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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.

PROGRESS REPORT

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 three years are summarized below under the following sections: (a) electron transfer reactions of peroxy radicals, concentrating on the characterization of new peroxy radicals derived from vinyl, phenyl, other aryl, and pyridyl, (b) solvent effects on electron transfer reactions of inorganic and organic peroxy radicals, including reactions with porphyrins, and (c) electron transfer and alkylation reactions of metalloporphyrins and other complexes.

(a) Electron Transfer Reactions of Peroxy Radicals.

This part of our work is concerned with electron transfer reactions of organic peroxy radicals, which can be conveniently studied by pulse radiolysis. These radicals are important as intermediates in radiation chemistry and biology as well as in environmental and industrial processes, and the results on their reactions are expected to lead to an improved theoretical understanding of electron transfer and other reactions.

Most peroxy radicals studied in the past were derived from aliphatic compounds and exhibited optical absorption only in the UV region, which made it difficult to follow the formation and reactions of these radicals through their absorption. Instead, rate constants for reactions of these radicals were measured by following the formation of transient species from other reactants. During the past two years, we have studied vinylperoxy, phenylperoxy, and related radicals, which have not been reported before and which were found to exhibit substantial optical absorption in the visible range.

Phenyl radicals were produced by reduction of aryl halides with hydrated

electrons. The rate constant for the reaction of 4-carboxyphenyl with O_2 was determined

from the rate of buildup of the peroxy radical absorption at 520 nm as a function of $[O_2]$ and found to be $1.6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. Phenyl radicals react with 2-PrOH by H-abstraction; a rate constants of $4 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ was determined for 4-carboxyphenyl by competition with the reaction of this radical with O_2 . Phenylperoxy radicals react with 4-methoxyphenolate ions, trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), ascorbate ions, chlorpromazine [2-chloro-10-(3-dimethylaminopropyl)phenothiazine hydrochloride], and ABTS [2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate ion)] by one-electron oxidation. The rate constants for such reactions, determined from the rate of

formation of the one-electron oxidation product as a function of substrate concentration, were found to be near $10^8 - 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. The reaction with neutral phenols, however,

was much slower and could not be observed under the pulse radiolysis conditions.

Phenylperoxy radicals are found to be much more reactive than methylperoxy and more reactive than most substituted methylperoxy, except for the halogen substituted radicals. Electron withdrawing substituents at the 4-position of phenylperoxy increase the rate constant and electron donating groups decrease the rate constant for oxidation by this radical, and there is a good correlation between the reactivities and the Hammett substituent constants.

Other aryl radicals (phenyl, 4-biphenyl, 2-naphthyl, 1-naphthyl, and 9-phenanthryl) were produced by the reaction of the corresponding aryl bromide with solvated electrons and reacted rapidly with oxygen to produce the arylperoxy radicals. These radicals exhibit optical absorptions in the visible range, with λ_{max} at 470, 550, 575, 650, and 700 nm, respectively. These arylperoxy radicals also react with ABTS, chlorpromazine, and Trolox; the rate constants k in different solvent mixtures vary between 4×10^6 and $2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. In the same solvent, k increases in the order: phenyl-, 4-biphenyl-, 2-naphthyl-, 1-naphthyl-, and 9-phenanthryl-peroxy, the same order as the absorption peaks of these radicals. To attempt a quantitative correlation between these two sets of data, we corrected the experimental rate constants, k_{obs} , for the effect of the diffusion-controlled limit, k_{diff} , to obtain the activation-controlled value, k_{act} , according the equation $1/k_{act} = 1/k_{obs} - 1/k_{diff}$. Correlations of $\log k_{act}$ with the energy ($E = hc/\lambda$) of the absorption peak show a nearly linear dependence in all cases. Since the Marcus theory relates $\log k_{act}$ with the driving force (or ΔG°) for the reaction, the correlation found here suggests that the energy of the absorption peak is inversely related to the driving force for the reaction (i.e. to the redox potential or electron affinity of the peroxy radical). Possibly, as the π -system becomes more extended, all the energy levels are compressed, and this reduces the distance between the singly occupied molecular orbital (SOMO) and the penultimate occupied molecular orbital (E of the peak in the visible range) as well as the distance between the SOMO and the continuum level (ionization potential). As the ionization potential decreases, the electron affinity

increases and, assuming similar effects of solvation in the whole series, the redox potential will become more positive. This implies strong interaction between the aromatic π -system and the unpaired electron on the terminal oxygen, which affects the absorption spectrum as well as the reactivity.

