153. Norrish Type I Cleavage of Aliphatic Carboxylic Acids and Esters in Solution. A CIDNP.-Study

by Tony Kaiser and Hanns Fischer

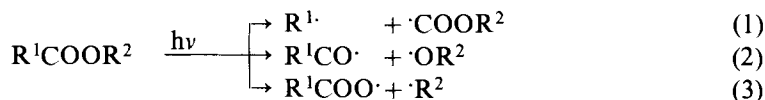Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH–8057 Zürich

Herrn Prof. *A. S. Dreiding* zum 60. Geburtstag gewidmet

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Summary

UV.-irradiation of pivalic and isobutyric acid and their methyl esters as well as of α-hydroxy isobutyric and malonic acid in solution lead to chemically induced dynamic nuclear polarization (CIDNP.) of parent compounds and of various reaction products. CIDNP.-effects and product distributions confirm α-cleavage of the $C(\alpha)$, CO bond to be the major mode of photodecomposition. Scavenger experiments indicate that decomposition of the molecules from a triplet excited state is roughly equally or more probable than from a singlet excited state. Quantum yields of educt disappearance are also given for the methyl esters of pivalic and isobutyric acid.

1. Introduction. – Chemically induced dynamic nuclear polarization (CIDNP.) is an established method to investigate free radical reaction mechanisms. It allows the determination of the multiplicity of the radical precursor states, the product formation steps and ratios, and the detection of unstable products such as enols. This has amply been demonstrated for photochemical radical reactions of aliphatic ketones and aldehydes [1]. To explain the observed photoproduct distributions [2] [3] for aliphatic carboxylic acids and esters three homolytic photochemical cleavage reactions have been suggested. Recently we have published ESR.-results on free radical formation during photolysis of a variety of aliphatic carboxylic acids and esters, and have shown that $C(\alpha)$, CO-bond cleavage (1) is the main primary

$$R^1COOR^2 \xrightarrow{\ h\nu\ } \begin{cases} R^{1\cdot} + \cdot COOR^2 & (1) \\ R^1CO\cdot + \cdot OR^2 & (2) \\ R^1COO\cdot + \cdot R^2 & (3) \end{cases}$$

process for α-hydroxy, α-alkoxy and α-di- and tri-alkyl substituted carboxylic acids and esters [4]. Reaction (2) was found to be of minor importance while no evidence could be obtained for reaction (3). This is confirmed in this study which deals with

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the CIDNP.-effects, the product distributions and the quantum yields of reactand disappearance for the photodecomposition of pivalic acid, isobutyric acid and their methyl esters, a-hydroxy isobutyric acid and malonic acid in solution. Only very few previous attempts to obtain quantitative mechanistic information on the photochemistry of related carboxylic acids and esters have been reported [2] [3] [5–10].

2. Experimental Procedures. – If not otherwise stated, 0.5M solutions of the carboxylic compounds in methanol-d_4, cyclohexane-d_{12} or water were photolyzed at room temperature in thin wall quartz tubes (*Stohler* ST 19) within a modified probe [11] of a *Varian* HA-100 D-proton-NMR.-spectrometer. Tetramethylsilane (10% by volume) was added to the organic solvents to provide the lock signal. The optical arrangement was similar to that described in [12], but in this work a *Hanovia* 1000 W/Xe/Hg-lamp (977 B-1) was employed. The light was focussed onto the light pipe by means of an elliptical mirror [13] and two *Suprasil* lenses. The dispersion of the quantum flux $I(\lambda)$ in the NMR.-tube is expected to be very similar to that given elsewhere [4]. NMR.-spectra and integrals were taken before, during and after irradiation. The transitions were assigned to the various products by adding small amounts of the expected substances and by comparison of line positions. Chemicals were obtained from *Fluka AG* (Buchs) and *Chemische Fabrik Uetikon* (Uetikon) (methanol-d_4, cyclohexane-d_{12}) in the purest available form. The methyl and ethyl esters of monochloroacetic acid, methyl pivalate and isobutyrate were distilled twice with a spinning band column. All other chemicals were used without purification.

