The Radiation-induced Isomerization of 2-Butenes

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The cis-trans isomerization of 2-butenes has been investigated under various conditions in order to obtain some critical information about the nature and reactivity of the double bond. Gas-phase thermal isomerization has been known to be of a unimolecular reaction, in which there is a transition to an excited state, which can then undergo a radiationless transition to the ground state with isomerization.[1]

The cis-trans isomerization of 2-butenes through the triplet state provides a straightforward means of conducting the multiplicity exchange:

$$\text{Sensitizer (triplet)} + \text{2-Butene (singlet)} \longrightarrow \text{2-Butene (triplet)} + \text{Sensitizer (singlet)} \quad (1)$$

Hammond, Leermarkers and Turro[2] have suggested that it is possible to study the mechanisms of various photochemical reactions by determining the formation of the triplet intermediates from the reactants in the presence of such a sensitizer as benzophenone. Cundall and Palmer[3] have also studied the gas-phase

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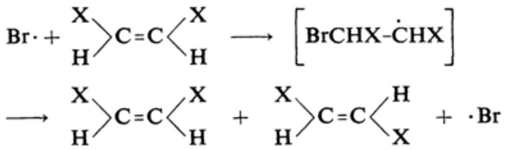
[1] B. S. Rabinovitch and K. W. Michel, *J. Am. Chem. Soc.*, **81**, 5065 (1959).

[2] G. S. Hammond, P. A. Leermarkers and N. J. Turro, ibid., **83**, 2395 (1961).

[3] R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

isomerization of 2-butene in the presence of various photosensitizers, such as mercury, sulfur dioxide, benzene and a variety of other organic photosensitizers, and have shown that the multiplicity exchanges that lead to the isomerization can be accomplished if the photosensitizing species have energy in excess of approximately 60 kcal. mol.$^{-1}$ above the ground state. If this latter condition is satisfied, reaction 1 occurs at every collision.

It has long been known that a trace of bromine or iodine initiates the cis-trans isomerization of such substances as dimethyl maleate and stilbene; early works in this field have been reviewed by Mayo and Walling.[4] Such an isomerization has been suggested to be a radical-chain process, and the isomerization of dimethyl maleate to dimethyl fumarate by bromine in carbon tetrachloride is known to be induced by light. Thus the isomerization takes place through the reversible addition of bromine atoms, which occurs in the initial step of the reaction:



Since the incipient radical formed can readily rotate around the C–C bond axis, the elimination of the halogen atom gives both isomers, although the more stable isomer is yielded preferentially. The same incipient intermediate radical is also involved in the addition reaction; therefore, the addition reaction usually competes with the isomerization reaction.

In high-energy radiation chemistry, a similar situation arises. The radiation-induced reactions involve a transfer of electronic excitation from one molecule to another. Moreover, all possible excited states, ions and electrons may be produced, and so little or no selectivity can be expected in the product formation. In the process of being thermalized, an electron may induce the excitation of a molecule to a triplet state, and the number of such states may also result from the neutralization of positive ions by electrons, or indirectly by transition from higher excited states. Radicals can also be made by various processes, and different radicals may display different chemical behavior in the overall reaction process.

It, therefore, appears of interest to study a system where such a species leads to the cis-trans isomerization of 2-butenes by either chemical change or energy degradation.

Experimental

Materials.—*cis* and *trans*-2-Butenes were Takachiho research-grade materials. The *trans*-2-butene contained less than 0.05% of the cis material, and the *cis*-2-butene contained less than 0.05% of the trans isomer and 0.05% of butane. 1-Butene, purchased in a cylinder, was purified by repeated distillations in a vacuum. The purities of these materials were confirmed by gas chromatography. Spectrally-pure argon, helium, nitrogen, hydrogen, oxygen, carbon dioxide and carbon monoxide supplied by Takachiho Chemical were used without any further purification. Benzene was washed with sulfuric acid, water and sodium carbonate solution, dried with calcium chloride, and purified by bulb-to-bulb distillation. Ethyl bromide was distilled and stored under vacuum. Nitric oxide and sulfur dioxide were dried with phosphorus pentoxide and purified by repeated vacuum distillations. Diphenyl disulfide, obtained from Tokyo Kasei, was purified by repeated recrystallizations in ethyl alcohol. All the other chemicals used were purified by conventional methods.

