

Electron Spin Resonance Studies of Primary Processes in Radiation-induced Reactions. III. 1,3-Butadiene in Organic Rigid Matrices

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The primary species formed from 1,3-butadiene following γ -irradiation in organic rigid matrices have been investigated. The cationic radical of butadiene is observed in polycrystalline carbon tetrachloride. A radical of the type $\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}-\text{CH}_2-\text{R}(\text{RI})$ is formed in butylchloride at 77 K. The positive charge scavenger triethylamine inhibits the formation of RI. Initiation by the butadiene cation has been indicated in the radiation-induced polymerization, yielding the radical RI in butylchloride. The butadiene anion has been observed at 77 K in 2-methyltetrahydrofuran but the formation of the radical RI has not been observed at 77 K. In hydrocarbon glasses of 3-methylpentane and 3-methylhexane the formation of the radical RI has been observed in the presence of either positive or negative charge scavengers. Both cationic and anionic initiation have been indicated at 77 K.

Some organic compounds form transparent glasses when they are rapidly cooled down to 77 K. Organic glasses act as rigid matrices which can trap reactive species produced by ionizing radiation; the trapped species may then be observed. Glasses such as 2-methyltetrahydrofuran (MTHF)¹ and triethylamine (TEA)² stabilize positive charge and then trap electrons stably. Glasses of alkyl halides such as butylchloride (BuCl) are known to capture electrons dissociatively and to stabilize negative charge as Cl^- ions. The anion and the cation radicals of styrene have been observed in MTHF and BuCl, respectively, after γ -irradiation.³ Glasses of branched alkanes such as 3-methylpentane (3MP) and 3-methylhexane (3MH) trap electrons and positive charges less stably than MTHF and BuCl, respectively. Trapped electrons and cation radicals have been observed in these alkane glasses.⁴

When solutes are irradiated in organic matrices, the reaction mechanism depends on the nature of the solute and the matrices. Anionic reactions are

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avored in matrices such as MTHF and TEA. Cationic reactions are favored in alkyl halides. Both cationic and anionic reactions can be expected in alkanes, according to the nature of the solutes. Glass matrices constitute a convenient method for investigating the effects of additives. The additives are distributed more uniformly at low temperature in glass matrices than in the crystalline or the adsorbed state.

In the present study 2-methyltetrahydrofuran, butylchloride, 3-methylpentane and 3-methylhexane were used as glass matrices. Carbon tetrachloride was used as a polycrystalline matrix, because it can stabilize negative charge and because γ -irradiation of this compound does not release hydrogen atoms, which could otherwise react with the solute. 1,3-Butadiene was chosen as solute. Electron spin resonance (ESR) studies of 1,3-butadiene have been carried out in different systems. The anion radical has been observed during electrolysis in ammonia⁵ and tetrahydrofuran.⁶ Allyl-type radicals have been observed in an aqueous redox system,⁷ during photolysis with di-*t*-butylperoxide,⁸ in the solid state after alkali metal treatment,⁹ in the adsorbed state after γ -irradiation¹⁰ and in the single crystal after γ -irradiation.¹¹ The cation radical is formed in the adsorbed state after γ -irradiation.¹⁰ Butadiene polymerizes with catalysts of either radical, cationic or anionic type.¹²

The aim of the present study is to identify the radicals formed by γ -irradiation and to determine the reaction mechanism in organic rigid matrices by means of ESR techniques. The investigation reported here gives a contribution to the elucidation of the primary processes of radiation-induced polymerization of 1,3-butadiene. The cation radical is observed in carbon tetrachloride. Evidence for cationic propagation in BuCl was obtained and the cationic radical is indicated to be the initiating agent of radiation-induced polymerization at 77 K. Radical post reactions occur thermally. The anion radical is observed in MTHF but initiation of polymerization does not occur. In alkane glasses both cationic and anionic propagation are indicated.

