Ion–Molecule Reactions in the Condensed-Phase Radiolysis of Hydrocarbon Mixtures. II. Cyclopentane and Cyclohexane[1a]

P. Ausloos, A. A. Scala,[1b] and S. G. Lias

Contribution from the Radiation Chemistry Section, National Bureau of Standards, Washington, D. C. 20234. *Received March 13, 1967*

Abstract: The radiolysis of c-C_5H_{10} and c-C_5H_{12}, as well as of equimolar c-C_5H_{10}–c-C_5D_{10} and c-C_5H_{12}–c-C_6D_{12} mixtures, has been investigated in the presence of 0.5 to 5 mole % $(CD_2)_3$, C_2D_2, C_2D_4, or CD_3CDCD_2. Isotopic analysis of the products formed in the radiolysis of cycloalkane–$(CD_2)_3$ mixtures points to the occurrence of the following ion–molecule reactions: (a) $C_nH_{2n}^+ + (CD_2)_3 \rightarrow C_nH_{2n-2}^+ + CD_2HCD_2CD_2H$ and (b) $C_nH_{2n}^+ + (CD_2)_3 \rightarrow C_nH_{2n-1}^+ + CD_2HCD_2CD_2$. The formation of *n*-propyl radicals in reaction b is confirmed by the production of $CD_3CD_2CD_2H$ as a major species in the radiolysis of C_nD_{2n}–$(CD_2)_3$–H_2S mixtures. The ion–molecule character of the reactions is further confirmed by the facts that addition of a known parent ion interceptor such as H_2S reduces G(propane), while addition of an electron scavenger such as CCl_4 raises G(propane). When cyclopentane is the solvent, the H_2-transfer reaction (a) is of major importance. The most efficient H_2-acceptor molecule for the cyclopentane parent ion is C_2D_4, and the least efficient is C_2D_2. When c-C_5H_{10}–c-C_5D_{10} (1 : 1) mixtures are irradiated in the presence of deuterated H_2-acceptor molecules such as C_2D_4 or C_2D_2, the ratio of products of reaction a, $C_2D_4H_2/C_2D_6$ or $C_2D_2H_2/C_2D_4$, is greater than unity, indicating the occurrence of charge-transfer processes favoring the formation of c-$C_5H_{10}^+$: (c) $c\text{-}C_5D_{10}^+ + c\text{-}C_5H_{10} \rightarrow c\text{-}C_5H_{10}^+ + c\text{-}C_5D_{10}$. A decrease in the mole per cent of the C_2D_4 or C_2D_2 from 6 to 2% raises $C_2D_4H_2/C_2D_6$ or $C_2D_2H_2/C_2D_4$ from 1.7 to 2.6, demonstrating that relatively high concentrations of H_2-acceptor molecules can interfere with the charge-transfer mechanism. When cyclohexane is the solvent, reaction b predominates over reaction a. A plot of the square root of the $(CD_2)_3$ concentration *vs.* G(propane) yields a straight line which goes through the origin, demonstrating the difficulty of obtaining chemical evidence for the presence of free ions.

In the first paper of this series,[2] we presented experimental evidence for the occurrence in the liquid-phase radiolysis of an H_2-transfer reaction of the type

$$C_nH_{2n+2}^+ + C_{m'}H_{m''} \longrightarrow C_nH_{2n}^+ + C_{m'}H_{m''+2} \qquad (1)$$

where $C_nH_{2n+2}^+$ is the parent ion of 2-methylbutane or 3-methylpentane, and $C_{m'}H_{m''}$ is acetylene, ethylene, propylene, cyclopropane, 1-butene, or 2-butene. It was demonstrated that the efficiency of reaction 1 depended on the structure of $C_{m'}H_{m''}$. Of the above-listed compounds, cyclopropane was shown to be the most efficient H_2-acceptor molecule, and 2-butene, the least efficient.

In the present communication, we intend to examine the occurrence of the H_2-transfer reaction in the radiolysis of cyclopentane and cyclohexane liquids containing various concentrations of cyclopropane or unsaturated hydrocarbons as solutes. It has already been demonstrated[3] in the course of radiolysis and photoionization studies of cyclopentane and cyclohexane that, in the gas phase, the parent cycloalkane ion ($C_nH_{2n}^+$) participates in the H_2-transfer reaction

$$C_nH_{2n}^+ + C_{m'}H_{m''} \longrightarrow C_nH_{2n-2}^+ + C_{m'}H_{m''+2} \qquad (2)$$

In these gas-phase studies, propylene was shown to be the most efficient H_2-acceptor molecule ($C_{m'}H_{m''}$). More recently,[4] the occurrence of reaction 2 proved most useful in establishing the occurrence of charge-transfer processes in the gas-phase photoionization of cycloalkane mixtures.

Our major concern in the present paper will be to determine to what extent the above-mentioned gas-phase observations apply to condensed-phase systems.

Experimental Section

The cyclopentane and cyclohexane used in this study were standard samples obtained from the American Petroleum Institute. The impurity in the cyclohexane was stated to be 0.007 ± 0.004% and in cyclopentane 0.01 ± 0.005%.

Cyclopentane-d_{10} contained 9.1% cyclopentane-d_9, and cyclohexane-d_{12} contained 8.7% cyclohexane-d_{11}. Propylene-d_6 and cyclopropane-d_6 contained respectively 5 and 7.4% C_3D_5H. Ethylene-d_4 contained 5% C_2D_3H. These isotopically labeled materials were rigorously purified by gas chromatography and were subsequently distilled in a vacuum line in order to remove traces of helium and water. The cyclohexane used to perform the experiments given in Figure 1 was stored in the vacuum line over a sodium mirror. The irradiation and analysis procedure has been described in the previous publication[2] of this series.

Results

The product yields are expressed as $G_{C_nH_{2n}}(X)$, that is, the number of molecules X formed per 100 ev absorbed by the cycloalkane (C_nH_{2n}). For mixtures, the assumption is tentatively made that initial energy absorption is partitioned between two or more components according to their electron fraction. Because in most experiments the concentration of the additives is relatively small, a deviation from the mixture law is not expected to cause a large error in the calculated value of $G_{C_nH_{2n}}(X)$.

Besides the results given in the tables and in Figure 1, the following information was collected.

