Ion–Molecule Reactions in the Condensed-Phase Radiolysis of Hydrocarbon Mixtures. III. Reactions of *i*-$C_4H_8^+$ and *tert*-$C_4H_9^+$ Ions Originating from Neopentane[1a]

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Abstract: The liquid-phase radiolysis of neopentane has been investigated in the presence of various hydrocarbons and electron scavengers. It is found that the neopentane parent ion dissociates to yield *tert*-$C_4H_9^+$ and *i*-$C_4H_8^+$ ions. The yields of these ions which are intercepted in these experiments under optimum conditions are ~2.4 and ~0.9, respectively. The *i*-$C_4H_8^+$ ion reacts with various added alkanes by the H_2^- transfer mechanism: $C_4H_8^+ + RH_2 \rightarrow i\text{-}C_4H_{10} + R^+$. The relative rates of reaction with different RH_2 additives have been determined and show the same trends as those observed for these reactions in the gas phase. That is, the rate is seen to increase with an increase in the exothermicity of the reaction (as calculated from gas-phase thermodynamic data). The effect of the ΔH of reaction is, however, more pronounced in the liquid than in the gas phase. The *tert*-butyl ion reacts more slowly with alkane additives than does the isobutylene ion, but reacts effectively with a negative ion from CCl_4 to form *tert*-C_4H_9Cl. Neutralization of the *tert*-butyl ion leads to the formation of isobutylene and propylene.

In the gas phase, the neopentane parent ion has a lifetime of 10^{-13} sec;[2] in the 70-eV mass spectrum of neopentane, at most only $4 \times 10^{-3}\%$ of the observed ions are parent ions. The $(CH_3)_4C^+$ ion undergoes dissociation mainly by a simple C–C bond cleavage which leads to the formation of a *tert*-butyl ion

$$(CH_3)_4C^+ \longrightarrow (CH_3)_3C^+ + CH_3 \quad (1)$$

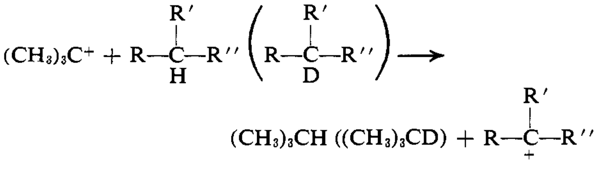
Under conditions where the *tert*-butyl ions are formed with excess energy, they may undergo further dissociation to form $C_3H_5^+$ ions; the importance of secondary fragmentation processes is, of course, dependent on the pressure in the system. However, even in experiments at relatively high pressures (200 Torr), no evidence has ever been found for collisional stabilization of parent neopentane ions.[3]

In addition to process 1, a fraction of the parent ions undergo the four-center molecular elimination process

$$(CH_3)_4C^+ \longrightarrow i\text{-}C_4H_8^+ + CH_4 \quad (2)$$

In the 70-eV mass spectrum of neopentane, as well as in the γ-ray irradiation at pressures up to 200 Torr, 2–3% of the parent ions dissociate through process 2.[3]

In a recent gas-phase radiolysis study[3] in which neopentane was irradiated in the presence of various alkanes, it was demonstrated that the *tert*-butyl ions formed in fragmentation process 1 undergo the hydride (or deuteride) transfer reaction(s)



$$(CH_3)_3C^+ + R\!-\!\underset{H}{\overset{R'}{C}}\!-\!R'' \left(R\!-\!\underset{D}{\overset{R'}{C}}\!-\!R'' \right) \longrightarrow (CH_3)_3CH\ ((CH_3)_3CD) + R\!-\!\underset{+}{\overset{R'}{C}}\!-\!R'' \quad (3)$$

The *tert*-butyl ion does not react with neopentane itself; in fact, reaction 3 occurs at a measurable rate only with compounds containing a tertiary hydrogen (deuterium) atom.[3]

