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Reprinted from the Proceedings of the NATIONAL ACADEMY OF SCIENCES
Vol. 48, No. 11, pp. 1877–1880. November, 1962.

*ELECTRON SPIN RESONANCE OF X-IRRADIATED ORGANIC INCLUSION COMPOUNDS**

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Communicated by Norman Davidson, September 24, 1962

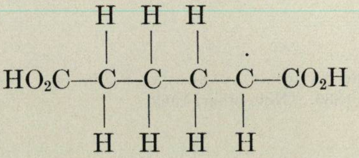
In recent years, there have been many electron-spin-resonance (ESR) investigations of X- and γ-irradiated single crystals of organic compounds.[1] Studies of the anisotropic hyperfine spectra of the trapped radicals have been used both to identify the radicals formed and to determine their electronic structure. However, there are two troublesome limitations to this technique: (1) Many organic compounds of theoretical importance are liquids at room temperature, and (2) the crystal structures of many compounds of interest have not been determined. The purpose of this note is to report the use of organic inclusion compounds for the investigation of long-lived free radicals produced by X-irradiation.

Inclusion compounds are crystalline compounds in which two or more components are associated without ordinary chemical bonds and in which one of the components fits into cavities formed by the other. The cavity formed by the host may be tube-shaped or cage-shaped, or it may consist of open layers.[2]

Perhaps the most useful for X-ray damage studies are the urea and thiourea crystalline inclusion compounds. In these compounds, the cavity formed by the host (e.g., urea) is tube-shaped. Crystallographic investigations of the urea and thiourea compounds have been reported,[3–6] and a large variety of organic molecules have been found to include with urea and thiourea[7–9] (in general linear molecules include with urea and highly branched or cyclic compounds include with thiourea). In addition, urea and thiourea have been reported to yield a negligible concentration of free radicals on exposure to X-irradiation.[10] Using urea compounds as examples, three applications of organic inclusion compounds are reported below. These are: (1) The identification of stable free radicals not observed in X-ray-damaged single crystals of the molecule itself, (2) the study of radiation damage in a molecule with unknown crystal structure, and (3) the investigation of X-ray damage of a compound which is a liquid at room temperature.

Single crystals of the adipic acid ($HO_2C(CH_2)_4CO_2H$)-urea inclusion compound were X-irradiated at room temperature. The ESR spectra indicate the presence of two stable free radicals, I and II, present in different concentrations.

The radical present in the greater concentration is



$$HO_2C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{\cdot}{\underset{H}{C}}-CO_2H$$

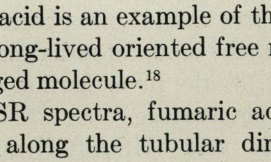
I

This radical has been thoroughly studied in a γ-irradiated single crystal of adipic acid.[11]

The ESR spectra of radical I in the urea inclusion compound unambiguously identified the orientation of I, and hence the direction of the tubular cavity, with respect to the external crystal morphology. The crystals grown from an aqueous solution elongate along the tube direction, making the adipic acid chain direction easily identifiable. From the ESR spectra, it is evident that all molecules of I are magnetically equivalent when the laboratory magnetic field is in a direction perpendicular to the tubular cavity. Therefore, there exists either a unique conformation of I in the cavity or two conformations related by a twofold rotation. As expected, all molecules of I are magnetically equivalent when the magnetic field is parallel to the tubular cavity.

In addition to the 6- to 8-line spectrum of I, a single line was observed and is attributed to the presence of radical II. Spectroscopic splitting factor data and limited C^{13} coupling constant data are reminiscent of the CO_2^- radical ion previously detected in γ-irradiated single crystals of sodium formate.[12] Radical II is apparently associated with the pink color acquired by the adipic acid-urea inclusion crystal during X-irradiation. Upon heat treatment, both the pink color and the ESR spectrum of radical II disappear, while the spectrum of I remains. A similar pink color persists for a few seconds after X-irradiation in single crystals of adipic acid, possibly indicating the presence of II as a transient radical in the adipic acid crystal. Sebacic acid analogues of I and II have also been observed in single crystals of the sebacic acid-urea inclusion compound.

The ESR spectrum of X-irradiated single crystals of the fumaric acid[13] (trans $HO_2CCH{=}CHCO_2H$)-urea inclusion compound is dominated by the six-line spectrum of radical III:



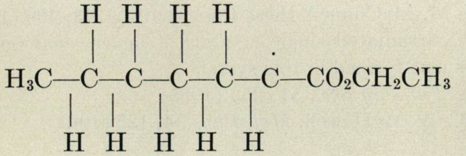
$$HO_2C-\overset{H}{\underset{H}{C}}-\overset{\cdot}{\underset{H}{C}}-CO_2H$$

III

This radical has previously been produced in X- and γ-irradiated single crystals of succinic acid[14, 15] and in X-irradiated single crystals of *dl*-aspartic acid.[16] The formation of III from fumaric acid is an example of the "hydrogen aufbau process"[17]; that is, the formation of a long-lived oriented free radical by the addition of a hydrogen atom to the undamaged molecule.[18]

As confirmed by the ESR spectra, fumaric acid-urea crystals, like those of adipic acid-urea, elongate along the tubular direction. There exist, however, multiple orientations of radical III in the tubular cavity.

The liquid compound investigated was ethyl heptanoate. The ESR spectrum of X-irradiated single crystals of the ethyl heptanoate-urea compound consists of six lines and is attributed to the radical



$$H_3C-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\cdot}{C}}-CO_2CH_2CH_3$$

IV

Again, the crystals (grown from methanol) were elongated along the tubular direction, simplifying the analysis of the spectra. At 300°K and with the magnetic field perpendicular to the tubular cavity, the spectrum of IV is isotropic. As the temperature is lowered, this spectrum broadens until at 77°K the spectrum consists of eight broad lines. This behavior suggests that at room temperature radical IV is undergoing a large degree of molecular motion, if not actually rotating in the tubular cavity. These observations are consistent with both dielectric absorption[19] and nuclear magnetic resonance[20] investigations of urea compounds with long-chain hydrocarbons and their derivatives.

In addition to the above compounds, ESR data have been taken of X-irradiated powders of nitrile, amide, carbonyl, alcohol, thiol, ether, unsaturated ($R_2C{=}CR_2$ and $RC{\equiv}CR$), and other derivatives of the straight chain hydrocarbons. Useful ESR data have also been recorded for organic inclusion compounds of thiourea and for the clathrates of hydroquinone. In particular, single crystals of cycloheptatriene-thiourea, cyclooctatetraene-thiourea, and formic acid-hydroquinone yield high concentrations of free radicals on exposure to X-irradiation. In all the above-mentioned urea, thiourea, and hydroquinone inclusion compounds, the free radical concentration produced from the host was negligible compared to that produced from the included molecules.

A detailed investigation of some of these organic inclusion compounds is in progress.

We are greatly indebted to A. L. Kwiram for helpful discussions.

* Supported by the National Science Foundation.

† National Science Foundation Predoctoral Fellow.

‡ Alfred P. Sloan Fellow.

§ Contribution No. 2889.

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