Electron Spin Resonance Studies of Carboxy Radicals. Adducts to Alkenes

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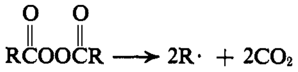
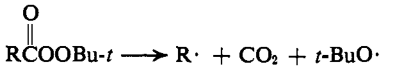
Abstract: The esr spectra of the adducts of carboxy radicals to a variety of alkenes are readily observed during the photolysis of dialkyl peroxydicarbonates and *tert*-butyl perbenzoate. In the absence of alkene, the spectra of the parent oxygen-centered radicals cannot be obtained in solution. Aliphatic diacyl peroxides and peresters under the same conditions afford only the spectra of the alkyl radicals as a result of decarboxylation. The structure and conformation of the carboxy adducts to alkenes are described. Structural effects on the decarboxylation of carboxy radicals as well as the addition of radicals to alkenes are also discussed.

The direct photolysis of diacyl peroxides and *tert*-butyl peresters has been used extensively for the selective generation and esr observation of a wide variety of alkyl radicals.[1]



$$\mathrm{R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R} \longrightarrow 2\mathrm{R\cdot} + 2\mathrm{CO_2} \qquad (1)$$

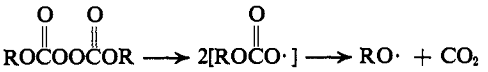


$$\mathrm{R\overset{O}{\overset{\|}{C}}OOBu\text{-}\mathit{t}} \longrightarrow \mathrm{R\cdot} + \mathrm{CO_2} + \mathit{t}\text{-}\mathrm{BuO\cdot} \qquad (2)$$

Product studies[2] indicated that the rate of decarboxylation of acyloxy radicals (as possible intermediates) was very fast, since in nearly all cases[3] no or little carboxylic acid derivatives were detected. The lifetime of such species (where R is methyl or an alkyl group) has been estimated to be 1.6×10^{-9} sec at 60° (E_a = 6.6 kcal/mol),[4,5] and the decarboxylation is exothermic ($\Delta H \approx -15$ kcal/mol).[6]

$$\mathrm{RCO_2\cdot} \longrightarrow \mathrm{R\cdot} + \mathrm{CO_2} \qquad (3)$$

Kinetic evidence[7] suggests that the rate of reaction 3 is dependent on the amount of s character in the α-carbon atom. Indeed, there is considerable information regarding the existence of discrete aroyloxy radicals such as $C_6H_5CO_2\cdot$, formed during thermolysis of benzoyl peroxide or *tert*-butyl perbenzoate either alone or in the presence of polymerizable olefins.[8-11] There are also indications that alkoxy radicals are generated during the decomposition of dialkyl peroxydicarbonates *via* $ROCO_2\cdot$ intermediates.[12,13]

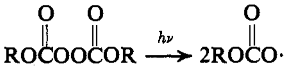


$$\mathrm{RO\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}OR} \longrightarrow 2[\mathrm{RO\overset{O}{\overset{\|}{C}}O\cdot}] \longrightarrow \mathrm{RO\cdot} + \mathrm{CO_2} \qquad (4)$$

In this report, we describe our attempts to observe a variety of carboxy radicals by electron spin resonance (esr) techniques, either directly or by the use of alkenes as traps. The results allow the existence of aliphatic acyloxy radicals to be probed, and the addition of radicals to alkenes to be delineated.

Photolysis of Dialkyl Peroxydicarbonates

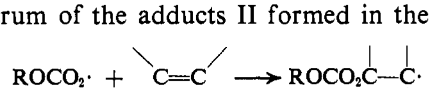
The photolysis of di-*n*-propyl, di-*sec*-butyl or diisopropyl peroxydicarbonates in cyclopropane solution with ultraviolet radiation (2500–3000 Å) at temperatures between −75 and −110° gave rise to no detectable esr spectrum. The microwave power as well as the modulation amplitude were varied widely in these experiments in order to optimize conditions for the observation of transient species. Our inability to observe (acyl)oxy radicals under these conditions is probably somewhat akin to the problems associated with line broadening due to relaxation effects in previous attempts at the observation of alkoxy radicals in solution.[14]



$$\mathrm{RO\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}OR} \xrightarrow{h\nu} 2\mathrm{RO\overset{O}{\overset{\|}{C}}O\cdot} \qquad (5)$$

I

The formation of alkoxycarboxy radicals I in high yields under these conditions was shown by the intense esr spectrum of the adducts II formed in the presence of alkenes as radical traps. The identity of the oxy radical adducts to ethylene, propylene, isobutylene, and



$$\mathrm{ROCO_2\cdot} + \mathrm{{>}C{=}C{<}} \longrightarrow \mathrm{ROCO_2\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot} \qquad (6)$$

II

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[1] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).

[2] R. A. Sheldon and J. K. Kochi, *ibid.*, **92**, 4395, 5175 (1970).

[3] The photolyses of *tert*-butyl perbenzoate and cyclopropanecarbonyl peroxide were notable exceptions.[2]

[4] W. J. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

[5] J. C. Martin, J. W. Taylor, and E. H. Drew, *J. Amer. Chem. Soc.*, **89**, 129 (1967).

[6] M. Szwarc, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience, New York, N. Y., 1962, p 153 ff; see also S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[7] T. G. Traylor, A. Sieber, H. Kiefer, and N. Clinton, *Intersci. Chem. Rep.*, **3** (4), 289 (1969).

[8] G. S. Hammond and L. M. Soffer, *J. Amer. Chem. Soc.*, **72**, 4711 (1950).

[9] H. J. Shine, J. A. Waters, and D. M. Hoffman, *ibid.*, **85**, 3613 (1963).

[10] (a) C. A. Barson and J. C. Bevington, *J. Polym. Sci.*, **20**, 133 (1956); (b) S. G. Cohen, *ibid.*, **2**, 511 (1947).

[11] For reviews see (a) L. A. Singer, "Organic Peroxide," Vol. I, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1970, p 265 ff; (b) R. Hiatt, *ibid.*, Vol. II, 1971, p 799 ff.

[12] (a) S. G. Cohen and D. B. Sparrow, *J. Amer. Chem. Soc.*, **72**, 611 (1950); (b) H. C. McBay and O. Tucker, *J. Org. Chem.*, **19**, 869 (1954); (c) F. Strain, *et al.*, *J. Amer. Chem. Soc.*, **72**, 1254 (1950); (d) G. A. Razuvaev, L. M. Terman, and D. M. Yanovskii, *Dokl. Akad. Nauk SSSR*, **161**, 614 (1965).

[13] (a) D. E. Van Sickle, *J. Org. Chem.*, **34**, 3446 (1969); (b) R. Hiatt and S. Szilagyi, *Can. J. Chem.*, **48**, 615 (1970); (c) G. A. Razuvaev and L. M. Terman, *Zh. Obsch. Khim.*, **30**, 2387 (1960); (d) M. E. Kurz and P. Kovacic, *J. Org. Chem.*, **33**, 266, 1950 (1968).

[14] (a) M. C. R. Symons, *J. Amer. Chem. Soc.*, **91**, 5924 (1969). (b) The esr spectra of carboxy radicals have been observed during γ-radiolysis of single crystals of maleic and related acids at 77°K: M. Iwasaki, B. Eda, *et al.*, *J. Chem. Phys.*, **55**, 3442 (1971); *J. Amer. Chem. Soc.*, **93**, 6415 (1971); see also *J. Chem. Phys.*, **57**, 3220 (1972).

