16. Free Radical Formation from Excited States of Aliphatic Carboxylic Acids and Esters in Solution as Studied by Electron Spin Resonance

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In Memoriam Professor *Heinrich Labhart*

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Summary

During UV.-irradiation of aliphatic carboxylic acids and esters in aqueous and nonaqueous solutions various alkyl and acyl type radicals derived from parent compounds and solvents have been observed by ESR.-spectroscopy. The structures of the radicals point to α-cleavage, β-dehalogenation and photoreduction as major photolytic processes of carboxylic acids and esters. The relative contributions of these processes to the overall photodecompositions depend on the carboxyl substituents, on solvent and temperature. Similarities of carboxyl and carbonyl group photochemistry are discussed.

1. Introduction. - For aliphatic carbonyl compounds free radical formation by cleavage or hydrogen abstraction reactions of excited states has been studied extensively and is well established by direct spectroscopic evidence for the radical intermediates [1]. For excited states of aliphatic carboxylic acids and esters a variety of radical generation steps and of fragmentation reactions of the primary radicals have been suggested to explain the observed product distributions [2-9] *(Scheme 1)* but direct evidence for these processes has been reported only for a few special cases: In particular, *Mittal, Mittal & Hayon* [10] have established reaction (1a) for aqueous solutions of acetic acid by the UV.-detection of $\cdot$ COOH, of malonic acid ($\cdot$ COOH and $\cdot$ CH_2COOH) and of dimethyl and diethylmalonate ($\cdot$ CH_2COOR^2). Alkyl radicals R^1 pointing to the same α-cleavage reaction have also been observed by ESR.-spectroscopy for aqueous solutions of tartaric [11], citric [12], alloxanic [13] and malonic [14] acid. Further, ESR.-spectroscopic evidence for the photoreduction (5a) in hydrogen donor solvents has been reported for formic acid and its esters (R^2 = Me, Et, *i*-Pr, *n*-Pr, *i*-Bu, *n*-Bu) in 2-propanol [15] and for several *n*-carboxylic acids in methanol and ethanol [16]. Thus, reactions (1a) and (5a) of *Scheme 1* seem well documented. However, there is no evidence for all the other reactions though product studies indicate that several of these (2a, 2b, 4, 5b) may be of major importance [2-9].

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In this paper we extend our previous work on the ESR.-spectroscopic detection of transient radicals during photochemical reactions in liquids [15] [17] [18] to aliphatic acids and esters and their α-hydroxy, α-alkoxy and α-halo derivatives in aqueous and nonaqueous solutions at various temperatures. The results confirm reactions (1a), (2a), (4) and (5a) as major primary processes. The relative contributions of these reactions to the overall photoreactions of carboxylic acids and esters are found to depend on substitution, solvent and temperature, similarly as known for carbonyl compounds. Quantitative aspects of the work as determinations of quantum yields, product distributions and multiplicities of the radical precursor states will be published subsequently.

2. Experimental Part. – Solutions of various carboxylic acids in water, methanol or 1-butene oxide (BO) (20% by volume for liquid, 40 mg/ml for solid compounds) were photolysed within the cavity of a *Varian*-E-4 ESR.-spectrometer. For solutions in methanol or BO a sample and cavity arrangement published previously [19] was used (1 mm cell width). For aqueous solutions the flat cell arrangement described in [18] was applied (0.4 and 0.6 mm cell width). Flow rates were between 0.12 and 0.59 ml/min. The solutions were deaerated prior to use by purging with He-gas. The light source was a *Hanovia* 1000 W/Xe/Hg-lamp (977 B-1) the light of which was focussed onto the sample by an elliptical mirror [20] and two suprasil lenses and was filtered by a Ni/Co-sulfate solution. *Figure 1* shows the dispersion of the quantum flux in the sample cell (1 mm cell width, arrangement as described [19]).

