Carbonium Ions in Radiation Chemistry. II. Isomerization Process in Protonated Cyclopropane and Cyclobutane Ions

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Abstract: The structures of propyl and butyl ions formed in the gas-phase radiolysis of appropriate alkanes have been deduced from the structures of the neutral products formed in proton transfer reactions with ammonia, or from the isotopic structures of hydride (or deuteride) transfer reaction products formed in labeling experiments. *n*-Propyl ions rearrange within 10^{-10} sec to the *sec*-propyl or the protonated cyclopropane structure. Rearrangement to the *sec*-propyl ion is favored under all conditions but increases in importance with increasing internal energy content of the ion. Both isomerization reactions are reversible, but the rate constants of the reverse reactions are very low owing to the energy requirements of these processes. The isomerization of the *sec*-butyl ion to the *t*-butyl structure is observed; this rearrangement also increases in importance with increasing internal energy content of the ion. The H (or D) atoms in the secondary and tertiary carbonium ions are seen to undergo energy-dependent hydrogen-scrambling processes. The protonated cyclobutane ion formed by proton transfer to cyclobutane isomerizes mainly to the *sec*-butyl structure. The results presented here demonstrate that most of the propyl and butyl ions formed in the dissociation of butane and hexane parent ions, respectively, originate as primary carbonium ions from simple C–C cleavage processes, rather than being formed initially with the secondary structure, as they are at the threshold energies.

Recently, isomerization reactions of hydrocarbon ions have become a subject of some interest in the literature.[1,2] A number of investigations have been reported, for instance, in which the nmr spectra of hydrocarbon ions were observed.[2] Thus, it has been demonstrated,[3] for example, that straight-chain carbonium ions isomerize to tertiary structures, and that various rearrangement processes occur[4] even in the stable tertiary structures.

Other investigations have concentrated on elucidating the paths of the isomerization reactions. Since there is now abundant experimental evidence for the existence of ions having the protonated cyclopropane structure,[5] the relationship of such cyclic structures to the classical carbonium ion structures and their role in isomerization reactions is of interest. In particular, studies have recently appeared[6] exploring the structures of the propyl and butyl ions formed in the deamination of 1-propylamine and isobutylamine and from brominated alkanes treated with aluminum bromide. These results do not reveal any evidence that the secondary propyl ions or protonated cyclopropanes, once formed, can isomerize to any other structures. On the other hand, a recent examination[7] of the nmr spectrum of ^{13}C-labeled *sec*-propyl ions has demonstrated that carbon scrambling does occur, although very slowly, indicating that some rearrangement processes occur in the *sec*-propyl ion.

$$\mathrm{CH_3\overset{+}{C}{}^*HCH_3} \rightleftharpoons \mathrm{CH_3\overset{+}{C}HC^*H_3} \tag{1}$$

Such apparent discrepancies may result from the fact that there is a large difference in the time scale of isomerization processes which can be observed by these two types of experiment. In the former experiments,[6] the ions are formed in an environment of reactive solvent molecules, and generally undergo reaction before slow rearrangements can occur. Under the conditions of the nmr experiments,[2-4] the ions do not undergo further chemical reaction, so very slow processes (such as reaction 1) can be seen, but on the other hand, certain fast isomerization processes cannot be detected by this technique.

In this study, the isomerization reactions of propyl and butyl ions will be investigated using a technique which permits the observation of processes on a time scale intermediate between those of the other two techniques discussed above. The ions are formed in the gas phase through fragmentation reactions of alkane ions generated by the absorption of high-energy radiation

$$\mathrm{A} \xrightarrow{\text{radiation}} \mathrm{A^+ + e \longrightarrow F^+ + R + e} \tag{2}$$

(where A is an alkane, F^+ is a fragment propyl or butyl ion, and R is a free radical). In these experiments, the ions exist for 10^{-8}–10^{-10} sec (depending on the pressure) before undergoing a collision. The structures of the ions are characterized from the isotopic structures of their hydride (or deuteride) transfer products formed in labeling experiments, as well as from the structures of

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(1) P. Ausloos in "Ion Molecule Reactions," J. L. Franklin, Ed., Plenum Press, New York, N. Y., 1970.

(2) G. A. Olah and P. von R. Schleyer, "Carbonium Ions," Vol. II, Interscience, New York, N. Y., 1970.

(3) (a) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227 (1967); (b) M. Saunders, E. L. Hagen, and J. Rosenfeld, *ibid.*, **90**, 6882 (1968); (c) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967).

(4) (a) M. Saunders and E. Hagen, *ibid.*, **90**, 2436 (1968); (b) D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc., London*, 147 (1964); (c) D. M. Brouwer, *Recl. Trav. Chem. Pays-Bas*, **87**, 210 (1968); (d) M. Saunders and J. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 7756 (1969); (e) D. M. Brouwer, *Recl. Trav. Chem. Pays-Bas*, **88**, 9 (1969).

(5) (a) C. J. Collins, *Chem. Rev.*, **69**, 543 (1969); (b) F Cacace, M. Caroselli, R. Cipollini, and G. Ciranni, *J. Amer. Chem. Soc.*, **90**, 2222 (1968).

(6) (a) G. J. Karabatsos, C. E. Orzech, Jr., J. L. Fry, and S. Meyerson, *ibid.*, **92**, 606 (1970); (b) G. J. Karabatsos, J. L. Fry, and S. Meyerson, *ibid.*, **92**, 614 (1970); (c) G. J. Karabatsos, N. Hsi, and S. Meyerson, *ibid.*, **92**, 621 (1970); (d) G. J. Karabatsos, R. A. Mount, D. O. Rickter, and S. Meyerson, *ibid.*, **92**, 1248 (1970).

(7) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

the products formed in proton transfer reactions between the ions of interest and ammonia. This approach, in principle, is the same as that utilized in the studies[6] of the deamination of amines, where the structures of the carbonium ions were also inferred from the structures of their final reaction products.

One distinctive feature of the investigation reported here is that the internal energy of the ions has been varied in order to test the effect of energy on the various isomerization reactions. This is accomplished by irradiating the alkane in the presence of a large excess of rare gas, so that the absorbed energy goes nearly entirely toward the formation of rare gas ions which then transfer their charge to the alkane molecules

$$X^+ + A \longrightarrow X + A^+ \qquad (3)$$

(where X is a rare gas and A is an alkane). Here the parent ion, A^+, is formed with an amount of energy which depends on the recombination energy of the rare gas.

