May, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***61****, 1527—1534 (1988)* 1527

ESR Study on the Reactions of 1,3-Diene Cation Radicals in Low-Temperature Matrices

Jun Fujisawa, Toshiyuki Takayanagi, Shin Sato,* and Kazuo Shimokoshi†
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152
†Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received October 3, 1987)

The reactions of the cation radicals of 1,3-butadiene, *cis-* and *trans*-1,3-pentadienes, 2-methyl-1,3-butadiene, and 2,3-dimethyl-1,3-butadiene have been investigated by low-temperature matrix ESR. The cation radicals produced in the irradiated solid solutions of CCl_2FCCl_2F were found to react with their neutral parents at temperatures above ca. 110 K, forming radicals with allylic ends. On the other hand, 1,3-pentadiene cation radicals in the matrices of CCl_4, CCl_3F, and CCl_3CF_3 were found to isomerize into cyclopentene cation radicals, irrespective of the cis and trans forms. The possible mechanisms for the reactions and their implications in the cationic polymerization of dienes are discussed.

The primary process in radiation-induced polymerization has long been a subject in radiation chemistry.[1] Traditional approaches, however, have mostly been confined to speculation about the mechanisms, since the high reactivity of the cation radicals prohibited any spectroscopic detection of the primary processes.

The method of radiolytic generation and stabilization of cation radicals in Freons has now widely been applied to a variety of organic compounds.[2] By measuring the ESR spectra of the cation radicals, thus prepared over a wide temperature range, direct information concerning their reactions has often been obtained.[3,4]

This technique, as it applies to the cation radicals of unsaturated hydrocarbons, is of special interest since some of them are supposed to initiate polymerization.[1] In fact, we have found that the cation radicals of ethylene and isobutene easily associate with their neutral parents to form chain end radicals.[5,6] This is in remarkable contrast to the deprotonation observed for the cation radicals of other olefins[6] and paraffins[3] giving neutral radicals.

In the present study, we have examined the reactions of a series of 1,3-diene cation radicals by the same method mentioned above. The isolated cation radicals of 1,3-pentadienes and 2,3-dimethyl-1,3-butadiene were newly observed by ESR, as well as those of 1,3-butadiene and 2-methyl-1,3-butadiene. The ESR observation for the formations of chain end allylic radicals from these cation radicals and the isomerization found for the cation radicals of 1,3-pentadiene are described.

Experimental

1,3-Butadiene from Takachiho Kagaku Kogyo Co., 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and cyclopentene from Tokyo Kasei Co. were used as received. Cis and trans isomers of 1,3-pentadiene were kindly supplied by Nippon Zeon Co. Ltd. All the dienes, except for 1,3-butadiene, can polymerize easily, even at room temperature. About 30 ppm of a polymerization inhibitor was kept incorporated with these compounds. Preliminary measurements using samples from which the inhibitor had been removed immediately before preparation gave the same results as described in this paper. The high purity (>97%) of each isomer was checked by NMR spectroscopy. Commercially available halocarbons (CCl_4, CCl_3F, CCl_3CF_3, and CCl_2FCCl_2F from Tokyo Kasei Co.) were used as a matrix media without further purification.

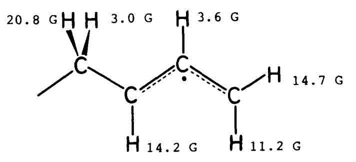
The procedure of sample preparation and ESR measurement have been described previously.[4-6] Solid solutions containing small amounts of the dienes (0.2—0.5 mol%) in various halocarbons were prepared in quartz tubes at 77 K, then irradiated to generate the cation radicals. The ESR measurement was carried out with a JES FE-2XG spectrometer calibrated with an NMR probe and a digital frequency counter. The sample temperature was regulated with a temperature controller, and the spectra were recorded at temperatures between 77 K and the melting point of each matrix with suitable intervals.

Results

1,3-Butadiene. The spectrum shown in Fig. 1a was recorded at 77 K after the irradiation of a solid solution of 1,3-butadiene in CCl_3CF_3. The spectrum consists of a quintet with an hfc (hyperfine coupling) constant of 10.4 G (1 G=10^{-4} T), which can readily be assigned to the cation radical of 1,3-butadiene. Essentially the same spectrum was observed for the solutions of CCl_3F and CCl_2FCCl_2F at 77 K. The cation radical of 1,3-butadiene in other matrices has been studied by several workers.[7-9] The present result is in good agreement with the previous results, as shown in Table 1.