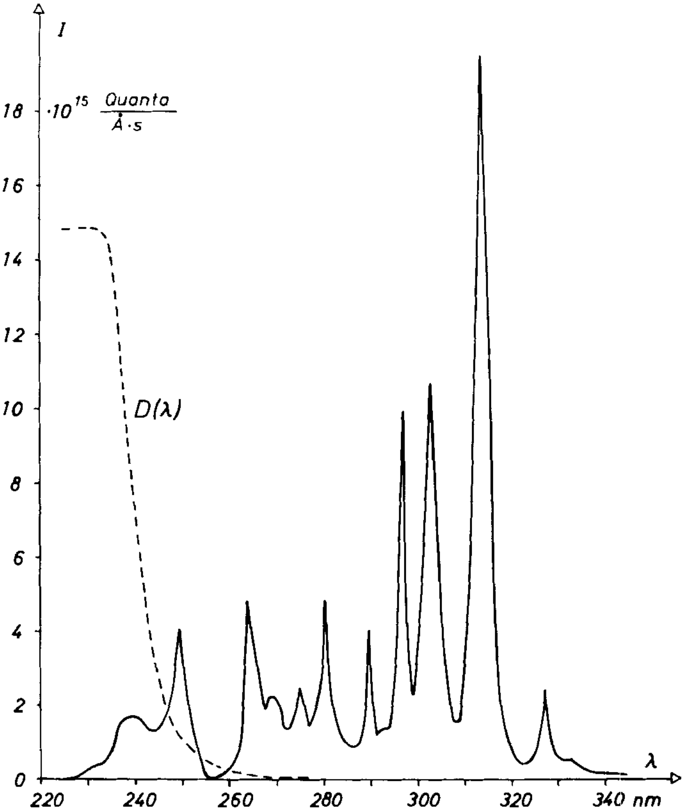
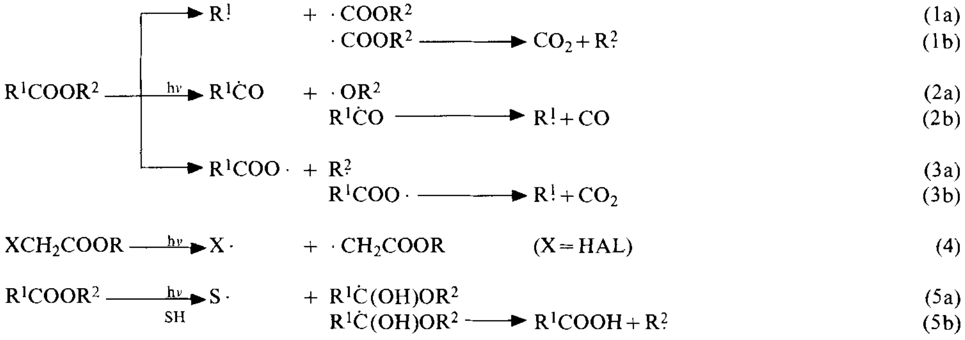


Fig. 1. *Optical Density D(λ) of Methyl pivalate in Methanol* (20% by vol., 1 mm pathlength, $D_{210} = 2.7$) *and Dispersion of the Quantum Flux*

Scheme 1. *Radical Formation from Excited Carboxylic Acids and Esters*



In general aliphatic carboxylic acids and esters absorb below $\lambda \simeq 240$ nm with a (first) $n\pi^*$-transition maximum at $\lambda \simeq 210$ nm [2]. The dashed line in *Figure 1* shows the optical density of a solution of methyl pivalate in methanol (20% by volume, 1 mm path length, $D_{210} = 2.7$). Comparison with the dispersion of the quantum flux shows that only a small portion of the available UV.-intensity is utilized for excitation of the carboxylic acids and esters. In our experiments this portion amounted to approximately 10^{17} absorbed photons/s.

All chemicals except fluoroacetic acid were purchased from *Fluka AG* (Buchs) in the purest available form and were used without further purifications. Fluoroacetic acid was obtained from *E. Merck AG* (Darmstadt). The ESR.-spectra were taken during continuous photolysis and were analysed by conventional procedures. Most of the radicals were identified by comparison of their coupling constants and g-factors with literature values [21] [22]. Radicals the ESR.-spectra of which had not previously been reported were identified by a comparison of their spectral parameters with those known for structurally related species.

3. Results and discussion.

- The radicals observed during photolysis of a variety of carboxylic acids and esters in different solvents and for various temperatures are listed in *Table 1*. The last column of the table gives the primary reactions of *Scheme 1* which we think responsible for the radical formation. To facilitate discussion we will now consider a few typical individual systems to some detail and draw general conclusions from the data of *Table 1* thereafter.

3.1. *Figure 2* shows a spectrum obtained during photolysis of isobutyric acid in methanol at −78°. The multiplets with extremely sharp lines exhibiting second

Fig. 2. *ESR.-Spectrum of Radicals during Photolysis of Isobutyric acid in Methanol*

Table 1. *Transient Radicals Observed during Photolysis of Aliphatic Carboxylic Acids and Esters in Solution*

