

Figure 11. Plot of the calculated excited-state equilibrium constant $*K_2$ as a function of the water content of the acetonitrile/water solvent mixtures. For details, see text.

poses, acetonitrile does not act as a practical base in the excited-state dissociation. In such a case, a new equilibrium (eq 5)

$$*BH^{+} + nH_{2}O \rightleftharpoons *B + H(H_{2}O)_{n}^{+}$$
(5)

should be considered, where n is the average number of water molecules acting as the proton-accepting "cluster". The relevant equilibrium constant then becomes

$$*K_{2'} = \frac{[*B][H(H_2O)_n^+]}{[*BH^+][H_2O]^n} = \frac{*K_2}{[H_2O]^n}$$
(6)

where $[H(H_2O)_n^+]$ is equal to the analytical HClO₄ concentration,

and [H₂O] represents the concentration of free water molecules (i.e., $[H_2O] = [H_2O]_0 - n[HClO_4]$, where $[H_2O]_0$ is the analytical water concentration). In principle, this model could also help to rationalize the dependence of $*K_2$ on HClO₄. In fact, if $*K_{2'}$ is the true equilibrium constant, then $*K_2$ is expected to depend on the acid concentration, as this concentration affects that of free water in the denominator of eq 6. While the value of n is not known a priori, it can be estimated by fitting the observed dependence of $*K_2$ on the water concentration. Three such plots corresponding to trial n values of 2, 3, and 4 are shown in Figure 11. It is seen that a quite satisfactory fitting is obtained for n= 3, but not for n = 2 or n = 4. Altogether, these results seem to indicate that in these acetonitrile/water mixtures the proton has an average hydration number of 3 ± 0.5 . Clusters of water molecules of various sizes acting as proton carriers in pure water or water/organic solvent mixtures have been suggested by several authors. Very recently, Robinson³⁴ suggested an average hydration number of 4 ± 1 for protons in methanol/water mixtures, based on a Markov random-walk analysis of solvent composition effects on the lifetime of 2-naphthol.

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Reactivities of Chlorine Atoms and Peroxyl Radicals Formed in the Radiolysis of Dichloromethane

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Radiolysis of dichloromethane (DCM) leads to formation of primary oxidizing radicals and carbon-centered radicals. The latter react with oxygen to yield peroxyl radicals. The yields and chemical behavior of these intermediates were studied by pulse radiolysis of DCM solutions containing various solutes: phenols, anilines, dimethoxybenzene, hexamethylbenzene, cyclohexene, dimethyl sulfoxide, and zinc tetratolylporphyrin. At low concentrations, some of these solutes were found to be oxidized by two peroxyl radicals, $CH_2ClO_2^*$ and $CHCl_2O_2^*$, with different rate constants. At higher concentrations, the solutes react also with the primary radicals: Cl atoms and the radical cations $CH_2Cl_2^{+*}$, with diffusion-controlled rate constants. The rates of these reactions were determined by competition kinetics because of the very short lifetimes of the species. Cl atoms were found to have a half-life of about 5 ns in DCM, reacting predominantly with the solvent by hydrogen abstraction. The radical cations decay within a fraction of a nanosecond. The total yield of these primary radicals was determined to be G = 3.6 and appears to be divided about equally between Cl and the radical cations. The total yield of oxidation, by the primary and the peroxyl radicals, was found to be G = 7.5. Cl atoms were found to be very reactive in electron transfer as well as addition and hydrogen abstraction reactions.

Introduction

Dichloromethane (DCM) is used frequently as a solvent to carry out electrochemical or radiolytic one-electron oxidation of solutes. Yet, although several organic compounds have been shown to undergo simple one-electron oxidation in irradiated DCM solutions, the exact nature and yields of primary radiation products in this solvent remain to be established. The primary action of radiation may be ionization and/or C-Cl bond rupture:

$$CH_2Cl_2 \rightarrow [CH_2Cl_2]^{+\bullet} + e^-$$
(1)

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$$CH_2Cl_2 \rightarrow CH_2Cl + Cl$$
 (2)

Subsequently, e⁻ reacts rapidly with the solvent:

$$e^{-} + CH_2Cl_2 \rightarrow {}^{\bullet}CH_2Cl + Cl^{-}$$
(3)

Cl atoms also react with the solvent:

$$Cl + CH_2Cl_2 \rightarrow CHCl_2 + HCl$$
 (4)

and if the radical cation deprotonates

$$[CH_2Cl_2]^{+\bullet} \rightarrow {}^{\bullet}CHCl_2 + H^+$$
(5)

the net reaction resulting from either mechanism 1 or 2 is

$$2CH_2Cl_2 \rightarrow CH_2Cl + CHCl_2 + HCl$$
(6)

Emmi et al.¹ suggested a decomposition of [CH₂Cl₂]^{+•} into Cl atoms and CH₂Cl⁺ and subsequent combination of this cation with the Cl⁻ produced in reaction 3 to give a solvated ion pair $[CH_2Cl^+\cdot Cl^-]$. Alternatively, they envisaged formation of ion pair between $[CH_2Cl_2]^{+}$ and Cl^- followed by elimination of HCl to yield •CHCl₂.

