

## Radiolysis of Methylcyclohexane. II. The Effect of Cumene on Hydrogen Formation from $\gamma$ -Irradiated Methylcyclohexane

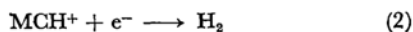
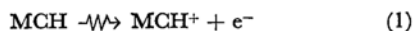
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The effect of cumene on the hydrogen yields from methylcyclohexane  $\gamma$ -irradiated at 100, 20,  $-72$ ,  $-120$  and  $-196^\circ\text{C}$  has been investigated. Cumene did not compete with  $\text{N}_2\text{O}$  for capturing electrons in methylcyclohexane and the yield of thermal H atoms in methylcyclohexane, determined by use of ethylene as an H atom scavenger, was smaller than the decrease in hydrogen yield in methylcyclohexane-cumene systems. Therefore, the decrease in hydrogen yield in methylcyclohexane-cumene systems can be ascribed mainly to positive charge transfer from methylcyclohexane to cumene. Further, the evidence of charge transfer from methylcyclohexane to cumene was found by the optical absorption method. The effect of cumene on the hydrogen yield from methylcyclohexane was similar in the temperature range from 100 to  $-196^\circ\text{C}$ , especially at high cumene concentration. The effect of an electron scavenger at high concentrations was also examined with *n*-butyl chloride. In the present work, we have found that although the effect of a positive ion scavenger on the hydrogen yield from methylcyclohexane in the liquid state differs little from that in the glassy state, the effect of electron scavengers on the former differs considerably from that on the latter.

In a previous paper<sup>1)</sup> we have reported the effects of temperature and electron scavengers on the hydrogen yield from  $\gamma$ -irradiated methylcyclohexane. We have shown that both in the liquid and glassy states the neutralization of a positive ion and an electron leads to the formation of a hydrogen molecule,



and that the efficiency of electron scavenging by solutes in the glassy state differs considerably from that in the liquid state. Some workers<sup>2,3)</sup> showed that the yields of scavengable electrons in hydrocarbon glasses were lower than those in liquid hydrocarbons, and that they are at most 1.6 (G unit).<sup>2)</sup> At present, the reason for this is not clear, but the following reasons may be considered; (1) the separation distances of positive ions and thermalized electrons in glasses are shorter than those in liquids, (2) positive ions may play a part in neutralization processes, for instance, in glasses charge transfer from positive ions to neutral molecules occurs rapidly and initial charge recombination is increas-

ed. Therefore it is of interest to know the behavior of positive ions both in liquid and glassy hydrocarbons.

Hitherto, studies of positive ions have been undertaken in several ways; observation of optical absorption spectra,<sup>4)</sup> measurements of HD formed from solutions containing deuterated compounds such as  $\text{ND}_3$  and  $\text{C}_2\text{H}_5\text{OD}$  as proton acceptors,<sup>5,6)</sup> measurements of methane produced from solutions containing neopentane,<sup>7)</sup> and observation of changes in product distribution by addition of ammonia.<sup>8)</sup> These methods, however, are not necessarily useful for our purpose, because we can observe only positive ions surviving after a large fraction of ion pairs have neutralized, and both deuterated ammonia and deuterated ethanol are not sufficiently soluble in methylcyclohexane glass at  $-196^\circ\text{C}$  for a major fraction of positive ions to be scavenged. Also, neopentane cannot be used to scavenge a large fraction of positive ions, since ionization potential of neopentane (10.35 eV) is higher than that of methylcyclohexane (9.85 eV).

4) W. H. Hamill, "Radical Ions," ed. by E. T. Kaiser and L. Kevan, John Wiley & Sons, Inc., New York (1968).

5) F. Williams, *J. Am. Chem. Soc.*, **86**, 3954 (1964).

6) J. W. Buchanan and F. Williams, *J. Chem. Phys.*, **44**, 4377 (1966).

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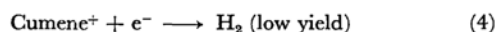
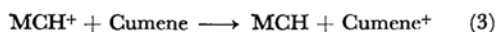
8) K. Tanno, S. Shida and T. Miyazaki, *J. Phys. Chem.*, **72**, 3496 (1968).

1) T. Kimura, T. Miyazaki, K. Fueki and Z. Kuri, *This Bulletin*, **41**, 2861 (1968).

