

An Electron Spin Resonance Study of the Photolysis of Carboxylic Acids, Neat or in Non-polar Solvents: Regiospecific Loss of a Hydrogen Atom from the α -Position

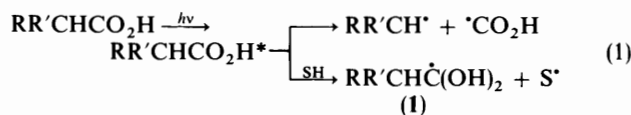
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When carboxylic acids RCH_2CO_2H ($R = H, Me, Et, \text{ or } Pr$) are photolysed, either neat or in carbon tetrachloride, the e.s.r. spectra of only the radicals $\dot{R}CHO_2H$ are observed. Isobutyric acid, Me_2CHCO_2H , similarly shows the spectrum of the radical $Me_2\dot{C}CO_2H$ at room temperature, but at lower temperatures the spectrum of the radical $Me_2CH\dot{C}$ can also be observed. Pivalic acid, Me_3CCO_2H , shows only the spectrum of the $Me_3C\dot{C}$ radical. This is in contrast to the behaviour of the acids in polar solvents, when they normally show Norrish I cleavage of the alkyl-acyl bond, or photoreduction by the solvent. Two models are considered, to account for the regiospecific formation of the radicals $\dot{R}CHCO_2H$. The first assumes that cleavage of a C-OH bond in a hydrogen-bonded dimer yields an $HO\cdot$ radical which is hydrogen-bonded to a carbonyl group of the acid [$RCH_2C(OH)=O \cdots HO\cdot$], and this species then undergoes regiospecific intramolecular transfer of α -H. The second assumes initial formation of the $RCH_2\dot{C}$ radical, which then abstracts hydrogen from a second molecule of acid.

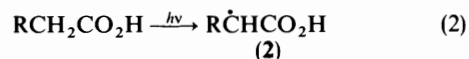
We are interested in the photogeneration of radicals in acidic media,¹ and in the course of this work have had occasion to study the e.s.r. spectra of the radicals which are formed when solutions in neat carboxylic acids, or in non-polar solvents containing the acids, are irradiated with ultraviolet light. This required an ancillary study of the photolysis of these solvent systems themselves, and the results are reported here: they are surprisingly different from those which have been reported previously for the photolysis of carboxylic acids dissolved in polar solvents.

The two principal processes which have previously been recognised to occur when carboxylic acids are photolysed in polar solvents such as water or alcohols parallel the Norrish I fragmentation and the photoreduction reactions of other carbonyl compounds such as ketones, and are shown in equation (1) (R and $R' = H$ or alkyl; $SH = \text{solvent}$).



Thus photolysis of formic acid in propan-2-ol,² or of various n-alkanecarboxylic acids in methanol or ethanol,³ showed the spectra of the reduction products (1). In a thorough e.s.r. study of the photolysis of aliphatic carboxylic acids in water, methanol, 0.1N-HCl or 1,2-epoxybutane, Fischer and co-workers showed that the principal reactions were those shown in equation (1),⁴ and a CIDNP study of the photolysis of isobutyric and pivalic acids in $[^2H_4]MeOH$ confirmed that α -cleavage was the principal reaction.⁵ The behaviour of carboxylic esters is broadly similar.⁴

We find that the photolysis of primary alkanecarboxylic acids RCH_2CO_2H ($R = H, Me, Et, \text{ or } Pr$) in the absence of a solvent, or in carbon tetrachloride, affords only the spectra of the corresponding radicals (2), resulting from loss of a hydrogen atom from the α -position, according to equation (2). Spectral parameters are listed in Table 1.



Photolysis of acetic acid, neat or in carbon tetrachloride between +20 and +85 °C, gave the spectrum of the radical $\cdot CH_2CO_2H$ as illustrated in Figure 1(a). No spectrum could be obtained using benzene as solvent, probably because it absorbs strongly in the region (ca. 220–240 nm) of the carbonyl group. Propionic acid, neat, between +35 and +104 °C, or in carbon tetrachloride showed the spectrum of the radical $Me\dot{C}HCO_2H$ [Figure 1(b)]. n-Butyric and valeric acids similarly showed only the spectrum of the corresponding radicals $\dot{R}CHCO_2H$, though with reduced intensity. Other workers have reported that they could not observe the spectra of any radicals when neat n-alkanecarboxylic acids were irradiated with u.v. light;⁶ the principal difference between those experiments and ours appears to be that they were carried out with only the higher acids,⁷ which may give very weak spectra.