The 1,3-butadiene cation radicals in CCl_3F and CCl_3CF_3 were found to remain isolated up to about 145 K. A further elevation of the temperature resulted in a uniform decay of the cation radical without giving any new paramagnetic species. This may be attributed to the neutralization between the cation radical and the chloride anion. On the other hand, the irradiated solution of 1,3-butadiene in CCl_2FCCl_2F

showed an irreversible change at around 110 K from the initial spectrum of the cation radical to a new one. Figure 1b shows the spectrum observed upon warming to 128 K. The spectrum was well reproduced by the simulation shown in Fig. 1c when an allylic structure **1** was assumed.[7]



1

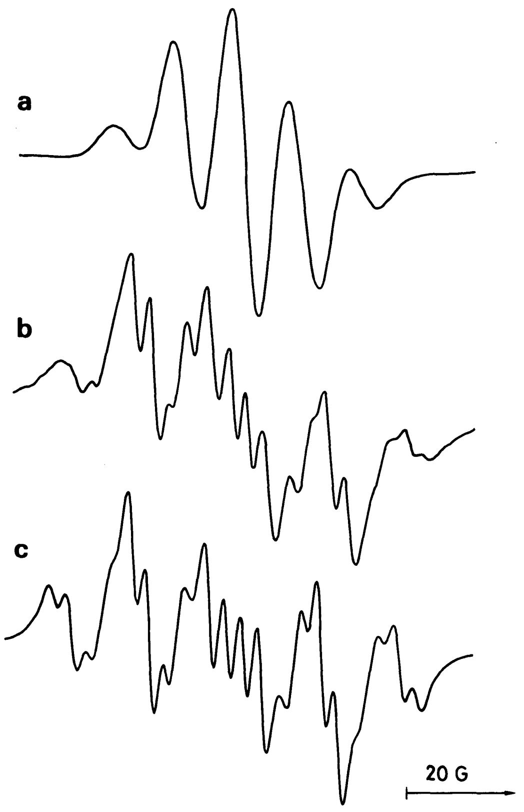
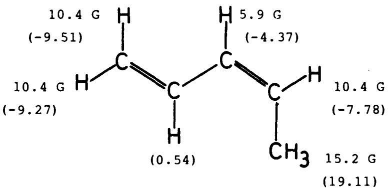


Fig. 1. (a) ESR spectrum of the cation radical of 1,3-butadiene in CCl_3CF_3 at 77 K. (b) ESR spectrum of the irradiated CCl_2FCCl_2F solution of 1,3-butadiene at 128 K, showing the features assigned to the allylic end **1**. (c) Simulation for (b) using the parameters given in Table 2 and a Lorentzian line width of ΔH_{msl}=5.0 G.

At elevated temperatures, it has often been observed that an irradiated CCl_2FCCl_2F solution allows molecular diffusion which may cause ion-molecule reactions.[4–6] The irreversible change of the spectrum, therefore, strongly suggests that the cation radical reacts with its neutral parents to form species whose radical end has an allylic structure **1**.

***cis*- and *trans*-1,3-Pentadienes.** The irradiated solutions of *cis*- and *trans*-1,3-pentadienes in CCl_2FCCl_2F exhibited the spectra shown in Figs. 2a and 3a, respectively. The former was successfully analyzed by using hfc constants of 15.2 G (3H), 10.4 G (3H), and 5.9 G (1H), as shown in Fig. 2b. Based on the results of INDO calculations (values in the parentheses in the diagrams **2**, **5**, and **6**),[10] the species giving the spectrum was assigned to the cation radical of *cis*-1,3-pentadiene (**2**). The analysis of the spectrum for the trans isomer (Fig. 3a) is less straightforward because of its low resolution. It was found, however, that the essential features of the spectrum closely resemble those of the cis isomer. This suggests the formation of



2

Table 1. Isotropic ESR Parameters of Diene Cation Radicals

Cation radical	Matrix	Temp/K	hfc constant/G			Ref.
			a(CH)	a(CH_2)	a(CH_3)	
CH_2=CHCH=CH_2^+	CCl_3CF_3	77		10.4		
	CCl_2FCCl_2F	77		11.4		
	Silica gel	77	3.2	11.4		7)
	CCl_4	130		10.1		8)
	CCl_3F	77	2.0	12.2		9)
CH_3CH=CHCH=CH_2^+ (cis isomer)	CCl_2FCCl_2F	108	5.9 10.4	10.4	15.2	
CH_2=C(CH_3)CH=CH_2^+	CCl_3CF_3	128		8.7 13.1	4.3	
	CCl_4	163	3.2	9.2 13.0	4.9	12)
CH_2=C(CH_3)C(CH_3)=CH_2^+	CCl_4	183		9.9	5.0	