Table I. Esr Parameters of Oxy Radical Adducts to Ethylene[a]

Addend	Adduct	T, °C	$\langle g \rangle$	Coupling constant, G $A_{H\alpha}$	 $A_{H\beta}$	Line broadening
$CH_3CH_2CH_2OCO_2\cdot$	$CH_3CH_2CH_2OCO_2–CH_2CH_2\cdot$	−116	2.00257	22.36	28.79	In-phase
$CH_3CH_2C(CH_3)$-$HOCO_2\cdot$	$CH_3CH_2C(CH_3)HOCO_2–CH_2CH_2\cdot$	−113	2.00257	22.34	28.74	In-phase
c	$CH_3CH_2OCO_2–CH_2CH_2\cdot$	−98	2.00258	22.32	28.07	In-phase
$C_6H_5CO_2\cdot$	$C_6H_5CO_2–CH_2CH_2\cdot$	−119	2.00257	22.20	28.19	In-phase
c, d	$CH_3CO_2–CH_2CH_2\cdot$	−119	2.00259	22.24	28.90	In-phase
c, d	$CH_3CH_2O–CH_2CH_2\cdot$	−111	2.00257	22.15	33.76	None
c	$CH_3CH_2CH_2CH_2O–CH_2CH_2\cdot$	−96	2.00256	22.04	33.54	None
c, d	$C_6H_5–CH_2CH_2\cdot$	−119	2.00268	22.14	31.64	None

[a] In cyclopropane solution. [b] See text for temperature ranges studied. [c] Adduct radical generated from corresponding β-substituted ethyl bromide and photochemically generated triethylsilyl radical. See reference 15. [d] Reference 18.

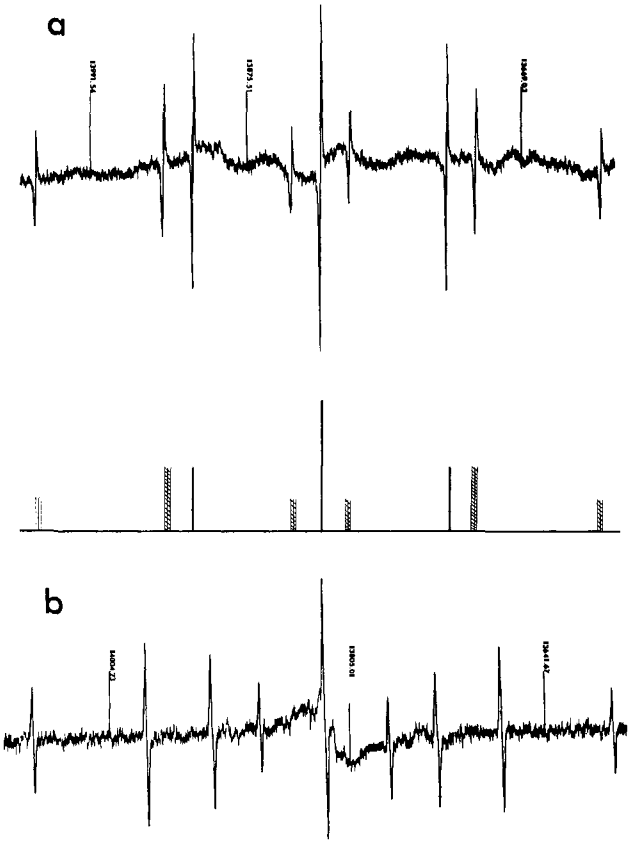
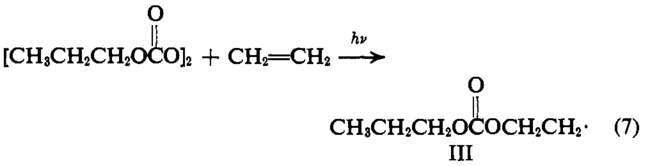


Figure 1. (Upper) Esr spectrum of $CH_3CH_2CH_2OCO_2–CH_2CH_2\cdot$ at −116° from the irradiation of di-*n*-propyl peroxydicarbonate and ethylene in cyclopropane solution. (Middle) Stick spectrum shows line broadening (shaded areas) due to in-phase modulation of the β hfs. (Lower) Esr spectrum of $CH_3CH_2OCH_2CH_2\cdot$ in cyclopane solution at −113°. Proton nmr field markers are in kHz.

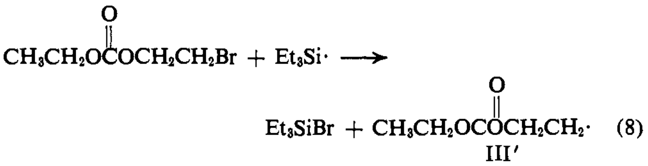
1,3-butadiene as representative olefins is presented in the following order.

Ethylene and Peroxydicarbonates. Photolysis of dialkyl peroxydicarbonates in cyclopropane solutions containing ethylene afforded well-resolved esr spectra over a range of temperatures. For example, the spectrum from di-*n*-propyl peroxydicarbonate at −116° consisted of a triplet of triplets characteristic of an ethylene adduct, the esr parameters of which are listed in Table I. The spectrum presented in Figure 1 clearly shows broadening of the "outer" lines corresponding to $M_I = \pm 1$ of the β-proton triplet, since these lines are considerably heightened at higher temperatures and approach the expected 1:2:1 intensity (peak–height) ratios. The spectrum is associated with the adduct III



$$[CH_3CH_2CH_2O\overset{O}{\overset{\|}{C}}O]_2 + CH_2{=}CH_2 \xrightarrow{h\nu} \underset{III}{CH_3CH_2CH_2O\overset{O}{\overset{\|}{C}}OCH_2CH_2\cdot} \quad (7)$$

of the *n*-propoxycarboxy radical (I, R = $CH_3CH_2CH_2$) to ethylene. The analogous ethyl species III′ could



$$CH_3CH_2O\overset{O}{\overset{\|}{C}}OCH_2CH_2Br + Et_3Si\cdot \longrightarrow Et_3SiBr + \underset{III'}{CH_3CH_2O\overset{O}{\overset{\|}{C}}OCH_2CH_2\cdot} \quad (8)$$

be generated independently from β-bromodiethylcarbonate and triethylsilyl radicals by a procedure that has been tested extensively.[15] The esr parameters for III′ consisted of $A_{H\alpha} = 22.32$ G, $A_{H\beta} = 28.07$, and $\langle g \rangle = 2.00258$ at −98°, which are essentially the same as those for III. Furthermore, the spectrum of III′ showed the same characteristic in-phase line broadening of the β protons as that of III with temperature variations.

The β-alkoxyethyl radical IV (R = CH_3CH_2, CH_3-

$$RO—CH_2CH_2Br + Et_3Si\cdot \longrightarrow Et_3SiBr + \underset{IV}{RO—CH_2CH_2\cdot}$$

$CH_2CH_2CH_2$) was also generated independently from several alkyl-β-bromoethyl ethers, in order to obviate the possibility that the observed species was an adduct derived from *n*-propoxy radical by prior decarboxylation (eq 9). In contrast to the esr spectra of III or III′,

$$CH_3CH_2CH_2OCO_2\cdot \longrightarrow CH_3CH_2CH_2O\cdot + CO_2 \quad (9)$$

$$CH_3CH_2CH_2O\cdot + CH_2{=}CH_2 \longrightarrow CH_3CH_2CH_2OCH_2CH_2\cdot \quad (10)$$

the spectrum of IV (R = CH_3CH_2), also shown in Figure 1, consisted of a triplet ($A_{H\alpha} = 22.04$ G) of triplets ($A_{H\beta} = 33.54$ G) with $\langle g \rangle = 2.00256$ and no detectable line broadening over the same temperature range. Analogous esr parameters have been reported previously for β-hydroxy-,[16] β-methoxy-,[17] and β-trifluoromethoxy-substituted[17] ethyl radicals.

Photolysis of a cyclopropane solution of di-*sec*-butyl peroxydicarbonate and ethylene also afforded an esr

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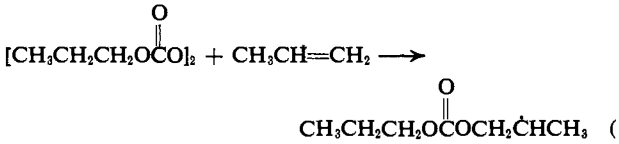
(15) A. Hudson and R. A. Jackson, *Chem. Commun.*, 1327 (1969); A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Lett.*, 5, 552 (1970).

(16) R. Livingston and H. Zeldes, *J. Chem. Phys.*, 44, 1245 (1966).

