Ion–Molecule Reactions in the Condensed Phase Radiolysis of Hydrocarbon Mixtures. I. 2-Methylbutane and 3-Methylpentane[1a]

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

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Abstract: When cyclopropane-d_6 is added to i-C_5H_{12}, $CD_2HCD_2CD_2H$ is formed as a product with a yield which at 77°K increases as the square root of the cyclopropane-d_6 concentration from a G value of 0.117 at 0.03 mole % $(CD_2)_3$ to 1.53 at 20 mole % $(CD_2)_3$, while all lower perprotonated hydrocarbon product yields diminish proportionately. Addition of an electron scavenger such as CCl_4 to an i-C_5H_{12}–$(CD_2)_3$ (1:0.03) mixture increases $G(CD_2HCD_2CD_2H)$ to a value as high as 2.85 while the G values of products such as C_2H_6, C_2H_4, or C_3H_8 drop by a factor of 5. On the other hand, addition of CH_3OH reduces $G(CD_2HCD_2CD_2H)$. These observations can be accounted for by an H-transfer reaction such as $C_4H_{12}^+ + (CD_2)_2 \rightarrow C_3H_5^+ + CD_2HCD_2CD_2H$. An analogous reaction is shown to occur with a comparable efficiency when 3-methylpentane is substituted for 2-methylbutane in the reaction mixture. H_2-Transfer reactions are also shown to occur to small unsaturated compounds. The relative probabilities for the transfer of an H_2 entity from $C_5H_{12}^+$ to cyclopropane, ethylene, propylene, 1-butene, acetylene, and 2-butene are 2.4, 1.4, 1.0, 0.9, 0.77, and <0.1, respectively. A change in temperature from 77 to 300°K has relatively little effect on the yields of products resulting from H_2-transfer reactions. Furthermore, experiments carried out with i-C_5H_{12}–i-C_5D_{12} and i-C_5D_{12}–i-C_6H_{14} mixtures indicate that charge transfer from i-$C_5D_{12}^+$ to i-C_6H_{14} is unimportant when more than 0.6 mole % of cyclopropane is present in the mixture.

In a recent communication,[2] we reported a few typical results which demonstrated the occurrence of specific ion–molecule reactions in the condensed phase radiolysis of hydrocarbon mixtures. In the present paper, which is the first in a series dealing with ion–molecule reactions initiated by radiolysis of alkanes in the liquid phase, we are presenting a detailed account of the experimental evidence which led us to postulate the occurrence of H_2-transfer reactions of the general type

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

In this investigation, $C_nH_{2n+2}^+$ 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.

Experimental Section

Materials. The 2-methylbutane and 3-methylpentane used in this study were standard samples obtained from the American Petroleum Institute and had sufficient purity that they could be used without any further purification. 2-Methylbutane-d_{12} and 2-methylbutane-2-d_1 ($(CH_3)_2CDCH_2CH_3$) were obtained from Merck Sharp and Dohme and required extensive purification by gas chromatography. This was accomplished by consecutive injections of small amounts (0.1 g) of material on a gas chromatograph provided with a squalane column. The material trapped from the helium stream was subsequently reinjected on a silica gel column in order to remove the last traces of diethyl ether which was the major impurity. Mass spectrometric analysis indicated that the 2-methylbutane-d_{12} contained 6% 2-methylbutane-d_{11}. At least 90% of the 2-methylbutane-2-d_1 was correctly labeled with the deuterium atom at the tertiary carbon atom. The cyclopropane-d_6, propylene-d_6, ethylene-d_4, and acetylene-d_2, which contained respectively 5% cyclopropane-d_5, 4% propylene-d_5, 5% ethylene-d_3, and 4% acetylene-d_1, were thoroughly purified by gas chromatography until no chemical impurities could be detected.

Irradiation. The samples were irradiated in the 50,000-curie National Bureau of Standards cobalt-60 source. The compounds to be irradiated were contained in Pyrex tubes (5 cm long, 0.5 cm in diameter) provided with break-seals. The tubes were, after thorough degassing, filled with about 0.5 ml of the hydrocarbon mixture. The volume of the vapor phase above the liquid level is estimated to be about 1 ml. In order to minimize the amount of alkane in the vapor phase, most experiments were carried out at 195°K rather than at room temperature. The mixtures were usually made up in the vapor phase in a mercury-free line and, subsequently, condensed in the reaction cells at 77°K. Three or four of these cells were then put in a dewar which, depending on the experiment, contained a Dry Ice–acetone mixture or liquid nitrogen. The dewar was enclosed in an aluminum can which could be lowered into a reproducible position in the center of the pool-type γ-ray source. Dose rates were determined by the Fricke dosimeter. Assuming that $G(Fe^{3+}) = 15.45$,[3] the rate of energy absorption by 2-methylbutane was calculated to be 0.8×10^{19} ev/mole sec in Feb 1966.