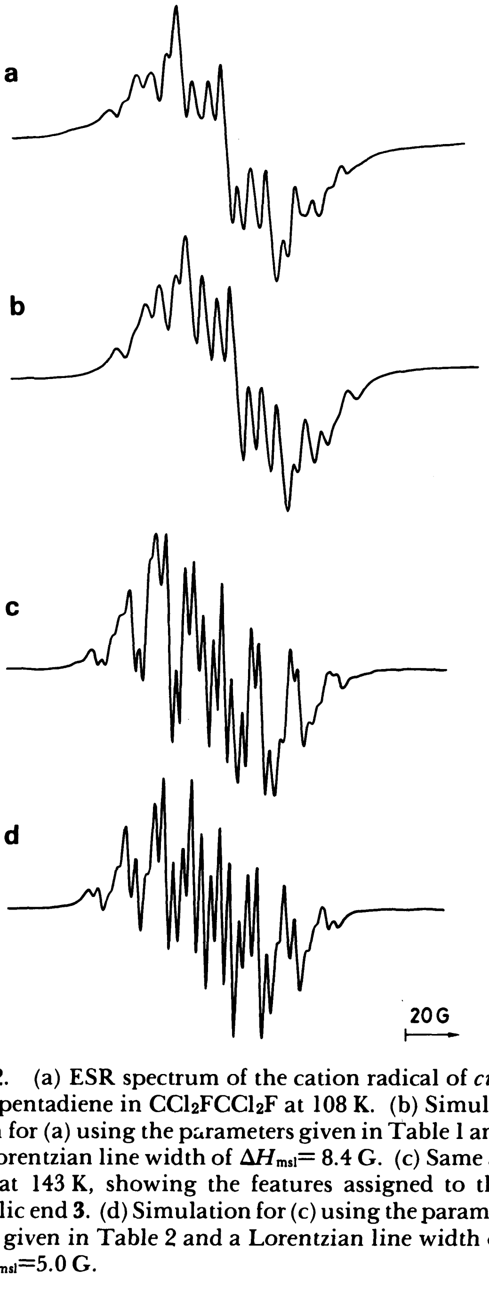


Fig. 2. (a) ESR spectrum of the cation radical of *cis*-1,3-pentadiene in CCl_2FCCl_2F at 108 K. (b) Simulation for (a) using the parameters given in Table 1 and a Lorentzian line width of ΔH_{msl}= 8.4 G. (c) Same as (a) at 143 K, showing the features assigned to the allylic end **3**. (d) Simulation for (c) using the parameters given in Table 2 and a Lorentzian line width of ΔH_{msl}=5.0 G.

a *tarns*-1,3-pentadiene cation radical, though the cause of the apparent difference in the resolution between the isomers is not clear.

The essential differences between cis and trans isomers of the cation radicals were characterized by their reactions. Upon warming, the spectra of these cation radicals changed irreversibly into different patterns, as shown in Figs. 2c and 3b, respectively. Taking the small variations of the hyperfine interaction into account, both could be reproduced by simulations, as shown in Figs. 2d and 3c. Such a variation has often been observed for allylic radicals with different conformations;[6,11] the spectra can consistently be assigned to the allylic ends with cis **3** and trans **4** skeletons.

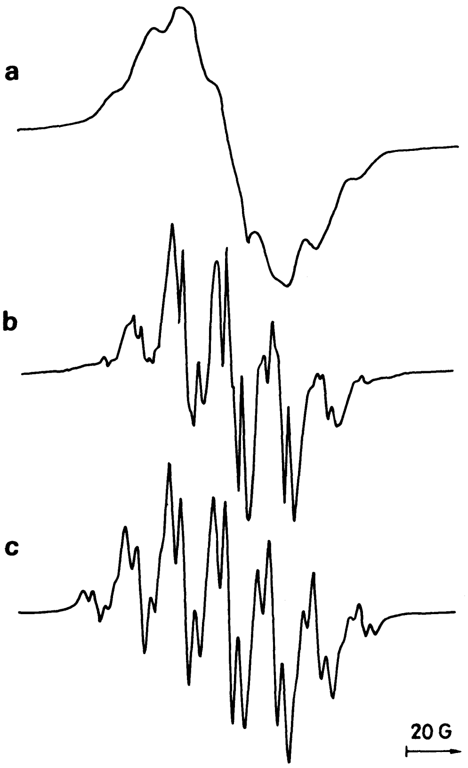
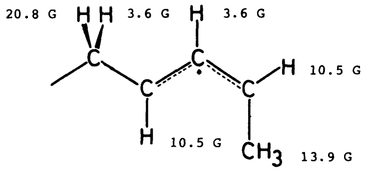
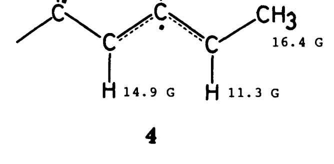


Fig. 3. (a) ESR spectrum of the cation radical of *trans*-1,3-pentadiene in CCl_2FCCl_2F at 77 K. (b) Same as (a) at 128 K, showing the features assigned to the allylic end **4**. (c) Simulation for (b) using the parameters given in Table 2 and a Lorentzian line width of ΔH_{msl}=5.2 G.



