Carbonium Ions in Radiation Chemistry. Reactions of *t*-Butyl Ions with Hydrocarbons[1]

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Abstract: *t*-Butyl ions, generated by the γ irradiation of neopentane, undergo hydride transfer reactions with alkanes having tertiary hydrogen atoms ($t\text{-}C_4H_9^+ + RH \rightarrow i\text{-}C_4H_{10} + R^+$) to form isobutane and a tertiary carbonium ion as products. By irradiating neopentane in the presence of mixtures of two reactant molecules, one deuterated and one nondeuterated, the relative rates of the hydride transfer reaction for 22 C_5–C_8 alkanes were determined with an unusually high accuracy, from the observed ratios of $i\text{-}C_4H_9D$ to $i\text{-}C_4H_{10}$. Absolute rate constants for the reactions, based on a determination of the rate of depletion of the isobutane yield when ammonia is added, are given. The rate constants are generally very low [10^{-11}–10^{-10} cm^3/(molecule sec)], but are shown to depend on the heat of reaction and steric factors involving van der Waals interactions between the approaching ion and hydrogen atoms or methyl groups on the carbon atom β to the tertiary carbon. The evidence indicates that the hydride transfer reactions of the *t*-butyl ion have an activation energy, $E_{act} \leq 0.15$ eV. In another series of experiments, unsaturated hydrocarbons were added to neopentane–isopentane mixtures, and the rates of the condensation reaction of these additives with *t*-butyl ions were determined by measuring the rate of depletion of the isobutane yield. The rate constants for the condensation reactions are in the range 10^{-10}–10^{-9} cm^3/(molecule sec). Some insight into processes occurring in the radiolysis of neopentane can be gained from these results. It is shown, for example, that in the absence of reactive additives, not more than about 14% of the *t*-butyl ions undergoes processes resulting in the formation of isobutene.

The hydride transfer reactions of small alkyl ions such as $C_2H_5^+$ and $C_3H_7^+$ with alkanes have been studied extensively.[2a–c] In addition, proton transfer and condensation reactions of these ions with unsaturated hydrocarbons and inorganic molecules such as ammonia are well known.[2a–c]

The *t*-butyl ion is less reactive than the normal and secondary C_1–C_4 carbonium ions;[2] the hydride transfer reactions between the *t*-butyl ion and alkane molecules

$$t\text{-}C_4H_9^+ + RH_2 \longrightarrow i\text{-}C_4H_{10} + RH^+ \qquad (1)$$

are endothermic for many alkanes, and therefore do not occur at a rate great enough to compete with homogeneous or heterogeneous neutralization of the ion. Indeed, in an earlier study from this laboratory of the radiolysis of neopentane,[3] we failed to observe any isobutane from reaction 1 in pure neopentane or in neopentane–cyclohexane mixtures, even though the *t*-butyl ion is the major fragment ion formed in the dissociation of the neopentane ion

$$neo\text{-}C_5H_{12}^+ \longrightarrow t\text{-}C_4H_9^+ + CH_3 \qquad (2)$$

($M[t\text{-}C_4H_9+]/N^+$ in the 70-eV mass spectrum, 0.41).

Recently, a high-pressure mass spectrometric study[4] appeared in which the reactions of *t*-butyl ions with olefins were explored. In addition, a rate constant of 10^{-11} cm^3/(molecule sec) was determined for the hydride transfer reaction (reaction 1) between the *t*-butyl ion and 2,2,4-trimethylpentane. Another study concerning the gas-phase radiolysis of neopentane[5] has showed that *t*-butyl ions transfer a proton to ammonia.

Since the earlier study[3] of the radiolysis of neopentane was performed in this laboratory, our sophistication, in both experimental techniques and in the understanding of ion–molecule reaction mechanisms, has increased greatly. We therefore felt that a systematic examination of the ion–molecule reactions of the *t*-butyl ion might prove fruitful at this time. It was expected, for example, that the rate of the hydride transfer reaction between the *t*-butyl ion and larger alkanes containing a tertiary hydrogen atom might be measured precisely using the technique of end product analysis in deuterium-labeled mixtures.[2b] Variations in the observed rates with the structures of the reacting molecules should yield information about the rate controlling factors of such reactions. In addition, a further exploration of the rates of reaction of this ion with unsaturated hydrocarbons and with ammonia would complement the information on these systems in the literature.

Experimental Section

All undeuterated hydrocarbons used in this study were American Petroleum Institute standard samples which were of sufficiently high purity that no further purification was necessary. All isotopically labeled materials used in this study were purified by gas chromatography and low-temperature distillation. The $neo\text{-}C_5D_{12}$ contained 8% $C_5D_{11}H$; $i\text{-}C_5D_{12}$ contained 6% $i\text{-}C_5D_{11}H$. Mass spectrometric analysis indicated that at least 95% of the 2-methyl butane-2-d_1 and 3-methyl pentane-3-d_1 was correctly labeled with the deuterium atom at the tertiary position.

The samples were irradiated in the NBS high-intensity ^{60}CO γ-ray source, which, at the time these experiments were performed, had an intensity of 0.3915×10^{-6} eV sec^{-1} electron^{-1}.

The irradiation and analytical procedures were identical with those described before.[3] The relative amounts of different deuterated isobutane products ($i\text{-}C_4H_{10}$, $i\text{-}C_4H_9D$, $i\text{-}C_4H_8D_2$, etc.) were determined mass spectrometrically using standard cracking patterns.

Results

Relative rates of reaction of the *t*-butyl ion with saturated alkanes were determined in this study using the technique of competitive reaction.[2b] Neopentane ions,

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(1) This research was supported by the Atomic Energy Commission.

(2) (a) F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. React. Kinet.*, **1**, 67 (1961); (b) P. Ausloos, *ibid.*, **5**, 113 (1969); (c) J. H. Futrell and T. O. Tiernan, "Fundamental Processes in Radiation Chemistry," Wiley, New York, N. Y., 1968, p 171; (d) F. W. Lampe and F. H. Field, *J. Amer. Chem. Soc.*, **81**, 3238 (1959).

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(5) T. Miyazaki and S. Shida, *Bull. Chem. Soc. Jap.*, **39**, 2344 (1966).

Table I. Isobutane Formed in the Radiolysis of *neo*-C_5H_{12}–*i*-C_5D_{12} Mixtures in the Presence of Hydrocarbon Additives[a]

i-C_5D_{12} pressure, Torr	Additive	Relative yields			
		CH_2DCD-$(CH_3)_2$	$(CH_3)_3CD$	$(CH_3)_3CH$	k_1/k_3[b]
11.2	None	0.067	1.00		
4.0	*c*-C_6H_{12}, 38.8	0.14	1.00	0.066	<0.0068
2.0	$(CH_3)_3CCH_2CH_3$, 100.4	1.35	1.00	0.38	<0.0075
3.5	*n*-C_5H_{12}, 57.1	0.17	1.00	0.43	<0.026
3.0	*n*-C_6H_{14}, 38.8	0.080	1.00	0.68	<0.053
17.0	$(C_2H_5)_2CHCH_3$, 10.0	0.057	1.00	1.04	1.77
0	$(C_2H_5)_2CHCH_3$, 10.0 + $(C_2H_5)_2CDCH_3$, 10.0	0.015	1.00	1.64	
2.3	$(CH_3)_3CCH(CH_3)_2$, 2.3	0.10	1.00	2.10	2.10
15.4	*c*-$C_5H_9(CH_3)$, 3.0	0.091	1.00	0.92	4.72
19.7	*c*-$C_5H_9(CH_3)$, 18.1	0.20	1.00	4.48	4.88
19.7	$(CH_3)_2CHCH(CH_3)_2$, 10.0	0.15	1.00	3.53	6.95

[a] All experiments contain 39 Torr of *neo*-C_5H_{12} and 5% NO or O_2 radical scavenger. [b] $[i\text{-}C_4H_{10}]/[i\text{-}C_4H_9D][i\text{-}C_5D_{12}]/[\text{additive}]$.

