been found from high resolution n.m.r. studies of polystyrene, which undergoes a characteristic conformational change as the chains are extended from about ten to about twenty monomer units.[22] There is, however, a disturbing discrepancy between our results and the 9-line e.s.r. spectra observed in experiments in which long chain polymethacrylate radicals were trapped in a gel.[23,24] The significance of this difference is at present unknown.

Like other vinyl-type monomers polymerizing in the solid state,[12,16] crystalline barium methacrylate dihydrate is transformed to a polymer which appears amorphous by the criterion of its X-ray diffraction pattern. It was suggested that evidence of the topochemical control[25] of solid state polymerization reactions may be reconciled with the formation of amorphous polymer if it is assumed that the active end of the propagating chain is attached to the surface of monomer crystallites, while the bulk of the chain lies in a separate amorphous phase.[11,12] This concept is consistent with the interpretation of the present investigation as outlined above since the monomer crystal breaks up in the course of the polymerization process into small crystallites which become increasingly disordered with respect to each other as the reaction attains a high degree of conversion.

Experimental

Barium methacrylate was prepared by neutralization of an aqueous solution of freshly distilled methacrylic acid (Rohm and Haas). Crystals of the dihydrate were grown from a filtered aqueous solution by slow evaporation at 20°. The crystals were diamond-shaped platelets whose long and short diagonals were found to be parallel to the b- and a-axes, respectively, of the unit cell as described in the preceding section. Single crystals of barium methacrylate dihydrate were enclosed in Spectrosil tubes sealed under vacuum. They were exposed at −196° to 0.5 Mrad of γ-radiation from a Co^{60} source.

The e.s.r. spectra of the irradiated crystals were recorded on a

(22) F. A. Bovey, G. V. D. Tiers, and G. Filipovich, *J. Polymer Sci.*, **38**, 73 (1959).

(23) G. K. Fraenkel, J. M. Hirshon, and C. Walling, *J. Am. Chem. Soc.*, **76**, 3606 (1954).

(24) S. E. Bresler, E. N. Kazbekov, and E. M. Seminskii, *Vysokomol. Soed.*, **1**, 132 (1959).

(25) A term introduced by Kohlschütter (*Z. anorg. Chem.*, **105**, 1 (1918)) to describe the dependence of a reaction on the geometrical arrangement of the reagent molecule in its crystal structure.
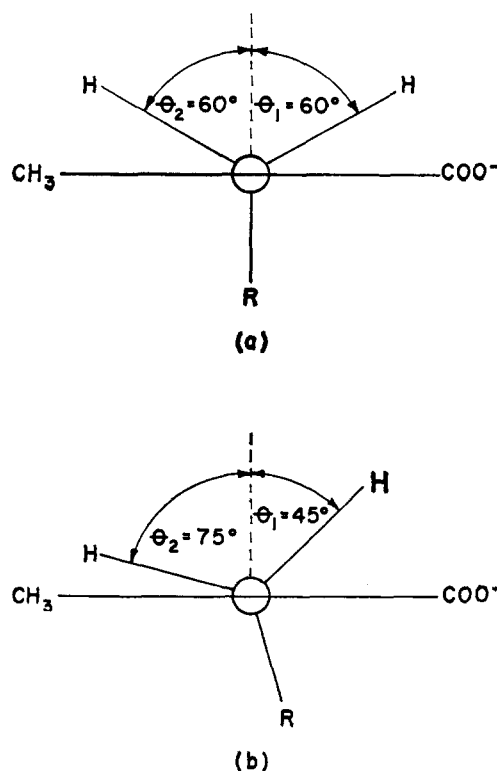
Fig. 2.—Conformation of the radical $RCH_2\dot{C}<^{CH_3}_{COO^-}$ with equivalent methylene hydrogens (a) and with one of the methylene hydrogens equivalent to the hydrogens in a freely rotating methyl group (b).

Varian Model V-4500-10A spectrometer in the X-band region using a 100-kc. sweep frequency. The low temperature spectra were taken with the sample enclosed in the Spectrosil tube and only crystal orientations in which the b-axis was perpendicular to the magnetic field could be studied under these conditions. At room temperature the spectra were found to be unaffected by exposure of the crystals to the atmosphere, apparently due to negligibly slow diffusion of oxygen through the crystals. Under these conditions the crystals could be removed from the tube, facilitating their orientation relative to the magnetic field. It was necessary to operate at a very low microwave power level, since there was a marked tendency for the resonance to saturate, so that additional lines appeared in the spectrum at higher microwave power, presumably due to species persent in very low concentration.

