ESR Studies on Primary Processes in Radiation-Induced Reactions. VI. Isoprene and 1,3-Pentadiene in Alkyl Halide Matrices

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ABSTRACT: The cation radical of isoprene was first detected by means of ESR. It was produced by γ-irradiation in carbon tetrachloride, and has proton coupling constants of $a_1 = 13.0$ G (2H), $a_2 = 4.9$ G (3H), $a_3 = 3.2$ G (1H), and $a_4 = 9.2$ G (2H). In *n*-butyl chloride glass at 77°K a linear allyl-type radical was formed from isoprene. The initiation of polymerization by the isoprene cation radical was suggested in *n*-butyl chloride glass at 77°K during γ-irradiation. A cyclohexadienyl-type radical was produced from *trans*-1,3-pentadiene by γ-irradiation in carbon tetrachloride, whereas a linear allyl-type radical was produced from *cis*-1,3-pentadiene. In a *n*-butyl chloride glass, a linear allyl-type radical was produced from both 1,3-pentadiene by γ-irradiation at 77°K. The cation radical were suggested to initiate radiation-induced polymerization in *n*-butyl chloride glass at 77°K.

KEY WORDS   ESR / γ-Irradiation / Isoprene / 1,3-Pentadiene / Cation Radical / Cyclohexadienyl-Type Radical / Allyl-Type Radical / *n*-Butyl Chloride Glass / Carbon Tetrachloride /

The anion radical of 1,3-butadiene and its derivatives formed by γ-irradiation were first detected by means of ESR in 2-methyl(tetrahydrofuran) glass at 77°K.[1] The cation radical of 1,3-butadiene was first observed by means of ESR following γ-irradiation on silica gel.[2] In this system the butadiene cation radical reacts further with butadiene molecules and produces the allyl-type radical (RI), $CH_2=CH-\dot{C}H-CH_2-$. The alkyl halides are well known as solvents and matrices suitable for studying cationic reactions. In a carbon tetrachloride polycrystalline matrix, the butadiene cation radical has been detected by means of ESR following γ-irradiation.[1] In a *n*-butyl chloride glass matrix, the radical RI is produced from 1,3-butadiene by γ-irradiation. Thus, it has been suggested that the butadiene cation radical initiates radiation-induced polymerization of 1,3-butadiene in a *n*-butyl chloride glass matrix at 77°K.[1] In the present study isoprene and 1,3-pentadiene are investigated in order to elucidate the primary processes of radiation-induced cationic reactions of these dienes by

using carbon tetrachloride and *n*-butyl chloride as matrices. It is also intended to detect the ESR spectra of the cation radicals of these dienes and to determine the coupling constants for them, because none of them has been reported yet.

EXPERIMENTAL

Alkyl halides were purified by distillation, then dried by storing on a molecular sieve 3 A which has previously been baked at 350°C for 8 hr under a pressure of 10^{-5} torr. Isoprene, *trans*-1,3-pentadiene, and *cis*-1,3-pentadiene were distilled in a vacuum line. Samples were prepared by adding known amounts of diene to a solvent in a vacuum line, then sealed off under a pressure of 10^{-5} torr. Irradiation was carried out at 77°K with a ^{60}Co γ-source at a dose rate of 2 Mrad/hr to a total dose of 1 Mrad. ESR measurements were made with a Varian E-3 X-band spectrometer with 100-kHz magnetic field modulation at a microwave power of 2 mW. This microwave power is the best

condition for ESR measurements with the presently used spectrometer. The lineshape of the spectrum is not distored by this microwave power.

RESULTS

Carbon Tetrachloride Matrix
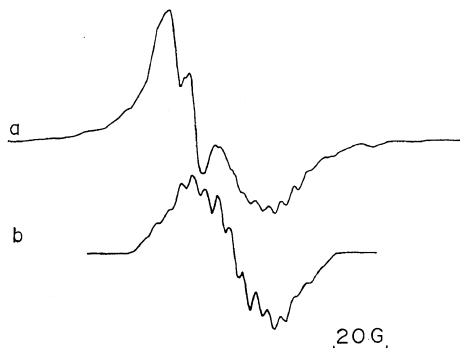
The ESR spectrum at 77°K is seriously masked