2-Pyridyl radicals were produced by the reaction of 2-chloro- or 2-bromopyridine with solvated electrons ($k \sim 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$) and reacted rapidly with oxygen ($k = 2.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$) to produce the 2-pyridylperoxyl radical. This radical exhibits optical absorption in the visible range, with λ_{max} at 440 nm. 2-Pyridylperoxyl radical is a fairly strong oxidant, which reacts with ABTS, chlorpromazine, and Trolox by one-electron oxidation. The rate constants k for these reactions, determined from the rate of formation of the one-electron oxidation products as a function of substrate concentration, vary between 2×10^6 and $2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ in various solvent mixtures. For each substrate, a good correlation was found between $\log k$ and the cohesive pressure of the solvent or solvent mixture, as found (see p. 15) for $\text{CCl}_3\text{O}_2\cdot$ radical reactions in nearly neat solvents. 3-Bromo, 3-chloro- and 4-chloropyridine also reacted rapidly with solvated electrons, but their radical anions underwent protonation on the nitrogen in competition with the dehalogenation process. Therefore, no pyridylperoxyl radicals were formed from these species in aqueous solutions and only partial yield was found in neat methanol.

Similarly, vinyl and phenylvinyl radicals were produced by reductive dehalogenation of vinyl bromide and β -bromostyrene with e_{aq}^- .

Vinyl was also produced by addition of H atoms to acetylene in acidic solutions.

Carboxyvinyl and dicarboxyvinyl radicals were produced in irradiated aqueous solutions from acetylenecarboxylic and acetylenedicarboxylic acid by addition of H atom to the triple bond or by reaction with e_{aq}^- , followed by protonation.

All these vinyl radicals react rapidly with oxygen to produce the corresponding vinylperoxyl radicals. Vinylperoxyl radicals exhibit optical absorptions in the UV (λ_{max} 250-290 nm) and in the visible range. The peaks in the visible range were at 440 nm for unsubstituted vinylperoxyl radical, between 480 and 520 nm for carboxylated vinylperoxyl, depending on pH and number of carboxyl groups, and at 540 and 690 nm for 2-phenylvinylperoxyl. These vinylperoxyl radicals oxidize organic reductants such as ABTS, chlorpromazine, ascorbate, and Trolox with rate constants between 4×10^5 and $2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, depending on the radical and the reductant. Vinylperoxyl radicals are more reactive than similarly substituted alkylperoxyl; carboxyl and phenyl substituents on the vinyl group increase the reactivity of the vinylperoxyl radical.

The rate constants for oxidation of ClPz, ABTS, and ascorbate by the vinylperoxyl radical are higher than those for oxidation by alkylperoxyl radicals. The rate constant for reaction of $\text{CH}_3\text{O}_2\cdot$ with ABTS was reported to be $< 1 \times 10^5$ and with ascorbate $1.7 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$. For the peroxyl radical derived from *t*-BuOH we estimate the rate constant for oxidation of ABTS and ClPz to be $< 1 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$. The rate constants for oxidation by vinylperoxyl are higher than those by alkylperoxyl by at least an order of

magnitude. This effect results from electron withdrawing by the vinyl group, which lowers the electron density on the oxyl site and thus increases its tendency to oxidize the substrates. Similar effects are exerted by other electron withdrawing substituents, such as halogens, carbonyl, cyano, or phenyl groups. A correlation has been demonstrated by us before between $\log k$ for oxidation of ascorbate by substituted alkylperoxyl radicals and the Taft σ^* substituent constant, which is a measure of the electron withdrawing effect of the substituent. However, if we compare the rate constants for vinylperoxyl and for phenylperoxyl with the values for other peroxyl radicals (with halogen, cyano, and carbonyl substituents), we find that in most cases the vinyl and phenyl substituted radicals exert a stronger effect than can be predicted on the basis of their σ^* values. For example, the oxidation of CIPz by $\text{CH}_3\text{COCH}_2\text{O}_2\cdot$ ($\sigma^* = +0.60$) takes place with $k = 2 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ whereas oxidation by $\text{C}_6\text{H}_5\text{O}_2\cdot$ (also $\sigma^* = +0.60$) occurs with $k = 1.5 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$; oxidation by $\text{CH}_2=\text{CHO}_2\cdot$ ($\sigma^* = +0.36$) has $k = 1 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ as compared with $k = 6.8 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ for $\text{CNCH}_2\text{O}_2\cdot$ ($\sigma^* = +1.30$). Similarly, oxidation of ABTS by $\text{C}_6\text{H}_5\text{O}_2\cdot$ ($\sigma^* = +0.60$) has $k = 6.6 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ as compared with oxidation by $\text{ClCH}_2\text{O}_2\cdot$ ($\sigma^* = +1.05$) which has a lower rate constant, $k = 4.4 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$. Oxidation of ascorbate by vinylperoxyl has a rate constant close to those for oxidation by $\text{ClCH}_2\text{O}_2\cdot$ and $\text{CNCH}_2\text{O}_2\cdot$; whose σ^* values are much higher. These comparisons suggest that the effect of the vinyl and phenyl groups is to withdraw electrons from the oxyl site to an extent that is greater than is expected on the basis of their σ^* values, suggesting that they act not only by an inductive effect but also interact with the oxyl site directly. Such interaction between the unpaired electron on the oxygen and the π -system of the phenyl or vinyl group may be also the cause of the absorption in the visible range (related theoretical studies by M. Krauss of NIST will be published).

