The Electron Spin Resonance of Irradiated Single Crystals of Dichloroacetamide

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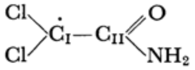
Although there have been many ESR studies of irradiated single crystals, only Pooley and Whiffen[1] have reported the chlorine coupling constant in organic radicals. We will here report the chlorine coupling found in X-irradiated single crystals of dichloroacetamide. Simultaneously we will report on the hyperfine couplings for N and H nuclei of the amide group, which have not been investigated so far.

Single crystals of dichloroacetamide were prepared from methanol solutions by slow evaporation. The crystals were prismatic, with a well-developed face. An orthogonal axis system, xyz, was defined for the sake of convenience. The x and the y axes were selected in the developed face, with the x axis parallel to the elongated direction of the crystal. The y axis was found by ESR measurements to be along the monoclinic unique axis.[2] The crystals were X-irradiated at room temperature to 1 Mrad. The ESR spectra of the irradiated crystals were measured at 9.5 kMc./sec.

Figure 1 shows a typical ESR spectrum of the irradiated single crystals of dichloroacetamide. The spectrum is a septet with an ill-resolved substructure and with an intensity ratio of approximately 1 : 2 : 3 : 4 : 3 : 2 : 1. The septet is to be expected for a radical with two equally coupling chlorine (spin 3/2) nuclei; this indicates that the radicals produced in dichloroacetamide are of the form;



A similar radical, $F_2C_IC_{II}ONH_2$, was found in

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1) D. Pooley and D. H. Whiffen, *Spectrochim. Acta*, **18**, 291 (1962).

2) C. Bodewig, *Z. Krist.*, **5**, 554 (1881).

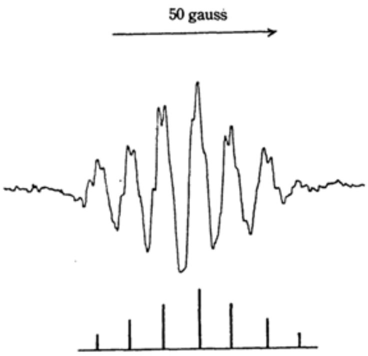

Fig. 1. Second-derivative ESR spectrum of an X-irradiated single crystal of dichloroacetamide for the magnetic field making an angle of 75° with the x axis in the xz plane.

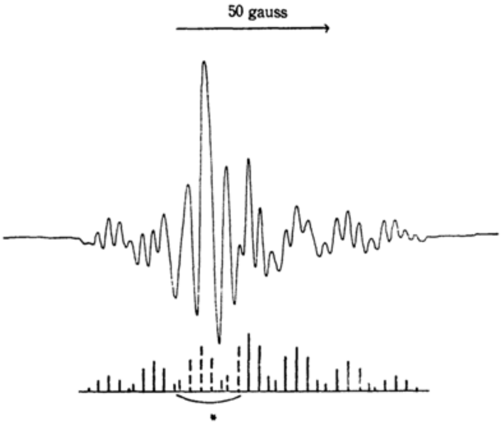

Fig. 2. Second-derivative ESR spectrum of an irradiated single crystal of dichloroacetamide for the magnetic field along the direction (0.28 0.63 0.72).

* There are overlapping lines due to alternative radicals whose orientations are related by the symmetry operations to each other.

TABLE I. PRINCIPAL VALUES AND DIRECTION COSINES FOR A^{Cl} OF THE RADICAL Cl_2CCONH_2

Principal values		Direction cosines with respect to the xyz axis system		
A_1^{Cl}	3G	0.96	∓ 0.20	-0.20
A_2^{Cl}	5G	0.02	± 0.75	-0.66
A_3^{Cl}	14G	0.28	± 0.63	0.72

irradiated trifluoroacetamide,[3] where the radial is planar and where the F_2CCON skeleton is in the nodal plane of a π orbital on C_I. The fluorine coupling constant has a cylindrical symmetry, with the cylindrical axis perpendicular to the radical plane. A similar situation may be anticipated in the case of dichloroacetamide. However, the chlorine quadrapole coupling gives rise to a breakdown in the usual selection rule, $\Delta M_I=0$; this makes it difficult to analyze the ESR spectra. Measurements show that the ESR spectra exhibit a considerably different appearance from the simple septet when the coupling constant of the chlorine is smaller than about $7\,G$.[4] A crude estimation has been made of the principal values of the coupling constant by a least-squares analysis of the angular dependence of coupling constants larger than $7\,G$. The results are shown in Table I; these results can be used in considering the radical orientation, but they are too rough to make it possible to discuss the electronic structure of the radical in detail.

The substructure of the septet is resolved into a quintet for a magnetic field perpendicular to the radical plane. The substructure is different from the superposition of the hyperfine structure due to ^{35}Cl and ^{37}C.[5] This can well be explained by equal couplings of one N and two H nuclei of the amide group, as is shown in Fig. 2. There is some delocalization of the unpaired electron in the π system from the carbon C_I to the nitrogen, and the unpaired electron would couple with N and H nuclei. The calculation of Hückel MO[6] shows that the spin density on the nitrogen of the amide group increases in the order of: F_2CCONH_2[3]$<$ $Cl_2CCONH_2 \approx FHCCONH_2$[7]$<R_2CCONH_2$ (R:H, CH_2 or CH_3). This indicates that $FHCCONH_2$ should give N and H couplings with the same order of magnitude as those in Cl_2CCONH_2. Moreover, R_2CCONH_2 and F_2CCONH_2 should give couplings with larger and smaller magnitudes respectively. The experimental data[3,6,8] are consistent with the prediction; this supports the preceding mechansim of the N and H couplings. The couplings will be treated in detail in discussing irradiated succinamide.[8]

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3) R. J. Lontz and W. Gordy, *J. Chem. Phys.*, **37**, 1357 (1962). According to this paper, the N and H couplings are too small to be detected.

4) The quadrapole effect is very intense when the quadrapole coupling is of a magnitude comparable to that of the hyperfine coupling. From this fact it may be inferred that the quadrapole coupling, $3eqQ/4I(2I-1)$, is$\sim 7G$(20 Mc.) and that, therefore, $eqQ=\sim 80$ Mc. in this radical.

5) T. G. Castner and W. Känzig, *J. Phys. Chem. Solids*, **3**, 178 (1957).

6) M. Kashiwagi, unpublished results.

7) R. J. Cook, J. R. Rowlands and D. H. Whiffen, *Mol. Phys.*, **7**, 31 (1963—1964). In this paper it is left undecided whether or not the observed couplings are due to N and H nuclei of the amide group.

8) M. Kashiwagi, *J. Chem. Phys.*, **44**, 2823 (1966).