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# ESR Studies on Radiation-Induced Polymerization of 1,3-Butadiene in Urea Canal Complexes[1]

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The ESR spectrum of $\gamma$-irradiated 1,3-butadiene in urea canal complexes at 77 K consists of 7 lines with a hyperfine splitting of 15 G and is assigned to the monomer radical $CH_3\text{–}CH\text{=}CH\text{–}\dot{C}H_2$ which may be produced by hydrogen addition to the 1,3-butadiene. Upon warming to room temperature the spectrum changes into a $6\times2$-line spectrum ($a_1=14$ G and $a_2=4$ G), which is attributed to the propagating radical $R\text{–}C_\beta H_2\text{–}C_\alpha H\text{=}CH\text{–}\dot{C}H_2$ occluded in the urea canals. On cooling back to 77 K, the $6\times2$-line spectrum is transformed into a 5-line spectrum ($a=14$ G); this spectral change is reversible with temperature and is interpreted in terms of oscillation of the propagating radical around the $C_\beta\text{–}C_\alpha$ bond. On further warming to 400 K, the propagating radical is converted to the "chain" allyl type radical $R\text{–}CH_2\text{–}CH\text{=}CH\text{–}\dot{C}H\text{–}CH_2\text{–}R'$, of which room-temperature spectrum consists of $7\times2$ lines ($a_1=14$ G and $a_2=4$ G). This radical conversion is explained by hydrogen atom transfer reaction within the propagating radical through the radical chain and/or between the propagating radical and a neighbouring polymer chain. Irradiated 1,3-butadiene-1,1,4,4-$d_4$ in urea canals is also examined and the results obtained confirm the above-mentioned identifications.

The polymerization of 1,3-butadiene in urea complexes was extensively investigated by White[2] and the formation of *trans*-1,4-polybutadiene was obtained by irradiation with high energy electron at low temperatures. The initiation of polymer chain growth inside the crystalline lattice[3] of canal complexes was reported to be quite difficult by other conventional means, *i.e.*, high pressure, heat, ultraviolet rays, and conventional initiators.[4]

High energy radiation, however, can penetrate into the crystalline lattice of canal complexes. As a result, active species may be produced inside the crystalline lattice. ESR results of irradiated aliphatic monomers

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[1] Presented at the 21st Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1968.

[2] D. M. White, *J. Amer. Chem. Soc.*, **82**, 5678 (1960).

[3] The structure of a urea lattice in hydrocarbon–urea complexes was reported to be hexagonal (A. E. Smith, *Acta Crystallogr.*, **5**, 224 (1952)). There are six urea molecules in the unit cell with lattice parameters $a=8.23$ Å and $c=11.0$ Å. Along the $c$ axis the urea molecules form the wall of a canal, of which diameter is 5—6 Å. 1,3-Butadiene molecules are packed in the canal.

[4] J. F. Brown, Jr., and D. M. White, *J. Amer. Chem. Soc.*, **82**, 5671 (1960).

(ketones, ethers, and esters) in urea canals[5] have showed that monomer radicals are trapped inside the urea canals. This suggests the possibility that monomer radicals from irradiated 1,3-butadiene–urea complexes may be produced inside the crystalline lattice of the urea complexes. The monomer radicals produced would be expected to initiate the polymerization of 1,3-butadiene.

In our preliminary experiments the irradiation of pure solid 1,3-butadiene did not produce appreciable amounts of polymers, while a 25% conversion to polymer was reported in irradiated 1,3-butadiene–urea complexes.[2] The results indicate that packing of 1,3-butadiene in urea canals is very effective for the polymerization of 1,3-butadiene. One of reasons for this is supposed to be due to the fact that walls formed by the urea molecules can prevent bimolecular termination reactions between growing polymer chains unless two growing polymer chains are both present in an urea canal.

Although the reaction processes of polymerization have been investigated in detail for several solid monomers including 1,3-butadiene by means of ESR,[6] there seems to be no report regarding the nature of active species produced during polymerization in urea canals. In order to elucidate the mechanism of polymerization in urea canals, ESR studies of irradiated 1,3-butadiene–urea complexes have been made at temperatures in the range 77—400 K. The results obtained have indicated that the monomer radical is produced by hydrogen addition to the 1,3-butadiene at 77 K, followed by changing into the propagating radical at elevated temperature. Further warming leads to conversion to the "chain" allyl type radical by intra- and/or intermolecular hydrogen transfer.

