163. Photochemical Free Radical Formation from Aliphatic Dicarboxylic Acids in Solution as Studied by Electron Spin Resonance Spectroscopy

by **Lotty Wymann, Tony Kaiser, Henning Paul** and **Hanns Fischer**

Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

Herrn Professor *Conrad Hans Eugster* zum 60. Geburtstag gewidmet

(15.V.81)

Summary

Various free radicals formed during UV.-irradiation of aliphatic dicarboxylic acids in aqueous and methanolic solution are identified by ESR.-spectroscopy. Their structures point to α-cleavage and photoreduction as the dominant primary photochemical decay processes. The relative contributions of these reactions to the overall photodecomposition depend on solvent and degree of α-alkylation of the acid. Emission ESR.-spectra are found for radicals formed by C, CO-bond cleavage of α-dimethyl substituted acids. The polarization is referred to the triplet mechanism of CIDEP. and indicates this cleavage reaction occurs from a triplet molecular state.

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1. Introduction. - The photochemistry of aliphatic carbonyl compounds has been studied extensively and the formation of free radicals from well known excited states of these molecules by cleavage and H-abstraction reactions has been established in numerous studies [1]. For aliphatic carboxylic acids and esters the published work, while less abundant than on the carbonyl compounds, indicates a similar photochemical behaviour [2] [3]. Especially, as in the case of the carbonyl compounds, the α-cleavage (1 and 2)

$$R^1COOR^2 \xrightarrow{h\nu} \begin{cases} \dot{R}^1 + \dot{C}OOR^2 & (1) \\ R^1\dot{C}O + \dot{O}R^2 & (2) \end{cases}$$

as well as the intermolecular photoreduction (3),

$$R^1COOR^2 + SH \xrightarrow{h\nu} R^1\dot{C}(OH)OR^2 + \dot{S} \qquad (3)$$

seem to be the dominant photochemical decay routes for aliphatic carboxyl compounds, as long as there are no alternative reaction pathways opened by special substituents such as halogen atoms [2] [3].

0018-019X/81/6/1739-13$01.00/0

The nature of the excited molecular states undergoing the decay processes 1-3 is not yet clear. *Coyle* [2] concluded from optical absorption and luminescence properties that the lowest excited singlet and triplet states of aliphatic carboxylic acids and esters have $^1n\pi^*$- and $^3\pi\pi^*$-character. Since ketones undergo α-cleavage and photoreduction most effectively from $n\pi^*$-states it may be inferred that the photodecomposition of carboxylic compounds occurs from the singlet $n\pi^*$-state. However, the CIDNP.-pattern obtained from the cleavage reaction 1 of some acids and esters revealed that this process occurred at least in part from a triplet state radical precursor [4].

In this paper we extend our previous ESR.-spectroscopic examination of transient radicals during the photochemical decomposition of carboxylic compounds [3] to some aliphatic dicarboxylic acids. The results confirm reactions 1 and 3 to be the dominant primary decay processes and indicate the occurrence of the cleavage 2. Further, for a few systems a strong CIDEP.-effect mainly due to the triplet mechanism (TM) [5] is found. Analysis of this polarization leads to the conclusion that the α-cleavage reaction 1 occurs, to a good approximation, exclusively from a triplet molecular state.

2. Experimental Part. - Solutions of various dicarboxylic acids in water and methanol (0.2-1.0 mol/dm^3, depending on solubility) were UV.-irradiated while slowly flowing (flow rate 0.3 cm^3/min) through a flat quartz cell inside the cavity of an *Varian* E-4 ESR.-spectrometer. Cell widths of 0.6 and 1.0 mm were chosen for the aqueous and methanolic solutions, respectively. All solutions were deaerated prior to use by purging with helium. Chemicals were purchased in their purest available form from *Fluka AG* (Buchs) and used without further purification. Only glutaric and dimethylglutaric acid were dissolved in toluene, cleaned with active charcoal, and recrystallized. The ESR.-spectra were recorded during continuous irradiation. The optical arrangement for focussing the UV.-light of a *Hanovia* 977 B-1 Xe-Hg short are lamp on the quartz cuvette has been described previously [3]. The quantum flux absorbed by the carboxyl chromophor having a first absorption maximum at $\lambda \simeq 210$ nm ($\varepsilon_{max} \simeq 50$-$100$ dm^3 mol^{-1} cm^{-1}) was approximately 10^{17} quanta/s. - The ESR.-spectra were analyzed by conventional procedures. Hyperfine coupling constants were determined with an accuracy of ±0.03 mT form line positions on the calibrated x-axis of the recorder

Table 1. *Coupling constants and g-factors of radicals identified during UV.-irradiation of dicarboxylic acids in methanolic solution at T= −60°*

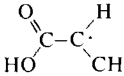
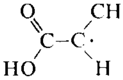
Radical	g-Faktor	Coupling constants [mT]
$HOOCCH_2CH_2\dot{C}HCH_3$	2.0027	H(α): 2.20; H(β,CH_3): 2.55; H(β,CH_2): 2.55
$HOOCCH_2CH_2\dot{C}(CH_3)_2$	2.0025	H(β,CH_3): 2.35; H(β,CH_2): 1.75
$HOOCCH(CH_3)\dot{C}HCH_3$	2.0027	H(α): 2.20; H(β,CH_3): 2.58; H(β,CH): 1.78
	2.0033	H(α): 2.06; H(β,CH_3): 2.51; H(γ,OH): 0.12
	2.0034	H(α): 2.00; H(β,CH_3): 2.55; H(γ,OH): 0.09
$HOOCCH_2\dot{C}(OH)_2$	2.0031	H(β,CH_2): 1.03; H(β,OH): 0.18
$HOOCCH_2CH_2\dot{C}(OH)_2$	2.0031	H(β,CH_2): 1.20; H(γ,CH_2): 0.25; H(β,OH): 0.08
$HOOCCH_2CH_2CH_2\dot{C}(OH)_2$	2.0029	H(β,CH_2): 1.33; H(γ,CH_2): 0.30; H(β,OH): 0.06
$HOOCCH(CH_3)CH_2\dot{C}(OH)_2$	2.0030	H(β,CH_2): 1.28; H(β,OH): 0.35
$HOOCCH_2CH(CH_3)\dot{C}(OH)_2$	2.0032	H(β,CH): 1.28; H(β,OH): 0.32

