14. Electron Spin Resonance of α-(Alkoxycarbonyl)alkyl Radicals in Solution

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Summary

High-resolution ESR. spectra of the radicals $\dot{C}H_2COOR$, $CH_3\dot{C}HCOOR$ and $(CH_3)_2\dot{C}COOR$ with $R = CH_3$, CH_2CH_3, $CH(CH_3)_2$ and $C(CH_3)_3$ in liquid solution confirm planar energy-minimum structures with substantial barriers to internal rotation about the $\dot{C}$,CO-bonds ($\simeq 40$ kJ/mol) and partial π-electron delocalization. The assignments of coupling constants to protons in isomeric positions and the conclusions on radical structures are supported by INDO-calculations.

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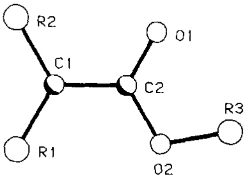
1. Introduction. – Many α-(alkoxycarbonyl)alkyl radicals have already been studied by ESR. spectroscopy in solids and in liquid solutions [1]. The ESR. parameters were generally discussed in terms of the general planar bonding structure **I** with some spin delocalization and a partial double-bond character of the $\dot{C}$,CO-bond. However, barriers to internal rotation have not yet been determined directly, and there is indirect evidence for both low and high barriers to $\dot{C}$,CO-bond rotation. Nearly unhindered rotation may be inferred from the values of proton coupling constants for $R^1, R^2 = H$ or CH_3 which are only slightly smaller than those of radicals with little spin delocalization, *i.e.* very similar to those of $(CH_3)_2\dot{C}H$ or $(CH_3)_3\dot{C}$. Further, in liquids and in solids near room temperature $\dot{C}H_2COOR^3$ and $(CH_3)_2\dot{C}COOR^3$ show equal α- or β-proton couplings which may point to rapid *exchange*. On the other hand, some delocalization is required to explain δ-couplings to R^3-protons of about 1 G, and $(CH_3)_2\dot{C}COOH$ in a solid matrix shows an onset of CH_3-group exchange only above 90° [2]. A high barrier is required also to explain the recent observation of two isomers of $CH_3\dot{C}HCOOH$ in a liquid at −60° [3]



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and of an isomerization reaction found for $CH_3\dot{C}HCOOD$ in a solid near room temperature [4]. Isomers were also found for $HO(CH_3)\dot{C}COOR$ and $HO(CH_3O)\dot{C}COOCH_3$ in liquids [5] [6], but not for various other related radicals [1].

Many previous studies employed conditions of rather low spectral resolutions, and small differences of coupling constants or the presence of isomers with similar parameters have not been detected. To clarify the situation we have now restudied a variety of α-(alkoxycarbonyl)alkyl radicals in liquid solutions using photochemical radical-generation techniques which allow small linewidths ($\leq$ 0.080 G). The results confirm the planar bonding structures and lead to substantial barriers to hindered rotation similar to those of α-(alkylcarbonyl)alkyl radicals $R^1R^2\dot{C}COR^3$ [7] [8].

2. Experimental. – The ESR. spectra and optical arrangements were as described previously [3]. Coupling constants were determined by NMR. and are accurate to ± 0.02 G. g-Factors are relative to DPPH with absolute accuracies of $\pm 1 \cdot 10^{-4}$ and relative accuracies of $\pm 4 \cdot 10^{-5}$. Three conventional methods for radical generation were used: *a*) photochemical Cl-elimination from α-chloroesters 20 vol-% in CH_3OH [9]. Besides $R^1R^2\dot{C}COOR^3$ the spectra showed the formation of $^{\cdot}CH_2OH$ from the reaction of Cl-atoms with the solvent; *b*) photolysis of di(*t*-butyl) peroxide 30 vol-% in *t*-butyl propionate or isobutyrates; *c*) photolysis of ethylene oxide solutions containing 20 vol-% di(*t*-butyl) peroxide, 10 vol-% triethylsilane and 1 vol-% of α-bromo-esters, particularly for studies at various temperatures.

The isopropyl esters of α-chloroacetic, propionic and isobutyric acids and *t*-butyl isobutyrate were prepared by standard procedures to purities larger than 95% as revealed by NMR. spectra. All other chemicals were commercial samples of the purest available forms.