An early study² on the γ radiolysis of DCM-cyclohexene mixtures found three products: chlorocyclohexane (G = 4.9), (chloromethyl)cyclohexane (G = 2.0), and bicyclohexenyl (G =3.8). These results indicated that CH_2Cl_2 radiolysis ruptures the C-Cl bond without any significant cleavage of the C-H bond. The reaction of Cl with DCM (reaction 4) was not important in this system because all Cl atoms were presumably captured by the cyclohexene present at high concentration. Another study³ indicated that the reaction of Cl atoms with DCM does not result in chlorine atom abstraction and can be formulated as in reaction 4. A more recent pulse radiolytic study⁴ on DCM/oxygen solutions examined the spectra and kinetics of haloalkyl and peroxyl radicals and considered the importance of reaction 4 on the short time scales. On the basis of an earlier⁵ estimate of $k = 6 \times 10^4$ M^{-1} s⁻¹ for the reaction of Cl with CHCl₃, it was suggested that reaction 4 was unimportant on the microsecond time scale. However, a rate constant of this magnitude is far too slow as compared with those measured in the gas phase.⁶ Indeed, in a very recent paper, Emmi et al.¹ conclude that Cl atoms react rapidly with the DCM solvent. Our results also indicate that reaction 4 takes place with a relatively high rate constant. Furthermore, we report here on the measurement of rate constants for reactions of Cl atoms with several organic compounds.

In aerated solution both chloromethyl and dichloromethyl radicals react with oxygen very rapidly to yield peroxyl radicals:

$$^{\bullet}CH_{2}Cl + O_{2} \rightarrow ^{\bullet}O_{2}CH_{2}Cl$$
(7)

$$^{\bullet}CHCl_{2} + O_{2} \rightarrow ^{\bullet}O_{2}CHCl_{2}$$
(8)

It is clear from the above discussion that a compound irradiated in aerated DCM may be oxidized by the radical cation, the Cl atom, and the two peroxyl radicals, each with a different yield and a different rate constant. The purpose of the present study is to shed some light on these mechanisms and to determine rate constants for the various radicals.

Experimental Section⁷

Dichloromethane (DCM) was a Mallinckrodt AR (ACS) reagent, dimethyl sulfoxide (DMSO) was Aldrich Gold Label, cyclohexene, 1,4-dimethoxybenzene, aniline, N,N-dimethylaniline (DMA), and N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) were obtained from Aldrich, hexamethylbenzene (HMB) was from Eastman, phenol and p-methoxyphenol (PMP) were from Sigma, pyridine, benzene, toluene, and cyclohexane were from Mallinckrodt, and zinc tetra-p-tolylporphyrin (ZnTTP) was from Midcentury Chemical Co. All chemicals were of the purest grade available and were used without further purification, except for aniline, which was distilled before use.

Fresh solutions were prepared before each experiment, and samples were transferred with a syringe to the irradiation cell. The pulse radiolysis apparatus was described before.⁸ It utilizes

(4) Emmi, S. S.; Beggiato, G.; Casalbore, G.; Fuochi, P. G. Fifth Tihany

50-ns pulses of 2-MeV electrons from a Febetron 705 accelerator. The dose per pulse could be varied from 3 to over 100 Gy, but most experiments were done with a dose of about 5 Gy. The kinetic spectrophotometric detection system consisted of a Varian 300-W xenon lamp, a 2-cm optical path length irradiation cell, a Kratos high-intensity monochromator, an RCA 4840 photomultiplier, and the proper shutters, lenses, and optical filters. The signals were digitized with a Tektronix 7612 transient recorder and analyzed by a PDP 11/34 minicomputer. Rate constants were derived from a series of experiments at varying concentrations and are generally accurate to $\pm 10\%$. However, rate constants derived for cases of overlapping reactions or from competition kinetics are less accurate, as indicated. Dosimetry was carried out with N2O-saturated aqueous KSCN solutions. All experiments were carried out at room temperature, 22 ± 2 °C.

