An Electron Spin Resonance Study of X-Irradiated Fumaric Acid–Urea Crystals[1a]

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Single crystals of the monoclinic fumaric acid–urea crystals were X-irradiated at room temperature and investigated by electron spin resonance. The urea molecules of this previously unreported crystal minimize polymerization of fumaric acid and permit an investigation of X-ray-produced monomer radicals. The dominant radical observed is the well-known $HO_2CCH_2\dot{C}HCO_2H$ radical. The α-proton tensor is obtained and the major orientations of this radical are related to the crystal morphology. Single crystals of succinic acid–urea and adipic acid–urea were also briefly investigated and the orientations of the X-ray produced carboxylic acid radicals ($R\dot{C}HCO_2H$) in all three "molecular compounds" were the same with respect to the three very similar crystal morphologies. The degree of radical motion in the fumaric acid–urea, succinic acid–urea, and adipic acid–urea crystals is much less than that of similar radicals in the hexagonal urea inclusion compounds.

Introduction

The electron spin resonance (e.s.r.) study of X- or γ-irradiated saturated crystalline dicarboxylic acids has provided useful information regarding the electronic structure, magnetic properties, and orientations of free radicals of the type $R\dot{C}HCO_2H^2$; and it is of interest to investigate X- or γ-ray damage in the unsaturated dicarboxylic acid, fumaric acid. However, γ-rays have been shown to polymerize acylamide, methacrylamide, vinyl stearate, acrylic acid, methacrylic acid, and related compounds in the solid state.[3,4] More recently several derivatives of maleic and fumaric acid have been found to dimerize in the solid state under the action of ultraviolet light.[5] For example, fumaronitrile and dimethyl fumarate photodimerize to yield tetracyanocyclobutane[6] and tetracarbomethoxycyclobutane,[7] respectively. It is therefore reasonable to expect that γ-irradiation of fumaric acid might cause polymerization in the solid state. Cook, Rowlands, and Whiffen[8] have shown that polymerization does occur in γ-irradiated fumaric acid by observing that the dominant radical present after irradiation is of the form $HO_2CCH(R)\dot{C}HCO_2H$. In addition, some of the minor lines of the spectra were tentatively assigned to the radical $HO_2CCH_2\dot{C}HCO_2H$.[9] Simultaneously with this work, single crystals of fumaric acid–urea were prepared and studied by e.s.r. in this laboratory.[10] These mixed crystals, although apparently not previously reported, were expected to be stable by analogy with the crystals formed between saturated dicarboxylic acids and urea reported by Schlenk.[11] These mixed

crystals effectively "dilute" the fumaric acid and suppress polymerization, thereby making feasible a study of the X-ray-produced monomer radicals. The identification and orientations of the major free radical ($HCO_2CH_2\dot{C}HCO_2H$) observed in the fumaric acid–urea crystals is discussed below and the orientations of this radical are compared to those of the free radicals in other dicarboxylic acid–urea crystals.

Experimental

The crystals of fumaric acid–urea were grown from a methanol solution containing mole ratios of fumaric acid–urea of from 1:3 to 1:10. The habit of the fumaric acid–urea crystals obtained from the methanol solution by slow evaporation is illustrated in Fig. 1, and the exterior angles are given in Table I. Defining the crystal faces as shown in Fig. 1, the crystals grew with face h in contact with the crystallizing dish. By titration with potassium permanganate the mole ratio of fumaric acid to urea in the crystal was found to be $1.0:2.0 \pm 0.2$. Fumaric acid–urea crystals were also grown from water and were obtained as needles elongated along the y axis. The e.s.r. spectra obtained from crystals grown in different solvents or with varying ratios of fumaric acid to urea in solution were essentially equivalent. Crystals of the other dicarboxylic acids investigated were grown from methanol by slow evaporation.

A Varian X-band spectrometer was used to obtain the e.s.r. data and the crystals were mounted in the microwave cavity by means of optical goniometer techniques. By this means, the orientations of the crystalline axes with respect to the magnetic field were known to within $\pm 30'$. The room-temperature e.s.r. spectra of the fumaric acid–urea crystals were complicated by the presence of more than one type of free radical, and several features of the spectra changed with time (due to the changing concentrations of the free radicals present[12]). Heating to 50–70° simplified the e.s.r. spectra (Fig. 2), and we will consider here only the e.s.r. spectra of the crystals which were heat-treated prior to ob-

(1) (a) Supported by the National Science Foundation under Grant No. GP-930; (b) National Science Foundation Predoctoral Fellow.

