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Differences in Electron Spin Resonance Spectra and Annealing Characteristics of Radicals Produced in Polycrystalline and Glassy Alkyl Iodides by  $\gamma$ -Radiolysis<sup>1</sup>

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Electron spin resonance spectra of alkyl halides irradiated with  $\text{Co}^{60}$   $\gamma$ -rays at 77°K. indicate that the nature of the detectable species formed, the yields of these species, and the annealing behavior at 77°K. and on warming are often much different for the glassy form than for the polycrystalline form. Several of the polycrystalline alkyl iodides give complex spectra of 15 lines or more, that for ethyl iodide containing 30 lines with a spread of 1000 gauss. Results of an exploratory survey of the radiolytic yields of the stable organic products of ethyl halides down to 4.2°K. are reported.

Alkyl halides activated by ionizing radiation, light, or nuclear processes show variations in product yields with phase (liquid, polycrystalline, rigid glass) which have not yet been satisfactorily rationalized.<sup>2</sup> For example, the product yields,  $G(\text{I}_2)$ <sup>3</sup> and  $G(\text{C}_2\text{H}_5)$ ,<sup>4</sup> from the  $\text{Co}^{60}$  radiolysis of  $\text{C}_2\text{H}_5\text{I}$  at 90°K. are substantially higher in glass samples than in polycrystalline samples. These observations have led us to seek to compare the electron spin resonance spectra of the irradiated glassy and polycrystalline forms of the eight alkyl iodides listed in Table I.

TABLE I  
COMPARISON OF E.S.R. SPECTRA OF  $\gamma$ -IRRADIATED GLASSY AND POLYCRYSTALLINE ALKYL IODIDES

Cpd.	State	No. of lines	Total spread, gauss	Approx. intensity ratio <sup>b</sup>	Approx. rapid anneal, °K.	M.p., °K.
$\text{C}_2\text{H}_5\text{I}$	Glass	6	160	1	100	165
	Cryst.	30	1000	0.005	158	
$i\text{-C}_3\text{H}_7\text{I}^a$	Cryst.	19	500	.02	145	182
$n\text{-C}_3\text{H}_7\text{I}$	Glass	6	160	.2	108	172
	Cryst.	7	160	.2	172	172
$n\text{-C}_4\text{H}_9\text{I}$	Glass	6	160	.5	106	170
	Cryst.	24	700	.03	170	170
$n\text{-C}_5\text{H}_{11}\text{I}$	Glass	6	160	.5	118	187
	Cryst.	6	160	.1	187	187
$n\text{-C}_6\text{H}_{13}\text{I}$	Glass	6	160	.2	123	205
	Cryst.	15	350	.05	205	205
$n\text{-C}_7\text{H}_{15}\text{I}^a$	Cryst.	6	160	.2	213	225
$n\text{-C}_8\text{H}_{17}\text{I}^a$	Cryst.	15	350	.05	227	227

<sup>a</sup> All attempts to obtain the glass were unsuccessful. <sup>b</sup> About 15 min. after completion of 20 min.  $7 \times 10^{19}$  e.v.  $\text{g}^{-1}$  irradiation.

A Varian V-4500 spectrometer employing 100-kc. modulation was used. Dried degassed samples in Suprasil tubes were irradiated at 77°K. with  $\text{Co}^{60}$   $\gamma$ -rays to a dose of  $7 \times 10^{19}$  e.v.  $\text{g}^{-1}$  at a rate of  $3.5 \times 10^{18}$  e.v.  $\text{g}^{-1}$  min.<sup>-1</sup>. Electron spin resonance spectra were determined starting 10 min. after irradiation. Anneal studies utilized the Varian variable temperature device. Reagents were, in general, Eastman White Label. Selective formation of glass or crystals, where possible, was controlled by the technique and rates of freezing. The two forms were distinguished by appearance, ability to induce transition to the other state, and color after irradiation.

There are four noteworthy ways in which the spectra of most of the polycrystalline samples differ from the glasses: (1) they have many more lines; (2) they are much wider, extending to 1000 gauss for  $\text{C}_2\text{H}_5\text{I}$ ; (3) the

intensity and hence the implied radiolytic yield of radicals is lower; (4) they persist much longer at 77°K. and are stable on rapid annealing almost up to the melting point.