Electron Spin Resonance in Irradiated Glycine Crystals

BY J. R. MORTON

Irradiated glycine crystals enriched with 55% $NH_3{}^+C^{13}H_2CO_2{}^-$ have been studied by electron spin resonance. The two radicals which are formed both exhibit C^{13} hyperfine interaction and are shown to be $NH_3{}^+CHCO_2{}^-$ and $CH_2CO_2{}^-$. The methylene group in $CH_2CO_2{}^-$ is apparently undergoing hindered rotation about the C–C bond.

Introduction

The interpretation of the electron spin resonance spectra of radiation-damaged glycine ($NH_3{}^+CH_2$-$CO_2{}^-$) has been the subject of some conjecture since the first experiments[1] in 1955. The spectrum of irradiated powdered glycine is a broad triplet variously assigned[1-3]

(1) W. Gordy, W. B. Ard, and H. Shields, *Proc. Natl. Acad. Sci. U. S.*, **41**, 983 (1955).

to the radicals $CH_2NH_3{}^+$, $CH_2CO_2{}^-$, and NH_2. Uebersfeld and Erb[4] obtained spectra from irradiated single crystals of glycine and concluded that two radicals were present. Ghosh and Whiffen[3,5] analyzed the single

(2) M. C. R. Symons, *J. Chem. Soc.*, 277 (1959).

(3) D. K. Ghosh and D. H. Whiffen, *ibid.*, 1869 (1960).

(4) J. Uebersfeld and E. Erb, *Compt. rend.*, **242**, 478 (1956).

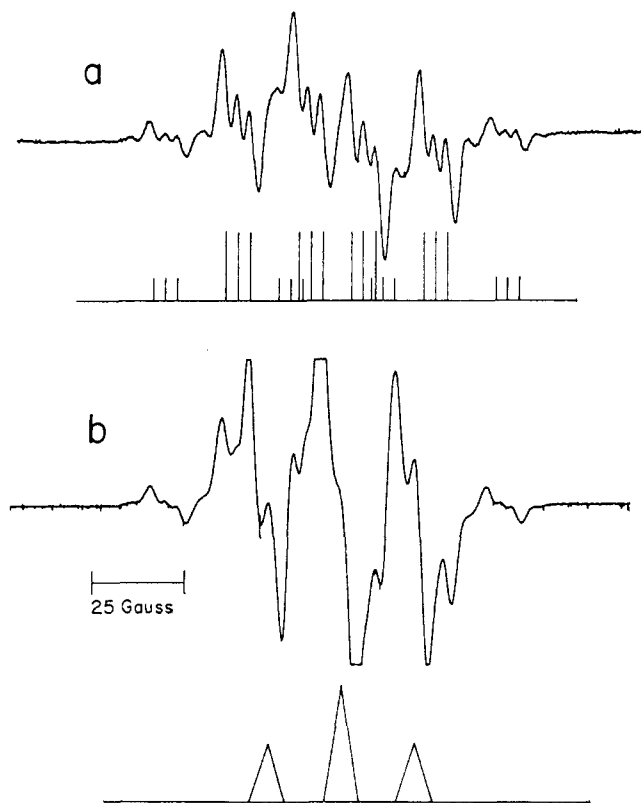(5) D. K. Ghosh and D. H. Whiffen, *Mol. Phys.*, **2**, 285 (1959).

Fig. 1.—First derivative spectra of glycine crystals for orientation (0.707, 0.000, −0.707) irradiated at: (a) 77°K., (b) 273°K.

crystal spectra in terms of $NH_3^+CHCO_2^-$ and NH_2. This interpretation was, however, recently disputed by Weiner and Koski,[6] whose analyses led them to conclude that the radicals were NH_4 and $CH_2CO_2^-$.

In the present work glycine substituted with C^{13} on the central carbon atom was used in an attempt to resolve the controversy.

Experimental

Glycine crystals were prepared by the slow evaporation of aqueous solutions. The C^{13}-glycine (central carbon) was purchased from Merck Sharpe & Dohme Ltd., Montreal, and contained 55% $NH_3^+C^{13}H_2CO_2^-$.