Analysis. After irradiation, the sample was expanded into a calibrated 1- or 2-l. bulb. An aliquot was subsequently introduced into a gas chromatograph provided with a flame ionization detector for quantitative analysis of the hydrocarbon products. The residual material was then introduced into another gas chromatograph from whose exit the hydrocarbon products, ethane, ethylene, propane, and butane, were trapped separately at 77°K. After removing the helium carrier gas, the various product compounds were introduced into a mass spectrometer. The mass spectra were interpreted using mass spectral cracking patterns of various deuterium-labeled hydrocarbons, which were, in some cases, especially prepared for this purpose. For the present study, it was of special importance to have reliable mass spectral patterns of the propanes, $CD_2HCD_2CD_2H$, $CD_2HCDHCD_3$, $CD_3CD_2CD_2H$, and CD_3CDHCD_3. Because the mass spectra of these propanes may be of interest to other investigators, they are given in Table I. Corrections for insufficient deuteration have not been made. It can, however, be estimated that the C_3D_7H contains 6% $C_3D_6H_2$. The contribution of $C_3D_5H_3$ to the $C_3D_6H_2$ mass spectral cracking patterns is close to 5%.

The mass spectral patterns of the ethanes used to calculate the isotopic compositions of the ethane fractions were closely comparable to those reported by Bell and Kistiakowsky.[4] It should be noted, however, that in those experiments where the contributions

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[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] P. Ausloos, A. A. Scala, and S. G. Lias, *J. Am. Chem. Soc.*, **88**, 1583 (1966).

[3] R. H. Schuler and A. O. Allen, *J. Chem. Phys.*, **24**, 56 (1956).

[4] J. A. Bell and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **84**, 3417 (1962).

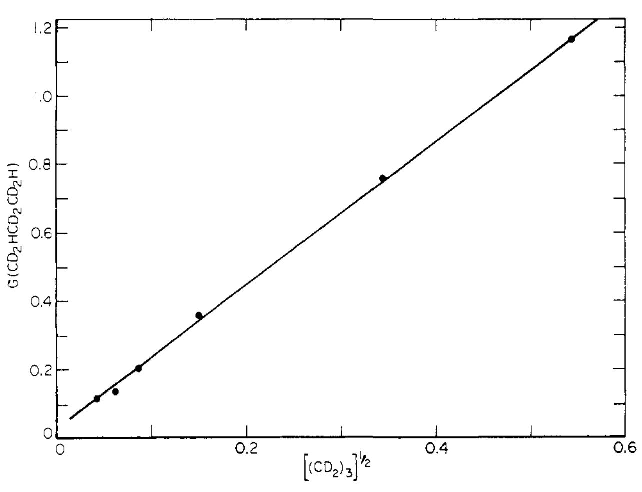

Figure 1. Radiolysis of 2-methylbutane–$(CD_2)_3$ mixtures at 77°K. Dependence of the $CD_2HCD_2CD_2H$ yield on the square root of the $(CD_2)_3$ concentration in moles/l.

of C_2D_6, C_2D_5H, and CD_2HCD_2H to the total ethane fraction are quite high, only the sum of the yields of C_2H_5D and C_2H_6 could be evaluated with any accuracy (Table V). Ethane-d_3 is also produced in most experiments, but because its yield is always less than 3% of the total ethane fraction, it is not given in Table V.

Table I. Mass Spectral Cracking Patterns of Propane-d_7 and Propane-d_6[a]

m/e	CD_3CD_2-CD_2H	CD_3CDH-CD_3	CD_3-$CDHCD_2H$	CD_2HCD_2-CD_2H
29	67.9	91.4	76.0	57.8
30	147.3	121.6	148.4	87.3
31	91.4	205.9	180.9	160.9
32	176.0	78.4	271.8	129.5
33	201.7	432.8	253.4	384.2
34	200.7	46.1	16.6	9.1
43	9.1	4.9	5.5	7.3
45	29.7	18.8	34.6	23.5
46	19.9	35.3	19.0	15.3
47	11.6	10.8	12.7	8.8
48	3.2	13.0	39.3	41.7
49	44.5	42.6	84.5	13.2
50	8.5	85.7	*100*	*100*
51	*100*	*100*		

[a] All patterns were obtained using a Consolidated Model 21-101 mass spectrometer at an ionizing current of 50 μa. (All patterns have been corrected for C_{13} abundance.)

Results

The product yields in this paper were expressed as $G_{C_nH_{2n+2}}(X)$, that is, the number of molecules of X formed per 100 ev absorbed by C_nH_{2n+2}. 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 $G_{C_nH_{2n+2}}(X)$.

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

1. No $CD_2HCD_2CD_2H$ is formed when an i-C_5H_{12}–$(CD_2)_3$–CCl_4 (1:0.02:0.02) glass is photolyzed at 77°K with the 1470-A (8.4 ev) xenon resonance line.[5] Nondeuterated alkane and alkene products were, however, produced in yields comparable to those obtained in the photolysis of a pure i-C_5H_{12} glass.[6] On the other hand, photolysis of the above mixture at 1048–67 A. (11.5–11.7 ev) did lead to the formation of $CD_2HCD_2CD_2H$ with a yield which was roughly equal to that of C_3H_8. The relative yields of all other products in this experiment were approximately equal to those formed in the photolysis of the pure i-C_5H_{12} glass[6] at these wavelengths.

2. The propane produced in the radiolysis of C_5H_{12}–C_3D_6 mixtures (Table II) and of C_6H_{14}–C_3D_6 mixtures (Table III) consists essentially only of $C_3D_6H_2$ and C_3H_8. The small amounts of $C_3D_5H_3$ found in the propane fractions of these experiments can in every case be entirely accounted for by the presence of the C_3D_5H impurity in the reacting cyclopropane-d_6 or propylene-d_6.