## Experimental

All the chemicals used for the preparation of the urea canal complexes, with the exception of 1,3-butadiene-1,1,4,4-$d_4$ (BD-*d*), were obtained from commercial source. The urea was recrystallized several times from water and was dried in a desiccator over anhydrous calcium chloride. The 1,3-butadiene without deuteration (BD-*h*) was distilled *in vacuo* from trap to trap. The BD-*d* was prepared by pyrolysis of the BD-*d*–$SO_2$ addition compound which was obtained by base-catalyzed deuterium exchange of the BD-*h*–$SO_2$ addition compound.[7]

The urea canal complexes of BD-*h* or BD-*d* were prepared by the method developed by White[2] with some modifications. A mixture of BD-*h* (60 wt%), urea (40 wt%), and methanol (traces) was sealed in a ESR sample tube and was kept in a low-temperature bath controlled at 218 K for 5 days. This temperature has been reported to be optimum for the formation of BD-*h*–urea complexes.[2]

Irradiation was carried out with a 3-KCi $^{60}$Co source at 77 K. The dose rate was $1.5\times10^5$ R/hr and the total dose was $2\times10^6$ R. ESR spectra were obtained with a Japan Electron Optics Lab. Co. (JEOL) X-band spectrometer with 100 KHz field modulation at various temperatures. A liquid-nitrogen Dewar was used for measurements at 77 K and a variabletemperature accessory supplied by JEOL was employed form easurements at higher than 90 K.

Polymer products obtained after irradiation of BD-*h*–urea complexes were confirmed to be *trans*-1,4-polybutadiene by comparison of their infrared spectra and intrinsic viscosities with the data reported by White.[2]

## Results and Discussion

*Monomer Radical.* Figure 1a shows the ESR spectrum of BD-*h*–urea complexes which were immediately measured at 77 K after irradiation at 77 K. The spectrum consists of 7 lines with a hyperfine splitting of 15 G. Any significant spectral change in the hyperfine structure did not take place after the sample was heated from 77 to 130 K and was cooled back to 77 K (Fig. 1b). The 7-line spectrum can be ascribed to the allyl type radical (radical I)

$$\underset{\mathrm{R_I}}{\overset{\beta}{\mathrm{CH_3}}-\overset{\alpha3}{\mathrm{CH}}=\overset{\alpha2}{\mathrm{CH}}-\overset{\alpha1}{\dot{\mathrm{C}}\mathrm{H_2}}.}$$

The formation of radical I may be accounted for by hydrogen addition to the conjugated double bond of BD-*h*.

Radical I has an unpaired spin coupling to four α and three β protons. The unpaired spin distribution of radical I is supposed to be approximately similar to that of the allyl radical $CH_2=CH-\dot{C}H_2$. The α-proton

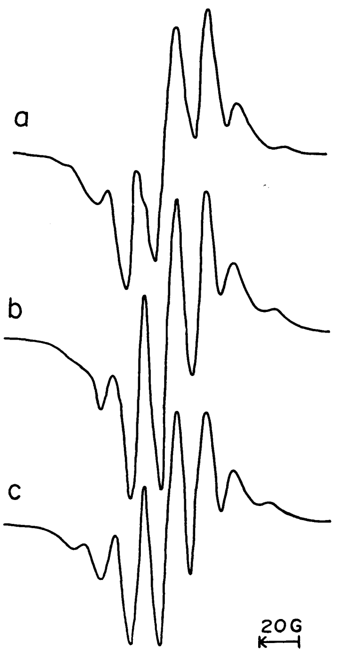

Fig. 1. ESR spectra of 1,3-butadiene-urea complexes irradiated at 77 K, (a) measured at 77 K immediately after irradiation; (b) measured at 77 K after warming to 130 K. (c) Computed spectrum of the monomer radical.

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[5] O. H. Griffith, *J. Chem. Phys.*, **42**, 2644, 2651 (1965); E. E. Wedum and O. H. Griffith, *Trans. Faraday Soc.*, **62**, 819 (1966).

