# Radiolysis of Tetrachloromethane†

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Electron spin resonance studies of tetrachloromethane after exposure to  ${}^{60}$ Co  $\gamma$ -rays at 77 K reveal the formation of  ${}^{\circ}$ CCl<sub>3</sub> and CCl<sub>4</sub><sup>+</sup> radicals. On warming in the presence of spin-traps, or on irradiating fluid solutions, nitroxide radical adducts have been detected that are characteristic of  ${}^{\circ}$ CCl<sub>3</sub> and chlorine atom adducts. In the light of this evidence and that of other investigators a mechanism for the radiolysis of tetrachloromethane is postulated.

In the presence of oxygen,  $\cdot$  CCl<sub>3</sub> radicals are converted into Cl<sub>3</sub>COO  $\cdot$  radicals. The use of spin-traps to detect these radicals is described and evaluated.

Mishra and Symons have analysed the solid-state e.s.r. spectra of  $^{12}CCl_3$  and  $^{13}CCl_3$ in various frozen media and the results make it clear that these radicals are non-planar, with extensive delocalization of the unpaired electron onto chlorine.<sup>1</sup> Hesse *et al.*<sup>2</sup> have shown that  $^{CCl_3}$  radicals give rise to complicated e.s.r. spectra in pure tetrachloromethane, and have suggested that there are two trapping sites for these radicals, which undergo 'free' rotation at 185 K.

Other studies have concentrated on pulse radiolysis with optical detection,<sup>3, 4</sup> and on the use of spin-traps to give stable nitroxide radicals where e.s.r. spectra give information concerning the original radicals,<sup>5, 6</sup> The former studies are not clear-cut because of the difficulty of assigning broad structureless ultraviolet absorption bands to specific intermediates. In the most recent work, it is suggested that a band at *ca*. 340 nm is due to  $CCl_4^{++}$  radicals, another at *ca*. 475 nm is due to  $CCl_4^{++}$ — $Cl^{-}$ ion-pairs, and a third in the 370 nm region is due to  $Cl_2^{-}$  ions.<sup>3</sup> In contrast, only neutral radicals are detected in spin-trapping experiments. In this case, however, evidence for  $\cdot CCl_3$  radicals is clear cut because of the detection of well resolved <sup>13</sup>C hyperfine coupling.<sup>5, 6</sup> Apparently the  $\cdot CCl_3$  radical has no absorption maximum above 230 nm,<sup>7</sup> and hence is not readily detected in pulse-radiolysis studies on pure tetrachloromethane, which is optically black in this region.

Our present aim is to use e.s.r. spectroscopy to distinguish between ionic and neutral radical mechanisms for the radiolysis of tetrachloromethane. Our interest in tetrachloromethane arises because it is a powerful hepatotoxic agent used in studies of liver injury,<sup>8,9</sup> ·CCl<sub>3</sub> radicals being implicated as significant intermediates.<sup>5,6,10</sup>

# EXPERIMENTAL

Chemicals were of the highest grade available and were used as supplied by the manufacturers without further purification: tetrachloromethane, (B.D.H. AnalaR); *N*-t-butyl- $\alpha$ -phenyl-nitrone (PBN), (Aldrich); 2-methyl-2-nitrosopropane (MNP), (Aldrich); tetrachloromethane, <sup>13</sup>C—CCl<sub>4</sub> (90.2 atom %), diluted as indicated, (British Oxygen Co Ltd).

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The radiolysis of tetrachloromethane in the presence of the spin-trapping agent was performed in silica e.s.r. tubes exposed to a source of  ${}^{60}$ Co y-rays either at 77 K or at room temperature. The mean dose was 10 krad.

When MNP was used as the spin trap, experiments were performed in the dark, to avoid photolysis. Solutions were degassed by the freeze-thaw technique, or oxygenated by passing a stream of oxygen through the solutions prior to freezing. In some experiments liquid oxygen was added to the fine powder obtained by dropping tetrachloromethane and a solution of the spin-trapping agent into liquid nitrogen.

Photolysis was performed using the full arc of a 400 W mercury source focused on the e.s.r. cavity at room temperature.

Spectra were measured on a Varian E-3 spectrometer fitted with a variable-temperature cavity.