In the liquid phase, where ions are produced in a medium of high density compared to the gas phase, it is generally believed that in most cases parent hydrocarbon ions undergo fragmentation to only a minor extent,[4] if at all. However, because of the exceptional instability of the parent neopentane ion in the gas phase, it was suggested some time ago[5] that even in the liquid phase, this ion might dissociate appreciably. The occurrence of ionic fragmentation process 1 has also been invoked[4] to explain the observed imbalance in yields between the methyl radicals and *tert*-butyl radicals [$G(CH_3) > G(tert\text{-}C_4H_9)$] in the liquid-phase radiolysis of neopentane. More recently, Ward and Hamill[6] irradiated neopentane in the liquid phase in the presence of ethanol and observed the formation of *tert*-butyl ethyl ether. This they explained by the occurrence of the well-known reaction sequence

$$(CH_3)_3C^+ + C_2H_5OH \longrightarrow (CH_3)_3COC_2H_5 + H^+ \quad (4)$$

Other investigators[7] have also proposed the occurrence of process 1 in the liquid phase on the basis of products observed in the presence of electron scavengers and proton acceptors. However, in none of the previous experimental studies was any evidence obtained for the presence of isobutylene ions in the liquid-phase radiolysis of neopentane.

This paper reports the results of an investigation in which the fragmentation of the neopentane ion and the reaction kinetics of the fragment ions in the liquid phase have been examined through the ion interception techniques which were used in the gas-phase study of neopentane.[3] That is, neopentane has been irradiated in the presence of additives which are known to undergo reaction with *tert*-butyl ions (such as reaction 3), as

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[1] (a) This research was supported by the U. S. Atomic Energy Commission; (b) guest worker, 1968–1969.

[2] H. D. Beckey, *Z. Naturforsch. A*, **16**, 505 (1961).

[3] P. Ausloos and S. G. Lias, *J. Amer. Chem. Soc.*, **92**, 5037 (1970).

[4] (a) R. A. Holroyd in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968, p 426; (b) R. A. Holroyd and G. W. Klein, *J. Amer. Chem. Soc.*, **87**, 4983 (1965); (c) R. A. Holroyd, *J. Phys. Chem.*, **65**, 1352 (1961).

[5] T. F. Williams, *Trans. Faraday Soc.*, **57**, 755 (1961).

[6] J. A. Ward and W. H. Hamill, *J. Amer. Chem. Soc.*, **89**, 5116 (1967).

[7] K. Tanno, T. Miyazaki, K. Shinsaka, and S. Shida, *J. Phys. Chem.*, 71, 4290 (1967).

Table I. Yields of Products Formed in the Radiolysis of Neo-C_5H_{12} in the Liquid Phase

Additive, %	Scavenger	CCl_4, %	Molecules per 100 eV absorbed by neopentane					
			Methane	Isobutylene	Isobutane	Ethane	*tert*-Butyl chloride	Propylene
None	None	0	4.4	1.4	0.43	0.33	0.00	0.12
None[a]	None	0	(3.7)	(1.6)	(0.45)	(0.45)		(0.18)
None	O_2	0	1.2	1.7	0.05	0.24	0.00	0.16
None[a]	I_2	0	(1.7)	(1.2)	(0.12)	(0.35)	0.00	(0.14)
None	O_2	3	1.1	0.83	0.09	0.24	1.4	0.05
N_2O, 3	O_2	3	1.1	1.1	0.06	0.18	0.33	
NH_3, 3	O_2	3	1.1	2.6	0.05	0.24	0.0	0.05
$(CH_3)_2NH$, 7	O_2	3	1.1	1.8	0.01	0.11	0.0	
CH_3OH, 5	O_2	3	1.0	0.01	0.04	0.25	0.11	0.10

[a] Values in parentheses from ref 4c.

well as with isobutylene ions, and the neutral products have been analyzed. Although indirect, end-product analysis is indeed still the only method available for the study of ion-molecule reactions in the condensed-phase radiolysis of saturated hydrocarbons.

Previous studies in this series[8] reported the observation of reactions between parent alkane ions and added olefinic molecules in the liquid-phase radiolysis of hydrocarbons. This investigation is an attempt to extend our knowledge of ion-molecule reaction kinetics in the liquid-phase radiolysis to alkyl ions and olefin ions.

