

drogen-atom transfer was envisioned to occur intramolecularly through "solvolysis" in the surface oxide ion. Recently, Pines³¹ summarized evidence that alumina acts as an effective solvent in the catalysis of hydrocarbons.

Whereas *n*-butene isomerization over silica-alumina seems to be relatively well understood, the mechanism

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over alumina continues to be elusive. The true picture probably is a composite of several mechanisms acting on different sites. Whatever mechanisms are considered, however, they must include C-H (or C-D) bond cleavage in the transition state.

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X-Ray-Induced Hydrogen-Atom Addition and Removal in Diethyl Glutaconate-Urea Crystals

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Abstract: X-Ray-produced free radicals in single crystals of the diethyl glutaconate-urea inclusion compound were investigated by esr at room temperature. The two long-lived free radicals are $\text{CH}_3\text{CH}_2\text{OOC}\dot{\text{C}}\text{HCH}=\text{CH}-\text{COOCH}_2\text{CH}_3$ (I) and $\text{CH}_3\text{CH}_2\text{OOC}\dot{\text{C}}\text{HCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$ (II). Spectra taken shortly after X-irradiation exhibit a remarkably low relative concentration of the allyl-type radical I. Heating experiments demonstrate that radical I is thermally more stable than radical II and that the two radicals decay independently. The relative concentration of radical I at 23° observed after X-irradiation at 77, 273, or 298°K is $20 \pm 10\%$. A table of proton coupling constants is given.

A large number of stable, oriented free radicals have been observed and studied in X- or γ -irradiated organic single crystals.¹⁻⁷ Among the chief goals of such studies are the understanding of the interaction of high-energy radiation with organic crystals and the prediction of the structures and stabilities of the resulting free radicals. Molecules containing carboxyl groups are frequently chosen for study because relatively intense and simple esr hyperfine patterns are observed. In many carboxylic acids or esters only one free radical is observed at room temperature. In some compounds this radical is related to its parent molecule simply by the removal of one α -hydrogen atom, and in other compounds it is obtained by the addition of one hydrogen to a position β to the carboxyl group. The purpose of this paper is to report a carboxylic ester in which long-lived radicals of both types are observed simultaneously. From a study of this compound, diethyl glutaconate ($\text{EtOOCCH}_2\text{CH}=\text{CHCOOEt}$), the relative concentrations and stabilities of the two general types of free radicals are determined in the same crystalline lattice.

(1) H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, *J. Am. Chem. Soc.*, **82**, 766 (1960).

(2) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

(3) D. Kivelson and C. Thomson, *Ann. Rev. Phys. Chem.*, **15**, 197 (1964).

(4) O. H. Griffith, *J. Chem. Phys.*, **41**, 1093 (1964).

(5) O. H. Griffith and A. L. Kwiram, *J. Am. Chem. Soc.*, **86**, 3937 (1964).

(6) O. H. Griffith, *J. Chem. Phys.*, **42**, 2644, 2651 (1965).

(7) R. J. Cook, J. R. Rowlands, and D. H. Whiffn, *Mol. Phys.*, **7**, 57 (1964).

Experimental Section

Diethyl glutaconate (Aldrich) was vacuum distilled before use. (However, using the unpurified compound did not result in observable differences in the spectra.) Crystals were grown by adding diethyl glutaconate to a mixture of three parts saturated solution of urea in methanol to one part methanol. This solution was cooled from room temperature to 7° over a period of 1 or 2 days in a 600-ml dewar containing 200 ml of water.

The crystals obtained were rinsed several times in cold methanol. The *z* axis was defined to lie along the needle axis of the hexagonal crystals, and the *xy* plane was perpendicular to the needle axis.