The quantum yields ϕ for photolysis were determined from initial decomposition rates r of the compounds, that of a standard (r_s) with known quantum yield ϕ_s and the absorbed light intensities *via* equation (4).

$$\phi = \phi_s \cdot \frac{r}{r_s} \cdot \frac{\Sigma_\lambda \, I(\lambda)(1-10^{-E_s(\lambda)}) \, \Delta\lambda}{\Sigma_\lambda \, I(\lambda)(1-10^{-E(\lambda)}) \, \Delta\lambda} \qquad (4)$$

Here, $I(\lambda)$ is the dispersion of the quantum flux [4], and $E(\lambda)$ and $E_s(\lambda)$ are the extinctions determined by UV.-spectroscopy corrected for the cylindrical shape of the sample cell. The summations were carried out with a stepwidth $\Delta\lambda = 1.25$ nm from $\lambda = 220$ nm, *i.e.* the short wavelength end of the quantum flux [4], to $\lambda = 270$ nm were the carboxylic compounds cease to absorb [2] [3] [14]. In all runs 0.5 ml of the solutions were irradiated in the NMR.-arrangement to $\leqslant 30\%$ conversion. The initial rates r for the compounds were determined at 20° from NMR.-integrals. A 0.5M aqueous solution of monochloroacetic acid was employed as a standard; r_s at 25° was obtained from titrations of the formed chloride with aqueous silver nitrate and potentiometric detection of the equivalence point. The quantum yield of chloride formation $\phi_s = 0.36$ was taken from the literature [15] [16] as appropriate for 25° and $\lambda = 240$ nm. To check the validity of the procedure the quantum yields of decomposition of the methyl and ethyl esters of monochloroacetic acid were measured. Our value $\phi = (1.1 \pm 0.2)$ for both esters agrees with [17]. The relative error of $\pm 20\%$ is estimated from experimental standard deviations and the uncertainties of the summations and of ϕ_s.

The CIDNP.-effects were analyzed *via Kaptein*'s rules [18] with known magnetic properties of the free radicals involved. Ratios of disproportionation *versus* combination of a radical pair k_d/k_c resulted from the CIDNP.-intensities of the products ΔJ by equation (5) [19]. The relaxation time constants T_1 were determined from the decay of the CIDNP.-signals after irradiation or by a rapid passage method [20].

$$\frac{\Delta J_d}{\Delta J_c} = \frac{k_d}{k_c} \cdot \frac{T_{1,d}}{T_{1,c}} \qquad (5)$$

3. Results. – 3.1. *Pivalic Acid. Figure 1* displays NMR.-transitions observed during and after photolysis of pivalic acid in methanol-d_4. *Table 1* lists the assignments of the transitions, the phases of the CIDNP.-effects (A = enhanced absorption, E = emission, A/E = multiplet effect of absorption/emission type [18]), yields of
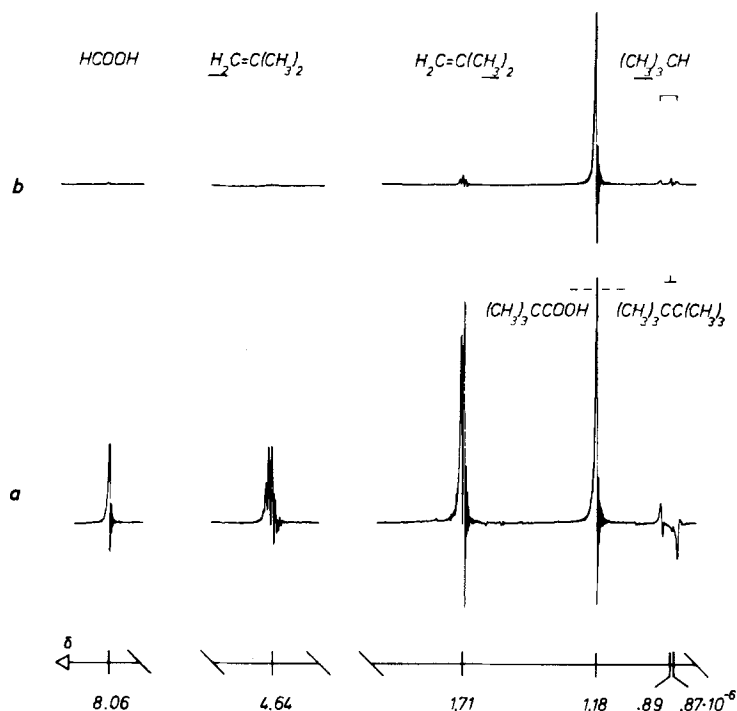
Fig. 1. *CIDNP.-Effects during Photolysis of 0.5M Pivalic Acid in Methanol-d₄:* a) during, b) after 20 min photolysis