The unit cell of the glycine crystal is monoclinic,[7,8] space group $P2_1/n$; $\beta = 111.7°$; dimensions $a = 5.102$, $b = 11.971$, $c = 5.457$ Å. The crystals are frequently prismatic in shape, developing the faces {011} and {210} and tend to be elongated along the c-axis. Advantage was taken of the pronounced cleavage on (010) to provide a surface perpendicular to the b-axis. There are four molecules per unit cell, but since the paramagnetic fragments formed from them also obey the symmetry operations of the crystal, only two radical "sites" may be distinguished.[6] When the magnetic field of the spectrometer explores the ac plane, or when it is parallel to the b-axis of the crystal, the spectral lines further coalesce into the spectrum for a single site.

The crystals were irradiated with 1-Mev. γ-rays from an 1100-curie Co^{60} source. The dose rate was 1 Mrad/hr., and dosages of up to 5 Mrads were given. The electron spin resonance spectra were obtained with a Varian V-4502 spectrometer equipped with the V-4012A magnet system. The technique employed to measure the magnetic field strength and microwave frequency has been described elsewhere.[9]

The irradiated crystals were mounted on a two-circle Teflon goniometer of the type described by Roberts and Derbyshire.[10] The crystal was mounted on its (010) cleavage face with the b-axis horizontal and could be rotated about the b-axis or about any

(6) R. F. Weiner and W. S. Koski, *J. Am. Chem. Soc.*, **85**, 873 (1963).
(7) G. Albrecht and R. B. Corey, *ibid.*, **61**, 1087 (1939).
(8) R. E. Marsh, *Acta Cryst.*, **11**, 654 (1958).
(9) J. R. Morton and W. E. Falconer, *J. Chem. Phys.*, **39**, 427 (1963).
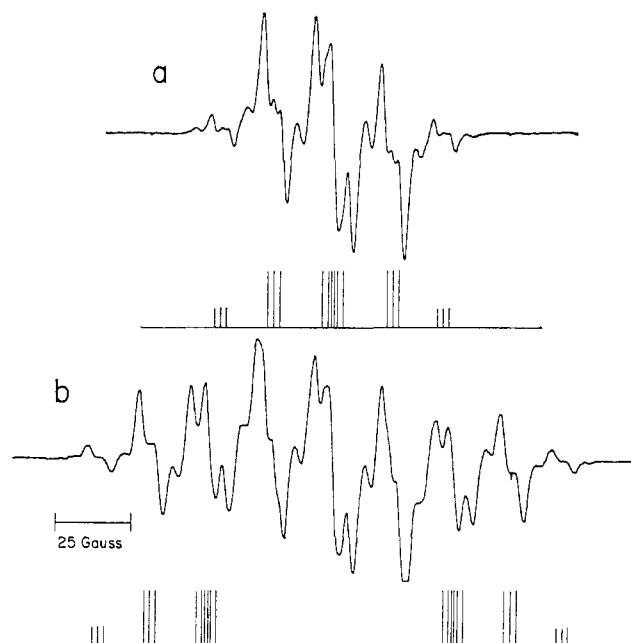(10) G. Roberts and W. Derbyshire, *J. Sci. Instr.*, **38**, 511 (1961).

Fig. 2.—First derivative spectra of glycine crystals irradiated at 77°K. for orientation (0, 1, 0): (a) normal glycine, (b) glycine containing 55% $NH_3^+C^{13}H_2CO_2^-$.

axis perpendicular to the b-axis without remounting the crystal. The axis of rotation was, of course, always perpendicular to the magnetic field of the spectrometer. The orientation of the crystals in the magnetic field is specified to within ±1.0° of arc by direction cosines of a right-handed a^*,b,c axis system. An isotropic g-value of 2.0023 was assumed.

Results and Discussion

The presence of two chemically distinct radicals in irradiated glycine crystals is demonstrated by the spectra reproduced in Fig. 1. These spectra were recorded at room temperature and are for the orientation (0.707, 0.000, −0.707). Figure 1(a) is that of a crystal irradiated at 77°K., while Fig. 1(b) is the spectrum of a crystal irradiated at 273°K. Figure 1(a) exhibits the many-lined spectrum of radical A, thought to be either[5,6] $NH_3^+CHCO_2^-$ or NH_4. Figure 1(b), however, is dominated by the broad triplet spectrum of radical B, variously identified[1-3] as $CH_2NH_3^+$, CH_2-CO_2^-, or NH_2. Clearly, irradiation at 77°K. prevents[11] the formation of radical B, thus facilitating a study of radical A. In the following sections the spectra of the two radicals will be discussed separately.