EXPERIMENTAL

1,3-Butadiene and 1,3-butadiene-1,1,4,4-*d*₄ were purified and dried, using a procedure described previously.¹⁰ MTHF, TEA, BuCl, 3MH, and 3MP were purified by distillation. MTHF and TEA were dried under reduced pressure while being mechanically stirred together with Na-K alloy in pyrex glass ampoules. 3MH and 3MP were dried in the same manner as MTHF after passage through a freshly activated silica gel column. BuCl and CCl₄ were dried by storing on the molecular sieve 3A which had previously been baked at 500°C for 12 h under 10⁻⁵ torr. Samples were prepared by adding known amounts of butadiene to a solvent through a breakable seal. The sample tubes were sealed off under a pressure of 10⁻⁵ torr. Irradiation was carried out at 77 K in the dark with a ⁶⁰Co γ -source at a dose rate of 0.8 Mrad/h to a total dose of 0.8 Mrad. ESR measurements were made at 77 K with a Varian E-9 X-band spectrometer with 100 kHz magnetic field modulation at a microwave power of 0.06 mW. The sensitivity of the ESR instrument was checked by using the standard pitch sample supplied with the apparatus. Photo-bleaching was achieved with the filtered light from a 1000 W iodine lamp.

RESULTS

Alkyl halide matrix. The spectrum from a sample containing 2.4 mol % of butadiene in BuCl consists of an odd number of lines (Fig. 1a). Comparison

with the spectrum from the pure BuCl glass (Fig. 1b) shows that an additional absorption is present. When the butadiene- d_4 was present at a concentration of 1.4 mol %, the central portion of the spectrum changed as shown in Fig. 1c. These observations show that a species designated RI derived from butadiene is responsible for the central part of the absorption. The presence of TEA at a concentration of 3.4 mol % inhibits the formation of RI and the spectrum is then essentially that of the butyl radical¹³ (Fig. 1d).

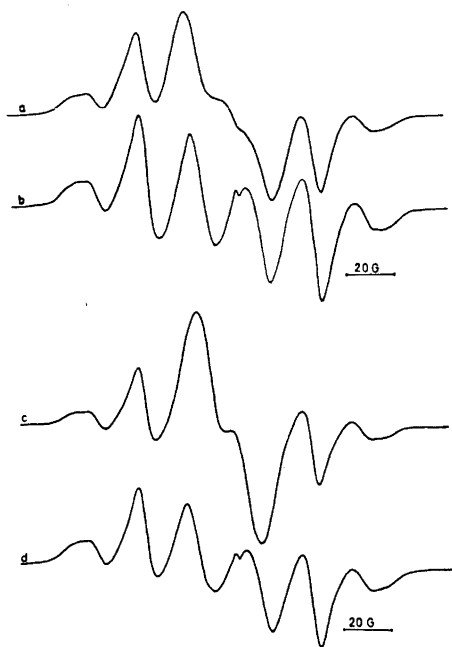


Fig. 1. ESR spectrum in butylchloride glass following γ -irradiation at 77 K to 8×10^5 rad, measured at 77 K. a, 2.4 mol % of 1,3-butadiene. b, pure butylchloride. c, 1.4 mol % of 1,3-butadiene-1,1,4,4- d_4 . d, 1.4 mol % of 1,3-butadiene-1,1,4,4- d_4 in the presence of 3.4 mol % of triethylamine.

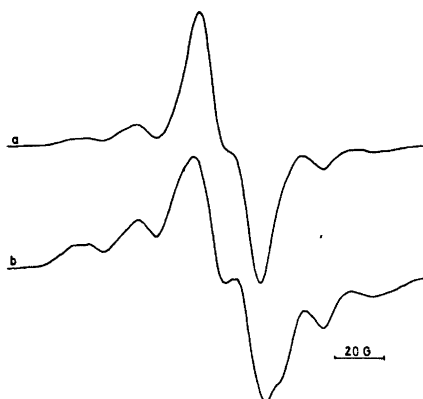


Fig. 2. ESR spectrum in butylchloride glass following γ -irradiation at 77 K to 8×10^5 rad, measured after storage for 7 days at 77 K. a, 1.4 mol % of 1,3-butadiene-1,1,4,4- d_4 . b, 1.4 mol % of 1,3-butadiene-1,1,4,4- d_4 in the presence of 3.4 mol % of triethylamine.