Results and Discussion

Reaction of Cl Atoms with Dichloromethane. It is clear from the Introduction that Cl is an important intermediate in the radiolysis of DCM and may be one of the crucial species when considering oxidation of solutes. To assess its role in the system, it is necessary first to determine its lifetime in solution. Since Cl has been reported to have an optical absorption with a maximum at 310 nm,9 we examined the transient absorption in pulse-irradiated DCM on the microsecond time scale. We could not detect any peak at 310 nm, and all absorptions in the UV were compatible with peroxyl radicals only. Therefore, we resorted to measuring the rate of reaction 4 by competition kinetics with an added solute.

A reaction of Cl with DMSO was reported to take place in irradiated DCM, chloroform, and CCl₄, with $k = 7 \times 10^9$ M⁻¹ s⁻¹, to yield a transient adduct absorbing at 400 nm:¹⁰

$$Cl + (CH_3)_2 SO \rightarrow (CH_3)_2 S(Cl)O$$
 (9)

We have confirmed the formation of the 400-nm peak in pulseirradiated DMSO/DCM solutions. The absorbance (A) at this peak increased gradually, by an overall factor of ~ 4 , upon increasing [DMSO] from 4.4 to 560 mM. If the competition is between reaction 9 and reaction 4 only, the dependence of absorbance on concentration can be expressed by the equation

$$\frac{1}{A} = \frac{1}{A_0} + \frac{1}{A_0} \frac{k_4 [\text{DCM}]}{k_9 [\text{DMSO}]}$$
(10)

A plot of 1/A vs [DCM]/[DMSO] gave a straight line. From the value of slope/intercept = k_4/k_9 and $k_9 = 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ we derive $k_4 = 9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, in very good agreement with the value reported by Emmi et al.¹ The experimental result actually means that the half-life of Cl atoms in neat DCM is 4.8 ns, and the above value of k_4 is correct if reaction 4 is the only one competing with reaction 9. Such a short lifetime for the Cl atoms cannot be ascribed to reactions with other radicals or with impurities and must be predominantly due to reaction 4. This result leads to the conclusion that in the absence of other reactive solutes all Cl atoms react with DCM within <0.1 μ s and, therefore, measurements on the microsecond time scale involve the two peroxyl radicals, ClCH₂O₂• and Cl₂CHO₂•. Since the optical absorption spectra of these two radicals are expected to be very similar, it would be impossible to distinguish between them on the basis of spectral measurements. However, it is known that the reactivity of peroxyl radicals increases with the number of halogen substituents and that Cl₂CHO₂ is more reactive than $ClCH_2O_2^{\bullet}$ toward several substrates.^{11,12} Therefore, it may be possible to confirm the presence of two peroxyl radicals by resolving the kinetics of their separate reactions with certain solutes. We chose ZnTTP and TMPD, which are readily oxidized by peroxyl radicals and, therefore, can be added at sufficiently low concentrations such that competition for Cl atoms is negligible.

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recognition or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified are necessarily the best available for the purpose

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Figure 1. Linear dependence of k_{obsd} on the concentration of ZnTTP-Pyr. Monitored at 640 nm in DCM solutions containing 1% pyridine for the fast (a) and the slow (b) processes demonstrated in the insert.

Oxidation of ZnTTP. Zinc porphyrins undergo one-electron oxidation to give the π -radical cations that absorb in the 600-700-nm range.¹³ Such an absorption was indeed found on pulse radiolysis of ZnTTP in CH₂Cl₂, and the kinetic measurements were carried out mostly at 640 nm. The rate of oxidation increased linearly with [ZnTTP], and from a plot of k_{obsd} vs [ZnTTP] over $(1-5) \times 10^{-5}$ M we derive a second-order rate constant of 3 \times 10⁹ M⁻¹ s⁻¹. Upon further increase in [ZnTTP] the observed rates deviated from linearity, indicating a contribution from a slower reaction. However, it was not possible to differentiate experimentally between the two reactions. The results suggest that ZnTTP is oxidized by CHCl₂O₂[•] with $k = 3 \times 10^9$ M⁻¹ s⁻¹ and by CH₂ClO₂[•] somewhat more slowly. The assignment is based on previous findings that the rate of oxidation by peroxyl radicals increases with the number of halogens on the α position.^{11,12} It may be possible to obtain better separation of the two processes by using a compound that is less readily oxidized. The complex ZnTTP·Pyr, obtained by addition of pyridine to the ZnTTP solution, is known to be oxidized more slowly than ZnTTP.¹⁴ In fact, when the oxidation was carried out in DCM solutions containing 1% pyridine, the rate constants were much lower and the two processes were easily separated, as demonstrated by the kinetic trace inserted in Figure 1. From plots of k_{obsd} for the fast process vs [ZnTTP] in the range $(2-10) \times 10^{-5}$ M and for the slow process in the range $(5-15) \times 10^{-4}$ M (Figure 1) we derive $k_{11} = 2.7 \times 10^{-4}$ M 10⁸ and $k_{12} = 2.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$:

$$CHCl_2O_2^{\bullet} + ZnTTP \cdot Pyr \rightarrow CHCl_2O_2^{-} + (ZnTTP \cdot Pyr)^{+\bullet}$$
(11)

$$CH_2ClO_2^{\bullet} + ZnTTP Pyr \rightarrow CH_2ClO_2^{-} + (ZnTTP Pyr)^{+\bullet}$$
(12)