Table 2. *Transient radicals observed during UV.-irradiation of dicarboxylic acids in solution*

Dicarboxylic acid	Solvent	T[°C] (pH)	Radicals observed	Reaction
Malonic acid	H_2O	29	$HOOC\dot{C}H_2$, $\dot{C}OOH$	1
$HOOCCH_2COOH$		(1.8)	$HOOC\dot{C}HCOOH$	2 and 4
			$HOOC\dot{C}(OH)_2$	6
	MeOH	−70	$HOOCCH_2\dot{C}(OH)_2$, $\dot{C}H_2OH$	3
Succinic acid	H_2O	29	$HOOCCH_2\dot{C}H_2$, $\dot{C}OOH$	1
$HOOC(CH_2)_2COOH$		(2.2)	$HOOCCH_2\dot{C}HCOOH$	2 and 4
			$HOOC\dot{C}(OH)_2$	6
	MeOH	−50	$HOOC(CH_2)_2\dot{C}(OH)_2$, $\dot{C}H_2OH$	3
Glutaric acid	H_2O	29	$HOOCCH_2CH_2\dot{C}H_2$, $\dot{C}OOH$	1
$HOOC(CH_2)_3COOH$		(2.0)	$HOOCCH_2CH_2\dot{C}HCOOH$	2 and 4
			$HOOC\dot{C}(OH)_2$	6
	MeOH	−52	$HOOC(CH_2)_3\dot{C}(OH)_2$, $\dot{C}H_2OH$	3
Methylmalonic acid	H_2O	28	$HOOC\dot{C}HCH_3$, $\dot{C}OOH$	1
$HOOCCH(CH_3)COOH$		(1.6)	$HOOC\dot{C}(CH_3)COOH$	2 and 4
			$HOOC\dot{C}(OH)_2$	6
			$RCH_2\dot{C}HCOOH$a)b)	7
	MeOH	−55	$HOOC\dot{C}HCH_3$c), $\dot{C}OOH$	1
			$\dot{C}H_2OH$	3, or 2 and 4
			$RCH_2\dot{C}OOH$a)c)b)	7
Methylsuccinic acid	H_2O	32	$HOOCCH_2\dot{C}HCH_3$, $HOOCCH(CH_3)\dot{C}H_2$,	1
$HOOCCH_2CH(CH_3)COOH$		(2.1)	$\dot{C}OOH$,	
			$HOOC\dot{C}(OH)_2$b)	6
	MeOH	−60	$HOOCCH_2\dot{C}HCH_3$, $\dot{C}OOH$	1
			$HOOCCH(CH_3)CH_2\dot{C}(OH)_2$, $\dot{C}H_2OH$	3
			$HOOCCH_2CH(CH_3)\dot{C}(OH)_2$	
Meso-2,3-Dimethylsuccinic acid	MeOH	−54	$HOOCCH(CH_3)\dot{C}HCH_3$, $\dot{C}OOH$	1
$HOOCCH(CH_3)CH(CH_3)COOH$			$\dot{C}H_2OH$b)	3, or 2 and 4
2-Methylglutaric acid	MeOH	−22	$HOOCCH_2CH_2\dot{C}HCH_3$, $\dot{C}OOH$	1
$HOOCCH_2CH_2CH(CH_3)COOH$			$\dot{C}H_2OH$	3, or 2 and 4
Dimethylmalonic acid	H_2O	30	$HOOC\dot{C}(CH_3)_2$d), $\dot{C}OOH$	1
$HOOCC(CH_3)_2COOH$		(1.7)	$HOOC\dot{C}(OH)_2$	6
			$RCH_2\dot{C}(CH_3)COOH$e)b)	f)
	MeOH	−62	$HOOC\dot{C}(CH_3)_2$c)d), $\dot{C}OOH$	1
			$RCH_2\dot{C}(CH_3)COOH$e)b)	f)
2,2-Dimethylsuccinic acid	H_2O	27	$HOOCCH_2\dot{C}(CH_3)_2$d), $\dot{C}OOH$	1
$HOOCCH_2C(CH_3)_2COOH$		(2.1)	$HOOC\dot{C}(OH)_2$b)	6
	MeOH	−20	$HOOCCH_2\dot{C}(CH_3)_2$d), $\dot{C}OOH$	1
			$HOOCC(CH_3)_2CH_2\dot{C}(OH)_2$, $\dot{C}H_2OH$	3
2,2-Dimethylglutaric acid	H_2O	30	$HOOCCH_2CH_2\dot{C}(CH_3)_2$d), $\dot{C}OOH$	1
$HOOCCH_2CH_2C(CH_3)_2COOH$		(2.1)	$HOOC\dot{C}(OH)_2$b)	6
	MeOH	−28	$HOOCCH_2CH_2\dot{C}(CH_3)_2$d), $\dot{C}OOH$	1
			$\dot{C}H_2OH$b)	3

a) Presumably $R = HOOC\dot{C}HCH_3$ or $R = \dot{C}OOH$. b) Spectrum shows additional weak lines due to further unidentified radicals. c) *cis-* and *trans*-isomer. d) ESR.-spectrum in emission. e) Presumably $R = HOOC\dot{C}(CH_3)_2$ or $R = \dot{C}OOH$. f) Addition of R to methacrylic acid.

paper. g-Factors were measured relative to those of the radicals $HOOC\dot{C}(OH)_2$ ($g = 2.00405$ [6]) and $\dot{C}H_2OH$ ($g = 2.00333$ [7]) which appear in the ESR.-spectra obtained in aqueous and methanolic solution, respectively. The relative error is estimated to be $\Delta g \simeq \pm 2 \cdot 10^{-4}$. Most of the radicals could be identified by comparison of their coupling constants and g-values with literature data [8] [9]. Species which have not been characterized previously or are not well documented in the literature [8] [9] are compiled in *Table 1*. They were identified by comparison of their spectral parameters with those known for structurally similar ones.