Table II. Isobutane Formed in the Radiolysis of *neo*-C_5H_{12}–*c*-$C_5D_9(CD_3)$ Mixtures in the Presence of Hydrocarbon Additives[a]

c-$C_5D_9(CD_3)$ pressure, Torr	Additive	$CH_2DCD(CH_3)_2$	$(CH_3)_3CD$	$(CH_3)_3CH$	k_1/k_3[b]
7.0	*c*-$C_5H_9(CH_3)$, 7.0	0.057	1.00	1.67	1.67
7.0	$(CH_3)_2CHCH_2CH_3$, 10.0	0.043	1.00	0.82	0.57
7.0	$(C_2H_5)_2CHCH_3$, 10.0	0.035	1.00	0.87	0.61
7.0	$(C_2H_5)_3CH$, 11.0	0.047	1.00	0.91	0.58
7.0	$(CH_3)_2CHCH_2CH_2CH_3$, 10.0	0.046	1.00	1.26	0.88
7.0	$C_2H_5CH(CH_3)CH_2CH_2CH_3$, 10.0	0.043	1.00	1.47	1.03
5.0	$(CH_3)_2CHCH(CH_3)CH(CH_3)_2$, 4.0	0.034	1.00	0.44	0.56
7.0	$(CH_3)_2CHCH(CH_3)CH(CH_3)_2$, 7.0	0.031	1.00	0.55	0.55
5.0	$(CH_3)_3CCH_2CH(CH_3)_2$, 4.0	0.058	1.00	0.10	0.13
7.0	$(CH_3)_2CHCH_2CH(CH_3)_2$, 10.1	0.036	1.00	0.68	0.47
8.0	$(C_2H_5)CH(CH_3)CH_2CH_2CH_2CH_3$, 10.75	0.058	1.00	2.55	1.90

[a] All experiments contain 50 Torr of *neo*-C_3H_{12} and 5% NO or O_2 radical scavenger. [b] $[i\text{-}C_4H_{10}]/[i\text{-}C_4H_9D][c\text{-}C_5D_9(CD_3)]/[\text{additive}]$.

generated in neopentane by high-energy irradiation, undergo fragmentation reaction 2 to form *t*-butyl ions. As mentioned above, *t*-butyl ions are unreactive toward the neopentane molecules. Therefore, if two alkanes, one deuterated and one nondeuterated, are mixed with the neopentane, the *t*-butyl ions will undergo reaction 1 with the nondeuterated compound and reaction 3 with the deuterated compound. The relative rate of reac-

$$(CH_3)_3C^+ + R'D_2 \longrightarrow (CH_3)_3CD + R'D^+ \qquad (3)$$

tion 1 *vs.* reaction 3, then, is simply given by

$$k_1/k_3 = \{(CH_3)_3CH/(CH_3)_3CD\}[R'D_2]/[RH_2] \qquad (I)$$

provided that $(CH_3)_3CH$ and $(CH_3)_3CD$ are formed only in reactions 1 and 3.

It should be mentioned that these experiments are performed in the presence of a free-radical scavenger, O_2, so that no isobutane is formed as a result of radical reactions. Besides reactions 1 and 3 of the *t*-butyl ion, the only sources of isobutane in these experiments are reactions of *i*-$C_4H_8^+$ ions[2a–c]

$$i\text{-}C_4H_8^+ + RH_2 \longrightarrow i\text{-}C_4H_{10} + R^+ \qquad (4)$$

$$i\text{-}C_4H_8^+ + R'D_2 \longrightarrow i\text{-}C_4H_8D_2 + R'^+ \qquad (5)$$

Although the product formed in reaction 4 cannot be distinguished from that formed in reaction 1, and relative rates of reaction of the *i*-$C_4H_8^+$ ions with the various alkanes considered here are not known, the fact that in most experiments the *i*-$C_4H_8D_2$ (reaction 5) makes up only about 2% of the total isobutane (see Tables I and II) allows us to assume that any contributions of reaction 4 to the *i*-C_4H_{10} yield will be small. The validity of this assumption was confirmed for at least one case by irradiating the same alkane mixture $[(CH_3)_2CHCH_2CH_3 + c\text{-}C_5D_9(CD_3)]$ in the presence of nondeuterated (Table II) and deuterated neopentane (Table III). In the latter case, reactions of the *t*-$C_4D_9^+$ ion

Table III. Isobutane Formed in the Radiolysis of *neo*-C_5D_{12}–*c*-$C_5D_9(CD_3)$ Mixtures in the Presence of Hydrocarbon Additives[a]

c-C_5D_9-(CD_3) pressure, Torr	Additive	$(CD_3)_3$-CD	$(CD_3)_3$-CH	k_6/k_7[b]
7.0	$(CH_3)_2CHCH_2CH_3$, 10.0	1.00	0.82	0.59
9.1	$(CH_3)_2CHCH_2CH(CH_3)$-C_2H_5, 12.3	1.00	0.95	0.74
9.0	$C_2H_5CH(CH_3)CH(CH_3)$-C_2H_5, 12.3	1.00	1.78	1.38
7.0	$(CH_3)_2CHCH_2CH_2CH_2$-CH_3, 10.0	1.00	2.05	1.53
9.0	$(CH_3)_2CHCH(CH_3)CH_2$-CH_2CH_3, 12.15	1.00	2.99	2.44
9.0	$(CH_3)_2CHCH_2CH_2CH$-$(CH_3)_2$, 12.0	1.00	3.03	2.51

[a] All experiments contain 50 Torr of *neo*-C_5D_{12} and 5% O_2 radical scavenger. [b] $[(CD_3)_3CH]/[i\text{-}C_4D_{10}][c\text{-}C_5D_9(CD_3)]/[\text{additive}]$.

$$(CD_3)_3C^+ + RH_2 \longrightarrow (CD_3)_3CH + RH^+ \qquad (6)$$

$$(CD_3)_3C^+ + R'D_2 \longrightarrow (CD_3)_3CD + R'D^+ \qquad (7)$$

lead to *i*-C_4D_9H and *i*-C_4D_{10}, while reactions of the *i*-$C_4D_8^+$ ion

$$\text{iso-}C_4D_8^+ + RH_2 \longrightarrow C_4D_8H_2 + R^+ \qquad (8)$$

$$\text{iso-}C_4D_8^+ + R'D_2 \longrightarrow C_4D_{10} + R'^+ \qquad (9)$$

lead to $C_4D_8H_2$ and C_4D_{10}, so that the product of reaction 4 in the first case shows up as the distinctive partially deuterated product, $C_4D_8H_2$, in the second case. The yield of this product was too small to be determined accurately, but was less than 2% of the total isobutane. Thus, in the relative rates listed in Tables I and II no correction has been made for i-C_4H_{10} originating from reaction 4; this means that these relative rates may be too high by 2–3%. In cases where the yield of i-C_4H_{10} from reaction 1 is very small, or where the yield of i-$C_4H_8^+$ ion is relatively large (as indicated by the observed i-$C_4H_8D_2$ yield), the relative rates of reaction 1, given in the last columns of Tables I and II, are not reliable, and should be regarded only as estimated maximum values. This is the case for the first four additive experiments listed in Table I.