Experimental Section

The samples were irradiated in the 50,000-Ci National Bureau of Standards cobalt-60 γ-ray source. At the time these experiments were performed, the rate of energy absorption by neopentane was 0.6×10^{19} eV/(mol sec). The irradiation and analytical procedures used in this study have been described previously,[8] as have the compounds used and the purification procedures which were followed.[3] The relative amounts of different deuterated isobutane products (i-C_4H_{10}, i-C_4H_9D, i-$C_4H_8D_2$, etc.) were, as before,[3] determined mass spectrometrically using standard cracking patterns.

All irradiations were carried out at a temperature of 300°K, except where otherwise specified. In most experiments, it will be noted, oxygen was added to the reaction vessel as a radical scavenger. This was accomplished by introducing 100 Torr of oxygen, measured at 77°K, into the reaction vessel containing the frozen reaction mixture. After the reaction vessels were sealed and the samples warmed to 300°K, part of the oxygen was dissolved in the sample by shaking the vessel vigorously. The solubility of oxygen in hydrocarbon under these conditions is about 0.3 mol %.[9] It should be noted that a change in the pressure of oxygen from 10 to 200 Torr had no effect on the yield or isotopic composition of the isobutane and *tert*-butyl chloride fraction in a $(CH_3)_4C$–c-C_5D_9-(CD_3) (1:0.3) mixture containing 3% CCl_4. It will be shown that these products originate in ionic processes; therefore, the fact that it is unaffected by changes in oxygen concentration indicates that, at least in the presence of CCl_4, the oxygen functions mainly as a radical scavenger.

Results

In the Discussion, the product yields are expressed as *G* values, in terms of the energy absorbed by neopentane only. For mixtures, the assumption is tentatively made that initial energy absorption is partitioned between two or more components according to their electron fractions.

In the radiolysis of a neo-C_5H_{12}–neo-C_5D_{12}–CCl_4 (1:1:0.1) mixture in the presence of O_2, 88% of the propylene consists of C_3H_6 and C_3D_6. The remaining propylene is C_3H_5D and C_3D_5H.

In the same experiment the *tert*-butyl chloride consists of *tert*-C_4D_9Cl (35.7%) and *tert*-C_4H_9Cl (64.3%).

In the irradiation of neo-C_5H_{12} in the presence of 5% of an equimolar i-C_5D_{12}–i-C_5H_{12} mixture, the isobutane consisted of $(CH_3)_3CH$ (58.1%), $(CH_3)_3CD$ (2.3%), and $(CH_3)_2CDCH_2D$ (39.6%).

Discussion

In the radiolysis of *pure* neopentane, the *G* values of the major products observed in this study are in reasonable agreement with those reported earlier (Table I). As pointed out before,[4] the occurrence of reactions in and outside the spur, involving H atoms, CH_3, *tert*-C_4H_9, and C_5H_{11} radicals, can explain the formation of most of the alkane products. Because the emphasis in this paper is on ion-molecule reactions, we will not elaborate further on the free-radical mechanisms; for information about these reactions, the reader is referred to the excellent account by Holroyd.[4] The addition of oxygen has the effect of inhibiting those radical reactions which occur outside the spur. In particular, the pronounced reduction in the yields of methane and isobutane can be ascribed to the removal of the *tert*-C_4H_9 and CH_3 radicals by O_2. The residual methane, formed in the presence of oxygen, originates largely in unimolecular dissociation or cage disproportionation processes, as indicated by the predominance of CD_4 and CH_4 in the methane formed in a neo-C_5D_{12}–neo-C_5H_{12}–O_2 mixture (Table II).

Table II. Radiolysis of Neo-C_5H_{12}–Neo-C_5D_{12} (1:1). Isotopic Distributions of Methane Products[a]

CCl_4, %	Total methane yield	% distribution				
		CD_4	CD_3H	CD_2H_2	CH_3D	CH_4
0	1.2	34.6	9.9	1.0	5.9	49.5
4	1.1	29.5	10.4	0.0	5.7	54.4

[a] O_2 present in all experiments.