3. An increase of the mole per cent of $(CD_2)_3$ added to i-C_5H_{12}–$(CD_2)_3$ mixtures not only reduces the yields of C_2H_6 and C_3H_8, as shown in Table II, but also proportionately reduces the yields of most other products such as propylene, n-butane, and the pentenes.

4. Addition of CCl_4 to pure i-C_5H_{12} or to an i-C_5H_{12}–deuterated additive mixture causes a drop in the yields of perprotonated products such as C_2H_6, C_2H_4, or C_3H_8 by as much as a factor of 5.

5. Addition of 5 mole % CH_3OH to an i-C_5H_{12}–$(CD_2)_3$–CCl_4 (1:0.05:0.01) mixture reduced $G(CD_2HCD_2CD_2H)$ from 2.12 to 1.53.

6. Butane formed in the radiolysis of an i-C_5H_{12}–i-C_5D_{12}–*cis*-2-C_4D_8–CCl_4 (1:1:0.03:0.03) mixture at 195°K has a G value of 0.114 and contains not more than 20% of $CD_3CDHCDHCD_3$. In the radiolysis of an i-C_5H_{12}–i-C_5D_{12}–1-C_4D_8–CCl_4 (1:1:0.03:0.03) mixture, butane is formed with a G value of 0.948 and consists of C_4D_{10} (1.00), C_4D_9H (0.25), and $C_4D_8H_2$ (1.76). Because cracking patterns of these partially deuterated butanes are unavailable, the concentrations of lighter butanes in the sample cannot be accurately calculated, but they are estimated to constitute less that 10% of the total butane fraction.

7. In the radiolysis of an i-C_5H_{12}–C_2D_4 (1:0.03) mixture at 195°K, $CD_2HCD_2CD_2CD_2H$ is formed as a product with a G value of 0.20. Propane having the structure $CD_2HCD_2CH_3$ is formed with a G value of 0.064.

Discussion

We will first attempt to demonstrate that H_2-transfer reactions do indeed occur in the condensed phase radiolysis of certain hydrocarbon mixtures. Subsequently, we intend to show that the parent ion is the reacting ion and will discuss some of the characteristics of these reactions as well as their importance to our understanding of the radiolysis of alkanes.

Evidence for H_2-Transfer Reactions. The results of Table II indicate that $CD_2HCD_2CD_2H$ is a major product when cyclopropane-d_6 is added to 2-methylbutane or to a 2-methylbutane–CCl_4 mixture. Similarly, $CD_2HCD_2CD_2H$ is formed with a high G value in 3-methylpentane-cyclopropane-d_6 mixtures (Table III). The fact that no other deuterium-labeled propanes are produced points to the occurrence of a reac-

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(5) The experimental techniques used in these experiments are described in detail elsewhere: P. Ausloos, R. E. Rebbert, and S. G. Lias, *J. Chem. Phys.*, **42**, 540 (1965).

(6) A. A. Scala and P. Ausloos, *J. Phys. Chem.*, to be published.

Table II. Radiolysis of i-C_5H_{12}–C_3D_6 Mixtures at 195°K

Mole %			$G(C_5H_{12})$ values (molecules per 100 ev absorbed by C_5H_{12})				
Hydrocarbon additive	CCl_4	i-C_5H_{12}	Propane	CD_2HCD_2-CD_2H	CD_3CD_2-HCD_2H	C_3H_8	C_2H_6
cyclo-C_3D_6							
0.3	..	99.7	0.93	0.24	...	0.69	1.27
2	..	98	1.12	0.62	...	0.50	1.05
6	..	94	1.40	0.98	...	0.42	0.80
12	..	88	1.51	1.14	...	0.37	0.72
21	..	79	1.84	1.53	...	0.31	0.60
3	1	96	2.44	2.12	...	0.32	0.86
3	5	92	2.59	2.40	...	0.19	0.50
3	7	90	2.71	2.56	...	0.15	0.41
3	9	88	2.85	2.69	...	0.16	0.44
3	39	58	2.97	2.85	...	0.12	0.32
CD_3CDCD_2							
5	9	86	2.06	...	1.76	0.30	0.12

Table III. Radiolysis of 3-Methylpentane–Cyclopropane-d_6 Mixtures

	Mole %			$G(C_6H_{14})$ values (molecules per 100 ev absorbed by C_6H_{14})				
Temp, °K	C_6H_{14}	cyclo-C_3D_6	CCl_4	Total propane	CD_2HCD_2-CD_2H	C_3H_8	C_3H_6	C_2H_4
77	97	3	...	1.51	1.48	0.03	0.92	0.48
77	95	3	2	2.44	2.42	0.02	0.39	0.18
195	97	3	...	1.37	1.31	0.06	1.22	0.52
195	95	3	2	2.63	2.60	0.03	0.50	0.25
298	97	3	...	0.67	0.61	0.06	1.40	0.69
298	95	3	2	1.80	1.76	0.04	0.89	0.26