2) T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki and Z. Kuri, presented at 22nd Annual Meeting of the Chemical Society of Japan, Apr., 1969, Tokyo.

3) M. Shirom and J. E. Willard, *J. Phys. Chem.*, **72**, 1702 (1968).

In this work we have used cumene as a positive ion scavenger. The reasons are that cumene is soluble at any concentration in the methylcyclohexane glass at  $-196^{\circ}\text{C}$ , the hydrogen yield from cumene is low (described later), and the ionization potential of cumene (8.69 eV) is lower than that of methylcyclohexane. Positive charge transfer from alkanes to olefins and aromatics and the subsequent decrease in hydrogen yields have been reported.<sup>9,10</sup> Thus it can be expected that cumene will scavenge the methylcyclohexane positive ion and suppress hydrogen formation.



Here we report the thermal H atom yield from  $\gamma$ -irradiated methylcyclohexane in the liquid and glassy states, determined by use of ethylene as an H atom scavenger, and the effect of cumene on the hydrogen yield at various temperatures. In addition to these results we will show evidence for positive charge transfer from methylcyclohexane to cumene by the optical absorption method and discuss primary processes in the radiolysis of methylcyclohexane in the liquid and glassy states.

### Experimental

The experimental procedure was almost the same as that described earlier.<sup>11</sup> Cumene was Nakarai guaranteed reagent and purified by distillation prior to use. *s*-Butyl chloride was Tokyo Kasei guaranteed reagent and was passed through a silica gel column after distillation. Tokyo Kasei guaranteed *n*-butyl chloride was passed through a silica gel column and fractionally distilled through 1.2 m long column filled with small cylindrical hollow glass packing. The purity of *n*-butyl chloride thus obtained was 99.8%. In the methylcyclohexane-cumene system,  $\gamma$ -irradiations were performed at 100, 20,  $-72$ ,  $-120$ , and  $-196^{\circ}\text{C}$ . Irradiations of samples at  $100^{\circ}\text{C}$  were performed in a Dewar filled with boiling water. In measurements of optical absorption spectra, samples were degassed in a glass tube and transferred in a rectangular quartz cell (10 mm  $\times$  5 mm), and sealed off. Irradiations were carried out at  $-196^{\circ}\text{C}$  in the dark. The dose was usually  $1.19 \times 10^{19}$  eV/g. Optical absorption measurements were made on a Hitachi EPU-2 spectrophotometer.

### Results

The hydrogen yields from pure methylcyclohexane, cumene, and *n*-butyl chloride irradiated at various temperatures and irradiation doses are listed in Table 1. The hydrogen yields from methylcyclohexane-ethylene systems irradiated at 20 and  $-196^{\circ}\text{C}$  are shown in Fig. 1. The decrease

TABLE 1. HYDROGEN YIELDS FROM PURE METHYLCYCLOHEXANE (MCH), CUMENE, AND *n*-BUTYL CHLORIDE (*n*-BuCl) AT VARIOUS TEMPERATURES AND DOSES

Sample	Irradiation temp. $^{\circ}\text{C}$	$G(\text{H}_2)$	Dose eV/g
MCH	100	5.4	$6.51 \times 10^{19}$
MCH	20	4.9	$2.93 \times 10^{20}$
MCH	$-72$	4.5	$2.60 \times 10^{20}$
MCH	$-120$	4.5	$6.51 \times 10^{19}$
MCH	$-196$	4.4	$2.60 \times 10^{20}$
Cumene	100	0.19	$6.51 \times 10^{19}$
Cumene	20	0.19	$2.93 \times 10^{20}$
Cumene	$-196$	0.11	$2.60 \times 10^{20}$
<i>n</i> -BuCl	$-196$	0.92	$2.60 \times 10^{20}$

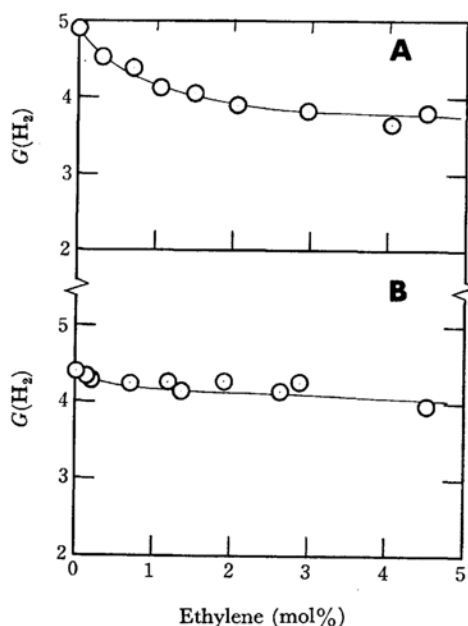


Fig. 1. Hydrogen yields from  $\gamma$ -irradiated methylcyclohexane-ethylene systems. (A), at  $20^{\circ}\text{C}$ ; (B), at  $-196^{\circ}\text{C}$   
Dose =  $2.93 \times 10^{20}$  eV/g

in hydrogen yield is about 1.0 G in the liquid state and 0.5 G in the glassy state.