Apparatus and Procedure. — A conventional vacuum apparatus was employed. The radiation-induced reactions were carried out in a Pyrex glass bulb 20 to 30 ml. in size. The sample in the gas phase was irradiated by a cylinder-type cobalt 60 source giving a radiation dose rate of 1.0×10^6 roentgen per hour. The dose rate was obtained from the Fricke ferrous-sulfate dosimeter, taking the G-value as 15.6, and from the Victoreen rate meter. All the irradiations were carried out at 45±1°C. At the end of the irradiation, the materials were removed for analysis from the reaction bulb to a system consisting of a series of traps and a manometer. The measured samples were analyzed with a Hitachi FID gas chromatograph, with a 90 m. squalane column at room temperature. The chromatograph was capable of handling a sample of 10^{-7} mol. with an accuracy of better than 2%.

Results and Discussion

The Radical Isomerization of 2-Butene.—The gamma irradiation of *trans*-2-butene was studied under various conditions. At room temperature and atmospheric pressure, the reaction did not occur markedly. The gas evolved consisted mainly of hydrogen and methane, together with a small amount of butene isomers. A detailed examination of the isomerization by the irradiation of *trans*-2-butene with a dose of 2.4×10^7 r. showed that little isomerization (only 0.7%) from trans to cis occured. Even the addition of hydrogen, nitrogen, helium, argon, carbon dioxide, carbon monoxide, oxygen or nitrous oxide had only a little effect on the isomerization of *trans*-2-butene, when the pressure was between 10 and 100 mmHg.

Recently the radiation-induced radical isomerization of 2-butene with hydrogen sulfide

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[4] F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

has been reported by this laboratory.[5] The cis-trans isomerization (ratio: 0.39) takes place through the formation of an incipient radical intermediate, together with the formation of small amounts of butyl mercaptan and butyl sulfide.

Usually in such a system there arises competition between addition and isomerization. Therefore, the radical isomerization of 2-butene in the vapor phase has been studied by using a variety of radicals formed by the irradiation of gamma rays. Figure 1 gives typical data for the conversion of 2-butene by the bromine radical as a function of the dose.

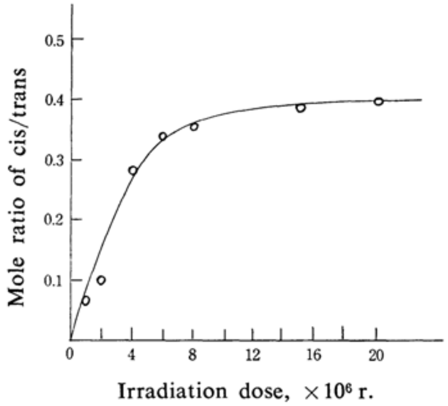

Fig. 1. Effects of ethyl bromide upon *trans*-2-butene as function of dose. (Ethyl bromide, 30 mmHg; *trans*-2-Butene, 100 mmHg)

The effect of the concentration of ethyl bromide upon the isomerization was examined at a constant dose. The isomerization of 2-butene took place very readily and was not affected by the change in the concentration of ethyl bromide, as Table I shows, suggesting that the reaction is a radical-chain process initiated by the bromine atom.

TABLE I. EFFECTS OF ETHYL BROMIDE ON THE 2-BUTENE ISOMERIZATION

trans-2-Butene mmHg	C_2H_5Br mmHg	cis/trans	1-Butene/*trans*-2-Butene $\times 10^{-2}$
100	10	0.40	0.82
100	20	0.366	1.13
100	30	0.394	1.11
100	40	0.389	0.89

Irraidiation dose: 1.5×10^7 r.

It is important to notice also that a very small quantity of bromine-containing by-products were observed.

The addition of an atom or a free radical to an olefin produces a vibrationally-excited adduct radical which contains all the energy of the newly-formed bond and the activation energy required for the reaction. However, such a radical may decompose without requiring any activation energy, or it may be deactivated by a suitable collision.[6] Its lifetime is substantially longer than the period of the internal rotation around the C–C bond, and the isomerization ensues. The work of Dainton shows that such a situation arises upon the addition of a Cl atom to dichloroethylenes; therefore, the isomerization observed in our experiments is explicable if one assumes that it is caused by a bromine atom.

$$C_2H_5Br \xrightarrow{\gamma} C_2H_5\cdot + \cdot Br$$

$$Br\cdot + trans\text{-2-Butene} \longrightarrow \cdot C_4H_8Br$$

$$\cdot C_4H_8Br \rightarrow cis\text{- or } trans\text{-2-Butene} + \cdot Br$$

This mechanism may be supported by the formation of small amounts of 1-butene and other by-products containing bromine.