Carboxyl Compound	Solvent	T[°]	Radicals Observed	Reactions
$HCOOH$	CH_3OH	−47	$H\dot{C}(OH)_2$, $\cdot CH_2OH$, $H\dot{C}(OH)OCH_3$a)	5a
$HCOOH$	0.1N HCl	+21	$H\dot{C}(OH)_2$, $\cdot O$b)c)	5a
$HCOOCH_2CH_3$	CH_3OH	−59	$H\dot{C}(OH)OCH_2CH_3$, $\cdot CH_2OH$	5a
$HCOOCH(CH_3)_2$	CH_3OH	−57	$H\dot{C}(OH)OCH(CH_3)_2$, $\cdot CH_2OH$c)	5a
$HCOOCH(CH_3)_2$	CH_3OH	−13	$H\dot{C}(OH)OCH(CH_3)_2$, $\cdot CH_2OH$, $CH_3\dot{C}HCH_3$, $H\dot{C}(OH)_2$d)c)	5a + 5b
CH_3COOH	CH_3OH	−46	$CH_3\dot{C}(OH)_2$, $\cdot CH_2OH$	5a
CH_3COOH	BO	−54	$CH_3\dot{C}(OH)_2$, $\cdot BO$e)	5a
CH_3COOH	0.1N HCl	+3	$\cdot CH_3$, $\cdot COOH$, $CH_3\dot{C}(OH)_2$, $\cdot CH_2COOH$, $\cdot O$b)	1a + 5a
CH_3COOCH_3	CH_3OH	−75	$CH_3\dot{C}(OH)OCH_3$, $\cdot CH_2OH$	5a
$CH_3COOCH_2CH_3$	CH_3OH	−35	$CH_3\dot{C}(OH)OCH_2CH_3$, $\cdot CH_2OH$	5a
$CH_3COOCH(CH_3)_2$	CH_3OH	−65	$CH_3\dot{C}(OH)OCH(CH_3)_2$, $\cdot CH_2OH$	5a
$CH_3COOC(CH_3)_3$	CH_3OH	−86	$CH_3\dot{C}(OH)OC(CH_3)_3$, $\cdot CH_2OH$, $\cdot C(CH_3)_3$	5a + 5b
$CH_3COOC(CH_3)_3$	CH_3OH	−44	$\cdot CH_2OH$, $\cdot C(CH_3)_3$	5a + 5b
CH_3CH_2COOH	CH_3OH	−25	$CH_3CH_2\dot{C}(OH)_2$, $\cdot CH_2OH$, $\cdot CH_2CH_3$f), $\cdot COOH$f)	1a + 5a
CH_3CH_2COOH	BO	−27	$\cdot CH_2CH_3$, $\cdot COOH$, $\cdot BO$e)g)	1a + 2a?
CH_3CH_2COOH	H_2O	+8	$\cdot CH_2CH_3$, $\cdot COOH$, $CH_3\dot{C}HCOOH$h)	1a + 2a?
CH_3CH_2COOH	0.1N HCl	+5	$\cdot CH_2CH_3$, $\cdot COOH$, $CH_3\dot{C}HCOOH$h), $\cdot O$b)	1a + 2a?
$CH_3CH_2COOCH_3$	BO	−58	$\cdot CH_2CH_3$, $\cdot COOCH_3$, $\cdot BO$e)g)	1a + 2a?
$CH_3CH_2COOCH_3$	CH_3OH	−25	$\cdot CH_2OH$	2a?
$CH_3CH_2COOCH_3$	CH_3OH	−70	$\cdot CH_2OH$	2a?
$CH_3CH_2COOCH_2CH_3$	CH_3OH	−74	$\cdot CH_2OH$	2a?
$CH_3CH_2COOC(CH_3)_3$	CH_3OH	−34	$\cdot CH_2OH$, $\cdot C(CH_3)_3$	5a + 5b
$(CH_3)_2CHCOOH$	CH_3OH	−78	$CH_3\dot{C}HCH_3$, $\cdot COOH$, $\cdot CH_2OH$f)	1a + 2a? or 5a?
$(COOH)_2$	H_2O	+30	$\cdot O$b)	1a
$CH_2(COOH)_2$	CH_3OH	−41	$HOOCCH_2\dot{C}(OH)_2$, $\cdot CH_2OH$	5a
$CH_2(COOH)_2$	H_2O	+30	$\cdot CH_2COOH$, $\cdot COOH$, $\cdot O$b)	1a
$CH_2(COOCH_2CH_3)_2$	CH_3OH	−38	$C_2H_5OOCCH_2\dot{C}(OH)OC_2H_5$, $\cdot CH_2OH$	5a
$(CH_2COOH)_2$	CH_3OH	−45	$HOOCCH_2CH_2\dot{C}(OH)_2$, $\cdot CH_2OH$	5a
$(CH_2COOH)_2$	H_2O	+30	$\cdot CH_2CH_2COOH$, $\cdot COOH$	1a
$ClCH_2COOH$	CH_3OH	−60	$\cdot CH_2COOH$, $\cdot CH_2OH$	4
$ClCH_2COOH$	BO	−43	$\cdot CH_2COOH$, $\cdot BO$e)	4
$ClCH_2COOH$	H_2O	+30	$\cdot CH_2COOH$	4
$ClCH_2COOCH_3$	CH_3OH	−61	$\cdot CH_2COOCH_3$, $\cdot CH_2OH$	4
$ClCH_2COOCH_3$	BO	−60	$\cdot CH_2COOCH_3$, $\cdot BO$e)	4
$ClCH_2COOCH_2CH_3$	CH_3OH	−35	$\cdot CH_2COOCH_2CH_3$, $\cdot CH_2OH$	4
$ClCH_2COOCH_2CH_3$	BO	−50	$\cdot CH_2COOCH_2CH_3$, $\cdot BO$e)	4
$ClCH_2COOC(CH_3)_3$	CH_3OH	−64	$\cdot CH_2COOC(CH_3)_3$, $\cdot CH_2OH$	4
$BrCH_2COOH$	CH_3OH	−57	$\cdot CH_2COOH$i)	4
$BrCH_2COOH$	H_2O	+30	$\cdot CH_2COOH$	4
$BrCH_2COOCH_2CH_3$	CH_3OH	−60	$\cdot CH_2COOCH_2CH_3$i)	4
FCH_2COOH	CH_3OH	−30	$\cdot CH_2COOH$, $\cdot CH_2COOCH_3$a), $\cdot CH_2OH$	4
FCH_2COOH	H_2O	+30	$\cdot CH_2COOH$	4
$CH_3CHClCOOH$	BO	−66	$CH_3\dot{C}HCOOH$, $\cdot BO$c)	4
$CH_3CHClCOOH$	H_2O	+30	$CH_3\dot{C}HCOOH$	4
$CH_3CHClCOOCH_3$	CH_3OH	−72	$CH_3\dot{C}HCOOCH_3$, $\cdot CH_2OH$c)	4
$CH_3CHClCOOCH_2CH_3$	CH_3OH	−54	$CH_3\dot{C}HCOOCH_2CH_3$, $\cdot CH_2OH$c)	4
$(CH_3)_2CBrCOOCH_2CH_3$	CH_3OH	−39	$(CH_3)_2\dot{C}COOCH_2CH_3$i)	4
CF_3COOH	CH_3OH	−62	$CF_3\dot{C}(OH)_2$, $\cdot CH_2OH$, $CF_3\dot{C}(OH)OCH$a)	5a