(1) The radiolysis of cyclopentane was investigated briefly at 77 and 195°K. At 195°K the following G values were obtained: CH_4, 0.025; C_2H_2, 0.03; C_2H_4, 0.31; C_2H_6, 0.040; CH_3CHCH_2, 0.15; C_3H_8, 0.05; $(CH_2)_3$, 0.11; 1-C_5H_{10}, 0.47; 2-C_5H_{10}, 0.05; n-C_5H_{12}, 0.11, c-C_5H_8, 1.91. Addition of 4 mole % CCl_4 reduces the yields of C_2H_4, $(CH_2)_3$, CH_3CHCH_2, and 1-

---

(1) (a) This research was supported by the U. S. Atomic Energy Commission; (b) National Academy of Sciences–National Research Council Postdoctoral Associate, 1964–1966.

(2) A. A. Scala, S. G. Lias, and P. Ausloos, *J. Am. Chem. Soc.*, **88**, 5701 (1966).

(3) (a) R. D. Doepker and P. Ausloos, *J. Chem. Phys.*, **42**, 3746 (1965); (b) P. Ausloos and S. G. Lias, *ibid.*, **43**, 127 (1965); (c) R. D. Doepker, S. G. Lias, and P. Ausloos, *ibid.*, in press.

(4) P. Ausloos and S. G. Lias, *Intern. J. Radiation Biol.*, in press.

Table I. The Radiolysis of Cycloalkanes in the Presence of Cyclopropane-d_6 at 195 °K

Mole %			Isotopic compositions				G values		
$(CD_2)_3$	CCl_4	O_2, atm	C_3D_8	CD_3CD_2-CD_2H	CD_2HCD_2-CD_2H	$(C_3D_2H_6 + C_3DH_7 + C_3H_8)$	Total propane	C_2H_4	1-C_5H_{10}
					c-C_5H_{10}				
0	0	0	...	...	...	0.04	0.04	0.31	0.47
2.9	0	0	0.002	0.017	1.00	0.081	0.687	0.25	0.42
9.1	0	0	0.004	0.029	1.00	0.047	1.08	0.19	0.33
2.9	4.0	0	0.002	0.025	1.00	0.004	2.10	0.12	0.13
					c-C_5H_{10} + c-C_5D_{10} (1:1)				
0	0	1	0.869	0.322	1.00	1.96	0.035		
4.7	0	0	0.308	0.135	1.00	0.021	1.19		
4.7	0	1	0.310	0.037	1.00	0.021	1.08		
4.3	4.3	0	0.357	0.171	1.00	0.004	2.18		
4.3	4.3	1	0.321	0.048	1.00	0.026	1.32		
					c-C_6H_{12}				
3.0	0	0	0.080	0.080	1.00	<0.003	0.289		
19.7	0	0	0.026	0.109	1.00	0.007	0.454		
8.8	3.4	0	0.038	0.106	1.00	...[a]	1.24		
					c-C_6H_{12} + c-C_6D_{12} (1:1)				
8.0	2.0	0	0.435	0.621	1.00	0.014	1.56		
2.9	8.8	0	0.307	0.674	1.00	<0.031	2.70		
8.0	2.0	1	0.350	0.200	1.00		0.70		

[a] Not determined.

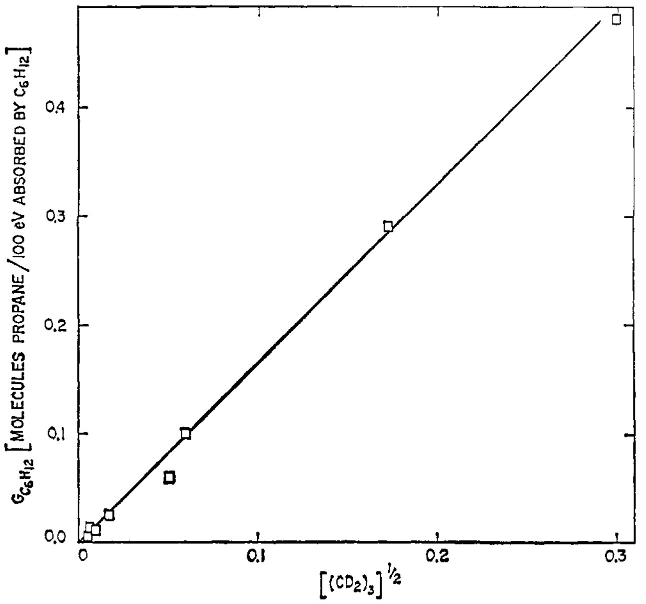

Figure 1. Radiolysis of cyclohexane–$(CD_2)_3$ mixtures at 195 °K. Dependence of G(propane) on the square root of the mole per cent of $(CD_2)_3$.

C_5H_{10} by approximately a factor of 3. On the other hand, the yields of ethane, propane, n-pentane, and cyclopentene show relatively little change. A decrease in temperature from 195 to 77 °K diminishes the yields of the lower alkanes and alkenes approximately threefold and twofold, respectively. The yields of 1-C_5H_{10} and c-C_5H_8 show, however, little change.

(2) Addition of CCl_4 to a c-C_6H_{12}–$(CD_2)_3$ (1:0.01) mixture irradiated at 195 °K increases G(propane) but does not appreciably change its isotopic composition ($CD_2HCD_2CD_3/CD_2HCD_2CD_2H$ = 0.1). The following values were obtained for G(propane): 0% CCl_4, 0.22; 0.35% CCl_4, 0.73; 1.1% CCl_4, 0.97; 3.2% CCl_4, 1.35. The increase of the mole per cent CCl_4 caused a gradual decrease of G(c-C_6H_{10}) from 3 to 1.05. No propane was observed upon irradiating a c-C_6H_{12}–CCl_4 mixture.

(3) Irradiation of a c-C_6H_{12}–$(CD_2)_3$–CCl_4 (1:0.1:0.05) at 77 °K yielded very little propane, G(propane) = 0.09. About 80% of this propane was $CD_2HCD_2CD_2H$.

(4) The hydrogen formed in the radiolysis of c-C_5H_{10}–$(CD_2)_3$ and c-C_6H_{12}–$(CD_2)_3$ consisted almost exclusively of H_2. For instance, the isotopic composition of hydrogen formed in the radiolysis of a c-C_6H_{12}–$(CD_2)_3$ (1:0.1) mixture at 195 °K was as follows: H_2, 1.0; HD, 0.025; D_2, 0.005. It should also be noted that G(methane) $\leqslant$ 0.025 in all experiments in which cyclohexane was used as solvent.