The Isobutylene Ion. As mentioned above, when O_2 is added to pure neopentane, the *tert*-C_4H_9 radicals are intercepted, and the yield of the isobutane product is diminished to a value of 0.05. However, when the neo-C_5H_{12} mixture is irradiated in the presence of methylcyclopentane-d_{12}, the yield of isobutane is augmented and increases with increasing concentration of methylcyclopentane-d_{12}. Most of this isobutane (Figure 1) is

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(8) (a) A. A. Scala, S. G. Lias, and P. Ausloos, *J. Amer. Chem. Soc.*, **88**, 5701 (1966); (b) P. Ausloos, A. A. Scala, and S. G. Lias, *ibid.*, **89**, 3677 (1967).

(9) C. B. Kretschmer, J. Nowa Kawska, and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946).

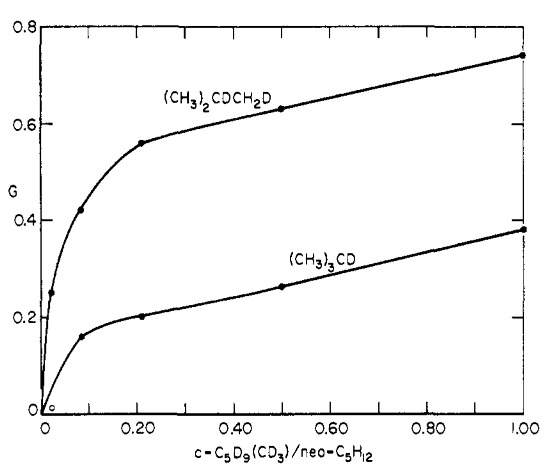

Figure 1. Yields of $(CH_3)_2CDCH_2D$ and $(CH_3)_3CD$ formed in neo-C_5H_{12}-c-$C_5D_9(CD_3)$ mixtures as a function of c-$C_5D_9(CD_3)$ concentration. The experiments were performed in the presence of 2.7% CCl_4 and ~0.3% dissolved oxygen.

seen to have the isotopic structure $(CH_3)_2CDCH_2D$, which suggests that it was formed in a reaction in which a D_2 species was transferred to a $(CH_3)_2C{=}CH_2$ entity. (Figure 1 also shows that $(CH_3)_3CD$ is formed in such mixtures; the formation of this product will be discussed later.) One likely mode of formation of the $(CH_3)_2CDCH_2D$ is the D_2^- reaction[10] between i-$C_4H_8^+$ ions[11] and c-$C_5D_9(CD_3)$

$$i\text{-}C_4H_8^+ + c\text{-}C_5D_9(CD_3) \longrightarrow (CH_3)_2CDCH_2D + C_5D_{10}^+ \quad (5)$$

In the gas phase, the rate constant for reaction 5 is 5.2×10^{-10} cm^3/(molecule sec).[10]

That the $(CH_3)_2CDCH_2D$ product was indeed formed in a reaction in which two D atoms are transferred to the isobutylene ion in one encounter was confirmed by an examination of the isotopic structure of the isobutane formed in the irradiation of neopentane in the presence of 5% of an i-C_5D_{12}-i-C_5H_{12} mixture (Results). This isobutane (which contains only about 2% $(CH_3)_3CD$) consists of $(CH_3)_3CH$ and $(CH_3)_2CDCH_2D$. This is what one would expect if this product was formed in the isobutylene ion reactions analogous to 5

$$i\text{-}C_4H_8^+ + i\text{-}C_5H_{12} \longrightarrow (CH_3)_3CH + C_5H_{10}^+ \quad (6)$$

$$i\text{-}C_4H_8^+ + i\text{-}C_5D_{12} \longrightarrow (CH_3)_2CDCH_2D + C_5D_{10}^+ \quad (7)$$

When carbon tetrachloride is added to a neo-C_5H_{12}-c-$C_5D_9(CD_3)$-O_2 mixture as an electron scavenger, the yield of $(CH_3)_2CDCDH_2$ is increased (Figure 2), indicating that this product does indeed have an ionic precursor. Earlier studies[8] have demonstrated that electron scavengers such as CCl_4 slow the neutralization process, and that, therefore, in their presence positive ions have a longer lifetime.