Thus ZnTTP-Pyr is oxidized at least an order of magnitude less rapidly than ZnTTP, and the two peroxyl radicals are readily



Figure 2. Yield of *p*-methoxyphenoxyl radicals as a function of *p*-methoxyphenol concentration. Given as absorbance measured at 420 nm immediately after the pulse (O) and at longer times (\bullet) after reaction of peroxyl radicals was complete.

differentiated. Nevertheless, both oxidations are complete at a porphyrin concentration of 1.5 mM, which is too low to compete for the Cl atoms to any appreciable extent (see below).

Oxidation of TMPD. The rate of oxidation of TMPD was followed at 570 nm, one of the reported peaks for the stable radical cation TMPD^{+•}.¹⁵ At [TMPD] = 0.4–3.2 mM the plot of k_{obsd} vs concentration was linear, and its slope gave $k_{13} = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$:

$$CHCl_2O_2^{\bullet} + TMPD \rightarrow CHCl_2O_2^{-} + TMPD^{+\bullet}$$
 (13)

At higher [TMPD] a slower process became apparent, but its rate constant could not be determined accurately because of overlapping processes.

The molar absorptivity of TMPD^{+•} in DCM, determined to be 12 200 M⁻¹ cm⁻¹ at 567 nm,¹⁵ can be used to calculate the yield of the radicals in irradiated DCM. Using thiocyanate dosimetry in N₂O-saturated solutions¹⁶ and correcting for the difference in electron densities between water and DCM, we find the yield of TMPD^{+•} at solute concentrations of 0.4–3.2 mM to be G = 3.6radicals/100 eV. This yield can be ascribed to the dichloromethylperoxyl radical reacting in reaction 13, i.e., the yield of °CHCl₂ radicals produced by reactions 4 and 5.

The overall yield of TMPD⁺ increased with concentration up to G = 7.5 at 0.34 M. This value is the total yield of radicals in DCM (see below).

Oxidation of p-Methoxyphenol. The yield and rate of oxidation of p-methoxyphenol (PMP) were examined over a wide range of concentrations, from 0.02 to 1.8 M, by following the formation of the p-methoxyphenoxyl radical absorption at 420 nm. At all concentrations the formation consisted of two distinct steps: a fast step, which was always complete within less than a microsecond, and a slower step occurring over 10-100 μ s. The ratio between the yield in the fast step to that in the slower step increased with concentration. The yields in both steps increased with [PMP] and leveled off at [PMP] ~ 1 M (Figure 2). The maximum yields correspond to G = 3.6 for the fast step and G= 6.8 for the total (assuming molar absorptivity of ~6000 M⁻¹ cm⁻¹ for the p-methoxyphenoxyl radical as in aqueous solution¹⁷).

The fast step may be due to reaction with Cl atoms:

$$CH_3OC_6H_4OH + Cl^{\bullet} \rightarrow CH_3OC_6H_4O^{\bullet} + HCl$$
 (14)

which is in competition with reaction 4, and possibly also to reaction with the radical cation, and the slow step represents the reaction with the peroxyl radicals:

$$CH_3OC_6H_4OH + RO_2^{\bullet} \rightarrow CH_3OC_6H_4O^{\bullet} + RO_2H$$
(15)

The rate of the slow step increased with [PMP], but the increase was not linear (Figure 3). In the lower range, [PMP] = 0.02-0.10 M, a plot of k_{obsd} vs [PMP] gave a straight line with a slope of

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Figure 3. Rate of reaction of peroxyl radicals produced in DCM as a function of concentration of *p*-methoxyphenol (see text).

 6×10^5 M⁻¹ s⁻¹. At higher [PMP] the slope of the line decreased by about a factor of 5. This decrease indicates that at low concentrations PMP reacts mainly with $CHCl_2O_2^{\bullet}$ (higher k) and at high concentrations PMP reacts with $CH_2ClO_2^{\bullet}$ (lower k). At high [PMP] most of the Cl atoms react with the solute rather than with the solvent and thus the yield of CHCl₂O₂ radicals is decreased. Therefore, a rate constant of $k = 2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ derived from the highest concentration can be ascribed to the reaction of PMP predominantly with CH₂ClO₂. At the low range of [PMP] reaction 4 becomes important, and then the slow step is a combination of the reaction of PMP with both peroxyl radicals. The slope of 6×10^5 M⁻¹ s⁻¹ derived from the lowest concentrations can be ascribed to the reaction of PMP with CHCl₂O₂, since at these concentrations the other peroxyl radical, which reacts more slowly, has a much lower contribution (due to the second-order decay competing with the slow oxidation).