[6] a) Y. Shioji, S. Ohnishi, and I. Nitta, *J. Polymer Sci.*, *A*, **1**, 3373 (1963). b) J. H. O'Donnell, B. McGarvey, and H. Morawetz, *J. Amer. Chem. Soc.*, **86**, 2322 (1964). c) M. J. Bowden and J. H. O'Donnell, *J. Phys. Chem.*, **72**, 1577 (1968). d) Y. Sakai and M. Iwasaki, *J. Polymer Sci.*, *A*,**7**, 1749 (1969). e) T. Shiga, A. Lund, and P. O. Kinell, *Int. J. Radiat. Phys. Chem.*, **3**, 145 (1971).

[7] The BD-*h*–urea addition compounds were synthesized by the reaction of BD-*h* and $SO_2$ under a high pressure (15 kg/cm$^2$).

coupling constants of radical I, therefore, are assumed to be $a_{\alpha 1}=a_{\alpha 3}=14$ G and $a_{\alpha 2}=4$ G from the values obtained for the allyl radical.[8]

The $\beta$-proton coupling constants of radical I can be estimated by the use of the relation[9]

$$a_\beta = 2Q_\beta \cdot \rho_\alpha \cdot \cos^2\theta. \qquad (1)$$

In Eq. (1), $Q_\beta$ is the constant, whose value is assumed to be 29.3 G from Ref. 8, $\rho_\alpha$ is the spin density on the $\alpha$3-carbon atom, of which value is assumed to be 0.58 from Ref. 8, and $\theta$ is the angle between the H–C$_\beta$–C$_{\alpha 3}$ plane and the axis of $p_z$ orbital on the $\alpha$3-carbon atom. Assuming that the methyl protons of radical I are rapidly rotating, $\cos^2\theta$ in Eq. (1) is averaged out, *i.e.*, $\langle\cos^2\theta\rangle=1/2$. As a result, $a_\beta$ for the rotating methyl protons is given by the expression

$$a_\beta(CH_3) = Q_\beta \cdot \rho_\alpha. \qquad (2)$$

Substitution of the values ($Q_\beta=29.3$ G and $\rho_\alpha=0.58$) into Eq. (2) gives $a_\beta=16$ G. Using these coupling constants estimated and the component lines with Gaussian shape, one obtains the computed spectrum as shown in Fig. 1c. It shows good agreement with the observed spectrum (Fig. 1b).

Maas and Volman[10] have reported the ESR spectrum of radical I produced from 1-buten-3-ol by ultraviolet irradiation; $CH_3-CH(OH)-CH=CH_2 \rightarrow CH_3-CH=CH-\dot{C}H_2+OH$. Its spectrum (7 lines with $a=15$ G) is quite similar to Fig. 1b. An ESR spectrum similar to Fig. 1b has been observed also by Morgan and White[11] in the hydrogen bombardment of BD-*h*; $CH_2=CH-CH=CH_2+H \rightarrow CH_3-CH=CH-\dot{C}H_2$.

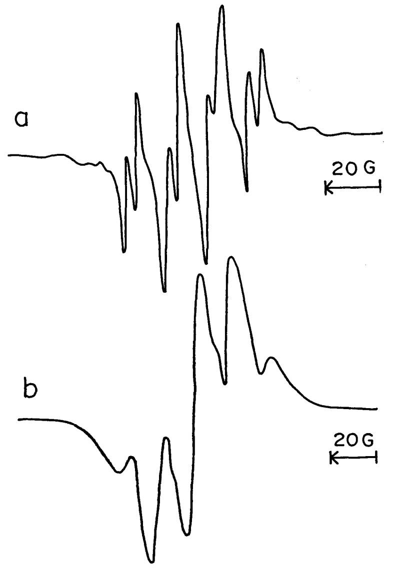

Fig. 2. ESR spectra of irradiated 1,3-butadiene–urea complexes after warming to room temperature. (a) Room-temperature spectrum. (b) 77 K spectrum.