The finding that the vinylperoxyl radical oxidizes CIPz with a measurable rate constant but does not oxidize ascorbic acid on the pulse radiolysis time scale suggests that the oxidation potential of this radical is near that of ascorbic acid ($\sim 1.0 \text{ V}$ vs NHE), i.e. clearly higher than that of methylperoxyl which was estimated to be $\sim 0.6\text{--}0.7 \text{ V}$.

Although the major thrust of our studies on the reactivity of peroxyl radicals has involved their electron-transfer reactions, we have also carried out studies of other important reactions of peroxyl radicals: on the self-reaction of these radicals and on their reactions with NO. This is allowing us to develop a more complete picture of the behavior of these radicals.

There have been a large number of studies of the self-reactions of organic peroxyl radicals in the liquid phase and in the gas phase, but few of these reactions have been studied in both phases, particularly as a function of temperature. In addition, there have been no studies of the temperature dependence of the self reactions of any primary peroxyl radical in the liquid phase, although there have been several studies in the gas phase. We, therefore, investigated the kinetics and absorption spectrum of the self reaction of the simple primary peroxyl radical derived from methanol, $\text{HOCH}_2\text{O}_2\cdot$ in the aqueous phase. The absorption spectrum measured for $\text{HOCH}_2\text{O}_2\cdot$ is similar to that measured for that radical in the gas phase, but slightly red shifted. The absorption coefficient at the maxima are almost identical. The kinetics, however, are somewhat different. At room temperature, the gas-phase rate constant is about five times greater

than the aqueous-phase value. Even more interesting is that the temperature dependence in the gas phase is negative (as it is for all of the primary peroxy radicals) but is positive in the aqueous phase. This suggests that the mechanism of the reaction changes on going from the gas to the aqueous phase. A particularly important reaction of peroxy radicals in the liquid phase is with nitric oxide. We have measured rate constants for the reaction of NO both with several organic peroxy radicals and with the superoxide anion, $O_2^{\cdot-}$. These reactions proved to be all very fast, $1-3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ for the organic peroxy radicals and $6.7 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ for $O_2^{\cdot-}$. Unlike in the gas phase, where the reactions proceed directly to the products $RO\cdot$ and NO_2 ; in the liquid phase a long-lived intermediate ascribed to the peroxyxynitrite was observed. The rate constant we measured for the reaction of $O_2^{\cdot-}$ with NO is about 200 times greater than that reported previously (and the misinterpretation in the previous work has been explained). An intriguing observation in our work was that the rate of decomposition of the intermediate organic peroxyxynitrite is strongly influenced by the solvent, becoming about 200 times faster in alcohol. This may suggest that the reaction products are also a function of solvent and that the effect of the reaction of $RO_2\cdot$ with NO will depend on whether the reaction takes place in the aqueous or the organic phase.

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

In recent years we have studied the redox behavior of a wide variety of inorganic radicals towards organic and inorganic compounds and utilized them for determination of redox potentials of several organic and inorganic radicals. All of these 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 10^6 to 10^{14} . The results suggested that although the reactions of the inorganic radicals with substitution-inert metal complexes 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 10^7 to 10^{14} . 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 $CCl_3O_2\cdot$ 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 $\text{SO}_4^{\cdot -}$ 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 Cl^- .

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) $\text{Cl}_2^{\cdot -} + \text{N}_3^-$, (2) $\text{Br}_2^{\cdot -} + \text{N}_3^-$, (3) $\text{Cl}_2^{\cdot -} + \text{SCN}^-$, (4) $\text{Br}_2^{\cdot -} + \text{SCN}^-$, (5) $\text{SO}_4^{\cdot -} + \text{Cl}^-$, (6) $\text{SO}_4^{\cdot -} + \text{CO}_3^{2-}$, (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/acetic acid mixtures, where k decreased and then increased upon addition of acetic acid, possibly due to dimer formation, which plays a role at low water content.

Rate constants have been measured for the reactions of the sulfate radical, $\text{SO}_4^{\cdot -}$, 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 $\text{SO}_4^{\cdot -}$ 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 $\text{SO}_4^{\cdot -}$ 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 (CIPz)

and trolox 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 ($R^2 = 0.53$) or δ^2 ($R^2 = 0.59$); all other parameters gave much lower R^2 values. A plot of $\log k$ vs. δ^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^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^2 and pK_a

$$\log k = C_0 + C_1\delta^2 + C_2\text{pK}_a \quad (11)$$

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 CIPz 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 ($R^2 = 0.84$) or δ^2 ($R^2 = 0.81$). Other single parameters gave poor fits. Combining δ or δ^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 , but only the trolox rate constants depended on solvent basicity. The solubility parameter, δ , 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: $\delta = [(\Delta H_v - RT)/V_M]^{1/2}$, where ΔH_v is the molar heat of vaporization at zero pressure and V_M is the molar volume. δ^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 or δ^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 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 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 solvents. This will be especially true for O-centered radicals due to hydrogen bonding in the transition state.