From +100 °C down to ca. +40 °C, photolysis of isobutyric acid showed only the spectrum of the radical $Me_2\dot{C}CO_2H$, together with some further, weak signals of an unidentified radical [see Figure 1(c)]. As the temperature was reduced to -37 °C, the spectrum of the isopropyl radical became increasingly apparent, together with a broad signal, $\Delta H_{pp} 2.2$ G, $g 2.0026$, which is probably to be assigned to the radical $\cdot CO_2H$. From the photolysis of isobutyric acid in methanol at -78 °C, Fischer detected only the isopropyl radical and the $\cdot CO_2H$ (or $\cdot CO_2^-$) radical, $g 2.0026$, together with some weak lines associated with the radical $\cdot CH_2OH$.⁴

Pivalic acid above its melting point (35 °C) showed only the spectrum of the t-butyl radical.

Any mechanism which we might propose for the formation of the α -radicals (2) must account for the following facts.

(i) The reaction with the acids RCH_2CO_2H or R_2CHCO_2H , neat or in carbon tetrachloride, proceeds quite differently from that when the acids are dissolved in polar solvents.

(ii) Only the radical resulting from loss of a hydrogen atom is detected; the fate of that hydrogen atoms is not spectroscopically apparent.

(iii) The loss of hydrogen occurs regiospecifically from the α -position.

A reaction involving abstraction of hydrogen by the photoexcited acid [equation (3)] seems unlikely because the familiar radicals (3)⁴ are not observed; we cannot rule out the

Table 1. E.s.r. spectra of radicals observed on photolysis of neat carboxylic acids

Acid	$T/^{\circ}\text{C}$	Radical observed	Hyperfine coupling constants (G) ^a		
			$a(\alpha\text{-H})$	$a(\beta\text{-H})$	g
MeCO_2H	20	$\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$	21.4(2 H)		
$\text{MeCH}_2\text{CO}_2\text{H}$	36	$\text{Me}\dot{\text{C}}\text{HCO}_2\text{H}$	20.4(1 H)	25.0(3 H)	2.0036
$\text{EtCH}_2\text{CO}_2\text{H}$	44	$\text{Et}\dot{\text{C}}\text{HCO}_2\text{H}$	20.0(1 H)	24.0(2 H)	2.0034
$\text{PrCH}_2\text{CO}_2\text{H}$	78	$\text{Pr}\dot{\text{C}}\text{HCO}_2\text{H}$	20.0(1 H)	23.1(2 H)	
$\text{Me}_2\text{CHCO}_2\text{H}$	18 ^b	$\text{Me}_2\dot{\text{C}}\text{CO}_2\text{H}$		21.5(6 H)	2.0032
$\text{Me}_3\text{CCO}_2\text{H}$	68	$\text{Me}_3\dot{\text{C}}^*$		22.7(9 H)	

^a The number of coupling hydrogen atoms is shown in parentheses. ^b Below room temperature, the spectrum of the radical Me_2CH^* could also be detected, and at -37°C , the two spectra had approximately equal intensities.

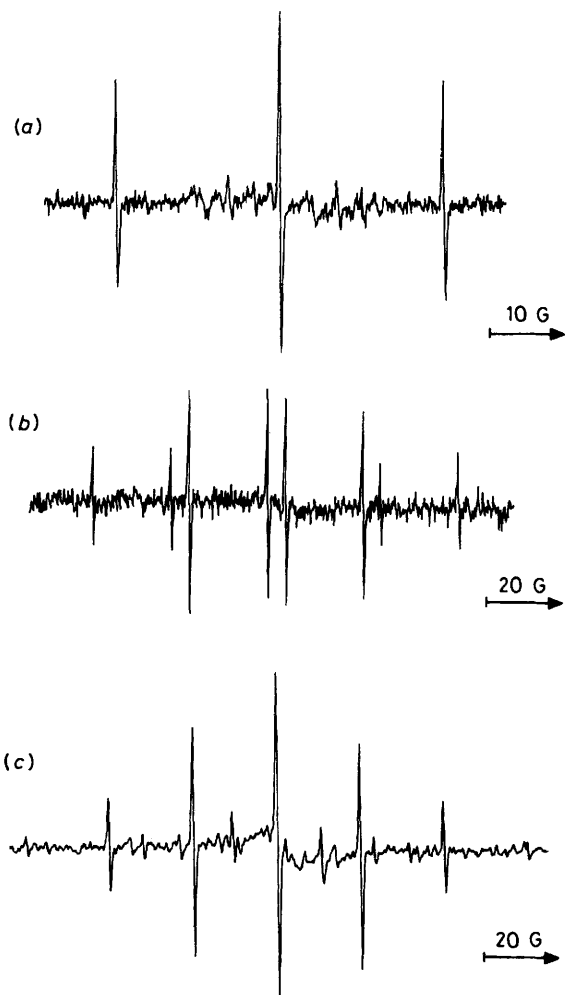
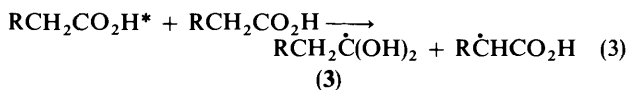