(17) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 93, 846 (1971).

spectrum consisting of a triplet ($A_{H\alpha}$ = 22.34 G) of triplets ($A_{H\beta}$ = 28.74 G) with $\langle g \rangle$ = 2.00257 at −113°. The same pronounced line broadening in the spectrum (due to in-phase modulation of the coupling constants associated with the β protons) indicates that the species is the analogous adduct [$CH_3CH_2CH(CH_3)OCO_2CH_2CH_2\cdot$] to ethylene (*vide infra*).[18a]

Propylene and Peroxydicarbonate. The esr spectrum observed during the photolysis of di-*n*-propyl peroxydicarbonate in cyclopropane solutions containing propylene consisted of a single species. It is clearly associated with an adduct to propylene, since the splitting pattern consists of a quartet (A_{CH_3} = 25.65) of triplets ($A_{H\beta}$ = 16.98 G) of doublets ($A_{H\alpha}$ = 22.08 G) with $\langle g \rangle$ = 2.00260 at −109°. The observation of in-phase line broadening in the esr spectrum strongly suggests the adduct to be V. We could find no evidence for the formation of allyl radicals under these conditions.



$$[CH_3CH_2CH_2O\overset{O}{\overset{\|}{C}}O]_2 + CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_2O\overset{O}{\overset{\|}{C}}OCH_2\dot{C}HCH_3 \qquad (11)$$

V

Isobutylene and Peroxydicarbonate. Photolysis of a mixture of di-*n*-propyl peroxydicarbonate and isobutylene in cyclopropane gave rise to an esr spectrum with a splitting pattern consisting of septets (A_{CH_3} = 23.41 G) of triplets ($A_{H\beta}$ = 11.04 G) with $\langle g \rangle$ = 2.00256 at −106°. The lines in the spectrum corresponding to M_I = ±1 of the β-proton triplet occurred with diminished peak-to-peak amplitude due to in-phase modulation of the hfs. This spectrum, by analogy with those, discussed earlier, was assigned to adduct VI.

$$[CH_3CH_2CH_2OCO_2]_2 + (CH_3)_2C{=}CH_2 \longrightarrow CH_3CH_2CH_2OCO_2CH_2\dot{C}(CH_3)_2 \qquad (12)$$

VI

No spectrum due to the 2-methallyl radical formed by hydrogen abstraction from isobutylene[19] or other adducts could be detected at various temperatures.

Butadiene and Peroxydicarbonate. Photolysis of a solution of di-*n*-propyl peroxydicarbonate in cyclopropane solution containing 1,3-butadiene at −105° afforded an esr spectrum with the parameters listed below.

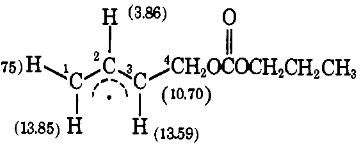
$A_H(1)$ = 3.86 G $A_H(1)$ = 13.59 G

$A_H(1)$ = 14.75 G $A_H(2)$ = 10.70 G

$A_H(1)$ = 13.85 G $\langle g \rangle$ = 2.00255

The spectrum exhibited no detectable line-width variations with temperature.

A variety of radicals add to 1,3-butadiene under these conditions, and only the characteristic esr spectrum of the *trans*-allylic adduct has been observed.[19,20] The coupling constants given above are consistent with such allylic radicals, and the assignments for the *n*-propoxycarboxy adduct VII are shown in parentheses (in gauss).



VII

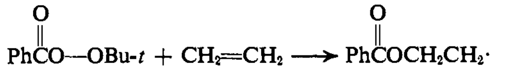
Photolysis of *tert*-Butyl Perbenzoate

The photolysis of *tert*-butyl perbenzoate can be carried out in cyclopropane solutions at temperatures as low as −120°. Benzoyl peroxide is less soluble in this medium and esr studies could be examined only at higher temperatures. Under no conditions were we able to observe an esr spectrum of an oxy radical or a phenyl radical in solution.[21]

$$PhCO_2{-}OBu\text{-}t \xrightarrow{h\nu} PhCO_2\cdot + t\text{-}BuO\cdot \qquad (13)$$

In the presence of alkenes, however, the esr spectra of adducts similar to those obtained with dialkyl peroxydicarbonates were readily observed.

Ethylene and Perbenzoate. The photolysis of a cyclopropane solution of *tert*-butyl perbenzoate and ethylene gave a weak, but readily analyzable, esr spectrum,[18b] which consisted of only one species showing a triplet ($A_{H\alpha}$ = 22.20 G) of triplets ($A_{H\beta}$ = 28.19 G) with $\langle g \rangle$ = 2.00257 at −119°. The characteristic in-phase broadening of the M_I = ±1 lines of the β-proton triplet suggested that the adduct VIII is derived from benzoyloxy radical (eq 14). The analogous acyloxyethyl radical VIII′, which can be generated independently from β-acetoxyethyl bromide and triethylsilyl radicals, shows the same selective line broadening behavior and proton coupling constants [$A_{H\alpha}(2)$ = 22.24 G, $A_{H\beta}(2)$ = 28.90 G, $\langle g \rangle$ = 2.00259 at −119°].



$$Ph\overset{O}{\overset{\|}{C}}{-}OBu\text{-}t + CH_2{=}CH_2 \longrightarrow Ph\overset{O}{\overset{\|}{C}}OCH_2CH_2\cdot \qquad (14)$$

VIII

The alternative possibility that the adduct was due to phenyl radical could be readily eliminated. The esr spectrum of the β-phenethyl radical IX is unambiguously derived from hydrocinnamoyl peroxide[1] as well as β-phenethyl bromide[18a] (reaction 15) and has parameters [$A_{H\alpha}$ = 22.14 G, $A_{H\beta}(2)$ = 31.64 G, $\langle g \rangle$ = 2.00268] at the same temperature which are distinctly different from either those of VIII or VIII′. Furthermore, the spectrum of IX shows no selective broadening of lines and is not present in detectable concentrations during the photolysis of *tert*-butyl perbenzoate and ethylene at temperatures up to −91°. Other adducts such as those derived from *tert*-butoxy and methyl radicals can also be readily ruled out.

$$[PhCH_2CH_2CO_2]_2 \longrightarrow \underset{\text{IX}}{PhCH_2CH_2\cdot} \longleftarrow PhCH_2CH_2Br + Et_3Si\cdot \qquad (15)$$

Propylene and Perbenzoate. The esr spectrum obtained during the photolysis of a cyclopropane solution

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[18] (a) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 7695 (1972). (b) Similar results were initially obtained by P. J. Krusic independently.

[19] (a) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968); (b) *Chem. Soc. Spec. Publ.*, **24**, 147 (1971).

[20] (a) T. Kawamura and J. K. Kochi, *J. Organometal. Chem.*, **30**, C8 (1971). (b) In *trans*-allylic radicals such as VII, the hfs of the syn protons on carbons 1 and 3 are usually the same.[11] Two previous exceptions have been observed in the thiyl adducts to 1,3-butadiene[17] and in the radical derived by hydrogen abstraction from the trimethylsilyl ester of crotonic acid: unpublished observations.

[21] For the esr spectrum of phenyl radical in a matrix see: P. H. Kasai, E. Hedaya, and C. B. Whipple, *J. Amer. Chem. Soc.*, **91**, 4364 (1969).