The reaction of $CCl_3O_2\cdot$ 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 $ArO\cdot$.

Subsequently, or concurrently, a proton is transferred from the solvent or from SH^+ to the incipient $CCl_3O_2^-$ to form CCl_3O_2H .

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 $k = 10^4 - 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ 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.

The studies of solvent effect on reactivity were extended to the reactions of porphyrins. The peroxy radical $\text{CCl}_3\text{O}_2\cdot$ reacts with porphyrins (P) to form the π -radical cations.

The rate constants were measured by following the formation of the porphyrin π -radical cation optical absorption at 700 nm as a function of porphyrin concentration. These studies have been carried out with free base porphyrins and not metalloporphyrins, because the latter are capable of binding solvent molecules as axial ligands, which will change their redox potential and the driving force for the reaction and will mask the other effects of the solvent. The rate constants were thus measured for several free base porphyrins in different solvents. The rate constants for hematoporphyrin-IX (HMP) in 14 solvents were found to vary between 3×10^7 and $2 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. Two other porphyrins, octaethylporphyrin and tetrasulfonatophenylporphyrin, were possible to measure only in a limited number of solvents; OEP was soluble only in non-polar and TSPP only in the more polar solvents. The results are insufficient for comparing the reactivities of the three porphyrins in any particular solvent. Only HMP was sufficiently soluble in a wide variety of solvents and, therefore, we use the results with this porphyrin to examine the solvent effect. The rate constants for reaction of $\text{CCl}_3\text{O}_2\cdot$ with HMP were correlated with the solvent cohesive energy density (Hildebrand's solubility parameter δ). The correlation was similar to that found for chlorpromazine, the correlation coefficient is $R^2 = 0.83$. Correlation of the rate constants with other solvent parameters was poorer.

The best correlation for the solvent effect on the rate constant was obtained with the cohesive energy density and not with the dielectric constant [$\log k$ vs. $1/\epsilon$ or $(\epsilon - 1)/(2\epsilon + 1)$], despite the fact that the reaction involves electron transfer and produces formally charged species. This finding suggests that the critical step in this reaction involves changes in the solvent cavity required for the reaction to proceed, whereas the electron transfer step within the activated complex is probably very fast. It should be noted also that the products of the reaction do not remain as the free ions in most cases. The hydroperoxide ion protonates to the neutral hydroperoxide, $\text{CCl}_3\text{O}_2\text{H}$, in a process that is concerted with the electron transfer. In low polarity solvents, P^+ may form ion-pairs with Cl^- (formed by reduction of CCl_4). Since the solvent dielectric constant is one of the factors that determine the cohesive energy, its effect on reactant polarization and electron transfer may be thus incorporated into the overall effect of δ . The main effect of δ on the reaction, however, is that of the other factors that contribute to δ , such

as hydrogen bonding and van der Waals forces. That the rate constant for the reaction increases with increasing solvent cohesion suggests that the reactants form an activated complex whose volume is less than the sum of those of the reactants, i.e. that the reaction has a negative volume of activation. This, however, could not be verified experimentally in our system.

A more quantitative correlation between the rate constants and solvent parameters can be achieved by using the Marcus relation if one can evaluate ΔG^0 for the reaction in each solvent. This, however, is not possible for the reaction of $\text{CCl}_3\text{O}_2\cdot$ with hematoporphyrin since the reduction potential of $\text{CCl}_3\text{O}_2\cdot$ is unknown and cannot be measured by electrochemical methods. Therefore, we attempted to measure other oxidation reactions of porphyrins, where the oxidation potentials of both reactants may be measurable. The best candidate for this purpose was found to be N-methylindole (MeIn).

which will then oxidize the porphyrin.