Table IV. Radiolysis of 2-Methylbutane at 195°K. Formation of Propane

Mole %				G(MB) values (molecules formed per 100 ev absorbed by 2-methylbutane)					
2-Methylbutane	Hydrocarbon additive	CCl_4	O_2, atm	Total propane	C_3D_8	C_3D_7H	CD_2HCD_2-CD_2H	C_3DH_7	C_3H_8
i-C_5H_{12} + i-C_5D_{12} (1:1)	cyclo-C_3D_6								
87	4	9	...	3.28	1.21	0.19	1.77	...	0.11
94	3	3	1	2.19	0.90	0.009	1.08	...	0.16
	CD_3CDCD_2						CD_3CDHCD_2H		
93	1	6	...	0.99	0.39	0.097	0.37	...	0.14
94	3	3	1	0.93	0.41	0.017	0.38	0.019	0.10
97	...	3	1	0.13	0.028	0.017	0.001	0.023	0.061

tion in which an H_2 molecule is transferred by a one-step mechanism to cyclopropane-d_6. On the same basis, the formation of CD_3CDHCD_2H in the radiolysis of a C_5H_{12}–CD_3CDCD_2–CCl_4 mixture (Table II) can also tentatively be ascribed to the transfer of a H_2 molecule across the double bond of the propylene molecule. It is clear, however, that in these systems propane-d_6 could conceivably also be produced by a mechanism involving the transfer of an H atom to C_3D_6 followed by an H-atom abstraction from the perprotonated alkane or by disproportionation with a nondeuterated radical in the system. It should, however, be noted that the absence of C_3D_7H as a product definitely excludes the occurrence of disproportionation reactions of the type

$$CD_2CD_2CD_2H + CD_2CD_2H \longrightarrow \mathit{CD_3CD_2CD_2H} + CD_2CDCD_2H \quad (2)$$

$$CD_3CDCD_2H + CD_3CDCD_2H \longrightarrow \mathit{CD_3CD_2CD_2H} + CD_2CDCD_2H \quad (3)$$

Conclusive proof for the formation of $C_3D_6H_2$ by an H_2-transfer reaction can be derived from the results given in Table IV. If propane-d_6 were produced by a two-step mechanism it is obvious that propane-d_7 would be a major product when a C_5H_{12}–C_5D_{12} (1:1) mixture is irradiated in the presence of cyclopropane-d_6 or propylene-d_6. The results of Table IV demonstrate that quite the opposite is the case. In the mixtures containing cyclopropane-d_6, C_3D_7H accounts for only 6% of the deuterium-labeled propanes. Addition of oxygen as a free-radical scavenger further reduces the contribution of C_3D_7H to as little as 0.4% of the sum of C_3D_8 and $C_3D_6H_2$.

When propylene-d_6, instead of cyclopropane-d_6, is added to equimolar i-C_5D_{12}–i-C_5H_{12} mixtures containing CCl_4 as an electron scavenger, C_3D_8 and CD_3CDHCD_2H are the major deuterium-labeled propanes produced. C_3D_7H accounts for 11.3 and 7.1% of all deuterated propanes formed in the absence and presence of oxygen, respectively. If one subtracts the propanes produced in the radiolysis of a C_5D_{12}–C_5H_{12}–CCl_4–O_2 mixture from those formed in the radiolysis of similar mixtures containing cyclopropane

Table V. Radiolysis of 2-Methylbutane–C_2D_4 Mixtures at 195°K. Formation of Ethane

Mole %				O_2,	G(MB) values (molecules per 100 ev absorbed by methylbutane)					
i-C_5H_{12}	i-C_5D_{12}	C_2D_4	CCl_4	atm	Total ethane	C_2D_6	C_2D_5H	$C_2D_4H_2$	C_2DH_5	C_2H_6
100					1.12					1.116
97		3			1.61			0.819		0.791
48.5	48.5	3			1.61	0.589	0.258	0.338	0.187	0.238
50	50				1.09	0.366	0.147		0.068	0.511
47	47	3	3		2.06	0.614	0.336	0.836	0.25	
47	47		3		0.445	0.111	0.063		0.067	0.204
47	47	3	3	1	1.38	0.599	0.033	0.595	0.15	
48	48		3	1	0.265	0.091	0.022		0.025	0.127

Table VI. Radiolysis of 2-Methylbutane–C_2D_2 Mixtures at 195°K. Formation of Ethylene

Mole %				O_2,	G(MB) values (molecules per 100 ev absorbed by 2-methylbutane)					
i-C_5H_{12}	i-C_5D_{12}	C_2D_2	CCl_4	atm	Total ethylene	C_2D_4	C_2D_3H	$C_2D_2H_2$	C_2DH_3	C_2H_4
49	49	2	...		0.798	0.209	0.12	0.310	0.015	0.144
50	50	...	...		0.413	0.141	0.005	<0.005	0.011	0.256
45.5	46.5	2	4		1.116	0.412	0.088	0.466	0.01	0.087
46	46	...	8		0.138	0.063	0.003	<0.003	0.004	0.068
47	47	3	3	1	0.742	0.335	0.007	0.307	0.018	0.075
48	48	...	3	1	0.119	0.052	0.001	<0.001	0.009	0.056

d_6, a value of 0.85 is obtained for the remaining C_3D_8/$CD_2HCD_2CDH_2$ ratio. Similarly a value of 1.0 is obtained for this ratio in the analogous mixtures containing propylene-d_6 instead of cyclopropane-d_6.