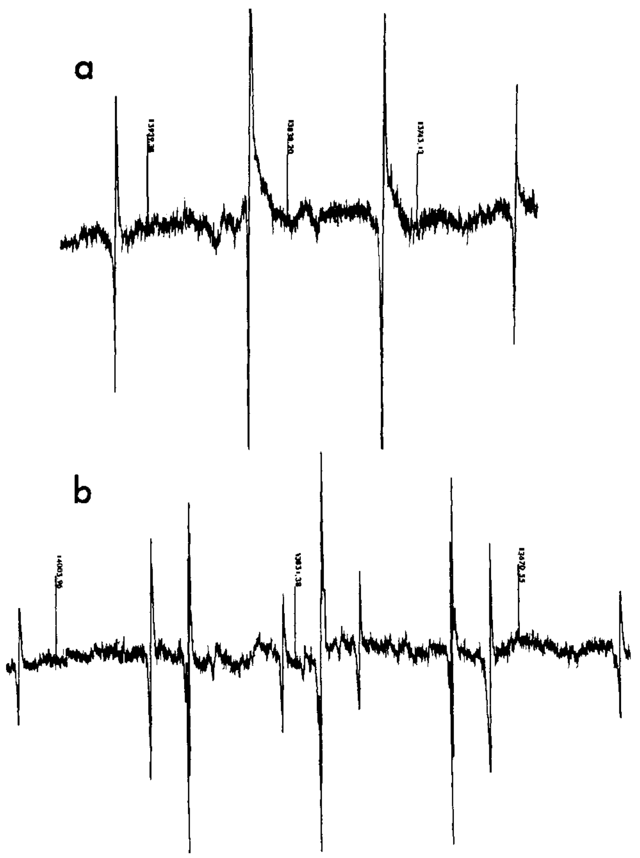
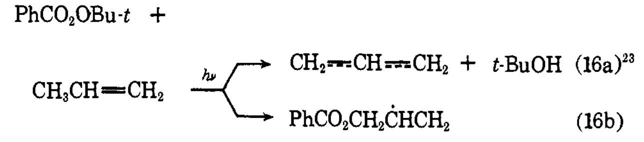


Figure 2. (Upper) Esr spectrum of the methyl radical from the photolysis of *tert*-butyl peracetate in ethylene at −150°. (Lower) Esr spectrum of $CH_3CO_2CH_2CH_2\cdot$ at −119° in cyclopropane solution showing selective (in-phase) line broadening.

of *tert*-butyl perbenzoate and propylene was the same as that recently reported under similar conditions.[22] It consisted of the spectrum of the readily identified allyl radical, presumably formed by abstraction of the allylic hydrogen from propylene by *tert*-butoxy radicals (eq 16a),[19] superimposed on the spectrum of a second

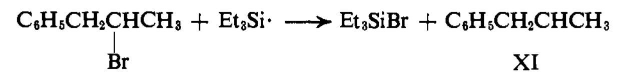


$$\mathrm{PhCO_2OBu\text{-}}t + \mathrm{CH_3CH{=}CH_2} \xrightarrow{h\nu} \mathrm{CH_2{\cdots}CH{\cdots}CH_2} + t\text{-}\mathrm{BuOH} \quad (16a)^{23}$$

$$\mathrm{PhCO_2OBu\text{-}}t + \mathrm{CH_3CH{=}CH_2} \xrightarrow{h\nu} \underset{\mathrm{X}}{\mathrm{PhCO_2CH_2\dot{C}HCH_2}} \quad (16b)$$

species X [$A_{H\alpha}(1) = 22.08$ G, $A_{H\beta}(2) = 17.38$ G, $A_{CH_3} = 25.51$ G, $\langle g\rangle = 2.00260$ at $-98°$]. We associate X with the adduct of benzoyloxy radical to propylene rather than phenyl adduct XI assigned earlier.[22,24]

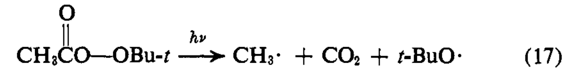
The 1-phenyl-2-propyl radical XI was separately



$$\mathrm{C_6H_5CH_2\underset{\underset{Br}{|}}{C}HCH_3} + \mathrm{Et_3Si\cdot} \longrightarrow \mathrm{Et_3SiBr} + \underset{\mathrm{XI}}{\mathrm{C_6H_5CH_2CHCH_3}}$$

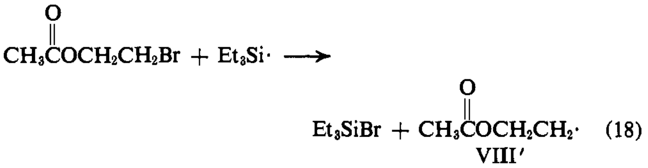
produced unambiguously from 1-phenyl-2-bromopropane and triethylsilyl radicals. The spectrum consisted of a doublet ($A_{H\alpha} = 21.93$ G) of quartets ($A_{CH_3} = 24.65$ G) of temperature-dependent triplets ($A_{H\beta} = 28.40$ G at $-111°$) due to the β-methylene protons with $\langle g\rangle = 2.00264$. The spectrum of XI is, thus, clearly distinguished from the adduct X derived from *tert*-butyl perbenzoate.

Photolysis of Aliphatic Acyl Peroxides. The photolysis of *tert*-butyl peracetate was carried out under the same conditions employed for *tert*-butyl perbenzoate. However, only the esr spectrum of the methyl radical was observed under all conditions employed. No evidence for the adduct to ethylene was found even when



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}O{-}OBu\text{-}}t \xrightarrow{h\nu} \mathrm{CH_3\cdot} + \mathrm{CO_2} + t\text{-}\mathrm{BuO\cdot} \quad (17)$$

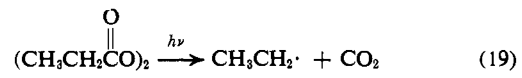
the photolysis was carried out in ethylene as solvent at temperatures as low at −160° (see Figure 2). The expected acetoxy adduct radical VIII′



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}OCH_2CH_2Br} + \mathrm{Et_3Si\cdot} \longrightarrow \mathrm{Et_3SiBr} + \underset{\mathrm{VIII'}}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}OCH_2CH_2\cdot}} \quad (18)$$

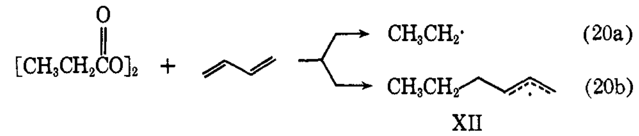
can be generated independently (see eq 18) and is sufficiently stable under these conditions to record the esr spectrum shown in the lower half of Figure 2 for comparison. Furthermore, the esr spectrum of *n*-propyl radical, the methyl adduct to ethylene, was also not in evidence.

Similar results were obtained when a solution of dipropionyl peroxide was photolyzed in the presence of alkenes. An intense esr spectrum of only the ethyl radical was observed during photolysis in ethylene,



$$\mathrm{(CH_3CH_2\overset{\overset{O}{\|}}{C}O)_2} \xrightarrow{h\nu} \mathrm{CH_3CH_2\cdot} + \mathrm{CO_2} \quad (19)$$

propylene, and isobutylene solutions. In the presence of butadiene, the esr spectrum consisted of the superposition of the esr spectra of ethyl radical and the adduct XII to butadiene.

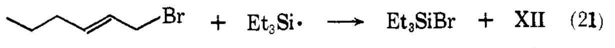


(20a)

(20b)

XII

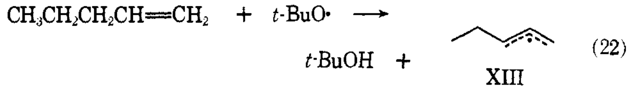
The esr spectrum of XII was identical with that produced independently from *trans*-1-bromohex-2-ene.[25]



(21)

There was no evidence for the adduct of propionoxy radical to butadiene.

The photolysis of acetyl peroxide in cyclopropane solutions of 1,3-butadiene also affords only the spectra of methyl radical and the adduct, *trans*-pentenyl radical XIII, which is the same as that generated independently



(22)

XIII

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(22) H. J. Hefter, T. A. Hecht, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 2793 (1972).

(23) From the intensities of lines in the spectrum it can be deduced that the relative steady-state concentration of allyl radical and X is roughly one. We surmise, thus, that allyl is derived from *tert*-butoxy (or phenyl) radical and X from benzoyloxy as shown in eq 16. The formation of allyl radical from benzoyloxy radical is probably unimportant. Benzoyl peroxide is too insoluble under these conditions to attain a sufficiently high concentration of radicals.

(24) The coupling constants of X compare with those reported for radical 5 in ref 22 ($A_{H\alpha} = 22.0$ G, $A_{H\beta} = 17.8$ G, and $A_{CH_3} = 25.4$ G) but not with those of the phenyl adduct XI.

(25) T. Kawamura, P. Meakin, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 8065 (1972).

