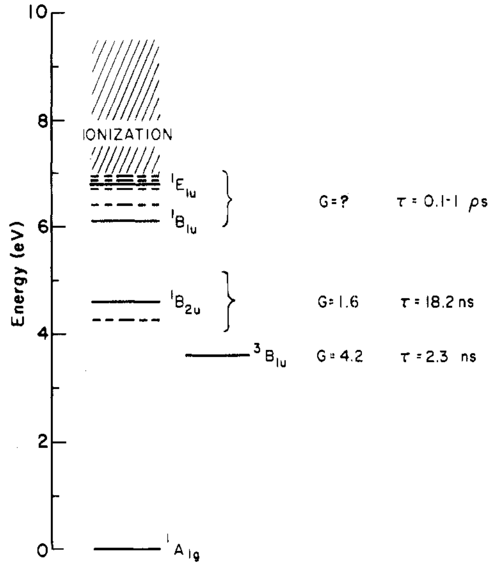

Figure 7. Term diagram for the lowest excited states of benzene. The lowest dashed line is a singlet excimer while the upper dashed lines are charge-transfer states. (See ref 19.)

for both products. It is also found that the isotopic composition of the hydrogen and acetylene produced from a 50:50 mixture of C_6H_6 and C_6D_6 does not depend on the irradiating particle,[9] indicating that similar mechanisms are operative in electron and in heavy-particle radiolysis. In the latter experiments HD is observed in a yield approaching that expected statistically, showing that hydrogen is not produced in any simple unimolecular process. However, the acetylene is predominantly from a single molecule although a small amount of scrambling does occur. Somehow energy must be localized in several molecules of benzene to produce these products before it is lost in decay processes. At this point a reasonable suggestion would seem to be second-order reaction between very short-lived excited states or possibly excited ions. The known excited states of benzene are indicated in Figure 7. The lifetime of the lowest lying singlet and triplet states would seem from the above discussion to be far too long to be involved here. If the shorter lived higher states are involved, then reaction between them would require second-order rate constants $\sim 10^{11}$ M^{-1} s^{-1}. It is, of course, disconcerting that a more complete mechanistic picture is not as yet available on a system that has been investigated so thoroughly as this one.

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Registry No. C_6H_6, 71-43-2; H_2, 1333-74-0.

Supplementary Material Available: Numerical tables (SI–SIV) of the experimentally observed H_2 yields and the data of Figures 2–4 (8 pages). Ordering information is given on any current masthead page.

One-Electron Oxidation in Irradiated Carbon Tetrachloride Solutions of ZnTPP, TMPD, and Phenols[†]

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One-electron oxidation of phenol, *p*-methoxyphenol, *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, chlorpromazine, and zinc tetraphenylporphyrin was studied by pulse radiolysis in carbon tetrachloride solutions. Phenols form phenoxyl radicals and the other compounds form cation radicals with yields strongly dependent on solute concentration. The highest yield in deoxygenated solutions approached $G = 4$. In the presence of oxygen an additional oxidation step is observed owing to $CCl_3\dot{O}_2$ radicals and the overall oxidation yield approached $G = 8$. ZnTPP was found to be oxidized to the cation radical without any side effects, unlike oxidation in 1,2-dichloroethane which was accompanied by demetallation owing to HCl production.

Introduction

Redox reactions involving porphyrins have been the subject of extensive investigation.[1] Recently, electron transfer between porphyrin π-cation radicals and neutral porphyrin molecules has been studied by pulse radiolysis.[2,3] The study was carried out with 1,2-dichloroethane solutions in which the formation of aromatic cation radicals had been known to occur.[4-7] The oxidation of porphyrins under these conditions, however, was complicated by the radiolytic production of HCl in this solvent, which causes demetallation of many metalloporphyrins. ZnTPP (TPP = tetraphenylporphyrin), MgTPP, and chlorophyll a were found to react rapidly with HCl under these conditions ($k \sim 10^8$ M^{-1} s^{-1} for the first step) to form H_4TPP^{2+} or pheophytin as the final product. The use of pyridine as an organic base prevented the demetallation but, on the other hand, pyridine binds to the metalloporphyrins (MP) as an axial ligand so that the redox reactions observed involve the pyridine–MP complexes rather than MP.[2,3]

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CCl_4 may be advantageous to $ClCH_2CH_2Cl$ for this purpose since formation of HCl by radiolysis, and thus demetallation, might possibly be prevented.