*Propagating Radical.* Upon warming to room temperature, the 7-line spectrum (Fig. 1b) changed as shown in Fig. 2. The spectrum measured at room temperature (Fig. 2a) is a well resolved spectrum, consisting of 6 lines ($a_1=14$ G) which respectively further split into 2 lines ($a_2=4$ G). On cooling back to 77 K, the 6×2-line spectrum changed into a 5-line spectrum with a hyperfine splitting of 14 G (Fig. 2b). This result indicates the conversion of radical I to another radical species at elevated temperature. When the sample was warmed again to room temperature, the 5-line spectrum reverted to the 6×2-line spectrum. This reversible spectral change may be attributed to a reversible conformation change of the 5-line species with temperature as discussed later.

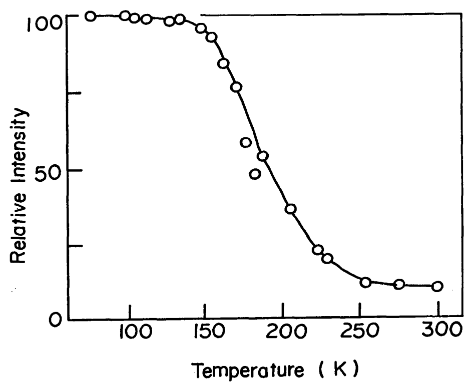

Fig. 3. Decay curve of radicals trapped in irradiated 1,3-butadiene–urea complexes.

Figure 3 shows the decay curve of radicals trapped in urea canals at 77 K. The relative intensity of the ESR signal was recorded after the sample had been annealed for 5 min at each elevated temperature. The radicals began to decay at 140—150 K and stopped decaying at 250—260 K. The radicals surviving after heat treatment up to 300 K were about 10% of the radicals initially trapped at 77 K and were stable at room temperature at least for several days.

Since White[2] has reported that the polymerization of irradiated BD-*h* in urea canals occurs at a low temperature of 195 K, the radical obtained after warming to room temperature is presumably attributable to the propagating radical (radical II) occluded in the urea canals:

$$R_I + n(CH_2=CH-CH=CH_2) \longrightarrow$$
$$R_I-(CH_2-CH=CH-CH_2)_{n-1}-\overset{\beta}{C}H_2-\overset{\alpha 3}{C}H=\overset{\alpha 2}{C}H-\overset{\alpha 1}{\dot{C}}H_2. \qquad (3)$$
$$R_{II}$$

As this radical also belongs to the allyl type radical, the unpaired spin distribution is supposed to be similar to that of radical I. The $\alpha$-proton coupling constants of radical II, therefor, are assumed to be the same as those of radical I, *i.e.*, $a_{\alpha 1}=a_{\alpha 3}=14$ G and $a_{\alpha 2}=4$ G. If both of the two $\beta$-coupling constants are 14 G, these five protons ($a_1=14$ G) and one proton ($a_2=4$ G) well account for the 6×2-line spectrum observed at room temperature. The computed spectrum (Fig. 4a) based upon these estimations is in good agreement with the observed spectrum (Fig. 2a).

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8) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

9) C. Heller and H. M. McConnell, *ibid.*, **32**, 1535 (1960); C. Heller, *ibid.*, **36**, 175 (1962).

10) K. A. Mass and D. H. Volman, *Trans. Faraday Soc.*, **60**, 1204 (1964).

11) C. U. Morgan and K. J. White, *J. Amer. Chem. Soc.*, **92**, 3309 (1970).

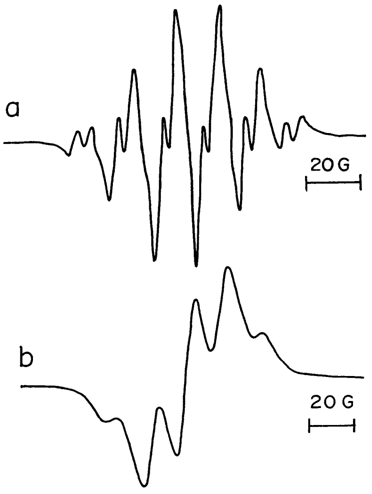


Fig. 4. Computed spectrum of the propagating radical. (a) Room-temperature spectrum. (b) 77 K spectrum.

