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Abstract

Full Text

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E.P.R. Spectra of γ-Irradiated Acetylene and Its Derivatives

In order to establish the relationship between the structure of the initial molecule and the structure of the radical arising from it, in the present work we studied the e.p.r. spectra of γ-irradiated acetylene, methylacetylene, methyl deuteroacetylene, ethyl- and butylacetylene, and also phenyl- and methylphenylacetylene at 77° K. The yield of radicals was determined as a function of the irradiation dose.

The compounds under investigation were irradiated in ampoules made of special glass that gives no e.p.r. spectrum at the γ-radiation doses used. Before the experiment the ampoules were evacuated to 10^{-3} mm Hg. Irradiation was carried out with a Co^{60} source. A superheterodyne-type radiospectroscope was used to record the e.p.r. spectra. Calibration of the magnetic field was performed from the e.p.r. spectra of the ion peroxylaminedisulfonate $[NO(SO_3)_2^{2-}]$ in chloroform. To determine the concentration of the radicals obtained, single crystals of cupric chloride ($CuCl_2 \cdot 2H_2O$) were used. The relative error in determining the radical yield was of the order of 20%; the g-factor of the line was determined from crystalline DPPH. The acetylenes studied were obtained and purified by known methods and had constants coinciding with the literature data.

The results of the experimental studies are given in Tables 1, 2 and in Fig. 1.

The simplest e.p.r. spectrum, as was to be expected, was obtained for irradiated methylacetylene. The spectrum is a symmetric quartet of equally spaced lines with an intensity ratio of $1 : 2$, $1 : 2$, $2 : 1$ and is apparently due to interaction of the unpaired electron with three protons.

The e.p.r. spectrum of irradiated deuteriomethylacetylene (which was obtained by decomposition of heavy water with lithium methylacetylide) indicates interaction of the unpaired electron in the radical with the protons of the CD and CH_2 groups.

On the basis of these data, the e.p.r. spectrum of γ-irradiated methylacetylene can be assigned to the radical (propynyl), having the structure (I):

$$[H_2C^1 = C^2 \equiv C^3H]^{\bullet} \qquad \text{(I)}.$$

The theoretical analysis carried out for the e.p.r. spectrum of the propynyl radical gives the best approximation to the experimental spectral curve when a certain nonequivalence of the hydrogen atoms at atoms C^1 and C^3 is taken into account. The magnitude of the "free" electron density in the region of the hydrogen nuclei of the methylene group must be somewhat greater (by $\sim 20\%$) than that of the methyl group.

The results of our work agree with the data obtained in the study of the e.p.r. spectrum of the radical arising under the action of ultraviolet light on methylacetylene at a temperature of 77° K ([1]). The formation of the propynyl radical (I) from methylacetylene is also quite justified from the energetic point of view. Radical (I) possesses a large energy of delocalization of the unpaired electron and requires a relatively smaller expenditure of energy for rupture of the C–H bond in the molecule at the moment of its birth.

The EPR spectra of γ-irradiated ethyl- and butylacetylene, which contain longer hydrocarbon chains than methylacetylene, become more complicated: they become asymmetric, and the number of lines and the total width of the spectra increase (Table 1).

Table 1

Integral γ-irradiation dose $\sim 10^7$ rad

No.	Initial compounds (b.p., °C)	Presumed radical	Number of lines	Total width in Oe[1]
1	$H_3C—C \equiv C—H$ (−23.3)	$\cdot H_2C—C \equiv C—H$ | · 1.	4	50.2 ± 1.4
2	$H_3C—C \equiv C—D$ (−23.3)	$\cdot H_2C—C \equiv C—D$ | · 1.	2	97.5 ± 1.4
3	$C_2H_5—C \equiv C—H$ (8.5)	$H_3C—\dot{C}H—C \equiv C—H$ | · 2. $H_2C=C=\dot{C}—H$ | · 1.	6 (8)	54.8 ± 1.6
4	$C_4H_9—C \equiv C—H$ (70.0)	$CH_3—CH_2—CH_2—\dot{C}H—C \equiv CH$ | · 2. $H_2C=C=\dot{C}—H$ | · 3. C_3H_7	11	104.4 ± 2.4
5	$C_6H_5—C \equiv C—H$[3]		–	–
6	$C_6H_5—C \equiv C—CH_3$ (71—72)	$C_6H_5—\dot{C}H—C \equiv C—CH_2$	3	34 ± 1.1
7	$HC \equiv CH$ (−83.6)[4]	1. $\dot{C}H—CH=CH—CH=CH—\dot{C}H$ $\vdots$ $\dot{C} \equiv C—H$ $H—C \equiv C—H$ $\vdots$ $H—C \equiv C—H$	10 (12)	112 ± 4