3. Results and discussion. – 3.1. *ESR. spectra. Figure 1* shows an ESR. spectrum obtained during photolysis of $CH_2ClCOOCH_2CH_3$ in CH_3OH. It shows lines of $^{\cdot}CH_2OH$ (arrows) and of one further radical. This species has three line groups 21.37 G apart, each split in a 1:2:1-triplet. The central group shows a further doublet splitting of 0.14 ± 0.02 G. The radical is undoubtedly $\dot{C}H_2COOCH_2CH_3$, since the triplet splitting of 1.53 G is typical for δ-CH_2-protons in α-(alkoxycarbonyl)alkyl radicals, and 21.37 G is a typical α-proton coupling [1]. The question of equivalency of the α-protons, however, can not be decided directly. The pattern is compatible with equivalent protons and a common coupling of 21.37 G since a second-order doublet splitting of the central group of 0.139 G would result [10]

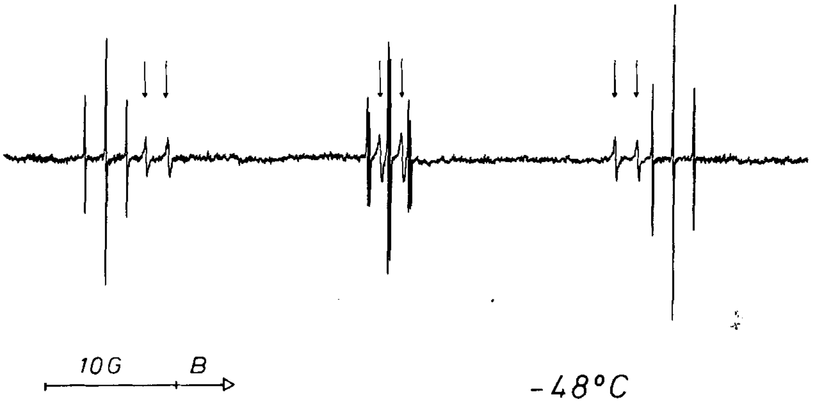


Fig. 1. *ESR. Spectrum of $\dot{C}H_2COOCH_2CH_3$ in CH_3OH* (Arrows denote $\dot{C}H_2OH$)

which is in agreement with the observation. On the other hand, the same pattern results from inequivalent protons with individual couplings of 21.30 and 21.44 G. Measurements in the range $-70 \leqq T < +60°$ lead to very similar spectra, and no line-broadening effects were found which would indicate the onset of proton exchange. The δ-proton coupling decreased by $1.7 \cdot 10^{-3}$ G/K and the α-proton coupling increased marginally by $2 \cdot 10^{-4}$ G/K with increasing temperature. Analogous results were obtained for $\dot{C}H_2COOCH_3$ and $\dot{C}H_2COOCH(CH_3)_2$ derived from the corresponding α-chloro-esters. The doublet splittings of the central groups of 0.13 ± 0.02 and 0.15 ± 0.02 G were again close to the expected second-order splittings. The δ-proton couplings decreased with increasing temperature.

$\dot{C}H_2COOC(CH_3)_3$ showed a partially resolved coupling to the *t*-butyl protons of 0.080 G which precluded the determination of the central doublet splitting. From analogy with the radicals discussed later on we believe in a substantial barrier for the species $\dot{C}H_2COOR^3$, which, for significant differences of the α-proton couplings in the energy-minimum configurations, would lead to line-broadening of the central group within the temperature range studied. Since this was not observed, the difference should be similar to or smaller than the second-order splitting. In this case of near degeneracy by accident, line-broadening by exchange is unobservable. In the first part of *Table 1* the ESR. parameters of the radicals $\dot{C}H_2COOR^3$ are summarized. Where a doublet splitting was observed the α-proton couplings are