Figure 1. E.s.r. spectra observed during the photolysis of (a) acetic acid at $+18^{\circ}\text{C}$, (b) n-butyric acid at $+36^{\circ}\text{C}$, (c) isobutyric acid at $+79^{\circ}\text{C}$, all without solvent

possibility that, when the acids are neat or in non-polar solvents, acid-catalysed dehydration of (3) might occur rapidly



to give acyl radicals, but this does not happen when the solvent is methanol, epoxybutane, or 0.1N-HCl .⁴

Further, it seems unlikely that the reaction of the carbonyl

triplet would be regiospecific for the α -position. For example, hydroxyl radicals, derived from hydrogen peroxide and titanium(III) chloride, react with n-butyric acid in water at pH 2 to show the e.s.r. spectra resulting from abstraction of hydrogen from the α -, β -, and γ -positions in the ratio of 1:5.2:1.9.⁸ Similarly, t-butoxyl radicals react with butyric acid in di-t-butyl peroxide at 17°C at the α -, β -, and γ -positions ($\alpha:\beta = 3.1:1$), and with valeric acid under the same conditions to give the α -, β -, and γ -radicals in the ratio 3.4:1:3.9.⁶

We have considered two mechanisms which at first sight appear to meet the above conditions.

The first assumes the intermediacy of the HO^{\cdot} radical, but with its regioselectivity modified by hydrogen bonding.

In a polar solvent such as water or an alcohol, a carboxylic acid will exist as the solvated monomer, but in a non-polar solvent, or in the absence of a solvent, the principal species will be the hydrogen-bonded dimer (4).^{9,10} In carbon tetrachloride at 25°C , the equilibrium constant, K , for the formation of the dimer is about $4 \times 10^3 \text{ mol}^{-1}$ l, varying little with the size of the alkyl group.¹⁰ In a 1M solution, only ca. 0.025% of the acid will be present as monomer. The absorption spectra of monomer and dimer are similar, and the primary photolytic process will involve the dimer, rather than the monomer which is involved in polar solvents.

With a carboxylic acid, $\text{RCH}_2\text{CO}_2\text{H}$, photoexcitation of the dimer is followed by cleavage of the C–OH bond rather than the C–CO₂H bond, to yield the hydrogen-bonded complex of the $\cdot\text{OH}$ radical [(5); equation (4)]. The other fragment would be a small acyl radical, with a broad e.s.r. spectrum which would be difficult to detect under our experimental conditions.¹¹

The acid then serves as a template for directing the attack of the hydrogen-bonded $\cdot\text{OH}$ radical to the α position [equation (5)] through a transition state involving a six-membered ring.

With isobutyric acid, homolysis of the C–C bond to give the more stable secondary alkyl radical is in competition with C–O cleavage at low temperatures, and with pivalic acid, C–C cleavage to give the t-butyl radical may be the dominant process.

The second mechanism assumes the intermediate formation of alkyl radicals. Gilbert and Young¹² have shown that when the $\text{SO}_4^{\cdot-}$ radical is generated photolytically in aqueous solution in the presence of carboxylic acids, $\text{RCH}_2\text{CO}_2\text{H}$, the spectrum of the alkyl radical RCH_2^{\cdot} is observed when the concentration of the acid is low. At higher concentrations, this spectrum is replaced by that of the radical $\text{R}\dot{\text{C}}\text{HCO}_2\text{H}$, which is believed to be formed by attack of the alkyl radical on the parent acid; the regioselectivity for the α -position would be in accord with previous observations.¹³

Our reaction might therefore proceed by the steps shown in equations (6) and (7).