Crystals were irradiated at 77°K or at 0° using a tungsten target X-ray tube operating at 44 kv and 35 ma. The irradiation time was 2 hr. Spectra were taken at room temperature on a standard Varian V4502 9.5 kMc/sec esr spectrometer. The scan rate was calibrated with peroxyamine disulfonate (Aldrich), assuming an over-all splitting of 26.0 gauss. A dual cavity, with the Varian strong pitch sample as a reference, was utilized for intensity measurements.⁸

Results and Discussion

Typical esr spectra of a diethyl glutaconate-urea crystal after X-irradiation at 77°K are shown in Figure 1. Spectrum 1a in the upper left-hand corner of Figure 1 was recorded with the magnetic field parallel to the *xy* plane immediately after the crystal was warmed to room temperature. Spectra obtained several hours later at room temperature were very nearly the same as the 1a spectrum. After heat treatment, however, a

(8) Using the Varian strong pitch sample as the standard, a rough calculation indicates 10^{14} free radicals in 1 mg of a diethyl glutaconate-urea inclusion crystal.

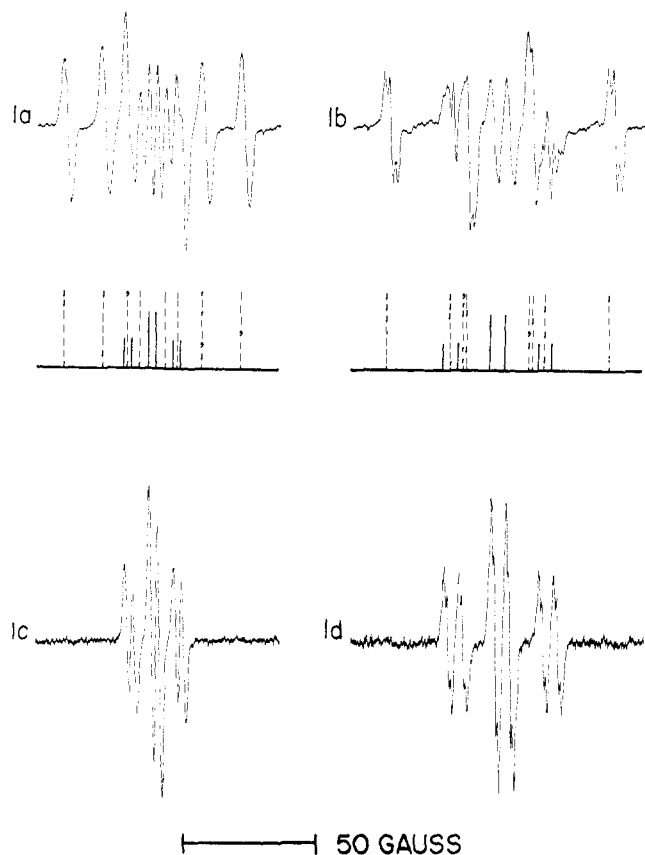
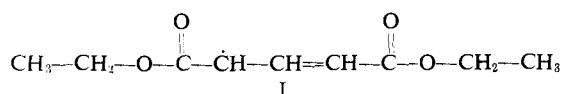


Figure 1. The room-temperature esr spectra with the magnetic field in the xy plane and along the z axis of a diethyl glutaconate-urea crystal. The single crystal was X-irradiated at 77°K, and the spectra 1a,b and 1c,d were recorded before and after heat treatment, respectively. The signal level of the 1a,b spectra differs from that of the 1c,d spectra. The stick spectra below 1a and 1b indicate the approximate positions of the peaks due to the two radicals, but not the fine splittings due to the ζ protons. The dashed lines refer to the hydrogen-addition radical, while the smaller solid lines refer to the allyl-type radical.

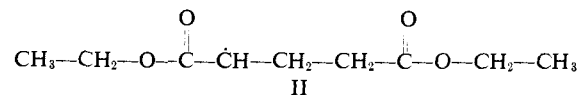
number of the esr lines slowly disappeared, leaving the simplified spectrum, 1c. Similar results were obtained with the magnetic field in the z direction as shown in spectra 1b and 1d of Figure 1. Further heating only decreased the intensity of the final spectra 1c and 1d. These observations clearly indicate that significant concentrations of two different free radicals were present at room temperature. Upon heating, the concentration of one of these two free radicals decreased much more rapidly than the concentration of the other radical.