3



4

When the matrix of CCl_4, CCl_3F, or CCl_3CF_3 was used instead, a completely different spectral pattern was observed. The spectrum shown in Fig. 4a was recorded at 77 K immediately after the irradiation of a solution of a *cis*-1,3-pentadiene in CCl_3F. Upon warming, the resolution of the spectrum was improved to give the spectrum shown in Fig. 4b at 128 K. Essentially the same spectra were obtained for *trans*-1,3-pentadiene, as shown in Figs. 4c and 4d. The spectra shown in Fig. 4 closely resemble that of a cyclopentene cation radical, reported by Shida and co-

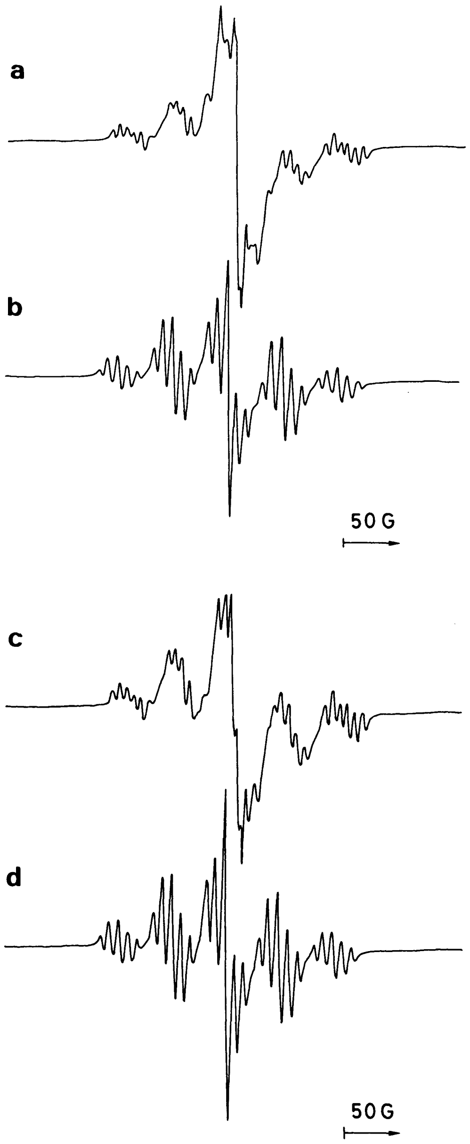


Fig. 4. (a) ESR spectrum of the irradiated CCl_3F solution of *cis*-1,3-pentadiene at 77 K, showing the features assigned to the cation radical of cyclopentene. (b) Same as (a) at 128 K. (c) Same as (a) for *trans*-1,3-pentadiene. (d) Same as (c) at 123 K.

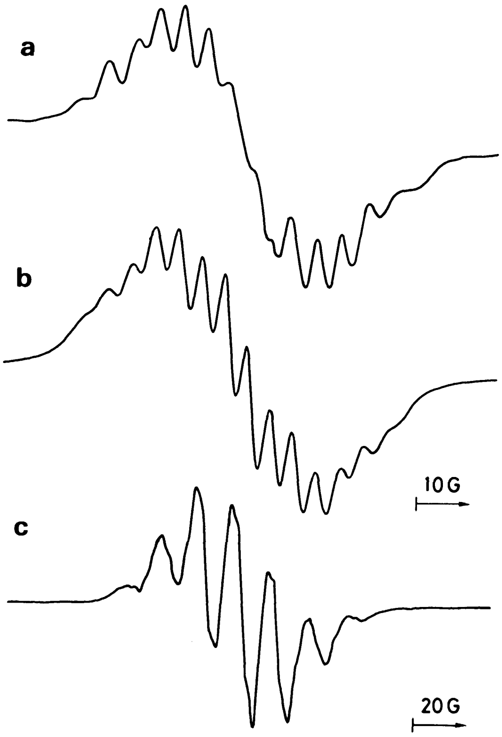
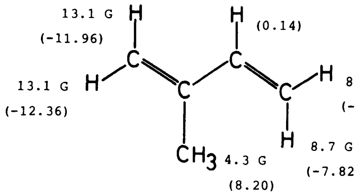