# **RESULTS AND DISCUSSION**

#### SOLID-STATE STUDIES

The most direct method of probing the mechanism of radiolysis is solid-state e.s.r. spectroscopy. Two well separated sets of features result, one set being that previously assigned to  $\cdot Ccl_3$  radicals,<sup>1,2</sup> and the other, shown in fig. 1(a), being tentatively assigned to  $CCl_4^+$  radicals. The central features are due to  $\cdot CCl_3$  radicals and radicals in the e.s.r. tube, but the other features are due to a species containing strongly coupled <sup>35</sup>Cl and <sup>37</sup>Cl nuclei (<sup>35</sup>Cl and <sup>37</sup>Cl have I = 3/2: the abundance of <sup>35</sup>Cl is 75.4% and that of <sup>37</sup>Cl is 24.6%). The possibility that this species is atomic chlorine can be rejected because the highest field line shows at least three features for <sup>35</sup>Cl and <sup>37</sup>Cl combinations. A two-chlorine radical such as  $Cl_2^-$  could be responsible for these features, but if it was we would expect only seven parallel features and  $g_{\parallel}$  would be ca. 1.95, whereas for  $Cl_2^-$  or  $(RCl - ClR)^+$  radicals,  $g_{\parallel}$  should be close to the free-spin value (2.0023). If three equivalent chlorine atoms are involved then there should be ten sets of features. On this interpretation,  $g_{\parallel} = 2.005$ ; this is a reasonable value for  $g_{\parallel}$  and lends support to the interpretation that the species  $\mathrm{CCl}_4^+$ . In this case, the high-field parallel (-9/2) line should have four components (3  ${}^{35}Cl$ ; 2  ${}^{35}Cl$ +1  ${}^{37}Cl$ ;  $1^{35}Cl + 2^{37}Cl; 3^{37}Cl$  in the approximate ratios 9:7:5:3. The first three components



FIG. 1.-For legend see facing page.

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FIG. 1.—First derivative X-band e.s.r. spectra for tetrachloromethane after exposure to <sup>60</sup>Co γ-rays at 77 K.
 (a) Showing features assigned to CCl<sub>4</sub><sup>+</sup> cations; central features are due to •CCl<sub>3</sub> radicals and radicals in the e.s.r. tube. (b) Showing features for RO<sub>2</sub><sup>-</sup> radicals formed in aerated solutions after annealing.

are well defined, but the last is largely hidden under the more intense -7/2 feature. The possibility of four equivalent chlorine nuclei can be ruled out because then there would be some low-field parallel lines outside the intense 'perpendicular' features, which were not detected.

As is frequently the case for powder spectra of such radicals, analysis of the 'perpendicular' feature is more difficult. However, the analysis suggested in fig. 2 does accommodate the form of the major low-field lines quite satisfactorily, and, in particular, it accommodates the nearly isotropic nature of the +5/2 set of lines, which is the most characteristic feature of the spectrum.

We suggest that this species is  $\text{CCl}_4^+$ . The only other reasonable species having three equivalent chlorine atoms is  $\cdot \text{CCl}_3$ , the spectrum of which is quite different.<sup>1, 2</sup> Following the loss of an electron, the tetrahedral  $\text{CCl}_4^+$  cation is bound to be distorted, according to the Jahn–Teller theorem, and our results suggest that this distortion is such that three chlorine atoms move so that the 'hole' is shared between them, leaving the fourth chlorine uncoupled. The resulting orbital is a linear combination of  $3p(\pi)$  orbitals on chlorine which are non-bonding with respect to carbon. A possible form for this orbital is shown, viewed along the axis of the unique chlorine, as structure I.





FIG. 2.--For legend see p. 2211.

Clearly the measured parallel and perpendicular components are not principal values for the individual 3p orbitals, but are intermediate between the true parallel and perpendicular values. Hence the estimated anisotropy should be smaller than the true anisotropy. If the data given in table 1 are analysed in the usual way<sup>11</sup> we obtain  $A_{iso} = 46.5$  G and 2B = 12.9 G, after correcting for the shift in  $g_{\perp}$ .

The correction for orbital magnetism is no greater than our experimental errors and is therefore neglected. (This analysis is based on like signs for  $A_{\parallel}$  and  $A_{\perp}$ . The choice of opposite signs leads to impossible values for calculated orbital populations.) These results can be converted into approximate orbital populations,<sup>11</sup> giving *ca.* 2.3% *s* character and 13% *p* character on each chlorine atom. The former value is high, but possible for spin polarisation. The latter value leads to a total spin density of 39%, which is far too low. As stressed above, this value should be low, owing to the fact that the experimental data are the values along the symmetry axes and not principal values.

We conclude that the assignment of these features to  $CCl_4^+$  cations is well supported and this is accepted in the following discussion. These features are much weaker than





FIG. 2.-For legend see p. 2211.

those for  $\cdot \text{CCl}_3$  radicals, which explains why they were not detected by others.<sup>2</sup> Nevertheless, since the lines are far broader than those for  $\cdot \text{CCl}_3$ , the two species are present in comparable concentrations.