Thus, in Table I are given the isotopic distributions of the isobutane products formed in a number of *neo*-C_5H_{12}–i-C_5D_{12}–RH_2–O_2 mixtures. In Table II, the isotopic distributions of the isobutane products formed in a series of *neo*-C_5H_{12}–c-$C_5D_9(CD_3)$–RH_2–O_2 mixtures are presented. In Table III are listed the results of experiments in which *neo*-C_5D_{12}–c-$C_5D_9(CD_3)$–RH_2–O_2 mixtures were irradiated. As mentioned above, in these last experiments i-C_4D_{10} will be formed in reaction 9 of the isobutene ion as well as in reaction 7 of the t-butyl ion. In the results presented in Tables I and II, the relative rates calculated according to eq I (listed in the last columns of the tables) will be a little too large because of the contributions of butene ion reactions to the C_4H_{10} yields; in the results presented in Table III, the relative rates are given by

$$k_6/k_7 = \{(CD_3)_3CH/(CD_3)_3CD\}[R'D_2]/[RH_2] \quad (II)$$

and thus will be too small if no correction is made for i-C_4D_{10} produced in reaction 9. An exact correction is impossible without further information, but since in the analogous experiments with undeuterated neopentane (Table II), the contribution of $C_4D_8H_2$ is always about 2% of the total isobutane produced, 2% of the total isobutane yield has been subtracted from the i-C_4D_{10} yield before calculating the relative rates of reaction given in the last column of the Table. This makes the comparison between the results given in Table III and those of Tables I and II somewhat better.

In cases where experiments on mixtures containing the same components at different concentrations were performed, it can be seen (Tables I and II) that the results are reproducible to within 3%. Where reaction with a given RH compound is compared to two different deuterated molecules (see 3-methylpentane and methylcyclopentane in Tables I and II), the observed relative rates given in the last column of the table, when corrected to the same base (see Discussion), agree within 2%. Similarly, when reaction of a deuterated t-butyl ion (Table III) is compared with reaction of a nondeuterated ion (Table II), the rates observed agree within 3%.

In the following discussion, product yields are given in units of $M(Y)/N_+$, or molecules of product Y formed per positive ion produced in neopentane. These values are obtained from the directly measured yields of product (in units of molecule cm^{-3} sec^{-1}, or molecules of product formed per second in one STP cm^3 of neopentane) by dividing by 18.5×10^{12} ions cm^{-3} sec^{-1}, the rate of ion formation in 1 cm^3 of neopentane, assuming W(neopentane) = 24 eV/N_+.

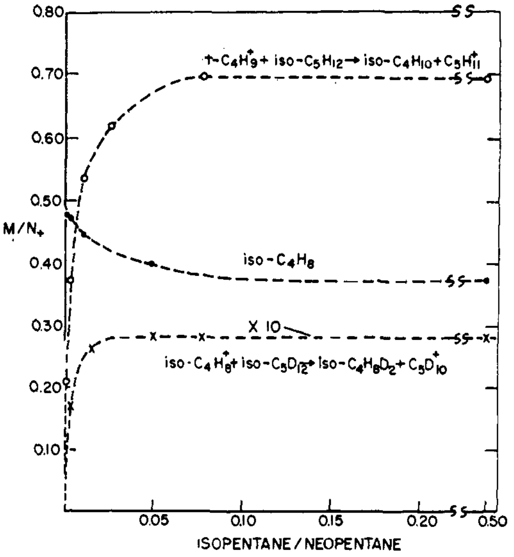

Figure 1. Variations in the yield of isobutene and of isobutane originating from reaction 11 as a function of isopentane concentration in *neo*-C_5H_{12}–i-C_5H_{12}–O_2 mixtures; also, the yield of i-$C_4H_8D_2$ (reaction 23) formed in *neo*-C_5H_{12}–i-C_5D_{12}–O_2 mixtures as a function of i-C_5D_{12} concentration. Pressure of *neo*-C_5H_{12} = 200 Torr in all experiments.

Discussion

Reaction of the t-C_4H_{9+} Ion with Isopentane. As mentioned above, an earlier attempt[3] to intercept the t-butyl ions formed in neopentane through reaction 1, with cyclohexane as RH_2, was unsuccessful. However, in view of the fact that molecules having tertiary hydrogen atoms are generally observed to undergo hydride transfer reactions more readily (as one would expect in view of the greater stability of the tertiary product ions over primary and secondary ions), we decided to irradiate neopentane in the presence of added isopentane. As expected, the irradiation of a *neo*-C_5H_{12}–$(CH_3)_2CDCH_2CH_3$–O_2 mixture (1:0.5:0.1) at 40 Torr resulted in the formation of $(CH_3)_3CD$ as a major product, $M/N_+ = 0.66$; the total amount of i-C_4H_{10} formed was approximately 5%, and could be accounted for by insufficient deuteration of the starting isopentane-d_1. This demonstrates not only that the hydride transfer reaction between the t-butyl ion and isopentane

$$(CH_3)_3C^+ + (CH_3)_2CDCH_2CH_3 \longrightarrow (CH_3)_3CD + C_5H_{11}^+ \quad (10)$$

occurs, but also that it involves the tertiary position of the molecule nearly exclusively.

Figure 1 shows the yield of isobutane, formed through the occurrence of reaction

$$(CH_3)_3C^+ + i\text{-}C_5H_{12} \longrightarrow (CH_3)_3CH + C_5H_{11}^+ \quad (11)$$

in mixtures of neopentane and O_2 with varying amounts of i-C_5H_{12} at a total pressure of 200 Torr. (The observed isobutane yields have been corrected for the presence of isobutane formed from i-$C_4H_8^+$ precursors.) It is seen that the measured yield of isobutane formed in reaction 11 is strongly influenced by the concentration of isopentane at isopentane concentrations lower than about 7 or 8%. This observation can be contrasted

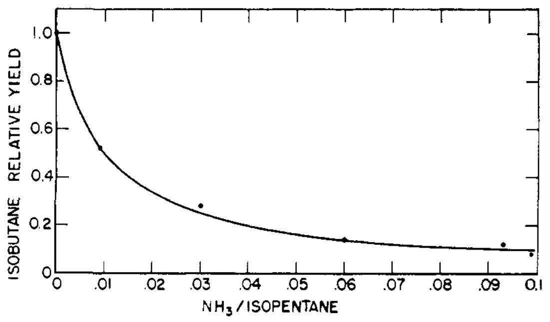

Figure 2. The relative yields of isobutane formed in the irradiation of a *neo*-C_5H_{12}–*i*-C_5H_{12}–O_2 (1:0.5:0.1) mixture in the presence of varying amounts of ammonia.

with results obtained in the radiolysis of methane,[6] where a similar situation prevails, namely that a major ion which is formed, $C_2H_5^+$, is unreactive with the parent compound; in that case, however, it was seen that nearly all of the unreactive ions were intercepted by as little as 0.01% of added higher hydrocarbon (propane, isobutane) with which the ion could undergo a hydride transfer reaction. It can only be concluded that reaction 11 of the *t*-butyl ion occurs at a much slower rate than the ethyl ion reactions occurring in the methane–alkane mixtures. Later in the discussion, we shall derive a rate for reaction 11 which indicates that only 1 collision in 100 is reactive.