MeIn is used in large excess over porphyrin so that the buildup of $\text{P}^{\cdot+}$ can be attributed exclusively to the second reaction. This measurement is possible also because $\text{MeIn}^{\cdot+}$ absorbs mainly at 600 nm with little absorbance at 700, where $\text{P}^{\cdot+}$ formation is monitored. The rate constants for oxidation of HMP by $\text{MeIn}^{\cdot+}$ in the different solvents vary between 1.5×10^8 and $1.8 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. This range is an order of magnitude higher than that for oxidation by $\text{CCl}_3\text{O}_2\cdot$; but there is no correlation between the rate constants for the two reactions. This indicates that the two reactions take place by different mechanisms; oxidation by $\text{MeIn}^{\cdot+}$ is an outer sphere electron transfer whereas oxidation by $\text{CCl}_3\text{O}_2\cdot$ is an inner sphere reaction that also involves solvent molecules intimately. The lack of correlation between the rate constants for the two reactions also implies that there is no correlation between the rate of oxidation by $\text{MeIn}^{\cdot+}$ and δ . We tested these and other solvent parameters, including various functions of the dielectric constant ϵ [$1/\epsilon$, $(\epsilon-1)/(2\epsilon+1)$, as well as $(1/n^2-1/\epsilon)$] but found very poor correlations.

To correlate the rate constants with the solvent reorganization energy and the free energy of the reaction, we attempted to measure the standard one-electron oxidation potentials of MeIn and HMP in various solvents by cyclic voltammetry (in collaboration with P. Hapiot from the Laboratory of Molecular Electrochemistry of the University of Paris 7). The values for MeIn were measurable in a number of solvents (using ultramicroelectrodes and very fast voltage scan rates) whereas those for HMP could not be measured with acceptable accuracy. We, therefore, tested several other free base porphyrins and found mesoporphyrin-IX dimethyl ester (MSPDME) to be the most suitable for accurate measurements of the one-electron oxidation potentials. This porphyrin is less soluble than HMP in protic solvents, but this is not a severe disadvantage since the potentials could not be measured in such solvents. Thus, the oxidation potentials of MeIn and MSPDME and the rate constants for reaction of $\text{MeIn}^{\cdot+}$ with MSPDME

were measured in the same solvents. The two sets of values were correlated with the solvent properties according to the Marcus theory.

The rate constant for an electron-transfer reaction is determined by the free energy of activation, $\Delta G^\ddagger$, and a collision frequency, Z .

$$k_{\text{act}} = Z e^{-\frac{\Delta G^\ddagger}{RT}} \quad (18)$$

The activation-controlled rate constants, k_{act} , were calculated from the experimental values, k_{obs} , by correcting for the effect of the diffusion-controlled limit, k_{diff} .

$$\frac{1}{k_{\text{act}}} = \frac{1}{k_{\text{obs}}} - \frac{1}{k_{\text{diff}}} \quad (19)$$

Values of $\Delta G^\ddagger$ were then calculated by taking the commonly used value of $Z = 1 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$. $\Delta G^\ddagger$ is related to the free energy of the reaction, ΔG° , calculated from the difference in standard one-electron oxidation potentials ($\Delta G^\circ = -nF\Delta E^\circ$), and the reorganization energy, λ .

$$\Delta G^\ddagger = \frac{(\Delta G^\circ + \lambda)^2}{4\lambda} \quad (20)$$

The work term ($Z_1 Z_2 e^2 / D r_{12}$) is zero since the reaction involves one uncharged species. We can assume that λ is mainly the solvent reorganization energy, which is given by:

$$\lambda = e^2 \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r_{12}} \right) \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) \quad (21)$$

where r_1 and r_2 are the radii of the reactants, r_{12} is the reaction distance, ϵ is the dielectric constant, and n is the refractive index. The term $f = 1/2r_1 + 1/2r_2 - 1/r_{12}$ should be the same in all solvents. In fact, the calculated values of f are nearly constant, within experimental error, and average to $(1.38 \pm 0.11) \times 10^7$.

Another way to test the agreement between the experimental rate constants and the theoretical values is to use the average value of f , as a constant for all solvents, to calculate the solvent reorganization energies, λ , and from these to calculate the rate constants k_{calc} from the above equations. These values of k_{calc} are found to be similar to the values of k_{act} (within a factor of 2).

It should be noted that the value of f is calculated from a quadratic equation and thus two values are obtained. The other value was rejected since it gives values of λ smaller than ΔG° and corresponds to the inverted region, which is unlikely for reaction 17, where the driving force is only of the order of 0.3 to 0.4 V. The value $f = 1.38 \times 10^7$ can be used to estimate the reaction radius from the radii of the reactants. For planar molecules such as the porphyrins and MeIn, there is a difficulty in calculating the radii r_1 and r_2 to fit to the above theory, which assumes spherical reactants. As suggested before, we can treat the reactants as approximate spheres and estimate the radii from the molar volumes. This approximation gives $r_1 = 5.8$ and $r_2 = 3.7 \text{ \AA}$ for MSPDME and MeIn, respectively. From these values, and f , we calculate $r_{12} = 12.2 \text{ \AA}$, larger than the sum of the individual radii. If we use larger values for the reactants, e.g. the radii of the planar structures, we obtain r_{12} still larger than the sum of r_1 and r_2 . Although this

treatment is not exact for planar reactants, these estimates suggest that the electron transfer does not require a very close approach of the reactants to each other and may take place with minimal overlap of the π -clouds of the two reacting species. This situation for the reaction of MeIn^+ with the porphyrin is clearly different from that indicated for the reaction of $\text{CCl}_3\text{O}_2^\cdot$, where the peroxy radical, the porphyrin, and solvent molecules are involved in the electron transfer and form a more condensed transition state.