Discussion

Cyclopentane. When c-C_5H_{10} is irradiated in the presence of cyclopropane-d_6, propane having the structure $CD_2HCD_2CD_2H$ appears as a major product (Table I). The same product propane was formed when 2-methylbutane or 3-methylpentane was irradiated in the presence of cyclopropane-d_6.[2] In that investigation, it was demonstrated that the parent ion of 2-methylbutane or 3-methylpentane participated in the reaction in which the propane-d_6 was formed. In the present investigation, it can again be demonstrated that the parent ion is a precursor of the product $CD_2HCD_2CD_2H$. For instance, the yield of $CD_2HCD_2CD_2H$ increases with an increase in the concentration of the additive $(CD_2)_3$; at the same time the yields of products, such as 1-pentene and C_2H_4, are reduced. 1-Pentene results largely from the rearrangement of neutral excited cyclopentane (c-$C_5H_{10}^*$) formed upon neutralization of the c-$C_5H_{10}^+$ ion, and C_2H_4 is formed mainly by fragmentation of c-$C_5H_{10}^*$.[5] The decrease in the yields of

---

(5) 1-Pentene is a rearrangement product formed in the condensed-phase photolysis of cyclopentane at 8.4 and 10 ev.[3c] Excited c-$C_5H_{10}^+$ ions are also known to rearrange to pentene ion, but only *cis*- and *trans*-2-C_5H_{10} have been observed as neutral products resulting from such a rearrangement: R. D. Doepker and P. Ausloos, *J. Chem. Phys.*, **44**, 1951 (1966). In the latter study it was also known that ethylene, cyclopropane, and propylene are products formed by fragmentation of $C_5H_{10}^*$.

these products with the addition of $(CD_2)_3$ to $c\text{-}C_5H_{10}$ can be explained, tentatively, by a competition between a reaction of the $C_5H_{10}^+$ ion with $(CD_2)_3$ and the neutralization step

$$C_5H_{10}^+ + e^- \longrightarrow C_5H_{10}^* \longrightarrow \text{1-pentene or fragments} \quad (3)$$

If this is indeed the case, addition of an electron scavenger such as CCl_4 would slow the neutralization of the parent ion[6] and give it a higher probability of reaction with cyclopropane. This is confirmed by the increase in $G(CD_2HCD_2CD_2H)$ upon addition of 4 mole % CCl_4 to a $c\text{-}C_5H_{10}\text{-}(CD_2)_3$ mixture (Table I). The corresponding decrease in $G(1\text{-}C_5H_{10})$ points to the inhibition of the neutralization step 3.

In the previous study, the formation of $CD_2HCD_2CD_2H$ was accounted for by the occurrence of an H_2-transfer reaction involving the parent 2-methylbutane or 3-methylpentane ion and the additive cyclopropane. The analogous reaction involving cyclopentane may be written[7]

$$c\text{-}C_5H_{10}^+ + (CD_2)_3 \longrightarrow c\text{-}C_5H_8^+ + CD_2HCD_2CD_2H \quad (4)$$

$$\Delta H_{\text{gas phase}} = -46 \text{ kcal/mole}$$

The parent ion participating in reaction 4 has, probably, the cyclic structure; in the liquid-phase radiolysis of cyclopentane,[8] the products ascribed to ring opening are very minor. In order to ascertain if the H_2 entity is indeed transferred in a single step in reaction 4, various $c\text{-}C_5H_{10}\text{-}c\text{-}C_5D_{10}\text{-}(CD_2)_3$ mixtures were irradiated. The isotopic analyses of the propane formed in these experiments are given in Table I. The results show that when oxygen has been added as a free-radical scavenger, C_3D_8 and $CD_2HCD_2CD_2H$ are the major propanes formed. Because propane is a very minor product ($G \sim 0.035$) in the radiolysis of pure cyclopentane–O_2 systems, it can be postulated that these propanes are nearly entirely formed by the transfer of an H_2 (or D_2) entity to cyclopropane-d_6 according to reactions 4 and 5. The fact that the product propane-d_6

$$c\text{-}C_5D_{10}^+ + (CD_2)_3 \longrightarrow C_5D_8^+ + C_3D_8 \quad (5)$$

formed in these experiments has the structure $CD_2HCD_2CD_2H$ indicates that the H_2 entity is transferred to two adjacent carbon atoms of cyclopropane-d_6 with the simultaneous breaking of the bond between them.

It should be pointed out that in the experiments where $(CD_2)_3$ is added to a $c\text{-}C_5H_{10}\text{-}c\text{-}C_5D_{10}$ (1:1) mixture in the presence of a free-radical scavenger (Table I), reactions 4 and 5 do not occur to the same extent. Indeed, the $CD_2HCD_2CD_2H$ produced in reaction 4 is formed with a yield more than three times larger than that of C_3D_8, formed in reaction 5. Because the ionization energy of the perdeuterated cyclopentane will be slightly higher than that of the perprotonated cyclopentane,[9] a plausible explanation of these results is the occurrence of charge-transfer reactions between the perprotonated and perdeuterated species which would favor the formation of $c\text{-}C_5H_{10}^+$ over $c\text{-}C_5D_{10}^+$. In a recent study of the gas-phase photoionization of cycloalkane mixtures,[4] definite evidence was obtained for the occurrence of a charge-transfer mechanism such as

$$c\text{-}C_6H_{12} + c\text{-}C_6D_{12}^+ \leftrightarrows c\text{-}C_6H_{12}^+ + c\text{-}C_6D_{12} \quad (6)$$

in which the formation of $C_6H_{12}^+$ was favored by as much as a factor of 3 over the formation of $C_6D_{12}^+$. It is of interest that, on the basis of the above interpretation, a value of 3 is obtained for $c\text{-}C_5H_{10}^+/c\text{-}C_5D_{10}^+$ while a similar $i\text{-}C_5H_{12}\text{-}i\text{-}C_5D_{12}\text{-}(CD_2)_3$ mixture yielded[4] a value of only 1.2 for $i\text{-}C_5H_{12}^+/i\text{-}C_5D_{12}^+$ in the gas phase.