3. Results and Discussion. – All the radicals which were identified during UV.-irradiation of a variety of dicarboxylic acid solutions in water and in methanol are listed in *Table 2*. The entries specify the acids, solvents, temperatures, and pH-values of the aqueous solutions, as well as the radicals observed and the reactions thought responsible for their formation. All compounds are given in their protonated form. The actual dissociation state depends on the pK-values and the pH of the solution. We first discuss a few typical systems in some detail and then draw general conclusions from *Table 2*.

3.1. *Figure 1* shows an ESR.-spectrum obtained during UV.-irradiation of a solution of succinic acid in methanol at T = –20°. As indicated by the stick plots two kinds of radicals are present, namely $HOOCCH_2CH_2\dot{C}(OH)_2$ (a) and $\dot{C}H_2OH$ (b). Their formation is most easily explained by the photoreduction reac-

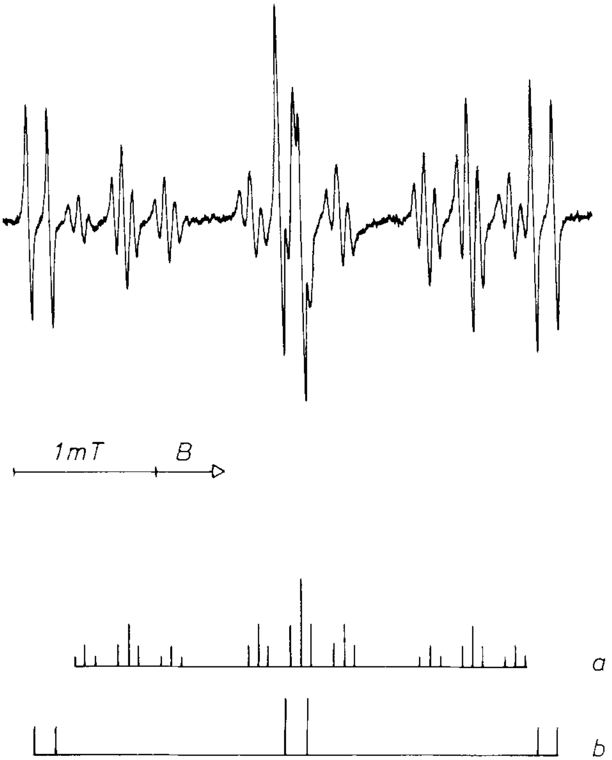


Fig. 1. *ESR.-spectrum of radicals during UV.-irradiation of succinic acid in methanol at T = –20°: $HOOCCH_2CH_2\dot{C}(OH)_2$* (a), *$\dot{C}H_2OH$* (b)

tion 3 which seems to be the by far dominant decay route for the photoexcited succinic acid in methanolic solution. Irradiation of the same acid in aqueous solution at T = 29° yields a completely different spectrum as is demonstrated in *Figure 2*. The intense resonances forming a triplet of triplets (stick plot b) can be attributed to the radical $HOOCCH_2\dot{C}H_2$ and the weak ones (doublet of triplets, stick plot a) to $HOOCCH_2\dot{C}HCOOH$. In addition, two singlets denoted by arrows are observed. Based on our previous work [3] we interpret the broad line at $g = 2.0006$ as the resonance of $\dot{C}OOH$ ($pK = 1.4$ [10]) and the narrow line at $g = 2.0041$ as due to $HOOC\dot{C}(OH)_2$ ($1.7 < pK < 4.5$ [6]). The generation of $HOOCCH_2\dot{C}H_2$ and $\dot{C}OOH$ points to reaction 1 with $\dot{R}^1 = HOOCCH_2\dot{C}H_2$ and $R^2 = H$. Thus, the photoexcited succinic acid decays predominantly by α-cleavage if a good H-donor such as methanol is not available.

Since the acid itself can act as a H-donor the low concentration of radicals $HOOCCH_2\dot{C}HCOOH$ observed in the ESR.-spectrum might indicate that in aqueous solution the photoreduction

$$2\,HOOCCH_2CH_2COOH \xrightarrow{h\nu} HOOCCH_2CH_2\dot{C}(OH)_2 + HOOCCH_2\dot{C}HCOOH$$

competes with the cleavage reaction 1. However, even at high sensitivity settings of the spectrometer we were unable to detect the counterradical $HOOCCH_2CH_2\dot{C}(OH)_2$. Thus, we favour an alternative source for $HOOCCH_2\dot{C}HCOOH$, namely the O,CO-bond cleavage 2. This would lead to hydroxyl $\dot{O}H$ and acyl type radicals $R^1\dot{C}O$ as primary species. Because of fast relaxation due to spin-rotation interaction [11] the acyl radical is expected to exhibit a very broad resonance line at $g \simeq 2.0006$ at room temperature [12] which at our low steady state radical concentrations should be undetectable in the ESR.-spectrum. The reactive $\dot{O}H$ radical, although not