The Rates of Reaction of *t*-Butyl Ions with Ammonia and Isopentane. The experiments described in the Results section provide relative rates of reaction of the *t*-butyl ion with different hydrocarbon molecules. It was, of course, of interest to obtain absolute rate constants for these reactions. In order to accomplish this, the rate of reaction 11 was determined relative to the rate of reaction of the *t*-$C_4H_9^+$ ion with ammonia

$$t\text{-}C_4H_9^+ + NH_3 \longrightarrow \text{products other than isobutane} \qquad (12)$$

Because reaction of the *t*-butyl ion with ammonia is highly exothermic, it is reasonable to assume that the total rate of reaction between the *t*-butyl ion and ammonia occurs at a rate equal to the collision rate. The collision rate constant can be calculated[7] to be 4.0 × 10^{-9} cm^3/(molecule sec). This value is close to the rate constant measured[8] in the mass spectrometer for reaction of methane ions with ammonia.

Figure 2 shows the yields of isobutane formed in a mixture of *neo*-C_5H_{12}–*i*-C_5H_{12}–O_2 (1:0.05:0.1) to which varying amounts of ammonia have been added. If we apply the steady-state treatment to the mechanism represented by reactions 2, 11, and 12 we obtain

$$\frac{[i\text{-}C_4H_{10}]_0}{[i\text{-}C_4H_{10}]} = 1 + \frac{k_{12}}{k_{11}}\frac{[NH_3]}{[i\text{-}C_5H_{12}]} \qquad \text{(III)}$$

where $[i\text{-}C_4H_{10}]_0$ represents the yield of isobutane formed in the absence of ammonia and $[i\text{-}C_4H_{10}]$ the yield of isobutane formed under the same conditions when the ratio of ammonia to isopentane is $[NH_3]/[i\text{-}C_5H_{12}]$. Applying this relation to the data given in Figure 2, we obtain a value of 99 ± 10 for k_{12}/k_{11}. Accepting that the rate constant for reaction with ammonia is equal to the collision rate constant, 4.0 × 10^{-9} cm^3/(molecule sec), a value for k_{11} of ~4.0 × 10^{-11} cm^3/(molecule sec) can be estimated.

Rates of Reaction of *t*-Butyl Ions with Saturated Hydrocarbons. Detailed descriptions of the experiments on which this discussion is based are given in the Results section. The experimental results are presented in Tables I, II, and III. For easy reference, all of the rate data given in Tables I, II, and III are expressed relative to the rate of reaction 11 and summarized in Table IV. Accepting a rate constant of 4.0 × 10^{-11} for reaction 11, the absolute rate constants for hydride transfer reaction 1 with the various hydrocarbons are given in the last column of Table IV. It is of interest that the absolute value of the rate constant [0.92 × 10^{-11} cm^3/(molecule sec)] for reaction with 2,2,4-trimethylpentane is in good agreement with the recently determined[4] value of 1 × 10^{-11} for this reaction.

Table IV. Relative Rates of Hydride Transfer Reaction between *t*-Butyl Ion and Saturated Hydrocarbons

Hydrocarbon	ΔH_f, eV (hydrocarbon)	Relative rate	k_1, cm^3/(molecule sec)
C_5			
n-Pentane	−1.518	<0.016	<0.06 × 10^{-11}
2-Methylbutane	−1.601	1.00	4.0
2-Methylbutane-2-d_1		0.61	2.4
2-Methylbutane-d_{12}		0.61	2.4
C_6			
n-Hexane	−1.732	0.032	0.12 × 10^{-11}
2-Methylpentane	−1.806	1.54	6.2
3-Methylpentane	−1.778	1.07	4.3
3-Methylpentane-3-d_1		0.66	2.6
2,2-Dimethylbutane	−1.923	<0.005	<0.02
2,3-Dimethylbutane	−1.843	4.24	17.0
C_7			
2-Methylhexane	−2.020	2.59	10.4 × 10^{-11}
3-Methylhexane	−1.993	1.80	7.2
2,4-Dimethylpentane	−2.094	0.82	3.3
3-Ethylpentane	−1.966	1.01	4.0
2,3,3-Trimethylbutane	−2.123	1.28	5.1
C_8			
2-Methylheptane	−2.233	4.89	19.6 × 10^{-11}
3-Methylheptane	−2.204	3.33	13.3
2,3-Dimethylhexane	−2.217	4.27	17.1
2,4-Dimethylhexane	−2.274	1.29	5.2
2,5-Dimethylhexane	−2.307	4.39	17.6
3,4-Dimethylhexane	−2.208	2.42	9.7
2,2,4-Trimethylpentane	−2.323	0.23	0.92
2,3,4-Trimethylpentane	−2.254	0.97	3.9
Cyclic			
Cyclohexane	−1.276	<0.004	<0.01 × 10^{-11}
Methylcyclopentane	−1.106	2.93	11.7
Methylcyclopentane-d_{12}		1.75	7.0

Examining the data presented in Table IV one sees that, as expected, the rate of reaction 1 is very low when RH_2 does not contain a tertiary hydrogen atom (see *n*-pentane, *n*-hexane, 2,2-dimethylbutane, and cyclohexane). In all other cases, it can safely be assumed that reaction involves the hydrogen(s) in the tertiary position(s) only. This is verified by the results of two experiments, one of which was mentioned above, in which neopentane was irradiated in the presence

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[6] P. Ausloos, S. G. Lias, and R. Gorden, Jr., *J. Chem. Phys.*, **39**, 3341 (1963).

[7] S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, **45**, 3107 (1967).

[8] M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **87**, 4242 (1965).

of 2-methylbutane-2-d_1 and of 3-methylpentane-3-d_1; in these experiments the isobutane consisted nearly entirely of $(CH_3)_3CD$.

Furthermore, the isotope effect, manifested by a lowering of the reaction rate when a tertiary H atom is replaced by a D atom, is 0.61 ± 0.01, regardless of the structure of the molecule or whether or not the molecule contains additional D atoms. (Compare methylcyclopentane-d_{12} with methylcyclopentane, 3-methylpentane-3-d_1 with 3-methylpentane, and 2-methylbutane-d_{12} or 2-methylbutane-2-d_1 with 2-methylbutane.) This indicates again that the reaction involves only heterolytic cleavage of the tertiary C–H (or C–D bond).

The variations in the rate of reaction 1 with the structure of the reacting molecule, RH_2, show some interesting and informative trends. For example, comparing the rates of reaction of isomers, we see that the position in the molecule of the tertiary hydrogen reaction site has a large influence on the rate of reaction 1. In the discussion which follows, we shall examine these variations in reaction rate in detail, and attempt to explain them.