As a nonpolar aprotic solvent, CCl_4 has been studied quite extensively by radiolysis,[8-29] but the mechanisms of the various radiolytic reactions are not yet very clear. Specifically, there is disagreement concerning the assignment of the transient spectra to the particular species and consequently in the *G* values reported for these species. It is, therefore, necessary to examine some aspects of CCl_4 radiolysis and, in particular, to determine the yield of oxidation products under various conditions before embarking on the use of this solvent for the study of one-electron oxidation of porphyrins.

In the pulse radiolysis of several aromatic amines in CCl_4 solutions[16] *G* values for the production of radical cations were determined mostly at one solute concentration. At 1×10^{-2} M concentrations of aniline, *p,p′,p″*-tribromotriphenylamine, tri-*p*-tolyamine, 2,4,6-tri-*tert*-butylphenol, and TMPD, the *G* values for production of solute radical or radical cations were 1.3, 1.19, 1.48, 2.05, and 2.98, respectively. Increase of the concentration of tri-*p*-tolyamine to 7.5×10^{-2} M did not have any influence on the *G* value of radical cations. In an earlier work[12] a *G* value of 0.8 was reported as a limit for the oxidation of aniline at concentration above 10^{-2} M. However, by correcting the ϵ used by the latter authors,[12] the *G* value becomes 4.8, in wide disagreement with the value measured in ref 16. We examined in more detail the case of TMPD and two phenols in deoxygenated and oxygen-saturated solutions and find a pronounced effect of concentration on the yield of oxidation in irradiated CCl_4 solutions.

Experimental Section

Carbon tetrachloride, Spectranalyzed from Fisher, was purified by passing through a column of activated basic aluminum oxide (Woelm). *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine (TMPD) dihydrochloride from Eastman was dissolved in water and the free base TMPD was precipitated with NaOH. Chlorpromazine hydrochloride was obtained from Sigma. The free base was extracted with CCl_4 from aqueous solutions after adding NaOH and the extract was dried over $CaCl_2$. *p*-Methoxyphenol from Aldrich was recrystallized from CCl_4. The other compounds used were of the purest grade commercially available and were used without further purification. Phenol was from Mallinckrodt, the porphyrins were from Midcentury Chemical Co., and the gases were from Linde.

Optical spectra were recorded with a Cary 219 spectrophotometer. Steady-state radiolysis was carried out in a Gammacell 220 ^{60}Co source with a dose rate of 3.2 krd/min. Pulse radiolysis experiments were carried out with the computer-controlled apparatus described previously.[30] The dose per pulse was in the range of 200–500 rd, determined by thiocyanate dosimetry and corrected for the electron density of CCl_4.

Results and Discussion

Radiolysis of CCl_4. Although the radiolysis of CCl_4 has been studied extensively,[8-29] the nature and yields of the intermediates is still under discussion. Before presenting our findings it is worthwhile to summarize the previous conclusions and controversies.

Carbon tetrachloride is a very effective electron scavenger.[31] Therefore, it is expected[16,18,21,25-29] that after the initial ionization

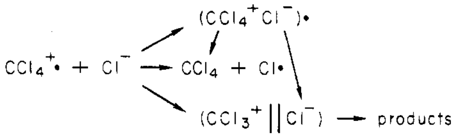
$$CCl_4 \rightsquigarrow CCl_4^{+\cdot} + e^- \qquad (1)$$

the electron would react very rapidly with the solvent

$$e^- + CCl_4 \rightarrow \dot{C}Cl_3 + Cl^- \qquad (2)$$

However, there are two approaches[18-29] to describe the reactions of the positive ions, differing in the estimation of the lifetime of CCl_4^+, and consequently in the subsequent mechanisms and in the interpretation of the intermediate spectra. Bühler et al.[18,19,22,28] suggested a very short lifetime for CCl_4^+, of the order of 200 ps, the decay involving decomposition and neutralization, resulting in CCl_3^+

$$CCl_4^{+\cdot} \rightarrow CCl_3^+ + Cl\cdot \qquad (3)$$



(4)

either free or in the solvent-separated ion pair $(CCl_3^+||Cl^-)$, which is also formed directly in the reaction

$$CCl_3^+ + Cl^- \rightarrow (CCl_3^+||Cl^-) \rightarrow \text{products} \qquad (5)$$