(- - - - amplitudes before irradiation)

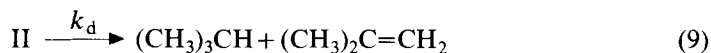Table 1. *CIDNP.-Effects during Photolysis of Pivalic Acid in Methanol-d₄*
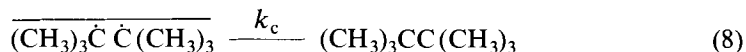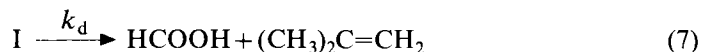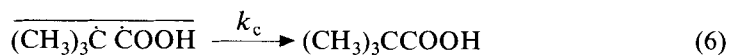
Product	$\delta \cdot 10^6$	T_1 [s]	CIDNP.	Yield [mM]
(CH₃)₃CCOOH	1.18[a])	3.1	A	
(CH₃)₂C=CH₂: CH₃	1.71	21.0	A+A/E	44[b])
CH₂	4.64		A+A/E	
HCOOH	8.06	46.0	A	36
(CH₃)₃CH	0.89		E[c])+A/E	24
(CH₃)₃CC(CH₃)₃	0.87		E[c])	

[a]) Reference: tetramethylsilane.
[b]) Concentrations after 20 min photolysis, conversion of pivalic acid 125 mM. All values ± 20%.
[c]) Weak.

several products and relaxation times. Previously we have shown that *t*-butyl and carboxyl are the major and that hydroxymethyl is a minor radical intermediate in this system. In accord with these findings all strong CIDNP.-effects observed here are explained by the occurrence of radical pairs I and II reacting *via* (6)–(9). One uses *Kaptein*'s rules [18], $g\,(CH_3)_3\dot{C})>g\,(\cdot COOH)$, $a_H((CH_3)_3\dot{C})>0$ [21] and the precursor parameter $\mu = 1$ (*i.e.* radical pair formation from a triplet precursor or by unreactive encounters of nongeminate radicals).

$$\overline{(CH_3)_3\dot{C}\ \dot{C}OOH} \xrightarrow{k_c} (CH_3)_3CCOOH \tag{6}$$

$$I \xrightarrow{k_d} HCOOH + (CH_3)_2C=CH_2 \tag{7}$$

$$\overline{(CH_3)_3\dot{C}\ \dot{C}(CH_3)_3} \xrightarrow{k_c} (CH_3)_3CC(CH_3)_3 \tag{8}$$

$$II \xrightarrow{k_d} (CH_3)_3CH + (CH_3)_2C=CH_2 \tag{9}$$

The weak net emission of isobutane and of 2,2,3,3-tetramethylbutane results from pair I as escape polarization. From the amplitudes of the polarizations the ratio of disproportionation to combination for pair I $k_d/k_c = 1.9 \pm 0.6$ is obtained *via* eq. (5).

As a further reaction of pair I the disproportionation

$$I \longrightarrow (CH_3)_3CH + CO_2 \tag{10}$$

may be envisaged. This reaction can not play a major role, however, since it would lead to strong enhanced absorption of isobutane which is not observed. The yields of the products also point to the dominance of reactions (6)–(9). Besides these, reactions

$$2\ \dot{C}OOH \longrightarrow HOOC–COOH \tag{11}$$

$$\longrightarrow HCOOH + CO_2 \tag{12}$$

(11) and (12) are also very likely, but oxalic acid was not detectable by NMR. in our system.