In investigations of the reactions of ions carried out in the mass spectrometer,[8] the structure of the reacting ions cannot be directly determined, although information about ionic structures has been derived by several diagnostic techniques, such as the observation of the modes of decomposition of partially deuterated molecule ions.[8] However, the structure of a given fragment ion formed in the dissociation of a particular alkane ion (see reaction 2) has often been inferred from a measurement of the appearance energy of the ion;[9] the results reported here will demonstrate that the often-made assumption that a given ion, formed in a particular compound, always has the isomeric structure of the ion formed in the threshold-energy fragmentation process, is generally incorrect. Not only is it possible that the ion, once formed in the fragmentation process, may undergo isomerization to alternate structures, but also, as the results presented here will show, at energies above the threshold energy, alternate higher energy fragmentation processes of the parent ion may occur.

Experimental Section

The results reported here are based on the analysis of the products formed in alkane-scavenger mixtures, which have been irradiated in the NBS ^{60}Co γ-ray source, which at the time these experiments were carried out had an intensity of 0.3915×10^{-6} eV sec^{-1} electron^{-1}.

The irradiation and analytical procedures were identical with those described before.[10] The temperature was 300°K.

All undeuterated hydrocarbons used in this study were American Petroleum Institute Standards 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.

Results

In order to improve the continuity of the Discussion, most of the more routine conclusions derived from the experimental results are discussed in the Results section. The Discussion can be read without reference to the Results section. The detailed derivations presented here are only for the benefit of those unfamilar with the techniques used in this type of study.

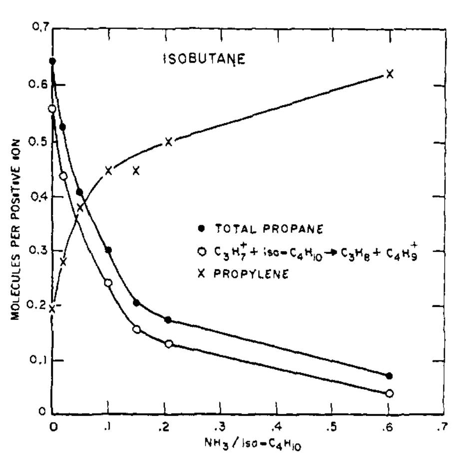

Figure 1. Yields of propane and propylene products formed in the radiolysis of isobutane–O_2 (1:0.1) mixtures in the presence of varying amounts of ammonia.

The Propyl Ion. A. In Isobutane. It has been demonstrated[11] that when isobutane is irradiated in the presence of a radical scavenger, such as O_2, most of the propane product (*i.e.*, 85% in an experiment performed at 20 Torr pressure) is formed as follows.

$$(CH_3)_3CH^+ \longrightarrow C_3H_7^+ + CH_3 \qquad (4)$$

$$C_3H_7^+ + (CH_3)_3CH \longrightarrow C_3H_8 + C_4H_9^+ \qquad (5)$$

Most of the remainder of the propane originates from reaction of the fragment $C_3H_6^+$ ion

$$C_3H_6^+ + (CH_3)_3CH \longrightarrow C_3H_8 + C_4H_8^+ \qquad (6)$$

When an equimolar i-C_4D_{10}–i-C_4H_{10}–O_2 mixture is irradiated, then the hydride transfer reactions of the propyl ions (analogous to reaction 5) result in the formation of C_3D_8, C_3D_7H, C_3H_7D, and C_3H_8 (while the reactions of the deuterated and nondeuterated propylene ions result in the formation of small amounts of C_3D_8, $C_3D_6H_2$, $C_3H_6D_2$, and C_3H_8). The cracking pattern[12] of the product C_3D_7H formed in the isobutane experiment indicates that, within the limits of detection (3–5%), it is entirely CD_3CDHCD_3. Thus, the propyl ions formed in isobutane are essentially all *sec*-propyl ions

$$CD_3\overset{+}{C}DCD_3 + (CH_3)_3CH \longrightarrow CD_3CDHCD_3 + (CH_3)_3C^+ \qquad (7)$$

Figure 1 shows the yields of some of the products formed in isobutane–O_2 mixtures irradiated in the presence of varying amounts of ammonia. Since NH_3 reacts efficiently with carbonium ions as a proton acceptor,[13] the observed diminution in the propane yield and increase in the propylene yield can be explained by

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(8) F. W. McLafferty, Ed., "Mass Spectrometry of Organic Ions," Academic Press, New York, N. Y., 1964.

(9) The appearance energy of an ion in the mass spectrometer corresponds to the enthalpy change of the reaction in which the ion is formed from the neutral species. Thus, for reaction 2, if the values of ΔH_f of A and R are known, $\Delta H_f(F^+)$ can be obtained from an appearance potential measurement. Where the heats of formation of the various isomeric ions are known, it is sometimes possible then to establish the structure of F^+ by matching its ΔH_f to that of the known isomeric structure.

(10) S. G. Lias and P. Ausloos, *J. Chem. Phys.*, 43, 2748 (1965).

(11) R. P. Borkowski and P. J. Ausloos, *ibid.*, 38, 36 (1963).

(12) The cracking pattern of the product C_3D_7H is obtained by subtracting out, first, the contributions from n-C_4D_{10}, and then correcting for the presence of $C_3D_6H_2$, on the basis of the m/e 49 peak. The contributions of the two C_3D_7H isomers to this mass are very similar, so an approximate correction for C_3D_7H at mass 49 is first made; then the residual mass 49 is assumed to be due to CD_3CDHCD_2H, whose pattern is then subtracted out. After a preliminary calculation of the relative amounts of the two C_3D_7H isomers, the contribution of these isomers to mass 49 is recalculated, the yield of $C_3D_6H_2$ is corrected, and so on, until balance is achieved.

