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The Dimerization of 2-Methylpropene Induced by γ-Radiation at High Temperatures and Pressures

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The dimerization of 2-methylpropene by γ-irradiation occurred at a temperature of 300 °C and a 2-methylpropene density of 0.1 g/cm^3, giving rise to the formation of 1,1,3-trimethylcyclopentane. The *G* value of this dimer was 50 at an absorbed dose rate of 4.3×10^{18} eV/g h and a total absorbed dose of 2.2×10^{19} eV/g. The *G* value of this dimer was inversely proportional to about 0.47 the power of the absorbed dose rate and was proportional to the 2-methylpropene density. The formation of this dimer was suppressed by the addition of oxygen or nitrogen monoxide. These facts led to the conclusion that the dimer was formed *via* chain reactions with the participation of the 2-methylallyl radical.

The radiation chemistry of 2-methylpropene has been studied by several investigators. Collin and Herman[1] examined the products of the radiolysis of gaseous 2-methylpropene, and they proposed some mechanisms leading to the formation of several low boiling-point products.

Many studies of the low-temperature radiation-induced polymerization of 2-methylpropene, both in the gas phase and in the liquid phase, have shown that the chain propagation was not the free-radical mode but the ionic one and that the most likely initiating species was the *t*-butyl cation, $t\text{-}C_4H_9^+$. For instance, Okamoto *et al.*[2] studied the gas-phase radiation-induced polymerization of 2-methylpropene and established the *t*-butyl cation mechanism. This cation was considered to be produced from the 2-methylpropene parent ion, $i\text{-}C_4H_8^+$, *via* an ion-molecule reaction:

$$i\text{-}C_4H_8 \rightsquigarrow i\text{-}C_4H_8^+ + e$$

$$i\text{-}C_4H_8^+ + i\text{-}C_4H_8 \longrightarrow t\text{-}C_4H_9^+ + C_4H_7\cdot \qquad (1)$$

From their mass spectrometric observations, Tal'rose and Lyubimova[3] showed that Reaction 1 did indeed occur, and Koyano[4] showed that this reaction had a very large cross section.

Collinson *et al.*[5] suggested that Reaction 1 also occurred in the radiolysis of liquid 2-methylpropene and that the $C_4H_7\cdot$ produced together with the *t*-butyl cation was most likely a methyl allyl radical.

On the other hand, McKinley *et al.*[6] studied the thermal polymerization of 2-methylpropene at 370—460 °C, at maximum pressures of from 37 to 370 atm, and at times of from one half hour to four hours. Under these conditions a cyclic dimer, 1,1,3-trimethylcyclopentane (**1**), was the main reaction product.

The present work showed that dimer **1** is not formed at 300 °C and a 2-methylpropene density of 0.1 g/cm^3 for five hours, but by γ-irradiation under the same conditions **1** is formed as a major dimer product, while, 2,4,4-trimethyl-2-pentene (**2**) is formed as a minor one. It will then be concluded that the dimerization of 2-methylpropene induced by γ-radiation proceeds mainly by means of a radical chain reaction whose chain carrier is $C_4H_7\cdot$ and that the contribution of the *t*-butyl cation to the dimerization is not greater than that of $C_4H_7\cdot$.

Experimental

Research-grade 2-methylpropene and all the other gaseous meterials except oxygen were degassed by repeating the freezing-pumping-thawing cycle several times.

The reaction vessel was a stainless steel autoclave (2 cm in inner diameter and with a volume of about 20 cm^3) which was surrounded by a mantle heater. The temperature was controlled at 300 ± 3 °C.

The samples were irradiated with γ-rays from ^{60}Co, and in most cases, the absorbed dose rate was 4.3×10^{18} eV/g h and the total absorbed dose was 2.2×10^{19} eV/g. The *G* values were calculated from the energy absorbed by the sample, where it was assumed that the absorbed energy was proportional to the electron density of the sample. The absolute energy absorption was determined by means of Fricke dosimetry, taking $G(\text{Fe}^{+3})=15.5$.

All the irradiations were carried out at a temperature of 300 °C and a 2-methylpropene density of 0.1 g/cm^3 except where otherwise specified.

After irradiation, the liquid products in the reaction vessel were collected in a trap immersed in liquid nitrogen by vaporizing and pumping them. In order to differentiate between the saturated compounds and the unsaturated compounds in the collected products, the products were hydrogenated in ethanol over Raney's nickel. Gas-liquid-phase chromatography and gas chromatograph-mass spectrography were applied to both the original and hydrogenated products for the identification and determination of the two dimers, **1** and **2**.

