of the trolox radical by two possible mechanisms. The first process is the de-protonation of the phenolic moiety, ArOH , by a solvent molecule, S , leading to the formation of the phenolate anion, which is much more reactive

than the neutral phenol in electron transfer reactions.

This process may occur to some extent prior to the reaction with the peroxy radical, but mainly in strongly basic solvents like TEA. The second mechanism is by removing a proton from ArOH in the transition state, in a process concerted with the electron transfer, to form the neutral radical $\text{ArO}^\cdot$.

Subsequently, or concurrently, a proton is transferred from the solvent or from SH^+ to the incipient CCl_3O_2^- to form $\text{CCl}_3\text{O}_2\text{H}$.

The basic approach we have taken to the correlation of our rate data has been empirical; essentially, we have sought solvent parameters which correlate with the observations and then have attempted to explain these correlations. Since these are electron-transfer reactions, an alternative approach is to start with electron-transfer theory to find appropriate parameters. The rate constant for an electron-transfer reaction is related to the solvent reorganization energy, λ :

$$\lambda = e^2(1/r_1 + 1/r_2 - 1/r_{12})(1/n^2 - 1/\epsilon)$$

where r_1 and r_2 are the radii of the reactants and r_{12} is the reaction distance, ϵ is the dielectric constant, and n^2 is the optical dielectric constant (the square of the refractive index, n). $\log k$ should be proportional to the free energy of activation, which is given by the expression

$$\Delta G^\ddagger = (\Delta G^\circ + \lambda)^2/4\lambda$$

where ΔG° is the free energy of the reaction. If ΔG° is small

compared to λ , or if λ is small compared to ΔG° , one may expect a correlation between $\log k$ and λ or $1/\lambda$, respectively. If none of these conditions hold, but ΔG° is only slightly solvent-dependent and is assumed to be solvent independent, one can correlate $\log k$ with a function of both λ and $1/\lambda$. Defining $R = (1/n^2 - 1/\epsilon)$, we attempted a correlation according to:

$$\log k = C_0 + C_1 R + C_2/R$$

but obtained very poor fits for both trolox and ClPz. In this treatment the solvent is viewed as a dielectric continuum and the solute-solvent interactions are not taken into account.

Therefore, we also attempted correlations that utilize the R and $1/R$ values in addition to the previous parameters:

$$\log k = C_0 + C_1 \delta_H^2 + C_2 pK_a + C_3 R + C_4/R$$

(the pK_a term is used only in the case of trolox). Correlation according to this equation leads to a noticeable improvement in the correlation coefficient obtained previously (for ClPz, R^2 increases from 0.81 to 0.86 and for trolox, without CCl_4 , the increase is from 0.92 to 0.94). These increases, however, come at the cost of two degrees of freedom and the error in the coefficients C_3 and C_4 are quite large. More rigorous treatment cannot be carried out at this time due to lack of information on the ΔG° values for these reactions in the different solvents.

Rate constants were measured also for the reactions of $CCl_3O_2^\cdot$ and $CBr_3O_2^\cdot$ radicals with unsaturated organic compounds in methanol solutions by competition kinetics, using ClPz as a reference. The rate constants were in the range $k = 10^4 - 10^7$ L

$\text{mol}^{-1} \text{ s}^{-1}$ and a good correlation was obtained between $\log k$ and the Taft substituent constants σ^* . Steric effects were also noticeable in some cases. The reactivities of the radicals were in the order $\text{CBr}_3\text{O}_2^\cdot < \text{CCl}_3\text{O}_2^\cdot < \text{C}_4\text{F}_9\text{O}_2^\cdot$, which is in contrast with the order observed in electron transfer reactions. The rate constants for reaction of $\text{CCl}_3\text{O}_2^\cdot$ with 2,3-dimethyl-2-butene (DMB) and cyclohexene (CH) were studied in 12 solvents. In all cases DMB is considerably more reactive than CH, indicating that at least in the case of DMB the reaction is predominantly via addition. The rate constant for addition of $\text{CCl}_3\text{O}_2^\cdot$ to DMB varies by a factor of 7 in the different solvents. No correlation was found between these rate constants and thermodynamic or polarity parameters of the solvents, although viscosity appears to have an effect.

In the past several years we have studied some reactions of halogen atoms in organic solvents. We found charge-transfer complexes of Br atoms with different bromoalkanes, which exhibit different spectra and reactivities. We then examined the possibility of charge-transfer complexes of Br atoms with chloroalkanes and alkanes. Bromine atoms were produced by photolysis of Br_2 (at 351 or 248 nm), by photolysis of bromoalkanes (at 248 nm), or by radiolysis of HBr or bromoalkanes dissolved in cyclohexane or in certain other organic solvents. The transient spectra, monitored within microseconds after the pulse, had absorption maxima that varied between 300 and 500 nm and are ascribed to complexes of Br atoms with the various

solvents or other solutes present. The absorption maxima for each group of complexes correlate with the ionization potential of the molecule bound to Br, suggesting the existence of charge-transfer complexes. The correlations for different groups, however, were different due to the specific atom to which the Br atom is bound.

The above studies on solvent effects on rate constants for reactions of peroxy radicals are now being extended to reactions of $\text{CCl}_3\text{O}_2\cdot$ with porphyrins.

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