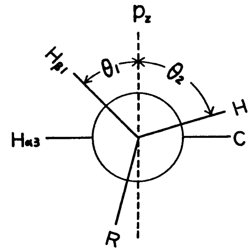


Fig. 5. Conformation of the propagating radical along the direction of the $C_\beta$–$C_{\alpha 3}$ bond.

It is well known that the coupling constants of $\beta$-methylene protons often exhibit temperature-dependent change[6c,d,12] due to hindered oscillation around the $C_\beta$–$C_\alpha$ bonds. At 77 K the motion of a $\beta$-methylene group in an aliphatic radical is usually considered to be almost frozen at a fixed conformation. The conformation of radical II at 77 K is depicted in Fig. 5 on the assumption of nonequivalent $\theta$ values for the two $\beta$ protons ($\theta_1 \neq \theta_2$); this leads to nonequivalent $\beta$-coupling constants ($a_{\beta 1} \neq a_{\beta 2}$) from Eq. (1). Each of the $a_\beta$ values can be determined by way of trial and error. When the $a_\beta$ values were respectively taken to be 19 G ($\theta_1=42°$) and 5 G ($\theta_2=68°$), the appropriate computed spectrum was obtained as shown in Fig. 4b. It is to be noted that the equivalent coupling of 14 G observed at room temperature is nearly equal to the averaged value of 19 and 5 G. This strongly suggests that the two $C_\beta$–H bonds undergo rapid exchange or large amplitude oscillation about the two equilibrium positions ($\theta_1=42°$ and $\theta_2=68°$).

This equivalency of the two $\beta$-proton couplings may partly contribute to the better resolution of the room-temperature spectrum. However, partial average of $\alpha$-proton anisotropic couplings due to overall rotation around the molecular chain axis of radical II would be the main cause of the sharper line width of the room-temperature spectrum; such a case has been often reported for radicals trapped in urea canals.[13]

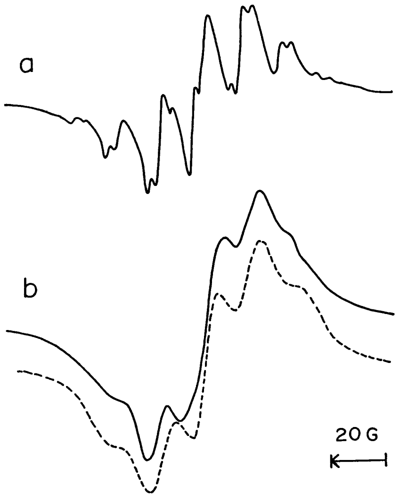


Fig. 6. ESR spectra of irradiated 1,3-butadiene–urea complexes after warming to 400 K. (a) Room-temperature spectrum. (b) 77 K spectrum. Dotted lines indicate the computed spectrum.

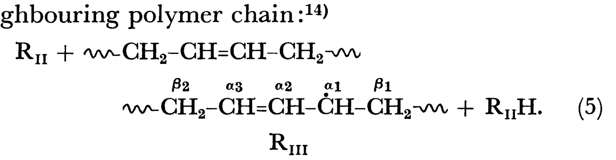
*Radical Conversion at 400 K.* When the sample was further warmed from 300 K to higher temperatures, radical II began to decay rapidly at 400 K and at the same time changed into another kind of radical. Its spectrum measured at room temperature consists of $7\times2$ lines ($a_1=14$ G and $a_2=4$ G) as shown in Fig. 6a, while the spectrum at 77 K consists of poorly resolved several lines (Fig. 6b). This spectral change was completly reversible with temperature in the range 77—300 K. The well resolved $7\times2$-line spectrum is obviously attributable to the interaction of an unparied spin with six equivalent protons ($a_1=14$ G) and one proton ($a_2=4$ G). This indicates that the radical species is probably an allyl type radical with one more proton ($a=14$ G) than radical II.

