γ-Radiolysis of Pure Acyl Chlorides at 77 K: an Electron Spin Resonance Study of Intermediate Radicals

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The matrix isolation technique, using e.s.r. spectroscopy, has been employed to investigate the nature of free radical intermediates of the γ-radiolysis of polycrystalline linear and branched acyl chlorides at 77 K. The main radicals are accounted for in terms of C–H, OC–Cl, and C–COCl bond scissions and their relative abundance is significantly influenced by the chemical structure of the parent molecules. A mechanism is suggested.

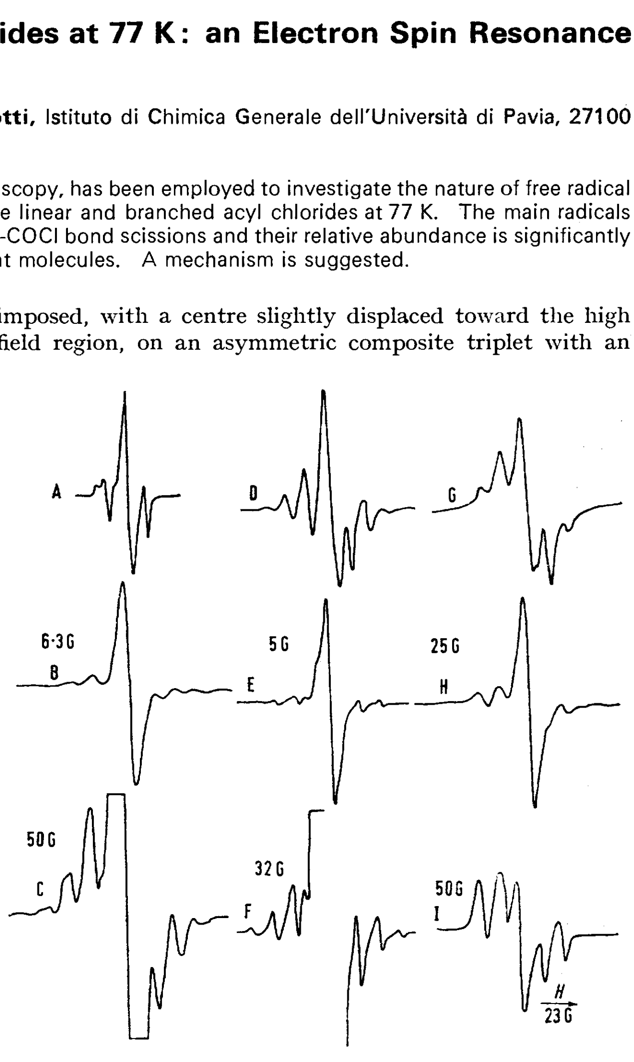
THIS paper is concerned with the interpretation of the e.s.r. spectra observed following the γ-irradiation at 77 K of some linear and branched acyl chlorides, *i.e.* CH_3COCl, $CH_3[CH_2]_3COCl$, $CH_3[CH_2]_{14}COCl$, Pr^iCOCl, Bu^tCOCl, and $CH_2{=}C(CH_3)COCl$. It was felt that the matrix isolation technique might result in the identification of at least some of the intermediate radicals involved in the radiolysis of these compounds thus making possible the elucidation of some aspects of the mechanism which are at present unknown.

EXPERIMENTAL

Polycrystalline samples of freshly redistilled commercially available acyl chlorides of the highest purity were sealed under high vacuum in Pyrex tubes and irradiated at 77 K in a ^{60}Co source with total doses of *ca.* 10 Mrad. After the irradiation the samples were placed in the rectangular cavity of the spectrometer and their e.s.r. spectra were recorded at 89 K and at various temperature up to 10—15° below the m.p.s. A Varian V 4500 spectrometer equipped with 100 kHz modulation and an X band klystron and a Varian accessory for the automatic control of the sample temperature in the cavity were employed. The approximate g values for the acyl radicals were measured by using diphenylpicrylhydrazyl (g *ca.* 2·0037) as a reference standard; these values correspond to the zero crossing of the first derivative of acyl radical singlets and may therefore differ significantly from the g_{iso} values as calculated either from solution spectra or from powder spectra when the g anisotropy is sufficiently resolved.[1]