Table 1 continued

Carboxyl Compound	Solvent	T[°]	Radicals Observed	Reactions
$\mathrm{CF_3COOH}$	0.1 N HCl	+19	$\cdot\mathrm{O}$[b]	1a?
$\mathrm{CF_3COOCH_3}$	$\mathrm{CH_3OH}$	−62	$\mathrm{CF_3\dot{C}(OH)OCH_3}$, $\cdot\mathrm{CH_2OH}$	5a
$\mathrm{(CH_3)_2CHCOOCH_3}$	$\mathrm{CH_3OH}$	−63	$\mathrm{CH_3\dot{C}HCH_3}$, $\cdot\mathrm{COOCH_3}$, $\cdot\mathrm{CH_2OH}$, $\mathrm{(CH_3)_2CH\dot{C}O}$[c]	1a+2a
$\mathrm{(CH_3)_2CHCOOCH_2CH_3}$	$\mathrm{CH_3OH}$	−83	$\mathrm{CH_3CHCH_3}$, $\cdot\mathrm{COOCH_2CH_3}$, $\cdot\mathrm{CH_2OH}$[f]	1a+2a?
$\mathrm{(CH_3)_2CHCOOCH_2CH(CH_3)_2}$	$\mathrm{CH_3OH}$	−63	$\mathrm{CH_3\dot{C}HCH_3}$, $\cdot\mathrm{COOCH_2CH(CH_3)_2}$, $\cdot\mathrm{CH_2OH}$	1a+2a?
$\mathrm{(CH_3)_2CHCOOCH_2CH_2CH_2CH_3}$	$\mathrm{CH_3OH}$	−63	$\mathrm{CH_3\dot{C}HCH_3}$, $\cdot\mathrm{COOC_4H_9}$, $\cdot\mathrm{CH_2OH}$	1a+2a?
$\mathrm{(CH_3)_3CCOOH}$	$\mathrm{CH_3OH}$	−74	$\cdot\mathrm{C(CH_3)_3}$, $\cdot\mathrm{COOH}$, $\cdot\mathrm{CH_2OH}$[f]	1a+2a?
$\mathrm{(CH_3)_3CCOOH}$	BO	−67	$\cdot\mathrm{C(CH_3)_3}$, $\cdot\mathrm{COOH}$	1a
$\mathrm{(CH_3)_3CCOOH}$	0.1 N HCl	+6	$\cdot\mathrm{C(CH_3)_3}$, $\cdot\mathrm{COOH}$, O[b]	1a
$\mathrm{(CH_3)_3CCOOCH_3}$	$\mathrm{CH_3OH}$	−85	$\cdot\mathrm{C(CH_3)_3}$, $\cdot\mathrm{COOCH_3}$, $\cdot\mathrm{CH_2OH}$,$\mathrm{(CH_3)_3C\dot{C}O}$[c]	1a+2a
$\mathrm{(CH_3)_3CCOOCH_2CH_3}$	$\mathrm{CH_3OH}$	−76	$\cdot\mathrm{C(CH_3)_3}$, $\cdot\mathrm{COOC_2H_5}$, $\cdot\mathrm{CH_2OH}$[f]	1a+2a?
$\mathrm{CH_3CH_2CH_2COOH}$	$\mathrm{CH_3OH}$	−80	$\mathrm{CH_3CH_2CH_2\dot{C}(OH)_2}$, $\cdot\mathrm{CH_2OH}$[g]	5a
$\mathrm{CH_3CH_2CH_2COOH}$	0.1 N HCl	+19	$\cdot\mathrm{CH_2CH_2CH_3}$, $\cdot\mathrm{COOH}$, $\cdot\mathrm{O}$[b]	1a
$\mathrm{CH_3CH_2CH(CH_3)COOH}$	BO	−62	$\mathrm{CH_3CH_2\dot{C}HCH_3}$, $\cdot\mathrm{COOH}$	1a
$\mathrm{CH_3CH_2CH(CH_3)COOH}$	$\mathrm{CH_3OH}$	−68	$\mathrm{CH_3CH_2\dot{C}HCH_3}$, $\cdot\mathrm{COOH}$, $\cdot\mathrm{CH_2OH}$	1a+5a?
$\mathrm{HOCH_2COOH}$	$\mathrm{CH_3OH}$	−53	$\cdot\mathrm{CH_2OH}$, $\cdot\mathrm{COOH}$[f]	1a
$\mathrm{HOCH_2COOH}$	$\mathrm{H_2O}$	+30	$\cdot\mathrm{CH_2OH}$, $\cdot\mathrm{COOH}$, $\cdot\mathrm{O}$[b]	1a
$\mathrm{CH_3OCH_2COOH}$	BO	−112	$\cdot\mathrm{CH_2OCH_3}$, $\cdot\mathrm{COOH}$	1a
$\mathrm{CH_3OCH_2COOCH_3}$	BO	−118	$\cdot\mathrm{CH_2OCH_3}$, $\cdot\mathrm{COOCH_3}$, $\cdot\mathrm{BO}$[e]	1a+2a?
$\mathrm{HOCH(CH_3)COOH}$	$\mathrm{H_2O}$	+30	$\mathrm{HO\dot{C}HCH_3}$, $\cdot\mathrm{COOH}$, $\mathrm{HO\dot{C}(CH_3)COOH}$[h], $\cdot\mathrm{O}$[b]	1a+2a?
$\mathrm{HOCH(CH_3)COOH}$	$\mathrm{CH_3OH}$	−68	$\mathrm{HO\dot{C}HCH_3}$, $\cdot\mathrm{COOH}$, $\cdot\mathrm{CH_2OH}$[f]	1a+2a?
$\mathrm{HOC(CH_3)_2COOH}$	$\mathrm{CH_3OH}$	−73	$\mathrm{(CH_3)_2\dot{C}OH}$, $\cdot\mathrm{COOH}$, $\cdot\mathrm{CH_2OH}$[f]	1a+2a?
$\mathrm{HOC(CH_3)_2COOH}$	BO	−80	$\mathrm{(CH_3)_2\dot{C}OH}$, $\cdot\mathrm{COOH}$, $\cdot\mathrm{BO}$[e]	1a+2a?
$\mathrm{HOC(CH_3)_2COOH}$	$\mathrm{H_2O}$	+30	$\mathrm{(CH_3)_2\dot{C}OH}$, $\cdot\mathrm{COOH}$, $\cdot\mathrm{O}$[b]	1a
$\mathrm{(CH_3)_2CHCH(OH)COOH}$	$\mathrm{CH_3OH}$	−70	$\mathrm{(CH_3)_2CH\dot{C}HOH}$, $\cdot\mathrm{COOH}$, $\cdot\mathrm{CH_2OH}$[f]	1a+2a?