The Spectra of Radical A.—The spectra of radical A in normal glycine exhibit hyperfine interaction with an N^{14} nucleus ($I = 1$), three equivalent protons, and a unique proton ($I = \frac{1}{2}$). In the spectrum shown in Fig. 1(a) the hyperfine interaction of the unique proton is approximately twice that of one of the three equivalent protons, giving the spectrum the appearance of a 1:3:4:3:1 sextet of triplets.

In Fig. 2 the spectrum of a normal glycine crystal irradiated at 77°K. (Fig. 2a) is compared with that (Fig. 2b) of a crystal containing 55% $NH_3^+C^{13}H_2CO_2^-$ also irradiated at 77°K. Both spectra are for the orientation (0, 1, 0). The wider spectrum of the irradiated C^{13}-glycine crystal, and, in particular, the characteristic triplets associated with radical A, prove without doubt that this radical is $NH_3^+CHCO_2^-$.

(11) A. Horsfield, private communication.

In the undamaged molecule the glycine zwitterions are held by hydrogen bonds in planes perpendicular to the b-axis. It has been shown[5] that the skeletal plane of the π-electron radical $NH_3^+CHCO_2^-$ is also approximately perpendicular to the b-axis, and so for this orientation the C^{13} hyperfine interaction should approach its maximum value of approximately 250 Mc.[12,13] The C^{13} hyperfine splitting calculated from the spectra of Fig. 2 was 226 Mc., being the difference between the total hyperfine interaction for normal glycine (212 Mc.) and for C^{13}-glycine (438 Mc.).

Assuming[5] that the total hyperfine interaction transforms as a tensor, this tensor was assembled for radical A in irradiated normal and C^{13}-glycines. These tensors are given in Table I and are referred to the right-handed a^*,b,c axis system. The total hyperfine tensor of normal glycine agrees reasonably well with that derived by Ghosh and Whiffen[5] when their diagonal elements are reduced by 12% to take into account a field calibration error,[3] and when it is realized[14] that they mis-identified the a- and c-axes of the crystal. The relative signs of the a^*b and bc elements of the two tensors were established by measuring the total hyperfine interaction for the *skew* direction $(+3^{-1/2}, +3^{-1/2}, +3^{-1/2})$. The observed values were 210 Mc. for normal glycine and 411 Mc. for C^{13}-glycine. Calculated values of the same parameter were 214 and 410 Mc. using the sign choice of Table I, but 222 and 363 Mc. for the alternate sign choice.

TABLE I

TOTAL HYPERFINE INTERACTION TENSORS^a OF $NH_3^+CHCO_2^-$ IN a^*bc AXIS SYSTEM

	Normal glycine			C^{13}-Glycine	
232.5	∓ 5.6	-33.2	287.8	∓ 43.8	0.0
∓ 5.6	212.5	± 13.8	∓ 43.8	438.2	∓ 34.9
-33.2	± 13.8	247.4	0.0	∓ 34.9	346.6

^{a} Units of all tensors are Mc.

By subtraction of corresponding elements of the two total hyperfine interaction tensors, the C^{13} tensor of the radical $NH_3^+C^{13}HCO_2^-$ in irradiated glycine was obtained. The ambiguity in the magnitude of the a^*b and bc elements was resolved by careful analysis of critical spectra. The C^{13} tensor, together with its principal values and their direction cosines, is given in Table II. The principal values obtained (254, 90, 37 Mc.)

TABLE II

C^{13} HYPERFINE INTERACTION TENSOR OF $NH_3^+C^{13}HCO_2^-$ IN a^*bc AXIS SYSTEM

	Tensor		Principal values, Mc.	Direction cosines
55.3	± 38.2	33.2	$(+)$ 36.7 $\pm$ 5.0	$(0.902, \mp 0.080, -0.424)$
± 38.2	225.7	± 48.7	$(+)$ 90.0	$(0.360, \mp 0.404, 0.841)$
33.2	± 48.7	99.2	$(+)$ 253.5	$(0.239, \pm 0.911, 0.335)$

may be compared with those from other π-electron radicals. The C^{13} tensor of the radical $C^{13}H(CO_2H)_2$ in irradiated malonic acid[12] had principal values 213, 42, and 23 Mc., whereas for $C^{13}H(SO_3)_2$ the corresponding values[13] were 260, 62, and 55 Mc. This correlation with earlier work establishes unequivocally that radical A is a π-electron radical, the unpaired electron occupying a 2p-orbital of the glycine central carbon atom.

