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ESR Study of Irradiated Single Crystals of Acetamidine Hydrochloride*

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Abstract

Two radicals have been identified in γ -irradiated single crystals of acetamidine hydrochloride. Material irradiated and observed at 77°K shows only the ESR spectrum characteristic of the V center Cl_2^- . On warming to 125°K the spectrum of the V center was replaced by that of a new radical which showed hyperfine interaction with two equivalent α protons plus weaker interaction with two more distant protons. This second radical is believed to be $[\cdot\text{CH}_2\text{C}(\text{NH}_2)_2]^+$ formed by abstraction of a methyl hydrogen of an undamaged acetamidinium ion by the hole center. The g and $A(\text{Cl})$ tensors for Cl_2^- and the hydrogen hyperfine splitting tensor $A(\text{H})$ for the second radical are reported and discussed.

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INTRODUCTION

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Halogen molecule-anions of the type Cl_2^- (called V centers or hole centers in solid state physics) are well-known in irradiated alkali and alkaline earth halides,¹ the ESR parameters of Cl_2^- have been determined

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1. T. Kastner and W. Känzig, J. Phys. Chem. Solids 3, 178 (1957);
F. W. Patten and M. J. Marrone, Phys. Rev. 142, 513 (1966); R. C. Catton
and M. C. R. Symons, J. Chem. Soc. (A), 446 (1969).

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for several irradiated ionic chlorides and the structure of V centers has been discussed.²

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2. P. W. Atkins and M. C. R. Symons, The Structure of Inorganic Radicals, Elsevier, New York, 1967.

Such species have only rarely been found when more complex halides are irradiated, breakage of covalent bonds often being the preferred process; however, the only identifiable radical in hydroxylamine hydrochloride³ irradiated at 77°K

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3. H. Ueda, J. Chem. Phys. 41, 285 (1964).

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was Cl_2^- and it was also found (along with an anion radical) in glycine hydrochloride⁴ irradiated at 4.2°K. The ESR parameters are rather similar

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4. H. C. Box, E. E. Budzinski and H. G. Freund, J. Chem. Phys. 50, 2880 (1969).

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for Cl_2^- in the latter two crystals, which are monoclinic, and in the alkali halides, except that the axial symmetry is lost in the crystals of lower symmetry. We report here an additional example of a V center which occurs as the only observable radical in acetamidine hydrochloride γ -irradiated at

77°K and observed at that temperature. The structure of a new radical, formed when the irradiated crystals are allowed to warm from 77°K to 125°K, is also proposed based on the observed proton hyperfine splitting tensors and the ESR spectra of deuterated crystals.

EXPERIMENTAL

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Acetamidine hydrochloride (Eastman Chemical Co.) was recrystallized from a saturated aqueous solution. The deuterated crystals were obtained by three recrystallizations from 99.84% D₂O (Stohler Isotope Chemicals). Single crystals were γ -irradiated at 77°K with a ⁶⁰Co γ -source for 3 hours with a dose rate of 2×10^6 rad/hr. The crystals were transferred without warmup to the TE₁₀₂ cavity of a Varian V-4502-04 ESR Spectrometer and spectra taken at 10° intervals in each of three mutually perpendicular crystallographic planes.

The unit cell and space group were determined by X-ray analysis. Unit cell dimensions were found to $a = 7.25 \text{ \AA}$, $b = 8.18 \text{ \AA}$, $c = 4.54 \text{ \AA}$, and $\beta = 104^\circ$. The crystal ^{is} monoclinic and systematic absences 001, $l = 2n$, correspond to space group $P2_1$ or $P2_1/m$. The observed density of 1.210 g/cc was measured by volume displacement in a mixture of n-pentane and carbon tetrachloride; also, a crystal of acetamidine hydrochloride dipped in liquid nitrogen was attracted to the walls of a silvered Dewar flask. Based on this latter observation and the experimental density, which leads to 2.01 molecules/unit cell, the space group $P2_1$ is assigned.