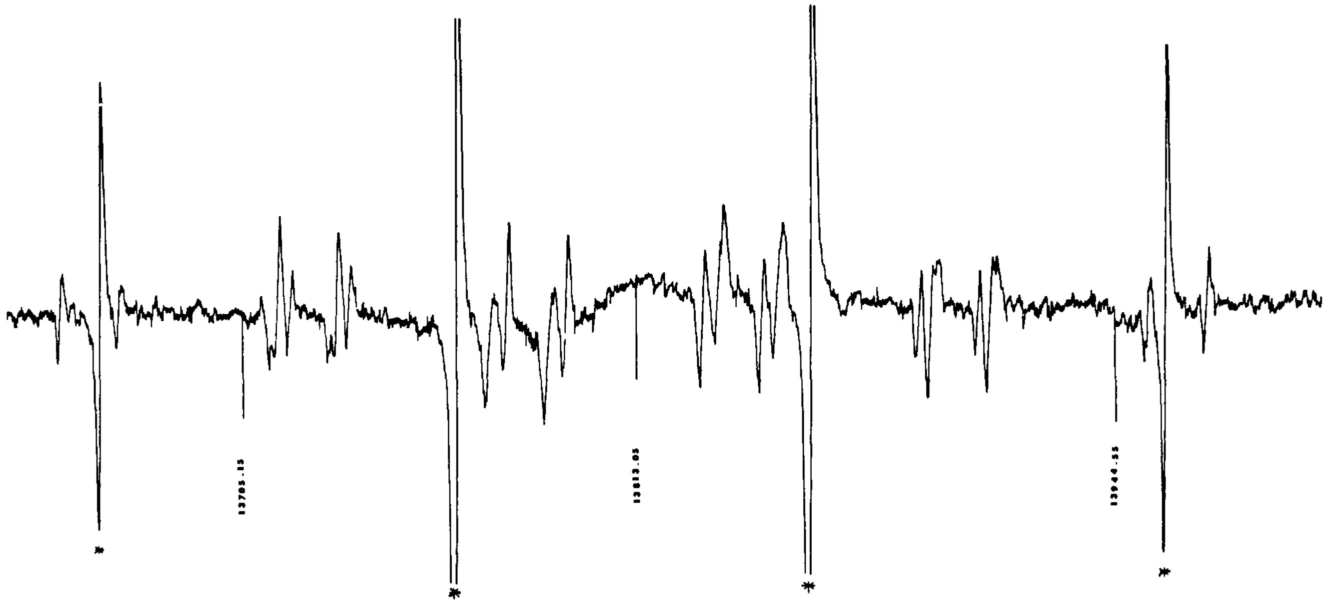


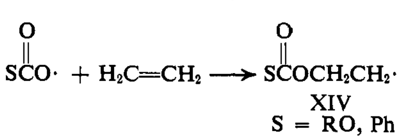
Figure 3. Esr spectrum obtained during the irradiation of acetyl peroxide in cyclopropane solutions containing 1,3-butadiene. Starred line due to methyl radical; others due to *trans*-1-pentenyl radical XII. Proton nmr field markers in kHz.

from pentene-1.[19] As shown in Figure 3, there is no evidence of the acetoxy adduct VIII′ in the spectrum.

Discussion

Electron spin resonance studies during photolytic decomposition of acyl peroxides in the presence of alkenes provide three basic types of information relating to: (a) the structure and conformation of carboxy radical adducts to alkenes, (b) the decarboxylation of carboxy radicals of different structural types, and (c) the competition between addition to a C=C bond and allylic hydrogen abstraction for various oxygen-centered radicals. Information about the latter (b and c) is also obtained in a more quantitative manner from kinetic and product studies, but esr does provide some unique insight into the static properties of the radical.

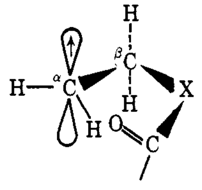
Structure and Conformation of Oxy Radical Adducts to Alkenes. The principal ethylene adducts derived from acyl peroxides in this study have the general structure XIV, in which the carbonyl function is three atoms



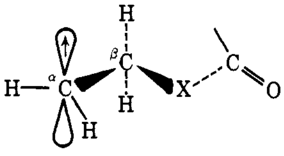
$$S\overset{O}{\overset{\|}{C}}O\cdot + H_2C{=}CH_2 \longrightarrow \underset{\text{XIV}}{S\overset{O}{\overset{\|}{C}}OCH_2CH_2\cdot} \qquad (23)$$

$S = RO, Ph$

removed from the radical center. We previously examined radicals of the same basic skeleton represented as esters (XV, $RO_2CCH_2CH_2CH_2\cdot$) and ketones (XVI, $RCOCH_2CH_2CH_2\cdot$).[18] The esr spectra of all three types of radicals (XIV–XVI) show interesting and unique line broadening behavior in which the "outer" lines ($M_I = \pm 1$) of the triplet corresponding to the β protons are selectively broadened at lower temperatures (compare upper Figure 1). This rather unusual alternation of line widths is associated with an in-phase modulation of the hfs of the pair of β protons.[18] Rate processes in which the β-methylene protons have hfs which are instantaneously equivalent at all times but modulated between two or more limiting values are consistent with this observation (since the width of a particular line is proportional to $(\tilde{M}_H)^2$).[26,27] A conformational change in which the β protons are always equivalent is represented by XVII.[18] Furthermore, in these radicals the magnitude and temperature dependence of the β hfs plotted in Figure 4 indicate that the conformation about the C_α–C_β bond is the same as that for other *n*-alkyl radicals in which the γ carbon lies close to the equatorial plane.[19b,28]



XVII



XVII′

$X = O, CH_2$

Other conformational changes are possible but must be limited to those in which the hfs of the β proton remain equivalent. The conformation shown in XVII also allows the π orbitals on the carbonyl group to interact with the p orbital of the radical center. The esr spectra of the (higher and lower) homologous radicals[18a] in this series only show selective line broadening due to the more commonly observed *out-of-phase* modulation of the β hfs arising from restricted rotation about the C_α–C_β bond.[17]

Successive substitution with α-methyl groups (*i.e.*, propylene V and isobutylene VI adducts) results in a marked decrease in the magnitude of the β hfs.[29] Sig-

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(26) (a) G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967). (b) P. D. Sullivan and J. R. Bolton, *ibid.*, **73**, 4387 (1969).

(27) There are few previous examples of selective line broadening attributable to in-phase modulation of the coupling constants. For a lucid discussion of alternating line-width effects see P. D. Sullivan and J. R. Bolton, *Advan. Magn. Resonance*, **4**, 39 (1970); and A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

(28) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971).

(29) The esr parameters of the propylene adduct V from alkoxycarboxy radical are analogous to the benzoyloxy adduct X in this regard.

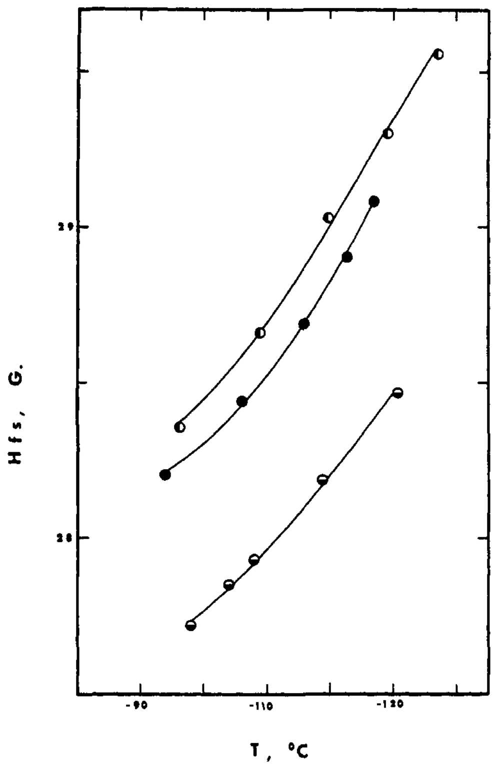
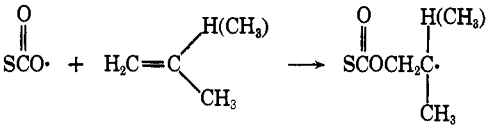
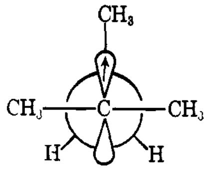