Brede *et al.* have assigned a band at *ca.* 340 nm to the  $CCl_4^+$  cation.<sup>3</sup> That there should be a relatively low-lying optical band is supported by the presence of ultraviolet or visible transitions for the isostructural radicals  $PO_4^{*2-}$  and  $SO_4^{*-}$ . They stress that the species must be distorted in order to prevent rapid charge transfer

$$\operatorname{CCl}_{4}^{*+} + \operatorname{CCl}_{4} \rightleftharpoons \operatorname{CCl}_{4} + \operatorname{CCl}_{4}^{*+}.$$
 (1)

Our results establish the nature of this distortion. The nature of the 475 nm species is less clear. Their assignment is to the ion-pair  $CCl_4^+\cdots Cl^-$ , which might well give rise to an intense charge-transfer band. Alternatively, reaction with  $Cl^-$  could give the  $\sigma^*$  radical, structure II, which could exhibit an intense  $\sigma \to \sigma^*$  absorption.



FIG. 2.-For legend see facing page.

Table	1E.s.r.	PARAMETERS
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	spin trap	hyperfine coupling constants/G <sup>a</sup>		
radical		<sup>14</sup> N	ιΗ	other
CCl <sup>+b</sup>				<sup>35</sup> Cl, 59.4, 40, iso 46.5
•CCl <sub>3</sub> <sup>c</sup>				<sup>35</sup> Cl, 20, <i>ca</i> . 0, iso 6.7
•13CCl <sub>3</sub>	PBN	13.5	1.5	<sup>13</sup> C, 9.4
$\cdot$ <sup>13</sup> CCl <sub>3</sub> <sup>d</sup>	PBN	14.10	1.74	<sup>13</sup> C, 9.68
•12CCl <sub>3</sub>	MNP	13.1		<sup>35</sup> Cl, 2.25
•13CCl <sub>3</sub> <sup>e</sup>	MNP	12.7		<sup>35</sup> Cl, 2.4
•Cl	PBN	12.2	0.7	<sup>35</sup> Cl, 6.1
•Cl <sup>f</sup>	PBN	12.12	0.75	<sup>35</sup> Cl, 6.05
Cl <sub>3</sub> COO•	MNP	27.0		
(Cl <sub>3</sub> COO· <sup>g</sup>	MNP	27.5		
$\int or Cl_3 CO^h$	MNP	27.0		
Cl <sub>3</sub> COO	PBN	13.5	1.6	
$RO \cdot or RO_2^{i}$	PBN	13.5-13.6	1.75-1.85	
RO <sup>,j</sup>	PBN	13.7	2.1	
$RO_2^{j}$	PBN	13.5	1.3	
$\cdot {}^{12}\text{CCl}_3{}^k$	MNP	6.75		<sup>13</sup> C, 5.7
				<sup>35</sup> Cl, 0.6

<sup>a</sup> 1 G =  $10^{-4}$  T. Isotropic unless indicated. <sup>b</sup>  $g_{\parallel} = 2.005$ ,  $g_{\perp} = 2.043$ . <sup>c</sup> Ref. (1). <sup>d</sup> Ref. (6). <sup>e</sup> Ref. (13). <sup>f</sup> E. G. Janzen, B. R. Knauer, L. T. Williams and W. B. Harrison, J. Phys. Chem., 1970, 74, 3025. <sup>g</sup> Ref. (14). <sup>h</sup> Ref. (15). <sup>i</sup> N. Ohto, E. Niki and Y. Kamiya, J. Chem. Soc., Perkin Trans. 2, 1977, 1770. <sup>j</sup> Ref. (17). <sup>k</sup> Probably ClCONO(CMe<sub>3</sub>).



FIG. 2.—First derivative X-band e.s.r. spectra for various spin-trap nitroxide radicals: (a) PBN + Cl-[(PhCH(Cl)NO(CMe<sub>3</sub>)], (b) PBN and  $\cdot^{12}$ CCl<sub>3</sub>, (c) PBN +  $\cdot^{13}$ CCl<sub>3</sub>, (d) MNP +  $\cdot^{12}$ CCl<sub>3</sub> and (e) MNP +  $\cdot^{13}$ CCl<sub>3</sub> in the presence of oxygen. Features  $\alpha$  (a) and  $\beta$  (a), (c) and (d) are due to PhCH(CCl<sub>3</sub>)NO(CMe<sub>3</sub>) and acyl nitroxides, respectively.