Table 1. *Magnetic properties of α-(alkoxycarbonyl)alkyl radicals at – 40°*

Radical	g-Factor	$a_{H\alpha}$ [G][a]	$a_{H\beta}$ [G][a]	$a_{H\delta}$ [G]	R.G.[b]
$\dot{C}H_2COOCH_3$	2.00315[c]	*c* 21.32 *t* 21.45		1.45	(a)
$\dot{C}H_2COOCH_2CH_3$	2.00315	*c* 21.30 *t* 21.44		1.53	(a)
$\dot{C}H_2COOCH(CH_3)_2$	2.00319	*c* 21.29 *t* 21.43		0.95	(a)
$\dot{C}H_2COOC(CH_3)_3$	2.00331	21.33[d]			(a)
c-$CH_3\dot{C}HCOOCH_3$[e]	2.00317	*t* 20.48	*c* 24.76	1.59	(a)
t-$CH_3\dot{C}HCOOCH_3$[e]	2.00322	*c* 20.30	*t* 24.92	1.28	
c-$CH_3\dot{C}HCOOCH_2CH_3$	2.00314	*t* 20.49	*c* 24.72	1.66	(a)
t-$CH_3\dot{C}HCOOCH_2CH_3$	2.00323	*c* 20.30	*t* 24.93	1.36	
c-$CH_3\dot{C}HCOOCH(CH_3)_2$	2.00314	*t* 20.47	*c* 24.75	1.00	(a)
t-$CH_3\dot{C}HCOOCH(CH_3)_2$	2.00316	*c* 20.30	*t* 24.91	0.84	
c-$CH_3\dot{C}HCOOC(CH_3)_3$	2.00319	*t* 20.56	*c* 24.57		(b)
t-$CH_3\dot{C}HCOOC(CH_3)_3$	2.00329	*c* 20.31	*t* 24.74		
$(CH_3)_2\dot{C}COOCH_3$	2.00316		*c* 21.49 *t* 21.68	1.29	(b)
$(CH_3)_2\dot{C}COOCH_2CH_3$	2.00317		*c* 21.44 *t* 21.69	1.29	(b)
$(CH_3)_2\dot{C}COOCH(CH_3)_2$	2.00306		*c* 21.43 *t* 21.68	0.88	(a)
$(CH_3)_2\dot{C}COOC(CH_3)_3$	2.00329		*c* 21.44 *t* 21.58		(b)

[a] *c* = *cis*, *t* = *trans* to the carbonyl O-atom. [b] Method of radical generation specifying the solvent, see text. [c] Absolute accuracy ±0.0001, relative accuracy ±0.00004. [d] Average value of the two α-protons. [e] *c* = CH_3 *cis*, *t* = CH_3 *trans* to the carbonyl O-atom.

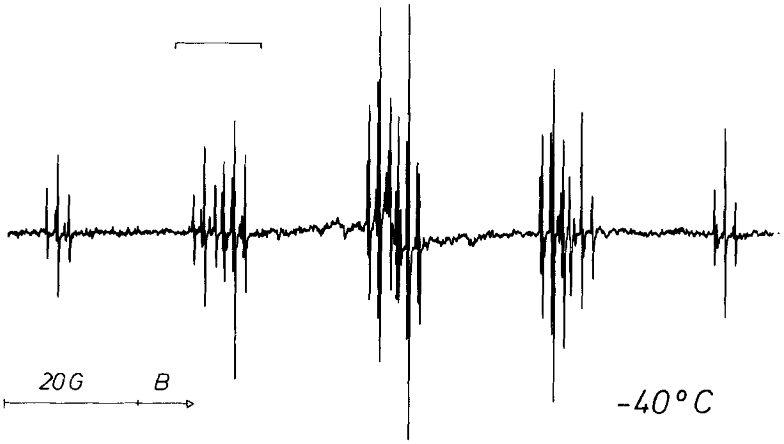


Fig. 2. *ESR. Spectrum of* $CH_3\dot{C}HCOOCH_2CH_3$ (Part in bracket expanded in *Fig. 3*)