Figure 1 (A, B) shows the contrast between the spectrum of  $\text{C}_2\text{H}_5\text{I}$  glass (6 lines) and that of polycrystalline  $\text{C}_2\text{H}_5\text{I}$  (ca. 30 lines plus the hydrogen doublet and quartz lines from the Suprasil (Fig. 1 G)) taken at a signal level 160 times more sensitive. The former is attributable to  $\text{C}_2\text{H}_5$  radical.<sup>4,5</sup> The latter seems to require coupling of the unpaired electron to iodine (spin  $5/2$ ) as well as to protons, possibly in a  $\text{C}_2\text{H}_4\text{I}$  radical. The spectra of 19, 24, 15, and 15 lines observed for polycrystalline  $i\text{-C}_3\text{H}_7\text{I}$ ,  $n\text{-C}_4\text{H}_9\text{I}$ ,  $n\text{-C}_6\text{H}_{13}\text{I}$ , and  $n\text{-C}_8\text{H}_{17}\text{I}$  seem also to require interaction with iodine. Previously reported e.s.r. spectra attributed to iodine include the gaseous atom<sup>6</sup> and the  $\text{I}_2^-$  ion.<sup>7</sup>

All of the alkyl iodide glasses with chain length  $\text{C}_3$  and above gave spectra nearly identical with Fig. 1C. This and the 19-line spectrum for  $i\text{-C}_3\text{H}_7\text{I}$  are similar to those reported for these compounds by Ayscough and Thomson,<sup>5</sup> who did not distinguish between glassy and crystalline samples. The forms they measured were, in general, those most easily obtained on rapid freezing. They have attributed the six-line spectrum of radicals of the type  $\text{RCH}_2\text{CH}_2\cdot$  to equal coupling to the two  $\alpha\text{-H}$  atoms and one  $\beta\text{-H}$  atom and unequal coupling to the other  $\beta\text{-H}$  atom, with overlapping of lines.<sup>5</sup>

On raising the temperature of the glassy samples at a rate of about 30° per hour, the spectra all disappeared at about 0.6 of the absolute melting point. The polycrystalline signals all persisted to 0.8 of the melting point and most were present until melting started. At least three of them showed qualitative changes on annealing [Fig. 1 (D, E, and F)], but the  $\text{C}_2\text{H}_5\text{I}$  (Fig. 1 B) maintained its original character to the melting point or on standing at 77° for 7 weeks. The 19 lines of  $i\text{-C}_3\text{H}_7\text{I}$  remained after 6 weeks at 77°K.

The most striking change at 77°K. occurred in  $\text{C}_2\text{H}_5\text{I}$  glass [Fig. 1 (H1, H2)]. Six very weak lines in the freshly irradiated sample, at higher  $g$ -values than the prominent central six-line pattern, grew on standing while the latter decreased after a week. The pattern then remained nearly constant for at least 3 weeks.

The greater yield of C-I bond rupture in glassy than in polycrystalline alkyl iodides indicated both by the e.s.r. spectra and by earlier studies of the radiolysis yields of  $\text{I}_2$ <sup>3,4</sup> may be due to one or more of the following: (1) a greater possibility of cage escape in the glass; (2) steric effects in the oriented molecular arrangement of the crystal such that the most probable orientation of the activated species does not split C-I bonds; (3) more C-I bond rupture in the random structure of the