During storage at 77 K for 7 days the butyl radicals decayed while the intensity of the absorption due to RI increased almost to the same extent (compare Fig. 2a with Fig. 1c, and Fig. 2b with Fig. 1d). Triethylamine had no obvious influence on this reaction. At 100 K the butyl radical had decayed completely. The remaining spectra differ, depending on whether ordinary or butadiene- d_4 had been used, as shown in Fig. 3. The quintet spectrum of Fig. 3a has an average splitting of 16 G. A more accurate estimate yields $a = 13.8$ G for the doublet obtained from the butadiene- d_4 sample.

At 77 K the spectrum from a sample containing 1.2 mol % butadiene in a polycrystalline CCl_4 matrix consisted of several lines separated by 10.6 G superimposed on a broad background at the low field side. This background decayed almost completely at 130 K and a quintet was then obtained, demonstrating a coupling constant of 10.1 G (Fig. 4a). This absorption is probably associated with a species formed from butadiene, since in the butadiene- d_4 sample a singlet of line width 8.1 G was observed at 77 K (Fig. 4b). At this temperature the background signal at the low field side which had decayed at 130 K (Fig. 4a) is present.

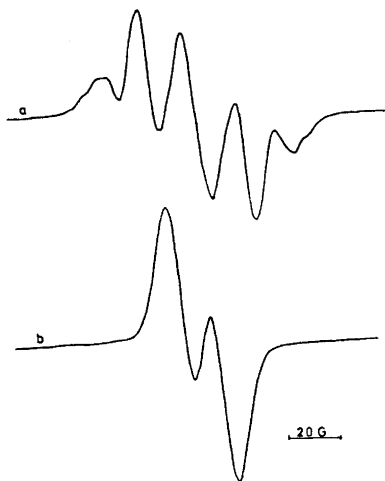


Fig. 3. ESR spectrum in butylchloride glass following γ -irradiation at 77 K to 8×10^5 rad, measured at 100 K. a, 2.4 mol % of 1,3-butadiene. b, 1.4 mol % of 1,3-butadiene-1,1,4,4- d_4 .

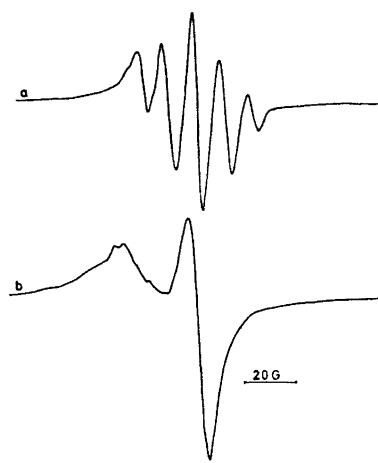


Fig. 4. ESR spectrum in carbon tetrachloride polycrystalline matrix following γ -irradiation at 77 K to 8×10^5 rad. a, 1.2 mol % of 1,3-butadiene measured at 130 K. b, 1.5 mol % of 1,3-butadiene-1,1,4,4- d_4 measured at 77 K. The background signal at low field side is due to a species formed from the carbon tetrachloride matrix.

MTHF matrix. The spectra obtained in the dark contained a small contribution from trapped electrons bleachable by IR light with $\lambda > 780$ nm, provided that the butadiene content was low (0.15 mol %). The intensity of the trapped electron signal is then about 10 % of the signal strength in the pure solvent. When BuCl is present at a concentration of 1.5 mol %, the resonance recorded is essentially that of the pure MTHF lacking the absorption of the trapped electrons. In a similar experiment with the higher butadiene content of 3.0 mol %, the spectrum of Fig. 5a was obtained in the dark. In this case the illumination with IR light with $\lambda > 780$ nm does not affect the spectrum; this indicates that trapped electrons are absent. The spectrum shown in Fig.