Results and Discussion

The yields of the liquid product from γ-irradiated 2-methylpropene were determined at temperatures between 30 and 300 °C. In the lower-temperature range, many kinds of products were formed, but their yields were poor. However, the yields increased with an increase in the temperature; moreover, the proportion of the **1** dimer in the product increased. It was expected that the dimerization proceeded by means of some chain mechanisms above 200 °C.

At 300 °C and a 2-methylpropene density of 0.1 g/cm^3, various scavengers were used in order to see whether the dimerization takes place by means of an ionic or radical mechanism. The experimental results are shown in Table 1.

The addition of ammonia, whose concentration range

Table 1. Effect of scavengers on the γ-radiation-induced dimerization of 2-methylpropene at a temperature of 300 °C and a 2-methylpropene density of 0.1 g/cm^3

Scavenger	Concn (mol %)	G value of dimer 1	G value of dimer 2
None		50	5
NH_3	1.0	48	2
	3.0	51	1
	5.0	52	1
O_2	0.05	30	4
	0.15	14	4
NO	0.5	41	5
	1.0	30	4
	5.0	15	5

The absorbed dose rate is 4.3×10^{18} eV/g h, and the total absorbed dose is 2.2×10^{19} eV/g.

was 0.5—5.0% in the molar fraction, suppressed the formation of **2**, but had little influence on the formation of **1**. This implied at least that the precursor of **1** was not a cation, while **2** was formed by the participation of some cations.

Oxygen and nitrogen monoxides of various concentrations were used as the radical scavengers. It was observed that the addition of small amounts of them suppressed the formation of **1**. On the other hand, the yield of **2** did not change upon the addition of the radical scavengers. Consequently, these observations were in marked contrast to those of ammonia addition.

It is well-known that the intermediary species formed during the γ-irradiation of 2-methylpropene are varieties of ions, radicals, and excited molecules. Among these species, the *t*-butyl cation and the $C_4H_7\cdot$ formed through Reaction 1 seem to be the most reasonable precursors of the 2-methylpropene dimers. Assuming this, it may be considered that, after the formation of the *t*-butyl cation and $C_4H_7\cdot$, they can bring about the subsequent reactions in the following ways:

$$t\text{-}C_4H_9^+ + i\text{-}C_4H_8 \longrightarrow C_8H_{17}^+ \longrightarrow \text{dimer} \longrightarrow \text{polymer} \qquad (2)$$

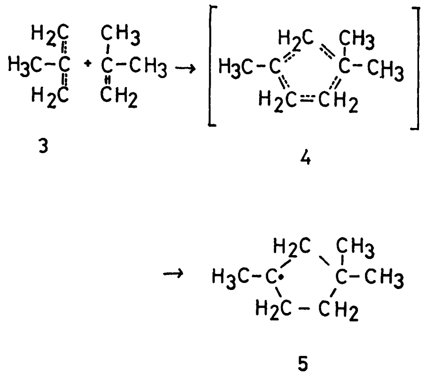
$$C_4H_7\cdot + i\text{-}C_4H_8 \longrightarrow C_8H_{15}\cdot \qquad (3)$$

$$C_8H_{15}\cdot + i\text{-}C_4H_8 \longrightarrow C_8H_{16} + C_4H_7\cdot \qquad (4)$$

It has been found that the *t*-butyl cation reacts predominantly with the terminal carbon in 2-methylpropene both in the gas phase[7] and in the liquid phase[8] to give $C_8H_{17}^+$, the 2,2,4-trimethylpentyl cation, and that this cation then produces mainly **2** by means of a proton-transfer reaction with 2-methylpropene. In the present work also, **2** is probably formed by means of the ionic reaction mentioned above. This speculation seems reasonable because of the observation that the formation of **2** was suppressed by the addition of ammonia. Ammonia is a well-known scavenger of the *t*-butyl cation[9]:

$$t\text{-}C_4H_9^+ + NH_3 \longrightarrow i\text{-}C_4H_8 + NH_4^+ \qquad (5)$$

On the other hand, it may be considered that $C_4H_7\cdot$ is a 2-methylallyl radical (structural formula (**3**)).[5] If so, **3** will readily react with 2-methylpropene to form a 1,3,3-trimethylcyclopentyl radical, (**5**), *via* an intermediary adduct, (**4**), and the radical **5** will subsequently abstract a hydrogen atom from 2-methylpropene; then, as a result of the abstraction, **1** and $C_4H_7\cdot$ (probably, the 2-methylallyl radical) will be formed. That is to say, the reformed $C_4H_7\cdot$ will serve as a chain carrier to repeat the above cyclic reaction and to cause a chain reaction:



In this case, it is assumed that the primary $C_4H_7\cdot$ is formed only by way of Reaction 1, not by other ways such as the decomposition of the excited 2-methylpropene molecule:

$$i\text{-}C_4H_8 \rightsquigarrow i\text{-}C_4H_8^* \longrightarrow C_4H_7\cdot + H\cdot \qquad (6)$$

No hydrogen or compounds formed by the participation of the hydrogen atom could be detected.