To see whether cumene scavenges an electron to form cumene anion, we have examined the nitrogen and hydrogen yields from methylcyclohexane solutions containing 3 mol % of  $\text{N}_2\text{O}$  together with various concentrations of cumene. These results are shown in Fig. 2. Though the experimental data are somewhat scattered because of the variation in the volume above the liquid surface in irradiation cells, the nitrogen yield is not affected by the presence of cumene. Moreover, it was found in  $\gamma$ -irradiated 3MP glasses containing biphenyl at  $-196^{\circ}\text{C}$ , the yield of biphenyl anions was not affected by the

9) G. R. Freeman, *J. Chem. Phys.*, **36**, 1542 (1962).

10) L. A. Rajbenbach and U. Kaldor, *ibid.*, **47**, 242 (1967).

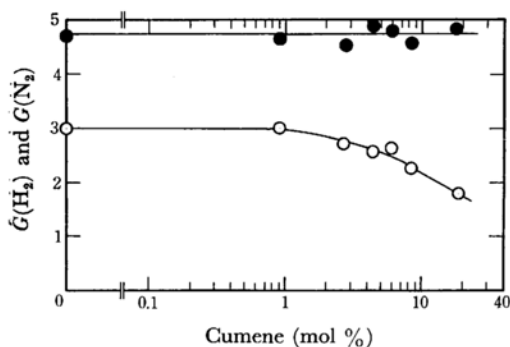


Fig. 2. The effect of cumene on hydrogen and nitrogen yields from methylcyclohexane containing 3 mol %  $N_2O$  irradiated at  $20^\circ C$ .

○  $G(H_2)$  ●  $G(N_2)$   
Dose =  $2.93 \times 10^{20}$  eV/g

presence of cumene in much higher concentrations than that of biphenyl.<sup>11</sup> Therefore it is concluded that cumene does not scavenge electrons.

The hydrogen yields from methylcyclohexane-cumene systems irradiated at 100, 20,  $-72$ ,  $-120$ , and  $-196^\circ C$  are shown in Fig. 3.

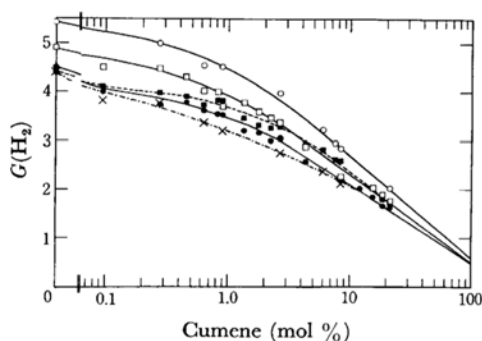


Fig. 3. Hydrogen yields from methylcyclohexane-cumene systems.

- (a) —○— irradiated at  $100^\circ C$   
(Dose =  $6.51 \times 10^{19}$  eV/g)
- (b) —□— irradiated at  $20^\circ C$   
(Dose =  $2.93 \times 10^{20}$  eV/g)
- (c) —●— irradiated at  $-72^\circ C$   
(Dose =  $2.60 \times 10^{20}$  eV/g)
- (d) —×— irradiated at  $-120^\circ C$   
(Dose =  $6.51 \times 10^{19}$  eV/g)
- (e) —■— irradiated at  $-196^\circ C$   
(Dose =  $2.60 \times 10^{20}$  eV/g)