The intermediate absorption with $\lambda_{max} \sim 500$ nm is assigned to CCl_3^+ with $\epsilon_{500} = 6000\ M^{-1}\ cm^{-1}$,[28] and is thought to be the same for the free cation and for the ion pair. The absorption with $\lambda_{max} \sim 330$ nm was ascribed to $CCl_2\cdot$ which is formed from a highly excited state of CCl_4.[19]

Several authors,[20,21,26] on the other hand, identified the latter absorption as CCl_4^+, with a lifetime of the order of 100 ns, and assign the absorption at ~500 nm to $[CCl_4^+\cdots Cl^-]$ formed directly by the neutralization reaction

$$CCl_4^+ + Cl^- \rightarrow [CCl_4^+\cdots Cl^-] \qquad (6)$$

They also include reaction 3 in their mechanism but do not assign any absorption to CCl_3^+. Bühler recently[28] criticized this model and the interpretation of the spectra on the basis of kinetic considerations.

Evaluation of the *G* values for the intermediates depends on the mechanism assumed and was based on conductivity measurements[25] and on scavenger experiments.[12,16] Conductivity data fit the model of geminate ion recombination in a nonpolar system and the *G* value of free ions was measured to be 0.095 at 20 °C.[25] The initial yield of ionization was extrapolated to be 5 or 2.3, depending on the model used to describe the initial ion distribution.

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The ionization potentials of CCl_4 (IP = 11.47 eV[32]) and CCl_3 (8.78 eV[32]) are different enough to expect different reactivities for CCl_4^+ and CCl_3^+ and also indicate that CCl_3^+ may be a longer-lived species. But the similarities between CCl_4^+ and CCl_3^+ and the necessity to use high concentration of scavengers makes it difficult to distinguish between reactions involving these two ions. Besides there are also other intermediate and final products in the radiolysis of CCl_4, whose reactions have to be considered:

$$Cl\cdot + Cl^- \rightarrow Cl_2^- \quad (7)$$

$$Cl\cdot + Cl\cdot \rightarrow Cl_2 \quad (8)$$

$$CCl_3\cdot + CCl_3\cdot \rightarrow C_2Cl_6 \quad (9)$$

$$CCl_3\cdot + Cl\cdot \rightarrow CCl_4 \quad (10)$$

Cl^- is the main negative ion formed in reaction 2, but no *G* value was reported. The residual absorption with a maximum around 340 nm was assigned[21] to *Cl_2^-* but again no *G* value was reported. *Cl_2 and C_2Cl_6* were the only products determined after γ-radiolysis of dry, air-free CCl_4. The *G* value of both products was 0.7–0.8[8,9,11] and was interpreted as the yield of $\dot{C}l$ and $\dot{C}Cl_3$ which escape spur reactions. According to unpublished data of Dolenc, Hurni, and Bühler (cited in ref 28) $G(Cl_2)$ was 3.6 and $G(C_2Cl_6)$ was 3.4, after single-pulse irradiation owing to the higher concentration of radicals in the pulse radiolysis which favor reactions 8 and 9. Low yields of C_2Cl_4 were also reported.[15,17] *$CCl_3\cdot$ and $Cl\cdot$* attracted special attention as the precursors of Cl_2 and C_2Cl_6. The maximum *G* value for each of them, from experiment with scavengers, was 7–8.[15,17] $CCl_3\cdot$ radicals were also identified by ESR in frozen media.[27,33]

$\dot{C}Cl_3$ radicals are thought to play an important role in hepatotoxicity of CCl_4.[34,35] However, most oxidation reactions ascribed originally to $\dot{C}Cl_3$ turned out to be caused by another radical, $CCl_3\dot{O}_2$, produced very rapidly in the presence of even traces of oxygen.

$$\dot{C}Cl_3 + O_2 \rightarrow CCl_3\dot{O}_2 \quad (11)$$

This radical is an oxidizing agent and a number of its reactions have been reported.[36] It has been suggested[37] that this radical in aqueous system could decompose to produce a ClO radical

$$CCl_3O_2 \rightarrow COCl_2 + ClO \quad (12)$$

which is also an oxidizing species. In fact, $COCl_2$ was found as a product of radiolysis of CCl_4 saturated with O_2.[11] Packer et al., however, did not find any evidence for reaction 12.[36c]

Cl is also reactive and, for example, forms donor–acceptor complexes with aromatic molecules.[21,38]

$$Cl\cdot + Ar \rightarrow [Cl\leftarrow Ar] \quad (13)$$

The product of reaction 13 can be easily recorded by its strong absorption around 500 nm.