Rate constants for oxidation of MSPDME by MeIn^+ were also measured in CH_2Cl_2 , pyridine, and acetophenone, although the oxidation potentials could not be measured in these solvents. From the factor $f = 1.38 \times 10^7$ and k_{act} for these three solvents, we can estimate the difference in redox potential, ΔE^0 . By assuming the same extent of agreement between k_{act} and k_{calc} as found above, we estimate the errors in the calculated ΔE^0 values to be ± 0.05 V, approximately three times the errors in the measured values.

The rate constants for oxidation of HMP by MeIn^+ are lower than those of MSPDME, probably due to a small difference in the oxidation potentials. For the seven solvents in which the rate constants were measured for both porphyrins, we find that the ratio of rate constants is 2.3 ± 0.4 , practically constant within the experimental error limits. This ratio may be used to estimate, from the above calculations using the same f factor, that the potential for one-electron oxidation of HMP is ca. 90 mV higher than that of MSPDME. The above calculations permit us to estimate redox potentials from the measured rate constants and thus provide us with a method to estimate the potentials in solvents in which these are not measurable.

(c) 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 enable their application 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} -TPP is reduced to Cr^{II} TPP when the Cr center bears L_wL_i , but yields the Cr^{III} TPP $^-$ when the Cr bears L_iL_i or L_wL_s . Pyrrole-substituted porphyrins, whose macrocyclic rings have lower electron affinities than TPP, 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 ($\cdot CH_3, \cdot C_2H_5, \cdot C_4H_9, \cdot CH_2CO_2^-, \cdot CH(CO_2^-)_2, \cdot CH_2CN$) and fluoroalkyl ($\cdot CF_3, \cdot CF_2Cl$) radicals with Ni-, Fe-, and Mn-porphyrins (P) by radiolytic techniques in various solvents. All the radicals (R) react with Fe^{II} P to form $R-Fe^{III}$ P with stable Fe-C bond. These products are oxidized by O_2 to Fe^{III} P. Although Ni^I P and Ni^{II} P also react rapidly with the radicals to form Ni-C bonds, only the reactions of fluoroalkyl radicals with Ni^I P yield stable products. Reactions of alkyl radicals with Ni^I P result in unstable $R-Ni^{II}$ P products ($t_{1/2}$ several seconds) that eventually yield Ni^{II} P. Reactions of alkyl radicals with Ni^{II} P are reversible and the short lived $R-Ni^{III}$ P products ($t_{1/2} \sim \text{ms}$) disappear through radical reactions, with recovery of Ni^{II} P. Alkyl radicals react rapidly with Mn^{II} P, probably via addition to the metal, but the adduct gives Mn^{III} P immediately. $\cdot CF_3$ radicals also react with Mn^{III} 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 $R-Cr^{III}$ MSP and $R-Cr^{IV}$ MSP, respectively. Whereas Cr^{II} MSP is oxidized by O_2 very rapidly to Cr^{III} MSP, $R-Cr^{III}$ MSP is oxidized more slowly to give the same product, Cr^{III} MSP, and $R-Cr^{IV}$ MSP is oxidized very slowly to give a product oxidized on the porphyrin ring. The observed stability of $R-Cr^{IV}$ 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) [$M^{II}(\text{N-Me})\text{TSP}$] 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, [$M^{II}(\text{N-Me})\text{TSP}$] $^-$. These species were found to undergo two competing reactions, (a) disproportionation and protonation to yield the two-electron reduced phlorin anions, $M^{II}(\text{N-Me})\text{TSPH}$, 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, $\text{MeM}^{\text{III}}\text{TSPP}$. Both pathways were observed with the Co and Ni derivatives, and their contributions depended on the experimental conditions. Moreover, the Ni derivative produced $\text{MeNi}^{\text{III}}\text{TSPP}$ which was unstable and gave $\text{Ni}^{\text{II}}\text{TSPP}$ and methyl radicals. Independent experiments on the reaction of methyl radicals with $\text{Ni}^{\text{II}}\text{TSPP}$ 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 $\text{Cu}^{\text{II}}(\text{N-Me})\text{TSPP}$ 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 $(\text{Cu}^{\text{II}}\text{TAP})^\cdot$.