The isotopic composition of ethane fractions produced in the radiolysis of 2-methylbutane–ethylene-d_4 mixtures (Table V) further demonstrates that a hydrogen molecule can also be transferred to ethylene. The fact that CD_2HCD_2H is the only deuterium-labeled ethane produced in the second experiment of Table V is consistent with the occurrence of an H_2-transfer process but does not necessarily prove it. The formation of $CD_2HCD_2CD_2CD_2H$ in this experiment (see Results) clearly demonstrates that CD_2HCD_2 radicals are produced, and that, therefore, reaction 4 followed by 5 might equally well account for the formation of CD_2HCD_2H. The third experiment given in Table V demonstrates,

$$CD_2CD_2 + H \longrightarrow CD_2HCD_2 \tag{4}$$

$$CD_2HCD_2 + i\text{-}C_5H_{12} \longrightarrow CD_2HCD_2H + C_5H_{11} \tag{5}$$

however, that when C_2D_4 is added to an i-C_5H_{12}–i-C_5D_{12} mixture, C_2D_6 and CD_2HCD_2H are both produced in yields which are larger than that of C_2D_5H. This is also true when one subtracts from the above ethanes the yields of C_2D_6 and C_2D_5H produced in the radiolysis of a pure C_5H_{12}–C_5D_{12} (1:1) mixture. The occurrence of an H_2-transfer mechanism is still more clearly demonstrated in the next to last experiment given in Table V, where both CCl_4 and oxygen are added to a C_5H_{12}–C_5D_{12}–C_2D_4 (1:1:0.03) mixture and C_2D_6 and CD_2HCD_2H account for about 95% of all deuterium-labeled product ethanes. It is again of interest to note that in this experiment, the yield of C_2D_6 is comparable to that of CD_2HCD_2H. After subtracting the ethanes produced in the last experiment on Table V, a value of 0.85 is obtained for C_2D_6/CD_2HCD_2H.

Following a similar argument, it can be derived from the results given in Table VI that a hydrogen molecule can also be transferred to acetylene by a one-step mechanism. This follows from the isotopic compositions of the ethylene fractions produced in the radiolysis of C_5H_{12}–C_5D_{12}–CCl_4 mixtures containing C_2D_2. From the last two experiments given in Table VI it can furthermore be deduced that the relative probability for transfer of a D_2 molecule as compared to the transfer of an H_2 molecule is 0.92.

The Nature of the H_2-Transfer Reaction. A. Evidence for Ion–Molecule Reaction. That we are indeed dealing with an ion–molecule reaction is shown by the following observations.

1. If one accepts[7] that the ionization energy of isopentane in the condensed phase is approximately 1 ev lower than the gas-phase value of 10.3 ev,[8] ionization does occur in photolysis at the argon resonance line (11.5–11.7 ev) but not at the major xenon resonance line corresponding to 8.4 ev. Therefore, the fact that in the photolysis of an i-C_5H_{12}–$(CD_2)_3$ mixture at 77°K (see Results), $CD_2HCD_2CD_2H$ is formed when argon resonance radiation is used, but not at higher wavelengths, indicates that ions are involved in the H_2-transfer reaction. Similar observations have been reported in the gas-phase photolysis.[9] For instance, in the photolysis of cyclohexane (ionization potential, 9.88 ev) in the presence of cyclopropane-d_6, $CD_2HCD_2CD_2H$ is a product at 10 ev but not at 8.4 ev. Comparison of the product distributions obtained in the photolysis at the xenon line and at the argon line indicate that the relative probabilities of the primary modes of dissociation of the neutral excited molecule change with increasing energy, but no new processes appear.

2. Addition of CCl_4 to C_5H_{12}–$(CD_2)_3$ mixtures (Table II) or C_6H_{14}–$(CD_2)_3$ mixtures (Table III) strongly enhances $G(CD_2HCD_2CD_2H)$. It is well established that CCl_4 is an efficient electron scavenger.[10] As

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(7) C. Vermeil, M. Matheson, S. Leach, and F. Muller, *J. Chim. Phys.*, **61**, 596 (1964).

(8) K. Watanabe, T. Nakoyama, and J. Mottle, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962).

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

noted before,[11] addition of this compound will, therefore, increase the opportunity of the cations to react prior to neutralization. The observed increase of $G(CD_2HCD_2CD_2H)$ would thus support our hypothesis that this molecule is indeed formed by reaction of a cation. It is of incidental interest to note that addition of CCl_4 reduces the yields of perprotonated hydrocarbon products which are known[6] to result largely from decomposition of neutral excited 2-methylbutane molecules. The latter observation is consistent with earlier studies[12,13] in which it was noted that neutralization of an alkane ion by an anion rather than by an electron usually leads to a reduction in the formation of products which most likely have a neutral excited molecule as precursor.

3. The addition of methanol to a C_5H_{12}–$(CD_2)_3$–CCl_4 mixture reduced the yield of $CD_2HCD_2CD_2H$ (see Results). Methanol, which has a high proton affinity, will react with larger alkane ions to accept a proton. Positive hole trapping by proton transfer in 3-methylpentane glasses containing alcohols or amines is well established by Hamill and co-workers.[14] Such a reaction would compete with the H_2-transfer reaction resulting in the observed reduction of $G(CD_2HCD_2CD_2H)$.

B. H_2 Donor Is Parent Alkane Ion. Several considerations indicate that the cation which reacts to transfer the H_2 species must be the parent alkane ion. At least, the following alternative interpretations can be excluded.