However, we have not obtained any evidence for such species, nor have we been able to detect  $Cl_2^-$  anions, which were also postulated by Brede *et al.*<sup>3</sup>



## structure II

If oxygen is not removed from the system, a new species is detected after annealing,<sup>2</sup> the e.s.r. spectrum of which is given in fig. 1 (b). This has  $g_{\parallel} = 2.037$  and  $g_{\perp} = 2.003$ , these values being characteristic of ROO radicals. These must be Cl<sub>3</sub>COO radicals since (Cl<sub>3</sub>C—ClOO ·)<sup>+</sup> or ClOO would have quite different spectra.<sup>12</sup>

## USE OF SPIN TRAPS

Two different traps were used, PBN and MNP (structures III and IV). PBN usually adds radicals ( $R \cdot$ ) to carbon to give a nitroxide, structure V, and MNP usually adds to nitrogen, giving structure VI.



 $Me_3C - NO$ 

MNP, structure IV

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Radicals of structure V display hyperfine coupling to <sup>1</sup>H, <sup>14</sup>N and to atoms directly bonded to carbon that are  $\beta$  to the electron on nitrogen and interact *via*  $\sigma$ - $\pi$  overlap (hyperconjugation). Radicals of structure VI give a <sup>14</sup>N triplet with hyperfine features due to coupling to  $\alpha$  and  $\beta$  nuclei in R. Thus, for example,  $\cdot$ <sup>13</sup>CCl<sub>3</sub> radicals of structure V should exhibit strong coupling to <sup>13</sup>C but none to <sup>35/37</sup>Cl, whereas radicals of structure VI should give resolved coupling to both types of nuclei.

Our results are summarised in table 1. Only PBN gave an adduct with chlorine atoms, and this was unstable above *ca.* 270 K. The spectrum is, however, quite distinctive [fig. 2(*a*)], showing features for <sup>35</sup>Cl and <sup>37</sup>Cl, and a large value of  $A_{iso}$ , as expected for  $\beta$  chlorine atoms with good  $\sigma - \pi$  overlap. Thus the formation of chlorine atom intermediates is established. This accords with the optical detection of  $Cl_2^-$  radicals,<sup>3</sup> presumably formed from Cl<sup>-</sup> and Cl<sup>-</sup>. Also present in the e.s.r. spectrum are features for  $\cdot$  CCl<sub>3</sub> adducts ( $\alpha$ ), which are stable and can be seen clearly at room temperature. This spectrum shows only coupling to <sup>14</sup>N and <sup>1</sup>H [fig. 2(*b*)], but when <sup>13</sup>C-enriched CCl<sub>4</sub> was used, another set of lines displaying coupling to <sup>13</sup>C was also resolved [fig. 2(*c*)]. The coupling of 9.4 G is again characteristic of a  $\beta$ -carbon atom with good  $\sigma - \pi$  overlap.

In contrast, with MNP the  $\cdot^{12}$ CCl<sub>3</sub> adduct gave clear coupling to all three chloride nuclei [fig. 2(*d*)], a result which is diagnostic of  $\cdot$ CCl<sub>3</sub> radicals. The coupling to  $^{35}$ Cl and  $^{37}$ Cl nuclei of 2.25 G agrees reasonably with the literature value<sup>13</sup> (table 1).

These results with spin traps confirm the formation of  $\cdot CCl_3$  radicals and establish the presence of Cl· atoms. Taken alone, they would seem to support the homolysis mechanism

$$\operatorname{CCl}_4 \to \operatorname{CCl}_4^{+} + e^- \tag{2}$$

$$\operatorname{CCl}_4^{\cdot +} + e^- \to (\operatorname{CCl}_4)^* \to \operatorname{CCl}_3 + \operatorname{Cl}^{\cdot}$$
(3)

in which  $(CCl_4)^*$  is an electronically excited molecule. However, the solid-state results show that  $\cdot CCl_3$  radicals are formed together with  $CCl_4^+$  cations in the primary process, so this sequence is inadequate. To explain the presence of  $CCl_4^+$  cations, electrons must react elsewhere and we suggest that the reaction

$$CCl_4 + e^- \rightarrow \cdot CCl_3 + Cl^- \tag{4}$$

well known in protic media, must also occur. However, this should prevent the occurrence of step (3). In that case, the simplest way of explaining yields of chlorine atoms comparable with those of  $\cdot$ CCl<sub>3</sub> radicals is by the dissociation

$$\operatorname{CCl}_{4}^{+} \leftrightarrows \operatorname{CCl}_{3}^{+} + \operatorname{Cl}^{\bullet} \tag{5}$$