Many of the radiolysis products of CCl_4 could have oxidizing properties in the presence of the appropriate reagents, but variations in their reactivity and lifetime make the oxidation process quite complex, especially when other processes, such as substitution or hydrogen abstraction, can take place in parallel with electron transfer. To test the oxidation, we chose reactants whose one-electron oxidation products are known from measurements in other solvents. We have also repeated and extended some earlier results in CCl_4.

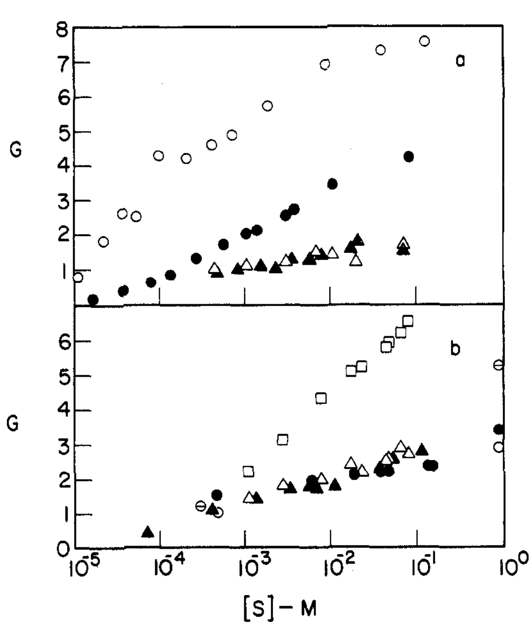

Figure 1. Concentration dependence of the *G* values of radicals in pulse-irradiated CCl_4 solutions saturated with N_2 or O_2: (a) TMPD, N_2 (●), O_2 (○); chlorpromazine, N_2 (▲), O_2 (△); (b) phenol, N_2 (●), O_2, initial *G* values (○) and maximum (⊖) *G* values; *p*-methoxyphenol, N_2 (▲), O_2, initial *G* values (△) and maximum values (□).

TABLE I: Spectral Data of the Observed Radicals and Kinetics of Their Formation

	radical		
compd (S)	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	$k_{(S + CCl_3\dot{O}_2)}$, M^{-1} s^{-1}
TMPD	572	11 870[a]	$(2.1 \pm 0.3) \times 10^9$
p-methoxyphenol	410	5 450[b]	$\leq 8 \times 10^6$
phenol	400	3 000[c]	$\leq 7.5 \times 10^4$
chlorpromazine	525	10 700[d]	*e*
ZnTPP		10 000[f]	$(1.2 \pm 0.2) \times 10^9$

[a] Measured in CCl_4 solutions, ref 16. [b] Data from aqueous solution, ref 39. [c] Data from aqueous solution, ref 40. [d] Data from aqueous solution, ref 43. [e] Rate constant could not be measured because of rapid decay of cation radical in these experiments. [f] ϵ at 660 nm, ref 1.

Deoxygenated Solutions

TMPD. Pulse radiolysis of CCl_4 solutions of TMPD shows formation of the spectrum of the $TMPD^{+}\cdot$ cation radical which absorbs in the range of 450–750 nm and has two peaks at ~575 and 615 nm. For calculation of yields we used $\epsilon_{572} = 1.187 \times 10^4$ M^{-1} cm^{-1} determined in CCl_4 from chemically prepared $TMPD^{+}\cdot$.[16] This cation radical is extremely sensitive to light and, therefore, we have carried out all the experiments using narrow band-pass filters to minimize photolysis by the analyzing light. The results (Figure 1a) show a considerable increase in the *G* value with concentration, indicating that the yield depends on the competition between the oxidation reactions and the decay of the intermediates. The yield reaches a value of $G \sim 4.2$. Since TMPD is oxidized very readily (see also redox potentials and rate constants determined in aqueous solutions),[39] we carried out experiments with compounds of higher oxidation potentials.