The radical isomerization for 2-butene was investigated further in a heterogeneous or a homogeneous system. The results are shown in Table II. The relative rate of the isomerization of 2-butene with halogenated compounds decreased in the order, Br>Cl>I, being small with chlorine and less with iodine.

As we have seen in the bromine system, the isomerization caused by a reversible Cl-atom addition is extremely rapid. However, in contrast to the cases with chlorine and bromine, the radical addition of iodine to 2-butene is a marginal proposition. The heat of formation[7] of the C_4H_8I radical may be very roughly estimated as 25 kcal. mol^{-1}.* Therefore, the radical formed from 1-butene may be said to be quite unstable, and that formed from 2-butene, slightly more so. On the other hand, Christie et al.[8] have found values of a few kcal. mol^{-1} for the heat of formation of several complexes formed by the interaction of an iodine atom and a hydrocarbon molecule. Rand and Strong[9] have also found a complex formation between an iodine atom and benzene when iodine was flash-photolyzed in a benzene solution.

If the mechanism of the isomerization may be described by the following reactions:

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[5] K. Sugimoto, W. Ando and S. Oae, This Bulletin, **38**, 224 (1965).

[6] P. B. Ayscough, A. J. Cooker and F. S. Dainton, *Trans. Faraday Soc.*, **58**, 284 (1962).

[7] M. H. Back and R. J. Cvetanovic, *Can. J. Chem.*, **41**, 1396 (1963).

[8] M. I. Christie, R. G. Norrish and G. Porter, *Proc. Roy. Soc.*, **A216**, 152 (1953).

[9] J. Rand and R. L. Strong, *J. Am. Chem. Soc.*, **82**, 5 (1960).

* Values used in this estimation; $H_{f25}(C_4H_{10})=-29.8$, $D(s\text{-}C_4H_9\text{-}H)=D(s\text{-}C_3H_7\text{-}H)=94$, $D(H_2)=103.2$, $D(I_2)=35.35$, $D(s\text{-}C_4H_9\text{-}I)=48$, $D(s\text{-}C_4H_8I\text{-}H)=D(s\text{-}C_4H_9\text{-}H)$.

TABLE II. RADICAL ISOMERIZATION OF 2-BUTENE IN THE GAMMA IRRADIATION

Radical source	mmHg	cis/trans	1-Butene / *trans*-2-Butene
C_2H_5I	30	0.0127	0.0091
C_2H_5Br	30	0.394	0.0111
C_2H_5Cl	30	0.0654	—
CCl_4	30	0.025	—
$CHCl_3$	30	0.0213	—
$(C_6H_5S)_2$	1 g.	0.365	—

trans-2-Butene, 100 mmHg; Irradiation dose, 1.5×10^7 r.

$$C_2H_5I \xrightarrow{\gamma} C_2H_5\cdot + \cdot I \qquad (1)$$

Isomerization

$$\left\{\begin{array}{ll} I\cdot + trans\text{-2-Butene} \rightarrow C_4H_8I\ (\text{radical}) & (2) \\ C_4H_8I\ (\text{radical}) \rightarrow I\cdot + \alpha\ trans\text{-2-Butene} & \\ \qquad + (1-\alpha)\ cis\text{-2-Butene} & (3) \end{array}\right.$$

No isomerization

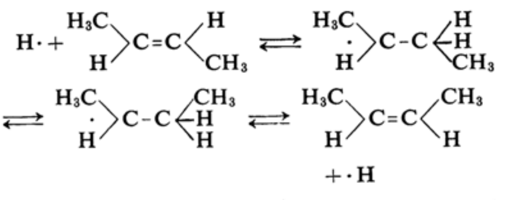
$$\left\{\begin{array}{ll} I\cdot + trans\text{-2-Butene} \rightarrow C_4H_8I\ (\pi\text{-complex}) & (4) \\ \pi\text{-Complex} \longrightarrow trans\text{-2-Butene} + I\cdot & (5) \\ \pi\text{-Complex} + I\cdot \rightarrow trans\text{-2-Butene} + I_2 & (6) \end{array}\right.$$

the complex formed in 4 may be more stable than the radical and have a lower energy barrier for formation. The easy formation of a π-complex is in agreement with the low isomerization of 2-butene.

Other chemical systems have also been examined for the radical isomerization, with special attention being paid to the effect of radiation-sensitive hydrocarbons. Particularly interesting is the isomerization of 2-butene in hexane or cyclohexane, because they readily liberate hydrogen atoms on irradiation and would eventually lead to the isomerization of 2-butene (Table III).