In an attempt to choose between these two alternatives, we have carried out two sets of experiments. In the first, the alkyl

Table 2. Photolysis of acetyl and propionyl peroxides in the presence of acetic and propionic acids

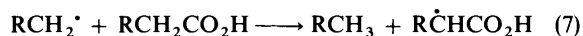
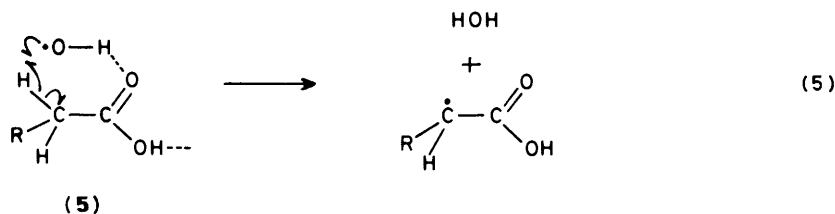
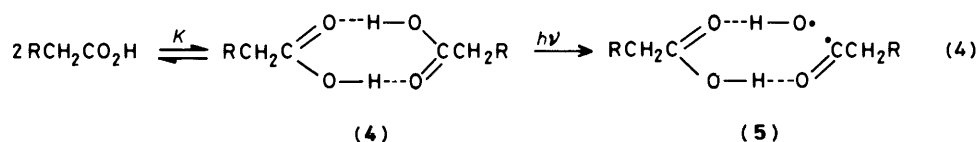
Experiment	Reagents	Solvent	$T/^\circ\text{C}$	Conditions	Radical observed
1	(MeCO ₂) ₂	Et ₂ O ^a	-52 to +32	$h\nu$	Me [•]
2	(EtCO ₂) ₂	Et ₂ O-C ₈ H ₁₈	-1 to +73	$h\nu$	Et [•]
3	(MeCO ₂) ₂ + MeCO ₂ H	Et ₂ O ^a	-31 to +32	$h\nu$	Me [•]
4	(EtCO ₂) ₂ + EtCO ₂ H	C ₈ H ₁₈	-2 to +82	$h\nu$	Me [•] CHCO ₂ H
5	MeCO ₂ H + EtCO ₂ H		+82	$h\nu$	Me [•] CHCO ₂ H
6	(MeCO ₂) ₂ + MeCO ₂ H	<i>a</i>	+80 to +101	Δ	
7	(EtCO ₂) ₂ + EtCO ₂ H	C ₈ H ₁₈	+81	Δ	Me [•] CHCO ₂ H
8	(MeCO ₂) ₂ + MeCO ₂ H + EtCO ₂ H	<i>a</i>	+88	Δ	Me [•] CHCO ₂ H

^a Some dimethyl phthalate was also present as the peroxide was stored in this solvent for safety.

Table 3. Photolysis of acetic and propionic acids and of acetyl and propionyl peroxides in the presence of pentamethylnitrosobenzene as a spin trap

Experiment	Reagents	Solvent	$T/^\circ\text{C}$	Radicals ^a observed	Hyperfine coupling constants (G)	
					$a(\text{N})$	$a(n\text{-H})$
1	(MeCO ₂) ₂	DMP ^b	+23	ArN([•] O)Me ^c	14.0	12.7(3) ^d
2	(EtCO ₂) ₂	DMP	+20	ArN([•] O)Et	14.0	11.6(2) ^e
3	MeCO ₂ H		+5	ArN([•] O)COMe ^f	13.7	^g
				ArN([•] O)CH ₂ CO ₂ H	14.75	9.25(2)
				ArN([•] O)Me	14.7	13.4(3)
4	EtCO ₂ H		+70	ArN([•] O)Me ^h	14.8	13.4(3)
			+20	ArN([•] O)COEt	14.3	
				ArN([•] O)CHMeCO ₂ H	13.6	9.0(1)
				ArN([•] O)Et	14.35	12.25(2) ⁱ

^a For assignment, see text. ^b DMP = dimethyl phthalate, which was used as a safe storage solvent for the peroxides. ^c Ref. 14 quotes $a(\text{N})$ 13.8, $a(3\text{H})$ 12.3, g 2.0058, in benzene at 26 °C. ^d g 2.0058. ^e g 2.0062. ^f Ref. 14 quotes $a(\text{N})$ 13.2, g 2.0058 in benzene at 26 °C. ^g g 2.0058. ^h The sample was photolysed at +5 °C, then the light was shuttered, and the sample was heated to +71 °C. ⁱ g 2.0058.



radicals RCH_2^\bullet ($\text{R} = \text{H}$ or Me) were generated from the diacyl peroxides under our solvent conditions, and the radicals which were formed were monitored by e.s.r. spectroscopy. In the second, the acids were photolysed in the presence of pentamethylnitrosobenzene¹⁴ as a spin trap, and the nitroxyl radicals which were formed were examined. The results of these experiments are shown in Tables 2 and 3.