Figure 1. ESR spectra in carbon tetrachloride polycrystal following γ-irradiation at 77°K, measured at 163°K: a, 1.5 mol% of isoprene; b, computed spectrum using the parameters, $a_1=$ 13.0 G (2H), $a_2=4.9$ G (3H), $a_3=3.2$ G (1H), $a_4=$ 9.2 G (2H), and a Gaussian linewidth of 4.5 G.
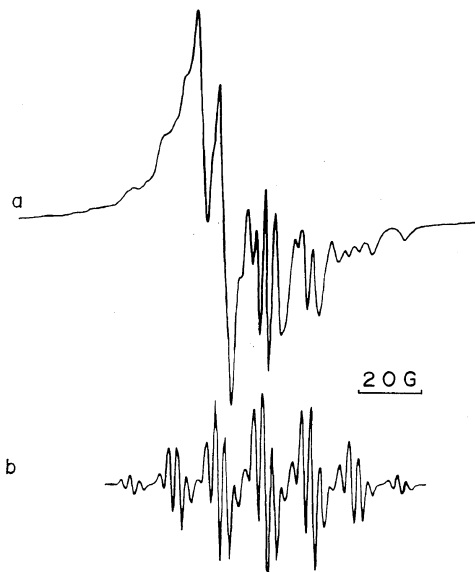

Figure 2. ESR spectra in carbon tetrachloride polycrystal following γ-irradiation at 77°K, measured at 120°K: a, 1.0 mol% of trans-1,3-pentadiene; b, computed spectrum using the parameters, $a_1=$ 48.5 G (4H), $a_2=8.6$ G (4H), $a_3=2.8$ G (2H), and a Gaussian linewidth of 3.5 G.
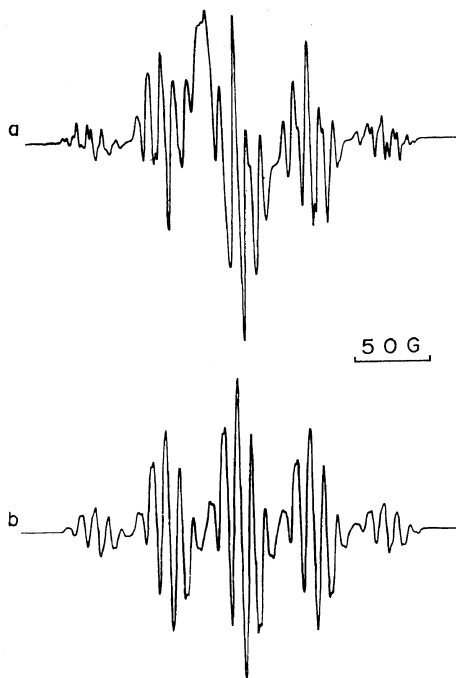

Fugure 3. ESR spectra in carbon tetrachloride polycrystal following γ-irradiation at 77°K, measured at 163°K: a, 1.0 mol% of cis-1,3-pentadiene; b, computed spectrum using the parameters, $a_1=$ 12 G (2H), $a_2=15$ G (3H), $a_3=14$ G (1H), $a_4=2.7$ G (2H), and a Gaussian linewidth of 1.5 G.

by the signal originating from the carbon tetrachloride. This signal could be partly removed by heating a sample, then the signal from the dienes was observed. The spectrum on a low half field is still superimposed with the signal originating from the matrix with larger g factor, $\dot{C}Cl_3$.[3]

The spectrum from 1.5 mol% of isoprene at 163°K is shown in Figure 1a. The spectrum from 1 mol% of trans-1,3-pentadiene at 120°K is presented in Figure 2a, and that corresponding to cis-1,3-pentadiene at 163°K in Figure 3a. The spectrum in Figure 2a consists of the quintet spectrum with coupling constant of 48.5 G.

n-Butyl Chloride Glass Matrix

The spectra at 77°K from 1 mol% of isoprene, trans-1,3-pentadiene, and cis-1,3-pentadiene are shown in Figures 4, 5a, and 5b respectively. They appear similar to the spectrum from 1,3-butadiene.[1] The subtraction of the spectrum

Fugure 4. ESR spectrum of isoprene 1 mol% in *n*-butyl chloride glass matrix measured at 77°K following γ-irradiation at 77°K.
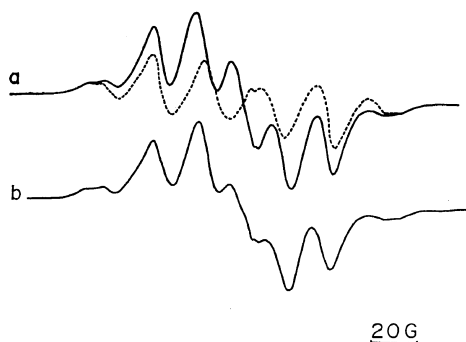

Figure 5. ESR spectra of 1,3-pentadiene in *n*-butyl chloride glass matrix measured at 77°K following γ-irradiation at 77°K: a, 1 mol% of *trans*-pentadiene (——), *n*-butyl radical (- - -); b, 1 mol % of *cis*-pentadiene.