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

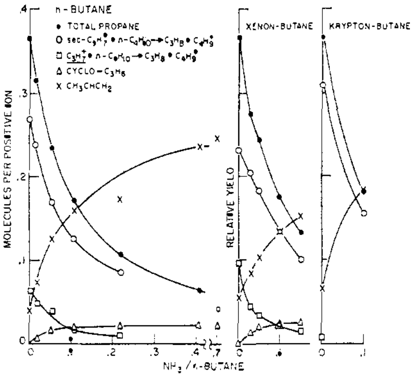

Figure 2. Yields of propane, propylene, and cyclopropane products formed in the radiolysis of *n*-butane–O_2 (1:0.1) mixtures in the presence of varying amounts of ammonia, and of excess (18:1) xenon and krypton. The yields of the propane products originating from ions of different structures have been deduced from the isotopic structures of propanes formed in mixtures of C_4D_{10}–C_4H_{10} (see Discussion).

the fact that the reaction

$$CH_3\overset{+}{C}HCH_3 + NH_3 \longrightarrow CH_3CHCH_2 + NH_4^+ \qquad (8)$$

competes with reaction 5. Since the increase in the yield of propylene does not quite match the decrease in the yield of propane, some (~20–30%) of the propyl ions apparently react with ammonia to form some other product, perhaps a condensation ion

$$CH_3\overset{+}{C}HCH_3 + NH_3 \longrightarrow C_3H_7NH_3^+ \qquad (9)$$

It should be pointed out that in the presence of ammonia, cyclopropane is formed as a product, but in miniscule yields (0.001 molecule formed per positive ion in the system in the presence of 20% NH_3). When an isobutane–NH_3–O_2 (1:0.2:0.1) mixture is irradiated in the presence of a large excess of xenon or krypton (17:1), the parent isobutane ions, formed by charge transfer from the rare gas ions

$$X^+ + (CH_3)_3CH \longrightarrow X + (CH_3)_3CH^+ \qquad (10)$$

have known amounts of energy which depend on the recombination energies of the particular rare gas (12.12 and 13.43 eV for xenon, 14.00 and 14.66 eV for krypton); the cyclopropane product formed in these experiments remained very minor (0.11 or 0.35% of the combined propane and propylene yields in the xenon and krypton radiolysis, respectively).

Since it has been noted before[11,14] that there is some reshuffling of the hydrogen atoms in a *sec*-propyl ion, experiments designed to reexamine this phenomenon were performed. When $(CH_3)_3CD$ is irradiated in the presence of a free-radical scavenger, the observations reported above allow us to write the mechanism for propane formation as

$$(CH_3)_3CD^+ \longrightarrow C_3H_6D^+ + CH_3 \qquad (11)$$

$$C_3H_6D^+ + (CH_3)_3CD \longrightarrow C_3H_6D_2 + (CH_3)_3C^+ \qquad (12)$$

If reshuffling of the hydrogen atoms in the parent ion is unimportant (as is apparently the case[15]), one would expect the $C_3H_6D^+$ ion initially formed to have the structure $CH_3\overset{+}{C}DCH_3$ and react to form $CH_3CD_2CH_3$.

Table I. Structure[a] of $C_3H_6D_2$ Formed in the Radiolysis of $(CH_3)_3CD$–O_2 (1:0.1)

Isobutane pressure, Torr	Rare gas, Torr	CH_3CHDCH_2D/$CH_3CD_2CH_3$	Estimated % rearrangement[b] A	B	C
19		0.96	98	49	16
749		0.53	69	35	8
20	Xe, 100	0.56	72	36	9
20	Kr, 100	1.7	165	63	28
90	Ar, 2800	1.7	165	63	28

[a] Calculated from mass spectra of product $C_3H_6D_2$ using the following partial standard cracking patterns: $CH_3CD_2CH_3$ (*m/e* 45) = 15% of parent peak (*m/e* 46); $CH_2DCHDCH_3$ (*m/e* 45) = 71% of parent peak (*m/e* 46). The $CH_2DCHDCH_3$ yield was corrected for the contribution from the propylene ion reaction analogous to reaction 6. [b] (A) Estimated on the assumptions (a) that the mechanism of hydrogen shuffling is reaction 44 and (b) an H or a D on the center carbon atom in the transition state has an equal probability of ending up on the methyl group. If in fact an isotope effect[6d] exists, favoring H shift over D by a factor of 1.2–1.3, these estimated percentages should be raised by about 20%. (B) Estimated on assumptions that (a) the mechanism of hydrogen shuffling is reaction 44 but (b) the D^- ion moves to the methyl group at almost the same time as the H^- ion moves to the center carbon. (C) Estimated on the assumption that in every act of scrambling, the H's and D's may be statistically distributed throughout the ion. These are the minimum possible amounts of hydrogen scrambling which could account for the observed ratios.

If reshuffling of hydrogen atoms occurs, some of the ions will have the structure $CH_2DC^+HCH_3$ and will react to form $CH_2DCHDCH_3$. Thus the ratio of these two product propanes gives a measure of the amount of randomization which occurs in the *sec*-propyl ion. Table I shows the ratios of these two product propanes in several direct and rare-gas-sensitized radiolyses of $(CH_3)_3CD$–O_2 mixtures. The results indicate that shuffling of hydrogen atoms decreases as the pressure is increased and increases as the energy supplied to the parent ion increases.

B. In *n*-Butane. In irradiated *n*-butane, as in isobutane, the propane product formed in the presence of a radical scavenger is known[16] to be formed mainly in the hydride transfer reaction of the fragment propyl ion

$$CH_3CH_2CH_2CH_3^+ \longrightarrow C_3H_7^+ + CH_3 \qquad (13)$$

$$C_3H_7^+ + n\text{-}C_4H_{10} \longrightarrow C_3H_8 + C_4H_9^+ \qquad (14)$$

with a small contribution (~14% in an experiment at 20 Torr) from the reaction of the fragment propylene ion

$$C_3H_6^+ + n\text{-}C_4H_{10} \longrightarrow C_3H_8 + C_4H_8^+ \qquad (15)$$

When an equimolar *n*-C_4D_{10}–*n*-C_4H_{10}–O_2 mixture at a total pressure of 20 Torr is irradiated, the C_3D_7H product shows a mass spectrum,[12] indicating that the product is about 81% CD_3CDHCD_3 and 19% CD_3CD_2-CD_2H. This result demonstrates that there are two distinct propyl ions which react in *n*-butane. One of these is the *sec*-propyl ion

$$CD_3\overset{+}{C}DCD_3 + n\text{-}C_4H_{10} \longrightarrow CD_3CDHCD_3 + C_4H_9^+ \qquad (16)$$

while the other, which we shall designate as $C_3H_7^+$ or $C_3D_7^+$ until we can characterize its structure more definitively, reacts to form the product one would expect from an ion with the primary structure

$$C_3D_7^+ + n\text{-}C_4H_{10} \longrightarrow CD_3CD_2CD_2H + C_4H_9^+ \qquad (17)$$

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(14) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, 90, 6881 (1968).

(15) F. E. Condon, *ibid.*, 73, 4675 (1951).