If the yield of the fast oxidation step represents only the competition between reaction 4 and reaction 14, the dependence of yield on [PMP] should provide the relative reactivities (k_4/k_{14}) . A plot of 1/A vs [DCM]/[PMP], according to an equation parallel with eq 10, should be linear and provide the value of k_4/k_{14} from slope/intercept. Of the 10 data points in Figure 4a, 8 may fit a reasonably straight line, but the 2 points for the lowest solute concentrations (high [DCM]/[PMP]) deviate from the line. Although the deviations may be partly due to experimental errors in the measurement of low A values, they may indicate that the competition involves more than one radical, i.e., Cl atoms and possibly a solvent radical cation. To examine this possibility, it would be advantageous to use solutes that are oxidized by Cl atoms and other strong oxidants but not by the peroxyl radicals, so that the yield of the fast step can be determined accurately without interference by the slower step. For this purpose we examined phenol and aniline, and the results obtained with these compounds (see below) confirm the involvement of two radicals. On that basis we analyze the results for PMP.

Exact mathematical analysis is not possible, but we can use the results for the three lowest concentrations to represent one set of competing reactions and the results for the highest concentrations to represent another set of competing reactions. The line drawn through the lowest concentrations (Figure 4a) has an intercept of 76, which corresponds to an absorbance of 0.013. This absorbance value represents the yield of the species involved in the competing reactions at low [PMP]. Since the total yield of the fast process (Figure 2) is 0.023, it appears that the two species involved in the fast step are formed with somewhat similar yields. By using the line drawn in Figure 4a, we can correct the results for the highest concentrations and draw another line (Figure 4b) that represents the other competition. The correction is made by calculating the value of A_0 for each concentration from the line in Figure 4a, then deriving $A' = A - A_0$ and plotting 1/A' vs [DCM]/[PMP]. The two lines in Figure 4 provide only ratios of rate constants. For the Cl atoms this would be the ratio k_4/k_{14} and for the radical cation this would be the ratio between the rate of its decomposition (e.g., reaction 5) to that of PMP oxidation. Let us assume that the results at the lower concentrations represent



Figure 4. Dependence of 1/A on [DCM]/[PMP]: (a) dependence over the whole range and the line for the competition at low PMP concentrations; (b) dependence for high PMP concentration with use of A', derived by subtracting the respective values of A_0 of the line in Figure 4a from the experimental A values.

the competition for Cl atoms. By using the lifetime of the Cl atoms in DCM determined above and the slope/intercept of the line in Figure 4a, we derive a rate constant of 5×10^9 M⁻¹ s⁻¹ for reaction 14. If we assume that the other oxidizing radical reacts with PMP at least as rapidly as does Cl, we can derive from the line in Figure 4b a rate constant of $>7 \times 10^9$ s⁻¹ for the decay of this species. If we reverse the assignment of the lines in Figure 4 to the respective radicals, we obtain a much lower rate constant for reaction 14, only 1×10^8 M⁻¹ s⁻¹, which is unreasonable.¹⁸ Therefore, we tentatively conclude from these results that two strong oxidants are produced in the radiolysis of DCM, with nearly equal yields: Cl atoms, which oxidize PMP with $k_{14} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and probably the radical cations CH₂Cl₂^{+•}, which oxidize PMP at least as rapidly and decay on the picosecond time scale. These conclusions are supported by the results for phenol and aniline described below.

Oxidation of Phenol. The oxidation of phenol by the peroxyl radicals is expected to be slower than that of p-methoxyphenol and was not observed in our experiments, owing also to the relatively rapid decay of phenoxyl radicals. However, the fast oxidation step was clearly seen at all concentrations (from 4 mM to 1 M), and its yield was used to obtain the rate constant for the reaction of phenol with Cl atoms:

$$C_6H_5OH + Cl^{\bullet} \rightarrow C_6H_5O^{\bullet} + HCl$$
 (16)

A plot of 1/A vs [DCM]/[phenol] showed a considerable curvature (Figure 5a), suggesting again that more than one species is involved in the oxidation. Treatment of the data as described above for PMP gives the two lines in Figure 5. From the results for the low concentration range we derive $k_{16} = 2.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, and if we assume again that the radical cation oxidizes phenol with a similar rate constant, we derive $k = 8 \times 10^9 \text{ s}^{-1}$ for the rate of its self-decay, in agreement with the value estimated above from the results with PMP. From the intercept in Figure 5a, which is 42, we calculate A = 0.024 for the contribution of Cl atoms to the yield of phenoxyl radicals. Since the total yield at high

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Figure 5. Dependence of 1/A on [DCM]/[phenol]. The data and lines in a and b are as explained under Figure 4.

concentrations gave A = 0.045, we find again that the two species involved in the fast oxidation reactions are formed with similar yields.