Table I. Spin densities and proton coupling constants of the isoprene cation radical

	CH₃	
C—C—C—C		a_H (G)
1 2 3 4		

C_i	Spin density	Calcd[a].	Obsd.
1	0.391	11.5	13.0
2	0.136	—	—
3	0.112	3.2	3.2
4	0.322	9.2	9.2
CH_3		7.7[b]	4.9

[a] Calculated with the formulae in ref 3.
[b] Calculated with the formula in ref 4.

of the *n*-butyl radical (dotted line in Figure 5a) as a background spectrum from Figures 4 and 5 gives the signals from isoprene, *trans*-1,3-pentadiene, and *cis*-1,3-pentadiene respectively. Due to a large linewidth of the spectra it is difficult to judge whether the spectra obtained after subtraction procedure are quintet or septet spectra. However, it is clear that their peaks are separated by about 15 G, and that they do not contain the coupling constant of 48.5 G which is observed in *trans*-1,3-pentadiene in carbon tetrachloride (Figure 2a).

DISCUSSION

The analysis of the spectra which are super-imposed on the signal originating from carbon tetrachloride on a low half field is attempted on the spectra on a high half field. The simulation spectrum for Figure 1a is obtained by using parameters of $a_1=13.0$ G (2H), $a_2=4.9$ G (3H), $a_3=3.2$ G (1H), $a_4=9.2$ G (2H), and a Gaussian linewidth of 4.5 G. Possible radical structures which have 8 protons are the cation radical of isoprene or the allyl-type radical, $CH_2=C(CH_3)—\dot{C}H—CH_2—$, which is the same type of radical as observed in 1,3-butadiene, (RI). In the case of the allyl-type radical, $a_4=$ 9.2 G is too small for the coupling constant. The spin densities on carbons of the isoprene cation radical are listed in Table I, which are obtained by Hückel method including a hyperconjugation for the methyl group. The coupling constants expected from the spin densities are obtained by the formulae given by Snyder and Amos[4] which have predicted fairly well the coupling constants of the cation radical of 1,3-butadiene.[2] The coupling constants of the methyl protons are obtained by the formula given by Levy.[5] The agreement of the calculated coupling constants for protons on $C_1—C_4$ with those of experimentally obtained coupling constants is good. Therefore, the spectrum presented in Figure 1 is assigned to the isoprene cation radical. The formula given by Levy does not predict the coupling constant of the methyl protons of the isoprene cation radical. The other small peak at a higher field than the simulation spectrum is a part of the signal originating from the matrix.

The simulated spectrum (Figure 2b) for the spectrum from *trans*-1,3-pentadiene gives coupling constants of $a_1=48.5$ G (4H), $a_2=8.6$ G (4H), $a_3=2.8$ G (2H), and a Gaussian linewidth of 3.5 G. The coupling constants of 47.71 G, 8.99 G,

Table II. Calculated spin densities and proton coupling constants of 1,3-pentadiene anion radical

| C—C—C—C—CH₃		a_H, G[a]
1 2 3 4		
C_i	Spin density	
1	0.344	9.9
2	0.105	2.9
3	0.165	4.8
4	0.303	8.2
CH₃		16.4[b]

[a] Calculated with the formulae in ref 3.
[b] Calculated with the formula in ref 4.

2.65 G and 13.04 G have been reported for the cyclohexadienyl radical.[6] Thus, the coupling constants estimated from Figure 2 indicate reasonably well that the cyclohexadienyl-type of radical is produced in a carbon tetrachloride matrix. The spectrum in Figure 2a is assigned to
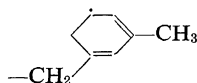

The reaction mechanism for the formation of this radical is not clear. As a possible mechanism cyclic dimerization or further reactions could be considered followed by the abstraction of hydrogen:
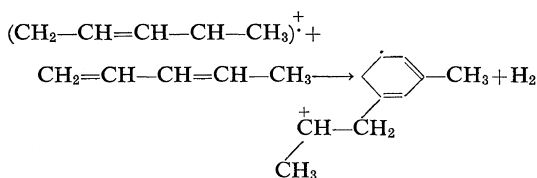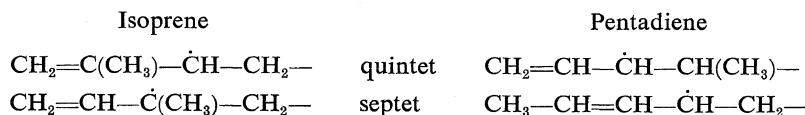