(16) R. P. Borkowski and P. J. Ausloos, *J. Chem. Phys.*, 39, 818 (1963).

Table II. Relative Rates of Reactions of $\mathrm{C_3H_7^+}$ Ions with Ammonia and with Butanes[a]

	$k_{\text{reaction with butane}}/k_{\text{reaction with ammonia}}$	
	In isobutane	In *n*-butane
sec-$\mathrm{C_3H_7^+}$	0.065 ± 0.005 (3.1)	0.10 ± 0.02 (4.8)
Precursor of propylene	0.067 ± 0.024 (3.2)	0.086 ± 0.018 (4.1)
$C_3H_7^+$		0.022 ± 0.005 (1.1)
Precursor of cyclopropane		0.022 ± 0.005 (1.1)

[a] Values in parentheses are absolute rate constants (in cm^3/(molecule sec) × 10^{10}) for the reaction $\mathrm{C_3H_7^+ + C_4H_{10} \rightarrow C_3H_8 + C_4H_9^+}$, based on the assumption that $k(\mathrm{C_3H_7^+ + NH_3 \rightarrow products}) = 4.8 \times 10^{-9}$ cm^3/(molecule sec).

Table III. Distributions[a] of *sec*-Propyl and Protonated Cyclopropane Ions as a Function of Pressure

	% of total $\mathrm{C_3H_7^+}$							
	Protonated cyclopropane				*sec*-Propyl ion			
Pressure	Hydride transfer product	Proton transfer product	Other reactions[b]	Total	Hydride transfer product	Proton transfer products	Other reactions[c]	Total
20 Torr	3.6	3.5	10.5	17.6	28.6	42.9	10.7	82.2
200 Torr	4.1	4.2	12.6	20.9	31.7	37.9	9.5	79.1
760 Torr	5.7	5.1	15.4	26.2	26.5	37.8	9.4	73.7
1598 Torr	5.0	5.3	16.0	26.3	30.3	34.5	8.6	73.4

[a] Derived from yields of observed reaction products (as indicated) in the radiolysis of a *n*-$\mathrm{C_4D_{10}}$–*n*-$\mathrm{C_4H_{10}}$–$\mathrm{NH_3}$–$\mathrm{O_2}$ (1:1:0.4:0.1) mixture. [b] Reaction 19; contributions are calculated on the assumption (from the data of Figure 2) that $k_{19}/k_{18} = 3$ and is invariant with pressure. [c] Reaction 9; contributions are calculated on the assumption (from the data of Figure 1) that $k_9/k_8 = 0.25$ and is invariant with pressure.

(We make the assumption that $C_3D_7^+$ does not react to form $\mathrm{CD_3CDHCD_3}$ also. Reaction rate data given below seem to verify this.)

Figure 2 shows the yields of some of the products formed in irradiated *n*-$\mathrm{C_4D_{10}}$–*n*-$\mathrm{C_4H_{10}}$ mixtures in the presence of $\mathrm{O_2}$ as a radical scavenger and varying amounts of $\mathrm{NH_3}$. The results of analogous experiments in the presence of large excesses (17:1) of xenon and krypton are also given. The mass spectra of the $\mathrm{C_3D_7H}$ products have in every case been separated into $\mathrm{CD_3CDHCD_3}$ and $\mathrm{CD_3CD_2CD_2H}$. The yield calculated for the propyl ion, therefore, has been divided up according to the proportion of these two products into *sec*-$\mathrm{C_3H_7^+}$ (*sec*-$\mathrm{C_3D_7^+}$) and $C_3H_7^+$ ($C_3D_7^+$), so the diminution in the yields of these ions as a function of ammonia concentration can be followed separately. Again, the decrease in the *sec*-propyl ion yield and the increase in the propylene yield can be attributed to the occurrence of reaction 8; in fact, the increase in the propylene yield is just what one would predict if reaction 8 is totally responsible for the increment in this compound (assuming that the ratio of reaction 8 to reaction 9 observed in the isobutane–ammonia experiments is correct).

The yield of propane from reaction of $C_3H_7^+$ also decreases when ammonia is added to the system. A product of the proton transfer reaction between this ion and ammonia is apparently cyclopropane, which appears as a fairly important product when ammonia is added to *n*-butane (in contrast to the isobutane–ammonia experiments discussed above).

$$C_3H_7^+ + \mathrm{NH_3} \longrightarrow c\text{-}\mathrm{C_3H_6} + \mathrm{NH_4^+} \qquad (18)$$

Thus, it is possible that the ion which undergoes reaction has a cyclic structure, *i.e.*, that it is the protonated cyclopropane ion.[5,6] However, the increase in the yield of cyclopropane only amounts to about 25% of the decrease in the yield which can be attributed to $C_3H_7^+$, indicating either that the balance of these ions undergo an alternate reaction with $\mathrm{NH_3}$, such as a condensation reaction

$$C_3H_7^+ + \mathrm{NH_3} \longrightarrow \mathrm{C_3H_7NH_3^+} \qquad (19)$$

or that $C_3H_7^+$ is actually a mixture of two ionic structures. It is also possible that some of the $C_3H_7^+$ ions form propylene in the proton transfer reaction with ammonia; however, the reaction rate data discussed below seem to indicate that this is not very important.

A comparison of the rates of depletion of the propane products with ammonia and the rates of formation of propylene and cyclopropane could shed some light on this question. Table II summarizes the relative rates of reaction of the propyl ions in isobutane and *n*-butane calculated from the data given in Figures 1 and 2. The table also shows the relative rates of reaction of the precursors of the propylene and cyclopropane products. Absolute rate constants are based on the assumption that the ions react at every collision with ammonia. The collision rate constant for a $\mathrm{C_3H_7^+}$ ion and ammonia can be calculated[17] to be 4.8×10^{-9} cm^3/(molecule sec).

In order to determine the effect of pressure on the relative amounts of the products formed in reactions of the two different propyl ions, a mixture of *n*-$\mathrm{C_4D_{10}}$–*n*-$\mathrm{C_4H_{10}}$–$\mathrm{NH_3}$–$\mathrm{O_2}$ (1:1:0.4:0.1) was irradiated at different pressures from 20 Torr to 1600 Torr. The results are presented in Table III, and are expressed in terms of percentages of the total yield which can be attributed to propyl ions; this method of presentation is chosen rather than absolute yields of products, since fragmentation process 13 is quenched over this pressure range to some extent (and the amount of secondary decomposition of the $\mathrm{C_3H_7^+}$ ions varies also).