Assuming that the maximum yield of $(CH_3)_2CDCH_2D$ formed in neo-C_5H_{12} in the presence of 33% c-$C_5D_9(CD_3)$ (reaction 5) and 12% CCl_4 approximately represents the yield of isobutylene ions, we have from the data given in Figure 2

$$G(i\text{-}C_4H_8^+) \approx 0.9$$

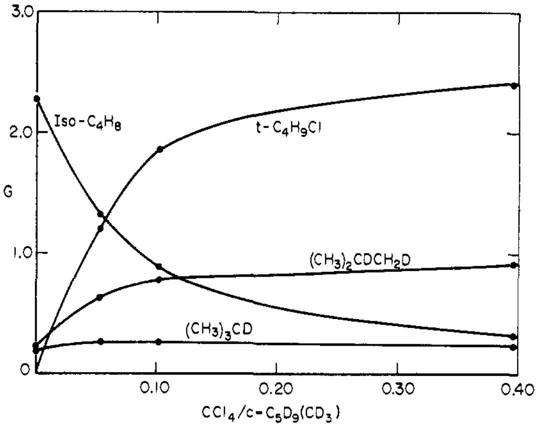

Figure 2. Yields of *tert*-butyl chloride, isobutylene, and isobutane products formed in the radiolysis of neo-C_5H_{12}-$C_5D_9(CD_3)$ (1:0.5) mixtures in the presence of 0.3% O_2 and varying amounts of CCl_4.

If isobutylene ions are formed exclusively in the parent-ion fragmentation process 2, one would expect one methane molecule to be formed for each isobutylene ion. The fraction of the methane product which is formed in unimolecular elimination processes can be estimated from the isotopic composition of the methane formed in neo-C_5D_{12}-neo-C_5H_{12}-O_2 mixtures (Table II). From these isotopic distributions and the methane yields shown in Table I, we obtain a maximum value for the yield of methane originating from unimolecular dissociation processes

$$G(CH_{4\text{unimolecular}}) \approx 0.7\text{-}0.8$$

Because it has recently been shown that in the liquid phase[12] about 25 eV is expended in the production of an ion pair in neopentane, the assumption that all the isobutylene ions and/or "unimolecular" methane can be attributed to process 2 would lead us to the conclusion that about 20% of the parent ions dissociate to form isobutylene ions. This estimate is unusually high when compared with the isobutylene ion yields (2-3%) observed in the gas-phase radiolysis of neopentane. Such four-center molecular elimination processes are usually effectively quenched[13] at high pressures or high densities such as those encountered in the liquid phase; such processes, even though they have low energy requirements,[14] occur from long-lived ions which must assume a constrained conformation before undergoing dissociation.

An alternate explanation for the high yield of isobutylene ions observed in the liquid-phase radiolysis of neopentane is the occurrence of a reaction in the spur between *tert*-butyl ions and methyl radicals.

$$(CH_3)_3C^+ + CH_3 \longrightarrow i\text{-}C_4H_8^+ + CH_4 \qquad \Delta H = -0.39 \text{ eV} \quad (8)$$

Since the yield we have attributed to isobutylene ions (0.9) is somewhat higher than the yield of methane which might originate from unimolecular processes (0.7-0.8), it is likely that a bimolecular process such as 8 does

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[10] (a) S. G. Lias and P. Ausloos, *J. Amer. Chem. Soc.*, **92**, 1840 (1970); (b) J. Herman, K. Herman, and P. Ausloos, *J. Chem. Phys.*, **52**, 28 (1970); (c) L. W. Sieck, S. K. Searles, and P. Ausloos, *J. Amer. Chem. Soc.*, **91**, 7627 (1969).

[11] The formation of $(CH_3)_2CDCH_2D$ through a reaction of the isobutylene product molecule with c-$C_5D_9(CD_3)^+$ ions can be excluded, since when 0.4% i-C_4D_8 was added to a neo-C_5H_{12}-c-$C_5D_9(CD_3)$-O_2 mixture, the isobutane still consisted mainly of $(CH_3)_2CDCDH_2$; only 5% of the isobutane consisted of i-C_4D_{10}.

[12] W. F. Schmidt, *Radiat. Res.*, **42**, 73 (1970).

[13] (a) P. Ausloos and S. G. Lias, *Actions Chim. Biol. Radiat.*, **11**, 1 (1967); (b) D. P. Stevenson, *Radiat. Res.*, **10**, 610 (1959).

[14] B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, **34**, 189 (1961).

contribute to the formation of these products, but it is impossible to assess the relative importance of processes 2 and 8.