1. The H_2 donor is not an ion with molecular weight less than that of the parent ion. The only lower molecular weight ion for which an exothermic H_2-transfer reaction with all the compounds added in this study can be written would be the pentene ion. At any rate, fragmentation of the parent isopentane ion to form C_2, C_3, or C_4 ions is of minor importance in the liquid phase, as was shown in a recent study of the radiolysis of pure isopentane[6] at 195 and 77°K, so reactions of these ions with the H_2-acceptor molecule do not have to be considered. C_5H_{10} ions would be produced in the H_2-transfer reaction itself, but olefinic ions will not undergo H_2-transfer reactions with unsaturated additives, since condensation reactions would be a preferred mode of reaction, as has been demonstrated for analogous systems.[15]

2. The reacting ion is not a dimer or other complex ion with a molecular weight higher than that of the alkane which is being irradiated. This is demonstrated by the fact that in the irradiation of C_5H_{12}–C_5D_{12} (1:1) mixtures containing oxygen as a free-radical scavenger the entity transferred is always H_2 or D_2, but never HD.

3. The ion–molecule reaction which occurs in the presence of the additive molecules can, at least in some instances, not readily be explained as a charge transfer to the additive molecule ($C_{m'}H_{m''}$) followed by an exothermic H_2^--transfer reaction.

$$C_nH_{2n+2} + C_{m'}H_{m''}^+ \longrightarrow C_nH_{2n}^+ + C_{m'}H_{m''+2} \qquad (6)$$

The gas-phase ionization potentials of ethylene (IP = 10.5 ev) and acetylene (IP = 11.4 ev) are considerably higher than that of 2-methylbutane (10.3), and, therefore, charge transfer to these molecules would be excluded unless we make the unlikely assumption that a large fraction of the 2-methylbutane ions are excited and could efficiently transfer their excitation energy to acetylene or ethylene. Additional evidence that the observed reaction is not an H_2^--transfer reaction is found in the fact that the structure of the propane formed in the reaction involving cyclopropane is $CD_2HCD_2CD_2H$. In the gas-phase radiolysis of cyclo-C_6H_{12}–$(CD_2)_3$ mixtures, no evidence could be obtained[16] for the formation of such a product when the charge was carried by cyclopropane-d_6 rather than by cyclohexane. It should nevertheless be noted that, in mixtures containing butene or propylene, transfer of the positive charge to the olefinic molecule followed by reaction 6 cannot, except by analogy, be excluded.

4. The observation that addition of increasing amounts of $(CD_2)_3$ to i-C_5H_{12} (Table II) diminishes the yields of perprotonated hydrocarbons also indicates that a parent ion is the H_2 donor. In view of the fact that these perprotonated noted products seem to be formed mainly by decomposition of neutral excited isopentane molecules formed[5] upon neutralization, the variations in product yields given in Table II can best be accounted for by the competitive mechanism

$$C_5H_{12}^+ + e \longrightarrow C_5H_{12}^* \longrightarrow \text{perprotonated products} \qquad (7)$$

$$C_5H_{12}^+ + (CD_2)_3 \longrightarrow CD_2HCD_2CD_2H + C_5H_{10}^+ \qquad (8)$$

Efficiency of the H_2-Transfer Reaction. By comparing the G values of the products formed in the H_2-transfer reactions from an ion to a series of different compounds under comparable experimental conditions, accurate values can be obtained for the relative efficiencies with which an H_2 entity is transferred to the various acceptor molecules. The relative efficiencies compiled in Table VII were derived from the G values of the products formed in the radiolysis of i-C_5H_{12}–i-C_5D_{12}–CCl_4 (1:1:0.06) mixtures which contained 3 mole % C_2D_2, C_2D_4, C_3D_6, or C_4D_8, and which were irradiated under a pressure of 1 atm of oxygen.

Table VII. H_2 Transfer from 2-Methylbutane to Various Additives

		Relative efficiencies		
H_2 acceptor	IP, ev	Liquid phase (195°K)	Gas phase (300°K, 750 torr)	Δ*H*, gas phase
C_2D_2	11.41	0.77	0.17	−41.63
C_2D_4	10.51	1.4		−32.65
$(CD_2)_3$	10.06	2.4	0.19	−37.50
$CD_2{=\!=}CDCD_3$	9.73	1.0	1.00	−29.62
$CD_2{=\!=}CDCD_2CD_3$	9.58	0.9		−30.03
$CD_3CD{=\!=}CDCD_3$	9.13	<0.1	<0.1	−28.39

There are apparently rather wide variations in the relative efficiencies of the H_2-transfer reactions. Although much more experimental information will be needed before one can attempt to interpret the results

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(10) See, for instance, P. S. Rao, J. R. Nash, J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 500 (1962).

(11) M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *ibid.*, **84**, 4230 (1962).

(12) P. R. Geissler and J. E. Willard, *ibid.*, **84**, 4627 (1962).

(13) G. Scholes and M. Simic, *Nature*, **202**, 895 (1964).

(14) See, for instance, J. B. Gallivan and W. H. Hamill, *J. Chem. Phys.*, **44**, 2378 (1966).

(15) R. D. Doepker and P. Ausloos, *ibid.*, **44**, 1951 (1966).

(16) P. Ausloos and S. G. Lias, *ibid.*, **43**, 127 (1965).

given in Table VII, several interesting features should be pointed out.