(2) For a review see: R. G. Shulman, *Ann. Rev. Phys. Chem.*, **13**, 325, (1962).

(3) R. B. Mesrobian, P. Ander, D. S. Ballantine, and G. J. Dienes, *J. Chem. Phys.*, **22**, 565 (1954).

(4) A. J. Restaino, R. B. Mesrobian, H. Morawetz, D. S. Ballantine, G. J. Dienes, and D. J. Metz, *J. Am. Chem. Soc.*, **78**, 2939 (1956).

(5) G. W. Griffen, J. E. Basinski, and A. F. Vellturo, *Tetrahedron Letters*, **3**, 13 (1960).

(6) G. W. Griffen, J. E. Basinski, and L. I. Peterson, *J. Am. Chem. Soc.*, **84**, 1012 (1962).

(7) G. W. Griffen, A. F. Vellturo, and K. Furukawa, *ibid.*, **83**, 2725 (1961).

(8) R. J. Cook, J. R. Rowlands, and D. H. Whiffen, *J. Chem. Soc.*, 3520 (1963).

(9) We have observed certain features of the e.s.r. spectra of X-irradiated *cis*-1,2-ethylenedicarboxylic acid (maleic acid) which *suggest* that similar radicals are produced in this system (no detailed investigation of maleic acid is planned in this laboratory).

(10) The initial results of this work were briefly mentioned in a note reporting uses of X-irradiated urea inclusion compounds. [O. H. Griffith and H. M. McConnell, *Proc. Natl. Acad. Sci. U. S.*, **48**, 1877 (1962).]

(11) W. Schlenk, Jr., *Ann.*, **565**, 204 (1949).

(12) In addition to the lines attributed to the $HCO_2CH_2\dot{C}HCO_2H$ radical (I), the freshly X-irradiated fumaric acid–urea crystals exhibited four to eight partially resolved lines which probably arise from just one other type of radical (II). The maximum splitting attributed to II is 175 Mc./sec. and the g-value of II is similar to that of I. It is possible that II is related to the vinyl radical, which has been observed by Fessenden and Schuler[20c] in solution and by Adrian, Cochran, and Bowers ["Free Radicals in Inorganic Chemistry," American Chemical Society, Washington, D. C., 1956, p. 50] in an argon matrix (see ref. 20c, footnote 48). Radical II could also be a conformational isomer of I in which the value of θ (see discussion of β-proton coupling constants) of one of the β-protons is nearly 90°. (This could be caused, for example, by hydrogen addition perpendicular to the plane containing the carbon atoms of fumaric acid. II might then be a precursor to I.) The protons of urea and the carboxyl groups of fumaric acid were simultaneously exchanged for deuterium by repeated recrystallization from D₂O. The e.s.r. spectra of the X-irradiated deuterated crystals did not provide positive identification of II due to extensive overlapping of lines. However, a large concentration of the radical $DO_2CCH(D)\dot{C}HCO_2D$ relative to the concentration of radical I was observed in the deuterated crystal. In view of the fact that the α-proton tensors of the minor orientations of radical I could not be obtained, further work on this system would more profitably await a complete X-ray crystallographic investigation of the fumaric acid–urea crystals. (Multiple twinning or the presence of crystal defects, for example, would hinder the identification of additional radicals and are not always easily recognizable from the e.s.r. spectra.)
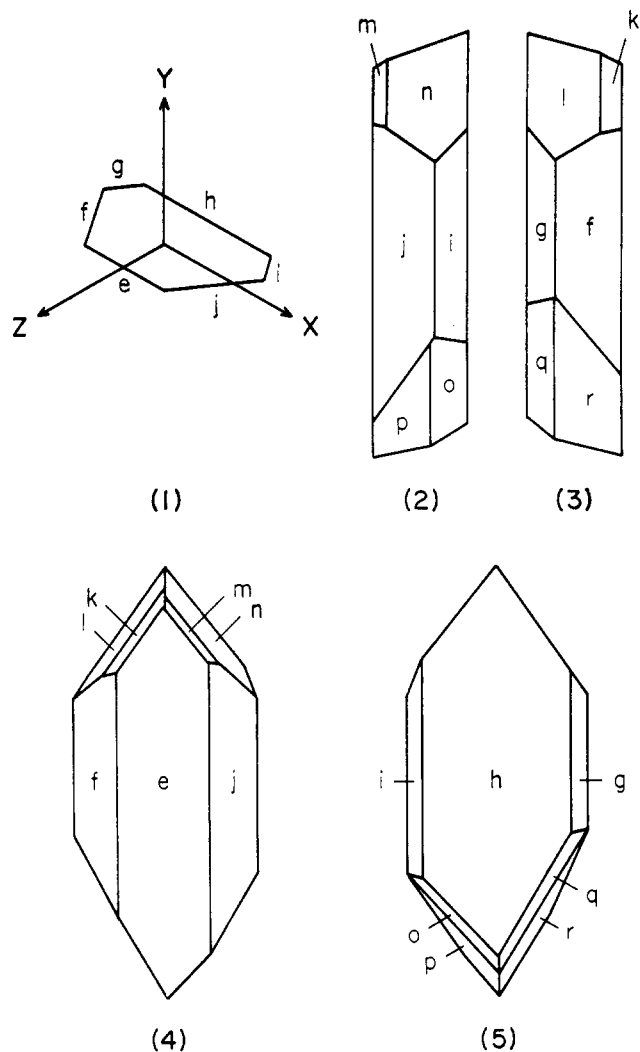
Fig. 1.—One typical habit of the fumaric acid–urea crystal. (1) The definition of the axis system with respect to the crystal morphology. (2)–(5) The views of the crystal along the x, $-x$, z, and $-z$ directions, respectively.