The observation of pairs I indicates that the cleavage of pivalic acid follows, at least predominantly, pathway (1). However, since these pairs are formed not only in the primary cleavage process, but also by unreactive encounters of nongeminate radicals, the finding of $\mu = 1$ for the CIDNP.-effects of the products of reactions (6) and (7) does not directly imply $\mu = 1$ for the geminate part of the pairs. Therefore, radical scavenging experiments with CCl_4 as scavenger were performed. *Table 2* shows the CIDNP.-phases for the products observed during photolysis of pivalic acid in CD_3OD/CCl_4-mixtures. In addition to the aforementionned products, *t*-butylchloride, chloroform and 1,1,1-trichloro-2,2-dimethylpropane appear. They are very likely due to reactions (13)–(15).
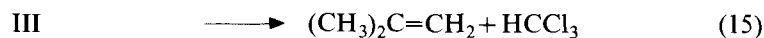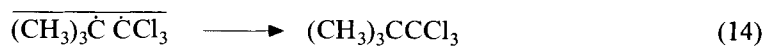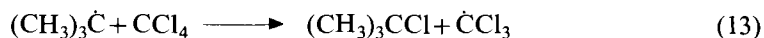
$$(CH_3)_3\dot{C} + CCl_4 \longrightarrow (CH_3)_3CCl + \dot{C}Cl_3 \tag{13}$$

$$\overline{(CH_3)_3\dot{C}\ \dot{C}Cl_3} \longrightarrow (CH_3)_3CCCl_3 \tag{14}$$

$$III \longrightarrow (CH_3)_2C=CH_2 + HCCl_3 \tag{15}$$

Table 2. *CIDNP.-Effects during Photolysis of Pivalic Acid in Methanol-d_4/CCl_4-mixtures*

Product	$[CCl_4] = 0$	0.009	0.025	0.1	1.5 M
$(CH_3)_3CCOOH$	A	A	A	A	A
HCOOH	A	A	A	A	A
$(CH_3)_2C=CH_2$	A + A/E	A[a]) + A/E	E + A/E	A + A/E	A + A/E
$(CH_3)_3CH$	E[a]) + A/E	A/E	A/E	O[b])	O
$(CH_3)_3CC(CH_3)_3$	E	E	E	O	O
HCCl$_3$	O	E	E	E	E[a])
$(CH_3)_3CCl$	O	E	A	A	E
$(CH_3)_3CCCl_3$	O	E	E	E	O

[a])   Weak.
[b])   O: Not detectable, also not observed as product.

The dependence of the CIDNP.-effects on the scavenger concentration may then be understood as follows: Pivalic acid and formic acid exhibit enhanced absorption for all concentrations, implying pairs I and reactions (6) and (7) to operate with $\mu = 1$ for all concentrations. Chloroform and $(CH_3)_3CCCl_3$ show emission for all but the highest concentration. These effects are in accord with the formation of these products from pairs III with $g(\cdot CCl_3) > g(\cdot C(CH_3)_3)$ [21]. Isobutane and 2,2,3,3-tetramethylbutane show CIDNP.-effects pointing to pair II as the origin. They decrease sharply in intensity as the scavenger concentration is increased as the scavenging reaction (13) increasingly suppresses the formation of pair II. The double phase change of the net effects observed for isobutene and t-butyl-chloride, finally, is also in accord with the scavenger reactions: the emission of the chloride at low and at high CCl_4-concentrations characterizes this compound as escape product from pair I. At intermediate concentrations, where pair III occurs, the polarization originating from this pair dominates. Similarly, isobutene acquires its polarization at low and high CCl_4-concentrations from pair I and at medium concentration predominantly from pair III. These findings now allow a conclusion on the parameter μ for the geminate pair I formed from cleavage of pivalic acid: With increasing CCl_4-concentration the formation of pairs II and III by encounters of nongeminate radicals is increasingly suppressed *via* reaction (13) and does not occur at $[CCl_4] = 1.5$ M. This then must also hold for the nongeminate fraction of pair I. Since the CIDNP.-effects from this pair are still observed for $[CCl_4] = 1.5$ M they must be formed from the geminate fraction. The CIDNP.-phases then are only compatible with $\mu = 1$ for this fraction, *i.e.* the photodecomposition of pivalic acid occurs at least in part from an excited triplet state (see also the discussion section).