At elevated temperature two types of reaction processes may be possible for the conversion of radical II. The one is migration of the unpaired spin site accompanied by intramolecular 1,3 and/or 1,5 hydrogen transfer through the polymer chain of radical II:

$$\sim\!\text{CH}_2\text{-CH=CH-CH}_2\text{-CH}_2\text{-}\dot{\text{C}}\text{H-CH=CH}_2 \longrightarrow \sim\!\text{CH}_2\text{-CH=CH-}\dot{\text{C}}\text{H-CH}_2\text{-CH}_2\text{-CH=CH}_2; \quad (4a)$$

$$\sim\!\text{CH}_2\text{-CH=CH-CH}_2\text{-CH}_2\text{-CH=CH-}\dot{\text{C}}\text{H}_2 \longrightarrow \sim\!\text{CH}_2\text{-CH=CH-}\dot{\text{C}}\text{H-CH}_2\text{-CH=CH-CH}_3. \quad (4b)$$

The other is hydrogen abstraction of radical II from a neighbouring polymer chain:[14]



$$\text{R}_{\text{II}} + \sim\!\text{CH}_2\text{-CH=CH-CH}_2\!\sim \quad \overset{\beta 2}{\text{CH}_2}\text{-}\overset{\alpha 3}{\text{CH}}\text{=}\overset{\alpha 2}{\text{CH}}\text{-}\overset{\alpha 1}{\dot{\text{C}}\text{H}}\text{-}\overset{\beta 1}{\text{CH}_2} \text{ (R}_{\text{III}}\text{)} \sim + \text{R}_{\text{II}}\text{H}. \quad (5)$$

$\sim$CH₂-CH=CH-ĊH-CH₂$\sim$ is labelled R$_{\text{III}}$

All the reaction processes result in the formation of the

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[12] S. Ohnishi, S. Sugimoto, and I. Nitta, *J. Chem. Phys.*, **37**, 1283 (1962); M. Kashiwagi and Y. Kurita, *ibid.*, **39**, 3165 (1963); C. Corvaja, *ibid.*, **44**, 1958 (1966).

[13] B. Birrell and O. H. Griffith, *J. Phys. Chem.*, **75**, 3489 (1971).

[14] Probably, most of the walls of the urea canals are melted and destroyed by this heat treatment, because remarkable decrease of a cavity Q value which is due to loss of microwave power caused by melting urea molecules is observed for measurement at 400 K. Therefore, the reactions between polymer chains must be taken into consideration.

same "chain" allyl type radical (radical III).

At room temperature all the $\beta$-coupling constants of radical III are reasonably expected to become 14 G because of the motion of the $\beta$-methylene group as suggested in the case of radical II. The $\alpha$-proton coupling constants of radical III are supposed to be similar to those of radical II; $a_{\alpha1}=a_{\alpha3}=14$ G and $a_{\alpha2}=4$ G. Consequently, radical III at room temperature has these six equivalent protons ($a_1=14$ G) and one proton ($a_2=4$ G), giving the $7\times2$-line spectrum.

It is difficult to determine unequivocally the number of component lines from the broad spectrum measured at 77 K. The spectrum, however, agrees closely with the computed spectrum consisting of broad 7 lines ($a=15$ G) with the intensity ratios of 1: 6: 15: 20: 15: 6: 1, as shown in Fig. 6b by dotted lines. This indicates that radical III at 77 K has six equivalent protons with the coupling constants of about 15 G. The 15-G splitting should be due to the protons at the $\alpha1$, $\alpha3$, $\beta1$, and $\beta2$ positions and a small 4-G splitting expected from the coupling with the $\alpha2$ proton should be smeared out by the broad line width ($\Delta H=15$ G).

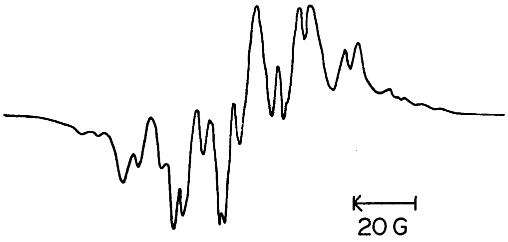


Fig. 7. ESR spectrum of irradiated trans-1,4-polybutadiene-urea complexes measured at room temperature.

It is interesting to note that a $7\times2$-line spectrum of Fig. 7 which is similar to Fig. 6a is obtained from irradiated *trans*-1,4-polybutadiene-urea complexes.[15] In this case, it seems probable that the radical species is formed by removal of a hydrogen atom from the polymer chain:

$$\sim\!\!\sim CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}\!\sim\!\!\sim \longrightarrow$$

$$\sim\!\!\sim CH_2\text{-}CH{=}CH\text{-}\dot{C}H\text{-}CH_2\text{-}\!\sim\!\!\sim + H. \quad (6)$$

This results would seem to support the identification of the $7\times2$-line spectrum of Fig. 6a as radical III.