taining the e.s.r. spectra. Prolonged heat treatment only diminished the e.s.r. signal intensity and did not change the splittings or relative intensities of the major lines of the spectra.

Results

The e.s.r. spectra obtained with the magnetic field along the x, y, and z crystalline directions are given in

TABLE I
INTERFACIAL ANGLES OF THE FUMARIC ACID–UREA CRYSTALS

Angle[a]	Intersecting faces[b]
13° 40'	l:k, n:m, p:o, r:q
32° 55'	f:k, m:j, i:o, q:g
40° 25'	l:f, j:n
56° 25'	g:h, h:i, j:e, e:f, g:l, n:i, r:f, j:p
65° 20'	k:e, m:e, o:h, q:h
67° 25'	f:g, i:j
100° 55'	h:n, h:l, e:p, e:r
107° 15'	l:n, k:m, o:q, p:r

[a] The exterior angles (±15') formed by the lines normal to the two intersecting faces. [b] The faces are those of the habit illustrated in Fig. 1.

Fig. 2. The g-value of the e.s.r. spectra was nearly isotropic, and the maximum range for the xy, yz, and xz planes was from 2.0027 to 2.0046 ± 0.0003. The spec-
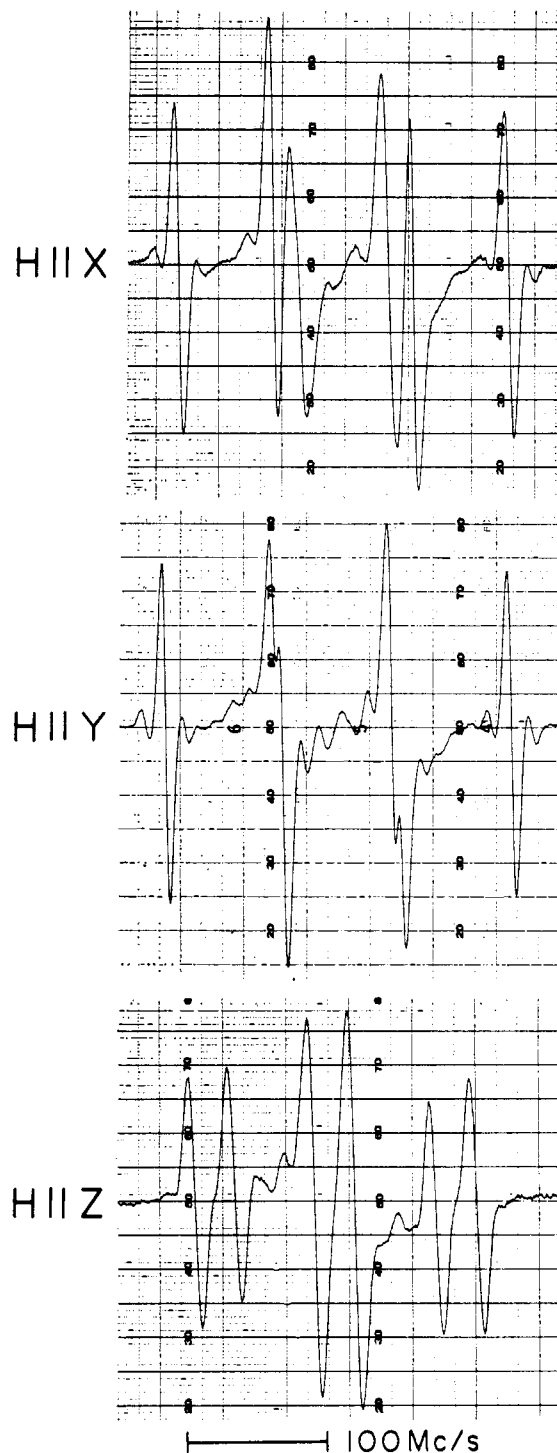
Fig. 2.—The e.s.r. spectra of an X-irradiated fumaric acid-urea crystal with the magnetic field parallel to the x, y, and z crystalline axes, respectively. The crystal was heated (50–70°) for 1 hr. prior to recording these spectra. Continued heating decreased the intensity but left the major features of the spectra unchanged.

tra of Fig. 2, and all other e.s.r. spectra obtained from the (heat-treated) crystals are attributed to the radical

$$HO_2C - \overset{H_\beta}{\underset{H_\beta \ H_\alpha}{C_2}} - \overset{\cdot}{C_1} - CO_2H$$
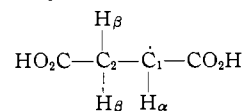
This radical has previously been produced by the *removal* of one α-proton from succinic acid[13,14] and from

(13) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).
(14) D. Pooley and D. H. Whiffen, *Mol. Phys.*, **4**, 81 (1961).