It is first of interest to point out that for the two homologous series for which results are presented in Table IV (the 2-methylalkanes and the 3-methylalkanes) a logarithmic plot of k_{relative} *vs.* the heat of formation of the neutral reactant molecule shows a straight-line relationship (see Figure 3). This can be interpreted to mean that for a particular homologous series log k is proportional to the heat of reaction 1

$$\Delta H_f(i\text{-}C_4H_{10}) + \Delta H_f(R^+) - \Delta H_f(t\text{-}C_4H_9^+) - \Delta H_f(RH_2) = \Delta H \quad \text{(IVa)}$$

$$-8.62 \text{ eV}^9 + \Delta H_f(R^+) - \Delta H_f(RH_2) = \Delta H \quad \text{(IVb)}$$

since the values of $\Delta H_f(R^+)$ (which unfortunately are unknown for the product tertiary ions we are considering)[10] of a particular homologous series follow the same trends as the values of ΔH_f for the corresponding neutral molecules; increments in ΔH_f between two successive members of a series are, however, larger in the ions than in the molecules.[11] Of course, the rate of reaction is not generally influenced by the overall heat of reaction, but rather by the activation energy; thus, the relationship graphically presented in Figure 3 suggests that there is an activation energy for reaction 1 which is proportional to the heat of reaction. Such a proportionality between heats of reaction and activation energies has been seen before. The well-known Evans–Polanyi Rule,[12] for example, states that for a homologous series of exothermic radical abstraction reactions, the change in activation energy is related to the change in heat of reaction by the relation

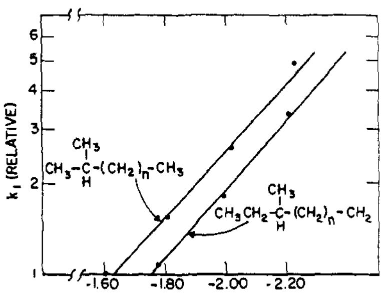

Figure 3. Logarithmic plot of the relative values of k_1 *vs.* ΔH_f(RH) for the 2-methyl alkanes and 3-methyl alkanes. The 2-methyl alkanes range from isopentane (lowest point) to 2-methylheptane; *i.e.*, n = 1–4. The 3-methyl alkanes range from 3-methylpentane (lowest point) to 3-methylheptane; *i.e.*, n = 1–3.

$$\Delta E_{\text{act}} = \beta \Delta H_{\text{reaction}} \quad \text{(V)}$$

(where β is a constant for a given homologous series).

Until now, activation energies have never been ascribed to *exothermic* ion molecule reactions. Most of the reactions which have been studied in the mass spectrometer, however, are highly exothermic. If indeed the energy of activation decreases as the exothermicity of such a reaction increases, one would expect the activation energies for highly exothermic ion–molecule reactions to approach zero. Further evidence that an activation energy does exist for reaction 1 is found in the above-mentioned isotope effect. The replacement of an H atom by a D atom at a reaction site does not change the overall heat of reaction, but in studies of free-radical abstraction reactions, such a replacement has been observed[13] to increase the energy of activation by about 0.048 eV. The magnitude of the isotope effect observed here would correspond to a smaller change, of about 0.008 eV, in the energy of activation. It should be pointed out that for the more highly exothermic ion–molecule reactions which have negligible activation energies, no deuterium isotope effects are observed.[14]

If we assume that the transmission coefficient for reaction 1 is unity for the alkanes containing tertiary hydrogen atoms, we can estimate that the maximum values for the activation energy of reaction 1 range from ~0.08 eV (for 2-methylheptane) to 0.15 eV (for 2,2,4-trimethylpentane).

Let us now analyze the effects of molecular structure on the rate of reaction 1. Since no information is available which allows us to compare the heats of formation of the product ions of differing structures, we cannot at the present time completely explain all the factors which cause the rate of reaction 1 to vary for isomeric molecules. However, in certain cases the observed trends can be predicted by considering possible

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[9] $\Delta H_f(t\text{-}C_4H_9^+)$ = 7.24 eV, as determined by F. P. Lossing and G. P. Semeluk, *Can. J Chem.*, in press.

[10] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, NBS-NSRD 26, U. S. Government Printing Office, Washington, D. C., 1969.

[11] It was suggested several years ago [J. L. Franklin, *J. Chem. Phys.*, **21**, 2029 (1953)] that the heats of formation of carbonium ions can be calculated empirically by assuming that each "group," consisting of a C atom and its attached H atoms (*i.e.*, CH_3, CH_2, H_2C^+, etc.), wherever it occurs in a molecule, always contributes the same absolute amount to the overall heat of formation of the ion or neutral molecule. According to this hypothesis, the heats of formation of all carbonium ions of a given structure (primary, secondary, or tertiary) would differ from the heats of formation of the corresponding neutral molecules by the same increment, and all of the reactions considered here would have the same heat of reaction. Recently determined [J. M. Williams and W. H. Hamill, *ibid.*, **49**, 4467 (1968)] values of ΔH_f for the ethyl (9.55 eV), propyl (9.18 eV), and n-butyl (8.50 eV) ions, when compared with the heats of formation of the corresponding alkanes, ethane (−0.877 eV), propane (−1.076 eV), and n-butane (−1.307 eV), demonstrate that the heats of formation of carbonium ions are indeed simply related to the heats of formation of the corresponding neutral molecules, but that the contribution of a given group (say CH_2) is larger in the ion than in the molecule.

[12] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1933 (1936); **34**, 22 (1938).

[13] See, for instance, W. M. Jackson, J. R. McNesby, and B. deB. Darwent, *J. Chem. Phys.*, **37**, 1610 (1962).

[14] P. Ausloos and S. Lias, *ibid.*, **36**, 3163 (1962).

steric interactions between the methyl groups of the *t*-butyl ion when it is within a reasonable bonding distance of the tertiary hydrogen atom and H atoms or methyl groups of the reacting molecule. In order to predict which interactions would be most likely to occur, we must consider the conformational preferences of the molecules. For example, as mentioned above, we see (Table IV) that for the methylpentanes, methylhexanes, and methylheptanes, the rate of reaction is lower by a factor of 0.69 when the methyl group is located on the third, rather than the second, carbon atom of the chain. In 3-methylpentane, the preferred conformations are the zigzag linear structure (with two *gauche*-butane interactions) and the other conformer with two *gauche* interactions resulting from the rotation of an ethyl group; in both of these conformations, there is the possibility of a van der Waals repulsion arising between the attacking butyl ion and hydrogen atoms of the 1 and 5 methyl groups. The conformer with three *gauche* interactions is most exposed to the attack by the ion having only one possible unfavorable interaction with the ion, but is present in considerably smaller concentration than the other two conformers. In the faster reacting 2-methylpentane, on the other hand, the linear conformer which is most favored at equilibrium presents only one unfavorable interaction to the attacking ion, that of the hydrogen on the 4-carbon atom. Similar reasoning also applies to the larger members of the two homologous series.

Continuing this reasoning, 3-ethylpentane reacts more slowly than the isomeric 3-methylhexane; in this case, the most favorable conformer has three hydrogen atoms (on the three terminal methyl groups) which may undergo van der Waals interactions with the methyl groups of the *t*-butyl ion.

2,2,3-Trimethylbutane presents two such interactions, from the hydrogen atoms on the two branching methyl groups at the 2-carbon. This molecule reacts at a rate intermediate between that of 3-methylhexane and 3-ethylpentane, but as pointed out above, detailed interpretations of the relative rates are impossible without information about the relative stabilities of the various product ions. It should be pointed out that the fact that 2,2,3-trimethylbutane reacts at all demonstrates that these unfavorable van der Waals interactions do not prohibit reaction from occurring, since in this molecule, there is no possible conformation which is free from possible interaction.