Relative Rates of Reaction of Isobutylene Ions. Since the above results have indicated that isobutylene ions formed in neopentane are intercepted by added alkanes with which they can undergo a H_2^- (D_2^-) transfer reaction, it is possible to determine the relative rates of reaction of isobutylene ions with various alkanes in such experiments. Neo-C_5H_{12}–i-C_5D_{12}–CCl_4–O_2 mixtures were irradiated in the presence of nondeuterated hydrocarbons. The isobutylene ions will undergo reaction with the i-C_5D_{12} to form i-$C_4H_8D_2$ as a product (reaction 7) and reaction with the nondeuterated alkane additive to form i-C_4H_{10}

$$i\text{-}C_4H_8^+ + RH_2 \longrightarrow (CH_3)_3CH + R^+ \qquad (9)$$

The concentrations of the reactive additives, i-C_5D_{12} and RH_2, were kept low enough that more than 80% of the isobutane product originated from reactions 7 and 9. (That is, less than 20% of the isobutane in these experiments was formed in reactions of other species, to be discussed below.) Thus, the rates of reaction(s) 9 relative to reaction 7 are given simply by the ratios of the product isobutanes, i-C_4H_{10}/i-$C_4H_8D_2$, taking into account the relative concentrations of i-C_5D_{12} and RH_2 in the particular mixture. Table III gives the values of k_9/k_7 derived from such experiments. These relative rates are compared with those observed in the gas phase.[10]

Table III. Relative Rates of Reaction of Isobutylene Ions with Various Alkanes[a]

RH_2	RH_2/ i-C_5D_{12}	k_9/k_7 (liquid)	k_9/k_7 (gas)[b]	ΔH, eV, reaction 9 (gas)
n-C_6H_{14}	1.62	~0.042	0.4	
c-C_5H_{10}	5.03	~0.097	0.7	−0.29
c-C_6H_{12}	5.00	0.17	n.d.	−0.55
i-C_5H_{12}	0.83	1.5	1.5	−0.66
$(CH_3)_2CHCH_2CH_2CH_3$	0.64	1.6	n.d.	
c-$C_5H_9(CH_3)$	0.49	2.2	2.5	
$(CH_3)_2CHCH(CH_3)_2$	0.41	2.6	n.d.	−1.0

[a] 2.7% CCl_4 and O_2 added in all experiments. [b] Data from ref 10b.

The results given in Table III show that the trends in the rates of reaction 9 for various alkane molecules are the same in the liquid and in the gas phase. It is interesting that the relative rates seem to follow exactly the same trends as the gas-phase exothermicities of the H_2^- transfer reactions.[15]

The *tert*-Butyl Ion. As mentioned before, the rate of reaction of the *tert*-butyl ion with saturated hydrocarbons (reaction 3) is, in the gas phase,[3] generally an order of magnitude or more slower than the reaction of the butene ion. Therefore, we anticipate that in the liquid phase a considerably higher concentration of a reactive alkane will be needed to intercept *tert*-butyl ions quantitatively than would be the case for the isobutylene ion. The results given in Figure 1 do show an increase in the yield of isobutane-d_1 with increasing amounts of methylcyclopentane-d_{12}. However, although this product may indeed[3] be formed in the hydride transfer reaction

$$(CH_3)C^+ + c\text{-}C_5D_9(CD_3) \longrightarrow (CH_3)_3CD + C_6D_{11}^+ \qquad (10)$$

its yield even at relatively high concentration of methylcyclopentane is considerably below the yield of the *tert*-butyl ions estimated on the basis of previous studies,[4,6,7] or on the basis of some of the results given in Table I. For example, when ammonia or dimethylamine is added to neopentane, the *tert*-butyl ions would be expected to undergo the very efficient proton transfer reaction

$$(CH_3)_3C^+ + NH_3 \longrightarrow (CH_3)_2C{=}CH_2 + NH_4^+ \qquad (11)$$

or

$$(CH_3)_3C^+ + (CH_3)_2NH \longrightarrow (CH_3)_2C{=}CH_2 + (CH_3)_2NH_2^+ \qquad (12)$$

The results given in Table I show that in the presence of 2.3% CCl_4 (which, as mentioned above, would increase the lifetime of positive ions in the system), the yield of isobutylene is increased from 0.8 to 2.6 in the presence of ammonia, or to 1.8 in the presence of dimethylamine.