dl-aspartic acid[15] (by X- or γ-irradiation). However, in X-irradiated fumaric acid–urea crystals the above radical is formed by the *addition* of a hydrogen atom to an undamaged fumaric acid molecule. Observations of free radicals formed by H atom addition at room temperature are relatively infrequent compared to observations of radicals produced by removal of H atoms (or carboxyl groups, etc.). H atom addition has, however, been observed in X-irradiated tiglic acid[16] and in X- and γ-irradiated furoic acid.[16,17]

The e.s.r. spectra of X-irradiated fumaric acid–urea crystals are complex for arbitrary orientations of the magnetic field, and there are apparently several magnetically distinguishable orientations of the above radical. However, the spectra are always dominated by at most two orientations of the radical, and these two orientations account for at least two-thirds of the total e.s.r. signal intensity. We will be concerned here with the two major orientations of the radical and will not discuss further the multiple orientations which produce low-intensity e.s.r. spectra (it was not possible to resolve completely these low-intensity signals).

The two major orientations of the fumaric acid radical gave the same e.s.r. spectra in the yz plane and approximately the same spectra in the xz plane. These were the only two planes for which reasonably accurate coupling constant data could be obtained. As shown in Fig. 2, the e.s.r. spectra of all radical orientations are approximately superimposed when the magnetic field is along the x, y, or z crystalline axes. Along these three directions the values of the approximately magnetically equivalent β-proton coupling constants are 86, 85, and 84 Mc./sec. (± 3 Mc./sec.), respectively. The β-proton splittings for other orientations of the magnetic field differ at most by a few Mc./sec. from these values.