RESULTS

Acetyl Chloride CH_3COCl.—Following γ-irradiation at 77 K, the e.s.r. spectrum consists of a strong singlet superimposed, with a centre slightly displaced toward the high field region, on an asymmetric composite triplet with an overall spread of *ca.* 54 G (Figure A). The latter component has a shape characteristic of a species with a CH_2 group



E.s.r. spectra of polycrystalline acyl chlorides recorded at 89 K after γ-irradiation at 77 K: A, acetyl chloride; B, C, valeryl chloride at different gains; D, isobutyryl chloride; E, palmitoyl chloride; F, palmitoyl chloride after annealing for *ca.* 11 h at 262 K; G, methacryloyl chloride; H, I, pivaloyl chloride at different gains

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[1] R. W. Fessenden and R. H. Schuler, *Adv. Radiation Chem.*, 1970, **2**, 35.

undergoing restricted rotation[2,3] and might therefore be attributed to the radical $\dot{C}H_2COCl$ (II). The singlet has an average g value at the zero crossing smaller than the free spin value (g *ca.* 2·0012) and a shape and line width (*ca.* 16 G) suggesting the presence of an unresolved hyperfine structure; these features may be considered diagnostic of a σ type radical containing some weakly interacting protons such as the acetyl radical $CH_3\dot{C}=O$ (I) ($g_{iso} = 2{\cdot}0005$ $a_{H\ iso} = 5{\cdot}0$ G).[4] On warming the irradiated sample to 143 K both the radicals (I) and (II) begin to decay at different rates, the decay of (I) being faster.

Radicals from γ-irridation of acyl chlorides

	Radicals	
Compounds	89 K	After annealing at higher temperature
CH_3COCl	$CH_3\dot{C}=O$ (I) [a] $\dot{C}H_2COCl$ (II) [b]	(II) (I) [a]
$CH_3[CH_2]_3COCl$	$CH_3[CH_2]_3\dot{C}=O$ (III) [a] $CH_2\dot{C}HCH_2$ (IV) and/or $CH_3\dot{C}HCH_2$ (V) [b] $CH_3[CH_2]_2\dot{C}HCOCl$ (VI)	
$CH_3[CH_2]_{14}COCl$	$CH_3[CH_2]_{14}\dot{C}=O$ (VII) [a] (IV) $CH_3[CH_2]_{13}\dot{C}HCOCl$ (VIII) [b]	(VIII)
Pr^iCOCl	$(CH_3)_2\dot{C}COCl$ (IX) [a] $Pr^i\dot{C}=O$ (X) [c]	(IX)
Bu^tCOCl	$Bu^t\dot{C}=O$ (XI) [a] $(CH_3)_3\dot{C}$ (XII) [b]	(XI) [a]
$CH_2=C(CH_3)COCl$	(IX) [a] $CH_2=C(CH_3)\dot{C}=O$ (XIII) [c]	$CH_2\dot{C}(CH_3)COCl$ (XIV)

[a] Major component. [b] Minor component. [c] Barely detectable.

Valeryl Chloride $CH_3[CH_2]_3COCl$.—The prominent feature of the low temperature spectrum of polycrystalline valeryl chloride is again a singlet (g *ca.* 2·0014) probably due to the acyl radical $CH_3[CH_2]_3\dot{C}=O$ (III) (the couplings of the two β-protons are expected to be smaller than the experimental line width); the presence of other species may also be inferred from the underlying structure which probably consists of eight equally spaced lines with a splitting of *ca.* 21 G (Figures B, C). Eight lines patterns with almost identical hyperfine separations were obtained by Ayscough from radicals produced by low temperature dissociative electron attachment of the alkyl halides $CH_3CH(X)CH_2R$ and $RCH_2CH(X)CH_2R$;[4] on this basis it might tentatively be suggested that the octet is generated by radicals (IV) and/or (V). Figure C does not allow positive identification of other species; however progressive thermal annealing experiments made with glassy samples of valeryl chloride in a temperature range where chemical reactions are not expected to occur (89—113 K) strongly suggest that the radical (VI) is probably formed.