[a] Presumably formed from the excited methyl ester.

[b] $\cdot\mathrm{O}$ denotes $\mathrm{HOOC\dot{C}(O^-)OH}$ or $\mathrm{HOOC\dot{C}(OH)_2}$ (see text).

[c] Spectrum shows additional weak lines due to further unidentified radicals.

[d] Presumably formed from excited HCOOH.

[e] $\cdot$BO is a radical formed by H-abstraction from BO (= 1-butene-oxide). Its spectrum shows many sharp lines and has not yet been analysed.

[f] Weak signal.

[g] At microwave powers ⩾5 mW a broad single line with $g \simeq 2.0007$ can be observed which may be due to an acyl type radical $\mathrm{R\dot{C}O}$.

[k] Presumably formed by attack of an electrophilic radical (HO · ?) on the parent acid.

[i] $\cdot\mathrm{CH_2OH}$ not observed.

order structure are immediately recognized as due to the isopropyl radical $\mathrm{CH_3\dot{C}HCH_3}$. The weak lines denoted by arrows belong to $\cdot\mathrm{CH_2OH}$. Further a broad single line, indicated by a circle, is observed. Its g-factor is 2.0006 ± 0.0001 and points to $\cdot\mathrm{COOH}$ ($g = 2.0002$ [23] or $\cdot\mathrm{CO_2^-}$ ($g = 2.0007$ [24], $\mathrm{p}K_\mathrm{a} = 1.4$ [25]). The line width of this species increases sharply with increasing temperature (0.08 mT at −87°, 0.21 mT at +25°). It does not saturate at microwave powers $P \leq 100$ mW. From g-factor and line width we conclude that the radical has a σ-electronic structure and relaxes mainly through spin-rotational interaction similar to other acyl type radicals [18] [26].

The observation of $CH_3\dot{C}HCH_3$ and $\cdot COOH$ is obviously due to reaction (1a) which reads for isobutyric acid

$$(CH_3)_2CHCOOH \xrightarrow{h\nu} CH_3\dot{C}HCH_3 + \cdot COOH \qquad (6)$$

The appearance of a weak signal of $\cdot CH_2OH$ may be rationalized in various ways:

a) Reaction (2a) followed by H-abstraction from methanol by $\cdot OH$:

$$(CH_3)_2CHCOOH \xrightarrow{h\nu} (CH_3)_2CH\dot{C}O + \cdot OH \qquad (7)$$

$$\cdot OH + CH_3OH \longrightarrow H_2O + \cdot CH_2OH \qquad (8)$$

b) Reaction (3a) followed by H-abstraction from methanol by $(CH_3)_2CHCOO\cdot$ or $\cdot H$:

$$(CH_3)_2CHCOOH \xrightarrow{h\nu} (CH_3)_2CHCOO\cdot + H\cdot \qquad (9)$$

$$(CH_3)_2CHCOO\cdot + CH_3OH \longrightarrow (CH_3)_2CHCOOH + \cdot CH_2OH \qquad (10)$$

$$H\cdot + CH_3OH \longrightarrow H_2 + \cdot CH_2OH \qquad (11)$$

c) Photoreduction (5a):

$$(CH_3)_2CHCOOH \xrightarrow{h\nu} (CH_3)_2CH\dot{C}(OH)_2 + \cdot CH_2OH \qquad (12)$$