Fig. 5. (a) ESR spectrum of the cation radical of 2-methyl-1,3-butadiene in CCl_3CF_3 at 128 K. (b) Simulation for (a) using the parameters given in Table 1 and a Lorentzian line width of $\Delta H_{msl}=7.5$ G. (c) ESR spectrum of the irradiated CCl_2FCCl_2F solution of 2-methyl-1,3-butadiene at 133 K, showing the features assigned to the allylic end **7**.

workers.[9] We performed the same experiment and confirmed that these spectra coincide almost exactly with the spectra from cyclopentene. Therefore, it may be concluded that the cation radical of cyclopentene was formed immediately after the irradiation of the CCl_3F solutions of *cis*- and *trans*-1,3-pentadienes. The employment of other matrices of CCl_4 and CCl_3CF_3 also gave similar results.

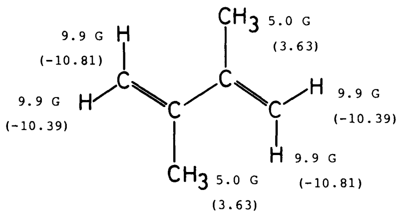
2-Methyl- and 2,3-Dimethyl-1,3-butadienes. The irradiated 2-methyl-1,3-butadiene in CCl_3CF_3 yielded the spectrum shown in Fig. 5a at 128 K. The spectrum is quite similar that previously observed in CCl_4.[12] The hfc constants of 13.1 G (2H), 8.7 G (2H), and 4.3 G (3H) were derived from the simulation shown in Fig. 5b and were ascribed to the 2-methyl-1,3-butadiene cation radical (**5**).



5

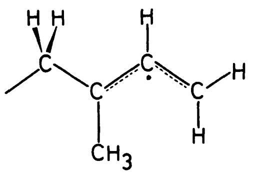
For an irradiated solution of 2,3-dimethyl-1,3-butadiene in CCl_3CF_3, a poorly resolved spectrum was obtained. Well-resolved structures were observed by using CCl_4 instead (Fig. 6a). Although some background signals due to the matrix radicals[13] are superimposed at the low-field side of the spectrum, the main spectral pattern can easily be identified as a quintet of septets with hfc constants of 9.9 G (4H) and 5.0 G (6H) (Fig. 6b); those agree well with the values expected for the cation radical of 2,3-dimethyl-1,3-butadiene (**6**).

Irreversible spectral changes were also observed for these systems upon warming. Figure 5c shows the spectrum observed for an irradiated CCl_2FCCl_2F solution of 2-methyl-1,3-butadiene at 118 K. The

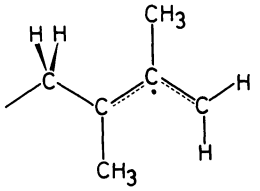


6

septet structure separated by about 13 G may be assigned to the allylic end **7**, though possible differences in hfc constants among six protons are not clear from the spectrum. A similar septet pattern was also obtained for an irradiated solution of 2,3-dimethyl-1,3-butadiene at 128 K (Fig. 6c). The formation of another type of allylic end **8** may be responsible.



7



8

The observed ESR parameters for the cation radicals of dienes and the allylic end radicals are summarized in Tables 1 and 2, respectively.

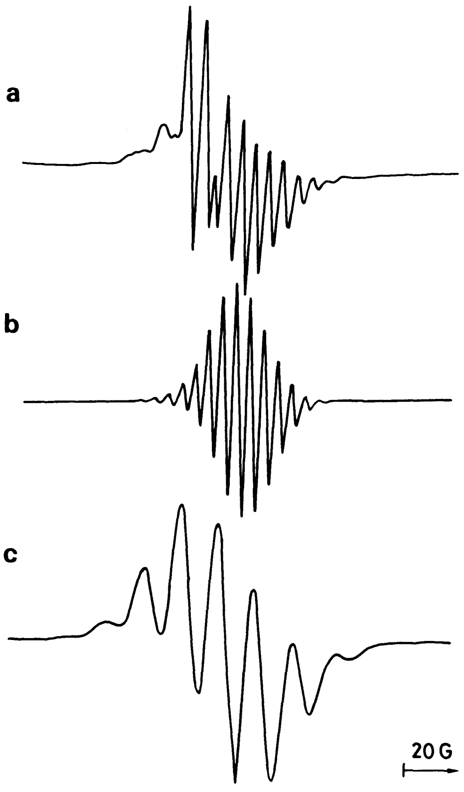


Fig. 6. (a) ESR spectrum of the cation radical of 2,3-dimethyl-1,3-butadiene in CCl_4 at 183 K. (b) Simulation for (a) using the parameters given in Table 1 and a Lorentzian line width of ΔH_{msl}=3.0 G. (c) ESR spectrum of the irradiated CCl_2FCCl_2F solution of 2,3-dimethyl-1,3-butadiene at 128 K, showing the features assigned to the allylic end **8**.