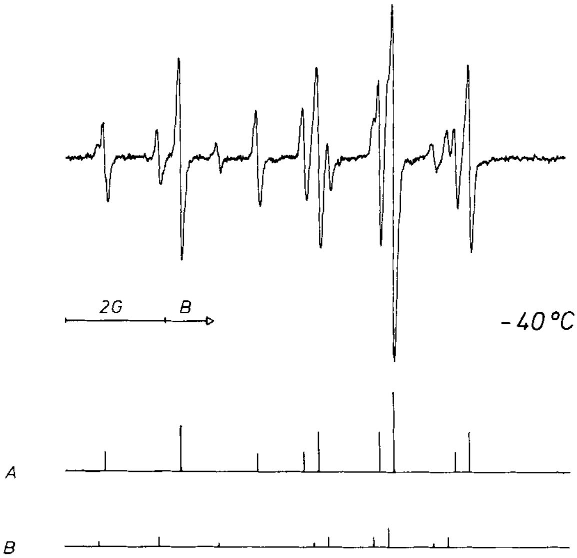


Fig. 3. *Expanded part of* Figure 2 (A and B are stick plots of the isomers of $CH_3\dot{C}HCOOCH_2CH_3$)

listed as being inequivalent. The assignments to specific positions will be explained later.

Figure 2 displays an ESR. spectrum obtained from $CH_3CHBrCOOCH_2CH_3$ in ethylene oxide at −40°. It consists of eight line groups, the more prominent lines of each exhibit a 1:2:1-splitting of 1.66 G, *i.e.* typical for δ-CH_2-groups. The main features may be explained in terms of $CH_3\dot{C}HCOOCH_2CH_3$ with coupling to three equivalent β-CH_3-protons, one α-proton and the δ-CH_2-protons. However, there are

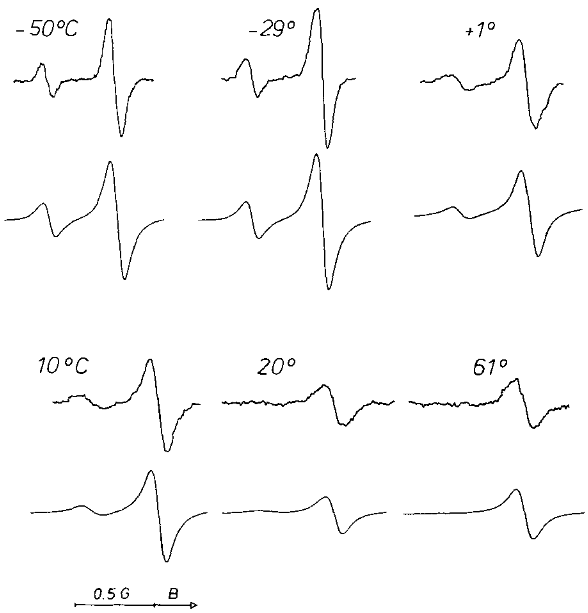


Fig. 4. *ESR. Lines of* $CH_3\dot{C}HCOOCH_2CH_3$ *isomers*

weak lines which point to more than one species. In fact, expansion of the line groups as in *Figure 3* reveals the presence of two radicals **A** and **B** with different abundancies (**A**/**B** $\cong$ 4:1), the same coupling patterns and slightly different coupling constants. We attribute **A** and **B** to two isomers of $CH_3\dot{C}HCOOCH_2CH_3$. Analogous results were obtained for $CH_3\dot{C}HCOOCH_3$, $CH_3\dot{C}HCOOCH(CH_3)_2$ and $CH_3\dot{C}HCOOC(CH_3)_3$ at $-40°$. The second part of *Table 1* lists the ESR. parameters for the isomers of $CH_3\dot{C}HCOOR$, with the first set of constants referring to the more abundant species.

To assess rate constants for the isomerization $\mathbf{A} \rightleftharpoons \mathbf{B}$ the temperature dependence of the spectra of $CH_3\dot{C}HCOOR^3$ was studied. For all radicals two isomers were observable for $T \leqq 10°$. The coupling constants of their α- and β-protons varied not significantly and the δ-couplings decreased by about $2 \cdot 10^{-3}$ G/K with increasing temperature. For $T \geqq -30°$ line-broadening due to isomer exchange set in, and for $T \geqq 30°$ only one average species could be detected. A quantitative study was carried out for $CH_3\dot{C}HCOOCH_2CH_3$ in ethylene oxide solution. The exchange between the central lines of the δ-proton triplets in the left part of *Figure 3* was chosen for quantitative fits since the positions of these lines are unaffected by the temperature dependence of the δ-proton coupling. *Figure 4* shows the two lines at various temperatures. The line-broadening is particularly evident for the less abundant species **B**. Also shown are theoretical line profiles calculated using the exchange program *ESREXN* [11] in the following way: the relative populations of **A** and **B** were estimated from the spectra for $T \leqq 10°$ and extrapolated to $T > 10°$. They reflect the ratio of rate constants $\bar{k}$ for $\mathbf{B} \rightarrow \mathbf{A}$ and k for $\mathbf{A} \rightarrow \mathbf{B}$ and are required as input