Figure 4. Temperature dependences of the hfs due to the β protons of the ethylene adducts in cyclopropane solutions: (◐) $CH_3CH_2CH(CH_3)OCO_2CH_2\dot{C}H_2$, (●) $CH_3CH_2CH_2OCO_2CH_2\dot{C}H_2$, (⊖) $C_6H_5CO_2CH_2\dot{C}H_2$.



$$\overset{O}{\overset{\|}{SC}}O\cdot + H_2C{=}C\begin{matrix}H(CH_3)\\ CH_3\end{matrix} \longrightarrow \overset{O}{\overset{\|}{SC}}OCH_2\overset{H(CH_3)}{\underset{CH_3}{C\cdot}} \quad (24)$$

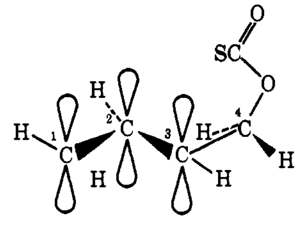
nificantly, the sign of the temperature dependence shown in Figure 5 is *opposite* to that of the ethylene adduct XIV. Since the previous analysis[17] of the magnitude and sign of the temperature dependence of the β hfs for the *tert*-amyl radical indicated it to be in a symmetric conformation XVIII about the C_α–C_β bond, we



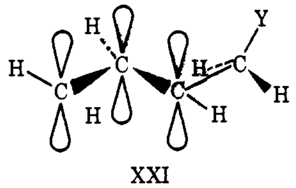
XVIII

conclude that adducts V and VI exist in an analogous conformation.[30] The observation of *in-phase* modulation of the β hfs in V and VI also suggest conformational changes which may be described by XIX.

An equivalent effect on conformation exerted by a γ-carbonyl group is also shown in the adducts VII to 1,3-butadiene.[31] The magnitude of the temperature-dependent triplet splitting ($A_{H_4} \simeq 10.5$ G; see Figure 5) represents the averaged value $[0.5(A_{H_4} + A_{H_4'})]$ for the two nonequivalent β protons in conformation XX

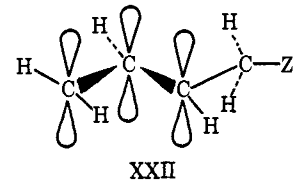


XX



XXI

in which the C_4–O bond eclipses the π orbitals. This conformation is analogous to that of a series of adducts XXI derived from sulfur- and group IVB-centered radicals (Y = SR, SiR_3, GeR_3, SnR_3), which show the same temperature-dependent behavior of the β hfs.[25] Moreover, XX and XXI are in contrast to the conformation XXII (Z = CH_3, *tert*-BuO) adopted by



XXII

Z = CH_3, $(CH_3)_3CO$

the methyl and *tert*-butoxy adducts to butadiene, in which the hfs of the two equivalent β protons are larger (A_{H_4} = 14 and 16 G, respectively).[17]

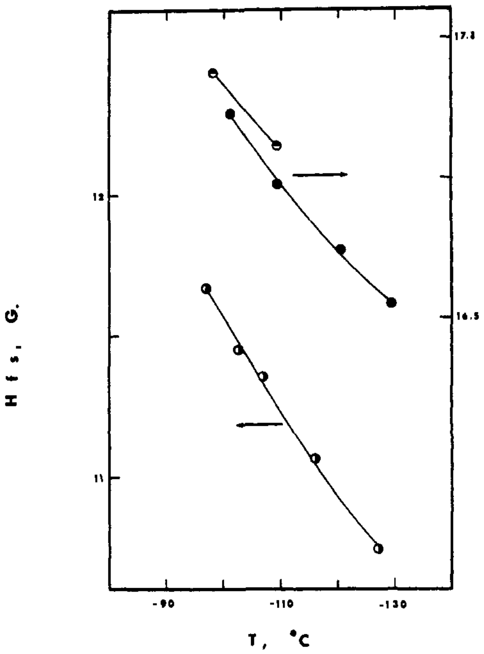
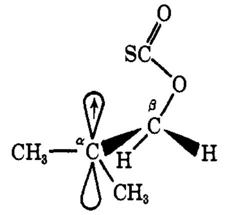
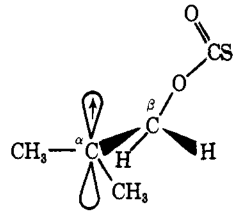


Figure 5. Temperature dependences of the hfs due to the β-methylene protons of the propylene and isobutylene adducts in cyclopropane solutions: (⊖) $C_6H_5CO_2CH_2\dot{C}HCH_3$, (●) $CH_3CH_2OCO_2CH_2\dot{C}HCH_3$, (◑) $CH_3CH_2CH_2OCO_2CH_2\dot{C}(CH_3)_2$.



XIX



XIX'

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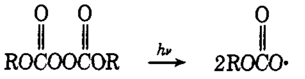
[30] However, the much smaller value of the β hfs for VI compared with XVIII suggests that the β protons in VI are closer to the nodal plane, a configuration which could be brought about by distortion about the β-carbon atom in a manner described previously.[17,19b]

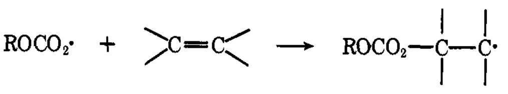
[31] The addition of a variety of radicals to 1,3-butadiene under these conditions has been shown to occur only to the s-trans form.[19] Cis–trans isomerism of the allylic adducts is too slow to observe.

The isotropic g values β-oxy-substituted alkyl radicals are all slightly (but consistently) less than those of the corresponding hydrocarbon analogs. The g values, moreover, are independent of the conformational location of oxygen, as shown by a comparison of III, V, and VI.

Decarboxylation of Carboxy Radicals. A variety of carboxy radicals can be potentially generated from the homolysis of acyl peroxides.[11] For example, acyloxy radicals $RCO_2\cdot$ and $ArCO_2\cdot$ are derived from thermolysis of diacyl peroxides and peresters, whereas alkoxycarboxy radicals $ROCO_2\cdot$ result from peroxycarbonates of various types. The observation of a strong esr spectrum of adducts XI during ultraviolet irradiation of dialkyl peroxydicarbonates in the presence of alkanes also suggests the following process.[32,33]



$$RO\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}OR \xrightarrow{h\nu} 2RO\overset{O}{\overset{\|}{C}}O\cdot \quad (5)$$



$$ROCO_2\cdot + {>}C{=}C{<} \longrightarrow ROCO_2\text{—}\overset{|}{\underset{|}{C}}\text{—}\overset{|}{\underset{|}{C}}\cdot \quad (6)$$

The absence of adducts derived from alkoxy radicals[34] indicates that decarboxylation of alkoxycarboxy radicals (eq 25) is not competitive[35] with addition (eq 6).