Of these we favour the sequences (7)/(8) because we were unable to detect H-atoms and radicals of the type $(CH_3)_2CH\dot{C}(OH)_2$ which should be easily observable in the system. The acyl radical $(CH_3)_2CH\dot{C}O$ should exhibit a very broad line ($\Delta H_{ms} = 0.23$ mT at $-95°$) at $g = 2.0007$ [18] and may easily escape detection. Thus, for isobutyric acid the α-cleavage (1a) is the major photolytic pathway in methanol, other reactions as (2a), (3a) or (5a) are only of minor importance. The findings for isobutyric acid are typical for a variety of systems including esters of isobutyric acid, pivalic acid and esters, isovalerianic acid, α-hydroxy and α-alkoxy acids and esters in various solvents as well as for acetic and propionic acid and esters in non hydrogen donor solvents (see *Table 1*). Reaction (1a) was previously established by ESR.-spectroscopy also for tartaric, citric, alloxanic and malonic acid in aqueous solutions at room temperature [11-14]. The authors did not report the detection of $\cdot COOH$ (or $\cdot CO_2^-$), and we suppose that the large line width of this radical has prevented its observation.

From the relative abundances of $(CH_3)_3C\cdot$ and $\cdot CH_2OH$ we conclude that the cleavage of the C—CO-bond is preferred over that of the CO—O-bond.

3.3. *Figure 4* gives an example for the β-dehalogenation reaction (4) which seems to be the dominating processes for all carboxyl compounds monohalogenated in the α-position (see *Table 1*, [2] [7]). The spectrum has been measured during irradiation of the methyl ester of monochloracetic acid and demonstrates the presence of $\cdot CH_2OH$ (lines denoted by circles) and of $\cdot CH_2COOCH_3$. These radicals indicate the reaction sequence

$$ClCH_2COOCH_3 \xrightarrow{h\nu} \cdot Cl + \cdot CH_2COOCH_3 \tag{16}$$

$$\cdot Cl + CH_3OH \longrightarrow HCl + \cdot CH_2OH \tag{17}$$

From *Table 1* it may be noted that the α-bromo compounds do not lead to the formation of $\cdot CH_2OH$ in methanol, *i.e.* bromine atoms do not abstract hydrogen atoms from methanol under our conditions.

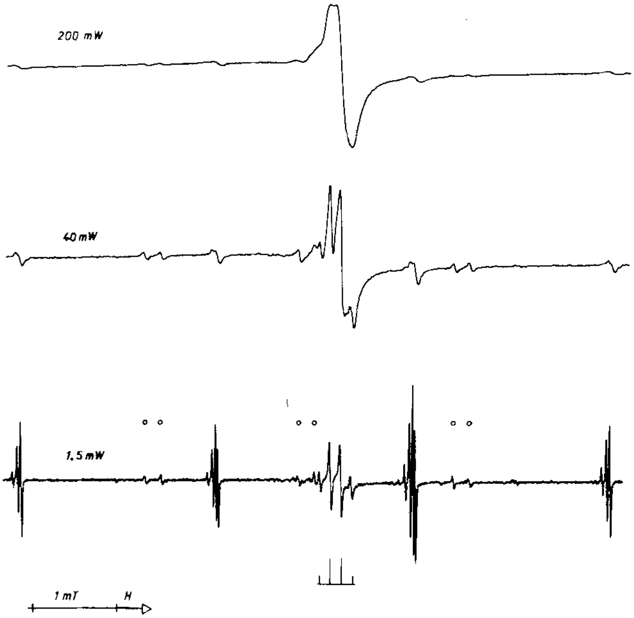


Fig. 3. *Details of ESR.-Spectra during Photolysis of Methyl pivalate in Methanol at different Microwave powers*

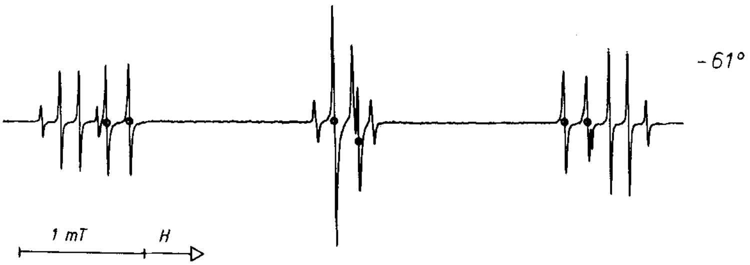


Fig. 4. *ESR.-Spectrum of Radicals during Photolysis of Methylchloro acetate in Methanol*

β-Elimination of chlorine, bromine and iodine atoms is a well known photochemical process also of carbonyl compounds for which, however, fluorine elimination has not been reported [2] [18]. Our observation of fluorine elimination from monofluoroacetic acid *(Table 1)* seems surprising, however, the process is energetically feasible since the bond energy of the C-F bond (~485 kJ/mol) is lower than the excitation energy under our conditions (498 kJ/mol for $\lambda = 240$ nm).