The hydrogen atom formed from hexane or cyclohexane was found to attack the double bond of *trans*-2-butene, and the formation of new C–H bond easily expelled the other hydrogen atom of 2-butene.

$$C_6H_{14} \xrightarrow{\gamma} C_6H_{13}\cdot + H\cdot$$



Steinmetz and Noyes,⁽¹⁰⁾ by measuring the relative rates of exchange and isomerization, concluded that the rate constant for the exchange process is about twice that for the rotation process that lead to the isomerization, but that the two have almost identical activation energies of somewhat greater than 3 kcal. The difference is probably caused by the barrier to rotation in the intermediate radical.

TABLE III. THE EFFECTS OF HYDROCARBON ON THE ISOMERIZATION

trans-2-Butene mmHg	C_6H_{14} mmHg	cyclo-C_6H_{12} mmHg	Mole ratio cis/trans	1-Butene / *trans*-2-Butene
100	25		0.1005	0.0060
100		25	0.1025	0.0051

Irradiation dose: 2.4×10^7 r.

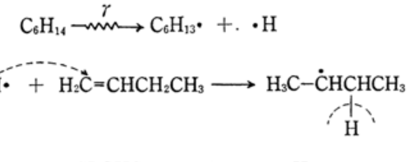
To demonstrate these possibilities, the exchange of the hydrogen atom was studied by investigating the isomerization of 1-butene in hexane or cyclohexane in the gas phase. The results are shown in Table IV.

TABLE IV. ISOMERIZATION OF BUTENE-1 IN HYDROCARBON

1-Butene mmHg	C_6H_{14} mmHg	cyclo-C_6H_{12} mmHg	Mole ratio	
			trans-2-Butene / 1-Butene	*cis*-2-Butene / 1-Butene
100	25		0.0777	0.00142
100		25	0.0481	0.00231

Irradiation dose: 2.4×10^7 r.

If the hydrogen exchange reaction does not occur, the isomerization from 1-butene to *trans*- or *cis*-2-butene should not take place. The results showed the rapid isomerization of 1-butene to 2-butene, leading us to the conclusion that the hydrogen-exchange reaction is actually involved. If one assumes the isomerization of 1-butene as arising from the exchange of hydrogen, the reaction involved may be diagramed as:



$$C_6H_{14} \xrightarrow{\gamma} C_6H_{13}\cdot + \cdot H$$

$$H\cdot + H_2\dot{C}{=}CHCH_2CH_3 \longrightarrow H_3C{-}\dot{C}HCHCH_3$$

$$\longrightarrow H_3CHC{=}CHCH_3 + \cdot H$$

A similar path can probably account for the isomerization of 1-butene in cyclohexane vapor, and also the fact that hydrogen exchanges in the 1-butene isomerization lead to a similar process for the isomerization of 2-butene. With other hydrocarbons, therefore, one can also find similar processes for isomerization.

The Isomerization Involving Transfer of Electronic Energy.—There are a large number of known elementary processes which involve

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10) H. Steinmetz and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 4141 (1952).

atoms or molecules in excited electronic states.

Benzene photosensitzation has been successfully applied by Sato et al.[11] to the isomerization of 2-butene. Cundall and Criffiths[12] have also reported that a large amount of benzene triplets are formed during the irradiation of a benzene solution with varying concentrations of *cis*-2-butene, and they have presented strong evidence for the energy transfer from benzene to *cis*-2-butene.

Similar experiments have thus been carried out in the gas phase. The results for the benzene - *trans*-2-butene system are shown in Fig. 2 as function of the dose. The conversion of *trans*-2-butene to the cis isomer increased with the irradiation dose; equilibrium was attained at a cis/trans ratio of around 0.33. Even when the benzene pressure was varied with respect to that of *trans*-2-butene, the rate of isomerization remained nearly constant, as may be seen in Table V.

The process in the gas phase isomerization of 2-butene is not simple in contrast to the case in a solution. As we have seen in the previous section, a considerable isomerization of 2-butene was observed with hexane or cyclohexane. Therefore, if hydrogen atoms are formed in the irradiation of benzene, the isomerization should occur in the radical-chain process. However, as Cundall and Mine have suggested,[13] if the isomerization takes place by an energy transfer mechanism involving the benzene triplet, the triplet 2-butene formed by intersystem crossing would not isomerize to 1-butene or isobutene. The possibility of radical-chain reaction in causing isomerization can be seen from the formation of a small amount of 1-butene. In order to study this problem further, experiments were also carried out using 1-butene and benzene (Table VI).