5c was obtained after subtraction of the photobleached pure MTHF component shown in Fig. 5b. This component is also present in the sample containing 0.15 mol % butadiene.

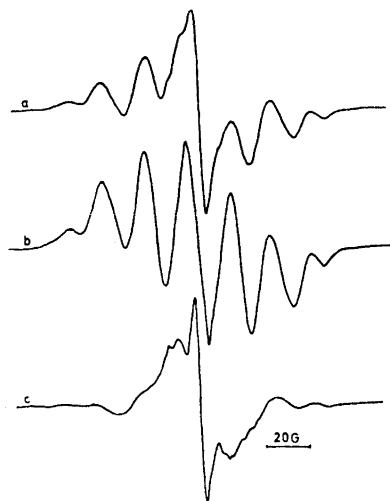


Fig. 5. ESR spectrum in 2-methyltetrahydrofuran glass following γ -irradiation in the dark at 77 K to 8×10^5 rad, measured at 77 K. a, 3.0 mol % of 1,3-butadiene in the dark. b, pure 2-methyltetrahydrofuran after the illumination with IR light ($\lambda > 780$ nm). c, difference spectrum obtained by subtraction of b from a.

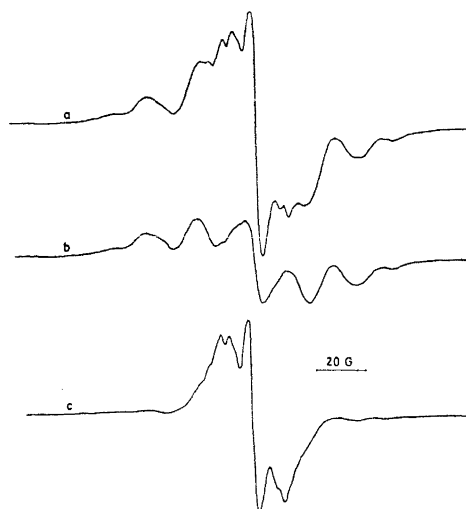


Fig. 6. ESR spectrum of 3.0 mol % of 1,3-butadiene in the presence of 8.0 mol % of triethylamine in 2-methyltetrahydrofuran following γ -irradiation in the dark at 77 K to 8×10^5 rad, measured at 77 K. a, after the illumination with IR light ($\lambda > 780$ nm). b, after the illumination with visible light ($\lambda > 395$ nm). c, the component bleached with visible light, obtained by subtraction of b from a.

Butylchloride at a concentration of 10 mol % completely scavenged the formation of the component represented in Fig. 5c. In the presence of TEA at a concentration of 8.0 mol % the spectrum did not contain any contribution from trapped electrons bleachable by light with $\lambda > 780$ nm (Fig. 6a). Following illumination with visible light with $\lambda > 395$ nm, the decaying component of Fig. 6c was obtained by subtracting the remaining signal of Fig. 6b. The decaying species seems to be identical with that formed in the absence of TEA.

Hydrocarbon matrix. The spectrum from a sample containing 1.7 mol % butadiene in a 3MP glass matrix changed during storage for one week at 77 K. This change became obvious when butadiene- d_4 was used (Fig. 7a). The remaining component (Fig. 7b) has a line profile which is similar to the absorption observed in BuCl (Fig. 3b) and can therefore be attributed to RI. The decaying component is due to the 3-methylpentyl radical.¹⁴ During storage the signal strength of RI remained approximately constant.