These  $G$  values were obtained based on the energy absorbed only in methylcyclohexane. It can be seen from the data in Table I that the contribution of hydrogen formation from cumene by the direct effect of radiation is at most  $\sim 1\%$  of the total hydrogen even at the highest cumene concentration studied, 21.5 mol 1%. Comparing the hydrogen

yields from methylcyclohexane-cumene systems (Fig. 3) with those from methylcyclohexane-ethylene systems (Fig. 1), we see that the decrease in hydrogen yield in the former cannot be explained only by H atom scavenging by cumene because H atom scavenging is a minor process for the suppression of hydrogen formation, especially in the glassy state at  $-196^\circ C$ , as shown in Fig. 1. The experimental curves (Fig. 3) which represent the hydrogen yield *vs.* cumene concentration are very similar to each other, practically at high cumene concentrations. The hydrogen yields at  $-72$  and  $-120^\circ C$  (Fig. 3. c and d) are somewhat lower than those at 20 and  $-196^\circ C$  (Fig. 3. b and e). This may be partly due to inaccuracy in the evaluation of the energy absorbed in cooling agents.

Though the effect of cumene on the hydrogen yields in the liquid state at  $20^\circ C$  is practically the same as that in the glassy state at  $-196^\circ C$  (Fig. 3. b and e), the effect of electron scavengers on the former is considerably different from that on the latter.<sup>1)</sup> Therefore, in the present work we have extended the study of the effect of electron scavengers in the glassy state to higher concentrations than before.<sup>1)</sup> For this purpose we have examined the hydrogen yield from methylcyclohexane glass with *n*-butyl chloride as an electron scavenger, since it has been found that *n*-butyl chloride is soluble at any concentration in methylcyclohexane glass at  $-196^\circ C$ . The results are shown in Fig. 4 together with the previous data<sup>1)</sup> for comparison. The values were obtained based on the energy absorbed only in methylcyclohexane. The observed hydrogen yield at the highest concentration of *n*-butyl chloride (26.8 mol %) is 2.8 G, which contains the hydrogen yield from *n*-butyl chloride by 0.33. Since the observed decrease in hydrogen yield at the highest concentration of *n*-butyl chloride is 1.6 G,

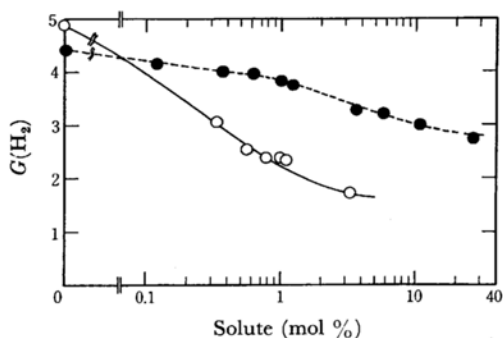


Fig. 4. Hydrogen yields from methylcyclohexane solutions.

- $G(H_2)$  from methylcyclohexane-iodobenzene systems irradiated at  $20^\circ C$   
(Dose =  $3.06 \times 10^{20}$  eV/g)<sup>1)</sup>
- $G(H_2)$  from methylcyclohexane *n*-butyl chloride systems irradiated at  $-196^\circ C$   
(Dose =  $2.60 \times 10^{20}$  eV/g)

11) N. Kato, K. Fueki and Z. Kuri, unpublished results.

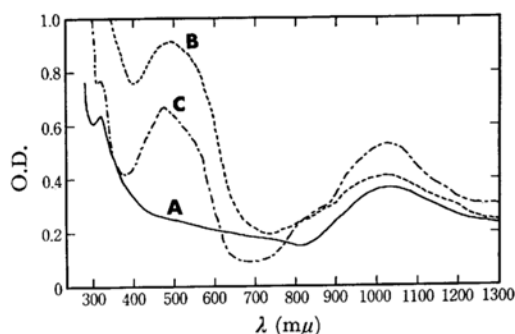


Fig. 5. Optical absorption spectra of (A) methylcyclohexane containing 3 mol %  $N_2O$  and 3.5 mol % cumene after  $\gamma$ -irradiation (Dose =  $1.19 \times 10^{19}$  eV/g); of (B) *s*-butyl chloride containing 7.9 mol % cumene after  $\gamma$ -irradiation (Dose =  $2.38 \times 10^{19}$  eV/g); of (C) the same sample as (B) after photobleaching with visible light from a tungsten lamp at  $-196^\circ C$ .

the corrected decrease, that is the scavenged electron yield, is estimated to be 1.9 G.