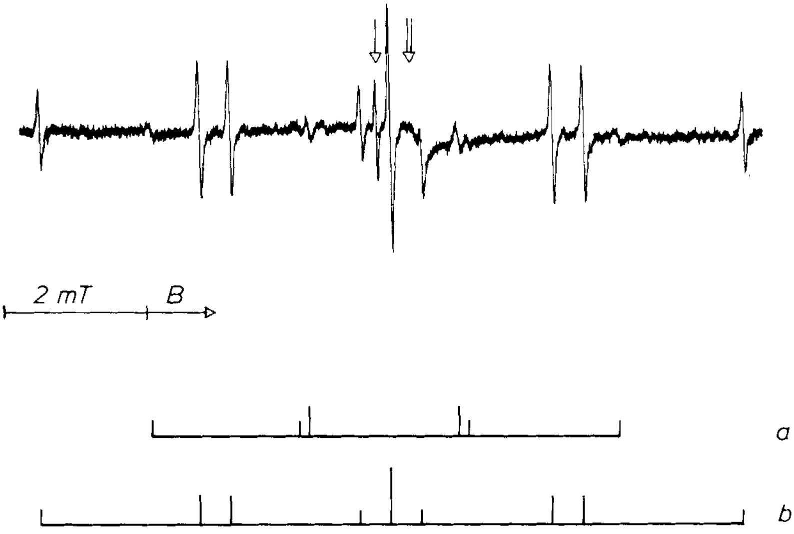


Fig. 2. *ESR.-spectrum of radicals during UV.-irradiation of succinic acid in water at T = 29°:* $HOOCCH_2\dot{C}HCOOH$ (a), $HOOCCH_2\dot{C}H_2$ (b), $\dot{C}OOH$ ($\Downarrow$), $HOOC\dot{C}(OH)_2$ ($\downarrow$)

directly observable in the spectrum, would certainly abstract a H-atom from the acid (see equ. 4),

$$\mathrm{RH} + \dot{\mathrm{O}}\mathrm{H} \longrightarrow \dot{\mathrm{R}} + \mathrm{H_2O} \qquad (4)$$

and in this way generate the observed species $\dot{\mathrm{R}} = \mathrm{HOOCCH_2\dot{C}HCOOH}$.

Finally, we interpret the formation of $\mathrm{HOOC\dot{C}(OH)_2}$ radicals in aqueous solution as originating from oxalic acid formed as a reaction product by combination of carboxyl radicals $\dot{\mathrm{C}}\mathrm{OOH}$. The radical $\mathrm{HOOC\dot{C}(OH)_2}$ might then be formed from oxalic acid in two ways, either by photoreduction (5),

$$\mathrm{HOOCCOOH} + \mathrm{RH} \xrightarrow{h\nu} \mathrm{HOOC\dot{C}(OH)_2} + \dot{\mathrm{R}}, \qquad (5)$$

or by an electron transfer reaction with the carboxyl radical anion (6). Several

$$\begin{array}{lll} \mathrm{HOOCCOOH} + \dot{\mathrm{C}}\mathrm{OO^-} \longrightarrow & \mathrm{HOOC\dot{C}(O^-)OH} + \mathrm{CO_2} & \\ & \quad\updownarrows & \\ & \mathrm{HOOC\dot{C}(OH)_2} & (6) \end{array}$$

arguments are in favour of reaction 6 which was considered by *Norman* [13] and examined to some detail by *Zeldes* [6]:

a) Reaction 5 requires absorption of UV.-light by oxalic acid. However, its absorption band is largely screened by that of the highly concentrated succinic acid.

b) Gas evolution was observed during UV.-irradiation, not only for succinic acid but also for all other systems showing the ESR.-absorption of $\mathrm{HOOC\dot{C}(OH)_2}$ (see *Table 2*). This strongly supports reaction 6 which produces carbondioxide.

c) The electron transfer process 6 is known to proceed much faster in aqueous than in alcoholic solution [6]. In accord with this, the ESR.-absorption of $\mathrm{HOOC\dot{C}(OH)_2}$ is detectable for aqueous systems only. For acids undergoing the cleavage reaction 1 in methanolic solution (see *Table 2* and [3]) $\dot{\mathrm{C}}\mathrm{OOH}$ but never $\mathrm{HOOC\dot{C}(OH)_2}$ is observed in the ESR.-spectrum.

The photochemical behaviour of succinic acid, namely photoreduction in methanolic and α-cleavage in aqueous solution, is representative for other non substituted aliphatic dicarboxylic acids. Analogous results were obtained for malonic and glutaric acid *(Table 2)*.

3.2. Several radicals are observed during UV.-irradiation of methylmalonic acid in aqueous solution at $T = 28°$ *(Fig. 3)*. The stick plots a–c mark the ESR.-line positions of the species $\mathrm{HOOC\dot{C}HCH_3}$ (c), $\mathrm{HOOC\dot{C}(CH_3)COOH}$ (b), and a radical which would have a structure $\mathrm{RCH_2\dot{C}HCOOH}$ (a) according to its ESR.-parameters $a_{\mathrm{H}}(\mathrm{CH}) = 2.10$ mT, $a_{\mathrm{H}}(\mathrm{CH_2}) = 2.23$ mT, and $g = 2.0033$. In addition, two singlets due to $\dot{\mathrm{C}}\mathrm{OOH}$ and $\mathrm{HOOC\dot{C}(OH)_2}$ are denoted with arrows. The spectrum contains a few further resonances of low intensity which were not interpreted. - The species $\mathrm{HOOC\dot{C}HCH_3}$ and $\dot{\mathrm{C}}\mathrm{OOH}$ give evidence for a photochemical decomposition via C,CO-bond cleavage 1. With the same reasoning as given above for succinic acid the most satisfactory explanation for the generation of $\mathrm{HOOC\dot{C}(CH_3)COOH}$ is a competing primary photodecomposition by O,CO-bond cleavage (2) followed by reaction 4, *i.e.* H-abstraction from the acid by the hydroxyl radical. The formation of $HOO\dot{C}(OH)_2$ is again attributed to reaction 6. Finally, the most probable source for the radicals $RCH_2\dot{C}HCOOH$ seems to be an addition reaction (7),

$$\dot{R} + CH_2{=}CHCOOH \longrightarrow RCH_2\dot{C}HCOOH, \qquad (7)$$

of some radical $\dot{R}$ to acrylic acid, formed as a product by disproportionation of $HOOC\dot{C}HCH_3$ with itself or other radicals.