Some isomerization to the other isomer did occur from 2-butene, but in view of other evidence, it seems that the radical-chain reaction is not the main process in the isomerization.

TABLE V. EFFECT OF BENZENE ON *trans*-2-BUTENE

trans-2-Butene mmHg	C_6H_6 mmHg	Mole ratio	
		cis/trans	1-Butene / *trans*-2-Butene
100	5	0.244	0.00762
100	10	0.152	0.00562
100	20	0.171	0.00445
100	30	0.216	0.00308
100	40	0.166	0.00338

Irradiation dose 1.5×10^7 r.

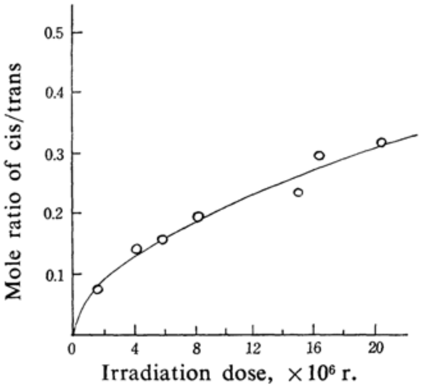

Fig. 2. Effect of dose upon 2-butene with benzene. (*trans*-2-Butene, 100 mmHg; Benzene, 30 mmHg)

TABLE VI. EFFECT OF BENZENE ON 1-BUTENE

1-Butene mmHg	C_6H_6 mmHg	Mole ratio	
		trans-2-Butene / 1-Butene	*cis*-2-Butene / 1-Butene
100	5	0.00228	0.00076
100	10	0.00166	0.00088
100	20	0.00318	0.00159
100	40	0.00556	0.00185

Irradiation dose: 1.5×10^7 r.

These experiments demonstrate that a large number of triplets are formed during the irradiation of benzene and that the energy transfer appears to occur in preference to the radical-chain process for the isomerization of 2-butene. The mechanism which accounts for this is the following:

$$\text{Benzene} \xrightarrow{r} \text{Benzene (triplet)}$$

$$\text{Benzene (triplet)} + \textit{trans}\text{-2-Butene (singlet)} \rightarrow$$

$$\text{2-Butene (triplet)} + \text{Benzene (singlet)}$$

$$\text{2-Butene (triplet)} \rightarrow \textit{cis}\text{- or } \textit{trans}\text{-2-Butene}$$

Similar experiments were carried out in the gas phase using a variety of organic compounds. The data are summarized in Table VII.

The use of toluene and acetone illustrates a similar energy transfer process for the 2-butene isomerization. Here the case is, however, less unambigous and involves a partial contribution by the radical-chain process to the isomerization. Meanwhile, the effect of acetophenone or acetaldehyde on the isomerization does not seem to be through a clear process of energy transfer. The formation of a large amount of

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[11] S. Sato, K. Kikuchi and M. Tanaka, *J. Chem. Phys.*, **38**, 239 (1963).

[12] R. B. Cundall and P. A. Griffiths, *J. Am. Chem. Soc.*, **85**, 1211 (1963).

[13] R. P. Cundall and D. G. Mine, ibid., **83**, 3902 (1961).

TABLE VII. EFFECT OF ORGANIC SUBSTANCES ON *trans*-2-BUTENE

Substance	mmHg	Mole ratio	
		cis/trans	*trans*-2-Butene / 1-Butene
C_6H_6	50	0.348	0.0033
$C_6H_5CH_3$	10	0.288	0.0046
$(CH_3)_2CO$	30	0.195	0.0044
$CH_3COC_6H_5$	1 ml.	0.0368	0.0286
CH_3CHO	50	0.0203	0.0187
$(CH_3CO)_2$	50	—	0.0147

trans-2-Butene, 100 mmHg; Irradiation dose 2.4×10^7 r.

1-butene may be brought about by the radical-chain process.

The possibility of the triplet states of naphthalene and anthracene causing the isomerization of 2-butene in the irradiation was studied. It is probably safe to assume that energy transfer will not take place readily in these heterogerneous systems; therefore, it is likely that the isomerization proceeds through the radical-chain process by means of a hydrogen atom formed in the irradiation of naphthalene and anthracene.

The Effects of Inorganic Substances on the Isomerization.—It has been suggested that the radiation-induced isomerization of 2-butene can take place either by a free-radical chain process or by the energy transfer with a triplet state of an organic molecule with π-electrons, or by both.