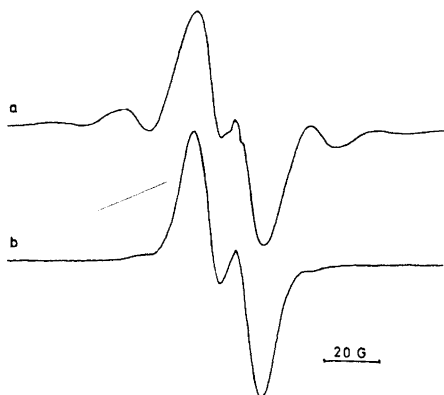


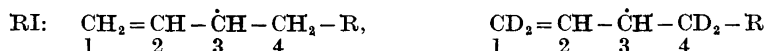
Fig. 7. ESR spectrum of 1.7 mol % of 1,3-butadiene-1,1,4,4- d_4 in 3-methylpentane glass following γ -irradiation in the dark at 77 K to 8×10^5 rad. a, measured at 77 K. b, measured at 77 K after storage for 7 days at 77 K.

In the presence of 3.5 mol % BuCl the concentration of RI is approximately doubled by comparison with a sample which contained 4.1 mol % TEA as an additive. The latter sample contained 1.4 mol % butadiene- d_4 , and here also a doublet structure associated with RI was obtained.

Similar experiments were repeated with 3MH as glass matrix. In this glass and with a butadiene- d_4 content of 1.7 mol %, a component was present which could be bleached by IR light with $\lambda > 1000$ nm; this indicates the presence of trapped electrons. The concentration is an order of magnitude less than in the pure 3MH. The 3-methylhexyl radical was still present in the sample after storage for a week at 77 K. Following heat treatment, this radical decayed and the doublet spectrum of RI was obtained. The results from experiments using additives are analogous to those described for 3MP glass.

DISCUSSION

Radical structure. The species RI, which forms in all the glass matrices used except MTHF, has a splitting constant typical of the allyl-type of radical. The influence of deuteration shows that this radical is most probably derived from radiation-induced reactions with the solute butadiene. A species of the type



is consistent with the observed spectra in the case of the ordinary and the deuterated samples, respectively. In the latter case, the value $a_3 = 13.8$ G coincides with the splitting constant observed in the solution.⁸ Because of the large line width in the glassy state, about 12 G, the resolution of the smaller splittings from the deuterons and from the proton at position 2 could not be obtained. The observation of an odd number of lines when ordinary butadiene was used requires that the two β protons at position 4 should be nonequivalent. Either one coupling is approximately twice that of a_3 and the other is comparable with a_3 , or one coupling is the same as a_3 and the other is small and unresolved.¹⁵ It is known that $a_1 \approx a_3$.⁸ Taking into account the excessive

line width, an odd number of lines can then be expected in both models, *i.e.* 7 or 5 peaks. The intensity distribution in Fig. 3a across the resolved components seems to favour the latter alternative.

The formation of a radical of the type RII by hydrogen atom abstraction



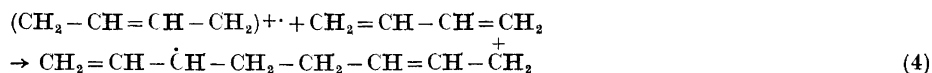
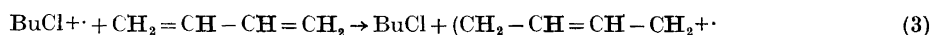
from the solvent and subsequent addition to the solute can only occur to a very minor extent. According to data from the solution⁸ the coupling constants of the methyl protons and those of the protons on carbon 1 and 3 are comparable. From the reasonable assumption of free rotation for the methyl group, a triplet structure can be expected in the butadiene-*d*₄ sample; this is at variance with the observed doublet.