All of the repulsive interactions postulated above have involved molecular configurations in which H atoms on carbon atoms β to the tertiary carbon atom are in a position close to the reactive tertiary hydrogen atom. If these interactions do indeed inhibit reaction, one would expect a more serious inhibition when these interacting H atoms are replaced by methyl groups, *i.e.*, when there is branching at the carbon atom β to the reaction site. This is indeed the case; 2,4-dimethylpentane 2,4-dimethylhexane, 2,2,4-trimethylpentane, and 2,3,4-trimethylpentane all react much more slowly than their respective isomeric molecules. In each of these cases, it can be shown that when the molecule is in its most favorable conformation, the tertiary hydrogen(s) is (are) placed very close to methyl group(s); approach of the bulky $t\text{-}C_4H_9^+$ ion would be seriously inhibited.

Reasoning analogous to that followed above can be used to explain why 3,4-dimethylhexane (with two potential van der Waals interactions at each possible reaction site in the most favorable configuration) reacts more slowly than 2,3-dimethylhexane (with two interactions at the 3-tertiary hydrogen but only one at the 2-tertiary hydrogen). However, the fact that 2,5-dimethylhexane (with only one potential van der Waals interaction at each possible reaction site in the most favorable configuration) reacts at a rate very close to that of 2,3-dimethylhexane demonstrates that other factors must also be operative in determining these reaction rates.

It is very likely, for example, that differences in the stabilities of isomeric tertiary product ions will also be reflected in the relative reaction rates. This is demonstrated most clearly in the case of 2,3-dimethylbutane, which reacts with the *t*-butyl ion much faster than any other C_6H_{14} isomer. Yet, in the most favorable conformations of this molecule, the tertiary reaction sites would each lie in the vicinity of two H atoms which would interact unfavorably with an attacking ion. The product ion resulting from reaction with this molecule, however, has recently been shown[15] to be the most stable $C_6H_{13}^+$ ion.

It should be emphasized that if reaction 1 were more exothermic (*i.e.*, if the energy of activation were much smaller), the simple relationships we have seen between rate and molecular structure or product ion stability would not be evident. For example, the hydride transfer reactions of the *sec*-butyl ion

$$sec\text{-}C_4H_9^+ + RH \longrightarrow n\text{-}C_4H_{10} + R^+ \qquad (13)$$

are more exothermic than the corresponding reactions of the *t*-butyl ion, and occur at rates about one order of magnitude greater than the rates of reaction 1. In order to illustrate this difference, some $n\text{-}C_6D_{14}$–RH–NO mixtures (1:0.83:0.10) were irradiated. Deuterated *sec*-butyl ions are formed and react with $n\text{-}C_6D_{14}$

$$sec\text{-}C_4D_9^+ + n\text{-}C_6D_{14} \longrightarrow n\text{-}C_4D_{10} + C_6D_{13}^+ \qquad (14)$$

or with the additive

$$sec\text{-}C_4D_9^+ + RH \longrightarrow n\text{-}C_4D_9H + R^+ \qquad (15)$$

The results of these experiments and values for k_{15}/k_{14} derived from the ratios of $n\text{-}C_4D_9H$ to $n\text{-}C_4D_{10}$ are given in Table V. Although the RH molecules listed in Table V react with the *t*-butyl ion at rates which vary over more than a factor of 5, the corresponding variation in the rates of reaction 15 is only about a factor of 2. The inhibiting effect involving branching at a carbon atom β to the reaction site noted above for reaction 1 does not exist for reaction 15. Further-

Table V. Irradiation of $n\text{-}C_6D_{12}$–RH–NO (1:0.83:0.10) Mixtures. Isotopic Distributions of *n*-Butane Product

RH	*n*- C_4D_{10}	*n*- C_4D_9H	*n*- $C_4D_8H_2$	k_{15}/k_{14}
2,3-Dimethylbutane	0.61	0.28	0.11	0.58
2,4-Dimethylpentane	0.60	0.31	0.087	0.68
2,2,3-Trimethylbutane	0.57	0.35	0.074	0.47
2,3,4-Trimethylpentane	0.57	0.41	0.021	1.10

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(15) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 4739 (1967).

Table VI. Radiolysis of a Neopentane–Isopentane–O_2 (1:0.5:0.08) Mixture in the Presence of Added Unsaturated Hydrocarbons

Additive	Additive/i-C_5H_{12}	i-C_4H_8[a]	Total i-C_4H_{10}	t-$C_4H_9^+$ [b]	k_{16}/k_{11}	k_{16}, cm^3/(molecule sec)
None	0.00	0.21	0.71	0.66		
1-C_4H_8	0.050	N.d.	0.50	0.45	9.3	3.7×10^{-10}
$CH_2{=}CHCH_2CH(CH_3)_2$	0.050	0.23	0.43	0.39	13.9	5.6
$CD_2{=}C(CD_3)_2$	0.10	N.d.	0.30[c]	0.20	23.0	9.0
	0.10	N.d.	0.31[d]	0.21	21.4	
$CH_2{=}CHCH{=}CH_2$	0.10	N.d.	0.23	0.19	24.7	9.9
C_6H_6	0.10	N.d.	0.37	0.33	10.0	4.0
trans-2-C_6H_{12}	0.05	0.28	0.33	0.28	27.1	11.4
	0.15	0.26	0.17	0.12	30.0	

[a] N.d., not determined. [b] Isobutane formed in reaction 11. [c] 0.096 = $C_4D_8H_2$. [d] 0.084 = $C_4D_8H_2$.

more, the nonnegligible rate of reaction of the *sec*-$C_4D_9^+$ ion with *n*-hexane demonstrates that reaction of this ion is not confined to tertiary hydrogen reaction sites.

Rates of Reaction of the *t*-Butyl Ion with Unsaturated Compounds. In order to investigate the rates of reaction of the *t*-butyl ion with unsaturated compounds, a neopentane–isopentane–O_2 (1:0.5:0.08) mixture was irradiated in the presence of added olefins and of benzene. The yields of isobutane and, in some cases, isobutene measured in these experiments are given in Table VI. In such a mixture, the reaction of the *t*-butyl ion with isopentane to form isobutane (reaction 11) competes with reaction with the unsaturated compound

$$t\text{-}C_4H_9^+ + A \longrightarrow \text{products} \qquad (16)$$

(where A is an olefin, a diolefin, or an aromatic compound). A recent mass spectrometric investigation of the reactions of the *t*-butyl ion with olefins[4] demonstrated that the product of reaction 16 is generally a condensation ion [$C_4H_9A^+$]. In some cases, a simple proton transfer reaction

$$t\text{-}C_4H_9^+ + A \longrightarrow i\text{-}C_4H_8 + AH^+ \qquad (17)$$

may occur also. Although it is difficult to derive quantitative results about the relative importance of reaction 17 from the increments in the isobutene yield, we can say roughly that this reaction constitutes less than 10% of the total reaction between the *t*-butyl ion and 4-methyl-1-pentene, and not more than 25% of the total reaction between the *t*-butyl ion and *trans*-2-hexene. In fact, in the cases of 1-butene and 4-methyl-1-pentene, proton transfer from a *t*-butyl ion is almost certainly endothermic.[10] Applying the steady-state treatment to the mechanism represented by reactions 11 and 16, (where (16) is assumed to represent all the reactions between the *t*-butyl ion and A), one obtains

$$\frac{[i\text{-}C_4H_{10}]_0}{[i\text{-}C_4H_{10}]} = 1 + \frac{k_{16}}{k_{11}}\frac{A}{[i\text{-}C_5H_{12}]} \qquad \text{(VI)}$$

(where $[i\text{-}C_4H_{10}]_0$ and $[i\text{-}C_4H_{10}]$ are the yields of i-C_4H_{10} originating from reaction 11 in the absence and presence, respectively, of added unsaturated compound). Values for k_{16}/k_{11} derived from these results and absolute values for k_{16} [accepting that $k_{11} = 4.0 \times 10^{-11}$ cm^3/(molecule sec)] are given in the last two columns of the table. The rate constant for reaction of the *t*-butyl ion with 1-butene, 3.8×10^{-10} cm^3/(molecule sec), is in fairly good agreement with the value of 2.7×10^{-10} cm^3/(molecule sec) measured[4] for this rate constant in the mass spectrometer.