We are now examining the case of rhodium porphyrins. Certain rhodium porphyrins have been shown to photocatalyze the formation of H_2 from 2-propanol and the reduction of CO_2 , but the mechanism of the latter process is unclear. Rhodium porphyrins (RhP) have been prepared with the metal center at various oxidation states. The stable form under aerobic conditions is the $\text{Rh}^{\text{III}}\text{P}$ state. This can be reduced to $\text{Rh}^{\text{II}}\text{P}$ and $\text{Rh}^{\text{I}}\text{P}$, which are unstable in the presence of O_2 . $\text{Rh}^{\text{I}}\text{P}$ can react with a proton to form the hydride, $\text{HRh}^{\text{III}}\text{P}$. $\text{Rh}^{\text{II}}\text{P}$ can dimerize by forming a Rh-Rh bond. The dimerization of this radical-like species could be prevented in porphyrins with strong steric hindrance to dimerization, such as those bearing two ortho substituents on the meso-phenyl groups. Numerous studies utilized 5,10,15,20-tetramesitylporphyrin (TMP) as the ligand to stabilize the monomeric Rh^{II} state. Monomeric $\text{Rh}^{\text{II}}\text{TMP}$, however, is very reactive in other reactions, such as addition to double bonds or reaction with H_2 to form the hydride. We utilized radiolytic techniques to effect controlled reduction of rhodium porphyrins in alcohol solutions, first at the metal center and subsequently at the ligand. Further, we examined alkylation of these porphyrins and the possibility of CO_2 reduction, catalyzed by the reduced complex, or CO_2 insertion into alkyl-metal bonds.

We find that $\text{Rh}^{\text{III}}\text{TMP}$ undergoes radiolytic reduction in deoxygenated alkaline alcohol solutions to produce a transient $\text{Rh}^{\text{II}}\text{TMP}$ and then a stable $\text{Rh}^{\text{I}}\text{TMP}$. When the solvent was 2-PrOH and the KOH concentration was $>0.02 \text{ mol L}^{-1}$, the radiolytic yield

of reduction was considerably higher than the total yield of reducing radicals, indicating a chain reaction. For the chain reaction to proceed, we suggest that $\text{Rh}^{\text{II}}\text{TMP}$ reacts with a solvent molecule in a base-catalyzed process to form $\text{Rh}^{\text{I}}\text{TMP}$ and another reducing radical. The possibility that this occurs by direct hydrogen abstraction

is not likely, since the bond energy for H-Rh in the product (259 kJ mol^{-1} for hydridorhodium octaethylporphyrin) is lower than that for the H-C bond in 2-PrOH (381 kJ mol^{-1}). Therefore, most probably, the mechanism involves binding of $\text{Rh}^{\text{II}}\text{TMP}$ with a solvent molecule as an axial ligand, where this deprotonates to the $(\text{CH}_3)_2\text{CHO}^-$ anion, and then an intramolecular hydrogen transfer is assisted by the hydroxide anion.

The chain process may be terminated by reaction of the $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ radicals with $\text{Rh}^{\text{II}}\text{TMP}$ or by radical-radical reactions. No chain reaction was observed with $[\text{KOH}] < 0.01 \text{ mol L}^{-1}$ or when the solvent was MeOH. With pyridine as an axial ligand, reduction occurs on the porphyrin ring to yield $\text{Rh}^{\text{III}}\text{TMP}^-$, which then yields the stable $\text{Rh}^{\text{I}}\text{TMP}$. Further radiolytic reduction of $\text{Rh}^{\text{I}}\text{TMP}$ in 2-PrOH takes place at the porphyrin ring to yield the chlorin and more highly reduced products.

Unlike the results in alkaline solutions, radiolysis of $\text{Rh}^{\text{III}}\text{TMP}$ in 2-PrOH solutions under neutral or acidic conditions leads to production of alkyl- $\text{Rh}^{\text{III}}\text{TMP}$. These are produced by reaction of the intermediate $\text{Rh}^{\text{II}}\text{TMP}$, formed upon the first one-electron reduction, with alkyl radicals that are also formed by the radiolysis ($\cdot\text{CH}_3$ and $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$). Further reduction of alkyl- $\text{Rh}^{\text{III}}\text{TMP}$ occurs at the porphyrin ligand to produce alkyl- Rh^{III} -chlorin and alkyl- Rh^{III} -isobacteriochlorin. In the presence of CO_2 , the radiolytic reduction yields are increased, and only after extensive irradiations do we find evidence that a small amount of CO_2 may be reduced to CO. The extent and the mechanism of this process are under investigation.

Because reduction of CO_2 to CO probably requires binding of the compound to the metal center, and because this process and the insertion of CO_2 into alkyl-metal bonds may be inhibited by the rigid structure of the metalloporphyrin, we have also considered the use of other metal complexes to examine the feasibility of such reactions. We studied complexes derived from dimethylglyoxime, which are smaller in size than porphyrins, do not possess an extended π -system, and have a more flexible planar geometry.