Table 2. Isotropic ESR Parameters of Allylic End Radicals

Chain end	Monomer	Temp/K	hfc constant/G			Ref.
			a(CH)	a(CH$_2$)	a(CH$_3$)	
$\dot{C}H_2CH{=}CHCH_2$–	$CH_2{=}CHCH{=}CH_2$[a)]	128	3.6 14.2	11.2 14.7 3.0 20.8		
	$CH_2{=}CHCH{=}CH_2$[b)]	195	4.2 14.9	13.8 13.8 12.8 12.8		7
$(CH_3)\dot{C}HCH{=}CHCH_2$– (cis isomer)	$CH_3CH{=}CHCH{=}CH_2$[a)] (cis isomer)	143	3.6 10.5 10.5	3.6 20.8	13.9	
$(CH_3)\dot{C}HCH{=}CHCH_2$– (trans isomer)	$CH_3CH{=}CHCH{=}CH_2$[a)] (trans isomer)	128	3.8 11.3 14.9	3.8 20.8	16.4	

a) In a CCl_2FCCl_2F matrix. b) Adsorbed on silica gel.

Discussion

The cation radicals of 1,3-butadiene and its methyl and dimethyl derivatives were stabilized in halocarbon matrices upon irradiation at 77 K. From the results of ESR measurements (Table 1), it can be seen that the coupling constants of CH_2 protons vary little among the species. This indicates that the cation radicals of 1,3-dienes possess essentially the same π-structures as that of 1,3-butadiene, where an unpaired electron is located mainly on the terminal (1,4-position) carbons.

The radicals derived from these cation radicals were characterized by their allylic ends, which reflect the conformations of the corresponding parent cation radicals. In particular, cis and trans isomers of 1,3-pentadiene cation radicals in CCl_2FCCl_2F were found to give allylic ends with cis and trans skeletons, respectively. This indicates that the radicals formed by reactions, as well as the parent cation radicals, retain their geometrical identities of neutral dienes. A similar stereospecificity has also been found for reactions of the *cis*- and *trans*-2-butene cation radicals.[6)]

Regardings the ESR parameters of the radical from the 1,3-butadiene cation radical, there is a noticeable difference between the present result and the previous one;[7)] i.e., large inequivalence between the two β-methylene proton couplings, 20.3 and 3.0 G, has not been previously observed (see Table 2). The difference may be ascribed to the lower temperature at which the present measurement was carried out. In this case, the motional averaging between two protons may be prohibited. Such an inequivalence of β-methylene proton couplings has been observed for other allylic end radicals,[14)] and the present values seem to be appropriate for this type of radical.

So far, a number of studies have been reported concerning the primary processes in the radiation-induced polymerization of 1,3-butadiene.[1a,7,8,15)] The formation of primary cation radicals or allylic end radicals has been observed, depending on the conditions. The concentration effect on the processes was investigated by Lund et al.[7)] for the irradiated 1,3-butadiene adsorbed on silica gel. They reported that the cation radical was observable at a low 1,3-butadiene content, but absent when the allylic end radical occurred at high concentrations. The following reaction scheme has been proposed for 1,3-butadiene:[7,8,15c)]

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\rightsquigarrow} CH_2{=}CH{-}CH{=}CH_2^{+\!\cdot} + e^-, \tag{1}$$

$$CH_2{=}CH{-}CH{=}CH_2^{+\!\cdot} + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \dot{C}H_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2^+, \tag{2}$$

$$\dot{C}H_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2^+ + n[CH_2{=}CH{-}CH{=}CH_2] \longrightarrow \dot{C}H_2{-}CH{=}CH{-}CH_2(-CH_2{-}CH{=}CH{-}CH_2-)_nCH_2{-}CH{=}CH{-}CH_2^+. \tag{3}$$

In the present study, the formation of the allylic end was characterized as the ion-molecule reaction of 1,3-butadiene cation radical. This may be considered as direct evidence for the initiation reaction 2. During the subsequent step, the polymerization has been thought to proceed cationically as in reaction 3. The present result is compatible with this scheme in that the spectra of allylic end radicals can be assigned without taking into account any branched structures which often occur in radical propagation.