Recently, Shiga *et al.*[6e] found a $7\times2$-line spectrum similar to Fig. 6a in an irradiated single crystal of 1,3-butadiene after warming to 143 K and assigned the spectrum to the same species as radical III. The formation of radical III in the crystal was explained by a reaction mechanism similar to (4a) on the assumption of the presence of the propagating radical which was not able to be confirmed. In our case, the conclusive evidence has been obtained for the presence of the propagating radical which is stable even at room temperature. This difference with regard to radical stability might be due to the difference of crystal structure, *i.e.*, the propagating radical in the crystalline lattice of pure 1,3-butadiene might undergo rearrangement to radical III at lower temperature than that in the crystalline lattice of urea canal complexes does.

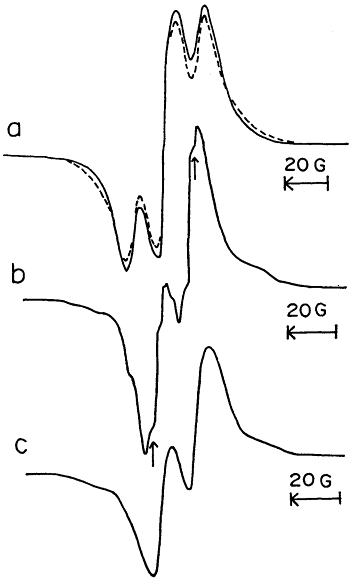
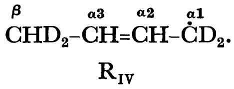


Fig. 8. ESR spectra of irradiated 1,3-butadiene-1,1,4,4-d$_4$-urea complexes. (a) 77 K spectrum measured immediately after irradiation. Dotted lines indicate the computed spectrum. (b) Room temperature spectrum. Arrows indicate the presence of small splittings. (c) 77 K spectrum after warming.

*Radicals from 1,3-Butadiene-1,1,4,4-d$_4$.* Using BD-*d*-urea complexes, a parallel experiment has been made in order to confirm the preceding identifications of the radicals formed in BD-*h*-urea complexes. The ESR spectrum of BD-*d* in urea canals irradiated and measured at 77 K consists of 3 lines with a hyperfine splitting of 15 G (Fig. 8a). There are two possible addition reactions for the formation of the monomer radical, *i.e.*, the hydrogen or deuterium addition to the conjugated double bond of BD-*d*. If the hydrogen addition is the case, the radical to be formed is



$$\overset{\beta}{CHD_2}\text{-}\overset{\alpha3}{CH}{=}\overset{\alpha2}{CH}\text{-}\overset{\alpha1}{\dot{C}D_2}.$$

$R_{IV}$

The 3-line spectrum would be interpreted on the assumption; $a_{\alpha1}{}^{H}=2.2$ G, $a_{\alpha2}{}^{H}=4.0$ G, $a_{\alpha3}{}^{H}=14$ G, $a_{\beta}{}^{H}=16.0$ G, and $a_{\beta}{}^{D}=2.5$ G, where the deuteron coupling constants are taken from the relation $a^{D}=0.153\ a^{H}$. The computed spectrum obtained by the use of these coupling constants is shown in Fig. 8a by dotted lines. It shows good agreement with the observed spectrum. Small splittings from the $\alpha2$ proton and the deuterons are smeared out because of the broad line width ($\Delta H=7$ G).

On the other hand, the deuterium addition would be excluded, because the expected spectrum of the radical $CD_3\text{-}CH{=}CH\text{-}\dot{C}D_2$ consists of 2 lines from the splitting due to the $\alpha3$ proton. These results suggest that the origin of the hydrogen added may be determined to be either urea or BD-*d* if radicals formed from BD-*d*-urea-*d*$_4$ complexes are identified as either $CD_3\text{-}CH{=}CH\text{-}\dot{C}D_2$ or $CD_2H\text{-}CH{=}CH\text{-}\dot{C}D_2$. An attempt to prepare the BD-*d*-urea-*d*$_4$ complexes, however, was not successful.