Bis(dimethylglyoximato)cobalt(III) complexes and their alkyl derivatives were reduced by solvated electrons and by various radicals in solution. $\text{Cl(py)}(\text{dmgH})_2\text{Co}^{\text{III}}$ was reduced to the Co^{II} state and then to the Co^{I} state. Pulse radiolysis experiments indicated that upon reduction to the Co^{II} state the complex loses its Cl^- and pyridine axial ligands within $\leq 0.5 \mu\text{s}$ and upon further reduction to the Co^{I} state the complex takes up pyridine with a rate constant of $4.6 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$. $(\text{dmgH})_2\text{Co}^{\text{II}}$ reacts with alkyl radicals (R) to form a Co-C bond. $\text{R(py)}(\text{dmgH})_2\text{Co}^{\text{III}}$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5\text{CH}_2, 4\text{-carboxybenzyl}$) react rapidly with e_{aq}^- to give transient reduced species ascribed to $\text{R}(\text{dmgH})_2\text{Co}^{\text{II}}$. These species disappear by reaction with the starting material,

$R(py)(dmgH)_2Co^{III}$ ($k = 3.1 \times 10^7$ for $R = CH_3$ and $2.2 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ for $R = \text{benzyl}$ at pH 7) to result in formation of dialkylcobalt complexes, whose absorption is slightly red-shifted and more intense as compared with that of the alkylcobalt complex. γ -Radiolysis experiments also show the formation of the dialkylcobalt complex upon reduction of $R(py)(dmgH)_2Co^{III}$ with concomitant production of alkyl radicals from RX. These results are in contrast with those obtained from chemical and electrochemical experiments, where reduction of alkyl-cobaloxime led to dealkylation. $\dot{CO}_2^-$ radicals were found to react with the various forms of the above complexes by electron transfer, either rapidly or slowly, depending upon complex and conditions, but did not react at all via formation of metal-carbon bonds. Attempts to insert CO_2 into the less stable dialkylcobalt complex indicated very slow reaction and lack of any insertion product. CO_2 insertion probably requires not only unstable metal-carbon bond, which can be in equilibrium with the free radical, but also conditions for reducing CO_2 , since CO_2 does not react rapidly with carbon-centered radicals as does $\dot{CO}_2^-$. If R-M is split into R $\cdot$ and a strongly reducing metal ions, then this metal ion might reduce CO_2 to $\dot{CO}_2^-$, which will react with R $\cdot$ to produce RCO_2-M (this is most likely the mechanism for the observed photoinduced CO_2 insertion into R-In III P).

During the past year, we also have examined briefly the electron transfer reactions between porphyrins and fullerenes (in collaboration with Guldi and Asmus, Hahn-Meitner-Institut, Berlin). π -Radical anions of several metalloporphyrins (tetraphenyl- and tetrapyrrolyl-porphyrins) reduced C_{60} with rate constants of $1 - 3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, whereas metalloporphyrins which are reduced at the metal center (Ni I , Cu I , Cr II) reacted with C_{60} somewhat more slowly, with rate constants of $0.7 - 2.3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. Sb $^{VOEP\cdot}$ (octaethylporphyrin) did not reduce C_{60} ($k \leq 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$), probably because the reverse reaction is favored, and Sn $^{IV}(Ph)_3(Py)P\cdot$ reacted in an equilibrium process ($K = 14$). Electron transfer from C_{60} to several aromatic radical cations (derived from naphthalene, biphenyl, m-terphenyl, and t-stilbene) also took place rapidly ($k = 2.5 - 7.9 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$) to produce $C_{60}^{+\cdot}$; the radical cations of anthracene and chrysene did not react with C_{60} . In general, it was found that electron transfer to or from C_{60} took place with rate constants that are very close to the diffusion-controlled limit, even when the driving force for the reaction (the difference in reduction potentials) is relatively small. This suggests a very high self-exchange rate between C_{60} and its radical anion or cation, probably due to the high degree of delocalization of the unpaired electron and the unchanged geometry upon electron transfer. Only reducing species which are not delocalized radical anions, such as the low oxidation state metalloporphyrins, reacted with C_{60} somewhat more slowly.

In addition to the results summarized above under (a)-(c), we have studied other systems: halogen atom complexes in irradiated DMSO and their electron transfer reactions, Br atom complexes with various organic solvents, proton transfer reactions of some radical cations of heterocyclic compounds, reduction and decomposition of some substituted nitroalkanes, the mechanism of dimerization of several substituted phenoxyl radicals, and the reductive defluorination of pentafluorophenol to form tetrafluorophenoxyl radical. Most of the studies summarized above utilize the pulse radiolysis technique to obtain kinetic and mechanistic information on reactions of short-lived

intermediates in solution, with emphasis on electron transfer reactions. Currently, we are continuing to study aromatic peroxy radicals and redox and alkylation reactions of various metalloporphyrins.

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