Unlike the nonsubstituted dicarboxylic acids, methylmalonic acid essentially undergoes the same primary photochemical reactions in methanolic solution as it does in water. This is demonstrated in *Figure 4* by an ESR.-spectrum obtained from a methanolic solution at $T = -55°$. Indicative of a C, CO-bond rupture (s. equ. 1) are the intense resonance of $\dot{C}OOH$, marked in *Figure 4* with a broad arrow, as well as the ESR.-lines of the radical $HOOC\dot{C}HCH_3$, which is present at this low temperature in two distinct conformations having slightly different ESR.-parameters (stick plots c and c′). Comparison of the coupling constants and *g*-factors (see *Table 1*) with literature data [14] suggests an interpretation of the spectra c and c′ as due to the *cis*- and *trans*-isomer, respectively (*cis* and *trans* with respect to the hydroxyl and methyl group). In addition, the radical $\dot{C}H_2OH$ is identified in the ESR.-spectrum

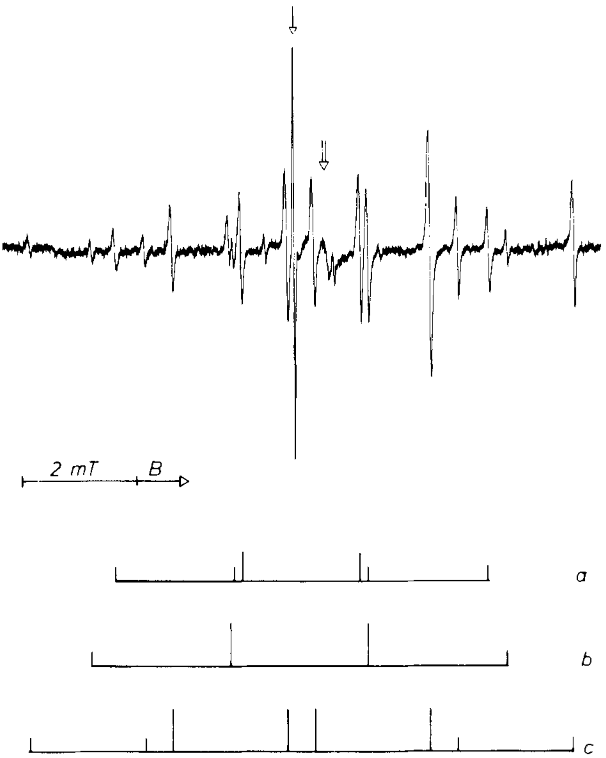


Fig. 3. *ESR.-spectrum of radicals during UV.-irradiation of methylmalonic acid in water at T = 28°:* $RCH_2\dot{C}HCOOH$ (a), $HOOC\dot{C}(CH_3)COOH$ (b), $HOOC\dot{C}HCH_3$ (c), $\dot{C}OOH$ (⇓), $HOOC\dot{C}(OH)_2$ (↓)

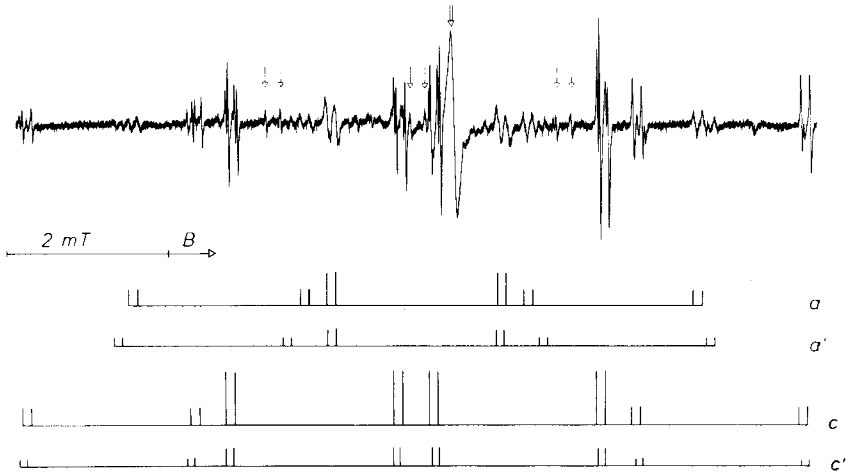


Fig. 4. *ESR.-spectrum of radicals during UV.-irradiation of methylmalonic acid in methanol at T= −55°: 2 isomers of* $RCH_2\dot{C}HCOOH$ (a, a'), cis- *and* trans-$HOOC\dot{C}HCH_3$ (c, c'), $\dot{C}OOH$ (⇓), $\dot{C}H_2OH$ (↓)

by its characteristic line pattern which in *Figure 4* is denoted by narrow arrows. It is present in low concentration only and might have been generated by intermolecular photoreduction (3) or by O, CO-bond cleavage (2) followed by H-abstraction from methanol by the primarily formed hydroxyl radicals.

The secondary radical $RCH_2\dot{C}HCOOH$ attributed to the addition reaction 6 is observable in the ESR.-spectrum as it was in aqueous solution. At T= −55°

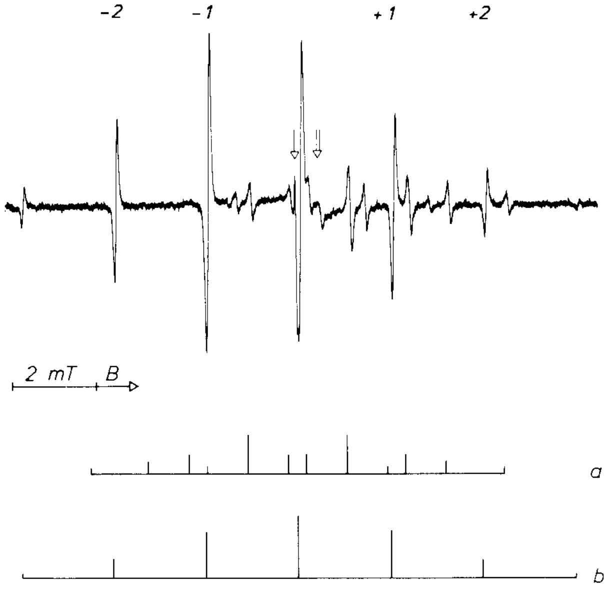


Fig. 5. *ESR.-spectrum of radicals during UV.-irradiation of dimethylmalonic acid in water at T= 30°:* $RCH_2\dot{C}(CH_3)COOH$ (a), $HOOC\dot{C}(CH_3)_2$ (b), $\dot{C}OOH$ (⇓), $HOOC\dot{C}(OH)_2$ (↓)