Hydrogen scrambling in the propyl ions originating from *n*-butane was investigated by irradiating $\mathrm{CD_3CH_2CH_2CD_3}$ in the presence of 20% ammonia and examining the isotopic composition of the propylene and cyclopropane products formed. The results are given in Table IV. The mass spectrum of the propane formed in this experiment is too complicated to interpret, but the H and D atoms in the precursor ions have definitely undergone scrambling processes.

The appearance energy of the propyl ion in *n*-butane is much too low to allow the possibility that the propyl

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

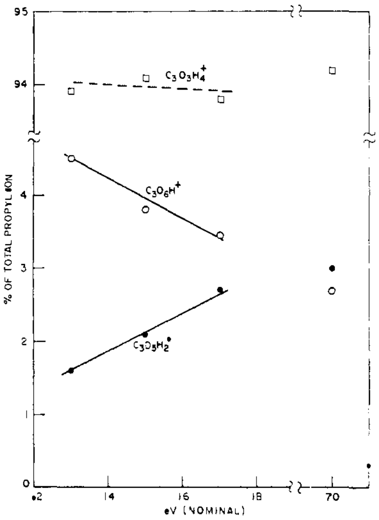

Figure 3. The yields of the $C_3D_3H_4^+$, $C_3D_5H_2^+$, and $C_3D_6H^+$ ions formed in the dissociation of $CD_3CH_2CH_2CD_3^+$ in the mass spectrometer at low energies.

ion formed at the onset energy originates from a direct C–C cleavage process.[18] (The heat of formation of this ion, derived from the appearance potential measurements, indicates that it has the *sec*-propyl structure.) In order to investigate possible modes of formation of this ion at low energies, the mass spectrum of $CD_3CH_2CH_2CD_3$ was measured at several low energies. These results are given in Figure 3.

Table IV. The Radiolysis of $CD_3CH_2CH_2CD_3$–NH_3 (1:0.2) Mixtures. Isotopic Structures of Neutral Products Formed in Reactions between $C_3D_3H_4^+$ and Ammonia

Reaction	Neutral product	Rel yield, %
$c\text{-}C_3D_3H_4^+ + NH_3 \rightarrow NH_4^+ +$	*c*-$C_3D_3H_3$	62
$c\text{-}C_3D_3H_4^+ + NH_3 \rightarrow NH_3D^+ +$	*c*-$C_3D_2H_4$	38
sec-$C_3D_3H_4^+ + NH_3 \rightarrow NH_4^+ +$	$C_3D_3H_3$ (propylene)	73
sec-$C_3D_3H_4^+ + NH_3 \rightarrow NH_3D^+ +$	$C_3D_2H_4$ (propylene)	27

The Butyl Ion. A. In *n*-Hexane. When a mixture of $n\text{-}C_6D_{14}$–$n\text{-}C_6H_{14}$–O_2 (1:2:0.1) is irradiated in the presence of excess xenon or krypton, the $n\text{-}C_4D_9H$ products show a mass spectral cracking pattern indicating that they consist of about 85% $CD_3CD_2CDHCD_3$ and 15% $CD_2HCD_2CD_2CD_3$ in the krypton-sensitized radiolysis, 92% $CD_3CD_2CDHCD_3$ and 8% $CD_2HCD_2CD_2CD_3$ in the xenon-sensitized radiolysis. Thus, apparently there are butyl ions of two structures which react to form *n*-butane in *n*-hexane. The most abundant of these is the *sec*-butyl ion

$$CD_3\overset{+}{C}DCD_2CD_3 + n\text{-}C_6H_{14} \longrightarrow CD_3CDHCD_2CD_3 + C_6H_{13}^+ \quad (20)$$

The other may be an *n*-butyl ion, but will be designated as $C_4H_9^+$ or $C_4D_9^+$ in view of the possibility[6] that it may have some alternate (cyclic) structure

$$C_4D_9^+ + n\text{-}C_6H_{14} \longrightarrow CD_2HCD_2CD_2CD_3 + C_6H_{13}^+ \quad (21)$$

When *n*-hexane is irradiated in the presence of 20% ammonia, (added as a proton acceptor[13]), neither methylcyclopropane nor cyclobutane was formed in significant yields; small quantities (<1%) of these products could not, however, have been detected.

The rate constant for reaction between a *tert*-butyl ion and *n*-hexane to form isobutane has been determined recently[19] to be $<1.3 \times 10^{-12}$ cm³/(molecule sec); this means if any $C_4H_9^+$ ions formed in pure *n*-hexane should isomerize to the *tert*-butyl structure,[3] the reaction of this ion with the parent molecule would be so slow that it could not compete effectively with neutralization or reaction with accumulated products. Therefore, in order to intercept any *tert*-butyl ions formed in *n*-hexane, it is necessary to add a suitably reactive alkane (an alkane having a tertiary hydrogen atom) with which the *tert*-butyl ion can undergo a hydride transfer reaction.[19] For this reason, a mixture of $n\text{-}C_6D_{14}$–$(CH_3)_2CHCH_2CH_2CH_2CH_3$–$O_2$, at a total pressure of 20 Torr, was irradiated; $(CD_3)_3CH$ was observed as a product with a yield about 12% of the total yield of *n*-butane. In the presence of excess krypton at a pressure of 200 Torr, the yield of $(CD_3)_3CH$ was about 52% of the total yield of *n*-butane. Within experimental error, all the isobutane product consisted of $(CD_3)_3CH$, indicating that it was produced in the reaction

$$(CD_3)_3C^+ + (CH_3)_2CHCH_2CH_2CH_2CH_3 \longrightarrow (CD_3)_3CH + C_7H_{15}^+ \quad (22)$$

$$k_{22} = 1.0 \times 10^{-10}\ \text{cm}^3/(\text{molecule sec})^{19}$$

B. In Isopentane. When the isopentane parent ion dissociates, there are two possible direct C–C bond cleavage processes which could yield $C_4H_9^+$ ions. In order to determine the relative importance of these two processes we examined the mass spectral cracking pattern of $(CH_3)_2CHCH_2CD_3$, where the fragmentation which leads to the formation of the *sec*-butyl ion

$$(CH_3)_2CHCH_2CD_3^+ \longrightarrow CH_3\overset{+}{C}HCH_2CD_3 + CH_3 \quad (23)$$

will always give $C_4H_6D_3^+$, while the fragmentation which leads to the formation of the isobutyl ion

$$(CH_3)_2CHCH_2CD_3^+ \longrightarrow (CH_3)_2CHCH_2^+ + CD_3 \quad (24)$$

would result in the formation of $C_4H_9^+$. The 70-eV mass spectral cracking pattern of this partially deuterated isopentane after correction for insufficient deuteration (3.3%) showed that more than 80% of the butyl ions have the formula $C_4H_6D_3^+$, demonstrating that the formation of isobutyl ions by direct fragmentation in isopentane (reaction 24) is a relatively unimportant process. Initially, mainly *sec*-butyl ions are formed in irradiated isopentane.