TABLE VIII. SULFUR DIOXIDE INDUCED ISOMERIZATION OF *trans*-2-BUTENE

trans-2-Butene mmHg	cis/trans $\times10^{-2}$	1-Butene / *trans*-2-Butene $\times10^{-3}$
10	15.3	7.13
20	10.6	6.25
40	8.69	2.67
60	7.58	2.31
80	7.08	3.44
100	6.64	0.833

Sulfur, dioxide 50 mmHg; Irradiation dose, 1.5×10^7 r.

TABLE IX. SULFUR DIOXIDE INDUCED ISOMERIZATION OF 1-BUTENE

1-Butene mmHg	*trans*-2-Butene / 1-Butene $\times10^{-3}$	*cis*-2-Butene / 1-Butene $\times10^{-3}$
10	9.37	—
20	5.26	—
40	4.50	0.45
60	4.66	0.66
80	3.45	1.14
100	2.89	0.48

Sulfur dioxide, 50 mmHg; Irradiation dose, 1.5×10^7 r.

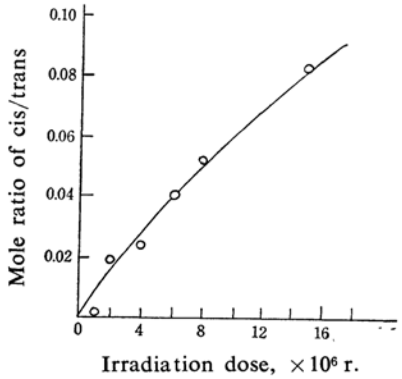

Fig. 3. Effects of sulfur dioxide upon *trans*-2-Butene as function of irradiation dose. (Sulfur dioxide, 100 mmHg; *trans*-2-Butene, 100 mmHg)

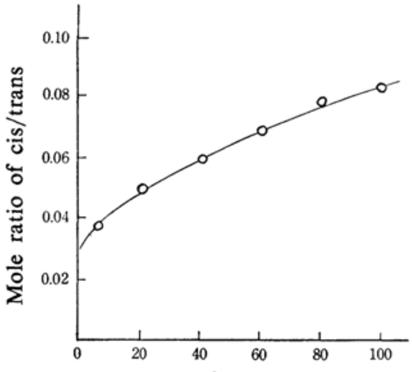

Fig. 4. Effects of sulfur dioxide upon the *trans*-2-butene isomerization (*trans*-2-butene, 100 mmHg; irradiation dose, 15×10^6 r.).

It is, therefore, interesting to see the effect of simple inorganic compounds in the radiation-induced isomerization. Recent work of Cundall and Palmer on the sulfur dioxide-photosensitized isomerization is very interesting in this connection; they have regarded it as involving the triplet state of sulfur dioxide.[3] Their results are in agreement with those of Dainton and Ivin,[14] who showed that the photochemical reactions of sulfur dioxide are due to the formation of the first triplet state (73.4 kcal. mol.$^{-1}$. [15]).

A similar experiment was applied to radiation chemistry with gamma rays. The effects of sulfur dioxide upon the isomerization were

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[14] F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 374 (1950).

[15] A. D. Walsh, *J. Chem. Soc.*, **1953**, 2266.

examined in a mixture of *trans*-2-butene and sulfur dioxide (Tables VIII and IX).

A marked isomerization was found to occur from trans to cis, but little isomerization to 1-butene was found to take place. The isomerization from 1-butene to *trans*- or *cis*-2-butene was also almost negligible. Further observations as to the function of the dose and the pressure of sulfur dioxide are shown in Figs. 3 and 4.

The isomerization can be explained similary by the following mechanism, which assumes the interaction of the triplet state of sulfur dioxide:

$$SO_2 \xrightarrow{\gamma} SO_2 \text{ (triplet)}$$

$$SO_2 \text{ (triplet)} + \textit{trans}\text{-2-Butene (singlet)} \rightarrow$$

$$\text{2-Butene (triplet)} + SO_2 \text{ (singlet)}$$

$$\text{2-Butene (triplet)} \rightarrow \textit{cis}\text{- or } \textit{trans}\text{-2-Butene}$$

However, the formation of small amounts of sulfinic acid and of the polymer on the walls of reaction vessels in the case of both 2-butene and 1-butene seems to suggest that at least a portion of the isomerization proceeds via the chain process shown below:

$$\textit{trans}\text{-2-Butene} + SO_2^* \rightarrow \cdot C_4H_8SO_2\cdot$$

$$\cdot C_4H_8SO_2\cdot \rightarrow \textit{trans}\text{- or } \textit{cis}\text{-2-Butene} + \text{1-Butene} + SO_2$$

$$\cdot C_4H_8SO_2\cdot + M \rightarrow \text{Products}$$

Experiments were also conducted with nitric oxide and carbon disulfide. Nitric oxide has been used extensively as a free-radical trap in gas kinetics, and recently the possibility of an attack of nitric oxide on substrate molecules has been considered.[16,17] The effects of nitric oxide upon the isomerization are shown in Tables X and XI, with the function of the dose and the pressure of butene respectively.

