RECEIVED BY DTIC FEB 18 1970

MASTER

COO-1385-32

V Centers and Hydrogen Atoms in Irradiated Hydrazinium Dihalides

M. T. Rogers and J. C. Watson

Department of Chemistry, Michigan State University, East Lansing, Michigan 48823

Several paramagnetic hole centers of the type $X'X^{\bullet}$ ($X, X' = \text{Cl}, \text{Br}, \text{F}, \text{I}$) have been detected and studied in irradiated alkali and alkaline earth halides.^{1,2} They have also been observed in a few more complex

1. T. G. Kastner and W. Känzig, J. Phys. Chem. Solids, 3, 178 (1957).
2. W. B. Fowler, Ed., Physics of Color Centers, Academic Press, New York, 1968.
3. R. C. Catton and M. C. R. Symons, J. Chem. Soc. 2155 (1968).

irradiated halides including glycine hydrochloride,⁴ hydroxylamine hydrochloride⁵

4. H. C. Box, E. E. Budzinski and H. G. Freund, J. Chem. Phys. 50, 2880 (1969).
5. H. Ueda, J. Chem. Phys. 41, 285 (1964).

and acetamidine hydrochloride.⁶ These molecular ions have been called V centers¹

6. J. C. Watson and M. T. Rogers, unpublished results.

in solid state physics and show axial symmetry in the simple cubic crystals of the alkali and alkaline earth halides. The axial symmetry is lost in the monoclinic crystals⁴⁻⁶ but the g values and chlorine hyperfine interactions are not greatly changed, the principal difference being a larger isotropic splitting in the crystals of lower symmetry. We report here an ESR study

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Notwithstanding the United States, nor the Commission, nor any person acting on behalf of the Commission

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, in the extent that such employee or contractor of the Commission, or employee of such contractor, provides access to, or any information pursuant to the employment or contract with the Commission, or the employment with such contractor.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

of Cl_2^- in irradiated single crystals of hydrazinium dichloride, $\text{N}_2\text{H}_6\text{Cl}_2$, and of Br_2^- in $\text{N}_2\text{H}_6\text{Br}_2$, both at 77°K. Strangely, $\text{N}_2\text{H}_6\text{F}_2$ irradiated at 77°K did not show F_2^- but rather hydrogen atoms.

ESR studies of hydrazine and several of its salts have been reported but apparently none of the dihalides. Hydrazine itself is said to give the N_2H_3^+ radical⁷ while the presence of N_2H_4^+ in γ -irradiated

-
7. V. I. Tupikov, V. I. Tsivenko, S. Y. Pshezhetskii, A. G. Kotov and V. K. Milinchuk, Russ. J. Phys. Chem. 37, 65 (1963).
-

hydrazinium oxalate has been convincingly established by a complete single-crystal ESR investigation.⁸ This radical has also been found in an ESR

-
8. O. Edlund, A. Lund and Å Nilsson, J. Chem. Phys. 49, 749 (1968).
-

study of γ -irradiated ferroelectric lithium hydrazinium sulfate⁹ ($\text{LiN}_2\text{H}_5\text{SO}_4$),

-
9. R. Blinc, M. Schara and S. Poberaj, J. Phys. Chem. Solids, 24, 559 (1963).
-

using both polycrystalline material and single crystals, and in γ -irradiated hydrazinium monochloride powder.¹⁰ On the other hand γ -irradiated hydrazinium

-
10. A. G. Kotov and S. Y. Pshezhetskii, Russ. J. Phys. Chem. 38, 1046 (1964).
-

sulfate has been reported to give N_2H_4^+ from an analysis of the ESR spectra of polycrystalline material^{10,11} but on the basis of a partial single-crystal study the species was reported^{12,13} to be N_2H_5^+ . It is likely that all these studies

-
11. J. A. Brivati, J. M. Gross, M. C. R. Symons and D. J. A. Tinling, J. Chem. Soc. 6504 (1965).