This may be an overall reaction occurring by more complicated routes, but we stress that  $CCl_3^+$  is isostructural with stable molecules such as  $SO_3$ , so reaction (5) may not be too unfavourable. Also  $CCl_3^+$  cations would be rapidly removed by reaction with  $Cl^-$  ions formed in step (4). In view of the evidence for  $CCl_4^+Cl^-$  ion-pairs,<sup>4</sup> and the expected rapid formation of ion-pairs in this low dielectric medium, the step

$$\operatorname{CCl}_4^+\operatorname{Cl}^- \to \operatorname{CCl}_4 + \operatorname{Cl}^{\bullet}. \tag{6}$$

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is a source of Cl<sup> $\cdot$ </sup> atoms that avoids the formation of CCl<sup>+</sup><sub>3</sub> cations. Steps (2), (4) and (6) give all the required products, and so we favour these as the most probable process for the radiolysis of tetrachloromethane.

#### **REACTION WITH OXYGEN**

Our solid-state results confirm the rapid and irreversible reaction of  $\cdot$ CCl<sub>3</sub> radicals with oxygen. Reactions of RO · and ROO · radicals with spin traps show that MNP is by far the most useful, as a characteristic species with a greatly increased coupling to <sup>14</sup>N is produced (*ca.* 27 G). However, for ROO · radicals there is some confusion about identification, since the <sup>14</sup>N coupling constants obtained in reactions with ROO · radicals<sup>14</sup> are similar to those obtained with RO · radicals.<sup>15</sup> The <sup>14</sup>N isotropic coupling is greatly increased for nitroderivatives because these radicals are pyramidal at nitrogen whereas simple dialkyl nitroxides are planar, or nearly so.<sup>16</sup> We expect that RO<sup>-</sup> and ROO<sup>-</sup> derivatives will have very similar properties in this respect, and hence that  $A(^{14}N)$  will be similar. Evidence for RO<sup>-</sup> rather than ROO<sup>-</sup> adducts came from the observation of only one coupled <sup>17</sup>O nucleus. However, it is not certain that both oxygen nuclei should give rise to detectable coupling. Whatever the correct identification, the detection of radicals having a large coupling to <sup>14</sup>N (*ca.* 27 G) remains diagnostic of ROO · radicals in the present systems.

In contrast, reaction of PBN with ROO  $\cdot$  radicals gave rise to a species having coupling constants to <sup>14</sup>N and <sup>1</sup>H similar to those for many other radicals, including  $\cdot$ <sup>12</sup>CCl<sub>3</sub>, and we would hesitate to claim that the slight differences are diagnostic of RO<sub>2</sub> formation. However, using  $\cdot$ <sup>13</sup>CCl<sub>3</sub> radicals plus oxygen, no <sup>13</sup>C splitting was observed, showing that the trapped species was not CCl<sub>3</sub>. Merritt and Johnson<sup>17</sup> have suggested that in this case also, RO  $\cdot$  rather than ROO  $\cdot$  radicals are trapped. Their results for these two types of radicals (table 1) are quite similar, and since our results lie between them it is impossible for us to decide which derivative we are studying.

We have attempted to make the result more positive by using <sup>17</sup>O-enriched oxygen. Unfortunately, the lines are broadened by spin exchange with dioxygen in these experiments, and we were unable to detect any coupling to <sup>17</sup>O nuclei.

# FORMATION OF RCONO(R) RADICALS

In many cases, especially in the presence of oxygen, we have detected radicals having  $A(^{14}N) \approx 7G$  ( $\beta$  in fig. 2). These radicals are almost certainly acyl nitroxide RCONO(R), radicals. These are frequently detected in reactions with spin traps and a variety of mechanisms have been proposed to explain their formation. We do not intend to discuss this further except to mention our results for  $\cdot^{13}CCl_3$  radicals with MPN. In addition to a coupling of 6.75 G to  $^{14}N$ , we detected a small coupling of *ca*. 0.6 G to one chlorine and a clear coupling of *ca*. 5.7 G to  $^{13}C$  [fig. 2(*e*)]. The radical is almost certainly Cl<sup>13</sup>CONO(CMe<sub>3</sub>), but we hesitate to propose a route for its formation.

#### PHOTOLYSES

In order to check the e.s.r. spectra of some of these spin-trap adducts, we also studied the photolysis of tetrachloromethane in the presence of PBN and MNP. The major species formed were  $\cdot$  CCl<sub>3</sub> adducts, but considerable yields of acyl nitroxides were also obtained.

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#### RADIOLYSIS OF TETRACHLOROMETHANE

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