Reactions 4 and 5 are probably not the only modes of reaction between cyclopentane parent ions and $(CD_2)_3$, as is indicated by the results given in Table I. It is seen, for instance, that propane-d_7 is formed as a product in the radiolysis of $c\text{-}C_5H_{10}\text{-}(CD_2)_3$ mixtures and in $c\text{-}C_5D_{10}\text{-}c\text{-}C_5H_{10}\text{-}(CD_2)_3$ mixtures. Because oxygen prevents the formation of $CD_3CD_2CD_2H$ and reduces the total propane yield, we may tentatively conclude that n-propyl radicals are the precursors of C_3D_7H. This interpretation is supported by the fact that $CD_3CD_2CD_2H$ is a major product in the radiolysis of a $c\text{-}C_5D_{10}\text{-}(CD_2)_3\text{-}H_2S$ mixture (Table II); propyl radicals will preferentially react with H_2S to form propane[10]

$$C_3D_7 + H_2S \longrightarrow C_3D_7H + HS \quad (7)$$

Assuming that all C_3D_7 radicals formed in this mixture react with H_2S according to reaction 7, we can ascribe the C_3D_8 formed (Table II) to the D_2-transfer reaction (5). Because H_2S is also known to interact with parent ions,[11] no importance should be attached to the actual yields of C_3D_7H and C_3D_8 formed in this experiment.

Table II. Cycloalkane–$(CD_2)_3$–H_2S Mixtures Irradiated at 273°K

Mole % $(CD_2)_3$	H_2S	CCl_4	Isotopic compositions C_3D_8	$CD_3CD\text{-}HCD_3$	$CD_3CD_2\text{-}CD_2H$	G values Total propane
			Cyclopentane-d_{10}			
0	5.7	0	1.00	0.51	0.26	0.038
6.0	5.4	0	1.00	0.06	0.75	0.81
			Cyclohexane-d_{12}			
1.9	5.5	0	1.00	0.0	2.43	0.54
5.5	1.9	0	1.00	0.0	2.09	1.39
5.4	5.4	0	1.00	0.0	2.47	1.06
5.1	5.1	5.1	1.00	0.0	2.82	1.35

Because cyclopropane is relatively inert toward free radicals, it seems most logical, especially at the relatively low cyclopropane concentrations used in these experiments, that the propyl radical is formed as a result of an ion–molecule reaction. The most plausible reactions are

$$c\text{-}C_5H_{10}^+ + (CD_2)_3 \longrightarrow CD_2HCD_2CD_2 + C_5H_9^+ \quad (8)$$

$$c\text{-}C_5D_{10}^+ + (CD_2)_3 \longrightarrow CD_3CD_2CD_2 + C_5D_9^+ \quad (9)$$

---

[6] P. S. Rao, J. R. Nash, J. P. Guarino, M. R. Ronayne, and W. H. Hamill *J. Am. Chem. Soc.*, **84**, 500 (1962).

[7] All values for $\Delta H_{\text{gas phase}}$ are based on (1) the ionization energies of ions reported by F. H. Field and J. L. Franklin in "Electron Impact Phenomena," Academic Press Inc., 1957, N. Y., and by K. Watanabe, T. Nakajama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962); (2) ΔH_f values of neutral molecules reported in "Selected Values of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, API Research Project 44; (3) ΔH_f values of free radicals from J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966. Whenever available, revised data are used.

[8] R. A. Holroyd and G. W. Klein, *J. Am. Chem. Soc.*, **87**, 4983 (1965).

[9] V. H. Dibeler and R. M. Reese, *J. Res. Natl. Bur. Std.*, **68A**, 409 (1964).

[10] R. D. Doepker and P. J. Ausloos, *J. Chem. Phys.*, **44**, 1951 (1966).

[11] G. Meissner and A. Henglein, *Ber. Bunsenges. Physik. Chem.*, **69**, 264 (1965).

Table III. The Radiolysis of c-C_5H_{10}–c-C_5D_{10} (1:1) in the Presence of Deuterated Unsaturated Hydrocarbons[a]

Mole % Additive	Mole % CCl_4	O_2, atm	Isotopic compositions					$G_{\text{cyclohexane}}$
			I. C_2D_4					
			C_2D_6	C_6D_5H	CD_2HCD_2H	$(C_2D_2H_4 + C_2DH_5 + C_2H_6)$		Total ethane
0	0	0	0.61	1.03	1.00[b]	$\sim$2.0		0.040
0	0	1	0.69	0.41	1.00[b]	$\sim$1.5		0.029
1.8	0	0	0.36	0.39	1.00	<0.03		1.22
0.5	3.9	1	0.34	0.00	1.00	<0.05		1.07
1.8	3.9	1	0.39	0.00	1.00	<0.05		1.99
6.0	3.9	1	0.57	0.00	1.00	<0.05		2.84
1.8[c]	3.9	1	0.67	0.22	1.00	<0.05		0.49
			II. C_2D_2					
			C_2D_4	C_2D_3H	CDHCDH	C_2DH_3	C_2H_4	Total ethylene
0	0	0	1.00	0.055	0.00	0.035	1.24	2.30
0	0	1	1.00	0.010	0.00	0.06	1.28	0.27
2.0	3.9	1	0.38	0.005	1.00		0.14	1.18
6.0	3.9	1	0.65	0.056	1.00			2.05
			III. C_3D_6					
			C_3D_8	C_3D_7H	CD_3CDHCD_2H	$(C_3D_2H_6 + C_3DH_7 + C_3H_8)$		Total propane
0	0	1	0.87	0.32	1.00	$\sim$2.0		0.035
2.0	3.9	1	0.65	0.07	1.00	0.023		1.03

[a] All experiments performed at 195°K, except where otherwise indicated. [b] Structure of ethane-d_4 not necessarily entirely CD_2HCD_2H. [c] 77°K.

Hydrogen- or deuterium-atom-transfer reactions such as (8) or (9) have recently been observed in a mass spectrometric[12] study in which cyclopropane was bombarded by c-$C_6H_{12}^+$ ions with approximately 0.4 ev kinetic energy. In view of the fact that no reshuffling of hydrogen atoms occurs in the H_2- or D_2-transfer reaction, it is reasonable that reaction 8 or 9 would lead to the formation of a n-propyl radical. In the radiolysis of c-C_5H_{10}–$(CD_2)_3$ mixtures, $CD_2HCD_2CD_2$ formed by reaction 8 will mainly abstract an H atom from c-C_5H_{10} to form $CD_2HCD_2CD_2H$; at these low temperatures, however, a small fraction of the $CD_2HCD_2CD_2$ radicals may disproportionate (10) as is indicated by

$$CD_2HCD_2CD_2 + CD_2HCD_2CD_2 \longrightarrow CD_2HCDCD_2 + CD_2HCD_2CD_3 \quad (10)$$

the presence of a small amount of $CD_2HCD_2CD_3$ as a product in these experiments.