12. I. Barbur, Phys. Stat. Sol. 34, 711 (1969).

13. Since $N_2H_5^+$ would have an even number of electrons and the radical does not appear to be in a triplet state, the radical possibly should be $N_2H_5^{++}$.

(except Ref. 10) were made of the species stable at room temperature although this is not always clearly stated; Kotov and Pshezhetskii did note that both $N_2H_6SO_4$ and $N_2H_4 \cdot HCl$, when irradiated and observed at 77°K, gave quite different ESR spectra than did material irradiated and observed at room temperature. Our results have been obtained using single crystals γ -irradiated and observed at 77°K; under these conditions the ESR lines from any radicals derived from the hydrazinium ion are quite weak compared with the very strong lines from the V centers in both $N_2H_6Cl_2$ and $N_2H_6Br_2$. Only in the case of $N_2H_6F_2$ are the lines from the hydrazinium radical-ion sufficiently intense to analyze and the radical does not appear to be any of those previously observed.¹⁴ The present report deals only with the

-
14. M. T. Rogers and J. C. Watson, unpublished results.

paramagnetic species stable at 77°K and not containing nitrogen.

EXPERIMENTAL

Single crystals of hydrazinium dichloride (Fisher Scientific Co.) were grown from a saturated aqueous solution. Hydrazinium dibromide and difluoride were prepared by neutralizing 95% hydrazine solution (Eastman Organic Chemicals) with 48% HBr solution (Matheson, Coleman and Bell) or 49% HF solution (J. T. Baker Chemical Co.), respectively, using the stoichiometric ratio of materials; single crystals were obtained by slow evaporation

of the resulting solutions. The salts are, in every case, hygroscopic and were stored in a desiccator.

Irradiations were carried out using a ^{60}Co γ -ray source or a 1 mev. G. E. Resonant transformer. The ^{60}Co source delivered a dose rate of 2×10^6 rad/hr and irradiations of 3 - 10 hours were employed. The dose rate from the resonant transformer is about 3×10^6 rad/min and radiation times were 3 - 8 minutes. The crystals were floated on the surface of liquid nitrogen during irradiation and were then transferred under liquid nitrogen to a crystal mount which was placed in a quartz Dewar flask which fit into the Varian Multipurpose Cavity. The ESR spectra were recorded as a function of magnetic field orientation at 77°K using a Varian V-4503-10 ESR spectrometer without at any time permitting the temperature to rise appreciably above 77°K.

The crystal structures of two of the salts are known. Hydrazinium dichloride is cubic with $a = 7.89 \text{ \AA}$, $Z = 4$ and space group $\text{Pa}\bar{3}$; hydrazinium difluoride¹⁶ is rhombohedral with $a = 5.43 \text{ \AA}$, $\alpha = 38^\circ 10'$, $Z = 1$ and space

15. J. Donohue and W. N. Lipscomb, J. Chem. Phys., 15, 115 (1947)

16. M. L. Kronberg and D. Harker, J. Chem. Phys. 10, 309 (1942).

group $\text{R}\bar{3}\text{m}$. Since no x-ray results had been reported for $\text{N}_2\text{H}_4\text{Br}_2$ we have determined the unit cell and space group for this study. Weissenberg and Precession photographs showed the cell to be monoclinic with $a = 3.86 \text{ \AA}$, $b = 7.53$, $c = 10.28$ and $\beta = 94^\circ$. Systematic absences occur only for 00ℓ with $\ell = 2n$. The density, measured in a mixture of methylene bromide and

carbon tetrachloride, was 2.144 g/ml leading to $Z = 2$ molecules per unit cell. A crystal was attracted to the walls of a silvered Dewar flask containing liquid nitrogen. All these data are consistent with space group $P2_1$.

