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RADIATION-INDUCED CHAIN ISOMERIZATION OF *cis*-2-BUTENE IN BENZENE SOLUTION

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Radiation-induced isomerization of *cis*-2-butene was found to proceed in benzene solution by an ionic chain mechanism when total radiation dose is low. The yield of *trans*-2-butene reaches 10^3 in G unit under optimum conditions. Scavenging studies indicate that charge transfer from benzene cations to *cis*-2-butene and direct isomerization of *cis*-2-butene cations take place. Outlines of the results are presented.

We have found that *cis*-*trans* isomerization of 2-butene proceeds by a chain mechanism when *cis*-2-butene is irradiated with ionizing radiations in benzene solution at low doses. High radiation-chemical yields of *trans*-2-butene, $G(trans)$, were obtained not only by γ-irradiation but also by high-LET heavy ion-irradiation under similar conditions. In this communication we wish to report outlines of the results obtained by γ-irradiation and to discuss briefly the reaction mechanism that predominates at low doses and at a 2-butene concentration in the vicinity of 0.1 mol dm^{-3}.

cis-2-Butene was Takachiho's standard gas and was used without further purification. Reagent-grade benzene was dried over calcium chloride before distillation; purified solvent was degassed and stored in a Pyrex bulb. Four milliliters of benzene was distilled into an irradiation cell in vacuo to prepare solution. The concentration of *cis*-2-butene was 0.1 mol dm^{-3} except for a series of experiments on the concentration dependence. γ-Irradiation was carried out at room temperature using 12-kCi ^{60}Co. Dose rate was 35 — 440 rad min^{-1}. Analysis of *cis*- and *trans*-2-butene was made by gaschromatography using a 5-m benzyl cyanide-$AgNO_3$ column at 10 °C.

Dose dependence of $G(trans)$ for 0.1-mol dm^{-3} solution is shown in Table I. The yield increases abruptly to the order of 10^3 at a dose of the order of 10^2 rad, indicating that a chain process occurs in this dose range. At a dose $\sim 10^7$ rad $G(trans)$ is about 1, in agreement with the values obtained for the systems in which isomerization is believed to take place *via* triplet *cis*-2-butene.[1)]

Table I. Dependence of *cis*→*trans* isomerization yield, $G(trans)$, on γ-ray dose. Concentration of *cis*-2-butene is 0.1 mol dm^{-3}.

Total dose (rad)	Dose rate (rad min^{-1})	$G(trans)$
3.2×10^2	35	1.4×10^3
6.4×10^2	35	4.2×10^3
1.9×10^3	150	1.4×10^2
3.4×10^3	150	19
3.4×10^4	440	8.0

Pronounced effects on $G(trans)$ of additives and of solvents were observed. Table II shows the effect of scavengers on $G(trans)$ for 0.1-mol dm^{-3} solutions at a total dose of 6.4×10^2 rad. Carbon tetrachloride and naphthalene, which are regarded as electron scavengers, increase $G(trans)$ by one order of magnitude. Triethlyamine reduces $G(trans)$ to practically zero (*i.e.*, no detectable amount of *trans*-2-butene is produced). In ethanol or cyclohexane solution subjected to low-dose irradiation, no *trans*-2-butene was detected.

Table II. Effect of scavenger on $G(trans)$ for 0.1-mol dm^{-3} *cis*-2-butene solution in benzene. Dose is 6.4×10^2 rad and dose rate is 35 rad min^{-1}.

Scavenger	Concentration (mol dm^{-3})	$G(trans)$
None	——	4.2×10^3
Naphthalene	2.8×10^{-3}	4.3×10^4
Carbon tetrachloride	3.7×10^{-2}	5.4×10^4
Triethylamine	3.8×10^{-2}	0

These results may be interpreted as indicating cationic species that play an exclusive role in the chain isomerization process. Electrons produced in the early stage of the process will be scavenged by electron scavengers before recombination with cationic species, resulting in the increase in their lifetime. Scavenging of electrons should thus enhance *G*(*trans*), inasmuch as the cationic species are assumed to be a chain carrier. Drastic reduction in *G*(*trans*) resulting from the addition of the positive-charge scavenger supports this assumption. In ethanol or cyclohexane, parent cation is known to undergo rapid ion-molecule reaction or decomposition producing stable cations.

On the basis of the present results, we assume that a benzene cation or a hole may transfer its charge to *cis*-2-butene and that the resulting cation of *cis*-2-butene is involved in the chain process

$$\mathrm{B} \xrightarrow{\gamma\text{-rays}} \mathrm{B}^{+} + e^{-}, \qquad \mathrm{B}^{+} + cis \longrightarrow \mathrm{B} + cis^{+}$$

$$cis^{+} \longrightarrow trans^{+}, \qquad trans^{+} + cis \longrightarrow trans + cis^{+}$$

(where B is benzene and *cis* and *trans* stand for corresponding 2-butenes) plus a chain termination step involving neutralization.

Ionization potentials determined by a photoionization method have been reported to be 9.245 ± 0.01 eV for benzene and 9.13 ± 0.01 eV for *cis*- and *trans*-2-butene.$^{3)}$ No chain *trans*→*cis* isomerization was observed under the optimum conditions for the *cis*→*trans* process. It should also be noted that *G*(*trans*) is dependent upon the *cis*-2-butene concentration.

Radiation-induced isomerizaiton of olefinic compounds including 2-butene in benzene solutions has been studied from the viewpoints of energy transfer from excited benzene molecules and of the yield of the benzene triplet;$^{2,4-7)}$ radiation dose is usually higher ($>10^{5}$ rad) than that in the present study and, therefore, *G*(isomer) is low. An ionic mechanism has been proposed by Hatano *et al.*$^{8)}$ for isomerization of *cis*-2-butene in pure liquid, but it is not a chain.

Chain isomerization has been reported for photolysis and radiolysis of gaseous mixtures of *cis*-2-butene with $SF_6$$^{9,10)}$ and of cyclohexane solutions containing 2-pentene and some additives;$^{11)}$ a contribution of ionic species is not established, however. Hentz *et al.*$^{12,13)}$ have reported that the radiation-induced isomerizaiton of *cis*-stilbene in benzene solution proceeds by an ionic chain mechanism at ∿ 0.1 mol dm^{-3}; they emphasize the role of stilbene anions formed in electron-capture processes.

In this communication, evidence supporting a cationic chain mechanism was presented. Although no explanation was given to the reason why the chain mechanism occurs preferentially in low-dose irradiation, these results may give important insight into low-dose radiolysis studies and behavior of benzene cations or holes as well. Extensive studies of γ and heavy-ion radiolysis of the system are in progress. Although a study of the LET effect using 0.5-MeV protons has been made from the viewpoint of energy transfer,6) our preliminary results of the chain isomerization by heavy-ion (C and N ions) irradiation seem to imply interesting features of primary processes in high-LET radiation chemistry. Details will be published.

References and Notes

1) *G*(*trans*) was found to be dependent on the *cis*-2-butene concentration when radiation dose is as high as 10^7 rad, increasing linearly with increasing concentration to reach a plateau of about 2 at 0.2 mol dm^{-3} (Ref. 2).

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