the species is present in two conformations (stick plots a and a′) which might be a *cis*- and a *trans*-isomer, in analogy to the interpretation given above for the two conformations of the related $HOOC\dot{C}HCH_3$ radical. As to the nature of $\dot{R}$ it is noted that the ESR.-spectra of the two conformations of $RCH_2\dot{C}HCOOH$ coalesce for $T \gtrsim -20°$, whereby the coupling constants and the *g*-factor of the resulting spectrum become equal to those measured for $RCH_2\dot{C}HCOOH$ at $T = 28°$ in water. Thus, in aqueous and methanolic solution the same radical $\dot{R}$ seems to add to acrylic acid leaving $\dot{R} = HOOC\dot{C}HCH_3$ or $\dot{R} = \dot{C}OOH$ as the most likely candidates.

3.3. *Figure 5* shows an ESR.-spectrum observed during UV.-irradiation of dimethylmalonic acid in aqueous solution at $T = 30°$. It consists of the resonance lines of the two radicals $HOOC\dot{C}(CH_3)_2$ (stick plot b) and $\dot{C}OOH$ (broad arrow) due to C,CO-bond cleavage 1, the species $HOOC\dot{C}(OH)_2$ (narrow arrow) due to reaction 6, and a radical $RCH_2\dot{C}(CH_3)COOH$ (stick plot a) which presumably stems from the addition of some species $\dot{R}$ to methacrylic acid, the disproportionation product of the primary radical $HOOC\dot{C}(CH_3)_2$. The same radicals, except $HOOC\dot{C}(OH)_2$, are formed during UV.-irradiation of this acid in methanolic solution. Thus, the photochemical behaviour of dimethylmalonic acid, namely decay by C,CO-bond rupture in water and in methanol, is identical to that observed for the monomethyl substituted acid.

The ESR.-spectrum of $HOOC\dot{C}(CH_3)_2$ in *Figure 5* shows a remarkably strong effect of Chemically Induced Dynamic Electron Polarization (CIDEP.) [5]. All the

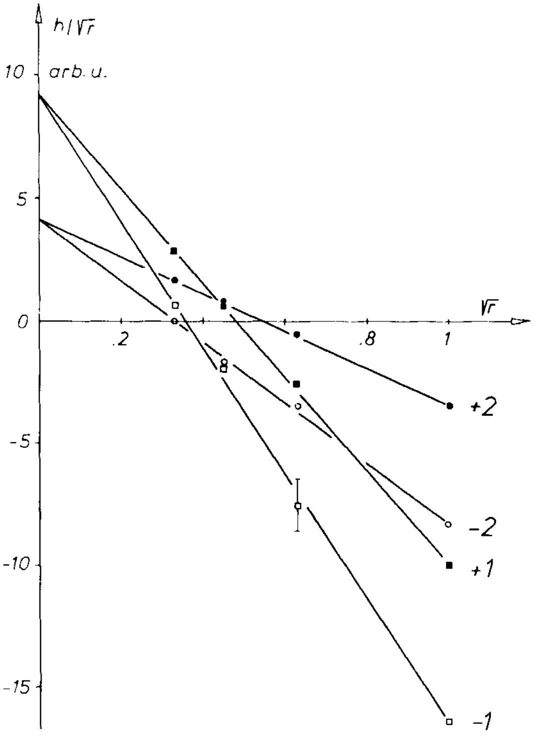


Fig. 6. *ESR.-line heights h of* $HOOC\dot{C}(CH_3)_2$ *as function of the initiation rate* $I = rI_0$

seven lines of the septet are in emission, *i.e.* the corresponding upper *Zeeman* levels are overpopulated. Two mechanisms are known as main sources for such non-equilibrium populations of the electron spin levels of transient radicals in solution. One is the triplet mechanism (TM.) [15]. It occurs if the radicals have as a precursor a molecular triplet state, the sublevels of which have been populated differently by intersystem crossing and decay into radicals faster than they equilibrate via relaxation. The second is the radical pair mechanism (RPM.) [16] [17], where the polarization is built up in reencounter sequences of spin correlated radical pairs by the successive action of exchange and *Zeeman* interaction. While the TM. should affect all hyperfine lines equally giving rise to an ESR.-spectrum with all the resonances in emission or in enhanced absorption, the RPM. normally produces E/A or A/E type multiplet effects, *i.e.* low field lines in emission and high field lines in enhanced absorption or *vice versa.*

In order to estimate the polarization of the electron spin levels of the $HOOC\dot{C}(CH_3)_2$ radicals in *Figure 5* we consider the initiation and the second order terminations of the radicals $\dot{C}OOH$ ($\dot{A}$) and $HOOC\dot{C}(CH_3)_2$ ($\dot{B}$) only. This leads to the reaction *Schemes 8* and *9a–9c*, where I is the rate of photochemical radical initiation and k_{AA}, k_{AB} and k_{BB} are the rate constants for bimolecular radical termination. As shown in the appendix, the height h of a polarized ESR.-line of $\dot{B}$ can then be written as in equation 10.

$$HOOCC(CH_3)_2COOH \xrightarrow{I} \dot{A}+\dot{B} \tag{8}$$

$$\dot{A}+\dot{A} \xrightarrow{k_{AA}} \text{products} \tag{9a}$$

$$\dot{A}+\dot{B} \xrightarrow{k_{AB}} \text{products} \tag{9b}$$

$$\dot{B}+\dot{B} \xrightarrow{k_{BB}} \text{products} \tag{9c}$$

$$h=C\sqrt{I}\,\{1+\sqrt{4k_{BB}I}\;T_1\,[p^I(TM.)+p^I(RPM.)+p^F(RPM.)]\} \tag{10}$$