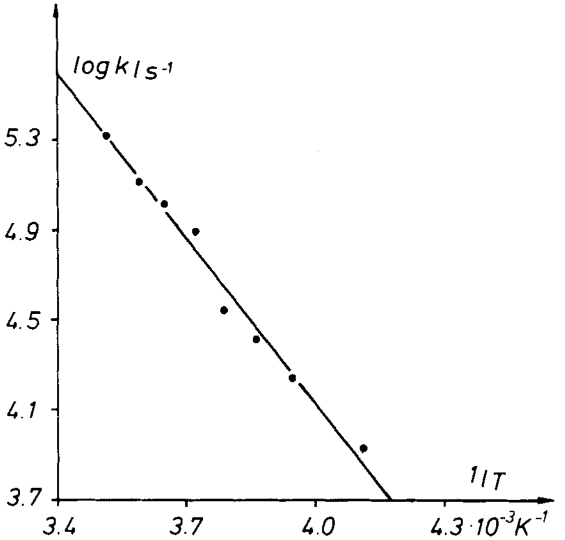


Fig. 5. *Rate constants for isomer exchange*

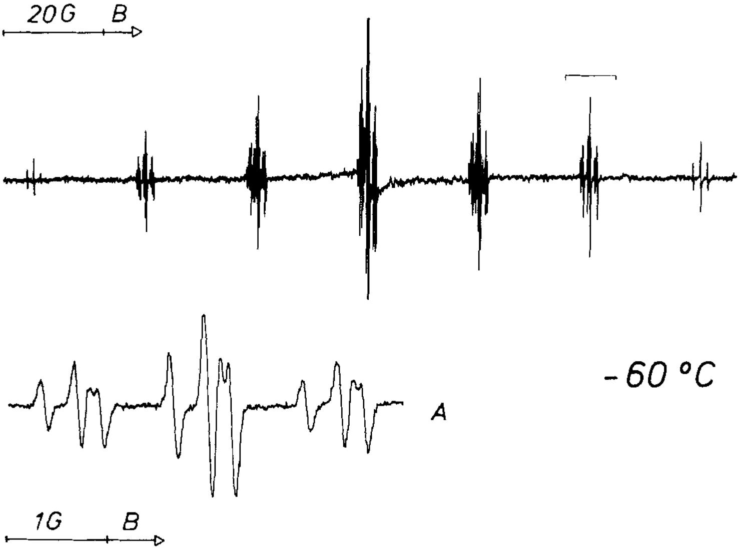


Fig. 6. *ESR. Spectrum of* $(CH_3)_2\dot{C}COOCH_2CH_3$ (upper part) (Insert A is an expansion of line group M = −2)

parameters. Only a small temperature variation of these populations was found indicating an energy difference of **A** and **B** of (2.5 ± 1.0) kJ/mol. The residual line width was estimated from low-temperature spectra and was assumed constant. Then spectra were calculated for various values of k, and k(T) was fixed such that reasonable agreement with experimental spectra resulted *(Fig. 4). Figure 5* shows