Phenol. The transient spectrum of the radical produced in pulse-irradiated solutions of phenol in CCl_4 is similar to that observed in aqueous systems, with two peaks around 380 and 400

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nm. For calculation of G values we adopted $\epsilon_{400} = 3000\ M^{-1}\ cm^{-1}$ from aqueous systems.[40-42] The results are summarized in Table I and Figure 1b. Phenol is found to be oxidized by the primary radicals rapidly, but less so than TMPD, and the yield of phenoxyl radicals reaches a value of only $G = 3.5$ at 1 M concentration. The phenoxyl radical produced under these conditions was found to be short-lived (first half-life ~ 60 μs at initial radical concentration ~ 2 μM).

p-Methoxyphenol. The *p*-methoxyphenoxyl radical exhibits absorption peaks at 290, 330, and 420 nm and a shoulder at 400 nm in aqueous solutions.[39] We obtained a very similar spectrum in CCl_4 solutions. The results (Table I and Figure 1b) are similar to those obtained with phenol. The *p*-methoxyphenoxyl radical decays by a second-order process with a first half-life of ~1 ms (at ~2 μM initial radical concentration).

Chlorpromazine. The chlorpromazine radical cation was also identified by comparison with data from aqueous solutions.[43] However, unlike the situation in aqueous systems, the radical cation was found to be short lived and the decay was composed of a fast component with a lifetime about 10 μs and ~30% of a longer-lived absorption. The results are presented in Table I and Figure 1a.

Other Compounds. We attempted to produce arylcarbenium ions which are known to be formed in dichloroethane solutions.[6,7] However, using the same solutes as before,[6,7] we obtained spectra in CCl_4 solutions different from those observed previously in dichloroethane. We also failed to obtain the radical cations from methoxybenzenes in CCl_4 solutions (using spectral data from aqueous systems).[44]

Oxygen-Saturated Solutions

As mentioned above, oxygen reacts very rapidly with $\dot{C}Cl_3$ radicals to form $CCl_3\dot{O}_2$, which is a good oxidizing agent in aqueous[36] and in CCl_4[45] solutions. However, this radical reacts more slowly than the primary oxidizing radicals from CCl_4. TMPD is oxidized by $CCl_3\dot{O}_2$ more radpily than any of the other compounds examined and produces a radical cation which is stable on the time scale used in the pulse radiolysis (ms). The results (Figure 1) show that in the concentration range of 1.1×10^{-5} to 1.3×10^{-1} M the G value for production of $TMPD^{+}\cdot$ radical cation increased from <1 to 7.5 and the rate constant for the reaction

$$TMPD + CCl_3\dot{O}_2 \rightarrow TMPD^{+}\cdot + CCl_3O_2^- \qquad (14)$$

was $k_{14} = (2.1 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$. The difference between the G value of the system with and without oxygen is about 3.5 (for concentrations > 10^{-4} M), indicating that the yield of $\dot{C}Cl_3$ radicals is $G \geq 3.5$ and also suggesting that in the oxygen-free system $\dot{C}Cl_3$ does not oxidize TMPD on the time scale of the pulse radiolysis.

The phenols and chlorpromazine react with $CCl_3\dot{O}_2$ more slowly than TMPD and their radicals are also relatively shorter lived. Therefore, the reactions did not take place quantitatively. The results are collected in Table I and Figure 1. In each case, an initial rapid oxidation was observed, with G values close to those observed with deoxygenated solutions. At longer times, further oxidation was seen, resulting from $CCl_3\dot{O}_2$ reactions. Again, in the limiting case for *p*-methoxyphenol the difference in yield between deoxygenated and oxygenated solutions reached $G \sim 3.5$, which is the yield of $\dot{C}Cl_3$ radicals. The initial oxidation step is, of course, due to the various primary radicals: CCl_4^+, CCl_3^+, Cl, and Cl_2^-, and the yield of oxidation strongly depends on the competition between the natural decay of these radicals and their reactions with the added scavengers. The more readily oxidized substrate, TMPD, scavenges most of these radicals, while the phenols and chlorpromazine are less efficient scavengers.

TABLE II: Electron Transfer between Phenoxyl Radicals and TMPD in N_2-Saturated CCl_4

solute	[TMPD], M	k,[a] $M^{-1}\ s^{-1}$	G-($TMPD^{+}\cdot$)	G-(PhO)[b]
phenol, $C = 1.7 \times 10^{-1}$ M	1.7×10^{-4}	4.3×10^8	3.6	2.4
	3.3×10^{-4}	4.7×10^8	3.6	
	6.2×10^{-4}	5.5×10^8	3.5	
p-methoxyphenol, $C = 6.4 \times 10^{-2}$ M	4.9×10^{-4}	1.3×10^8	3.0	2.5
	1.1×10^{-3}	1.5×10^8	3.7	
	2.1×10^{-3}	1.6×10^8	4.1	

[a] Rate of formation of ($TMPD^{+}\cdot$). [b] Initial.