It should be pointed out that 4-methyl-1-pentene contains a tertiary hydrogen atom and, therefore, can undergo reaction 1 as well as reaction 16. However, in view of the fact that reaction 16 generally proceeds at rates about one order of magnitude greater than those for reaction 1, the reported rate of reaction 16 for this molecule is probably too low by only a very slight amount.

When the additive, A, is isobutene, a special problem arises, for the product ion formed in reaction 17 is a *t*-butyl ion. In order, therefore, to investigate the reactions between a *t*-butyl ion and isobutene, i-C_4D_8 was added to the *neo*-C_5H_{12}–i-C_5H_{12}–O_2 mixture. In this case, reaction 17 can be written

$$t\text{-}C_4H_9^+ + i\text{-}C_4D_8 \longrightarrow i\text{-}C_4H_8 + t\text{-}C_4D_8H^+ \qquad (18)$$

Since the t-$C_4D_8H^+$ ion can now react with i-C_5H_{12} to form isobutane

$$t\text{-}C_4D_8H^+ + i\text{-}C_5H_{12} \xrightarrow{k_{11}} i\text{-}C_4D_8H_2 + C_5H_{11}^+ \qquad (19)$$

some of the isobutene product will consist of $C_4D_8H_2$. Results of a related study[16] demonstrate that the $C_4D_8H_2$ observed in this experiment is formed through reaction sequence 18–19, and not through an H_2^- transfer reaction involving a $C_4D_8^+$ ion. The requisite experiments for the elucidation of the relative importance of reaction 18 and the condensation reaction

$$t\text{-}C_4H_9^+ + i\text{-}C_4D_8 \longrightarrow C_8H_9D_8^+ \qquad (20)$$

are not included here; the rate constant given in the last column of Table VI, therefore, represents the total rate of reaction between the *t*-butyl ion and isobutene.

As suggested above, however, it can be assumed that the predominant mode of reaction between the *t*-butyl ion and the various olefins is condensation. Thus, some of the trends in reaction rate given in Table VI can be rationalized in terms of the stabilities of the product condensation ions. For example, it is not surprising that the reactions with 1-butene and 4-methyl-1-pentene, which lead to secondary product ions, are slower than reaction with isobutene, which forms a tertiary product ion, or with 1,3-butadiene, which forms an allylic ion. The high rate of reaction observed for *trans*-2-C_6H_{12} is unexpected and difficult to explain in terms of simple concepts.

The Yield of the *t*-Butyl Ion in the Radiolysis of Neopentane. The yields of isobutane formed in isobutane–isopentane–O_2 mixtures, shown in Figure 1, were all obtained in experiments in which not more than about

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[16] G. Collin and P. Ausloos, in preparation.

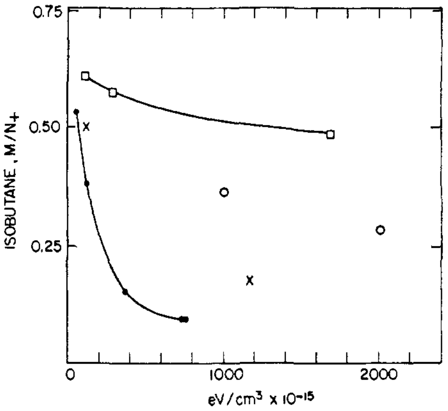

Figure 4. The yield of isobutane as a function of dose in neopentane–isopentane–O_2 mixtures which are 0.3% isopentane (●), 1% isopentane (×), 4.7% isopentane (○), and 33% isopentane (□).

0.002% of the neopentane molecules was decomposed (*i.e.*, a "conversion" of 0.002%). This corresponds to a dose of about 120×10^{15} eV/cm³. This constant, low dose was necessary if quantitative derivations based on the yields were to be made, since it was noted that the yield of isobutane was profoundly conversion dependent, as shown in Figure 4.

Taking, then, the experiments shown in Figure 1 which were performed at constant (0.002%) conversion, and plotting $1/[i\text{-}C_4H_{10}]$ *vs.* $1/[i\text{-}C_5H_{12}]$ in Figure 5, we obtain from the intercept an ion pair yield of 0.75 for the *t*-butyl ion in the radiolysis of neopentane at a pressure of 200 Torr.

From the results of a few experiments performed at a total pressure of 40 Torr, one can estimate that the approximate ion pair yield of the *t*-butyl ion at this pressure is 0.67. In the 70-eV mass spectrum of $neo\text{-}C_5H_{12}^+$ dissociating under a pressure of 10^{-5} Torr, the ion pair yield of this ion is 0.41. Accepting that the parent neopentane ion has a very short dissociative lifetime,[17] the increase in the yield of the *t*-butyl ion with increase in pressure can be accounted for by collisional deactivation of internally excited *t*-butyl ions which are formed in the primary dissociation reaction 2. It may indeed be assumed that except for the relatively minor importance of the dissociation reaction forming the $i\text{-}C_4H_8{+}$ ion

$$neo\text{-}C_5H_{12}^+ \longrightarrow i\text{-}C_4H_8^+ + CH_4 \qquad (21)$$

reaction 2 is the mode of dissociation of parent neopentane ions, and fragment ions other than $C_4H_9^+$ seen in the mass spectrum of neopentane originate in the dissociation of the *t*-butyl ion.

In the earlier radiolysis study[3] carried out in this laboratory at a neopentane pressure of 30 Torr, the total ion pair yield attributed to all observed fragment ions exclusive of $t\text{-}C_4H_9^+$ added up to 0.16. On this basis, the yield of ~0.67 attributed to the *t*-butyl ion in this pressure region is reasonable.

The isobutane formed in the irradiation of a $neo\text{-}C_5H_{12}\text{–}i\text{-}C_5D_{12}\text{–}O_2$ mixture consists mostly of $(CH_3)_3CD$ formed in the D^- transfer reaction

$$(CH_3)_3C^+ + i\text{-}C_5D_{12} \longrightarrow (CH_3)_3CD + C_5D_{11}^+ \qquad (22)$$

but, as discussed in the Experimental Section, also contains a small amount of $i\text{-}C_4H_8D_2$, formed by reaction of the isobutene ion

$$i\text{-}C_4H_8^+ + i\text{-}C_5D_{12} \longrightarrow i\text{-}C_4H_8D_2 + C_5D_{10}^+ \qquad (23)$$

The variations in the yield of $i\text{-}C_4H_8D_2$ with the amount of isopentane present in the mixture are shown in Figure 1; when the concentration of $i\text{-}C_5D_{12}$ in the mixture is greater than about 2.5%, we see that a constant yield, $(M[C_4H_8D_2]/N_+ = 0.028$ at 200 Torr) of this product is obtained. The yields of this product are not strongly conversion dependent. This observation, and the fact that the $i\text{-}C_4H_8^+$ ion is more readily intercepted by low concentrations of isopentane than the *t*-butyl ion (see Figure 1), leads to the conclusion that the isobutene ion reacts much more rapidly with isopentane than does the *t*-butyl ion.