[1] The indicated line widths refer to the first derivative of the absorption curve.
[2] The number of lines is difficult to determine, apparently because of overlap of the spectrum of incompletely deuterated methylacetylene.
[3] The spectrum was not obtained even at doses of $1—40 \cdot 10^6$ rad.
[4] The EPR spectrum was obtained at a dose of $1.5 \cdot 10^7$ rad.

increases (Table 1). Apparently, upon irradiation of acetylene derivatives of the type R—$CH_2C \equiv CH$, where R = C_2H_5, C_3H_7, etc., several radicals of the type R—$\dot{C}H$—$C \equiv CH$, R, and $\dot{C}H_2$—$C \equiv CH$ are formed. A change in the form of the spectrum as a function of the irradiation dose is also observed (the spectral width and the number of components change). This may indicate the occurrence of secondary reactions at 77° K. From Table 2 it follows that the yield

Table 2

Yield of radicals as a function of γ-irradiation dose

No.	Initial compounds	$1 \cdot 10^6$ rad, g-mol·10[21]	$1 \cdot 10^6$ rad, mol.%	$10 \cdot 10^6$ rad, g-mol·10[21]	$10 \cdot 10^6$ rad, mol.%	$12 \cdot 10^6$ rad, g-mol·10[21]	$12 \cdot 10^6$ rad, mol.%	$20 \cdot 10^6$ rad, g-mol·10[21]	$20 \cdot 10^6$ rad, mol.%	$40 \cdot 10^6$ rad, g-mol·10[21]	$40 \cdot 10^6$ rad, mol.%
1	$H_3C—C \equiv C—H$	0.15	0.02	1.1	0.18	2.1	0.34	4.4	0.73	1.8	0.30
2	$H_3C—C \equiv C—D$	2.4	0.42					(0.23)	0.04		
3	$C_2H_5—C \equiv C—H$	0.5	0.08	1.6	0.26	2.2	0.35	2.9	0.48	2.5	0.41
4	$C_4H_9—C \equiv C—H$	2.2	0.37	0.7	0.12						
5	$C_6H_5—C \equiv C—CH_3$	1.87[1]	0.23			0.47	0.09			0.16	0.03
6	$HC \equiv CH$					0.38[2]	0.06			0.13	0.02

[1] The radical yield was determined at a dose of 15 million rad.
[2] The radical yield was determined at a dose of 2 million rad.

of radicals at a given irradiation dose for methyl-, ethyl-, and butylacetylene increases somewhat with lengthening of the hydrocarbon chain. With an increase in the irradiation dose from 1 to 40 million rad, the yield of radicals also rises and reaches a maximum at a dose of ~ 20 million rad, and then begins to decrease.

It was shown above that in the propyl radical the unpaired electron is delocalized by means of the triple bond. Therefore it was of interest to investigate γ-irradiated methylphenylacetylene. In this case the results of the investigation proved somewhat unexpected. The EPR spectrum of γ-irradiated phenylmethylacetylene is a symmetric triplet. The observed spectrum can be explained in two ways. The hyperfine structure (h.f.s.) of the EPR spectrum, consisting of three lines, is caused by interaction of the unpaired electron with the protons of the methylene group in the radical of the structure: $-C\ C—\dot{C}H_2$, or the methyl

Fig. 1. EPR spectra of γ-irradiated acetylenes at T = 77°K: a – methylacetylene, b –methyldeuteroacetylene, c –ethylacetylene, d – butylacetylene, e –methylphenylacetylene, f –acetylene (a-d –integral dose 1 • 10 million rad., e –3 million rad., f –20 million rad.)