These results, as well as others, indicate that the mechanism for the isomerization appears to be similar to that with sulfur dioxide; when 2-butene encounters unpaired electrons, transitions otherwise forbidden may be induced, and the addition to the double bond, followed by dissociation, may occur.

Table X. Effects of nitric oxide upon *trans*-2-butene

Dose ($\times 10^6$ r.)	1	2	4	6	8	24
cis/trans ($\times 10^{-2}$)	10.3	14.5	13.3	15.1	13.8	16.5

Nitric oxide, 100 mmHg; *trans*-2-Butene 100 mmHg

Table XI. Effects of nitric oxide upon *trans*-2-butene and 1-butene

trans-2-Butene mmHg	cis/trans $\times 10^{-2}$	1-Butene / *trans*-2-Butene $\times 10^{-3}$
10	27.3	5.05
20	24.4	—
40	16.0	5.33
60	14.2	3.57
80	9.61	4.63
100	8.13	3.33

1-Butene mmHg	*trans*-2-Butene / 1-Butene $\times 10^{-3}$	*cis*-2-Butene / 1-Butene $\times 10^{-3}$
10	—	—
20	2.22	1.11
40	3.75	1.25
60	1.66	0.83
80	1.11	0.55
100	0.724	0.36

Nitric oxide, 50 mmHg; Irradiation dose, 3.5×10^6 r.

A brief study of the effect of carbon disulfide was made upon the mixture and 1-butene or 2-butene.

With 1-butene, some isomerization to 2-butene did occur, but a major portion underwent

Table XII. Effects of carbon disulfide upon *trans*-2-butene

trans-2-Butene mmHg	Carbon disulfide mmHg	cis/trans $\times 10^{-1}$	1-Butene / *trans*-2-Butene $\times 10^{-3}$
100	10	1.24	1.32
100	20	1.50	1.51
100	30	1.71	2.38
10	50	2.65	3.34
20	50	2.74	2.18
40	50	2.47	3.75
60	50	2.28	1.20
100	50	2.77	7.55

Irradiation dose: 1.5×10^7 r.

Table XIII. Effects of carbon disulfide upon 1-butene

1-Butene mmHg	*trans*-2-Butene / 1-Butene $\times 10^{-3}$	*cis*-2-Butene / 1-Butene $\times 10^{-3}$
10	7.14	—
20	10.0	2.0
40	3.8	0.95
60	3.86	0.77
80	5.13	1.71
100	3.84	0.96

Irradiation dose: 1.5×10^7 r.
Carbon disulfide: 50 mmHg

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16) B. W. Wojciechowski and K. Laidler, *Can. J. Chem.*, **38**, 1027 (1960); *Proc. Roy. Soc.*, **A260**, 103 (1961).

17) R. Blackmore and Sir C. Hinshelwood, ibid., **A268**, 21 (1962).

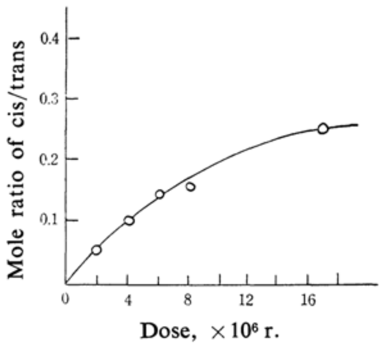


Fig. 5. Effect of dose of irradiation upon 2-butene by carbon disulfide. (Carbon disulfide, 25 mmHg; *trans*-2-butene, 100 mmHg)

decomposition. With 2-butene, carbon disulfide caused some isomerization, and here again the main product was a large amount of by-products, which consisted of some organo-sulfur compounds and elemental sulfur (Tables XII, XIII and Fig. 5).