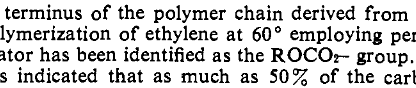
$$ROCO_2\cdot \longrightarrow RO\cdot + CO_2 \quad (25)$$

This conclusion is in complete accord with studies of thermally generated alkoxycarboxyl radicals,[12,13] in which decarboxyation reaction 25 is estimated to be endothermic ($\Delta H \approx 2$ kcal/mol) with an activation energy E_a of approximately 20 kcal/mol.[13a]

The esr studies also indicate that benzoyloxy radicals derived from the photolysis of *tert*-butyl perbenzoate are sufficiently long lived to be trapped by alkenes. The relatively slow first-order rate of decarboxylation of thermally generated benzoyloxy radicals (7.4×10^3 sec^{-1} at 60°, $E_a \cong 15$ kcal/mol)[38] is supported by chemical trapping experiments.[8-10] Recent experiments have shown a pathway involving direct photolytic decarboxylation of *tert*-butyl perbenzoate

$$C_6H_5CO_2\cdot \longrightarrow C_6H_5\cdot + CO_2 \quad (26)$$

(eq 27).[39] Phenyl radicals



$$C_6H_5\overset{O}{\overset{\|}{C}}OOBu\text{-}t \xrightarrow[-CO_2]{h\nu} [C_6H_5\cdots OBu\text{-}t] \text{ etc.} \quad (27)$$

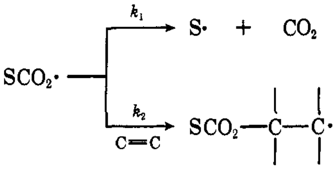
formed by this route or that of eq 26 are not detected by esr. Furthermore, the absence of lines in the esr spectrum attributable to adducts suggests that addition to alkenes is also not a facile process, an observation which is consistent with earlier flow studies in aqueous solution.[40]

The behavior of alkylcarboxy radicals derived from the photolysis of acyl peroxides of aliphatic acids is in strong contrast to alkoxycarboxy and arylcarboxy radicals. Esr studies show no evidence for the presence of such acyloxy radicals as intermediates, since only the alkyl radicals resulting from decarboxylation can be observed even at very low temperatures.

$$C_nH_{2n+1}CO_2\cdot \longrightarrow C_nH_{2n+1}\cdot + CO_2 \quad (28)$$

We attribute the absence of acyloxy adducts to the rapid rate of reaction 28 rather than inefficiency in the trapping of alkylcarboxy radicals.[41] Furthermore, esr results show that butadiene is able to trap methyl radicals during photolysis of acetyl peroxide despite the slower rate of addition of methyl radical compared to acyloxy (*i.e.*, alkoxycarboxy or aroyloxy) radicals.[42]

These esr studies give no direct information on the primary photochemical process which occurs during the photolysis of acyl peroxides. However, the most *economical* explanation for the differing availability of various carboxy radicals for trapping involves initial homolysis of the O–O bond. Such a formulation is consistent with the well-established mechanism of thermolysis of acyl peroxides, in which decarboxylation of acyloxy radicals takes place subsequent to cleavage of the O–O bond.[11,43] The trapping of carboxy radicals is then inversely related to the rate of decarboxylation, which is known to follow the order:[11,44] S = alkyl[4-6] ≫ aryl[8-10] > alkoxy.[12,13]



$$SCO_2\cdot \begin{cases} \xrightarrow{k_1} S\cdot + CO_2 & (29a) \\ \xrightarrow[C=C]{k_2} SCO_2\text{—}\overset{|}{\underset{|}{C}}\text{—}\overset{|}{\underset{|}{C}}\cdot & (29b) \end{cases}$$

More than one pathway for decomposition of the photoexcited state(s) of acyl peroxides is of course possible, as shown by the extrusion of carbon dioxide during the direct irradiation of *tert*-butyl perbenzoate.[39] We do not believe, however, that the difference between the photolysis of peroxybenzoates and alkyl peroxycarbonates, on the one hand, and peroxyacetates, etc., on the other, can be attributed solely to the participation of photoprocesses involving concerted scission

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(32) Alternatively, the adduct may result from a bimolecular reaction of a photoexcited peroxidic species directly (exciplex) with the alkene. Such a pathway cannot be entirely discounted, but lack of stereospecificity in perester photolysis[33] argues against molecular processes.

(33) P. Bakuzis, J. K. Kochi, and P. J. Krusic, *J. Amer. Chem. Soc.*, **92**, 1434 (1970), and studies to be published.

(34) For the addition of alkoxy radicals to alkenes see the rest of the text and footnote 50.

(35) The terminus of the polymer chain derived from the thermally initiated polymerization of ethylene at 60° employing peroxydicarbonates as initiator has been identified as the $ROCO_2$– group.[36] Quantitative analysis indicated that as much as 50% of the carbonyl content of the initiator has become incorporated in the polymer.[37] Thus, it seems clear that (barring induced decomposition)[12,13] even under these conditions the rate of decarboxylation of $ROCO_2\cdot$ is slow compared with its rate of addition to alkenes.

(36) H. N. Friedlander, *J. Polym. Sci.*, **58**, 455 (1962).

(37) E. M. Cernia and C. Mancini, *J. Polym. Sci., Part B*, **3**, 1097 (1965).

(38) J. C. Bevington and J. Toole, *J. Polym. Sci.*, **28**, 413 (1958).

(39) T. Koenig and J. A. Hoobler, *Tetrahedron Lett.*, 1803 (1972); *cf.* also T. Nakata, K. Tokumaru, and O. Simamura, *ibid.*, 3303 (1967), for sensitized decomposition.

(40) (a) A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. B*, 403 (1969). (b) The example cited in ref 22 is incorrect.

(41) There is no apparent chemical rationale for the rapid addition o arylcarboxy and alkoxycarboxy radicals but not alkylcarboxy radicals to alkenes.

(42) (a) For example, only the esr spectrum of methyl radical is produced during the photolysis of acetyl peroxide in the presence of ethylene, whereas *tert*-butyl perbenzoate or dialkyl peroxydicarbonates under the same conditions afford intense spectra of the oxy radical adducts. (b) See also W. A. Pryor, D. L. Fuller, and J. P. Stanley, *J. Amer. Chem. Soc.*, **94**, 1632 (1972).

(43) Except in those cases where multibond cleavage is facilitated by stabilizing alkyl groups.[11] Such assistance is not required in photolyses since ample energy is available for homolysis of the O–O bond.

(44) In CIDNP studies relating to decarboxylation of acyloxy radicals see (a) R. Kaptein, J. A. den Hollanden, D. Antheunis, and L. J. Oosterhoff, *Chem. Commun.*, 1687 (1970); (b) R. A. Cooper, R. G. Lawler, and H. R. Ward, *J. Amer. Chem. Soc.*, **94**, 545, 552 (1972); (c) C. Walling and A. R. Lepley, *ibid.*, **94**, 2007 (1972).

of the S–carbonyl and O–O bonds. More quantitative photochemical studies are required before this point can be established.

Addition of Oxygen-Centered Radicals to Alkenes. Competition with Allylic Hydrogen Abstraction. The facile addition of $ROCO_2\cdot$ and $PhCO_2\cdot$ to ethylene is indicated by the well-resolved esr spectra of the adducts obtainable during photolysis of the peroxidic precursors. Similar results have been observed with other oxygen-centered radicals such as $H\dot{O}$ from hydrogen peroxide,[45] $CF_3\dot{O}$ from bis(trifluoromethyl) peroxide,[19b] and $(CH_3)_3Si\dot{O}$ from trimethylsilyl-*tert*-butyl peroxide.[46] Of all these species examined heretofore, the *tert*-butoxy radical is unique in that it is the only one in which addition to ethylene is so slow that the esr spectrum of the adduct is not observed under comparable conditions. The *tert*-butoxy radical, of oxygen-centered species, is also unique in its ability to abstract allylic hydrogens.[47] The selectivity of the abstraction, in fact, forms the basis of the method for observing esr spectra of allylic radicals.[19] Thus, exposure of propylene to *tert*-butoxy radical results in the observation of only allyl radicals, whereas under similar conditions, $ROCO_2\cdot$ produces no allyl radicals. Hydrogen abstraction from propylene and isobutylene is also not observed with either $CF_3\dot{O}$[48] or $H\dot{O}$[22] and is minor (relative to addition) with $PhCO_2\cdot$[49] and $(CH_3)_3Si\dot{O}$.[46]

The quantitative rates of allylic attack relative to addition of a series of radicals collected in Table II have been determined by product studies at various temperatures. Again, *tert*-butoxy radical is uniquely disposed for hydrogen abstraction.