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[15] The complexes were prepared by storage of irradiated BD-*h*-urea complexes for several months at room temperature. Radicals trapped in the complexes almost disappeared during this storage.

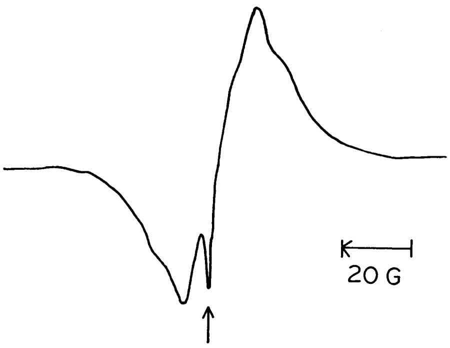

Fig. 9. ESR spectrum of polycrystalline 1,3-butadiene irradiated and measured at 77 K. A peak indicated by an arrow arises from color centers of the quartz sample tube.

It should be noted here that irradiated polycrystalline BD-*h* gives a poorly resolved spectrum at 77 K (Fig. 9) as compared with the spectrum obtained for BD-*h*–urea complexes (Fig. 1a). The formation of several types of radicals with different coupling constants may be the main cause of this poor resolution, as discussed by Shiga *et al.*[6e] Accordingly, the better resolution of Fig. 1a may be due to a selective formation of radical I in the presence of the urea molecules. The probable reaction mechanism explaining the selective radical formation would be proton transfer from the urea molecule to a butadiene anion radical which may be produced by attachment of an ejected electron:

$$(CH_2{=}CH{-}CH{=}CH_2)^- + CO(NH_2)_2 \longrightarrow CH_3{-}CH{=}CH{-}\dot{C}H_2 + CO(NH_2)(NH)^-. \quad (7)$$

Shida and Hamill[16] reported the formation of radical I in an irradiated 1,3-butadiene–methanol system and interpreted the radical formation in terms of a reaction mechanism similar to (7):

$$(CH_2{=}CH{-}CH{=}CH_2)^- + ROH \longrightarrow CH_3{-}CH{=}CH{-}\dot{C}H_2 + RO^-. \quad (8)$$

In an irradiated single crystal of fumaric acid-doped succinic acid, Iwasaki *et al.*[17] recently found the radical formed by the addition of an acidic proton of the host molecule to the fumaric acid-anion radical produced.

When the irradiated BD-*d*–urea complexes were warmed to room temperature and measured at room temperature, the 3-line spectrum at 77 K changed into a 2-line spectrum ($a$=14 G) with additional small splittings as shown in Fig. 8b. By this heat treatment, the formation of the propagating radical labeled by deuterium is expected from the results obtained for irradiated BD-*h*–urea complexes:

$$\begin{aligned}&CHD_2{-}CH{=}CH{-}\dot{C}D_2 + (CD_2{=}CH{-}CH{=}CD_2)_n \longrightarrow\\ &\quad CHD_2{-}CH{=}CH{-}CD_2{-}(CD_2{-}CH{=}CH{-}CD_2)_{n-1}\\ &\qquad \underbrace{{-}\overset{\beta}{CD_2}{-}\overset{\alpha3}{CH}{=}\overset{\alpha2}{CH}{-}\overset{\alpha1}{\dot{C}D_2}.}_{R_V} \qquad (9,\end{aligned}$$

On cooling back to 77 K, the small splittings disappeared, while the 2-line components unchanged (Fig. 8c).

It is evident that the 14-G splitting between the 2-line components should be due to the α3 proton and the small splittings should be due to the α1 deuterons ($a$=2.2 G), the α2 proton ($a$=4.0 G), and the β deuterons ($a$=2.2 G). It is to be noted that the 2-line spectrum of radical V does not show noticiable temperature-dependent changes as compared with the 6×2-line spectrum of radical II. This supports the interpretation that the spectral change of radical II is caused by the temperature dependent β-proton couplings.

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[17] M. Iwasaki, H. Muto, and K. Toriyama, *J. Chem. Phys.*, **55**, 1894 (1971).