RESULTS

The ESR spectrum of an irradiated single crystal of $N_2H_4Cl_2$, taken with the magnetic field along a $[110]$ axis, is shown in Fig. 1(a), and the lines calculated for Cl_2^- with $A(^{35}Cl) = 97.3$ G are shown below. It is clear that one paramagnetic species present is Cl_2^- . Since in this orientation $A(^{35}Cl)$ is a maximum (or very nearly so) the maximum principal value of $A(^{35}Cl)$ is about 97.3 and the Cl-Cl bond lies close to $[110]$. The smaller splittings for the magnetic field perpendicular to the Cl-Cl bond may also be estimated from this spectrum (Table I), although the probable error is rather large since there is considerable overlapping of lines from the two orientations of Cl_2^- and, in addition, some contribution from a nitrogen-containing radical stable at higher temperatures.

The ESR spectrum of a γ -irradiated single crystal of hydrazinium dibromide is shown in Fig. 1(b) at 77°K.

Since ^{79}Br and ^{81}Br each have nearly 50% natural abundance and the magnetic moments are 2.0991 and 2.2626, respectively, the outer multiplets appear as 1:2:1 triplets. Both the g tensor and hyperfine splitting tensor were obtained from ESR spectra taken every 10° in the a^*b , bc and a^*c planes (Table I). The anisotropy in the $A(^{81}Br)$ values is unusually large; in KBr the $A(^{81}Br)$ principal values are¹ (455, 80, 80 G). No previous reports of Br_2^- in crystals of symmetry lower than cubic have appeared.

When the crystals were warmed to 110-115°K the lines from Br_2^- disappeared and a single broad line ($g = 2.0043$) remained; this might be a peroxide. On warming to room temperature no ESR signals remained.

Single crystals of hydrazinium difluoride irradiated with 1 mev electrons at 77°K and observed at 77°K give the spectrum of Fig. 1(c) for $\text{H}||\text{c}$. The central group of five lines are part of a septet which possibly arises from N_2H_6^+ while the weak groups of lines on either side of the strong central group are from a radical pair; additional lines at $g \approx 4$ are present but are not shown. The two outer lines separated by 508 G are the hydrogen atom spectrum; presumably weak interactions with surrounding diamagnetic species are responsible for the linewidth of about 30 G. These lines do not change separation as the crystal is rotated so the H atom spectrum is isotropic within experimental error. On warming to 200°K the spectra from the radical pairs and from the hydrogen atoms disappear and only the lines from the N_2H_6^+ species remain. Hydrogen atoms are, however, unusually stable in this matrix since the spectrum persists up to about 200°K.

Table I. ESR parameters for V centers and for hydrogen atoms in irradiated hydrazinium dihalides at 77°K.

	Principal values (gauss)	Direction Cosines		
$\text{Cl}_2^{\cdot -}$ in $\text{N}_2\text{H}_6\text{Cl}_2$				
$A(^{35}\text{Cl})$	97.3 (33.6) ^a (33.6)	$A_{\text{max}} \parallel [110]$		
g	2.0035 2.0295 2.0295	$g_{\text{min}} \parallel [110]$		
$\text{Br}_2^{\cdot -}$ in $\text{N}_2\text{H}_6\text{Br}_2$				
$A(^{81}\text{Br})$	415.6 243.5 79.7	0.75 -0.61 0.26	0.64 0.57 -0.51	0.16 0.55 0.82
g	2.0635 2.0471 .9809	0.40 -0.59 0.70	0.08 0.78 0.61	-0.91 -0.19 0.36
H in $\text{N}_2\text{H}_6\text{F}_2$				
A	508	isotropic		
g	2.0023			

^a Values enclosed in parentheses have a rather large probable error.

Fig.1. (a) Second-derivative ESR spectrum of Cl_2^- in $\text{N}_2\text{H}_4\text{Cl}_2$ irradiated at 77°K. The magnetic field is along a cubic axis. (b) Second-derivative ESR spectrum of Br_2^- in irradiated $\text{N}_2\text{H}_4\text{Br}_2$ at 77°K. The magnetic field is 30° from the b axis in the bc plane. (c) Second-derivative ESR spectrum of irradiated $\text{N}_2\text{H}_4\text{F}_2$ at 77°K. The magnetic field is parallel to the c axis.