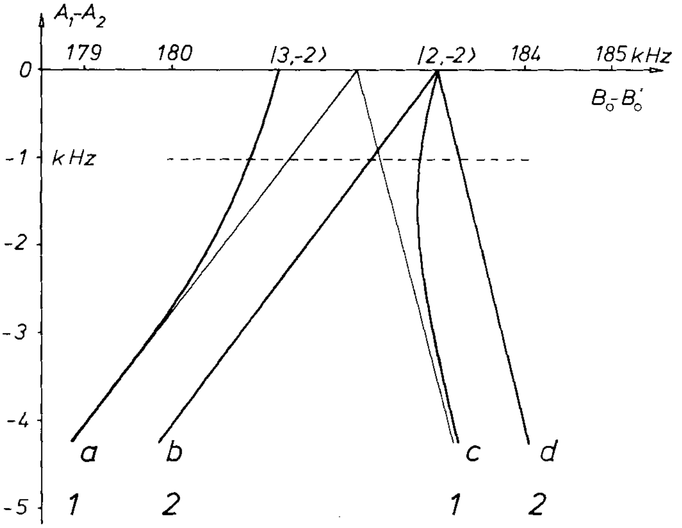


Fig. 7. *Positions of the* $M = -2$ *transitions* vs. *the difference of* CH_3*-couplings* (Units: ^{1}H-NMR. frequencies)

an *Arrhenius* plot of the rate constant for the isomerization $\mathbf{A} \rightarrow \mathbf{B}$. The straight line is a least-squares fit of the data and yields an activation energy of (47 ± 2) kJ/mol and $\log A/s^{-1} = 14.0 \pm 0.5$. In view of the uncertainties involved in the extraction of rate data from rather weak spectra we consider the values not to be more than estimates with possible systematic errors. Yet, the frequency factor is quite normal and similar to the values found for the isomerizations of $\dot{C}H_2COCH_3$ (12.9 ± 0.3) and allyl radical (13.5 ± 0.5) [7] [12].

The upper part of *Figure 6* displays an ESR. spectrum of $(CH_3)_2\dot{C}COOCH_2CH_3$ at −60°. It consists of seven equally spaced groups, each exhibiting the usual 1:2:1-splitting due to the δ-CH_2-protons. Insert *A* shows the substructure of the group bracketed in the total spectrum. Each member of the 1:2:1-triplet consists of four lines with intensity ratios of about 1:2:1:2 and irregular spacings. This may be analyzed in terms of higher order effects. If all six protons of the two CH_3-groups at $\dot{C}$ were equivalent the conventional second-order treatment predicts two lines with relative intensities 1:5 [10]. If the protons of the individual CH_3-groups are equivalent and the two CH_3-couplings are different four lines with the observed 1:2:1:2 intensity ratio result. The irregularity of the spacings are due to effects higher than second-order which become important if the difference of the coupling constants is small [13]. *Figure 7* shows calculated positions of the four lines (heavy curves) *vs.* the difference in coupling constants (field units in ^{1}H-NMR. frequencies). For zero difference they collaps to the 1:5-doublet. The dotted line describes the situation observed at −60° *(Fig. 6)*. The fine structure of the other inner groups of *Figure 6* could also be explained in terms of inequivalent CH_3-groups only. Analogous results were obtained for $(CH_3)_2\dot{C}COOCH_3$, $(CH_3)_2\dot{C}COOCH(CH_3)_2$ and $(CH_3)_2\dot{C}COOC(CH_3)_3$ at −40°. The difference of CH_3-coupling constants was about 0.2 G for each case. *Table 1* presents the g-factors and coupling constants measured at −40°.

Table 2. *Results of INDO-calculations*

Radical	$a_{H\alpha}$ [G]	$a_{H\beta}$ [G]^a)	$a_{H\gamma}$ [G]^a)	Barriers [kJ/mol]
$\dot{C}H_2COOCH_3$	*c* −17.29		0.14	V_α 62.0
	t −17.31			V_γ 21.5
cis-$CH_3\dot{C}HCOOCH_3$	*t* −16.20	*c* 23.32	0.13	V_α 53.9
				V_β 2.5
trans-$CH_3\dot{C}HCOOCH_3$	*c* −16.16	*t* 23.52	0.14	V_α 50.9
				V_β 1.3
$(CH_3)_2\dot{C}COOCH_3$		*c* 21.07	0.13	V_α 45.4
		t 21.33		$V_{\beta c}$ 1.6
				$V_{\beta t}$ 0.4

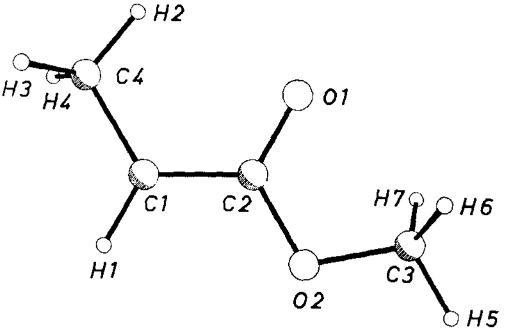
a) Rotational averages.