The optical absorption spectra of  $\gamma$ -irradiated methylcyclohexane glass containing cumene and  $N_2O$ , and of  $\gamma$ -irradiated *s*-butyl chloride glass containing cumene are shown in Fig. 5. The spectrum of methylcyclohexane glass containing 3 mol % of  $N_2O$  and 3.5 mol % of cumene has an absorption maximum at 1050 mμ (Spectrum A), which resembles that of toluene cation.<sup>4</sup> The spectrum of *s*-butyl chloride containing 7.9 mol % of cumene also has an absorption maximum at 1050 mμ. When  $\gamma$ -irradiated *s*-butyl chloride-cumene sample is photobleached with visible light from a tungsten lamp, the absorption spectrum changes from spectrum (B) to spectrum (C) and the 1050 mμ band increases in intensity. Thus, the 1050 mμ band can be assigned to the cumene cation. The dependence of the optical density at 1050 mμ on the cumene concentration in methylcyclohexane is shown in Fig. 6. The result is similar to that on toluene in 3MP glass<sup>4</sup> and indi-

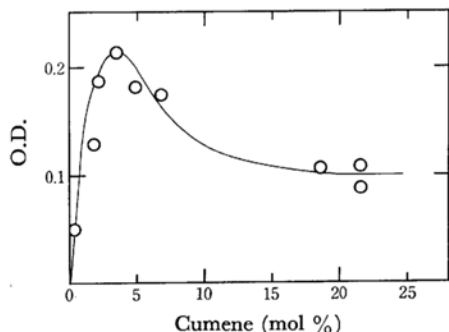


Fig. 6. Optical density vs. the concentration of cumene in methylcyclohexane glasses containing 3 mol %  $N_2O$ . Dose =  $1.19 \times 10^{19}$  eV/g.

cates that the cumene cation is produced by charge transfer from methylcyclohexane to cumene.

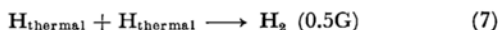
## Discussion

The decreased hydrogen yield in methylcyclohexane-ethylene systems can be ascribed to thermal H atom scavenging by ethylene.<sup>12</sup> The decrease in hydrogen yield in the liquid state (1.0 G) is twice that in the glassy state (0.5 G), as shown in Fig. 1. It should be noted that the difference between the hydrogen yields of pure liquid methylcyclohexane irradiated at  $20^\circ C$  and of pure glassy methylcyclohexane at  $-196^\circ C$  is 0.5 G. As we reported previously,<sup>1</sup> these results seem to suggest the following mechanism:

at room temperature



at  $-196^\circ C$



Thermal H atoms abstract H atoms from solvent molecules to produce hydrogen molecules (1.0 G), but they are unable to abstract H atoms at  $-196^\circ C$  and recombine with one another to produce hydrogen molecules (0.5 G).

Since cumene does not compete with  $N_2O$  for capturing electrons (Fig. 2), the decrease in hydrogen yield in methylcyclohexane systems (Fig. 3) cannot be attributed to electron scavenging by cumene. *s*-Butyl chloride matrix is widely used for trapping cation species.<sup>4</sup> Photobleaching of  $\gamma$ -irradiated *s*-butyl chloride-cumene glass causes the intensity of the 1050 mμ band to increase. This phenomenon is interpreted in terms of positive charge transfer from *s*-butyl chloride to cumene. It is known that the *s*-butyl chloride cation has an absorption maximum at 540 mμ<sup>13</sup> and can be excited by visible light to migrate over many molecules by resonant charge transfer.<sup>14</sup> The optical absorption measurements clearly demonstrate the formation of cumene cations in methylcyclohexane-cumene systems. It can also be seen from Fig. 6 that cumene cations are not produced by the direct ionization of cumene, but by charge transfer from methylcyclohexane to cumene. Thus, it may be said that the decrease in hydrogen yield in methylcyclohexane-cumene systems is mainly due to charge transfer from methylcyclohexane to cumene and partly due to thermal H atom scavenging by cumene.

Extrapolation of the curves in Fig. 3 to 100% cumene concentration gives hypothetical G values

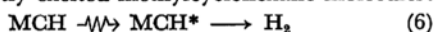
12) W. A. Cramer and G. J. Piet, *Trans. Faraday Soc.*, **63**, 1402 (1967).

13) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375 (1966).