The α-proton data were reduced to tensor form using the usual spin Hamiltonian[2] (neglecting the nuclear Zeeman term). It was found that the spectra arising from the major orientations of the radical could be reconstructed to within ± 1.5 Mc./sec. for an arbitrary direction of the magnetic field provided two α-proton tensors were used. These two tensors are related by a twofold rotation about the x axis and are given, along with the eigenvectors and eigenvalues, in Table II. (Two tensors related by a twofold rotation about the y axis reproduce the major features of the spectra, but the agreement is much poorer than it is for the tensors of Table II.) Although the tensors of Table II reproduce

TABLE II

α-PROTON TENSOR OF THE $HO_2CCH_2CHCO_2H$ RADICAL IN THE FUMARIC ACID–UREA CRYSTAL[a–c]

Tensor	Eigenvalues	Eigenvectors
$(-)\begin{pmatrix} +65.9 & \pm19.1 & \pm0.5 \\ \pm19.1 & +78.2 & -3.5 \\ \pm0.5 & -3.5 & +28.9 \end{pmatrix}$	$(-)92.2$ $(-)52.2$ $(-)28.5$	$(-0.586, \mp0.809, \pm0.040)$ $(+0.808, \mp0.580, \pm0.104)$ $(-0.061, \pm0.094, \pm0.994)$

[a] The tensor is in the x, y, z crystalline coordinate system defined in Fig. 1. [b] All tensor elements are reported in Mc./sec. The absolute values only are determined (the eigenvalues are known to be negative[2]). [c] The direction cosines relative to the x, y, z axes.

(15) T. S. Jaseja and R. S. Anderson, *J. Chem. Phys.*, **36**, 2727 (1962).

(16) A. L. Kwiram and H. M. McConnell, *Proc. Natl. Acad. Sci. U. S.*, **48**, 499 (1962).

(17) R. J. Cook, J. R. Rowlands, and D. H. Whiffen, *Mol. Phys.*, **7**, 57 (1963).

the α-proton coupling constants to within ± 1.5 Mc./sec., the absolute accuracy is limited to ± 3 Mc./sec. because of the imperfect superposition of the multiple orientations of the radical. Laue X-ray diffraction patterns of the fumaric acid–urea crystal indicate the crystal structure is monoclinic and that the twofold axis lies along the x direction. This confirms the results obtained from the anisotropic α-proton e.s.r. data.

E.s.r. data were also recorded for the succinic acid–urea crystals in order to compare the radical orientations with those of the fumaric acid–urea system. The morphology of the succinic acid–urea crystals is very similar to that of the fumaric acid–urea crystals (for example, f : g and g : h are 68° 5′ ± 15′ and 55° 55′ ± 15′, respectively, for the succinic acid–urea crystal). After X-irradiation at room temperature the only free radical observed is the one resulting from the removal of one α-proton from the succinic acid molecule, and it is therefore the same as the fumaric acid radical. The values of the α-proton coupling constants along the x, y, and z axes of the succinic acid–urea crystal are 69, 81, and 29 Mc./sec. and are identical, within the limits of experimental accuracy, with the values 69, 80, and 29 Mc./sec. along the corresponding axes of the fumaric acid–urea crystal. The β-proton coupling constants of the radicals in the two crystals are very nearly the same along the x, y, and z axes, respectively, and the e.s.r. spectra with the magnetic field in an arbitrary direction are qualitatively the same for the two crystals.

The crystals formed between adipic acid and urea and pimelic acid and urea were also briefly investigated. In both cases X-irradiation produced the usual long-lived free radical formed by the removal of one α-proton from the parent dicarboxylic acid. The morphology and radical orientations of the adipic acid–urea crystals are similar to those of the fumaric acid–urea and succinic acid–urea systems. However, the two β-protons of the adipic acid radical are nonequivalent, typical coupling constants being 105 and 83 Mc./sec., and the e.s.r. spectra due to a second radical are observed (this latter observation has been briefly mentioned elsewhere[10]). The two β-protons of the pimelic acid radical are also magnetically nonequivalent, and the e.s.r. spectra exhibit the usual anisotropy associated with an α-proton (in the absence of molecular motion). The crystals of pimelic acid–urea obtained from methanol had poorly developed faces and no radical orientation study of this system was attempted.