1. A plot of the efficiency of the H_2-transfer reactions *vs.* the ionization potential of the H_2-acceptor molecule shows a maximum in the neighborhood of of 10.1 ev. Because the appearance potential of the 2-methylbutane ion[17] (10.32 ev) lies rather close to this value, it is not inconceivable that resonance charge transfer between the two reactants in the reaction complex favors the occurrence of the H_2-transfer reaction. As pointed out by Durup,[18] such a phenomenon might lower the potential energy of interaction and thus increase the probability of reaction. Experiments on a wide variety of systems are needed in order to verify this point. It may be noted that there is definitely no obvious relationship between the efficiency of the H_2-transfer reaction and its exothermicity (Table VII).[19]

2. There is a drastic difference between the relative efficiencies of the H_2-transfer reaction observed in the liquid-phase radiolysis and those derived from a recent gas-phase study.[20] In the gas phase[16] the H-atom transfer reaction

$$C_nH_{2n+2} + C_{m'}H_{m''} \longrightarrow C_nH_{2n+1}^+ + C_{m'}H_{m''+1} \qquad (9)$$

can occur in addition to the H_2-transfer reaction. The relative probabilities of occurrence of the two competing reactions may be a sensitive function of the amount of energy in the reaction complex. If the complex has a lifetime larger than 10^{-12} sec, collisional deactivation may occur in the liquid phase. Because, H-atom transfer to cyclopropane is more exothermic than the H_2-transfer reaction by about 15 kcal, deactivation of the collision complex may favor the H_2-transfer reaction. Before pursuing this interpretation, it is essential to find out if the H-atom transfer reaction does actually occur in the liquid-phase radiolysis, especially when poor H_2-acceptor molecules such as 2-butene are involved. This is, however, not easy to determine because olefins also react to scavenge H atoms, forming product alkyl radicals which cannot readily be distinguished from those which might be formed in reaction.[9b] It should, further, be pointed out that in the liquid phase the occurrence of reactions other than 1 or 9 cannot *a priori* be excluded.

Effect of Concentration of $(CD_2)_3$ and CCl_4 and of Temperature. In Figure 1 it is demonstrated that a straight-line dependence exists between $G(CD_2HCD_2CD_2H)$ and the square root of the concentration[21] of $(CD_2)_3$, indicating that the latter quantity is related to the probability for reaction. A similar relationship was noted by Williams[22] in the radiolysis of cyclo-C_6H_{12}–ND_3 mixtures. HD was attributed to reaction between $C_6H_{12}^+$ or $C_6H_{13}^+$ and added ND_3 followed by neutralization of ND_3H^+. The yield of HD varied linearly with the square root of the concentration of ND_3 above a concentration of 10^{-2} *M* ND_3. As pointed out by Williams, the variations in reaction product yield with the square root of additive–reactant concentration parallel the trends predicted for scavenger competition with the geminate recombination of free radical. Because of experimental difficulties, no attempt was made in the present study to carry out experiments at concentrations of $(CD_2)_3$ lower than 1.77×10^{-3} *M*. On the other hand, at concentrations higher than 10^{-1} *M*, energy absorption by cyclopropane itself cannot be neglected.

It is now of interest to consider the maximum yield of $G(CD_2HCD_2CD_2H)$ which can be obtained. As noted before, addition of CCl_4 will delay the neutralization process and consequently favor reaction. This is well corroborated by the results given in Tables II and III. Apparently above 5 mole % of CCl_4, $G(CD_2HCD_2CD_2H)$ is quite insensitive to a further increase of the percentage of CCl_4 in the mixture. For instance, when CCl_4 is raised from 9 to 39 mole %, $G(CD_2HCD_2CD_2H)$ increased by not more than 5% (Table II). The maximum value of 2.97 obtained for $G(CD_2HCD_2CD_2H)$ in the radiolysis of i-C_5H_{12}–$(CD_2)_3$–CCl_4 mixtures is actually quite close to the maximum value of 3.0 reported by Hamill and coworkers[13] for $G(C_{12}H_{10}^-)$ measured spectrophotometrically in the radiolysis of 2-methyltetrahydrofuran–biphenyl mixtures at 77°K, or the *G* value of 2.6 obtained by Smith and Pieroni[23] for the trapped electrons in pure 2-methyltetrahydrofuran at 77°K by esr measurements.

Charge Transfer

The occurrence of charge transfer in the liquid phase from the parent ion of a given saturated hydrocarbon to an alkane molecule having lower ionization potential has been postulated in the past, although recent investigations[24–27] have yielded evidence that such reactions are of minor importance when ΔIP is less than 1 ev. The irradiation of an i-C_5D_{12} (IP 10.32)–C_6H_{14} (IP 10.08) mixture in the presence of varying small amounts of cyclopropane-d_6 (Table VIII) constitutes a direct test for the occurrence of such charge-transfer processes. If charge transfer from i-$C_5D_{12}^+$ to C_6H_{14} competes with a D_2-transfer reaction to the $(CD_2)_3$ additive, the observed ratio $(CD_2HCD_2CD_2H/C_3D_8)$ should increase as the concentration of $(CD_2)_3$ is decreased. At the same time, the total yield of propane resulting from reaction of the two parent ions with cyclopropane will, of course, decrease, as discussed above. The last column of Table VIII shows that after the yield of C_3D_8 is corrected for C_3D_8 formed in the radiolysis of pure isopentane (Table IV), the ratio of H_2-transfer to D_2-transfer reactions occurring in the mixture does increase only very slightly when the mole per cent of cyclopropane-d_6 is diminished

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[17] The adiabatic ionization potential may be somewhat lower; see B. Steiner, C. F. Giese, and M. C. Inghram, *J. Chem. Phys.*, **34**, 189 (1961).