14) W. F. Louwrier and W. H. Hamill, *J. Phys. Chem.*, **72**, 3878 (1968).

for hydrogen formation based on the energy absorbed only in methylcyclohexane, where all the effects of cumene on the radiolysis of methylcyclohexane are assumed to be completed. It should be noted that (1) the curves are very close to each other, and (2) the hypothetical hydrogen yields at 100% cumene are approximately the same (0.5–0.7 G). To interpret the results, two different effects of cumene are considered: H atom addition to cumene at low cumene concentrations and charge transfer to cumene at high concentrations.<sup>9)</sup> Thus at high cumene concentrations the curves are interpreted to indicate positive ion scavenging curves at each irradiation temperature. One of the most notable features in the curves is that they differ little from each other in the temperature range from 100°C to –196°C. It is certain that in the glassy state at –196°C the mechanism of charge migration is resonant charge transfer. Since the curve of positive ion scavenging in the liquid state differs little from that in the glassy state, charge transfer in the liquid state may possibly be resonant. According to Freeman's calculation,<sup>15)</sup> more than 10 mol % of scavenger is required to scavenge positive ion completely. Assuming the number of molecules surrounding a positive ion is six, it is shown that 13 mol % of scavenger is required for scavenger molecule to be adjacent to a positive ion. Therefore, it is difficult to discern between charge transfer by resonance and that by diffusional collision. Further study is needed to establish the charge transfer mechanism in liquid.

The hypothetical hydrogen yields at 100% cumene do not coincide with the hydrogen yields from pure cumene, as is seen from Table 1, and are tentatively considered to be the hydrogen yields from directly excited methylcyclohexane molecules:



The decrease in hydrogen yields in Fig. 4 is assumed to be equal to the yields of scavenged electrons. This interpretation is reasonable especially in the case of methylcyclohexane. It has been proposed by many workers that Eq. (2) holds in the radiolysis of liquid hydrocarbons, but some workers have shown by ESR studies that charge neutralization does not lead to decomposition of hydrocarbon glasses at –196°C,<sup>9)</sup> although others have shown by product analysis studies that Eq. (2) holds even in the glassy state at –196°C.<sup>1,16)</sup> In the previous work on methylcyclohexane,<sup>1)</sup> we

have shown that the scavenged electron yield is equal to the decrease in hydrogen yield at –196°C as well as 20°C. Further, the hydrogen yield from pure methylcyclohexane irradiated at 20°C is not so different from that at –196°C. Thus, Eq. (2) seems to be valid at –196°C as well as 20°C, and we could evaluate by the decrease in hydrogen yield both the scavenged electron and the scavenged positive ion yield in methylcyclohexane.

As already described, the efficiency of electron scavenging in liquids differs considerably from that in glasses at –196°C (Fig. 4), though the efficiency of positive ion scavenging in liquids scarcely differs from that in glasses at –196°C (Fig. 3). Further, the yield of scavenged electrons in methylcyclohexane-*n*-butyl chloride glasses at –196°C is at most 1.9 G at the highest concentration of *n*-butyl chloride where a *n*-butyl chloride molecule exists adjacent to a positive ion. Therefore, assuming the total ion-pair yield of methylcyclohexane is  $\sim 4$ , we can say that more than half of the electrons cannot be scavenged at such a high solute concentration. To explain these experimental facts, we are forced to state as follows; a significant fraction of charge transfer in glasses will be completed before electrons ejected from molecules by radiation are thermalized. Since molecules in a glass at –196°C are not allowed for translational motions, charge transfer must be resonant. Hamill has suggested that resonant charge transfer is a very fast process.<sup>14)</sup> Our results are consistent with the following mechanism: positive ions transfer their charge to solute molecules or trapping sites of the matrix before ejected electrons are thermalized, and then thermalized electrons return to positive ions or are scavenged by electron scavengers. One of the causes for the scavenged electron yield in glasses to be less than half of the total ejected electrons may be the shorter separation distances between trapped positive ions and thermalized electrons in glasses. However, it is not so easy to give a theoretical explanation for this reasoning.

We have found that the scavengable electron yield in glasses is  $\sim 2\text{G}$ . If this value is used in the previous calculation of electron scavenging in methylcyclohexane-iodobenzene glasses,<sup>1)</sup> the experimental points fit well in the calculated curve without the assumption of aggregation of iodobenzene molecules at –196°C. Since positive ions do not move after electrons are thermalized, the previous calculation will be valid except for uncertainty in the initial ion-pair yield assumed in glasses.

15) G. R. Freeman, *J. Chem. Phys.*, **46**, 2282 (1967).

16) N. H. Sagert, *Can. J. Chem.*, **46**, 89 (1968).