Discussion

The Relation between the Free Radical Axes and the Crystal Coordinates.—Free radicals of the type $R\overset{.}{C}HCO_2H$ have been extensively studied by e.s.r. in X-irradiated crystalline dicarboxylic acids and the diagonal tensor elements of all of these radicals are approximately the same.[2] From a comparison of the eigenvalues of the α-proton tensor (Table II) with the values reported for similar radicals in crystals with known crystal structures, it is readily seen that the eigenvalues 28, 52, and 92 Mc./sec. correspond, respectively, to (1) the direction along the C_1–H_α bond, (2) the axis of the 2p orbital on C_1, and (3) a direction perpendicular to (1) and (2). These directions are commonly referred to as the molecular Cartesian z', x', and y' axes, respectively. The direction cosines of the x',

y', z' axes with respect to the crystalline x, y, z axes are given in Table II. From Table II it is seen that the C_1-H_α bonds of both radical orientations lie nearly along the crystalline z direction and the 2p orbitals containing the unpaired electrons lie approximately in the xy plane and are inclined $\sim 36°$ to the x axis of the crystal.

The β-Proton Coupling Constants.—The β-proton coupling constants a_β, in the absence of molecular motion, are given by the approximate relation $a_\beta = R(\theta)\rho_C{}^\pi = \rho_C{}^\pi B^0 \cos^2\theta$ where B^0 is a constant, $\rho_C{}^\pi$ is the spin density in the $2p_{x'}$ orbital on C_1, and θ is the angle between the axis of the $2p_{x'}$ orbital on C_1 and the projection of the C_2-H_β bond onto a plane which is perpendicular to the C_1-C_2 bond.[13] [$R(\theta)$ is just the constant of proportionality between $\rho_C{}^\pi$ and a_β.] If there exist small amplitude oscillations about the C_1-C_2 bond, then the principal effects on the above equation relating a_β and θ are to decrease the apparent value of B^0 and to add a small constant term, A^0.[18,19] However, if there exist very large molecular motions about the C_1-C_2 bond (e.g., free rotation) then the θ-dependence will be averaged out and $a_\beta \simeq \rho_C{}^\pi B^0/2$. Therefore, the equivalence of the two β-protons of the fumaric acid radical indicates that one of the four following situations exist: (1) the value of θ for each β-proton is $30°$; (2) the value of θ for each β-proton is $60°$[20]; (3) the β-protons are undergoing limited torsional motion about the 30 or 60° positions; or (4) the β-protons are undergoing very large amplitude oscillations about the C_1-C_2 bond. The choice between these possible explanations is made by comparing the values of a_β calculated from the above equation with the experimentally observed a_β, assuming a known value of $\rho_C{}^\pi B^0$. Taking $\rho_C{}^\pi B^0$ to be in the range 130–140 Mc./sec. obtained from similar radicals with rotating methyl groups attached to C_1,[2,19] a^β for $\theta = 30°$ ranges from 97 to 105 Mc./sec. The observed values lie somewhat below this range, suggesting that the β-protons of the fumaric acid radical are undergoing limited motion about the 30° equilibrium positions. Therefore, the time-average positions of all four carbon atoms and the α-proton lie in one plane, and the β-protons are inclined 60° to this plane. The orientation of this plane is obtained from the α-proton tensor data of Table II.

Comparison of the Fumaric Acid–Urea Crystal with Other Dicarboxylic Acid–Urea Crystals.—Urea has been found to form mixed crystals with a wide variety of molecules and these crystals have been the subject of numerous investigations. The urea inclusion compounds are the best known of these systems and they are formed between urea and the derivatives of the straight-chain hydrocarbons. The inclusion compounds are hexagonal crystals in which the hydrocarbon molecules fit loosely into cavities formed by hydrogen-bonded urea molecules. The centers of the oxygen atoms of the urea molecules lie in the edges of a regular hexagonal prism, and the unit cell is composed of six urea molecules spiraled about the prism.[21,22] Because of the absence of strong interactions between the urea molecules and the hydrocarbon molecules, the latter undergo a high degree of complex molecular motion in the tubular cavities.[19,23] Another distinguishing property of the inclusion compounds is that the urea and hydrocarbon molecules do not, in general, crystallize in whole-number ratios.[11,22,24] This follows from the fact that the tubular structures have more or less fixed dimensions, whereas the hydrocarbon molecules may vary in length. These three properties of the urea inclusion compounds: (1) hexagonal crystal structures, (2) large degree of motion of the guest molecule, and (3) definite, but (in general) nonintegral composition, provide convenient means of identifying the urea-inclusion compounds.