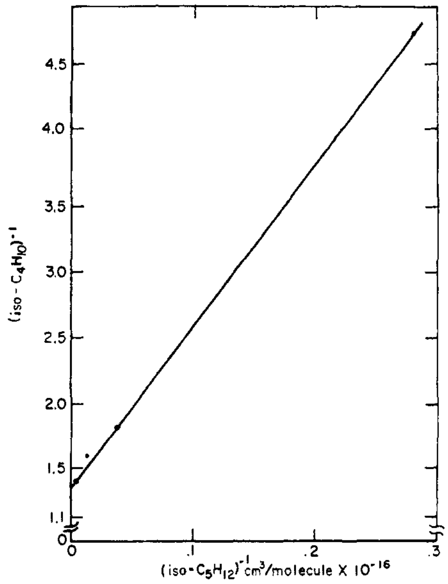

Figure 5. The reciprocal of the yield of isobutane formed in reaction 1 plotted as a function of the reciprocal of the isopentane concentration.

The Formation of Isobutene in the Radiolysis of Neopentane. In the earlier study of neopentane carried out in this laboratory,[3] it was noted that the yield of isobutene was diminished by at least a factor of 3 when neopentane was irradiated in a graphite-coated cell or in the presence of benzene; it was suggested that the isobutene which disappeared under these circumstances (having an ion pair yield of 0.32) had the *t*-butyl ion as precursor. The results of the present study indicate that this is not entirely correct. The yields of isobutene measured in the presence of varying amounts of isopentane are given in Figure 1; it is seen that at all concentrations of isopentane, the diminution of the isobutene yield is much smaller than the yield of intercepted *t*-butyl ion.

From the data given in Figure 1 for experiments at 200 Torr, a value of 0.14 for the fraction of *t*-butyl ions which end up as isobutene can be estimated. We further derive values of 0.43 or 0.21 for the ion pair yield of isobutene originating from sources other than the *t*-butyl ion at 200 and 40 Torr (see Table VII an above discussion for pertinent data), respectively.

The origin of the isobutene which does not have the *t*-butyl ion as precursor and the explanation of

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

Table VII. The Radiolysis of Neopentane in the Presence of Added Ammonia. Yields of Products[a]

	M/N_+		
	0% NH_3	1.5% NH_3	5.0% NH_3
Methane	0.17	0.16	0.16
Acetylene	0.040	0.031	0.031
Ethylene	0.10	0.10	0.098
Ethane	0.069	0.062	0.058
Propane	0.020	0.019	0.021
Propylene	0.081	0.095	0.085
Isobutene	0.30	0.67	0.68

[a] Pressure of neopentane = 40 Torr in all experiments.

the effects of benzene or a graphite surface on the yield of this product are not known at the present time.

Reaction of the *t*-Butyl Ion with Ammonia. Recently Miyazaki and Shida[5] irradiated neopentane in the presence of varying amounts of ammonia. They noted that owing to the occurrence of reaction 24, the yield

$$(CH_3)_3C^+ + NH_3 \longrightarrow (CH_3)_2CCH_2 + NH_4^+ \qquad (24)$$

of isobutene increases markedly upon the addition of even a small amount of ammonia, and becomes constant at higher ammonia concentration. Taking the increment in the isobutene yield as equal to the yield of the *t*-butyl ion, they derived an ion pair yield of 0.42 (G = 1.76), for the *t*-butyl ion in the radiolysis of neopentane at 180 Torr. Table VII gives the yields of products formed in the radiolysis of neopentane–O_2 mixtures in the presence of ammonia; we see that at a pressure of 40 Torr, the increment in the isobutene yield is 0.38.[18]

Taking into account the fact that in the absence of ammonia about 25–30% of the isobutene has the *t*-butyl ion as precursor, we derive a value of 0.47 as the ion pair yield of *t*-butyl ions undergoing reaction 24. Since we have attributed an ion pair yield of 0.67 to the butyl ion formed in the radiolysis of neopentane at this pressure, it is clear that only about 70% of the *t*-butyl ions reacting with ammonia undergoes reaction 24; the remainder in all likelihood undergoes a condensation reaction

$$t\text{-}C_4H_9^+ + NH_3 \longrightarrow C_4H_9NH_3^+ \qquad (25)$$

Taking these corrections into account, the data of Miyazaki and Shida lead to an estimated ion pair yield of ∼0.72 for the *t*-butyl ion at 180 Torr, assuming that k_{25}/k_{24} is independent of pressure. This estimated yield is in quite reasonable agreement with the yield of 0.75 at 200 Torr reported above.

Acknowledgment. The authors are indebted to Dr. Abraham Schneider, Research and Development Division, Sun Oil Co., who suggested that the variations in the rate of reaction of the *t*-butyl ion with various alkanes could in many cases be explained in terms of a conformational analysis of the reacting molecules.

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[18] Differences between our data and those of Miyazaki and Shida[5] can be explained by the fact that our ammonia additive experiments are performed at a lower pressure (40 Torr). As noted above, the yields of both the *t*-butyl ion and the isobutene not originating from a *t*-butyl ion precursor are pressure dependent over this range.

Reversible Triplet Energy Transfer and Thermally Activated Delayed Phosphorescence

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Abstract: The lowest triplet states of the benzophenone and triphenylene chromophores in the ester of 2-hydroxymethyltriphenylene and 4-benzoylbenzoic acid in a cured poly(methyl methacrylate) film are in thermal equilibrium over the temperature range 82–298°K. This leads to a temperature-dependent phosphorescence spectrum and triplet decay time for the compound.

Mixed molecular systems of weakly interacting components which possess excited state energy levels lying within an energy range comparable to kT often exhibit strongly temperature-dependent luminescence properties and excitation transfer characteristics.[1-3] We report here on the interesting temperature-dependent luminescence properties of a compound which has two chromophores whose triplet levels lie within about 2 kcal/mol of each other. This represents an intramolecular analog of the mixed crystal experiments of Harrigan and Hirota.[3]

The phosphorescence spectrum of the ester (BT) of 2-hydroxymethyltriphenylene (T) and 4-benzoylbenzoic acid, recorded from a solution in "cured" polymethylmethacrylate near liquid nitrogen temperature, is similar to the sum of the corresponding spectra of T and B, the 4-methylbenzyl ester of 4-benzoylbenzoic acid, in the ratio 2:3, respectively (Figures 1 and 2). However, at room temperature the phosphorescence spectrum of BT resembles that of B. Analyses of the temperature dependences of the phosphorescence spectra, yields, and decay times of BT, B, and T have been carried out. The results fit a model in which triplet excitation transfer back and forth between the two chromophores in BT is sufficiently fast over the temperature range studied

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