Identification of the two free radicals is straightforward. The esr hyperfine patterns 1c and 1d of Figure 1 result from two equivalent anisotropic proton coupling constants and a third anisotropic proton coupling constant. These lines are further split by four equivalent small coupling constants which are resolved only at certain orientations of the magnetic field (Figure 1, spectrum 1d). The free radical associated with spectra 1c and 1d is clearly the allyl-type radical



Referring again to Figure 1, the spectrum of the less thermally stable free radical can be reconstructed with

two nonequivalent but nearly isotropic proton coupling constants and one anisotropic proton coupling constant. The lines are further split by two small coupling constants when the magnetic field is parallel to the z axis. Recalling that β -proton coupling constants, in contrast to α -proton coupling constants, are nearly isotropic, the only reasonable choice for the structure of the radical is



The proton coupling constant data (which were found to be independent of the temperature of irradiation) of radicals and I and II are summarized in Table I.

All room-temperature esr spectra of the diethyl glutaconate-urea crystal are invariant with respect to rotations of the laboratory magnetic field vector in the crystalline xy plane but are anisotropic with respect to arbitrary rotations out of the xy plane. This behavior is characteristic of organic inclusion compounds⁴⁻⁶ and is a direct result of free-radical motion in the tubular cavities formed by the urea molecules. As shown previously,⁴ an estimate of the isotropic component a_0 of a proton coupling constant can be obtained from the relation

$$a_0 = (2a_{xy} + a_z)/3 \quad (1)$$

where a_{xy} and a_z are the values of the proton coupling constant measured with the magnetic field in the xy plane and parallel to the z axis, respectively. Using this relation, the data of Table I can be compared with data previously reported for similar radicals.

Heller and Cole⁹ have thoroughly investigated by esr single crystals of glutaconic acid X-irradiated at room temperature. The only radical observed is the allyl-type radical $\text{HO}_2\text{CCH=CH}\dot{\text{C}}\text{HCO}_2\text{H}$, and the isotropic components of the three proton coupling constants are 12.7, 4.3, and 12.7 gauss.⁹ From Table I and the above relation for a_0 , the isotropic components of the three proton coupling constants for radical I are 12.3, 3.8, and 12.3 gauss. The differences between the two sets of values are within the combined limits of error but could also result from slight differences in radical structure and conformation. Both sets of data are consistent with the values obtained by Fessenden¹⁰ for the allyl radical in irradiated liquid cyclopropane, and there can be little doubt that radical I is a π radical of the allyl type.

Radical II, formed by hydrogen addition to diethyl glutaconate, is of the same general type as the radicals observed by hydrogen-atom removal from saturated esters in X-irradiated urea inclusion compounds.⁴ The β -proton coupling constants depend strongly on the degree of molecular motion but the α -proton coupling constants of the radicals can be compared directly. The average values of the α -proton coupling constants with $H_{||z}$ and $H_{||xy}$ reported for saturated esters are 29.5 and 14.9 gauss, respectively. These values are essentially identical with the values 30.2 and 14.8 gauss observed for radical II. The isotropic component of the α -proton coupling constants and the ζ -proton coupling

(9) C. Heller and T. Cole, *J. Chem. Phys.*, **37**, 243 (1962).

(10) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

Table I. Proton Hyperfine Coupling Constants^a

Radical	$H_{ z}$, gauss		$H_{ xy}$, gauss	
$\begin{array}{c} \text{O} \quad \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{CH}_3\text{CH}_2\text{OCCHCH}=\text{CHCOCH}_2\text{CH}_3 \quad (\text{I}) \\ \zeta \quad 1 \quad 2 \quad 3 \quad \zeta \end{array}$	18.1 (1, 3)	5.7 (2) 0.8 (ζ)	9.4 (1, 3)	2.9 (2)
$\begin{array}{c} \text{O} \quad \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{CH}_3\text{CH}_2\text{OCCHCH}_2\text{CH}_2\text{COCH}_2\text{CH}_3 \quad (\text{II}) \\ \zeta \quad \quad \alpha \quad \beta \end{array}$	30.2 (α) 30.2 (β_2)	24.9 (β_1) 1.6 (ζ)	14.8 (α)	23.9 (β_1) 28.9 (β_2)