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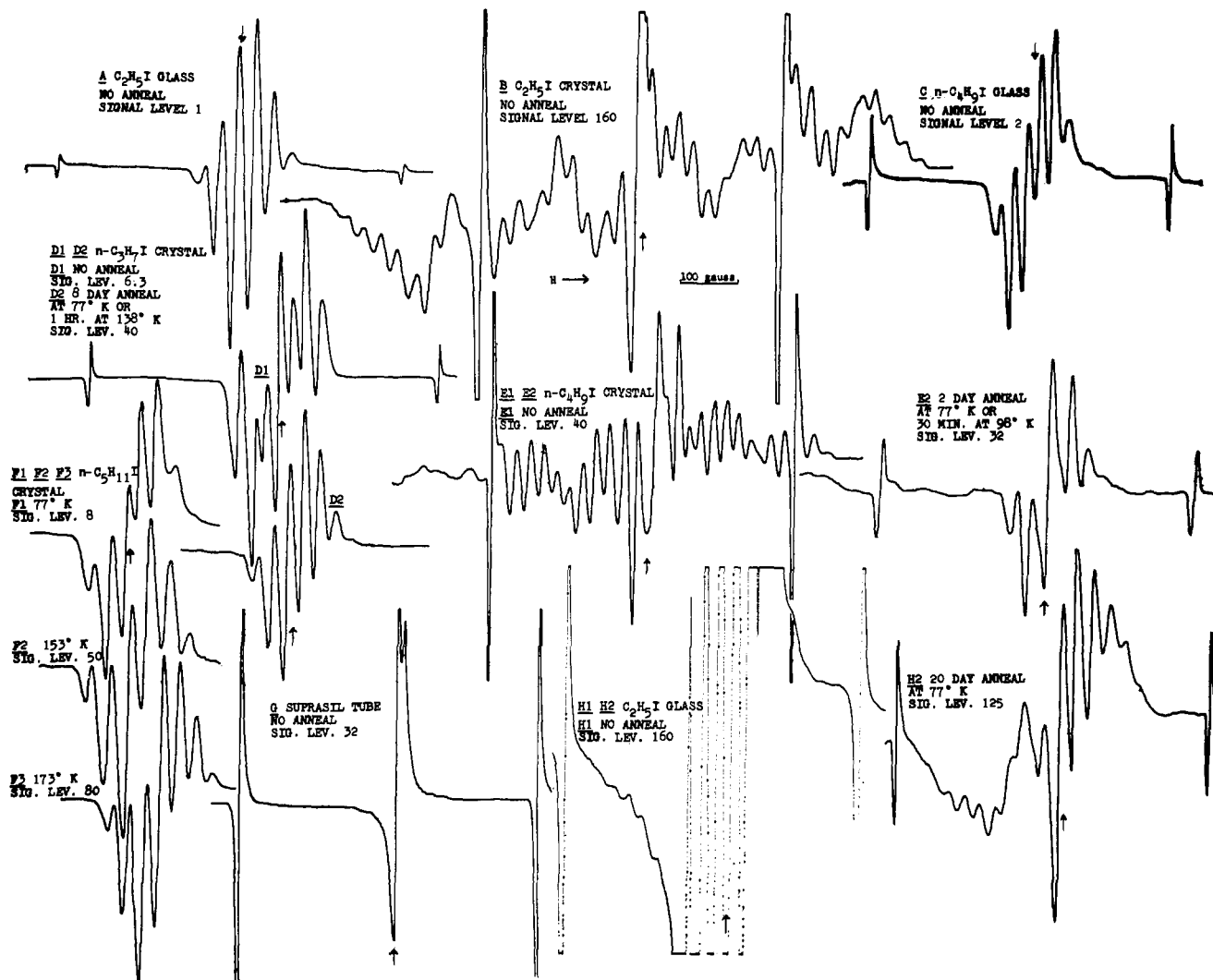


Fig. 1.—Spectra of alkyl iodides irradiated  $7 \times 10^{19}$  e.v.  $\text{g}^{-1}$  at  $77^\circ\text{K}$ . Vertical arrows indicate position of free electron  $g$ -value. All spectra are on approximately the gauss scale indicated in Fig. 1B.

glass as a result of greater localization of energy in the C-I bond as contrasted to the delocalization favored by the long-range order of the crystals; (4) ionic reactions in the glasses made possible by the trapping of electrons (the irradiated glasses show an intense blue color after irradiation while the crystals remain white).

$\text{C}_4\text{H}_9\text{Br}$  irradiated and examined at  $77^\circ\text{K}$ . shows the following glass-crystal differences and selective annealing: (1) a symmetrical six-line pattern for the glass, similar to Fig. 1C, which, at higher sensitivity reveals structure containing 15 or more poorly resolved additional lines extending between  $g = 1.85$  and  $2.25$ ; (2) a dominant six-line pattern for the crystal different from that for the glass but accompanied by somewhat similar structure at low and high fields; (3) the dominant six-line pattern of the glass disappears on annealing to about  $97^\circ$ , followed by the low-field pattern at  $104^\circ$ ;

(4) the spectrum of the polycrystalline sample persists to the melting point but undergoes an increase in intensity and change in character in the high  $g$ -value region between  $132$  and  $153^\circ$ .  $\text{C}_2\text{H}_5\text{Br}$  gave results similar to those in the literature.<sup>5,8</sup>

An exploratory survey showed that, in general, the same products, including ethylene, ethane, methyl, ethyl, propyl, and butyl halides, some dihalides, and some still less volatile compounds are produced from the radiolysis of  $\text{C}_2\text{H}_5\text{I}$ , of  $\text{C}_2\text{H}_5\text{Br}$ , and of  $\text{C}_2\text{H}_5\text{Cl}$  in the liquid, and in both the polycrystalline and glassy phases at both  $77$  and  $4.2^\circ\text{K}$ . Some yields are dependent on physical state. Most notable is the lower yield of butane in polycrystalline samples than in glassy samples.

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