3.2. *Methyl Pivalate. Table 3* summarizes the effects observed on photolysis of 0.5 M methyl pivalate in cyclohexane-d_{12}. Comparison with *Table 1* reveals a striking similarity of the product distribution and the CIDNP.-effects to those observed for pivalic acid. This means that reactions (6)-(9) and possibly (11) apply for methyl pivalate as well ($\cdot$COOH is replaced by $\cdot$COOCH$_3$). Noteworthy is the enhanced absorption of the CH$_3$-group. With $g(\cdot COOCH_3) = 2.0013 < g((CH_3)_3\dot C)$ [21] explanation via *Kaptein's* rules [18] and pair I requires a negative sign of $a_H(CH_3)$. Further, there are some differences in detail. The yield of isobutene is rather low,

Table 3. *CIDNP.-Effects during Photolysis of Methyl Pivalate in Cyclohexane-d$_{12}$*

Product		$\delta \cdot 10^6$	T_1 [s]	CIDNP.	Yield [mM]
$(CH_3)_3CCOOCH_3$	$(CH_3)_3$	1.15[a])	5.2	A	
	CH_3	3.55		–	
$(CH_3)_2C=CH_2$	CH_3	1.68	21	A + A/E	9[b])
	CH_2	4.64		A + A/E	
$HCOOCH_3$	H	7.88	96	A + A/E	32
	CH_3	3.62		A + A/E	
$(CH_3)_3CH$	CH_3	0.89		E[c]) + A/E	50
	H	1.68		A/E	
$(CH_3)_3CC(CH_3)_3$		0.87		E	14
CH_3OD	CH_3	3.35		N[d])	15

[a]) Reference: tetramethylsilane.
[b]) Yields determined for solutions in methanol-d$_4$, given as concentrations after 60 min photolysis, conversion of ester 150 mM. All values ± 20%.
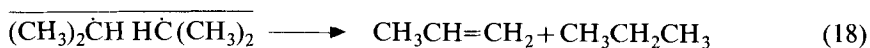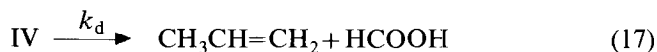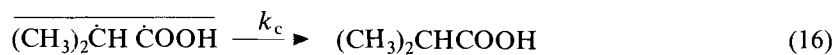[c]) Weak.
[d]) Unpolarized.

and dimethyloxalate expected from the coupling of two ·COOCH$_3$-radicals could not be found. As a tentative explanation we suggest the addition of carboxymethyl to isobutene. Further, we observe CH$_3$OD as product in about 10% yield. This points to the occurrence of the CO, O-cleavage reaction (2) besides the C(a), CO-split (1) followed by rapid D-abstraction by the reactive CH$_3$O· radical from the solvent [22]. From rate considerations this reaction should be about 1000 times faster than any possible bimolecular termination of CH$_3$O·. Thus, the yield indicates that about 10% of the ester molecules decompose *via* reaction (2).

From the CIDNP.-intensities and relaxation times the ratio of disproportionation to combination of the pair $\overline{(CH_3)_3\dot{C}\ \dot{C}OOCH_3}$ was found to be $k_d/k_c = 1.5 \pm 0.5$ *via* eq. (5). The quantum yield of photolysis of the ester was determined as $\phi = 0.4 \pm 0.1$. In our previous work [4] we reported the observation of the radicals $(CH_3)_3\dot{C}$, $CH_3OO\dot{C}$, $(CH_3)_3C\dot{C}O$ and ·CH$_2$OH during photolysis of methyl pivalate in methanol. The present results are fully compatible with these previous findings.