(12) T. Cole and C. Heller, *J. Chem. Phys.*, **34**, 1085 (1961).

(13) A. Horsfield, J. R. Morton, J. R. Rowlands, and D. H. Whiffen, *Mol. Phys.*, **5**, 241 (1962).

(14) D. H. Whiffen, private communication.

The p-orbital density direction is the direction of the largest C^{13} principal value $(0.239, \pm 0.911, 0.335)$ in the a^*bc axis system, and also of the intermediate $H_{(C)}$ principal value[5] $(0.43, \pm 0.75, 0.50)$ in the same axis system. The angle between these two directions is $17.5°$, reasonable correlation in view of the estimated[5] error of $\pm 15°$ in the principal directions of the $H_{(C)}$ tensor. In Table III are listed the atomic coordinates of a glycine molecule in the orthogonal a^*bc axis system, calculated from the data of Marsh.[8] The direction $(0.261, \pm 0.954, 0.131)$ is perpendicular to the $C_1O_1O_2$ plane, and the angle between this direction and the p-orbital density direction is $(\cos^{-1} 0.975)$ $12.8°$, establishing that the radicals are oriented similarly to the undamaged glycine molecules.

TABLE III

ATOMIC COORDINATES OF ONE GLYCINE MOLECULE IN THE a^*bc AXIS SYSTEM

Atom	a^*	b	c
C_1	0.3575	1.4937	0.2182
C_2	0.3098	1.7357	-1.2852
N	1.4285	1.0750	-1.9813
O_1	1.4498	1.1285	0.7085
O_2	-0.7004	1.6944	0.8633

The Spectra of Radical B.—Glycine crystals irradiated at 273°K. exhibit for all orientations the broad triplet apparently associated with the two equivalent protons of radical B, in addition to the complex spectrum of $NH_3^+CHCO_2^-$ discussed in the previous section. Figures 1(b) and 3(a) show the spectra from normal glycine crystals irradiated at 273°K. for the orientations $(0.707, 0.000, -0.707)$ and $(0, 1, 0)$, respectively.

In Fig. 3(b) is reproduced the spectrum of a glycine crystal enriched with C^{13} on the central carbon atom, and irradiated at 273°K. This spectrum is for the orientation $(0, 1, 0)$ and, by comparison with Fig. 3(a) and 2(b), it will be noted that a C^{13} hyperfine interaction in radical B is observed. The C^{13} and the proton hyperfine interactions together prove that radical B must be $CH_2CO_2^-$, in agreement with the assertion of Weiner and Koski.[6] The alternate suggestions[1,3] $CH_2NH_3^+$ and NH_2 cannot be entertained for various reasons: the former radical would exhibit hyperfine interactions with four or five protons, and the latter would not show C^{13} hyperfine interaction.

By the same procedure as that described in the previous section, the C^{13} tensor of $CH_2CO_2^-$ in irradiated glycine was evaluated and in Table IV the proton and

TABLE IV

HYPERFINE INTERACTION TENSORS OF $CH_2CO_2^-$ IN a^*bc AXIS SYSTEM

Nucleus	Tensor			Principal values, Mc.	Direction cosines
H^1	48	0	0	$(-)$ 69 $\pm$ 5	$(0.00, \pm 0.32, 0.95)$
	0	57	± 4	$(-)$ 56	$(0.00, \pm 0.95, -0.32)$
	0	± 4	68	$(-)$ 48	$(1.00, 0.00, 0.00)$
C^{13}	118	0	-50	$(+)$ 221 $\pm$ 10	$(0.24, \pm 0.83, -0.50)$
	0	177	∓ 73	$(+)$ 19 $\pm$ 20	$(0.42, \pm 0.38, 0.83)$
	-50	∓ 73	78	$(+)$ 133	$(0.87, \mp 0.41, -0.26)$