It is assumed that the termination reaction can be expressed as follows:

$$C_4H_7\cdot(\text{or } C_8H_{15}\cdot) + R \longrightarrow \text{Products} \qquad (7)$$

where R denotes the $C_4H_7\cdot$ radical, the $C_8H_{15}\cdot$ radical, or other radicals in this system, for instance, the fragment radicals such as $CH_3\cdot$ or $C_3H_5\cdot$ from the radiolysis of 2-methylpropene. Unfortunately, in this work, the termination reactions could not be defined because it was not possible to determine accurately each product derived from the respective termination reactions because of the uncertainty of the gas-chromatographic analysis. However, it may be considered that $C_4H_7\cdot$ and $C_8H_{15}\cdot$ are the most important radicals and that the other radicals are negligible. Therefore, it is assumed that the overall velocity of the termination reaction is $k_t[C_4H_7\cdot][C_8H_{15}\cdot]$, where k_t is the rate constant.

In the reaction sequence mentioned above, provided a stationary state holds for the radicals of both $C_4H_7\cdot$ and $C_8H_{15}\cdot$, **1** can form only *via* Reactions 3 and 4; further, the rate of the formation of primary $C_4H_7\cdot$ (Reaction 1) is proportional to the absorbed dose rate, and the *G* value of **1** is inversely proportional to one-half the power of the absorbed dose rate and is proportional to the 2-methylpropene density:

$$G(\mathbf{1}) = k_4(k/k_t)^{1/2} I^{-1/2}[i\text{-}C_4H_8]$$

where k and k_4 are the rate constants of Reactions 1 and 4 respectively, and where I is the absorbed dose rate.

The variations in the *G* value of **1** with the absorbed dose rate and the 2-methylpropene density are shown in Figs. 1 and 2 respectively. The *G* value of **1** was

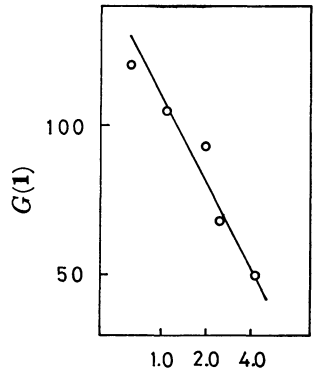


Fig. 1. A plot of G value of **1** *vs.* absorbed dose rate. The absorbed dose, about 2.2×10^{19} eV/g.

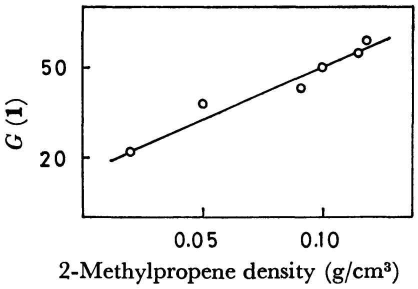


Fig. 2. A plot of G value of **1** *vs.* 2-methylpropene density. The absorbed dose rate, 4.3×10^{18} eV/g h and the total absorbed dose, 2.2×10^{19} eV/g

inversely proportional to about the 0.47 power of the absorbed dose rate and was proportional to the 2-methylpropene density. These experimental results were consistent with the schematic consideration. Therefore, it seems reasonable to conclude that, on γ-irradiation, 2-methylpropene dimerizes to form the cyclic dimer, **1**, by means of a radical chain mechanism where the chain carriers are both $C_4H_7\cdot$ and $C_8H_{15}\cdot$.

Lampe[10)] showed a $G(C_4H_7\cdot)$ of 4.2 and $G(t\text{-}C_4H_9{}^+)=G(C_4H_7\cdot)$ in the liquid-phase polymerization of 2-methylpropene, where the *t*-butyl cation formed *via* Reaction 1 was a polymerization initiator. If it can be assumed that a $G(C_4H_7\cdot)$ of 4.2 is little affected by the phase of 2-methylpropene and the irradiation conditions, this value is equal to the initial G values of Reaction 1, that is, to the initial G values of $C_4H_7\cdot$ or the *t*-butyl cation under the conditions of this work. Therefore, the chain dimerizations concerned in the formation of **1** have chain-lengths of about 12, as evaluated by $G(\mathbf{1})/G(C_4H_7\cdot)=50/4.2$.

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