Urea also forms crystals which are not of the inclusion compound type. Schlenk[11] has found that crystals formed between urea and acetone (1:2.8), adiponitrile (1:1), suberonitrile (1:5.7), trichloroacetic acid (1:1), malonic acid (1:2), succinic acid (1:2), adipic acid (1:2), and several dihalogenated hydrocarbons of short-chain length exhibit X-ray powder diffraction patterns unlike those of the hexagonal urea inclusion compounds. Oxalic acid–urea crystals (1:2) and dioxane–urea crystals (1:1, 1:2) also differ from the hexagonal inclusion crystals.[21,25] (The numbers in parentheses following all of these compounds are the mole ratios of the hydrocarbon derivatives to urea.) Most of these crystals are composed of whole-numbered ratios of the two components and are often referred to as "molecular compounds." The only one of the above crystals which has been studied in detail by X-ray crystallography is the oxalic acid–urea crystal.[25] Oxalic acid–urea crystals are monoclinic (space group P2$_1$/c) and possess a layer structure in which the oxalic acid molecules and urea molecules are held together by strong hydrogen bonds. The layers are held together by van der Waals forces and there is no indication that the crystal is a salt formed between the acid and urea molecules.

It is evident from the e.s.r. data and Laue X-ray data that the fumaric acid–urea crystals are not urea inclusions compounds of the type discussed above. The crystal structure is not hexagonal, the motion of the fumaric acid radical is very limited, and the composition of the crystal is $\sim 1:2$. Although our data does not permit a detailed analysis of the structure of these crystals, it is of interest to compare the e.s.r. data with those of the other dicarboxylic acids. The orientations of the free radical in the fumaric acid–urea crystals are essentially the same as those of the succinic acid–urea crystal. Since the free radicals normally remain in nearly the same positions as the undamaged molecules, this is a strong indication that the orientations of the undamaged molecules in the two crystals are the same.

The e.s.r. spectra of adipic acid–urea crystals and of pimelic acid–urea crystals indicate that the radical

(18) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

(19) O. H. Griffith, *ibid.*, in press.

(20) Throughout this discussion it is assumed that the σ-bonds involving carbon atom 1 are sp^2 hybridized. Therefore the H–C$_1$–H dihedral angle is taken to be 120°, and (in the absence of motion) the values of θ must be either 30 or 60° in order for the β-protons to be magnetically equivalent. These points have been discussed extensively in the literature. See for example: (a) T. Cole, H. O. Pritchard, N. R. Davidson, and H. M. McConnell, *Mol. Phys.*, **1**, 406 (1958); (b) H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, *J. Am. Chem. Soc.*, **82**, 766 (1960); (c) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); and (d) J. R. Rowlands and D. H. Whiffen, *Mol. Phys.*, **4**, 349 (1961).

(21) A. E. Smith, *Acta Cryst.*, **5**, 224 (1952).

(22) K. A. Kobe and W. G. Domask, *Petrol. Refiner*, **31**, No. 3, 106 (1952).

(23) D. F. R. Gilson and C. A. McDowell, *Mol. Phys.*, **4**, 125 (1961).

(24) O. Redlich, C. M. Gable, A. K. Dunlop, and R. W. Miller, *J. Am. Chem. Soc.*, **72**, 4153 (1950).

(25) J. H. Sturdivant, A. Schuch, and L. L. Merritt, Jr., *Struct. Rept.*, **13**, 477 (1950). (Also, J. H. Sturdivant, unpublished results.)

orientations are not related by hexagonal (or trigonal) symmetry operations and therefore the crystals are not hexagonal urea inclusion compounds. Sebacic acid–urea crystals, on the other hand, are hexagonal and the e.s.r. spectra indicate that the sebacic acid radical is undergoing large amplitude oscillations.[19] This motion removes the α-proton anisotropy in a plane perpendicular to the hexagonal needle axis, and produces an easily recognizable isotropic spectrum in this plane. Similar results are obtained for 1,12-dodecanedioic acid, and crystals of sebacic acid–urea and 1,12-dodecanedioic acid–urea are apparently urea inclusion compounds. Therefore, there is a transition from hexagonal urea inclusion crystals to crystals of lower symmetry as the saturated dicarboxylic acid chain length is shortened.[26] From the e.s.r. data it is evident that

(26) This transition was first noted in the series of acids: succinic acid, adipic acid, and sebacic acid by Schlenk[11] from X-ray powder diffraction

some of the short-chain length acid molecules have similar orientations in the nonhexagonal crystals. In particular it is interesting to note that the orientations of the acid radicals are the same in the two crystals, succinic acid–urea and fumaric acid–urea. The positions of the urea molecules cannot be determined from e.s.r. data since urea does not produce stable paramagnetic damage sites at room temperature.

data. Of course, neither the powder diffraction data nor the single crystal e.s.r. data are a substitute for a (single crystal) X-ray crystallographic investigation. However, e.s.r. does provide a method for investigating the structure, positions, and molecular motion of the X-ray produced free radicals in the crystals.