The question should then be asked as to what the actual fate of the *tert*-butyl ion in the irradiated neopentane–methylcyclopentane mixture is. Some information about this may be obtained from the results given in Figure 2, where it is shown that when CCl_4 is added to the reaction mixture, $(CH_3)_3CCl$ appears as a product. The yield of the *tert*-butyl chloride increases with increasing CCl_4 concentration to a value of 2.4 when the ratio CCl_4/c-$C_5D_9(CD_3)$ is 0.4. It is clear that this product is not formed by a free-radical mechanism because the experiments were carried out in the presence of oxygen, which, as shown above, seems to effectively inhibit product formation through free-radical reactions. Furthermore, as indicated in the Results section, a variation in the concentration of oxygen has no effect on the yield of this product. The *tert*-butyl chloride also cannot originate from reactions involving butene ions in view of the fact that the yield of $(CH_3)_2CDCH_2D$ is not diminished upon addition of CCl_4. The effects of various additives on the yield of this product indicate that it indeed originates in a reaction of the *tert*-butyl ion. For example, in the presence of ammonia or dimethylamine, which intercept *tert*-butyl ions through reactions 11 or 12, respectively, the formation of *tert*-butyl chloride is entirely inhibited. Also, in the presence of 5% methanol, which is known to react with *tert*-butyl ions

$$(CH_3)_3C^+ + CH_3OH \longrightarrow (CH_3)_3COCH_3 + H^+ \qquad (13)$$

the yield of *tert*-butyl chloride is strongly diminished. In addition, if this product indeed originates from a reaction of the *tert*-butyl ion, the *tert*-butyl chloride formed in a mixture of neo-C_5H_{12}–neo-C_5D_{12}–CCl_4–O_2 should consist entirely of *tert*-C_4D_9Cl and *tert*-C_4H_9Cl, as it does (Results).

The formation of *tert*-butyl chloride in a reaction between CCl_4 and the *tert*-butyl ion

$$(CH_3)_3C^+ + CCl_4 \longrightarrow (CH_3)_3CCl + CCl_3^+ \qquad (14)$$

is energetically unfavorable (1.2 eV endothermic in the gas phase) and, therefore, can be ruled out. In fact,

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(15) Although the absolute exothermicities of these reactions will be different in the liquid and the gas phase, it is reasonable to assume that the trends in the ΔH values will be the same in the two phases. Only those gas-phase exothermicities are given for which reliable thermodynamic data have been reported in a recent compilation: J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Rev. Data Ser., Nat. Bur. Stand.*, 26 (1969).

all the experimental evidence points to the formation of this product in a reaction between the *tert*-butyl ion and a negative ion formed from CCl_4

$$(CH_3)_3C^+ + CCl_4^-(Cl^-) \longrightarrow (CH_3)_3CCl + CCl_3 \qquad (15)$$

When N_2O is added (Table I), it competes with CCl_4 for the electrons. Thus, the fact that the yield of *tert*-butyl chloride is diminished when N_2O is added indicates that it is indeed the negative ion formed from CCl_4 which participates in the reaction to form *tert*-butyl chloride.

In an earlier study of the liquid-phase radiolysis of neopentane,[7] methylamine was added to neopentene as a proton acceptor, and the increment in isobutylene, traceable to the occurrence of the reaction

$$(CH_3)_3C^+ + CH_3NH_2 \longrightarrow (CH_3)_3CH + CH_3NH_3^+ \qquad (16)$$

was taken as the yield of the *tert*-butyl ion. The value obtained was $G(tert\text{-}C_4H_9^+) = 1.0$, a value which is lower than the estimated yield presented here. However, at high densities, proton transfer from a *tert*-butyl ion to an amine is not necessarily the only mode of reaction between these partners. This is demonstrated by the fact (Table I) that the yield of isobutylene formed in the presence of $(CH_3)_2NH$ (reaction 12) is not as high as that formed when ammonia is added (reaction 11). In fact, the increment in isobutylene observed in the presence of dimethylamine is 1.0, in agreement with the increment observed in the earlier study in the presence of methylamine.[7] Actually, the increment in the isobutylene yield observed in the presence of CH_3NH_2 would not be expected to give an accurate measure of the *tert*-butyl ion yield, since the isobutylene ion can be expected to transfer its charge to methylamine

$$i\text{-}C_4H_8^+ + CH_3NH_2 \longrightarrow (CH_3)_2C{=}CH_2 + CH_3NH_3^+ \quad \Delta H = -0.28 \text{ eV} \qquad (17)$$