Table II. Rates of Allylic Attack Relative to Addition of $\dot{X}$ on $RCH_2CH{=}CH_2$

$\dot{X}$	Source	T, °C	k_{abs}/k_{add}	Ref
$(CH_3)_3C\dot{O}$	$(CH_3)_3COCl$	40	30	*a*
$RO\dot{O}$	Autoxidation	100	1.0	*b*
$\dot{C}H_3$	$(CH_3CO_2)_2$	100	0.3	*c*
$PhC\dot{O}_2$	$(PhCO_2)_2$	70	0.2	49
$\dot{C}l$	Cl_2	−9	0.13	*d*
$\dot{C}Cl_3$	$BrCCl_3$	78	0.02	*e*
$\dot{C}F_3$	$CF_3N{=}NCF_3$	50	0.02	*f*
$R\dot{S}$	RSH		Very small	*g*

[a] C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83**, 3877 (1961). [b] F. R. Mayo, *ibid.*, **80**, 2497 (1958). [c] (a) R. J. Cvetanovic and R. S. Irwin, *J. Chem. Phys.*, **46**, 1694 (1967); (b) N. Yokoyama and R. K. Brinton, *Can. J. Chem.*, **47**, 2987 (1969). [d] M. Poutsma, *J. Amer. Chem. Soc.*, **87**, 2172 (1965). [e] E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961). [f] J. M. Tedder, *Progr. React. Kinet.*, **4**, 39 (1967). [g] R. M. Kellogg, *Methods Free-Radical Chem.*, **2**, 1 (1969).

The clear separation into factors which affect the relative rates of addition and abstraction is not apparent from these results as yet. Previously, Hammond, *et al.*,[22] suggested a relationship with the electron affinity of the attacking radical and predicted that acyloxy radicals would preferentially abstract hydrogen. Our results clearly show, however, that the converse is true. An examination of the results suggests that steric properties[50] may play an important role, but in the absence of more direct information continued discussion is not fruitful. It remains, nonetheless, that the dichotomy is interesting as well as important and merits further study.

Experimental Section

Esr spectra were taken with a modified Varian X-band spectrometer utilizing 100-kHz modulation. The microwave bridge was designed around a three-port ferrite circulator. A backward diode (Philco L4154B) was employed as detector in conjunction with a low-noise, wide-band preamplifier (Philco P301). The latter was provided with an impedance-matching input circuit and a simple dc circuit to monitor the crystal current by means of a sensitive galvanometer. The input transformer was wound in a ferrite pot core (Ferroxcube Inc.) and was carefully shielded with many layers of high magnetic permeability foil. An attenuator was placed before the tunable detector mount and was used during tuning to avoid excessive microwave power on the detector. The field of a Varian V3600 12-in. magnet was swept very linearly by a Varian V3508 magnet flux stabilizer and slow-sweep unit. The spectral scans were accurately calibrated by means of a field marker operating in conjunction with a Harvey-Wells G502 nmr gaussmeter and a Hewlett-Packard frequency counter. The field marker causes the superposition of markers at accurately known field values directly onto the spectral record. The microwave frequency was determined directly using a Hewlett-Packard 5255A frequency converter and a Hewlett-Packard X281A microwave adapter in conjunction with a Hewlett-Packard 5248L frequency counter. The g factors were determined with the perylene cation radical (g = 2.00258)[53] as a daily standard in the configuration employed. A correction, usually 5×10^{-5}, was made to the measured values. The accuracy of such measurements is thought to be ±0.00003, and g factors made under these conditions were in agreement with those obtained by Fessenden and Schuler.[54] In most cases hfs were determined by positioning each line precisely, applying second-order corrections,[55] and then recomputing the distance between each line.

The light source, variable-temperature equipment, and the sample tubes are as described previously.[17] The temperature in the tube was calibrated with a thermocouple and accurate to ±5°. The photolyses were carried out in typical cases as follows.

For the photolysis of diacyl peroxides, acyl peresters, and dialkyl peroxydicarbonates a small amount of the peroxide (*ca.* 100 mg) was dissolved in a relatively large volume (15:1) of cyclopropane or cyclopropane–ethane mixtures. For diacyl peroxides it was also possible to employ diethyl ether or ether–pentane mixtures as solvent to enable lower temperatures to be obtained before crystallization became a problem. Photolytic reactions in the presence of alkenes were carried out with the volumes of the peroxide, cyclopropane, and alkene in a ratio of 1:8:2. When spectra were weak or not observed, the amounts of the various components were varied to obtain optimum concentrations. For photolytic reduction of alkyl halides, equal volumes of di-*tert*-butyl peroxides and triethylsilane were diluted with sufficient cyclopropane (and ethane) to give a final ratio of approximately 1:1:1:4. The halide was usually the bromide. All samples were thoroughly degassed using a freeze–pump–thaw cycle.

Materials. *tert*-Butyl perbenzoate was obtained from Wallace and Tiernan and redistilled before use. Di-*n*-propyl, di-*sec*-butyl,

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(48) Unpublished results.

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(50) Such experiments have not yet been systematically carried out with other primary and secondary alkoxy radicals, but there is some indication[51] that methoxy radicals add to propylene. Examples of intramolecular additions are, of course, well known.[52]

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and diisopropyl peroxydicarbonates were gifts from PPG Industries, Inc., Chemical Division and used without further purification. Ethylene, isobutylene, butadiene, and cyclopropane were from Matheson and propylene from Baker Chemical Co. Di-*tert*-butyl peroxide was obtained from the Shell Chemical Co. and washed and redistilled at reduced pressure prior to use. Triethylsilane was obtained from Columbia Organic Chemical Co. Other acyl peroxides used in this study were prepared previously.[2]

2-Bromoethyl *n*-butyl ether was prepared from the mono-*n*-butyl ether of ethylene glycol and phosphorus tribromide by the method given for the ethyl ether[56] (bp 170–171°).

2-Bromoethyl ethyl carbonate was prepared from 2-bromoethanol and ethyl chloroformate using the general method of Ritchie for the preparation of unsymmetrical dialkyl carbonates[57] (mp 7–10°).

2-Bromo-1-phenylpropane was prepared by treatment of the corresponding alcohol with phosphorus tribromide[58] (bp 100–101° (10 mm), lit. 114° (21 mm)).[58]

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Mechanisms of Free-Radical Reactions. I. Interconversion of Homoallyl and Cyclopropylcarbinyl Free Radicals

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Abstract: A section of the C_4H_7 potential surface connecting and including the homoallyl and cyclopropylcarbinyl free radicals has been investigated by *ab initio* molecular orbital theory. Both isomers are stable minima, the former being the lower in energy, and are connected by a small but finite activation barrier.

Concerted interconversions between stable hydrocarbon free radicals generally require moderate activation energies; low enough for the processes to occur facilely at ordinary temperatures, and yet sufficiently high to allow for characterization of individual species by conventional spectroscopic and chemical methods.[2] Significant progress has been made in recent years both toward the synthesis of specific precursor free radicals and in the routine interpretation of electron spin resonance (esr) spectra of increasing complexity,[3] and it would seem to this author that radical systems may soon provide a unique opportunity for the study of organic reaction mechanisms. Nonempirical theoretical techniques applicable to the study of the energetics of radicals have also evolved impressively during the past decade. Although their applications have for the most part thus far been restricted to studies of equilibium geometry[4] and conformational behavior,[5] indications are that meaningful results might be obtained from explorations of reaction potential surfaces. In this paper we report an application of *ab initio* molecular orbital theory to a section of the C_4H_7 potential surface including and connecting the homoallyl and cyclopropylcarbinyl free radicals. Our primary intent is to establish whether or not the individual species are stable minima on the C_4H_7 surface, and if so the nature of the transition state connecting them. Comparison of our findings with the recent esr results of Krusic and coworkers[6] is inevitable, and it is hoped that such might form a guide for later theoretical studies where experiments have not as yet been performed or have led to ambiguous findings. We shall also be interested in a comparison of the energetic surface for homoallyl–cyclopropylcarbinyl interconversion with our previously reported studies on the analogous carbocationic species.[7] In this previous work it was shown that the distant interaction of a formally vacant orbital with an area of high electron density led to a collapse of the acyclic homoallylic structure to cyclopropylcarbinyl. It will be interesting to probe the consequences of the related (radical center–ethylene π system) interaction.

Methods. We employ standard single determinant

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[1] The Laboratoire de Chimie Théorique is part of the Laboratoire de Physico-Chimie des Rayonnements and is associated with the CNRS.

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