3.4. *Figure 5* shows a spectrum of radicals from acetic acid in methanol. Besides the lines of $\cdot CH_2OH$ (circles) it shows a quartet of triplets which is attributed to $CH_3\dot{C}(OH)_2$. No other radicals are observed, thus photoreduction (5a) seems to be the dominating process:

$$CH_3COOH + CH_3OH \xrightarrow{h\nu} CH_3\dot{C}(OH)_2 + \cdot CH_2OH \qquad (18)$$

As *Table 1* reveals the same reaction occurs for formic acid and derivatives, for esters of acetic acid, for malonic acid and esters, for succinic acid and for propionic acid in hydrogen donor solvents. In aqueous solution most of these compounds undergo α-cleavage, however.

3.5. Evidence for the fragmentation reaction (5b) following photoreduction (5a) was obtained for the isopropyl ester of formic acid and for the *t*-butyl esters of acetic and propionic acid in methanol. This process (5b) must be activated, as *Figure 6* shows. During photolysis of the *t*-butyl ester of acetic acid at −86° one observes lines due to $\cdot CH_2OH$ (circles), $(CH_3)_3C\cdot$ (stick diagram) and $CH_3\dot{C}(OH)OC(CH_3)_3$ (the remaining quartet of doublets). At −44° the latter radical can not be observed whereas the signal of $(CH_3)_3C\cdot$ is present with increased intensity. These findings point to

$$CH_3COOC(CH_3)_3 + CH_3OH \xrightarrow{h\nu} CH_3\dot{C}(OH)OC(CH_3)_3 + \cdot CH_2OH \qquad (19)$$

$$CH_3\dot{C}(OH)OC(CH_3)_3 \longrightarrow CH_2COOH \quad + \cdot C(CH_3)_3 \qquad (20)$$

as the major reactions.

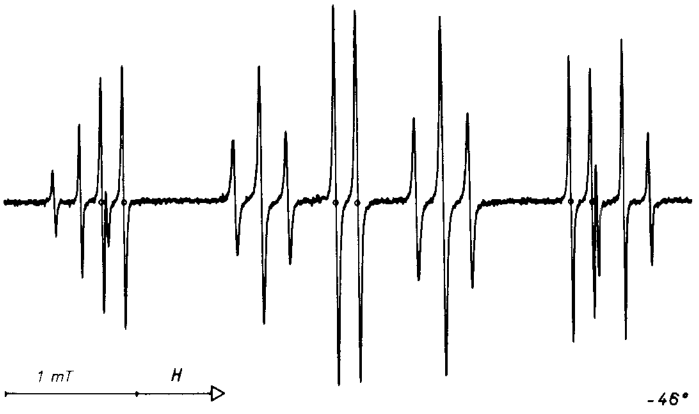


Fig. 5. *ESR.-Spectrum of Radicals during Photoreduction of Acetic acid in Methanol*

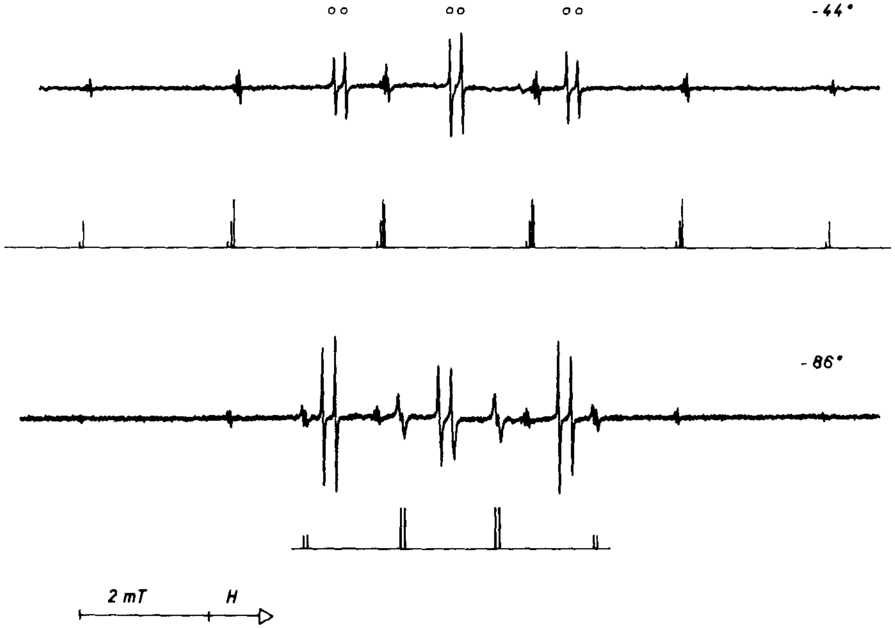


Fig. 6. *Effect of Temperature on the ESR.-Spectra during Photoreduction of* t-*Butyl acetate in Methanol*