The computed spectrum in Figure 3b is obtained by using parameters of $a_1=12$ G (2H), $a_2=15$ G (3H), $a_3=14$ G (1H), $a_4=2.7$ G (2H), and a Gaussian linewidth of 15 G. The spin densities on carbon atoms and proton coupling constants which are expected for the cation

radical of 1,3-pentadiene are listed in Table II. The spin densities are calculated by the Hückel method including hyperconjugation for the methyl group. The coupling constants are calculated by the formulae given by Snyder and Amos[4] for protons on C_1—C_4, and by the formula given by Levy[5] for the methyl protons. The estimated coupling constants from Figure 3 are too large for those of the protons on C_1—C_4 of the 1,3-pentadiene cation radical. The spectrum in Figure 3a is more reasonably assigned to the allyl-type radical, CH₃—ĊH—CH=CH—CH₂—. In this radical one of the two β protons would have the small coupling of 2.7 G and another a similar value to that of the α proton. These coupling constants resemble those of the radical RI from 1,3-butadiene in n-butyl chloride and hydrocarbon glass matrices.[1] The reaction mechanism would be as follows using the analogy of 1,3-butadiene in n-butyl chloride glass.

$$(CH_3—CH—CH=CH—CH_2)\overset{+}{\cdot}+$$
$$CH_2=CH—CH=CH—CH_3 \longrightarrow$$
$$CH_3—\dot{C}H—CH=CH—CH_2—CH_2—$$
$$CH=CH—\overset{+}{C}H—CH_3$$
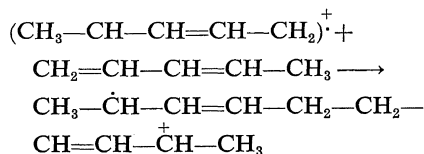
The signals from isoprene, *trans-*, and *cis-*1,3-pentadiene in n-butyl chloride glass are quintet or septet lines which are separated by about 15 G. They are reasonably assigned to the allyl-type radicals in which one of the two β protons has a small coupling constant less than a linewidth and another has a similar coupling to the α proton. These couplings of β protons are common to the allyl-type radicals from 1,3-butadiene, isoprene and 1,3-pentadiene in organic glass matrices. The magnitude of the β proton coupling is approximated to $a_\beta = B\cos^2\theta$, whereas B is 45—50 G and θ is the angle between the axis of the unpaired electron in its $2p_z$ orbital and the projection of the C_β—H bond on a plane orthogonal to the C_α—C_β bond.[7] From this relation the angle is estimated to have the values of about 45° and 75°.

Isoprene		Pentadiene
CH₂=C(CH₃)—ĊH—CH₂—	quintet	CH₂=CH—ĊH—CH(CH₃)—
CH₂=CH—Ċ(CH₃)—CH₂—	septet	CH₃—CH=CH—ĊH—CH₂—

The cation radicals of isoprene and 1,3-pentadiene would be more reactive at 1 position than at 4 position, when the reactivity could be predicted by the Frontier electron density.[8] If this is the case here, septet lines would be expected from the addition of the cation radicals of these dienes to the corresponding molecules. The initiation mechanism of the radiation-induced polymerization is analogic for 1,3-butadiene, isoprene, and 1,3-pentadiene in *n*-butyl chloride glass matrix at 77°K.

Several differences between carbon tetrachloride and *n*-butyl chloride matrices, *i.e.*, rigidity, ability for stabilizing the cation radical, monomer distribution and radical species formed from matrices could contribute to the observation of the isoprene cation radical in carbon tetrachloride and the allyl-type radical in *n*-butyl chloride at 77°K.

The formation of the cyclohexadienyl-type radical from *trans*-1,3-pentadiene and the linear allyl-type radical from *cis*-1,3-pentadiene in carbon tetrachloride suggests that these pentadienes have certain differences in their distribution in the matrix which leads to the different reaction mechanisms for *trans*- and *cis*-pentadienes in this matrix. On the other hand, in organic glass matrices, both pentadienes are probably distributed in such a way as to form the linear allyl-type radical.

REFERENCES

1. T. Shiga, A. Lund, and P. O. Kinell, *Acta Chem. Scand.*, **29**, 383 (1972); T. Shiga and S. Okamura, Abstract, 15th Discussion Meeting of Japanese Society of Radiation Chemistry, Osaka, October 30, 1972, p 64.
2. T. Shiga, A. Lund, and P. O. Kinell, *Int. J. Radiat. Phys. Chem.*, **3**, 131 (1971); T. Shiga, A. Lund, and P. O. Kinell, *Acta Chem. Scand.*, **25**, 1508 (1971).
3. J. Sohma, H. Kashiwabara, T. Komatsu, and T. Takahashi, *Hokkaido Univ. Kogakubu Kenkyu Hohkoku*, **35**, 511 (1964).
4. L. C. Snyder and T. Amos, *J. Chem. Phys.*, **42**, 3670 (1965).
5. D. H. Levy, *Mol. Phys.*, **9**, 233 (1966).
6. S. Ohnishi, T. Tanei, and I. Nitta, *J. Chem. Phys.*, **37**, 2402 (1962).
7. C. Heller and H. M. McConnell, *ibid.*, **32**, 1535 (1960).
8. T. Yonezawa, Ed., "Ryōshi Kagaku Nyumon", 3rd ed., Kagakudojin, Kyoto, 1969, p 218.