Other less plausible ion–molecule reaction schemes can be considered for the formation of propyl radicals in cyclopentane–$(CD_2)_3$ mixtures.[13] For instance, a proton-transfer reaction such as

$$c\text{-}C_5H_{10}^+ + (CH_2)_3 \longrightarrow n\text{-}C_3H_7^+ + C_5H_9 \quad (11)$$

followed by a neutralization step

$$n\text{-}C_3H_7^+ + e^- \longrightarrow n\text{-}C_3H_7 \quad (12)$$

would conceivably lead to the formation of n-propyl radicals. However, in the gas phase the n-$C_3H_7^+$ ion always rearranges to the thermodynamically more stable *sec*-$C_3H_7^+$ structure;[14] in reactions 11 and 12, one would have to assume that rearrangement does not occur. In addition, if $C_3H_7^+$ underwent neutralization, at least some of the excited n-$C_3H_7^*$ radicals would be expected to decompose. In the C_5H_{10}–$(CD_2)_3$ mixtures, however, there is no evidence for the formation of D atoms or CD_3 radicals (see Results).

Although it is perhaps true that information derived from experiments performed in the gas phase cannot necessarily be applied to condensed-phase systems, reactions 8 and 9 remain the most plausible mechanism for the production of propyl radicals in these experiments.

Ethane is a minor product in the radiolysis of c-C_5H_{10}-c-C_5D_{10}–O_2 mixtures, but when such mixtures are irradiated in the presence of a small amount of C_2D_4, C_2D_6 and CD_2HCD_2H become major products (Table III). This indicates the occurrence of an H_2- (or D_2-) transfer reaction from the parent ion to ethylene, similar to the parent ion–ethylene reaction which was demonstrated to occur in the radiolysis of 2-methylbutane–ethylene mixtures. By using the same argumentation for the experiments listed in Table III as was used for the analogous 2-methylbutane–ethylene experiments, the formation of C_2D_6 and CD_2HCD_2H as products can be explained by the ion–molecule reactions

$$C_5D_{10}^+ + C_2D_4 \longrightarrow C_5D_8^+ + C_2D_6 \quad (13)$$

$$C_5H_{10}^+ + C_2D_4 \longrightarrow C_5H_8^+ + CD_2HCD_2H$$

$$\Delta H_{\text{gas phase}} = -41 \text{ kcal/mole}$$

At 195°K, C_2D_5H is not formed at all in the irradiation of c-C_5H_{10}-c-C_5D_{10}-C_2D_4-O_2 mixtures, but, in an

---

(12) F. P. Abramson and J. H. Futrell, *J. Phys. Chem.*, 71, 1233 (1967).

(13) Because proton-transfer reactions between hydrocarbon molecules and their parent ions have often been proposed in liquid-phase hydrocarbon radiolyses, the alternate reaction sequence (i and ii) for the formation of propyl radicals in cyclopentene–$(CD_2)_3$ mixtures should be mentioned. This reaction sequence is unlikely, however, since

$$C_5H_{10}^+ + C_5H_{10} \longrightarrow C_5H_{11}^+ + C_5H_9 \quad \text{(i)}$$

$$C_5H_{11}^+ + (CH_2)_3 \longrightarrow C_5H_{10}^+ + CH_3CH_2CH_2 \quad \text{(ii)}$$

reaction ii is apparently endothermic. The values of ΔH_f of $C_5H_{11}^+$ and $C_5H_{10}^+$ depend, of course, on the structure of these ions. If one assumes that $C_5H_{11}^+$ has the normal secondary structure, and that $C_5H_{10}^+$ is the 1-$C_5H_{10}^+$ ion, then reaction ii is endothermic by 56 kcal/mole. There is no mass spectrometric evidence for the occurrence of reaction i.

(14) P. Ausloos and S. Lias in "Actions Chimiques et Biologiques des Radiations," Vol. 11, M. Haissinsky, Ed., Masson & Cie., Editeurs, Paris, 1967.

analogous experiment in the absence of oxygen, C_2D_5H is a significant product. When the radiolysis of such a mixture is carried out at 77°K instead of 195°K, it is seen (Table III) that, although C_2D_6 and $C_2D_4H_2$ are still the major ethane products formed, the yield of C_2D_5H is no longer negligible. This may be explained by the fact that under these conditions oxygen is an inefficient radical scavenger. In these experiments, C_2D_5 and C_2D_4H radicals may be formed as a result of hydrogen scavenging by the ethylene. These radicals may abstract an H or D to form C_2D_5H. The formation of ethyl radicals by ion–molecule reactions analogous to (8) and (9)

$$C_5H_{10}^+ + C_2D_4 \longrightarrow C_2D_4H + C_5H_9^+ \tag{14}$$

$$C_5D_{10}^+ + C_2D_4 \longrightarrow C_2D_5 + C_5D_9^+ \tag{15}$$

would be difficult to distinguish from the purely free-radical mechanism for their formation. However, reactions 14 and 15 must be relatively unimportant, since the combined yield of C_2D_6 and $C_2D_4H_2$ (that is, the yield of parent ions accounted for) is as high as 2.84 in the radiolysis of a $c\text{-}C_5H_{10}\text{–}c\text{-}C_5D_{10}\text{–}C_2D_4\text{–}CCl_4\text{–}O_2$ mixture containing 6% of C_2D_4.