Electron Transfer between Phenoxyl Radicals and TMPD. By analogy with aqueous systems,[39] the differences in redox potential between the two investigated phenols and TMPD suggest that a fast electron transfer from TMPD to phenoxyl radicals should take place in CCl_4 as well. Conditions were chosen such that the primary oxidation after the pulse will produce only phenoxyl radicals, which then react with TMPD to form $TMPD^{+}\cdot$ radicals in a process considerably slower than that in N_2-saturated solution without phenols. Owing to the large differences in spectra, it was easy to follow the kinetics of these processes. The data are presented in Table II. The trend in the rate constants agrees with the higher redox potential for phenol in comparison to *p*-methoxyphenol, but the G value measured for production of $TMPD^+$ radicals deserve some comments. These values are significantly higher than that expected from the yield of phenoxyl radicals (assuming that the ϵ values taken from aqueous systems for phenoxyl radicals are valid in CCl_4 solutions). This difference cannot be explained by higher reactivity of TMPD and competition with phenols for the primary products of CCl_4 radiolysis, because the experiments indicate that $TMPD^+$ formation occurs in one slow step only. A possible explanation for these results is that one of the primary radicals from CCl_4 can oxidize TMPD to $TMPD^{+}\cdot$ but reacts with phenols without producing phenoxyl radicals. Instead, it produces a molecular complex which does not absorb significantly at 400–500 nm. Upon addition of TMPD, both the phenoxyl radical ($G \sim 2.5$) and the molecular complex ($G \sim 1.5$) oxidize it to $TMPD^+$ with similar rates that appear as a single kinetic process. The molecular complex may involve phenol with Cl or Cl_2^-, for example, but this is only a speculation.

Initial Ionization in CCl_4. To estimate the initial ionization yields, we plotted the present results using the equation

$$G(P) = G_{fi} + G_{gi}\{(\alpha C)^{1/2}/[1 + (\alpha C)^{1/2}]\} \qquad (15)$$

which describes the scavenging efficiency as a function of concentration of the scavenger.[46] For TMPD, the results give a satisfactory fit to the equation only at concentrations higher than 3×10^{-4} M (Figure 2); at lower concentrations apparently different processes prevail, probably radical oxidation instead of ionization. Extrapolation to the high limit of TMPD concentration gives $G = 4.7$ for the initial ionization. In the case of phenol and *p*-methoxyphenol the same procedure gives $G = 2.8$, but the scatter of data is quite large. As mentioned above, some of the primary radicals are probably producing a species different than phenoxyl radical. Some conclusions could also be drawn from the results in oxygenated systems. The increase of G value in the presence of oxygen corresponds to CCl_3O_2 radicals and, consequently, to CCl_3 radicals. According to the mechanism, this value is equal to the yield of electrons plus the yield of $\dot{C}Cl_3$ directly formed from excited states. The efficiency of scavenging of $\dot{C}Cl_3$ by oxygen should be high enough to achieve conversion of the majority of $\dot{C}Cl_3$ to $CCl_3\dot{O}_2$. Our results indicate that the G value of $\dot{C}Cl_3$ radicals is in the range 3.5–4.5 for the higher concentration limit.

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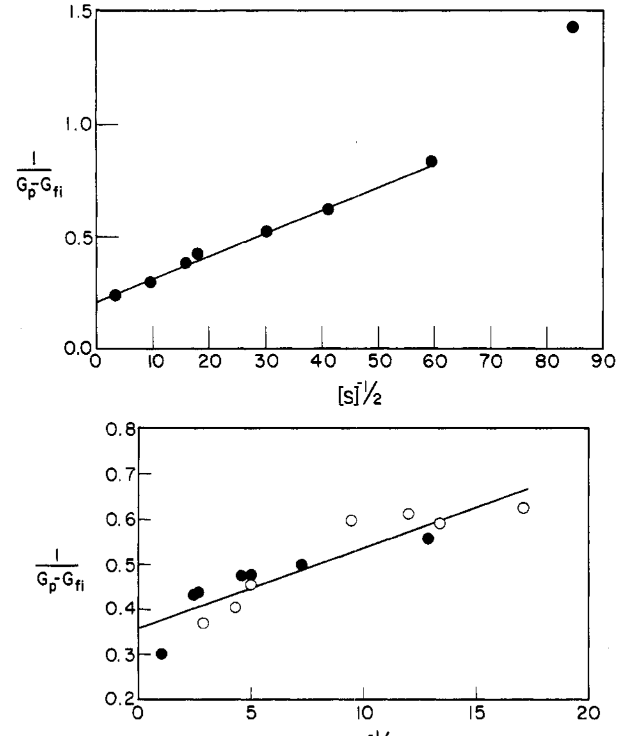