The reaction scheme implies two possible candidates for species with an allylic end: i.e., the dimer cation radical from reaction 2 and the propagating radical formed by reaction 3. Though the ESR measurement does not provide any direct information about this, the latter seems more probable since reaction 3 is known to take place with a nominal activation energy and, hence, at low temperature.[1a,15a)]

The results suggest that similar mechanisms are also applicable to the methyl and dimethyl derivatives of 1,3-butadiene. This was demonstrated by the formation of radicals with the specific conformations of methyl groups, as expected from the 1,4-addition reactions. The observed hfc constants of all the diene cation radicals indicate that the unpaired electron is mainly located on positions 1 and 4, which also accords well with this scheme.

For reactions of the cation radicals of 1,3-pentadienes and 2-methyl-1,3-butadiene, there are two possible structures in forming allylic ends, as illustrated in Fig. 7. These two structures are

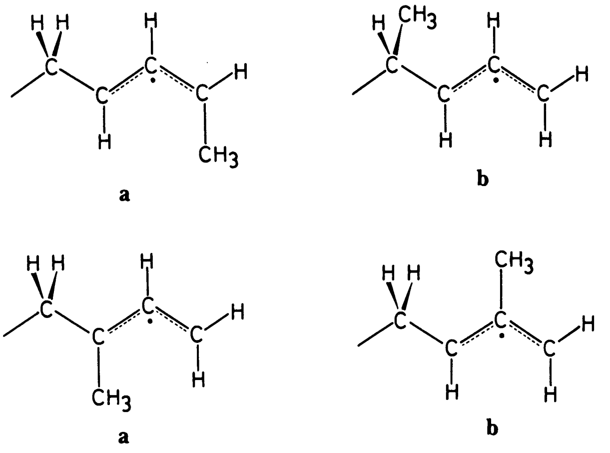
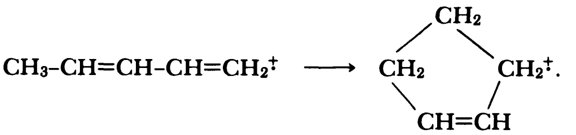


Fig. 7. Two possible structures of the allylic ends which may be formed by the polymerization of *cis*-1,3-pentadiene and 2-methyl-1,3-butadiene. Only the structures (a) were observed (see text). Similar scheme is applicable also to the reaction of *trans*-1,3-pentadiene cation radical.

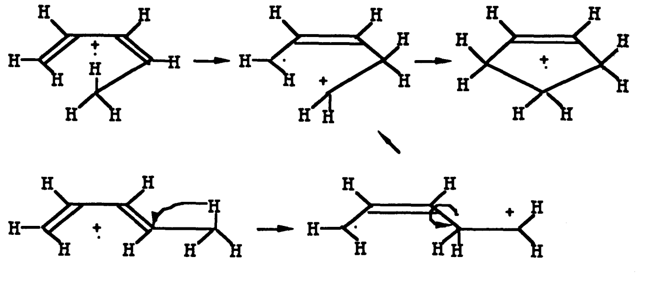
distinguishable from their ESR spectra. The results indicate that a specific structure **a** is formed exclusively for both of the cation radicals. This may be explained in terms of possible differences in hyperconjugative effects; i.e., the formation of the allylic ends **a** may be preferable because of their higher conjugation in π-systems.

As for the reactions of the cation radicals of 1,3-pentadienes, an alternative possibility of cation radical Diels–Alder reaction[16] has been discussed by Shiga and Okamura.[12] They observed a spectrum with a quintet structure separated by as much as 48.5 G for an irradiated CCl_4 solution of *cis*-1,3-pentadiene at 77 K and assigned it to a vinylcyclohexene-type cation radical. We obtained a similar spectra for irradiated solutions of *cis*- and *trans*-1,3-pentadienes in CCl_4, CCl_3F, and CCl_3CF_3 but found that these spectra could more reasonably be assigned to the cation radical of cyclopentene. Therefore, the absence of the primary cation radicals in these systems should be considered as being due to unimolecular isomerizations of the cation radicals of 1,3-pentadiene into the cation radical of cyclopentene.



(4)

It is noteworthy that the above reaction took place irrespective of the cis and trans forms of 1,3-pentadiene. They, in turn, have two possible conformations around the single bond: s-cis and s-trans. In forming the cyclopentene ring, however, the s-cis conformations seem preferable to s-trans conformations for both forms. In this case, the following mechanisms could illustrate the processes.



These mechanisms include 1,2-hydrogen atom shifts in froming the cation radical of cyclopentene. Another possible mechanism is a 1,4-hydrogen atom shift process. However, the necessary rearrangement of the carbon skeleton for the trans form is not conceivable in that case because of the double-bond nature of the 2,3-bond. Since isomerization was observed for both forms, the 1,2-hydrogen atom shift process is more appropriate.