When acetylene instead of ethylene is added to a $c\text{-}C_5H_{10}\text{–}c\text{-}C_5D_{10}\text{–}CCl_4\text{–}O_2$ mixture, C_2D_4 and CDHCDH appear as major products. Ethylene-d_4 is also a product when C_2D_2 is absent, but its yield is much smaller than that observed in the acetylene-containing mixtures. In view of the near absence of C_2D_3H as a product, it is suggested that C_2D_4 and CDHCDH are mainly formed by the single-step ion–molecule reactions

$$C_5H_{10}^+ + C_2D_2 \longrightarrow C_5H_8^+ + CDHCDH \tag{16}$$

$$C_5D_{10}^+ + C_2D_2 \longrightarrow C_5D_8^+ + C_2D_4 \tag{17}$$

$$\Delta H_{\text{gas phase}} = -50.4 \text{ kcal/mole}$$

The $c\text{-}C_5H_{10}\text{–}c\text{-}C_5D_{10}\text{–}C_2D_4$ and $c\text{-}C_5H_{10}\text{–}c\text{-}C_5D_{10}\text{–}C_2D_2$ experiments given in Table III show that an increase in the mole per cent of C_2D_4 or C_2D_2 lowers the product ratios $C_2D_4H_2/C_2D_6$ and $C_2D_2H_2/C_2D_4$, respectively. This indicates that the H_2- or D_2-transfer reaction can compete with the charge-transfer mechanism 6. The rather sharp increase of the yields of ethane and ethylene when the mole per cent of C_2D_4 or C_2D_2 is raised definitely indicates an increased efficiency of interception of the parent cyclopentane ions by the solute molecules.

H_2- and D_2-transfer reactions can also be written to account for the formation of C_3D_8 and $C_3D_6H_2$ in the radiolysis of a $c\text{-}C_5H_{10}\text{–}c\text{-}C_5D_{10}\text{–}CD_3CDCD_2\text{–}CCl_4\text{–}O_2$ mixture at 195°K (last row of Table III). In the latter experiment C_3D_7H is a minor product. The product $C_3D_6H_2$ has the structure CD_3CDHCD_2H, as may be expected if the H_2-transfer reaction occurs by way of a loose reaction complex.

$$C_5H_{10}^+ + CD_3CDCD_2 \longrightarrow C_5H_8^+ + CD_3CDHCD_2H \tag{18}$$

$$\Delta H_{\text{gas phase}} = -39 \text{ kcal/mole}$$

The high G values which can be attributed to reaction of the parent ion (Table III) indicate that fragmentation or rearrangement of the $c\text{-}C_5H_{10}^+$ ion must be of minor importance. Pentene ions are not expected to transfer H_2 species to unsaturated hydrocarbons.[2] That fragmentation does indeed play a minor role is indicated by the low yields of lower hydrocarbon products in the radiolysis of pure cyclopentane (see Results). Gas-phase mass spectrometric studies[15] indicate that there are two major primary fragmentation processes

$$C_5H_{10}^+ \longrightarrow C_2H_4 + C_3H_6^+ \text{ (AP} \leqslant 11.3 \text{ v)} \tag{19}$$

$$C_5H_{10}^+ \longrightarrow CH_3 + C_4H_7^+ \text{ (AP} \leqslant 11.0 \text{ v)} \tag{20}$$

At high densities secondary fragmentation can be ignored (see ref 10). The low yield of methane demonstrates that process 20 can be ignored. Ethylene is not a negligible product, but only a minor fraction of it can be ascribed to process 19. Indeed, the pronounced reduction of G(ethylene) with addition of CCl_4 (see Results) indicates that it is largely formed as a result of combination of a positive ion (probably the $c\text{-}C_5H_{10}^+$) with an electron.

On the other hand, it is significant that CCl_4 does not suppress G(propane). Although we are dealing here with a very minor product ($G \sim 0.045$), an attempt can be made to determine its mode of formation. In the presence of a radical scavenger, G(propane) and, in particular, $G(C_3D_7H)$ are reduced, indicating the formation of propyl radicals. The fact that the residual propane consists mainly, although not exclusively, of C_3D_8, $C_3D_6H_2$, $C_3D_2H_6$, and C_3H_8 actually indicates that it may be formed by the well-established H_2^--transfer reaction[10]

$$C_3H_6^+ + c\text{-}C_5H_{10} \longrightarrow C_3H_8 + c\text{-}C_5H_8^+ \tag{21}$$

If this interpretation is correct, only about 1 and 0.2% of the cyclopentane ions would decompose according to process 19 at 195 and 77°K, respectively.

Cyclohexane. The results given in Table I show that the addition of cyclopropane-d_6 to $c\text{-}C_6H_{12}$ leads to the formation of $CD_2HCD_2CD_2H$ as a major product. Using the same reasoning as was applied in the case of the analogous cyclopentane–cyclopropane-d_6 mixtures, the formation of this product can be explained by the occurrence of an H_2-transfer reaction between the $c\text{-}C_6H_{12}^+$ parent ion and cyclopropane.

$$c\text{-}C_6H_{12}^+ + (CD_2)_3 \longrightarrow CD_2HCD_2CD_2H + c\text{-}C_6H_{10}^+ \tag{22}$$

That propane is largely produced as a result of an ion–molecule reaction is confirmed by the fact (see Results) that its yield is increased by the delay of neutralization processes through the addition of an electron scavenger such as CCl_4.

In the radiolysis of a $c\text{-}C_6H_{12}\text{–}(CD_2)_3$ mixture, $CD_3CD_2CD_2H$ constitutes a much larger fraction of the total propane yield than it did in the radiolysis of the analogous cyclopentane mixtures (Table I). Similarly, the propane formed in the radiolysis of a $c\text{-}C_6H_{12}\text{–}c\text{-}C_6D_{12}\text{–}(CD_2)_3$ mixture contains a relatively large fraction (Table I) of propane-d_7. The addition of oxygen to the latter mixture reduced the yield of propane as well as the relative yield of C_3D_7H, indicating that the propane-d_7 formed in the $c\text{-}C_6H_{12}\text{–}c\text{-}C_6D_{12}$ mixtures has a free-radical precursor. This is confirmed by the fact that 70% of the propane formed in the radiolysis of a $c\text{-}C_6D_{12}\text{–}(CD_2)_3\text{–}H_2S$ mixture (Table II) consists of $CD_3CD_2CD_2H$. The ratio $CD_3CD_2CD_2H/C_3D_8$ increases by not more than 20% with an increase in the concentration of H_2S by a factor of 3, demonstrating that most of the $CD_3CD_2CD_2$ radicals have been inter-

---

(15) P. Natalis, B. Steiner, and M. G. Inghram, private communication.