3.3. *Isobutyric Acid. Figure 2* shows NMR.-transitions observed during and after photolysis of isobutyric acid in methanol-d$_4$. Apart from several small unexplained lines, these are due to polarized isobutyric acid, propene, propane and formic acid which were also found as products. Thus, the CIDNP.-effects parallel those observed for pivalic acid and may correspondingly be explained in terms of the reactions
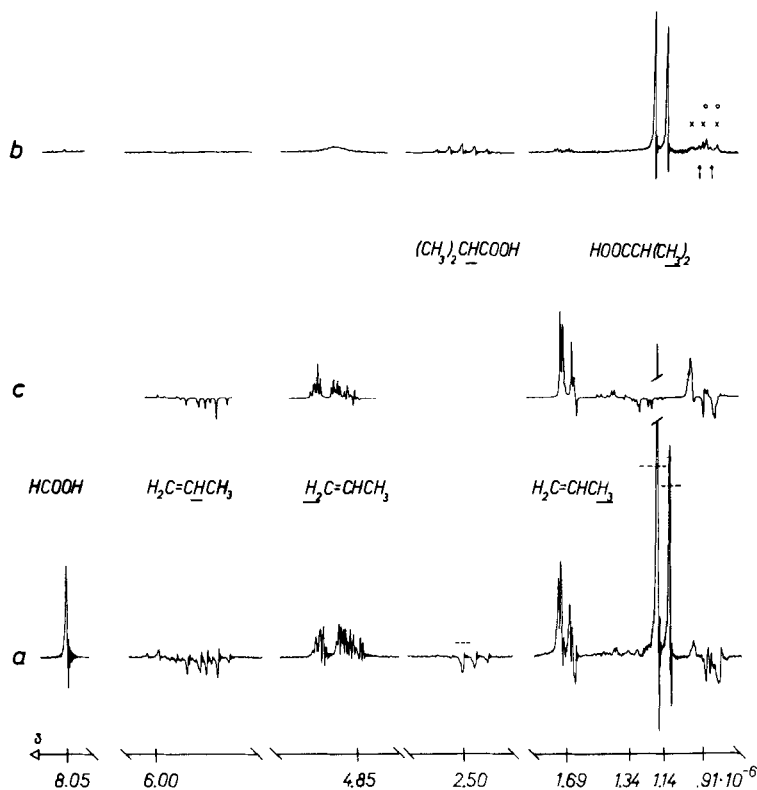
$$\overline{(CH_3)_2\dot{C}H\ \dot{C}OOH} \xrightarrow{\ k_c\ } (CH_3)_2CHCOOH \qquad (16)$$

$$IV \xrightarrow{\ k_d\ } CH_3CH=CH_2 + HCOOH \qquad (17)$$

$$\overline{(CH_3)_2\dot{C}H\ H\dot{C}(CH_3)_2} \longrightarrow CH_3CH=CH_2 + CH_3CH_2CH_3 \qquad (18)$$
$$V$$

Fig. 2. *CIDNP.-Effects during Photolysis of 0.5M Isobutyric Acid in Methanol-d₄:* a) during, b) after 30 min photolysis, c) simulated spectra

(– – – – amplitudes before irradiation, ○ : 2,3-dimethyl butane, × : propane, ↑ unidentified product)

Again reactions like (10) can be excluded. *Figure 2* also shows simulated spectra of propene and propane calculated with the programme described in [19] and [23] and based on the known radical parameters [21] with $\mu = 1$ for pairs IV and V. For propene a 1:1 superposition of the polarizations originating from both pairs was applied. Previously [4], we have shown that isopropyl and carboxyl are the dominant radicals in this system and have concluded that C (a), CO-cleavage (1) is the major photodecomposition mode of isobutyric acid. This is confirmed by the present results. They also revealed $k_d/k_c = 0.3 \pm 0.1$ for pair IV.

As for pivalic acid, addition of the radical scavenger CCl_4 results in the observation of additional products ($HCCl_3$, $(CH_3)_2CHCl$, $(CH_3)_2CHCCl_3$) and in changes of the CIDNP.-effects. Analysis as above (3.1) revealed that $\mu = 1$ holds also for the geminate fraction of pairs IV, *i.e.* the photodecomposition occurs at least in part from an excited triplet state.