The species RI does not form in the polycrystalline CCl₄ matrix containing butadiene. Carbon tetrachloride stabilize negative charge as Cl⁻ which then favours the formation of cations. The quintet structures observed is most probably caused by the butadiene cation. This theory is supported by the effect of deuteration. The experimental coupling constant of 10.1 G can be predicted correctly using a method similar to that applied by Snyder and Amos for the negative ion.¹⁶ A slightly larger coupling constant was obtained in the adsorbed state.¹⁰

The absorption found after subtraction of the pure solvent spectrum in the MTHF glass (Fig. 5c) is very probably associated with a species formed from the solute. The reduction of the trapped electron intensity suggests that in this system butadiene may act as an electron scavenger. The evidence for the formation of anionic species is obtained from the inhibiting action when BuCl is present as an electron scavenging additive. The fact that this species is formed in the presence of TEA rules out the possibility of cation formation. TEA should act as a cation scavenger, because it has a lower ionization potential (7.50 eV)¹⁷ than butadiene (9.18 eV)¹⁸ and also possesses a high proton affinity. A detailed assignment of the experimental spectrum based on isotropic coupling constants does not seem possible. Thus a simulation which includes the interactions with four equivalent protons having a coupling constant of 7.7 G gives a pattern in which the intensity of the central component appears too weak. This central line is not caused by the trapped electrons since IR light does not affect its signal strength. The spectrum is probably caused by the butadiene anion. In tetrahydrofuran the coupling constants $a_1 = 7.74$ G (4H) and $a_2 = 2.66$ G (2H) have been reported for the butadiene anion radical.⁶ In a glassy matrix the dipolar hyperfine interaction may broaden the lines due to an incomplete motional averaging. The broadening can occur to different extents for different transitions in the spectrum. Thus a deviation from the intensity ratio predicted from the isotropic coupling constants may occur.¹⁹

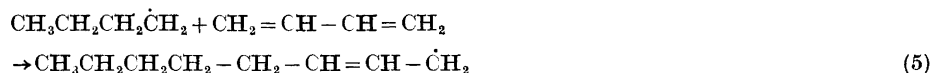
Mechanism. The observation of the butadiene cation in a CCl₄ matrix suggests the possibility of the initiation by radical cation in the alkyl halide glass matrices. It seems rather probable that reactions would occur more easily in the BuCl glass than in the polycrystalline CCl₄ matrix. This accords with the finding that the butadiene cation remains in the CCl₄ system but is

not observed in the BuCl system. The inhibiting effect of TEA on the formation of RI supports the hypothesis that this species is formed in a cationic process. A reaction mechanism consistent with the observations is as follows.



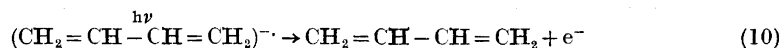
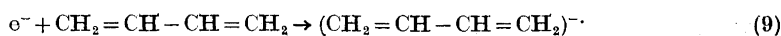
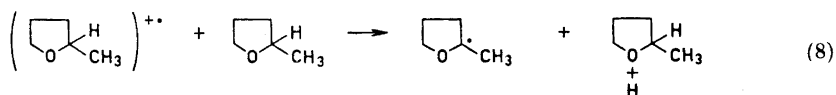
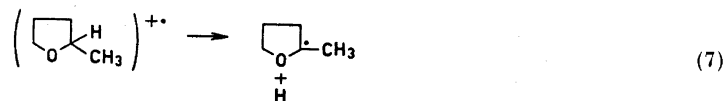
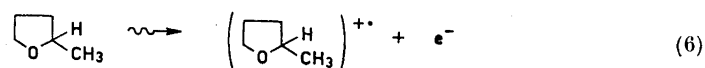
The successive addition of butadiene molecules through cationic propagation probably continues during irradiation, but this reaction cannot be evidenced by the ESR technique.