The maximum value for $G(C_4H_9Cl)$ obtained in our study is, however, in good agreement with the maximum G value of 1.9 obtained for the yield of $(CH_3)_3COC_2H_5$ in the radiolysis of neopentane–ethanol mixtures.[6]

Yields of Fragment Ions in Neopentane. If we now add up the maximum yields of products (Figure 2) which can be attributed to ionic precursors in these experiments (*i.e.*, *tert*-butyl chloride, isobutanes) we have

$$\Sigma G(\text{ion}) = 3.3\text{–}3.5$$

Then, since ions are formed in liquid neopentane with a G value of about 4.0, this result means that about 85% of the ions formed in neopentane are intercepted under optimum conditions. The ions we have accounted for are all fragment ions (or originate from fragment ions). Presumably, in the liquid, as in the gas phase, all, or nearly all, neo-$C_5H_{12}^+$ ions undergo fragmentation.

Further evidence that this is the case is provided by the fact that the yield of methane is not much affected by the presence of CCl_4 in the reaction vessel (Table I). This means that methane and isobutylene formation does not follow neutralization of the parent ion

$$(CH_3)_4C^+ + e \longrightarrow (CH_3)_2C{=}CH_2 + CH_4 \qquad (18)$$

Neutralization Processes of Fragment Ions. The yields of isobutylene and propylene (Table I) are strongly diminished by increasing concentrations of CCl_4. It is known that in the presence of an electron scavenger, the yields of products resulting from electron recombination processes will be diminished. Therefore, we can conclude that isobutylene and propylene are formed in such processes. Since the results given here indicate that all, or nearly all, of the parent neopentane ions dissociate (reactions 1 and 2) in the liquid-phase radiolysis of neo-C_5H_{12}, the neutralization of *tert*-butyl and/or isobutylene ions must lead to the formation of some of the observed products. It is likely that the propylene is formed in a dissociation of excited *tert*-butyl radicals formed by neutralization of *tert*-butyl ions

$$tert\text{-}C_4H_9^+ + e \longrightarrow tert\text{-}C_4H_9^* \qquad (19)$$

$$tert\text{-}C_4H_9^* \longrightarrow C_3H_6 + CH_3 \qquad (20)$$

(This propylene is indeed molecular, as indicated by the isotopic distribution of the propylene formed in neo-C_5D_{12}–neo-C_5H_{12} mixtures, given in the Results section.) The formation of propylene through a secondary decomposition of excited *tert*-butyl radicals (reaction 20) has been noted in the gas-phase photolysis of neopentane.[16] Reaction 20 has also been proposed as a mode of decomposition of vibrationally excited *tert*-C_4H_9 radicals formed in other systems.[17] Also, since *tert*-butyl radicals are observed in irradiated neopentane with a G value of 0.55, it is likely that some of the excited radicals formed in reaction 19 may be stabilized. In addition, the diminution in the yield of isobutylene with an increase in the CCl_4 concentration, both in pure neopentane (Table I) and in neopentane–methylcyclopentane mixtures (Figure 2), indicates that the neutralization of *tert*-butyl ions may lead to the formation of isobutylene

$$tert\text{-}C_4H_9^* \longrightarrow C_4H_8 + H \qquad (21)$$

The isobutylene yield in experiments carried out in the absence of CCl_4 is lower than the estimated *tert*-butyl ion yield, as one would expect if some of the excited *tert*-butyl radicals are stabilized and some dissociate to form propylene (reaction 20).

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(17) J. A. Kerr and A. C. Lloyd, *Quart. Rev., Chem. Soc.*, **22**, 549 (1968).