3.4. *Methyl Isobutyrate.* The CIDNP.-effects and products are those expected from reactions (16)–(18) ('COOH is replaced by ĊOOCH₃). $k_d/k_c = 0.3 \pm 0.1$ was determined for the reactions of the pair analogous to IV, and the quantum yield of

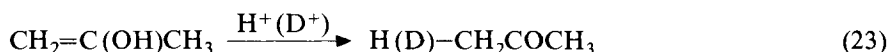Table 4. *CIDNP.-Effects during Photolysis of 0.4M α-Hydroxy Isobutyric Acid in Methanol-d_4*
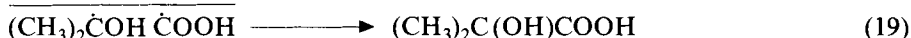
Product	$\delta \cdot 10^6$	CIDNP.
$(CH_3)_2C(OH)COOH$	1.40[a])	A
H_A — OH — CH_3 : H_A	1.74	A + A/E
C=C	3.90	A + A/E
H_B — CH_3 — H_B	3.69	A + A/E
HCOOH	8.05	A
CH_3COCH_3	2.14	A
CH_3COCH_2D	2.13	A
$(CH_3)_2CHOH$: CH_3	1.14	A/E
H	3.92	A/E
$(CH_3)_2C(OH)C(OH)(CH_3)_2$	1.19[b])	–

[a]) Reference: tetramethylsilane.
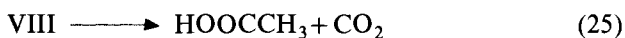[b]) Identified as product only, no CIDNP. observable.

photodecomposition was found to be $\phi = 0.6 \pm 0.1$. The yield of CH_3OD of 25% indicates that the cleavage reaction (2) does occur as for methyl pivalate. In our previous work [4] radicals arising from (1) and (2) have been observed. Thus, the photocleavage reactions of methyl isobutyrate are the same as those of the acids and of methyl pivalate.

3.5. *α-Hydroxy Isobutyric Acid.* The CIDNP.-effects summarized in *Table 4* are explained by reactions (19)–(23) and $\mu = 1$ for the pairs VI and VII, *i.e.* again the photocleavage (1) operates. The polarization of the acetones is created in the enol [23] [24] and transferred by the tautomerization (23). At $-50°$ no polarization of the ketone is observed indicating that at this temperature (23) is too slow to compete with relaxation [24]. In the previous ESR.-work the radicals $(CH_3)_2\dot{C}OH$ and $\dot{C}OOH$ were identified during photolysis of α-hydroxy isobutyric acid [4], in agreement with the presently observed reactions (19)–(23).

$$(CH_3)_2\dot{C}OH \ \dot{C}OOH \ \longrightarrow \ (CH_3)_2C(OH)COOH \qquad (19)$$

$$VI \ \longrightarrow \ CH_2=C(OH)CH_3 + HCOOH \qquad (20)$$

$$(CH_3)_2\dot{C}OH \ HO\dot{C}(CH_3)_2 \ \longrightarrow \ (CH_3)_2C(OH)C(OH)(CH_3)_2 \qquad (21)$$

$$VII \ \longrightarrow \ CH_2=C(OH)CH_3 + (CH_3)_2CHOH \qquad (22)$$

$$CH_2=C(OH)CH_3 \ \xrightarrow{H^+(D^+)} \ H(D)-CH_2COCH_3 \qquad (23)$$

3.6. *Malonic Acid.* During photolysis of a 0.5M aqueous solution emission is observed for the CH_2-protons of the parent compound and for the CH_3-protons of

acetic acid. The products are acetic acid (yield 35%) and succinic acid (11%). CIDNP.-effects and products are compatible with the reactions ($\mu = 1$)

$$\overline{HOOC\dot{C}H_2 \dot{C}OOH} \longrightarrow HOOCCH_2COOH \tag{24}$$

$$VIII \longrightarrow HOOCCH_3 + CO_2 \tag{25}$$

$$2\,HOOC\dot{C}H_2 \longrightarrow HOOCCH_2CH_2COOH \tag{26}$$

following the a-cleavage (1). The detection of polarization from reaction (25) is noteworthy since analogous reactions of pivalic and isobutyric acids could be excluded. Obviously, the primary radical $HOOC\dot{C}H_2$ is capable of abstracting the H-atom from $\cdot COOH$, whereas $(CH_3)_3\dot{C}$ and $(CH_3)_2\dot{C}H$ are not.