When an equimolar $i\text{-}C_5D_{12}$–$i\text{-}C_5H_{12}$ mixture is irradiated in the presence of a radical scavenger such as O_2, the *n*-butane product consists of $n\text{-}C_4D_{10}$, $n\text{-}C_4D_9H$, $n\text{-}C_4DH_9$, and $n\text{-}C_4H_{10}$. After subtracting out the contribution to the spectrum from $n\text{-}C_4D_{10}$, the residual mass spectrum of the $n\text{-}C_4D_9H$ product indicates that, within the limits of detection, the *n*-butane product formed in isopentane consists of $CD_3CDHCD_2CD_3$, demonstrating that it has the *sec*-butyl ion as precursor.

$$CD_3\overset{+}{C}DCD_2CD_3 + (CH_3)_2CHCH_2CH_3 \longrightarrow CD_3CDHCD_2CD_3 + C_5H_{11}^+ \quad (25)$$

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[18] F. P. Lossing and G. P. Semeluk, *Can J. Chem.*, **48**, 955 (1970).

[19] P. Ausloos and S. G. Lias, *J. Amer. Chem. Soc.*, 92, 1840 (1970).

The isobutane formed in the same experiment consists of i-C_4D_{10}, i-C_4D_9H, i-C_4H_9D, and i-C_4H_{10}, indicating that it is formed in a reaction of a C_4H_9 (C_4D_9) species which is not intercepted by radical scavengers. This is most likely a *tert*-butyl ion.

$$(CD_3)_3C^+ + i\text{-}C_5H_{12} \longrightarrow (CD_3)_3CH + C_5H_{11}^+ \qquad (26)$$

The fact that no $(CD_3)_2CDCD_2H$ was detected demonstrates that the isobutyl ions formed in process 24 all rearrange to more stable structures. It has recently been demonstrated[6c] that isobutyl ions rearrange mainly to the *tert*-butyl structure

$$(CH_3)_2CH\overset{+}{C}H_2 \longrightarrow (CH_3)_3C^+ \qquad (27)$$

but also may undergo rearrangement to the *sec*-butyl structure

$$(CH_3)_2CH\overset{+}{C}H_2 \longrightarrow CH_3\overset{+}{C}HCH_2CH_3 \qquad (28)$$

Radiolysis of the partially deuterated isopentane, $(CH_3)_2CHCH_2CD_3$, in the presence of O_2 as a radical scavenger, leads to the formation of n-$C_4H_7D_3$ and i-$C_4H_7D_3$ as the major butane products (again confirming that reaction 23 is the main fragmentation path leading to butyl ions in this compound). Unfortunately, the mass spectra of these partially deuterated products (Table V) are extremely complex, so the positions of the D atoms in the molecules cannot be ascertained with any certainty. However, from a comparison of these spectra with standard cracking patterns of $CD_3CH_2CH_2CH_3$ and $(CH_3)_2CH(CD_3)$, it can be said that the D atoms in both of these products have been "scrambled" from their original positions on one methyl group.

Table V. Observed Partial Mass Spectra[a] of $C_4D_3H_7$ Products Formed in the Radiolysis of $(CH_3)_2CHCH_2CD_3$–O_2 (1:0.1)

C$_3$ fragments m/e	$(CH_3)_2$-$CHCD_3$	Product i-$C_4D_3H_7$	CH_3CH_2-CH_2CD_3	Product n-$C_4D_3H_7$
41	8.7	7.1	9.3	7.1
42	8.3	11.2	7.0	8.9
43	23.4	21.1	34.7	20.9
44	10.6	20.1	7.2	19.5
45	8.5	26.3	5.7	25.8
46	40.5	14.1	36.1	17.7

[a] The sum of the peaks at masses 41 through 46 (the C$_3$ ions) has been set equal to 100%.

C. In 3-Methylpentane. For the 3-methylpentane parent ion, the only direct fragmentation process which can lead to a butyl ion is

$$CH_3CH_2CH(CH_3)CH_2CH_3^+ \longrightarrow CH_3CH_2\overset{+}{C}HCH_3 + C_2H_5 \qquad (29)$$

One would therefore expect that the primary fragmentation process in this compound would result in the formation of a *sec*-butyl ion. It is not surprising, therefore, that when a 3-methylpentane–3-methylpentane-d_{14} mixture is irradiated in the presence of oxygen as a radical scavenger, the n-butane-d_9 consists, within the limits of detection, entirely of $CD_3CDHCD_2CD_3$.

The mass spectra of $CH_3CH_2CH(CD_3)CH_2CH_3$ and $CH_3CH_2CD(CH_3)CH_2CH_3$ were measured; it was seen that the butyl ions, in the first case, all contained three D atoms, and in the second case, all contained the one D atom. This demonstrates that the fragmentation to form butyl ions involves a simple C–C bond cleavage rather than some process in which a parent ion rearrangement occurs.

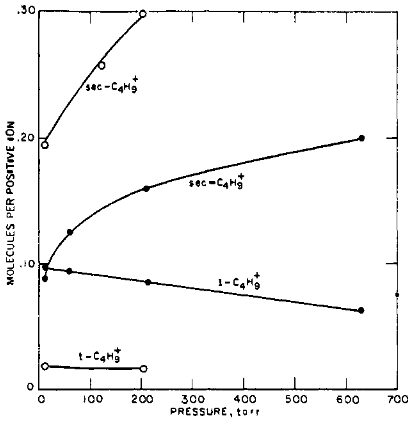

Figure 4. The yields of the butane products formed in krypton–3-methylpentane–O_2 (20:1:0.1) (●) and xenon–3-methylpentane–O_2 (20:1:0.1) (○) mixtures as a function of pressure.