cepted by H_2S. The independence of the relative yield of C_3D_7H formed in the radiolysis of a c-C_6H_{12}–$(CD_2)_3$ mixture with the concentration of cyclopropane (Table I) shows that the propyl radical is not formed by a reaction involving two cyclopropane entities. The experimental evidence cited above points to the formation of propyl radicals in an ion–molecule reaction mechanism similar to that proposed above for the formation of propyl radicals in the radiolysis of cyclopentane–cyclopropane mixtures. The D-atom-transfer reaction

$$C_6D_{12}^+ + (CD_2)_3 \longrightarrow CD_3CD_2CD_2 + C_6D_{11}^+ \qquad (23)$$

which has also been observed in the mass spectrometer,[12] is the most plausible source of the propyl radicals. From the experiments in which H_2S is added (Table II), it may be concluded that the probability of reaction 23 relative to that of the D_2-transfer reaction is approximately 2.5. This value is about three times higher than the analogous value derived for the experiments with cyclopentane and is in good agreement with the maximum value of 2.5 obtained for the ratio $C_3H_7D/C_3H_6D_2$ in the radiolysis of c-C_6D_{12}–$(CH_2)_3$–CCl_4–H_2S mixtures (Table IV) at 195°K. In the latter mixtures the formation of $CH_3CH_2CH_2D$ can be ascribed to the reaction sequence

$$C_6D_{12}^+ + (CH_2)_3 \longrightarrow CH_2DCH_2CH_2 + C_6D_{11}^+ \qquad (24)$$

$$CH_2DCH_2CH_2 + H_2S \longrightarrow CH_2DCH_2CH_3 + HS \qquad (25)$$

while at sufficiently high H_2S concentrations $CH_2DCH_2CH_2D$ is entirely formed by a D_2-transfer mechanism. Comparison of the experiments given in Table II with those given in Table IV demonstrates that there is little effect of temperature on the relative efficiency of D_2- to D-transfer reactions. They also show that an increase in the mole per cent of H_2S added to a constant cyclohexane–cyclopropane mixture, with or without CCl_4, lowers the yield of propane. It follows that H_2S is competing with cyclopropane for the parent ion. This is in accord with the conclusion drawn by Meissner and Henglein[11] on the basis of an extensive study of the liquid-phase radiolysis of H_2S–n-C_6H_{12} mixtures.

Table IV. The Radiolysis of c-C_6D_{12} + $(CH_2)_3$ + CCl_4 (1:0.02:0.02) in the Presence of H_2S at 195°K

	G value	Isotopic composition	
% H_2S	Total propane	CH_2DCH_2CHD	$CH_3CH_2CH_2D$
0	1.04	1.00	0.11
0.5	0.64	1.00	1.56
1.0	0.52	1.00	1.94
4.0	0.34	1.00	2.45
10.0	0.19	1.00	2.54

Figure 1 shows a plot of the variations in the yield of propane formed in the radiolysis of c-C_6H_{12}–$(CD_2)_3$ mixtures as a function of the square root of the concentration of cyclopropane. It should be mentioned that variations in the yield of propane are proportional to variations in the total amount of reaction between the cyclohexane parent ion and the cyclopropane, since the fraction of propyl radicals which will form propane is independent of the concentration of cyclopropane. Similar plots have been constructed for products of ion–molecule reactions in previous investigations,[3,16] and, as in the present case, a straight-line relationship is obtained. It is of interest to note that as the concentration of cyclopropane is decreased to very low values, there is no lower limiting yield of propane which could be attributed to "free ions"; in fact, the plot seems to pass through the origin. The lack of chemical evidence for the presence of free ions was also noted in a recent communication by Schuler, *et al.*[17] It should, however, be realized that although the cyclohexane and cyclopropane were highly purified, the presence of trace impurities can never be entirely excluded. A recent failure to obtain evidence for free ions in the radiolysis of c-C_6H_{12}–C_2H_5OD solutions was actually tentatively ascribed[18] to impurities.

It is of interest that the H_2-transfer reaction is also of relatively minor importance when C_2D_2, C_2D_4, and C_3D_6 are added as solutes to cyclohexane (Table V). Only the C_6H_{12}–C_6D_{12}–C_2D_4–O_2 mixtures yield fairly conclusive evidence for the occurrence of H_2- and D_2-transfer reactions, but the yield of this process is nearly an order of magnitude lower than the analogous reaction in the radiolysis of cyclopentane–ethylene mixtures. H_2 transfer from the cyclohexane ion to acetylene does not seem to occur even when as much as 16 mole % C_2D_2 is added to cyclohexane. The cyclohexane–C_3D_6 results are rather inconclusive but definitely show a low efficiency for the reaction

$$C_6H_{12}^+ + CD_3CDCD_2 \longrightarrow C_6H_{10}^+ + CD_3CDHCD_2H \qquad (26)$$

This is most surprising, because in the gas phase the latter reaction occurs at nearly every collision.[4]

Mechanism of the H_2-Transfer Process. The H_2- (or D_2-) transfer reactions have, up to this point, been pictured as one-step reactions which proceed through the formation of a reaction complex whose structure is well defined. Evidence for the latter point lies in the well-defined isotopic structure of the final products, which seems to indicate that any reshuffling of H (or D) atoms in the reaction complex can be ruled out. However, the reaction can also be envisioned as a two-step reaction, consisting of a charge transfer from the parent ion to the additive molecule followed by an H_2^--transfer process. This reaction sequence can be represented by eq 27 and 28 for c-C_5H_{10}–$(CD_2)_3$ mixtures. Of course, in order to explain the formation of product propane-d_6 with the structure $CD_2HCD_2CD_2H$ in reaction sequence 27 and 28, one has to assume that the reacting $C_3D_6^+$ ion has retained the cyclopropane ring structure or the open ring structure $CD_2CD_2CD_2^+$, rather than rearranging to the thermodynamically more stable propylene ion structure.

$$c\text{-}C_5H_{10}^+ + (CD_2)_3 \longrightarrow C_5H_{10} + c\text{-}C_3D_6^+ \qquad (27)$$

$$\Delta H_{\text{gas phase}} = \sim -11 \text{ kcal/mole}$$

$$c\text{-}C_3D_6^+ + C_5H_{10} \longrightarrow C_5H_8^+ + CD_2HCD_2CD_2H \qquad (28)$$

$$\Delta H_{\text{gas phase}} = -35 \text{ kcal/mole}$$

It should be pointed out that the distinction between the H_2-transfer reaction (4) and a reaction sequence such as (27) and (28) is meaningful only if the ion produced in the charge transfer does not always react with

---

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

(17) R. H. Schuler, J. L. McCrumb, and J. M. Warman, private communication.