Experiments 1 and 2 of Table 2 confirm the diacyl peroxides as suitable sources of the corresponding alkyl radicals. The methyl radicals however could not be caused to react with acetic acid (experiment 3), although propionic acid does quench the spectrum of the ethyl radicals to show the spectrum of the α -radical $\text{Me}^\bullet\text{CHCO}_2\text{H}$ (experiment 4). Experiment 5 shows that

photolysis of a mixture of acetic acid and propionic acid similarly yields the α -radical from only propionic acid.

Experiments 6–8 relate to thermolysis rather than photolysis. At +81 °C, ethyl radicals from propionyl peroxide react regioselectively with propionic acid to show the spectrum of the α -radical (experiment 7). Under similar conditions, no spectrum of either the methyl radical or the radical $\bullet\text{CH}_2\text{CO}_2\text{H}$ could be observed from acetyl peroxide in acetic acid (experiment 6), but, if propionic acid was added as a third component, the spectrum of the radical $\text{Me}^\bullet\text{CHCO}_2\text{H}$ became apparent.

Thus we have been able to demonstrate that methyl and ethyl radicals will react with propionic acid, but, under our conditions, methyl radicals apparently do not react with acetic acid.

Experiments 1 and 2 of Table 2 serve to identify the nitroxyl radicals which are formed when methyl and ethyl radicals add

to pentamethylnitrosobenzene. Photolysis of acetic acid in the presence of the spin trap at temperatures up to 36 °C affords a spectrum resulting from a mixture of nitroxyl radicals. The principal component was a simple triplet, $a(\text{N})$ 14.25 G, and weaker lines for a radical with $a(\text{N})$ 14.75, $a(2\text{H})$ 9.25 G could also be identified. The former spectrum may be ascribed to the radical $\text{Me}_5\text{C}_6\text{N}(\dot{\text{O}})\text{COMe}$, for which reference 14 reports $a(\text{N})$ 13.2 G (in benzene at 26 °C), and the latter may relate to the radical $\text{Me}_5\text{C}_6\text{N}(\dot{\text{O}})\text{CH}_2\text{CO}_2\text{H}$.

At these temperatures, the spectrum of the radical $\text{Me}_5\text{C}_6\text{N}(\dot{\text{O}})\text{Me}$ could also be detected, but if a sample showing only the triplet spectrum, $a(\text{N})$ 14.25 G, was heated in the dark to +70 °C, the triplet decayed, and was replaced by the spectrum of the radical $\text{Me}_5\text{C}_6\text{N}(\dot{\text{O}})\text{Me}$, perhaps implying that, at least under our conditions, the acyl adduct can undergo decarbonylation.

Similar experiments with propionic acid showed the formation of the radicals $\text{Me}_5\text{C}_6\text{N}(\dot{\text{O}})\text{Et}$, and, apparently, $\text{Me}_5\text{C}_6\text{N}(\dot{\text{O}})\text{CHMeCO}_2\text{H}$ and $\text{Me}_5\text{C}_6\text{N}(\dot{\text{O}})\text{COEt}$ at +20 °C.

We do not feel that any firm conclusions can be drawn from the experiments listed in Tables 2 and 3. The spin-trapping experiments appear to support the formation of the acyl radicals, but it may not necessarily be on the reaction path which leads to the α -radicals which are observed by e.s.r. spectroscopy. Under certain conditions, methyl and ethyl radicals can be trapped, but it is not clear whether they result from the primary photolytic process (6), or from decarbonylation of the acyl radicals formed in reaction (4).

The most diagnostic reactions appear to be experiments 3 and 6 of Table 2, which, taken at their face value, imply that reaction (7) ($\text{RCH}_2 = \text{Me}$) does not occur under our reaction conditions, but is permissive for the alternative template mechanism.

Carboxylic acids form hydrogen-donor complexes with many types of polar molecules such as amines, alcohols, and sulphoxides, and this template model suggests that it would be worthwhile investigating whether these systems could lead to similar regiospecific reactions.

Experimental

The acids (BDH Chemicals) showed the same e.s.r. spectra whether they were used with or without prior purification.¹⁵

The samples, neat or dissolved in an equal volume of carbon tetrachloride, were introduced into Suprasil silica tubes, and degassed with a stream of dry nitrogen, or by three freeze-thaw cycles. Photolysis was carried out in the cavity of a Varian E4 or E109 spectrometer, with light from a 500 W high-pressure mercury arc.

Acknowledgements

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