Figure 1: Fig. 1. EPR spectra of γ-irradiated acetylenes at T = 77°K: a – methylacetylene, b –methyldeuteroacetylene, c –ethylacetylene, d –butylacetylene, e –methylphenylacetylene, f –acetylene (a-d –integral dose 1 • 10 million rad., e –3 million rad., f –20 million rad.)

group of the initial compound, which initially absorbs the energy of γ-quanta, is preserved, and the EPR spectrum belongs to the radical of the phenyl ring Aŕ–C C–H.

Fig. 1. EPR spectra of γ-irradiated acetylenes at $T = 77^{\circ}$K: *a* –methylacetylene, *b* –methyldeuteroacetylene, *c* –ethylacetylene, *d* –butylacetylene, *e* –methylphenylacetylene, *f* –acetylene (*a*-*d* –integral dose $1 \cdot 10$ million rad., *e* –3 million rad., *f* –20 million rad.).

It is known([2]) that the h.f.s. of the EPR spectrum of the benzene ring is characterized by three components. However, in the case of irradiated benzene the total width of the EPR spectrum and of the individual components proved to be considerably greater than in the spectrum of γ-irradiated (simultaneously with benzene) methylphenylacetylene. In addition, the intensity of the EPR spectrum of γ-irradiated benzene is much smaller and, under the conditions used for recording the spectrum of phenylmethylacetylene, the benzene spectrum does not appear. Therefore we suppose that the h.f.s. of the EPR spectrum of γ-irradiated methylphenylacetylene is due to interaction of the unpaired electron with the protons of the methylene group, while the phenyl ring, by means of the triple bond C C, participates only weakly in the delocalization of the unpaired electron. This is also confirmed by the EPR spectrum of γ-irradiated ethylphenylacetylene, which contains five h.f.s. components.

Of particular interest is the EPR spectrum of γ-irradiated acetylene (Fig. 1). An intense EPR spectrum is observed only at large irradiation doses ($\sim 1.3 \cdot 10^7$ rad.), which indicates a considerable redistribution of energy in the system. This is manifested to an even greater extent in phenylacetylene, which gives no EPR spectrum even at high irradiation doses. The effective redistribution of absorbed energy in such systems is apparently associated with the presence of complexes formed between molecules. The EPR spectrum of γ-irradiated acetylene has a complex character (contains $\sim$ 12 lines); as the irradiation dose is increased to $4 \cdot 10^7$ rad., the appearance of the spectrum changes somewhat. The large number of h.f.s. lines in the EPR spectrum of γ-irradiated acetylene is due to interaction of the unpaired electron with several protons of the system. The observed EPR spectrum of γ-ir–

of irradiated acetylene can be explained in two ways: by the formation of poly-

meric radicals (polyacetylene)

$$-\dot{C}=CH-CH=CH-CH=CH-$$

or by the existence of radical complexes of the type

$$\begin{array}{c} \dot{C}\equiv C-H \\ \vdots \quad \vdots \\ H-C\equiv C-H \\ \vdots \quad \vdots \\ H-C\equiv C-H \end{array}$$

In a number of experiments we did in fact observe polymer films on the walls of the ampoule. The presence of complexes forming between acetylene molecules in the liquid phase is indicated in the works ([3,4]). The yield of radicals for acetylene decreases with increasing irradiation dose, while the yield of the polymer film increases. The g-factor of the centers of the single lines of the EPR spectra of all the compounds studied corresponds to the g-factor of crystalline DPPH.

Analysis of the EPR spectra studied for γ-irradiated compounds indicates the existence of a definite relationship between the structure of the initial molecule and the structure of the radical arising as a result of its decomposition under the action of radiation. It was found that, under the action of large doses of γ-radiation on frozen acetylene ($T = 77°$K), polymer formation occurs. The polymerization process apparently has a radical character, accompanied by the formation of complex radicals or radical complexes. It is important to note that, in the cases considered, radical formation is associated with rupture of the C –H bond of the methyl group of the starting compounds, which is due to the formation of a more stable radical.

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Note: Figure translations are in progress. See original paper for figures.