C^{13} tensors of the radical are given, together with their principal values and direction cosines. The signs of the principal tensor elements are not determinable from the spectra but are obtained by correlation with
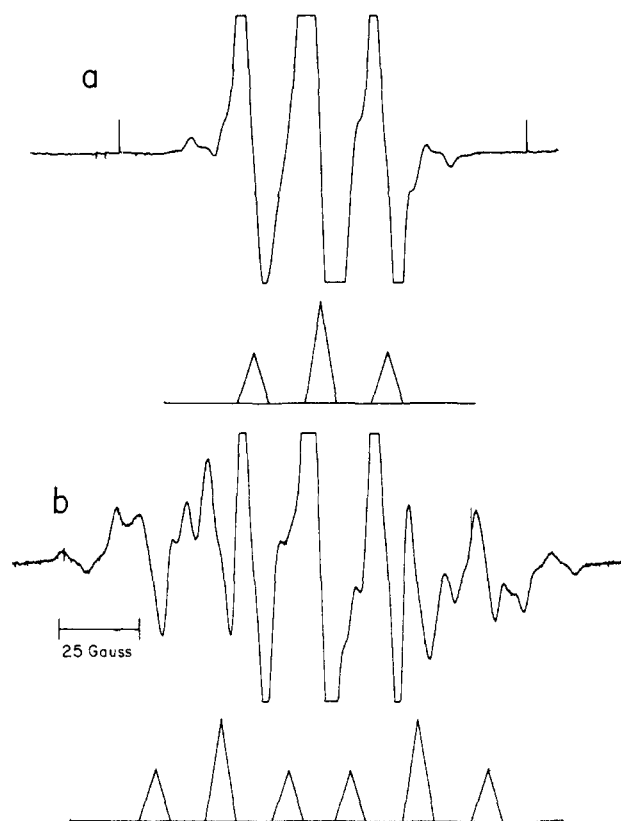
Fig. 3.—First derivative spectra of glycine crystals irradiated at 273°K. for orientation (0, 1, 0): (a) normal glycine, (b) glycine containing 55% $NH_3{}^+C^{13}H_2CO_2{}^-$.

theory.[15,16] The width of the lines due to radical B and the complexity of the underlying spectrum led to considerable uncertainty in the tensor elements, particularly the two smaller C^{13} principal values. The principal directions are correspondingly less well defined. In spite of the abnormal width (20 Mc., maximum slope) of the lines due to $CH_2CO_2{}^-$ there is no doubt as to the apparent equivalence of the two protons. It may be calculated from the α-proton tensors of CH_2CO_2H rigidly trapped in irradiated malonic acid[17] that the maximum separation of the central components of the quartet (i.e., the maximum difference in the proton hyperfine interactions) is 50 Mc. It is, therefore, virtually certain that if $CH_2CO_2{}^-$ were rigidly trapped in the glycine crystal the splitting of the central line of the triplet could be resolved. The proton tensors of $CH_2CO_2{}^-$ have axial symmetry and it may be calculated from the data of Tables III and IV that the directions of the C–C bonds in the host molecules are approximately parallel ($\cos^{-1} 0.99 = 8°$) to the unique directions of the proton tensors, and to the directions of the smallest C^{13} principal values ($\cos^{-1} 0.89 = 27°$). Moreover, it is apparent that the 221 Mc. principal value of the C^{13} tensor in $CH_2CO_2{}^-$ can reasonably be associated with a p-orbital density direction, and, within experimental error, this direction is perpendicular ($\cos^{-1} 0.21 = 78°$) to the unique direction of the proton tensor.

Symmetry considerations require that the in-plane principal directions of the C^{13} tensor in the radical CH_2-$CO_2{}^-$ be parallel and perpendicular to the C–C bond.
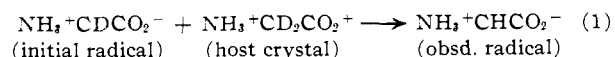
It will be noted that it is the smaller (19 Mc.) C^{13} principal value whose direction is approximately parallel to the unique direction of the proton tensor ($\cos^{-1} 0.90 = 25°$). A similar result was obtained[18] for the nitrogen-centered π-radical $NH_2{}^+SO_3{}^-$; at 300°K. the N^{14} hyperfine interaction perpendicular to the radical plane was 103 Mc., parallel to the S–N bond 17 Mc., and in-plane but perpendicular to the S–N bond, 33 Mc. These observations may be rationalized by resolving the effect[12,13] of spin polarization in two X–H bonds parallel and perpendicular to the HXH angle.