The temperature dependence of the ESR. spectra of $(CH_3)_2\dot{C}COOCH_2CH_3$ and $(CH_3)_2\dot{C}COOCH(CH_3)_2$ was studied in the range $-80 \leqq T \leqq +80°$. Line-broadening effects due to exchange of the CH_3-groups was observed. At temperatures $T \geqq 70°$ the CH_3-groups appeared equivalent as evident from the normal second-order pattern expected for six equivalent protons. We have not attempted a complete analysis. The temperature range of equilibration is similar to that found for $CH_3\dot{C}HCOOCH_2CH_3$ which means similar activation energies for exchange.

3.2. *Assignments and radical structures.* To assign the coupling constants of *Table 1* to protons in specific steric positions and to deduce to energy-minimum structures of the radicals we start from the structure of the ester group in non-radical molecules assuming that this is not changed by radical formation. There is overwhelming evidence for planarity of the $COOR^3$-group with R^3 *cis* to the carbonyl O-atom as drawn in **I** from crystal [14], liquid [15] and gas-phase [16] studies and theoretical calculations [17]. R^3 *trans* to the carbonyl O-atom is probably not an energy-minimum structure [16]. Therefore, isomeric structures of the $COOR^3$-group as explanation for our isomers are ruled out. The radicals $R^1R^2\dot{C}COOR^3$ must then have all-planar skeletons **I** with the substituents $R^1, R^2 = H$ or CH_3 in magnetically inequivalent positions *cis* or *trans* to the carbonyl O-atom.

Muto et al. [4] found an unstable isomer of $CH_3\dot{C}HCOOD$ in a γ-irradiated crystal of succinic acid which was transformed into a more stable isomer upon annealing at room temperature. The less stable isomer ($\bar{g} = 2.0034$, $\bar{a}_{H_\alpha} = 19.2$ G, $\bar{a}_{H_\beta} = 25.5$ G) was identified as having the CH_3-group *trans* to the carbonyl O-atom whereas the more stable species ($\bar{g} = 2.0032$, $\bar{a}_{H_\alpha} = 20.3$ G, $\bar{a}_{H_\beta} = 25.0$ G) had the CH_3-group *cis* to that atom. The magnetic properties of the isomers of $CH_3\dot{C}HCOOR^3$ observed in this work are very close to the literature values. Consequently we adopt the assignment of *Muto et al.* [4] for our species. As in the single crystal the isomers with CH_3 *cis* to the carbonyl O-atom are more stable. Unfortunately, for $CH_3\dot{C}HCOOH$ a wrong assignment was stated in [3]. Both α-proton and CH_3-protons of $CH_3\dot{C}HCOOR^3$ have larger coupling constants if they are in positions *trans* to the carbonyl O-atom. This leads to the immediate identification of the positions for the protons of $\dot{C}H_2COOR^3$ and $(CH_3)_2\dot{C}COOR^3$ as given in *Table 1.* The set of assignments obtained is self-consistent. Moreover, the coupling constants of the α-protons of the isomers of $CH_3\dot{C}HCOOR^3$ differ by only 0.18–0.25 G. This lends support to the nearly accidental equivalency of the α-protons of $\dot{C}H_2COOR^3$ inferred from the spectra and from the assumption of a barrier to hindered rotation similar to that of $CH_3\dot{C}HCOOR^3$ and $(CH_3)_2\dot{C}COOR^3$. Finally, the assignments of CH_3-couplings agree with those stated for $HO(CH_3)\dot{C}COOR$-type radicals [5].