The effect of gaseous carbon disulfide in the isomerization has not been reported previously. However, it has been shown that, under flash-photolysis conditions, the absorption spectrum taken a few millisenonds after the illumination of gaseous carbon disulfide gave the characteristic bands of S_2 and CS.[18,19] Therefore, one can safely assume the initial interaction of the double bond with the sulfur atom formed by the irradiation of carbon disulfide. The formation of by-products indicates that the isomerization must be carried out through interaction with CS and S, since S is formed in the primary act, while CS is formed both in the primary:

$$CS_2 \xrightarrow{\gamma} CS + S$$

and the secondary acts:

$$CS_2 + S \longrightarrow CS + S_2$$

The sulfur atom thus formed presumably induces isomerization by a direct radical attack on the double bond. The following basic processes may be proposed to explain the action of the sulfur atom in the induced isomerization:

$$trans\text{-2-Butene} + S \rightarrow \cdot C_4H_8S\cdot$$

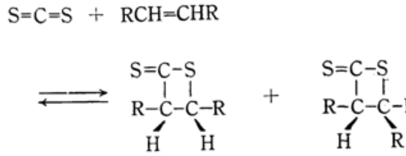
$$\cdot C_4H_8S\cdot \rightarrow cis\text{- or } trans\text{-2-Butene} + S$$

$$\cdot C_4H_8S\cdot + CS \rightarrow cis\text{- or } trans\text{-2-Butene} + CS_2$$

$$\cdot C_4H_8S\cdot + CS_2 \rightarrow cis\text{- or } trans\text{-2-Butene} + CS + S_2$$

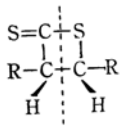
A similar reaction scheme can be postulated with CS, another radical formed by the initial irradiation of CS_2. Isomerization induced by the sulfur molecule would involve the formation of the free radical by the homolytic cleavage of the sulfur, with the subsequent addition of the free radical to the double bond. However, the contribution of this process would not be very large. The explanation of the isomerization mechanism involves the formation of a π-complex between sulfur and the double bond, as has been suggested for the thermal isomerization of polybutadiene with sulfur.[20] However, this mechanism does not reveal the exact nature of the bonding, either in the radical attack or the π-complex formation. The π-complex possibly involves the π-orbital of the olefin and the anti-bonding π-orbital of sulfur, but this is a mere conjecture; until further evidence is available, the discussion of the exact nature of bonding in such a complex will not be fruitful.

Another interesting mechanism is the one involving initial addition, followed by subsequent dissociation, as is shown below:



$$S{=}C{=}S + RCH{=}CHR \rightleftharpoons \begin{array}{c} S{=}C{-}S \\ R{-}C{-}C{-}R \\ H \quad H \end{array} + \begin{array}{c} S{=}C{-}S \\ R{-}C{-}C{-}H \\ H \quad R \end{array}$$

Here, the formation of a large amount of sulfur containing by-products can be also explained if one assumes that the dissociation takes place by A-type cleavage. A similar addition-dissociation was reported very recently



(A)

in the photochemical reaction between thiobenzophenon and olefins.[21] At present, it is difficult to single out the most plausible mechanism for this carbon disulfide-catalyzed isomerization. A detailed investigation of the nature of the by-products would, however, shed further light on the probable pathway of this reaction.

Summary

A detailed study of the radiation-induced trans-cis isomerization of 2-butenes has been made. The effects of halogenated compounds

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[18] R. G. Norrish and G. Porter, ibid., **A200**, 284 (1950).

[19] G. Porter, *Discussions Faraday Soc.*, **9**, 60 (1950).

[20] W. A. Bishop, *J. Polymer Sci.*, **55**, 827 (1961).

[21] E. T. Kaiser and T. F. Wulfers, *J. Am. Chem. Soc.*, **86**, 1898 (1964).

upon 2-butene can be explained by the attack of the halogen radicals formed in irradiation, and a radical chain process can be suggested for the isomerization.

The addition of hexane or cyclohexane to 2-butene in the gas phase has shown a rapid isomerization of trans to cis; it has been suggested that this is caused by the hydrogen atom formed in the irradiation of hexane or cyclohexane. The facile isomerization of 1-butene to *trans*-2-butene by the presence of such hydrocarbons suggests that the hydrogen is readily exchanged with the other hydrogen of olefin, thus leading to the isomerization.

Radiation-induced isomerizations brought by benzene, sulfur dioxide, nitric oxide, carbon disulfide and other molecules have also been examined. The effect of benzene on the trans-cis isomerization of 2-butene has been explained by production of vibrationally-excited triplet states. Results with sulfur dioxide have shown that radiation-induced isomerization is due not only to the formation of the first triplet state, but also to the addition to the double bond, followed by dissociation.

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