The hyperfine interaction tensor of the central atom of a π-electron radical is expected to possess axial symmetry about the p-orbital density direction, being of the form A + 2B parallel to this direction and A − B perpendicular to it. In the present case ($CH_2CO_2{}^-$) and also in the case[18] of the radical $NH_2{}^+SO_3{}^-$ considerable deviation from the expected symmetry is apparent. The divergence between the in-plane principal values of the central atom tensor may in part be explained by spin polarization in the bonds, but in the case of $NH_2{}^+SO_3{}^-$ was also shown[19] to be associated with hindered rotation of the $NH_2{}^+$ group about the N–S bond. The apparent equivalence of the two protons in $CH_2CO_2{}^-$ trapped in glycine at room temperature and the deviation from axial symmetry in the C^{13} tensor suggest that the CH_2 group in this radical is experiencing hindered rotation about the C–C bond. It is hoped eventually to study the changes in the spectrum of $CH_2CO_2{}^-$ when the glycine crystals are cooled to 77°K.

Conclusions

Having observed C^{13} hyperfine interactions in radicals A and B it is concluded that in irradiated normal glycine these radicals are $NH_3{}^+CHCO_2{}^-$ and CH_2-$CO_2{}^-$, respectively. It remains, however, to discuss the interesting results of earlier workers.

Weiner and Koski,[6] for example, identified radical A as NH_4 because they observed virtually identical spectra from irradiated crystals of $NH_3{}^+CH_2CO_2{}^-$ and (98%) $NH_3{}^+CD_2CO_2{}^-$, and this result has been substantiated by an independent authority.[11] With the present confirmation of radical A as $NH_3{}^+CHCO_2{}^-$, it must be concluded that in (98%) D_2-glycine radiolysis either leads to preferential damage of the 2% normal glycine molecules present, or else a radical–molecule exchange reaction occurs. It has already been shown that[20] the exchange between deuterons of ($ND_3{}^+$) groups in the host molecules of $CH_3(ND_3{}^+)CHCO_2{}^-$ and hydrogen atoms of the radical $CH_3CHCO_2{}^-$ leads eventually to conversion of the radical to $CD_3CDCO_2{}^-$. The results of Weiner and Koski[6] are, perhaps, best interpreted by the reaction

$$NH_3{}^+CDCO_2{}^- + NH_3{}^+CD_2CO_2{}^+ \longrightarrow NH_3{}^+CHCO_2{}^- \quad (1)$$
(initial radical)　　(host crystal)　　　(obsd. radical)

A comparison of the spectra of room-temperature irradiated $NH_3{}^+CH_2CO_2{}^-$ and $ND_3{}^+CH_2CO_2{}^-$ led Ghosh and Whiffen[5] to conclude that radical B was NH_2. Since radical B is now known to be $CH_2CO_2{}^-$, it seems that the reaction

(15) H. M. McConnell and D. B. Chesnut, J. Chem. Phys., 28, 107 (1958).
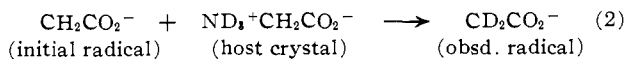
(16) H. M. McConnell and J. Strathdee, Mol. Phys., 2, 129 (1959).

(17) A. Horsfield, J. R. Morton, and D. H. Whiffen, ibid., 4, 327 (1961).

(18) J. R. Rowlands and D. H. Whiffen, Nature, 193, 61 (1962).

(19) J. R. Rowlands, Mol. Phys., 5, 565 (1962).

(20) I. Miyagawa and K. Itoh, Proc. Intern. Symposium on Molecular Structure and Spectroscopy, Tokyo, September, 1962.

$$CH_2CO_2^- + ND_3^+CH_2CO_2^- \longrightarrow CD_2CO_2^- \quad (2)$$
(initial radical)   (host crystal)   (obsd. radical)

takes place in irradiated D_3-glycine.

Whereas the exchange reactions between radical and host molecules were very slow in α-alanine (several years at 20°, 3 hr. at 150° for complete conversion), reactions 1 and 2 in irradiated glycines must be very fast since the postulated "initial " radicals were not observed.

It would therefore appear that caution must be exercised in the identification of radicals as a result of deuteration studies.