Figure 2. Plot of $1/(G_p - G_{fi})$ vs. $[S]^{-1/2}$. G_p is the yield of radicals, G_{fi} the yield of free ions in CCl_4 taken as 0.095: (top) S = TMPD; (bottom) S = phenol (●) and *p*-methoxyphenol (○).

The present results on the yield of oxidation products and of $\dot{C}Cl_3$ are in very good agreement with the measurements based on ionic conductivity[25] and suggest $G = 5$ as a better value for the initial ionization process.

Porphyrins

The range of concentrations normally used with porphyrins is 10^{-5}–10^{-4} M. In this range we can expect G values of <1 for oxidation in deoxygenated solutions and of $\sim$3–5 with oxygen present, if the reactivity is sufficiently high. In preliminary experiments with ZnTPP it has been shown[47] that in the dose range used in the pulse radiolysis experiments demetallation did not take place. ZnTPP was oxidized to form the π-cation radical whose spectrum is known from electrochemical measurements[1] to have a broad absorption band in the 500–700-nm range. Pulse radiolysis experiments in dichloroethane also gave such a spectrum.[2] In this work, as preliminary information of porphyrin oxidation in CCl_4, we present the dependence of the yield of ZnTPP π-cation radical on the concentration of the porphyrin in solutions saturated with oxygen or with nitrogen (Figure 3). To calculate the G values we take $\epsilon = 1 \times 10^4$ M^{-1} cm^{-1} at 660 nm for $(ZnTPP)^{+\cdot}$.[1] The rate constant of formation of the radical in oxygenated solutions was $(1.2 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, and without oxygen the reaction was too fast to measure. Thus, ZnTPP is oxidized by $CCl_3O_2\cdot$ nearly as rapidly as is TMPD, and the overall yield reaches $G \sim 8$ with both compounds. However, the differences between the G values in the presence and absence of O_2 are higher with ZnTPP than in the case of TMPD. This may indicate that one of the primary species, other than $\dot{C}Cl_3$, oxidizes the porphyrin only in the presence of O_2, as suggested above for phenol. In the absence of oxygen this unidentified species may either react with the porphyrin by a different mechanism or may preferentially react with other species.

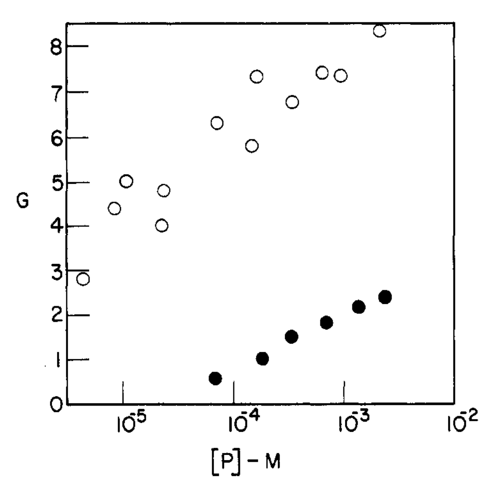

Figure 3. Concentration dependence of the G value of ZnTPP π-radical cation in CCl_4 solutions saturated with N_2 (●) or O_2 (○).

In conclusion, neat CCl_4 is a convenient solvent for studying one-electron oxidation reactions by pulse radiolysis, especially in the presence of oxygen. We are currently utilizing this system to investigate electron transfer reactions between porphyrins and porphyrin cation radicals.[47]

Registry No. ZnTPP, 14074-80-7; TMPD, 100-22-1; $TMPD^{+\cdot}$, 34527-55-4; $CCl_3O_2\cdot$, 69884-58-8; CCl_4, 56-23-5; O_2, 7782-44-7; phenol, 108-95-2; phenoxyl radical, 2122-46-5; *p*-methoxyphenol, 150-76-5; *p*-methoxyphenoxyl radical, 6119-32-0; chlorpromazine, 50-53-3; chlorpromazine radical cation, 34468-21-8.

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