As for the neutral molecules of 1,3-pentadienes, it is known that the s-trans is more stable from the results of the microwave spectra[17] and UV spectra.[18] In order to elucidate the stable conformations for the cation radicals of 1,3-pentadienes, we calculated the energies of these cation radicals by using the INDO method.[10] The result shows that the s-trans is more stable than s-cis conformation by ca. 10 kcal mol^{-1}. In a low-temperature matrix, nevertheless, these cation radicals might possibly have s-cis conformations as a result of matrix effects. In fact, it has been reported that the cation radicals of some alkanes do not have extended conformations but have less stable gauche conformations in the matrices of CCl_3F and CCl_3CF_3.[3,19] Therefore, we tentatively considered that the cation radicals of 1,3-pentadiene in CCl_4, CCl_3F, and CCl_3CF_3 specifically have s-cis conformations and are subject to the immediate isomerization into cyclopentene cation radicals. On the other hand, the cation radicals of 1,3-pentadiene in CCl_2FCCl_2F might remain as they are because of their s-trans conformations.

References

1) a) W. S. Anderson, *J. Phys. Chem.*, **63**, 765 (1959); b) P. C. Chang, N. C. Yang, and C. D. Wagner, *J. Am. Chem. Soc.*, **81**, 2060 (1959); c) K. Takeda, H. Yoshida, K. Hayashi, and S. Okamura, *Memo. Fac. Eng. Kyoto Univ.*, **32**, 213 (1966). d) K. Tsuji, H. Yoshida, K. Hayashi, and S. Ogasawara, *Polym. Lett.*, **5**, 313 (1967).

2) T. Shida, E. Haselbach, and T. Bally, *Acc. Chem. Res.*, **17**, 180 (1984).

3) K. Toriyama, K. Nunome, and M. Iwasaki, *J. Chem. Phys.*, **77**, 5891 (1982).

4) J. Fujisawa, S. Sato, K. Shimokoshi, and T. Shida, *Bull. Chem. Soc. Jpn.*, **58**, 1267 (1985).

5) J. Fujisawa, S. Sato, and K. Shimokoshi, *Chem. Phys. Lett.*, **124**, 391 (1986).

6) J. Fujisawa, S. Sato, K. Shimokoshi, and T. Shida, *J. Phys. Chem.*, **89**, 5481 (1985).

7) T. Shiga, A. Lund, and P-O. Kinell, *Int. J. Rad. Phys. Chem.*, **3**, 131 (1971).

8) A. Lund, T. Shiga, and P-O. Kinell, *Nobel Symp.*, **22**, 95 (1972).

9) T. Shida, Y. Egawa, H. Kubodera, and T. Kato, *J. Chem. Phys.*, **73**, 5963 (1980).

10) The INDO calculations were performed using the program coded by one of the authors (KS) (K. Shimokoshi, J. Fujisawa, K. Nakamura, S. Sato, and T. Shida, *Chem. Phys. Lett.*, **99**, 483 (1983).). The standard geometries of the neutral 1,3-dienes were used for the calculations.

11) J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **90**, 7157 (1968).

12) T. Shiga and S. Okamura, *Polym. J.*, **6**, 7 (1974).

13) T. Shida and Y. Takemura, *Red. Phys. Chem.*, **21**, 157 (1983).

14) T. Ohmori, T. Ichikawa, and M. Iwasaki, *Bull. Chem. Soc. Jpn.*, **46**, 1383 (1973).

15) a) Y. Tabata, H. Sobue, and E. Oda, *J. Phys. Chem.*, **65**, 1645 (1961); b) T. Shiga, A. Lund, and P-O. Kinell, *Int. J.*

Rad. Phys. Chem., **3**, 145 (1971); c) T. Shiga, T. Matsuyama, H. Yamaoka, and S. Okamura, *Makromol. Chem.*, **175**, 217 (1974); d) T. Shiga and S. Okamura, *Polym. J.*, **6**, 1 (1974).

16) a) N. L. Bauld, D. J. Bellville, R. Pabon, R. Chelsky, and G. Green, *J. Am. Chem. Soc.*, **105**, 2378 (1983); b) D. J. Bellville, D. D. Wirth, and N. L. Bauld, *J. Am. Chem. Soc.*, **103**, 718 (1981); c) P. G. Gassman and D. A. Singleton, *J. Am. Chem. Soc.*, **106**, 7993 (1984).

17) S. L. Hsu and W. H. Flygare, *J. Chem. Phys.*, **52**, 1053 (1970).

18) H. Booker, L. K. Evans, and A. E. Gillam, *J. Chem. Soc.*, **1940**, 1453.

19) G. Dolivo and A. Lund, *J. Phys. Chem.*, **89**, 3977 (1985).