Mercury-Photosensitized Decomposition and Collision Broadening of Resonance Line

BY KANG YANG

A low-pressure mercury lamp commonly employed in photochemical investigations emits 2537 resonance radiation with a Doppler half-breadth 4.35 times that of the absorption line. This mismatch in the two line shapes drastically reduces light absorption in spite of the high absorption coefficient; thus, a 4.8-cm. long cell with mercury at 25° absorbs only 56% of the incident light. The addition of foreign gases sharply increases the light absorption, because the absorption line becomes collision broadened. From the dependence of the light absorption on foreign gas pressures, the Lorentz half-breadths for various gases are determined under experimental conditions commonly used in photosensitized decompositions. Experimental broadening cross sections estimated from the Lorentz half-breadths agree well with theoretical ones if it is assumed that the line broadening occurs by the formation of a loosely bound activated complex. The quantum yield of hydrogen in the photosensitized decompositions of ethane, propane, n-butane, isobutane, and neopentane increases with increasing pressure; $\phi^{-1} = \phi_\infty{}^{-1} + bp^{-1}$ even after making appropriate corrections for the line broadening. The high pressure limit of quantum yield, ϕ_∞, is found to be approximately unity for all paraffins. In the decomposition of ethylene, the correction due to the line broadening does not alter the already known rate equation, $\phi^{-1/2} = \phi_0{}^{-1/2} + b'p$. This correction, however, significantly increases the estimated lifetime of excited ethylene. The only important primary process in ethylene decomposition is the formation of molecular hydrogen, because the low pressure limit of the quantum yield, ϕ_0, is found to be unity.

Introduction

The absorption of 2537 Å. light by ground-state mercury atoms results in the following transition

$$Hg(^1S_0) + h\nu \longrightarrow Hg(^3P_1) \qquad (1)$$
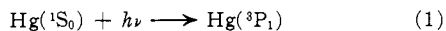
Resulting excited atoms have been extensively employed to photosensitize various gas phase reactions.[1] Elucidation of the mechanism of these reactions often demands detailed information on the dependence of the absorption coefficient, $k(\nu)$, on various experimental parameters. Among them, the pressure of foreign gases is of prime importance. Most gases employed in the photosensitized reactions do not absorb at 2537 Å.; nevertheless, they profoundly affect $k(\nu)$, because $k(\nu)$ becomes pressure broadened.[2]

Though its importance has been repeatedly emphasized,[1,2] the variation of $k(\nu)$ with foreign gas pressures is usually neglected in mechanism discussions. An ap-

(1) For example, see (a) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941; (b) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954.

(2) For example, see A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," The Cambridge University Press, Cambridge, 1961.

parent justification seems to be that, due to high $k(\nu)$, the light is completely absorbed; and any variation in the total amount of light absorbed is governed by the resonance lamp itself and not by possible changes in $k(\nu)$. This is true, provided one considers only a single frequency, ν_0, at which $k(\nu)$ is maximum. For example, the fraction of light passing unabsorbed through a 4.8-cm. long cell with mercury reservoir at 25° can be estimated to be only $\exp(-38.6)$.

More properly, however, the whole frequency range contributing to the resonance transition should be considered. Let $E(\nu)$ be the frequency distribution of the emission line; then the transmitted light between ν and $\nu + d\nu$ at a path length of l cm. is $E(\nu) \exp(-k(\nu)l)$; hence the absorption, A, becomes

$$A = 1 - \frac{\text{transmitted light}}{\text{incident light}}$$

$$= 1 - \frac{\int_0^\infty E(\nu) \exp(-k(\nu)l)d\nu}{\int_0^\infty E(\nu)d\nu} \qquad (2)$$