RESULTS

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The ESR spectrum of a single crystal of acetamidine hydrochloride irradiated and observed at 77°K is shown in Fig. 1(a) for the orientation in which the chlorine hyperfine splitting is a maximum. The basic seven-line pattern characteristic of Cl_2^- serves to identify this molecular ion and comparison with the calculated spectrum also given in Fig. 1(a) shows that other radicals, if present, do not provide strong enough ESR lines to permit their identification. The g and A tensors were evaluated from the ESR spectra in the usual manner⁵ and are given in Table I.

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5. A. Carrington and A. D. McLachlan, Introduction to Magnetic Resonance, Harper and Row, New York, 1967.
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When a crystal was allowed to warm from 77°K to 125°K the Cl_2^- spectrum disappeared and was replaced by a simpler spectrum which is basically a triplet of triplets with intensity ratios 1:2:1:2:4:2:1:2:1 as shown in Fig. 1(b) for $H \parallel c^*$. The magnitude of the larger triplet splitting indicates that it arises from two α hydrogens in a $\text{-CH}_{\alpha_1} \text{H}_{\alpha_2} \text{R}$ type radical. In certain orientations the spectrum becomes a quartet of triplets so the two α hydrogens have become inequivalent. The variation of the α_1 and α_2 proton splittings were therefore plotted as functions of magnetic field orientation (Fig. 2) and the hyperfine tensors for each determined from these plots by use of a computer program (Table I).

The smaller triplet splitting disappears for certain orientations of the magnetic field and is completely absent in the deuterated crystals as shown in Fig. 1(c) where again $H \parallel c^*$. The magnitude of this interaction

suggests that it arises from two amino hydrogens (γ hydrogens) which are equivalent at all orientations where it is observable. The corresponding tensor was estimated by Schonland's method⁶ and is given in Table 1 as H_{γ} .

6. D. S. Schonland, Proc. Phys. Soc. (London) 73, 788 (1959).

DISCUSSION

Cl₂⁻ Molecular-ion (77°K)

The values of the principal components of the chlorine hyperfine splitting tensor for Cl₂⁻ in irradiated acetamidine hydrochloride (103.1, 29.8, 10.0 gauss) may be compared with those reported for Cl₂⁻ in irradiated hydroxylamine hydrochloride³ (103.9, 32.1, 12.1), glycine hydrochloride⁴ (111, 42.5, 24.3) and potassium chloride¹ (101, 9, 9). The axial symmetry observed in the alkali halide matrices has been lost and the isotropic splitting is also larger in the monoclinic crystals. This behavior is reasonable since the Cl₂⁻ presumably interacts weakly with the surrounding molecules and these interactions will be asymmetric in monoclinic crystals. Also, the odd electron is essentially in a σ^* molecular orbital formed from p_z atomic orbitals on the chlorine atoms² and interactions with other species would tend to mix in some chlorine s orbital and increase the isotropic splitting. The components of the g tensor follow the general trend for V centers with one value near 2.000 and two near 2.004; the low g value and the large $A(Cl)$ value are parallel and define the direction of the C-Cl bond.

Radical Stable at 125°K

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The acetamidinium ion has a symmetrical structure which may be represented⁷ as a resonance hybrid of structures I and II. The radical

7. N. V. Sidgwick, The Organic Chemistry of Nitrogen, 3rd Ed., I. T. Millar and H. D. Springall, Eds., Oxford University Press, 1966.

we observe appears to have two nearly equivalent α hydrogens and this suggests that it has been formed by loss

of a hydrogen from the methyl group. Although the principal elements of the hyperfine tensors for the α hydrogens (-35.9, -23.1, 7.5 or -36.2, -19.0, -5.8) differ a bit from the usual values⁸ for a $\cdot\text{CHRR}'$ type radical

8. J. R. Morton, Chem. Rev. 64, 453 (1964).

[e.g., -32.4, -20.7, -10 in $\cdot\text{CH}(\text{COOH})_2$], and would equally well be accounted for as an $\cdot\text{NH} \begin{smallmatrix} \alpha_1 & \alpha_2 \end{smallmatrix} \text{H}$ coupling, we do not observe the rather large ^{14}N hyperfine interactions characteristic of the latter type of radical.⁹

9. K. N. Shrivistava and R. S. Anderson, J. Chem. Phys. 48, 4599 (1968).

They are sufficiently close to the values (-32.9, -21.9, -7.9) reported¹⁰

10. N. Cyr and W. C. Lin, J. Chem. Phys. 50, 3701 (1969).

for $\cdot\text{CH}(\text{CONH}_2)_2$ that we feel the radical is of the type $\cdot\text{CH}_2\text{R}$.