Palmitoyl Chloride $CH_3[CH_2]_{14}COCl$.—The effect of γ-irradiation on polycrystalline palmitoyl chloride is shown in Figure E; the e.s.r. spectrum is dominated by singlet of the acyl radical $CH_2\dot{C}=O$ which superimposes, with a centre displaced toward high magnetic field (g *ca.* 2·0009), on a weaker pattern with an overall spread of *ca.* 140 G. The latter structure is shown by progressive thermal annealing to consist of a sextet of *ca.* 27—28 G and of a quintet with an average splitting of 22 G attributable respectively to radicals of the type (IV) and $CH_2\dot{C}HCOCl$.[5] When the irradiated sample is submitted to prolonged thermal annealing above 193 K, the radicals $CH_2\dot{C}=O$ and (IV) decay at a slow rate leaving ultimately the pure quintet (Figure F).

Isobutyryl Chloride Pr^iCOCl.—The initial spectrum observed at 89 K is mainly composed of a septet of 22 G with a nearly binomial intensity ratio clearly arising from the radical (IX) (Figure 1). This signal is superimposed on an asymmetric singlet with a centre shifted toward high field (g *ca.* 2·0011) which may be attributed to minor amounts of radical (X). The singlet disappears gradually between 117 and 173 K leaving ultimately the pure septet.

Pivaloyl Chloride Bu^tCOCl.—The spectrum observed at 77 K after irradiation is shown in Figures H and I. It may be interpreted mainly in terms of two species, a singlet attributable to radical (XI) (g *ca.* 2·0014) and a decet of 23—24 G with a binomial intensity ratio, generated by the radical (XII). The presence of a third hyperfine component presumably consisting of an odd number of lines may also be inferred from the partially resolved peaks discernible on each side of the singlet; this structure however has not been identified. On warming to 193 K the decet disappears more rapidly leaving the pure singlet. Since radical (XII) is expected to be more stable than (XI), its higher rate of decay must be due to higher rate of diffusion because of the smaller molecular size.

Methacryloyl Chloride $CH_2=C(CH_3)COCl$.—The low temperature spectrum of methacryloyl chloride resembles closely that of isobutyryl chloride and may therefore be interpreted in terms of the presence of two main species; a septet generated by radical (IX) (formally arising from the addition of an hydrogen atom to the double bond), and a weak singlet, due to minor amounts of radical (XIII) (g *ca.* 2·0006) (Figure G). After warming to 143 K only the septet remains; this signal is stable up to 183 K but above this temperature it changes irreversibly into a nine line pattern characteristic of growing chain radicals in irradiated methacrylic systems. This change may be explained in terms of the onset of radical polymerization of methacryloyl chloride.

DISCUSSION

The Table summarizes the results stemming from the interpretation of the e.s.r. spectra together with an indication of the relative abundance of radicals at various temperatures. These results may be explained tentatively by the mechanism (1)—(7) which is based on the assumptions: (a) that the primary effect of the absorption of γ-radiation is ionization; (b) that the primary radical cation has its positive charge localized on the part of the molecule with maximum electron density, *i.e.* the COCl group; (c) that as in the case of carboxylic acids,[2] * recombination between cations and electrons to give excited molecules is unimportant; and (d) that the

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* The attribution of the quintet to the radical $CH_2\dot{C}HCOCl$ is mainly based on the comparison with the closely related radical $CH_2\dot{C}HCO_2H$ which is known to yield a quintet as a consequence of a particular orientation of the two C_β–H bonds (see for instance ref. 2). This interpretation is supported by the fact that on some occasions a more typical composite quartet was obtained.