Isobutane is also observed as a product, and reasoning analogous to that followed above leads us to the conclusion that it is produced in a reaction of a $C_4H_9^+$ ($C_4D_9^+$) ion. From the mass spectral cracking pattern of this product, we conclude that it consists entirely of $(CD_3)_3CH$, and, therefore, originates in a reaction of the *tert*-butyl ion. In view of the fact that the butyl ions are all formed in reaction 29, the *tert*-butyl ions must have been formed in an isomerization reaction.

The yields of the butane products formed in a krypton–3-methylpentane–O_2 mixture (20:1:0.1) are shown as a function of pressure in Figure 4. The yields of the butane products formed in a xenon–3-methylpentane–O_2 mixture are also given.

D. In Neopentane. The major fragment ion formed in the dissociation of the neopentane ion is the *tert*-butyl ion.[19] Experiments were performed to determine whether or not the H atoms in the *tert*-butyl ion undergo reshuffling. In order to do this, $(CH_3)_3CCD_3$ was irradiated in the presence of undeuterated isopentane. The partially deuterated *tert*-butyl ions formed in the fragmentation process

$$(CH_3)_3CCD_3^+ \longrightarrow (CH_3)_2\overset{+}{C}CD_3 + CH_3 \qquad (30)$$

react with the isopentane to form partially deuterated isobutane as a product

$$tert\text{-}C_4H_6D_3^+ + (CH_3)_2CHCH_2CH_3 \longrightarrow i\text{-}C_4H_7D_3 + C_5H_{11}^+ \qquad (31)$$

If no reshuffling has occurred, the partially deuterated isobutane product should consist entirely of $(CH_3)_2CHCD_3$. Table VI shows the mass spectra of the partially deuterated isobutane products formed in the xenon- and argon-sensitized radiolysis of $(CH_3)_3CCD_3$ in the presence of 10% i-C_5H_{12} and a free-radical scavenger. These fragmentation patterns are compared with that of a standard sample of $(CH_3)_2CHCD_3$. We see that in the standard cracking pattern of the unrearranged compound, the major peaks in the C$_3$ range are the two possible propyl ions, $C_3H_7^+$ and $C_3H_4D_3^+$, which are formed in a ratio of approximately 1:2. However, in the two-product i-$C_4H_7D_3$ samples, the $C_3H_7^+$ fragment is much less important, and diminishes

Table VI. Observed Partial Mass Spectra of i-$C_4H_7D_3$ Product Formed in the Radiolysis of $(CH_3)_3CCD_3$–$(CH_3)_2CHCH_2CH_3$–O_2 (1:0.1:0.05) Mixtures

	Standard cracking pattern		i-$C_4H_7D_3$ product	
m/e	$(CH_3)_2$-$CHCD_3$	Fragment	Xe-sensitized radiolysis	Ar-sensitized radiolysis
41	8.7	$C_3H_5^+$	12.3	6.0
42	8.3	$C_3H_6^+$	17.8	7.7
43	23.4	$C_3H_7^+$, $C_3H_3D_2^+$	15.3	9.7
44	10.6	$C_3H_4D_2^+$	18.3	23.0
45	8.5	$C_3H_3D_3^+$	9.1	16.2
46	40.5	$C_3H_4D_3^+$	37.1	37.3

in importance as the energy is raised, in going from the xenon- to the argon-sensitized radiolysis. The decrease in the importance of the $C_3H_7^+$ fragment is approximately compensated by increases in the peaks which can be attributed to the propyl ions of the isobutane $CH_3CH(CH_2D)CD_2H$. These spectra indicate that the hydrogen atoms of the *tert*-butyl ion do undergo reshuffling, and that the reshuffling process increases in importance with increasing energy.

E. In Methane–Cyclobutane Mixtures. When methane is irradiated in the presence of a radical scavenger, c-C_4D_8, and a perprotonated molecule such as i-C_5H_{12}, which will undergo hydride transfer reactions with butyl ions, butane will be formed by the mechanism

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \qquad (32)$$

$$CH_5^+ + c\text{-}C_4D_8 \longrightarrow C_4D_8H^+ + CH_4 \qquad (33)$$

$$C_4D_8H^+ + i\text{-}C_5H_{12} \longrightarrow C_4D_8H_2 + C_5H_{11}^+ \qquad (34)$$

The n-butane formed in such an experiment consisted of ~37% $CD_2HCDHCD_2CD_3$, ~12% $CD_3CH_2CD_2CD_3$, ~18% $CD_3CDHCDHCD_3$, and ~33% CD_3CDHCD_2-CD_2H. When the CH_4 was replaced by CD_4, the butane-d_9 within the limits of detection was CD_3CD-HCD_2CD_3, indicating that the straight-chain butyl ions formed in this system react mainly as *sec*-butyl ions.

Discussion

The Propyl Ion. A. The Structures of the Propyl Ions in *n*-Butane. The observations given in detail in the Results section can be summarized as follows. Propyl ions having at least two distinct structures are seen to undergo hydride transfer reactions in irradiated n-butane (see reactions 16 and 17). Some of the ions have the *sec*-propyl structure; the remaining propyl ions have been designated as $C_3H_7^+$ (or $C_3D_7^+$), and have a structure or structures as yet unspecified. The hydride transfer product of $C_3D_7^+$ has the structure $CD_3CD_2CD_2H$, indicating that its precursor may have the n-propyl ion structure. On the other hand, the formation of cyclopropane in a proton transfer reaction between $C_3H_7^+$ and ammonia indicates the presence of the protonated cyclopropane ion

$$c\text{-}C_3H_7^+ + NH_3 \longrightarrow c\text{-}C_3H_6 + NH_4^+ \qquad (35)$$

Furthermore, the fact that the rate of reaction 35 matches the rate of depletion of the hydride transfer product from the $C_3H_7^+$ ion in the presence of ammonia (see Table II) serves to establish the fact that most, if not all, of the $C_3H_7^+$ ions which react in n-butane have the protonated cyclopropane structure. Therefore, we can write for the hydride transfer reaction of the $C_3D_7^+$ species

$$c\text{-}C_3D_7^+ + C_4H_{10} \longrightarrow CD_3CD_2CD_2H + C_4H_9^+ \qquad (36)$$

(It should be pointed out that the n-propyl ion, if present, would be expected[1] to react with n-butane at a rate much faster than the *sec*-propyl ion, instead of the slower rate observed for the $C_3H_7^+$—that is, for the c-$C_3H_7^+$ ion.[20])