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

Table V. The Radiolysis of $c\text{-}C_6H_{12} + c\text{-}C_6D_{12}$ (1:1) in the Presence of Deuterated Unsaturated Hydrocarbons[a]

Mole fraction			O_2,	Isotopic composition					
Cyclohexane	Additive	CCl_4	atm						$G_{\text{cyclohexane}}$
					I. C_2D_4				
				C_2D_6	C_2D_5H	CD_2HCD_2H			Total ethane
0.94	0.018	0.038		1.00	1.21	2.42			0.668
0.94	0.019	0.038	1	1.00	0.76	2.08			0.198
					II. C_2D_2				
				C_2D_4	C_2D_3H	CDHCDH	C_2DH_3	C_2H_4	Total ethylene
0.95	0.012	0.037	1	1.00	0.15	0.51	0.68	1.40	0.023
0.92	0.046	0.037	1	1.00	0.23	0.58	0.17	0.92	0.054
0.81	0.16	0.032	1	1.00	~0.61	~1.09	~0.18	~0.5	0.084
					III. C_3D_6				
				C_3D_8	C_3D_7H[b]	$C_3D_6H_2$[b]	C_3H_8		Total propane
0.91	0.025	0.065		1.00	0.51	0.37	<0.023		0.381
0.93	0.037	0.028	1	1.00	0.43	0.53	0.13		0.277

[a] All experiments performed at 195°K. [b] Structure uncertain.

the entity to which it donated an electron. Since there is no reason to expect an isotope effect for reaction of a given ion with a deuterated or nondeuterated molecule, diffusion of the deuterated product ions away from the charge-transfer complex of reaction 27 would result in the observation of a 1:1 ratio for the transfer of an H_2 or D_2 species in the irradiation of a mixture of $c\text{-}C_5H_{10}$ and $c\text{-}C_5D_{10}$ (1:1) in the presence of an additive. As discussed above, the results given in Tables I and III show that the transfer of an H_2 species is favored over the transfer of a D_2 species when $c\text{-}C_5H_{10}\text{-}c\text{-}C_5D_{10}$ (1:1) is irradiated in the presence of $(CD_2)_3$, C_2D_4, or C_2D_2, indicating that the distinction between the H_2-transfer reaction and the charge-transfer reaction sequence is not meaningful at least for these mixtures. More to the point is the fact that, in the case of acetylene, a charge transfer from a cyclopentane parent ion is endothermic by about 20 kcal/mole (unless one makes the unlikely assumption that an inordinately large fraction of the reacting cyclopentane ions are excited[19] by more than 20 kcal). On the other hand, in the radiolysis of a $c\text{-}C_5H_{10}\text{-}c\text{-}C_5D_{10}\text{-}CD_3CDCD_2\text{-}O_2$ mixture (Table III) the product ratio $C_3D_8/C_3D_6H_2$ is closer to unity. This observation would support the occurrence of the charge-transfer reaction

$$C_5H_{10}^+ \text{ (or } C_5D_{10}^+) + C_3D_6 \longrightarrow C_5H_{10} \text{ (or } C_5D_{10}) + C_3D_6^+ \quad (29)$$

followed by reaction of $C_3D_6^+$ with C_5H_{10} and C_5D_{10} to form $C_3D_6H_2$ and C_3D_8 with approximately equal yield. Evidence for charge transfer from cycloalkane ions to propylene has been reported in the gas phase.[3,12]

Some further insight into the reaction mechanism may be obtained from a comparison of the relative efficiencies with which the H_2 (or D_2) entity is transferred to the various solute molecules. Results obtained in comparable experiments given in Tables I and III allow us to compare the efficiencies of the transfer of an H_2 or D_2 molecule from a cyclopentane ion to acetylene, ethylene, propylene, and cyclopropane. The values summarized in Table VI are based on a summation of the H_2- and D_2-transfer products formed in the radiolysis of $C_5H_{10}\text{-}C_5D_{10}$ mixtures containing CCl_4 and oxygen and a constant percentage of the H_2- (or D_2-) acceptor molecule. The most striking feature which emerges from Table VI is that, in the condensed phase, the highest efficiency for the H_2-transfer reaction is observed for the acceptor molecule, ethylene (IP = 10.51 ev), whose gas-phase ionization energy is closest to that of cyclopentane (IP = 10.53 ev). In the earlier investigation[2] of the H_2-transfer reactions involving the 2-methylbutane ion ($IP_{\text{2-methylbutane}} = 10.32$ ev), the most efficient acceptor molecule was seen to be cyclopropane (IP = 10.06 ev). It would, therefore, seem that, as pointed out before,[12] resonance charge transfer between the two reactants in the reaction complex increases the efficiency of the H_2-transfer reaction. It should, however, be noted that the additive molecule which reacts most efficiently with the parent ion (that is, has the highest yield of products from H-transfer plus H_2-transfer reactions) is not necessarily the molecule which undergoes the H_2-transfer reaction with a given parent ion most efficiently. Although using H_2S as a radical scavenger, the total reaction efficiency can readily be determined when $(CD_2)_3$ is the solute, it is more difficult to obtain this information for unsaturated solutes.

Table VI. H_2 Transfer from Cyclopentane to Various Additives

		Relative efficiencies		
H_2 acceptor	IP, ev	Condensed phase (195°K)	Gas phase (330°K)	ΔH gas phase
C_2D_2	11.41	0.9		−50.4
C_2D_4	10.51	1.96	0.17	−41.4
$(CD_2)_3$	10.06	1.20	0.088	−46.3
CD_3CDCD_2	9.73	1.00	1.00	−38.9

There are rather striking differences between the relative efficiencies of the H_2-transfer reactions involving various acceptor molecules observed in the gas phase and in the condensed phase. As noted before,[2] these differences may reflect a change in the probability of the H_2-transfer reaction relative to that of the corresponding H-transfer reaction rather than a difference in the total reactivity.

---

(19) Excited alkane ions have been reported (D. W. Skelly and W. H. Hamill, *J. Phys. Chem.*, 70, 1630 (1966)) to play a role in the radiolysis of alkane glasses, but since, as noted in the Discussion, fragmentation of the parent cyclopentane ion is of minor occurrence, it seems highly unlikely that in the radiolysis of cyclopentane excited ions are formed with a *G* value as high as 2 (Table III).