Oxidation of Aniline. One-electron oxidation of aniline was found to yield the radical cation, $[C_6H_5NH_2]^{+*}$, which then loses a proton over several microseconds to give the neutral radical, $C_6H_5NH^*$, as was observed before in aqueous solutions.¹⁹ The deprotonation was readily observable at 400–440 nm where the radical cation has a stronger absorption than the neutral radical. To avoid this complication, the kinetics of oxidation were monitored at 370 nm, where the deprotonation process does not cause any change in absorbance. Aniline was studied over a wide concentration range, 4 mM to 1 M, and all experiments showed oxidation in a fast and a slow step.

The slow step at low aniline concentrations (4-17 mM) took place with k_{obsd} increasing with concentration from 2.4×10^4 to $3.7 \times 10^4 \text{ s}^{-1}$. The dependence gave a rate constant of 1×10^6 $M^{-1} \text{ s}^{-1}$ which can be ascribed to the oxidation of aniline by $CHCl_2O_2^{\bullet}$ radicals. At higher aniline concentrations k_{obsd} increased up to $6 \times 10^4 \text{ s}^{-1}$ and then decreased somewhat. The value at 1 M aniline was $k_{obsd} = 5 \times 10^4 \text{ s}^{-1}$. The observed decrease is a result of decreased formation of $CHCl_2O_2^{\bullet}$ due to reaction of Cl with aniline, and thus at higher aniline concentrations the reaction of $CH_2ClO_2^{\bullet}$ becomes predominant. Therefore, the rate constant for this reaction is estimated to be $k = 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ from the value of k_{obsd} at 1 M aniline.

A plot of 1/A vs [DCM]/[aniline] according to eq 10 also gave a curved line similar to that found for phenol. Treatment of the data assuming two oxidizing radicals as described above gave k= 4×10^{10} M⁻¹ s⁻¹ for the reaction of Cl with aniline, and if we assume that the radical cation oxidizes aniline with a similar rate constant we estimate $k = 2 \times 10^{10}$ s⁻¹ for its self-decay (e.g., reaction 5).

Oxidation of N,N-Dimethylaniline. DMA was studied at concentrations of 0.2-220 mM. From the rate of the slow step at low concentrations we derive $k = 2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of CHCl₂O₂[•] with DMA. The reaction of the other peroxyl radical could not be determined properly because of the decay of DMA^{+•}. The yield of DMA^{+•} produced in the fast step increased by about a factor of 4 upon increasing [DMA] from

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2 to 220 mM. A plot of 1/A vs [DCM]/[DMA] gave a nearly straight line in this case, with somewhat scattered data points. Therefore, it was not possible to distinguish between two oxidizing radicals. From the slope/intercept we calculate a rate constant of 2×10^{10} M⁻¹ s⁻¹ for the oxidation of DMA by Cl atoms and by the radical cations.

Oxidation of p-Dimethoxybenzene. Dimethoxybenzenes are known to be oxidized by strong oxidants to form radical cations that have limited lifetimes.²⁰ The decay of the radical cation of DMB, followed at 460 nm, was faster than that observed in aqueous solutions, so that slow oxidation by the peroxyl radicals could not be observed. In any case, the peroxyl radicals are not expected to be capable of oxidizing DMB on thermodynamic grounds. The yield of DMB⁺⁺ in the fast oxidation step increased with concentration (2-360 mM), and a plot of 1/A vs [DCM]/[DMB] gave a somewhat straight line which did not permit clear distinction between the two oxidizing radicals. From the slope/intercept we calculate a rate constant of 1.8×10^{10} M⁻¹ s⁻¹ for the oxidation of DMB by Cl atoms and by the radical cations.

Determination of Rate Constants for Cl Atom Reactions by Competition with DMSO. The experiments described above provided the rate constants for reaction of Cl atoms with several compounds whose radical products could be followed spectrophotometrically. Rates for compounds that do not yield readily observable radicals may be determined by competition with DMSO as was done before.²¹ We have utilized this technique to obtain rate constants for Cl with several other representative compounds.