C is a proportionality constant, T_1 the spin-lattice relaxation time of $\dot{B}$, $p^I(TM.)$ and $p^I(RPM.)$ are the polarizations (expressed as multiples of the *Boltzmann* polarization) which $\dot{B}$ obtains in the initiation process *via* the TM. and the RPM. operative in the geminate pair, and $p^F(RPM.)$ measures all the polarizations of $\dot{B}$ that are generated by the RPM. during free radical encounters of $\dot{B}$ with radicals $\dot{A}$ or other radicals $\dot{B}$. If the rate of radical initiation is varied according to $I=rI_0$ (maximum initiation rate I_0, retardation factor $0<r\leq 1$) equation 10 leads to equation 11, where V_0, the experimental enhancement factor, is given by equation 12.

$$h/\sqrt{r}=C(1+\sqrt{r}\,V_0) \tag{11}$$

$$V_0=\sqrt{4k_{BB}I_0}\;T_1\,[p^I(TM.)+p^I(RPM.)+p^F(RPM.)] \tag{12}$$

Attenuating the UV.-light intensity by a set of calibrated wire gauzes we have analyzed the dependence of the ESR.-signal heights of the $HOOC\dot{C}(CH_3)_2$ radical on the initiation rate. As is shown in *Figure 6* relation 11 holds for the four lines denoted by ± 1 and ± 2 (see *Fig. 5*). The wing and centre lines could not be analyzed because of low intensity and overlap of other resonances, respectively. According to 11 the enhancement factors V_0 are obtained from *Figure 6* by dividing the slopes of the straight lines by their intercepts. The results listed in *Table 3*, show the enhancements to be a superposition of a strong net emission referable to the TM. with V_0(TM.) = −2.43 and an E/A type multiplet effect due to the RPM. with V_0(RPM.) = ±0.35 and V_0(RPM.) = ±0.60 for the lines ± 1 and ± 2, respectively.

The strong net emission suggests that most of the radicals are formed from strongly polarized triplet sublevels of the photoexcited dimethylmalonic acid. To check this more thoroughly we have to estimate p^I(TM.) and have to compare it with the maximum value predicted by theory [18] [19]. For comparable radicals in aqueous solution, the RPM. polarizes ESR.-lines about ± 2 mT from the centre of the spectrum by about $30 \lesssim |p^F(\text{RPM.})| \lesssim 60$ [5] [20] [21]. Thus, it seems safe to estimate for the lines ± 1 of $HOOC\dot{C}(CH_3)_2$ the total RPM. polarization to be $|p^I(\text{RPM.}) + p^F(\text{RPM.})| \gtrsim 30$. Since V_0(TM.) exceeds V_0(RPM.) for these lines by a factor of 7 we have to conclude from equation 12 that $p^I(\text{TM.}) \lesssim -210$. The theoretical prediction for p^I(TM.) is given in equation 13 [5] [18] [19], where k_{ISC} and k_S are the rate constants

$$p^I(\text{TM.}) = \frac{k_{ISC}}{k_{ISC} + k_S} \cdot F(w_x, w_y, w_z, D, E, \tau_T, \tau_c, \omega_0, P^{eq}) \tag{13}$$

for intersystem crossing and radical formation from the excited singlet state. The function *F*, which differs for different theoretical approaches [5] [18] [19], depends on the population probabilities w_x, w_y, w_z of the triplet zerofield states by intersystem crossing, the zerofield splittings D, E, the lifetime τ_T and reorientational correlation time τ_c of the triplet molecule, the magnetic field strength ω_0, and the *Boltzmann* polarization P^{eq}. In order to calculate *F* we assume isotropic reorientation and estimate $\tau_c \simeq 2.4 \cdot 10^{-11}$ s from $\tau_c = 4\pi a^3\eta/(3kT)$ taking the molecular volume $4\pi a^3/3 \simeq 10^{-22}$ cm³ from the *van der Waals* increments given by *Edward* [22]. Further, we take $|D| \simeq 0.14\ \text{cm}^{-1} \gg |E|$, values which have been found for the triplet states of aliphatic carbonyl compounds [23] [24]. The theoretical expressions derived by *Atkins et al.* [18] and *Pedersen et al.* [19] then both yield $F \simeq -190$ for the minimum of *F* which is obtained at $w_x = w_y = 0$, $w_z = 1$, sgn D = − 1, and $\tau_T \simeq 0.1$ ns. Thus, the experimental value $p^I(\text{TM.}) \lesssim -210$ just meets the maximum possible emission implying that $k_{ISC}(k_{ISC} + k_S)^{-1}$ must be close to unity, *i.e.* for the photoexcited dimethylmalonic acid the C,CO-bond cleavage reaction 1 occurs exclusively from a molecular triplet state. It is noted that the ESR.-spectra of the alkyl radicals formed by reaction 1 from 2,2-dimethylsuccinic acid and 2,2-dimethylglutaric acid are also observed in emission. Thus, they presumably stem from triplet state precursor molecules, as well.

Table 3. *Enhancement factors and polarizations of the ESR.-lines of* $HOOC\dot{C}(CH_3)_2$

Line	−2	−1	+1	+2
V_0[±0.08]	−3.03	−2.78	−2.08	−1.85
V_0(TM.)	−2.43	−2.43	−2.43	−2.43
V_0(RPM.)	−0.60	−0.35	+0.35	+0.60

Turning now to a concluding discussion, it is obvious from the compilation in *Table 2* that the photochemical behaviour of the three systems discussed is representative for other dicarboxylic acids, also. The dominant primary photochemical decay processes are C, CO-bond cleavage and/or intermolecular photoreduction. In addition, as discussed in 3.1 there is some indirect evidence for reaction 2, the O, CO-bond cleavage, as a further primary decay reaction. However, judged from the observed relative steady state radical concentrations this process occurs with a much lower quantum yield than the other two. This finding parallels our previous results obtained for the photochemical decay processes of aliphatic carboxylic esters [3] [4]. There, a partial decay *via* O, CO-bond cleavage 2 could be directly proven by ESR.-detection of the primarily formed acyl type radical $R^1\dot{C}O$. For the methyl ester of pivalic acid this reaction occurred with about a factor 10 lower quantum yield than the C, CO-bond rupture 1 [4]. With respect to the partitioning ratio of α-cleavage and intermolecular photoreduction the dicarboxylic acids behave in an analogous way to the monocarboxylic acids and esters [3]. The cleavage reaction is facilitated by α-alkylation, while the photoreduction is promoted by the presence of good hydrogen donors.