Partial Ionic Character of Diatomic Molecules

BY RAYMOND P. ICZKOWSKI

The partial ionic character of a diatomic molecule is derived from a semiclassical model. Total bond energy is treated as a sum of ionic and covalent contributions. The ionic component is a sum of coulombic, polarization, and partial ionization energies. Covalent energy is calculated by a generalization of Mulliken's method. The fractional ionic character is the value at which the total energy is a minimum. Application of the method to BrCl, ClF, BrF, and NaCl yields values of ionic character in rough agreement with values obtained from nuclear quadrupole coupling constants.

Introduction

Recently, relationships between electronegativity and partial ionic character have been formulated in terms of the concept of equalization of electronegativity.[1] As shown in Table I, this method yields values of percentage ionic character lower than the experimental values obtained from nuclear quadrupole coupling constants.[2] An alternative to this theory would be to derive the partial ionic character from a semiclassical model of a diatomic molecule. In a classical treatment of two oppositely charged spheres separated by an anharmonic nonconducting spring, the total energy of the system could be considered as a sum of the energy of compression of the spring plus the electrostatic energy of the two charged spheres. In this paper, the bond energy of a partially ionic molecule is considered as a sum of separate contributions due to the electrostatic energy and the energy of covalent binding.

has the effect of multiplying the electrostatic attraction by the term

$$\left[1 + \frac{\alpha_A + \alpha_B}{2r_e^3} + \frac{2\alpha_A\alpha_B}{r_e^6} \right]$$

where α_A is the polarizability of atom A. It was shown in a previous paper[4] how the energies of partial ionization $E_A(-N)$ and $E_B(N)$ could be evaluated from a plot of the total energies of atoms A and B as a function of degree of ionization. The polarizability also depends on the degree of ionization; e.g., for the molecule ClF, α_F would be intermediate between the values for F and F$^-$, and α_{Cl} would be intermediate between the values for Cl and Cl$^+$. The dependence of the polarizability on degree of ionization has been shown[5] to be of the form: constant $\times n^6/Z^4$, where n is the principal quantum number of the outermost electrons and Z is the effective nuclear charge.

TABLE I

	ClF	BrF	BrCl	LiBr	NaBr	KCl	KBr	RbCl	CsCl
% ionic character									
From equalization of electronegativity	9.86	13.4	8.15	39.4	40.9	48.9	46.1	50.0	52.0
From nuclear quadrupole coupling	25.9	32.9	5.6 or 11.0	94.4	91.1	100	98.5	99.2	96.8

Ionic and Covalent Components of the Bond Energy.—The ionic contribution, $E_i(N)$, at fractional ionic character N of a molecule AB, is easily calculated as a sum of four parts: (1) the energy $E_A(-N)$ required to remove a fraction of an electronic charge, Ne, from atom A; (2) the energy $E_B(N)$ required to place this charge on atom B; (3) the energy $-(Ne)^2/r_e$ due to the electrostatic attraction between two atoms of charge Ne separated by the internuclear distance r_e; (4) a correction[3] for polarization, i.e., the distortion of the electron clouds due to the electrostatic attraction. Polarization

According to Mulliken,[6] the energy of a covalent bond can be found from a semitheoretical formula which is a quantitative extension of the Slater–Pauling theory of maximum overlap. According to Mulliken's method this bond energy in a molecule is given by an attractive contribution $-AIS/(1 + S)$ due to electrons from each atom, which are paired in the molecule, together with a sum of repulsive contributions of the form: $^1/_2 n_A n_B \gamma A I S^2$ due to electrons from different atoms which are not involved in a bond; where $\gamma = 0.7$, $A = 1.16$ for σ-orbitals and 1.53 for π-orbitals, I is the average ionization energy of the two orbitals

(1) J. Hinze, M. A. Whitehead, and H. H. Jaffé, J. Am. Chem. Soc., **85**, 148 (1963); H. O. Pritchard, ibid., **85**, 1876 (1963); R. Ferreira, Trans. Faraday Soc., **59**, 1064, 1075 (1963); R. T. Sanderson, J. Am. Chem. Soc., **74**, 272 (1952); Science, **114**, 670 (1951).

(2) B. P. Dailey and C. H. Townes, J. Chem. Phys., **23**, 118 (1955).

(3) E. S. Rittner, ibid., **19**, 1030 (1951).

(4) R. P. Iczkowski and J. L. Margrave, J. Am. Chem. Soc., **83**, 3547 (1961).

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(6) R. S. Mulliken, J. Phys. Chem., **56**, 295 (1952).