As an example of an aromatic compound that is likely to undergo hydrogen abstraction we chose hexamethylbenzene. Pulse radiolysis of HMB in dichloromethane is expected to yield the corresponding benzyl radical, which will react with O_2 to form the peroxyl radical. We have observed a partial spectrum of this radical in the UV but found it inconvenient for competition kinetics. This radical has practically no absorption at 400 nm and, therefore, does not interfere in the monitoring of the DMSO chlorine atom adduct at this wavelength. Using 0.14 M DMSO and 0–0.16 M HMB, we find that the yield of the Cl-DMSO adduct decreases upon increasing [HMB]. The competition can be described by the equation

$$\frac{A_0}{A} - 1 = \frac{k(\text{Cl} + \text{HMB})[\text{HMB}]}{k(\text{Cl} + \text{DMSO})[\text{DMSO}] + k(\text{Cl} + \text{DCM})[\text{DCM}]}$$
(17)

where A_0 is the absorbance at 400 nm in the absence of HMB and A is the absorbance in the presence of HMB while [DMSO] is kept constant. From the linear plot of A_0/A vs [HMB] and with the rate constants for Cl with DMSO and with DCM (determined above), we calculate $k(\text{Cl} + \text{HMB}) = 2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

In these experiments it was noticed that an increase in [HMB] not only decreased the yield of Cl·DMSO adduct but also decreased the lifetime of the adduct produced. The decay of Cl-DMSO was found to follow first-order behavior with k_{obsd} linearly dependent on [HMB]. From this plot we derive a rate constant of $6.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, which we ascribe to the reaction of the Cl·DMSO adduct with hexamethylbenzene.

Similar results were obtained with cyclohexene. The rate constant for its reaction with Cl atoms was determined to be $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and for its reaction with Cl·DMSO adduct $2.6 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$.

Cyclohexane was less reactive than cyclohexene so that the competition experiments required higher concentrations of the hydrocarbon. However, the plot of the competition data did not give the expected linear behavior, probably because the high cyclohexane concentrations affected the radiation yields. Attempts

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TABLE I: Rate Constants for Reactions of Peroxyl Radicals in DCM

	$k, M^{-1} s^{-1}$	
compound	CH ₂ ClO ₂ •	CHCl ₂ O ₂ •
ZnTTP ZnTTP·Pyr TMPD PMP aniline DMA	$\sim 10^{9}$ 2.6 × 10 ⁷ 2 × 10 ⁵ $\sim 5 × 10^{4}$	$3 \times 10^{9} 2.7 \times 10^{8} 3 \times 10^{8} 6 \times 10^{5} 1 \times 10^{6} 2.5 \times 10^{7} $

to determine the rate constant for Cl with benzene and toluene by competition with DMSO were not successful because the addition of these compounds was found to increase rather than decrease the absorbance at 400 nm, possibly due to formation of a complex between Cl and the aromatic ring. Further experiments are planned to clarify this point.

Radiolytic Yields of Primary Radicals. The yield of TMPD+• formed in the fast step was determined to be G = 3.6, and the total yield after both fast and slow steps was G = 7.5. These are considered the most reliable results since the molar absorptivity of TMPD^{+•} was determined accurately in DCM solutions.¹⁵ For the other radicals derived from the phenols and anilines the molar absorptivities (ϵ) are known only for aqueous solutions and may be somewhat different in DCM. In the case of PMP, the values of ϵ from aqueous solutions led to G = 3.6 and 6.8, in reasonable agreement with the above values. However, using the maximal absorbance for phenoxyl radicals and the ϵ for phenoxyl in aqueous solution, we calculate G of only 2.6, indicating that ϵ must be different in the two solvents, probably because the peak of phenoxyl is very sharp. Similarly, the results for DMB give a lower G value if the ϵ from aqueous solutions is used; this is not surprising since the radical is charged and would be more highly solvated in water. The results for DMA also lead to a somewhat lower value of G. Therefore, we take G = 3.6 determined in the experiments with TMPD to represent the yield of primary oxidizing radicals, i.e., Cl atoms and radical cations. The distribution between these radicals is nearly 1:1 as discussed above. According to reactions 1-3, for each of the above radicals a $^{\circ}CH_2Cl$ radical is formed. After these radicals react with O_2 to give peroxyl, the overall yield of oxidizing species is expected to be about G = 7.2, in very good agreement with the above measurements. This yield is also similar to that determined before for CCl₄ solutions.²²