3.3. *Semiempirical quantumchemical calculations.* INDO-calculations were performed on the radicals $\dot{C}H_2COOCH_3$, *cis*- and *trans*-$CH_3\dot{C}HCOOCH_3$ (**1** and **2**, respectively) and $(CH_3)_2\dot{C}COOCH_3$ using standard geometries and bond angles [18]. Rotations about all single bonds gave the lowest energy conformations **1**–**3** and



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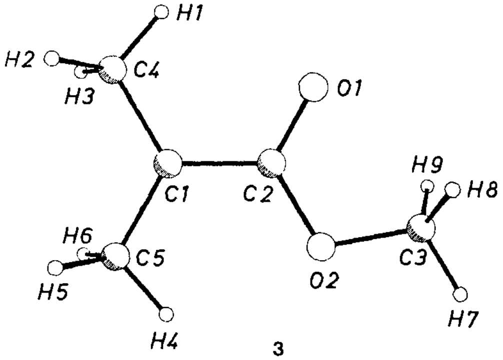

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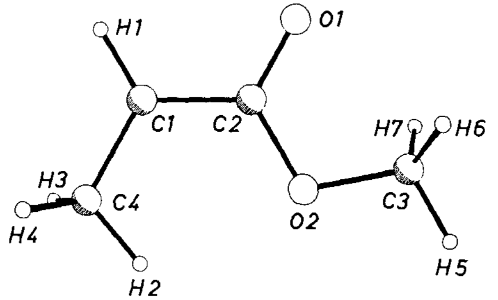

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the barriers to hindered rotation. *Table 2* lists relevant results. For all radicals substantial barriers to hindered rotation about the Ċ,CO-bond V_α were obtained. The orders of magnitude are in agreement with the observed barrier. The *cis*-isomer of $CH_3\dot{C}HCOOCH_3$ was found lower in energy than the *trans*-form by 3.0 kJ/mol also in agreement with the experimental value. Rather large barriers V_γ to rotation about the C,O-bond were calculated with maxima at 150° and 210°, whereas the barriers V_β of the $CH_3,\dot{C}$-bonds were small. For $(CH_3)_2\dot{C}COOCH_3$ markedly different barriers to rotation of the *cis*- and *trans*-CH_3 groups resulted. This explains the observation [19] that the rotation of the two CH_3-groups of $(CH_3)_2\dot{C}COOH$ freezes in at grossly different temperatures. Comparison of the coupling constants of *Tables 1* and *2* shows that too low values of $a_{H\alpha}$ and $a_{H\delta}$ are calculated, whereas $a_{H\beta}$ is correctly predicted. However, the assignments of *Table 1* and the near degeneracies of the α-protons of $\dot{C}H_2COOCH_3$ and of the β-CH_3-protons of

$(CH_3)_2\dot{C}COOCH_3$ are confirmed. ^{13}C-NMR. coupling constants of the radical C-atoms of 34.4, 30.9 and 27.9 G are calculated for $\dot{C}H_2COOCH_3$, *cis-* and *trans-*$CH_3\dot{C}HCOOCH_3$ and $(CH_3)_2\dot{C}COOCH_3$, in very reasonable agreement with literature data of 31.0 [20] and 29.4 G [21] for the former two radicals. Finally, the INDO-calculations predict a considerable spin delocalization over the alkoxycarbonyl groups. For radical C-atoms, carbonyl-C-atoms, the O-atoms of the C=O-group and the alkoxy-O-atoms the π-spin populations are 0.76, −0.26, 0.54 and −0.04 for $\dot{C}H_2COOCH_3$, 0.71, −0.25, 0.50 and −0.04 for *cis-* and *trans-*$CH_3\dot{C}HCOOCH_3$ and 0.67, −0.23, 0.48 and −0.03 for $(CH_3)_2\dot{C}COOCH_3$.

3.4. *Concluding remark.* The planar energy-minimum structures, the barriers to internal rotation about the $\dot{C}$,CO-bond and the magnitudes of the coupling constants combined with the results of semiempirical calculations suggest that α-(alkoxycarbonyl)alkyl radicals are partly allylic in character. The allyl radical has a barrier to internal rotation of 65.7 kJ/mol which corresponds to a delocalization energy of about 59 kJ/mol. The barrier observed here for $CH_3\dot{C}HCOOCH_2CH_3$ 47 kJ/mol indicates a delocalization energy of about 40 kJ/mol. It is larger than a previous estimate [20] and quite similar to that of α-(alkylcarbonyl)alkyl radicals [7] [8]. Interestingly, thermochemical experiments lead to the conflicting conclusion that there is no resonance stabilization of α-(alkylcarbonyl)alkyl radicals due to delocalization of the radical site [22].

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