No clear-cut decision is possible as to whether or not the two carboxyl chromophors of dicarboxylic acids undergo their photochemical decay processes independent of each other. For example, methylsuccinic acid undergoes C, CO-bond cleavage at both ends in water but only at the methyl substituted end in methanol. Thus, the two carboxyl chromophors seem to behave independently yielding a superposition of the photochemistry observed for succinic acid and 2, 3-dimethylsuccinic acid. The same is true for 2, 2-dimethylsuccinic acid in methanolic solution, where cleavage occurs at the methyl substituted end only, while the other one undergoes photoreduction. However, an independent photochemistry of the two carboxyl chromophors would require this acid to cleave at both ends in aqueous solution, but only $HOOCCH_2\dot{C}(CH_3)_2$ and no $\dot{C}H_2C(CH_3)_2COOH$ radicals are detected by ESR.-spectroscopy. A further argument against the independence of the two chromophors is the strong TM.-type CIDEP. of the radicals formed by C, CO-bond rupture from the dimethyl substituted malonic, succinic, and glutaric acid. No such polarization is observed for *t*-butyl radicals generated by photoexcitation of pivalic acid [3]. Thus, the presence of a second carboxyl group somehow influences either the decay *via* cleavage or the intersystem crossing process. Consequently, our conclusion from the TM.-type CIDEP. that C, CO-bond cleavage starts exclusively from a molecular triplet state might be true for the dimethyl substituted dicarboxylic acids only. For monocarboxylic acids there remains the result of our previous CIDNP. study [4] which showed the cleavage to be at least in part a triplet state reaction.

Support of this work by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* is gratefully acknowledged.

Appendix. – The steady state ESR.-signal of a radical system exhibiting CIDEP. is obtained from the *Bloch* equations 14, where all the symbols have their usual meaning [5] [21]. For radicals $\dot{B}$

$$\begin{aligned}
\dot{M}_x &= O = -T_2^{-1} M_x + (\omega - \omega_o) M_y \\
\dot{M}_y &= O = (\omega_o - \omega) M_x - T_2^{-1} M_y - \omega_1 M_Z \qquad (14) \\
\dot{M}_z &= O = \omega_1 M_y - T_1^{-1} M_Z + f,
\end{aligned}$$

obeying the reaction *Scheme 8* and *9* the function f is given by

$$\mathrm{f} = \mathrm{I}\mathrm{P}^{\mathrm{I}} + 2k_{\mathrm{BB}}[\dot{\mathrm{B}}]^2\mathrm{P}^{\mathrm{F}}_{\mathrm{BB}} + k_{\mathrm{AB}}[\dot{\mathrm{A}}][\dot{\mathrm{B}}]\mathrm{P}^{\mathrm{F}}_{\mathrm{AB}} + \mathrm{T}_1^{-1}[\dot{\mathrm{B}}]\mathrm{P}^{\mathrm{eq}}$$

It describes the CIDEP. of $\dot{\mathrm{B}}$, *i.e.* a production of z-magnetization during radical initiation and spin selective termination *via* self- and cross-reaction with $\dot{\mathrm{A}}$. The last term accounts for relaxation of M_z towards thermal equilibrium. Solution of the *Bloch* equations yields for the ESR.-signal height h the equation 15.

$$\mathrm{h} \propto -\mathrm{M}_y = \frac{\omega_1 \mathrm{T}_1 \mathrm{T}_2}{1 + \mathrm{T}_2^2(\omega - \omega_0^2) + \mathrm{T}_1\mathrm{T}_2\omega_1^2}\,\mathrm{f} \propto \mathrm{f} \qquad (15)$$

Assuming $k_{\mathrm{AB}} = 2\sqrt{k_{\mathrm{AA}}k_{\mathrm{BB}}}$ [25] the steady state rate laws for the reaction *Scheme 8* and *9* give equation 16.

$$\mathrm{I} = 4k_{\mathrm{BB}}[\dot{\mathrm{B}}]^2 \qquad \text{and} \qquad [\dot{\mathrm{A}}] = \sqrt{k_{\mathrm{BB}}/k_{\mathrm{AA}}}\,[\dot{\mathrm{B}}] \qquad (16)$$

Thus, f is given by equation 17, which is equivalent to equation 10 with $\mathrm{p}^{\mathrm{I}} \equiv \mathrm{p}^{\mathrm{I}}(\mathrm{TM.}) + \mathrm{p}^{\mathrm{I}}(\mathrm{RPM.})$ and $\frac{1}{2}(\mathrm{p}^{\mathrm{F}}_{\mathrm{BB}} + \mathrm{p}^{\mathrm{F}}_{\mathrm{AB}}) \equiv \mathrm{p}^{\mathrm{F}}(\mathrm{RPM.})$

$$\mathrm{f} = \frac{1}{2}\sqrt{\mathrm{I}/k_{\mathrm{BB}}}\,\mathrm{T}_1^{-1}\mathrm{P}^{\mathrm{eq}}\{1 + \sqrt{4k_{\mathrm{BB}}\mathrm{I}}\,\mathrm{T}_1[\mathrm{p}^{\mathrm{I}} + \frac{1}{2}(\mathrm{p}^{\mathrm{F}}_{\mathrm{BB}} + \mathrm{p}^{\mathrm{F}}_{\mathrm{AB}})]\} \qquad (17)$$

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