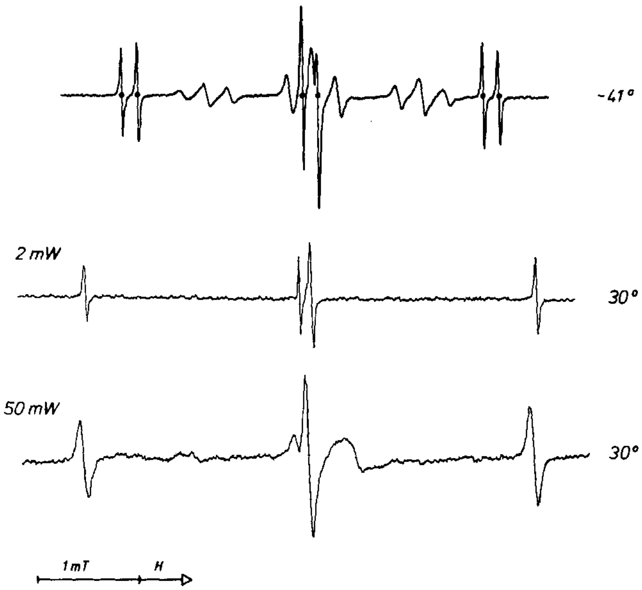


Fig. 7. *Effect of Solvent on ESR.-Spectra during Photolysis of Malonic acid in Methanol (top) and Water*

3.6. As mentioned before several acids undergoing photoreduction in methanol prefer α-cleavage (1a) in aqueous solution. A typical example is malonic acid. The top spectrum of *Figure 7* is observed for a methanolic solution at $-41°$ and shows lines due to the photoreduction radicals $\cdot CH_2OH$ (circles) and $HOOCCH_2\dot{C}(OH)_2$ (remaining lines, triplet of triplets). The two lower spectra are found for aqueous solutions at 30°. For low microwave power one observes a triplet ascribed to $\cdot CH_2COOH$ and a narrow single line at $g=2.0041 \pm 0.0001$. For high microwave power these are broadened by saturation, and a further broad singlet appears at $g=2.0004 \pm 0.0002$. This is very probably due to $\cdot COOH$ or $\cdot CO_2^-$ [23] [24]. $\cdot CH_2COOH$ and $\cdot COOH$ ($\cdot CO_2^-$) are most easily explained by the cleavage process

$$HOOCCH_2COOH \rightarrow HOOC\dot{C}H_2 + \cdot COOH \quad (21)$$

The narrow singlet with $g=2.0041$ has also been observed for all other acids undergoing α-cleavage in aqueous solution *(Table 1)* and seems to be typical for aqueous systems containing $\cdot COOH$ or $\cdot CO_2^-$ radicals. It can not be assigned with certainty to a particular radical, however it seems very likely to be due to reduced oxalic acid $HOOC\dot{C}(O^-)OH$ or its protonated form $HOOC\dot{C}(OH)_2$. This assignment is supported by the following facts: Firstly, oxalic acid is a product expected for all the systems showing the narrow line and is known to be readily reduced by one electron donors [27]. Secondly, $\cdot COOH$ and $\cdot CO_2^-$ are effective one electron donors [27], and finally *Zeldes & Livingston* [28] have measured the ESR.-spectrum of reduced oxalic acid in aqueous solutions at various pH-values and found a narrow single line with $g=2.00400$ at $pH<1$ and $g=2.00419$ at $pH=5.9$, which coincides with our findings.

Turning now to a concluding discussion of the information contained in *Table 1* it may be stated that we have obtained direct evidence for four of the five primary processes suggested in the literature and given in *Scheme 1* namely for the cleavage of the C-CO-bond (1a), the cleavage of the CO-O-bond (2a), β-dehalogenation (4) and photoreduction (5a). We have not found evidence for the cleavage of the $O-R^2$ bond (3a). This reaction has not been well documented in the past and has been considered to be of minor importance [3] so that one may doubt on whether it does occur at all. For the secondary process (5b) first suggested by *Ausloos* [4] clear evidence has been obtained. The remaining secondary processes (1b) and (2b) are known to be important only at temperatures higher than those applied in this study [18] [29] and were not expected to contribute under our conditions. Of the different pathways open for free radical formation from excited carboxyl compounds α-monohalo derivatives exclusively undergo β-elimination (4) and α-hydroxy and alkoxy derivatives cleavage of the C–CO bond (1a). The same behaviour has previously been found for the corresponding ketones [18]. For the other compounds the cleavage reactions (1a) and (2a) and the photoreduction process (5a) compete. Again as for ketones [18] the cleavage reactions are facilitated by α-alkylation, photoreduction is promoted by the presence of hydrogen donors. Of the two cleavage reactions the C–CO bond cleavage (1a) dominates over the CO–O bond rupture (2a). While this is in accord with bond strengths for the ground state molecules [3], the partitioning ratio is known to depend on the excitation wavelength, and (2a) may become dominant for $\lambda < 225$ nm [3-6]. Finally, we note that the radical reactions treated in this work are not the only deactivation processes for excited carboxyl compounds. Besides radiative and radiationless return to the ground state molecular processes leading to non radical products such as CO-elimination and *Norrish* Type II side chain elimination [2] [3] [31] [32] must be considered for many systems before a general description of the photochemistry of carboxyl compounds can be reached.

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