If simple loss of a methyl hydrogen, perhaps by reaction with Cl_2^- to give HCl and Cl^- , occurs the resulting species (III) should show interaction of the odd electron with two α hydrogens, two nitrogens and four amino nitrogens

if the geometrical arrangement of the radical was such that all the interactions were large enough to be observable. If this species (III) is indeed the radical which is stable at 125°K then the nitrogen hyperfine interactions must be less than the linewidths, which vary from 4 - 10G, and only two of the four amino hydrogens must be able to give an observable splitting. The first of these conditions is fairly often observed with no nitrogen splitting being observable⁸ in most amide radicals of the type $\cdot\text{CHRCOONH}_2$. The second condition is perhaps more difficult to believe although any hyperfine interaction from amino hydrogens in this type of radical is rare and it may be that only two of the hydrogen atoms are in the unusually favorable positions necessary to show an interaction. The only example of $\text{NH}(\gamma)$ type proton interactions appears to be the radical $\text{H}_2\text{NCOCH}_2\dot{\text{C}}\text{HCONH}_2$ in irradiated succinamide¹¹ where the amino protons

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

show a maximum hyperfine interaction of 6 G, very similar to our result.

It is, of course, possible that one of the amino groups has been lost from the radical but we have not been able to devise a plausible radical on the basis of such other possibilities. A knowledge of the crystal structure would help in settling this point.

ACKNOWLEDGMENT

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We are indebted to Professor H. A. Eick and Mr. Norman Fishel for assistance with the X-ray measurements.

Table 1. Principal values and direction cosines for the g and A tensors of radicals in irradiated acetamidine hydrochloride.

Tensor	Principal values <u>A</u> (or <u>g</u>)	<u>a</u> Isotropic	Anisotropic components	Direction Cosines (relative to a,b,c*)		
Cl ₂ ⁻ Molecular-anion						
A(³⁵ Cl)	103.1 gauss		55.5	0.01	0.99	-0.07
	29.8	47.6	-17.8	-0.52	0.07	0.85
	10.0		-37.6	0.85	0.03	0.52
g	2.0437			0.08	0.18	0.98
	2.0317			-0.97	-0.18	0.12
	2.0011			0.10	-0.96	0.16
$\left[\cdot\text{CH}_{\alpha_1} - \text{H}_{\alpha_2} - \text{C} \begin{matrix} \text{NH}_2 \\ \text{NH}_2 \end{matrix} \right]^+ \text{Radical}$						
A(H _{α₁})	-35.9		-13.7	0.79	0.49	-0.36
	-23.1	-22.2	-0.9	-0.58	0.44	-0.68
	-7.5		+14.7	-0.17	0.75	0.64
A(H _{α₂})	-36.2		-15.9	0.06	0.92	0.38
	-19.0	-20.3	+1.3	-0.61	0.34	-0.72
	-5.8		+14.5	-0.79	-0.19	0.58
A(H _Y)	-6.4		-2.3	0.83	-0.42	0.37
	-4.1	-4.1	0	0.40	-0.00	-0.91
	-1.7		+2.4	0.39	0.91	0.17

Fig. 1. (a) Second-derivative EPR spectrum of a 4-irradiated single crystal of acetanilide hydrochloride with the magnetic field 45° from the a axis in the ac plane. The spectrum was recorded at 77°K . The spectrum predicted for ^{14}N is shown underneath. (b) The spectrum of a crystal warmed to 125°K with the magnetic field parallel to the c axis. The spectrum computed from the parameters of Table I is shown underneath. (c) The spectrum of a crystal of irradiated $\text{CH}_3\text{C}(\text{NH}_2)_3\text{Cl}$ at the same temperature and in the same orientation as (b).

Fig.2. Angular variation of the hyperfine splitting for three protons of the radical stable at 135°K in Y-irradiated acetanilide perchlorate. Variation in the ab plane is shown at the top, in the bc plane in the center and in the ac plane at the bottom.