The increase of RI when the sample is stored after irradiation is probably not caused by a cationic mechanism since a positive charge scavenger like TEA had no inhibiting effect. The accompanying decrease in the butyl radical signal strength suggests a radical mechanism such as (5) which predicts that the

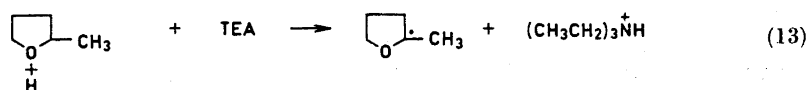
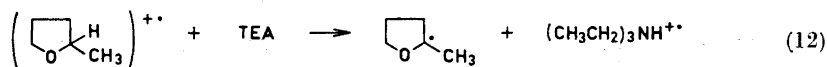
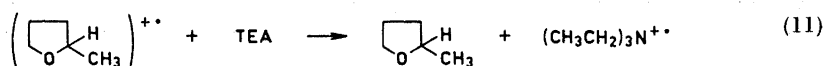


increase of RI and the decrease of butyl radicals will be equal, in accordance with the experimental findings. Other mechanisms which might be considered are more complex. The recombination or disproportionation of the butyl radical appears to be of less importance; RI cannot be formed in such reactions.

The solute spectra in MTHF shown in Figs. 5c and 6c may probably be assigned to the butadiene anion. The results do not support the occurrence of initiation reactions during irradiation. If such reactions occurred then radicals of the RI type would form. Evidence for anionic initiation forming RI has been obtained for butadiene treated with sodium at low temperature.⁹ The mechanism can be summarized as follows.



In the presence of BuCl reaction (2) occurs. In the presence of TEA



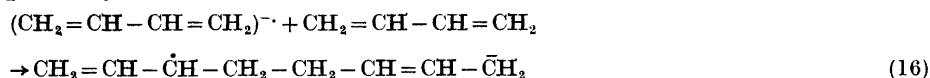
It is known that part of the MTHF absorption disappears simultaneously with the trapped electron signal by photobleaching.^{20,21} The bleached spectrum consists of the superimposed two spectra from the cations formed according to (6) and (7).²¹ The spectrum of Fig. 5c was obtained by subtraction of the MTHF signal after photobleaching. As a consequence this spectrum contains weak wings which are attributable to a bleached component of the solvent. When TEA is present the solvent cations may react with TEA to yield a neutral MTHF radical according to (11)–(13). The contribution from the cation signal to the background MTHF absorption becomes less and thus the solvent spectrum is bleached to a smaller extent by the light which bleaches the anion radical. Accordingly, Fig 6c is regarded as representing the spectrum of the anion radical more accurately than Fig. 5c. The decay of the anion is probably through electron detachment (10).

The reactions taking place in the hydrocarbon glasses 3MP and 3MH are similar and are therefore treated together. The formation of RI indicates that polymerization occurs. The initiation is not purely cationic since the formation of RI is not completely hindered by TEA. Similarly, a completely anionic mechanism is ruled out by the observation of RI when BuCl is present as an additive. Both cationic and anionic mechanisms therefore probably occur in these systems. Under the experimental conditions the amount of RI formed by a cationic mechanism would appear to be about twice the amount formed by an anionic mechanism.

The observation that the intensity of RI remains constant post irradiation at 77 K shows that a radical reaction between the solvent radical and the solute does not occur in branched hydrocarbon glasses, by contrast with the butylchloride system. The reaction mechanism can be summarized as follows.



The reaction (14) and (15) are followed by the reactions (9) and (4), respectively.



The propagation proceeds cationically and anionically following reactions (4) and (16), respectively. The 3MH glass affords a more rigid matrix so that electrons and 3-methylhexyl radicals become trapped more stably at 77 K.

CONCLUSIONS

The cation radical of 1,3-butadiene was observed in polycrystalline carbon tetrachloride following γ -irradiation. The initiation of the polymerization by the cation radical was indicated in butylchloride glass at 77 K during irradiation. The butadiene anion was observed in 2-methyltetrahydrofuran glass at 77 K following γ -irradiation. Both cationic and anionic initiation occurred in hydrocarbon glasses of 3-methylpentane and 3-methylhexane.

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