^a The assignments of the coupling constants obtained from the 25° esr spectra are designated in parentheses. Proton coupling constants 1, 2, and 3 of the allyl-type radical (I) and α , β_1 , and β_2 of radical II are believed to be accurate to ± 0.8 gauss. The ζ proton coupling constants of radicals I and II are accurate to within ± 0.3 gauss. All coupling constants are averages of several spectra of two or more crystals. $H_{||z}$ and $H_{||xy}$ indicate the spectra were obtained with magnetic field parallel to the z axis and the xy plane, respectively, of the diethyl glutaconate-urea crystal.

constants of radical II are also the same as those obtained for the saturated ester molecules.⁴ Furthermore, these data are consistent with coupling constants reported for similar radicals produced in solution by purely chemical means.¹¹ The identification of radical II is, therefore, clearly unambiguous.

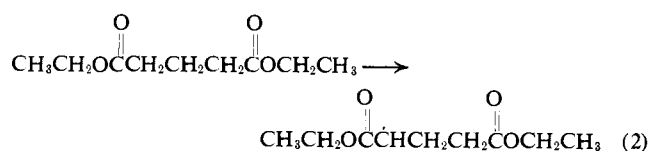
In crystals irradiated at 77°K, radical I initially represented between 14 and 28% of the total observed radical concentration, as determined from the spectra taken with the magnetic field in the z direction. After heating one crystal in the oven at 80° for 2 hr, radical II completely disappeared, while about 40% of radical I remained. In another crystal, heated at 60°, radical II was almost entirely eliminated at the end of 2 hr while 12% of radical I remained after 8 hr. Thus, we can conclude that although radical II was initially observed to be the predominant radical, it proved to be thermally less stable than radical I.

Although it is obvious that significant concentrations of radical I are not converted to radical II, it is possible to suggest that radical II is converted to radical I by the loss of two hydrogens, and that radical I subsequently decays. This would be an example of a simple consecutive reaction involving only irreversible first-order steps. If this type of reaction were occurring, an increase in the concentration of radical I should initially be observed as radical II decays.

A crystal of diethyl glutaconate-urea was heated at 55°, and esr spectra were taken (at room temperature) before heating and at 5-min intervals after heating. Radical II was observed to decay rapidly while radical I decayed relatively slowly, but there was no increase in the concentration of radical I. The relative con-

centrations were obtained from spectra taken with the magnetic field parallel to the z axis of the crystal, where less overlap of the lines due to the two radicals occurs. From these observations it can be concluded that the two radicals decay independently.

A separate check on this result was made by X-irradiating a single crystal of diethyl glutarate-urea inclusion compound. Diethyl glutarate loses hydrogen to form a radical identical with radical II.¹²



The X-irradiated crystal was heated at 55°, and spectra taken at time intervals similar to those of the previous run showed a rapid decay of radical II with no production of radical I.

The relative concentration of radical I was the same, within the limits of error of the experiment, whether the crystal was irradiated at 77°K or 0 or 24°C. The average value for radical I was about 20% of the total radical concentration. Spectra taken after irradiation of two crystals at room temperature without any temperature control gave approximately 40% of radical I, suggesting local heating effects.

Acknowledgment. The authors gratefully acknowledge the financial assistance received from the National Science Foundation (NSF GP-5509) for support of this work.

(11) P. Smith, J. T. Pearson, P. B. Wood, and T. C. Smith, *J. Chem. Phys.*, **43**, 1535 (1965).

(12) Coupling constants obtained from the spectra of this radical were essentially identical (± 0.5 gauss) with those calculated for radical II from the spectra of irradiated diethyl glutaconate-urea crystals.