[18] J. Durup, "Les Reactions entre Ions Positifs et Molecules en Phase Gazeuse," Gauthier-Villars, Paris, 1960.

[19] Solvation energies of the reactant ions and product ions in the condensed phase are not known, and therefore the Δ*H*s' of the reactions cannot be calculated with any accuracy. It is reasonable to assume, however, that the effect of solvation will be nearly the same for the product ion and the reaction ion, so that the over-all Δ*H*'s of the reactions should be comparable to those calculated using gas-phase data.

[20] A. A. Scala and P. J. Ausloos, *J. Chem. Phys.*, to be published.

[21] The data plotted in Figure 1 were taken from experiments performed at 77° rather than from the 195°K results given in Table II, because the concentration of cyclopropane in the mixture is more accurately known in the lower temperature experiments where preferential diffusion of cyclopropane from the liquid to the gas phase is excluded. A similar plot of the data given in Table II also gives a reasonably good straight-line relationship.

[22] F. Williams, *J. Am. Chem. Soc.*, **86**, 3954 (1964).

[23] D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **43**, 2131 (1965).

[24] J. A. Stone, *ibid.*, **42**, 2872 (1964).

[25] P. J. Dyne, *ibid.*, **43**, 1080 (1965).

[26] J. Y. Yang and I. Marcus, *J. Phys. Chem.*, **69**, 3113 (1965).

[27] J. A. Stone, A. R. Quirt, and O. A. Miller, *Can. J. Chem.*, **44**, 1175 (1966).

Table VIII. Liquid Radiolysis of C_5D_{12}–C_6H_{14} (1.5:1) Mixtures

%	G values[a]	% distribution			$\left(\frac{G(C_3D_6H_2)}{G(C_3D_8)}\right)\left(\frac{[C_5D_{12}]}{[C_6H_{14}]}\right)^b$
cyclopropane-d_6	total propane	C_3D_8	C_3D_7H	$C_3D_6H_2$	
6	2.53	46.4	2.0	49.2	1.33 (1.42)[c]
0.6	1.10	48.8	1.5	49.7	1.29 (1.49)
0.13	0.340	44.5	7.2	48.3	1.39 (2.62)

[a] G values calculated relative to energy absorbed by total alkane mixture. O_2 (1 atm) and CCl_4 (9%) added in all experiments. [b] $[C_5D_{12}]/[C_6H_{14}]$ = electron density ratio. [c] The values in parentheses are corrected for the formation of C_3D_8 by processes other than D_2 transfer.

from 6.0 to 0.6. This indicates that charge transfer probably does take place to a relatively minor extent when more than 1 mole % of cyclopropane is present. It should be pointed out that the ratio for the H_2- to D_2-transfer reaction obtained in the last experiment in the table is somewhat less reliable than the other values listed due to the fact that the correction mentioned above involves a relatively large fraction of the total propane formed in this experiment. The latter experiment, nevertheless, demonstrates that charge transfer may be important at very low concentrations of cyclopropane.

An interesting observation which emerges from the i-C_5H_{12}-i-C_5D_{12} (1:1) additive experiments is the fact that intermolecular isotope effects seem to be of minor importance. As pointed out earlier in the Discussion, values ranging from 0.85 to 1.0 are obtained for the probability for transfer of a D_2 species relative to that for the transfer of an H_2 species. This result also indicates that the $C_5D_{12}^+$ and $C_5H_{12}^+$ ions are, up to the time of reaction, present in comparable yields and that, therefore, preferential charge transfer from the perdeuterated to the perprotonated species, which may have a slightly lower ionization potential,[28] does not seem to be of importance in the presence of an H_2-acceptor molecule. This is in agreement with the results reported by Stone, *et al.*[27]

Conclusion

The experiments described in the present study show that considerable care should be exercised in the interpretation of the condensed phase radiolysis of alkanes containing relatively small concentrations of olefins. If the interpretation given in this paper is accepted, one must conclude that the positive hole trapping reported by Gallivan and Hamill[14] for 3-methylpentane–1-butene mixtures may not be due to charge transfer but should rather be ascribed to the occurrence of the H_2-transfer reaction. On the other hand, we cannot explain on the basis of our data why other olefins such as propylene or ethylene added to their system did not increase the observed yields of solvent-trapped electrons.

Ethylene-^{14}C has often been used as an additive in the liquid phase radiolysis as a means of determining the free-radical yields in pure alkanes. The results presented here show, however, that ethylene may react to given ethane and perhaps also C_2H_5 as a product by H_2-transfer and H-transfer reactions, respectively. Fortunately, in most of the studies carried out by Holroyd,[29] using this technique, the concentration of ethylene-C^{14} was kept sufficiently low that these effects may not have seriously affected the derived free-radical yields.

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(28) V. H. Dibeler, M. Krauss, R. M. Reese, and F. N. Harllee, *J. Chem. Phys.*, **42**, 3791 (1965).

(29) See, for instance, R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **69**, 194 (1965).