[2] P. B. Ayscough, K. Mach, J. P. Oversby, and R. K. Roy, *Trans. Faraday Soc.*, 1971, 360.

[3] R. Lefebvre and J. Maruani, *J. Chem. Phys.*, 1965, **42**, 1480.

[4] J. E. Bennet and B. Mile, *Trans. Faraday Soc.*, 1971, 1587.

[5] P. B. Ayscough and C. Thomson, *Trans. Faraday Soc.*, 1962, 1476; see also ref. 2.

formation of acyl radicals is based mainly on the capture of thermal electrons by COCl groups.[6]

$$RCH_2COCl \longrightarrow RCH_2COCl^{+} + e^{-} \qquad (1)$$

$$RCH_2COCl^{+} + RCH_2COCl \longrightarrow R\dot{C}HCOCl + RCH_2COHCl^{+} \qquad (2)$$

$$RCH_2COCl^{+} \longrightarrow RCH_2\cdot + COCl^{+} \qquad (3)$$

$$RCH_2COCl + e^{-}_{\text{thermal}} \longrightarrow RCH_2COCl^{-} \longrightarrow RCH_2\dot{C}{=}O + Cl^{-} \qquad (4)$$

$$RCH_2COCl^{-} \xrightarrow{RCH_2COCl} RCH_2CHO + R\dot{C}HCOCl + Cl^{-} \qquad (5)$$

$$RCH_2COHCl^{+} + Cl^{-} \longrightarrow RCH_2COCl + HCl \qquad (6)$$

$$COCl^{+} + Cl^{-} \left\{ \begin{array}{l} \longrightarrow COCl_2 \\ \longrightarrow CO + Cl_2 \end{array} \right. \qquad (7)$$

According to this mechanism, the difference observed in the relative extent of OC–Cl, C–H, and C–COCl bond scissions are explained in terms of competition between reactions (2) and (3) and (4) and (5), the choice being determined by the strength of C–H bonds available in the molecules. In isobutyryl chloride, the presence of a weak tertiary activated C–H bond should favour reactions (2) and (5); on the contrary in pivaloyl chloride, where only primary hydrogen atoms attached to carbon atoms β to COCl groups are available, reactions (3) and (4) are preferred. The linear acyl chlorides contain primary and secondary hydrogen atoms activated by COCl groups. As a consequence their behaviour might be thought to be intermediate between that of the branched chlorides and that reactions (2) and (5) would predominate.

The radiolytic behaviour of methacryloyl chloride is determined mainly by the vinyl double bond; consequently it cannot be explained by the mechanism suggested. However participation of reaction (4) can be inferred from the minor amount of acyl radicals detected.

As regards postirradiation reactions, we feel that no conclusion should be drawn from the e.s.r. spectra of low melting chlorides since, in these systems, the relative stabilities of the radicals are strongly influenced by the rates of diffusion which are functions of the molecular sizes (see pivaloyl chloride). Only in the case of the relatively high melting palmitoyl chloride, m.p. +12 °C, do the observed e.s.r. changes take place in a temperature range where the diffusion of radicals is inhibited. The changes may therefore be tentatively explained in terms of reactions (8)—(10). It must be pointed out however

$$CH_2CH_2\dot{C}{=}O + CH_2CH_2COCl \longrightarrow CH_2CH_2CHO + CH_2\dot{C}HCOCl \qquad (8)$$

and/or

$$CH_2CH_2\dot{C}{=}O \longrightarrow CH_2CH_2\cdot + CO \xrightarrow{CH_2CH_2COCl} CH_2CH_3 + CH_2\dot{C}COCl \qquad (9)$$

$$CH_2\dot{C}HCH_2 + CH_2CH_2COCl \longrightarrow CH_2\dot{C}HCH_2 + CH_2\dot{C}HCOCl \qquad (10)$$

that the conversion of the radicals precursors into CH_2-$\dot{C}HCOCl$ is far from being quantitative.

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[6] S. Noda, K. Fueki, and Z. Ichirokuri, *J. Chem. Phys.*, 1968, **49**, 3287.