Reactivities of the Peroxyl Radicals. Table I summarizes the rate constants determined in this study for the reactions of $CH_2ClO_2^{\bullet}$ and $CHCl_2O_2^{\bullet}$. They vary from $10^9 M^{-1} s^{-1}$ for ZnTTP down to less than $10^5 M^{-1} s^{-1}$. The rate constants for phenol and dimethoxybenzene could not be measured because they are considerably lower than $10^5 \text{ M}^{-1} \text{ s}^{-1}$. In all cases, the rate constant for the dichloromethylperoxyl radical is higher than that for the monochloro. As shown before, 11,22,23 the trichloro derivative reacts even faster. This trend is clearly due to the effect of increasing number of halogens, which increases the electron affinity of the radical. The mechanism of reaction of these radicals with ZnTTP and TMPD involves electron transfer from the substrate to the radical. Phenols and anilines that react more slowly may undergo electron transfer as well, although in these cases hydrogen abstraction may not be ruled out. Where the reaction involves electron transfer, the rate constant should be dependent on the driving force and on the self-exchange rate of each reactant. A comparison of aniline, DMA, and TMPD shows increasing rate constants in that order, in agreement with the order of redox potentials for these three compounds.^{17,24} On the other hand, PMP reacts more slowly despite the fact that its oxidation potential is lower than those of aniline and DMA. The low rate constant in this case results from the low self-exchange rate of phenols and

TABLE II: Rate Constants for Reactions of Cl Atoms in DCM

compound	$k, M^{-1} s^{-1}$	
dimethyl sulfoxide	7×10^9 (ref 21)	
dichloromethane	9×10^{6}	
<i>p</i> -methoxyphenol	5×10^{9}	
phenol	2.5×10^{10}	
aniline	4×10^{10}	
dimethylaniline	2×10^{10}	
dimethoxybenzene	1.8×10^{10}	
hexamethylbenzene	2.2×10^{10}	
cyclohexene	1.2×10^{10}	
methanol	2.7×10^9 (ref 21)	
n-pentanol	7.9×10^9 (ref 21)	

is in line with previous findings that one-electron oxidation of phenols is very much slower than that of phenoxide ions.¹⁷

Reactivity of Cl Atoms. The rate constants for reaction of Cl atoms determined in this study are summarized in Table II along with representative values from ref 21. It is obvious from the table that Cl atoms react very rapidly with numerous types of organic compounds. They oxidize phenols, anilines, and methoxybenzenes with diffusion-controlled rate constants k of the order of 10^{10} M^{-1} s⁻¹. The mechanism involves electron transfer in the case of TMPD and DMB while for the other compounds it may involve either electron transfer or hydrogen abstraction (or possibly both). The slight variations in rate constants are practically within the experimental error $(\pm 25\%)$.

Cl atoms react very rapidly also by hydrogen abstraction from allylic (cyclohexene) and benzylic positions (HMB). Hydrogen abstraction from alcohols also occurs rapidly, with rate constants gradually increasing from 2.7×10^9 for methanol to 7.9×10^9 M^{-1} s⁻¹ for *n*-pentanol.²¹ Only the deactivated hydrogens in DCM are abstracted considerably more slowly, $k = 9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Cl atoms also add rapidly to DMSO. Their reaction with cyclohexene may involve addition to double bonds as well as hydrogen abstraction.

This high reactivity of Cl contrasts with that of the complex radical ion Cl₂⁻. Oxidation by Cl₂⁻ takes place with rate constants²⁵ 2-3 orders of magnitude lower than those found for Cl in the present study. Even when both are measured in aqueous solutions, Cl was found to oxidize much more rapidly, e.g., Fe²⁺ ions.²⁶ For hydrogen abstraction reactions the difference is even greater. The rate constants for Cl reaction with alcohols are 4-6 orders of magnitude higher than those for Cl_2^{-25} . It is interesting to note that the complex radical DMSO-Cl also was found to be reactive toward HMB and cyclohexene. Although its reactivity cannot be compared with that of Cl_2^- in a quantitative fashion, it appears that both complex radicals exhibit somewhat similar reactivities. Recently, complexes of Cl atoms with benzene and pyridine also have been observed, and their reactivities found to be much lower than those of free Cl atoms.27,28

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Registry No. DCM, 75-09-2; TMPD, 100-22-1; PMP, 150-76-5; DMSO, 67-68-5; DMA, 121-69-7; DMB, 150-78-7; HMB, 87-85-4; ZnTTP, 19414-67-6; [CH₂Cl₂]^{+•}, 58165-12-1; Cl, 22537-15-1; *O₂CH₂Cl, 73761-32-7; *O₂CHCl₂, 73761-31-6; ZnTTP•Pyr, 57304-77-5; phenol, 108-95-2; aniline, 62-53-3; cyclohexene, 110-83-8; cyclohexane, 110-82-7; benzene, 71-43-2; toluene, 108-88-3; p-methoxyphenoxyl radical, 6119-32-0.

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