4. Discussion. – In the preceeding section we have shown that various aliphatic carboxyl compounds undergo $C(a)$, CO- and CO,O-cleavage reactions (1) and (2) after excitation as major and minor photolytic decomposition pathways in solution. Their photochemical behaviour is thus analogous to that of the corresponding ketones. This includes the magnitudes of the quantum yields [1] [2]. The nature of the excited states from which the cleavage reactions occur deserves further discussion. *Coyle* [3] has expressed the view that the lowest excited singlet state of saturated carboxylic acids and esters has n,π^*-character whereas the lowest excited triplet state has π,π^*-character. For the ketones it is known that a-cleavage occurs from n,π^*-states [1], and it may thus be inferred [3] that the cleavage of the carboxyl compounds occurs from the singlet n,π^*-state. On the other hand, we have shown (3.1 and 3.3) that the CIDNP.-effects from products of the geminate pairs produced by the a-cleavage (1) require $\mu = 1$ for explanation, *i.e.* the polarization indicates decomposition from a triplet state, at least to some extent. The following gives an estimation of the relative contributions of triplet and singlet channels to the cleavage: We realize that a triplet type CIDNP.-pattern for geminate pairs ($\mu = 1$) does not necessarily imply dominance of the triplet channel since the relative amplitudes of polarizations arising from triplet and singlet born pairs are different, and triplet polarization may be observed even if singlet pair formation strongly competes. Using the theoretical results of *Pedersen & Freed* [25] it may be stated, however, that $\mu = 1$ can only hold if

$$\phi_T > 3\,\phi_S \frac{1 - \chi - \Lambda \cdot t_f}{1 - \chi} \tag{27}$$

for competing triplet and singlet pathways with quantum yields ϕ_T and ϕ_S. In (27) $\chi \approx 0$, and $t_f = d/r_1$ is the transfer factor with d the reaction distance and r_1 the initial radical separation. Λ is the probability that a singlet pair with $r_1 = d$ ultimately leads to pair product formation in the absence of intersystem crossing. Usually $\Lambda \geq 0.8$ is adopted [25]. Eq. (27) shows that for $\Lambda \cdot t_f = 1$ and small χ the singlet pairs do not lead to appreciable polarization, and small triplet contributions already lead to $\mu = 1$. In our case we do not believe that $\Lambda \cdot t_f$ is close to unity, however, since the cleavage reaction (1) is exothermic by about 160 kJ/mol, as estimated from *the*

excitation wavelength (240 nm) and the standard enthalpies of formation of parent compounds and radicals [26]. Assuming with *Noyes* [27] that the excess energy is converted to energy of translation hindered by the viscous drag of the solution and adopting his formalism for the calculation of r_1 we obtain with $d \simeq 4.5$ Å, estimated from bond increments [28], $t_f \approx 0.7$. For $\Lambda = 0.8$, 0.9 and 1.0, respectively, and $\chi = 0$, eq. (27) then shows that $\mu = 1$ can be observed if $\phi_T > 1.3 \; \phi_S$, 1.1 ϕ_S and 0.9 ϕ_S, respectively. This means that for our systems (3.1 and 3.3) decomposition from triplet excited states is at least about equally probable as decomposition from singlet excited states, if it is not even the dominant process as for ketones.

Finally, the ratios of disproportionation to combination k_d/k_c require comment. They are 1.9 for $(CH_3)_3\dot{C} + \dot{C}OOH$, 1.5 for $(CH_3)_3\dot{C} + \dot{C}OOCH_3$ and 0.3 for $(CH_3)_2\dot{C}H + \dot{C}OOH(CH_3)$. Comparison with $k_d/k_c \approx 3$ for $(CH_3)_3\dot{C} + \dot{C}(CH_3)_3$ [29] and 0.65 for $(CH_3)_2\dot{C}H + H\dot{C}(CH_3)_2$ [30] reveals a diminution by a factor of 2 which is reasonable on statistical grounds.

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