B. Primary Fragmentation Processes in Butane Parent Ions. In isobutane, where the fragmentation of the parent ion can only lead to the formation of the *sec*-propyl ion (reaction 4), more than 99% of the products resulting from hydride transfer reaction with the parent isobutane molecule (reaction 5) or proton transfer with ammonia (reaction 8) can be attributed to ions having the secondary structure. Thus, the protonated cyclopropane ions which are observed in n-butane cannot be formed in a rearrangement of *sec*-propyl ions. Therefore, they must originate in a primary fragmentation process which does not produce *sec*-propyl ions; this point is of some interest, since it has been demonstrated that the propyl ions formed in n-butane at the threshold energy have a heat of formation which matches that of the *sec*-propyl ion.[18] Thus, even though at the onset energy, propyl ion formation in n-butane may proceed by way of some rearrangement path which results in the direct formation of *sec*-propyl ions

$$CH_3CH_2CH_2CH_3^+ \longrightarrow CH_3\overset{+}{C}HCH_3 + CH_3 \qquad (37)$$

at higher energies, we can surmise from these results that some other fragmentation process also takes place. This may be a direct C–C cleavage

$$CH_3CH_2CH_2CH_3^+ \longrightarrow CH_3CH_2\overset{+}{C}H_2 + CH_3 \qquad (38)$$

followed by a rearrangement within 10^{-10} sec to the protonated cyclopropane structure

$$CH_3CH_2\overset{+}{C}H_2 \longrightarrow c\text{-}C_3H_7^+ \qquad (39)$$

and, possibly, also to the *sec*-propyl structure

$$CH_3CH_2\overset{+}{C}H_2 \longrightarrow CH_3\overset{+}{C}HCH_3 \qquad (40)$$

or, alternatively, the protonated cyclopropane ion may be formed directly in the parent ion fragmentation process

$$CH_3CH_2CH_2CH_3^+ \longrightarrow c\text{-}C_3H_7^+ + CH_3 \qquad (41)$$

In order to assess which of these processes occur, and to what extent, it is first useful to assess the relative importance of process 37, the formation of the *sec*-propyl ion in a direct fragmentation, at high energies. Unfortunately, a quantitative answer to this question is not available at the present time, but the data given in Figure 3 indicate that the direct fragmentation to form the *sec*-propyl ion is probably unimportant at high energies. This statement is based on the premise that any mechanism for such a rearrangement occurring in $CD_3CH_2CH_2CD_3^+$ will lead to the formation of *sec*-propyl ions other than $C_3D_3H_4^+$. Vestal,[21] for ex-

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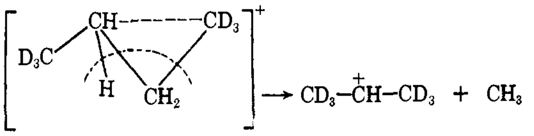
[20] Actually, in a preliminary report of this work which appeared earlier [P. Ausloos, R. E. Rebbert, and S. G. Lias, *J. Amer. Chem. Soc.*, **90**, 5031 (1968)], results were given which indicated that the precursor of $CD_3CD_2CD_2H$ did react with n-butane faster than the *sec*-$C_3D_7^+$ ion. However, the additional experiments reported here failed to confirm this observation. A reexamination of the early data indicates that the ratio of CD_3CDHCD_3 to $CD_3CD_2CD_2H$ calculated for the experiment in the absence of ammonia was based on a mass spectrum which was unreliable because of the small sample size.

ample, has suggested that the mechanism for direct formation of *sec*-propyl ions proceeds through a preliminary rearrangement of the *n*-butane parent ion to the isobutane parent ion, *i.e.*, for $CD_3CH_2CH_2CD_3^+$

$$\begin{aligned} &CD_3CH_2CH_2CD_3^+ \longrightarrow \\ &\quad (CD_3)_2CHCH_3^+ \longrightarrow CD_3\overset{+}{C}HCH_3 + CD_3 \quad (\sim 66\%) \\ &\quad\quad \longrightarrow CD_3\overset{+}{C}HCD_3 + CH_3 \quad (\sim 33\%) \end{aligned} \qquad (42)$$

Liardon and Gaumann[22] have proposed a mechanism for "internal methyl radical elimination," which, applied to $CD_3CH_2CH_2CD_3^+$, is



(43)

Either of these mechanisms could explain the direct formation of a *sec*-propyl ion from *n*-butane; in either case one would expect to see *sec*-propyl ions of the formula $C_3D_6H^+$ originating from $CD_3CH_2CH_2CD_3^+$. As the results given in Figure 3 show, $C_3D_6H^+$ ions are indeed formed from this parent ion, and the importance of this ion decreases as the energy increases. At 70 eV, $C_3D_6H^+$ comprises only 2.7% of the propyl ions. Although the formation of *sec*-propyl ions by alternate (unspecified) direct mechanisms cannot be excluded, it can logically be assumed that all such processes will show the same trends with energy.

The results given in Figure 3 also show that a propyl ion of the formula $C_3D_5H_2^+$ is formed in $CD_3CH_2CH_2CD_3$. This ion, which probably reflects the importance of hydrogen shuffling in the parent ion, comprises 3% of the propyl ions in the 70-eV spectrum but decreases in yield as the energy is decreased.

On the basis of the fact that a complex rearrangement process such as (37) is not important at high energies, we will assume that the equally complex rearrangement process 41 will also be unlikely (if it occurs at all) at high energies, and that nearly all propyl ions observed in *n*-butane originate in reaction 38 as *n*-propyl ions and undergo rearrangement reactions 39 and 40.

C. Relative Importance of Isomerization Paths of Primary Fragment Ions. The Effect of Energy and Pressure. In the foregoing discussion we have concluded that (a) more than 90% of the propyl ions formed in *n*-butane originate in direct C–C cleavage processes (reaction 38) and thus originate with the $CH_3CH_2\overset{+}{C}H_2$ structure, even at energies nominally only a few electron volts above the appearance energy (Figure 3); and (b) these $CH_3CH_2\overset{+}{C}H_2$ ions isomerize to the *sec*-propyl (reaction 40) and the protonated cyclopropane (reaction 39) structures.

Thus, neglecting the *sec*-propyl ions originating from direct fragmentation (reaction 37), we can obtain an approximate idea of the relative importance of isomerization reactions 39 and 40 by an examination of the relative yields which can be ascribed to the *sec*-propyl and protonated cyclopropane ions in *n*-butane. The relative importances of these two ions in the direct and inert-gas-sensitized radiolyses of *n*-butane are summarized in Table VII. The effect of pressure on the relative yields of the two ions is shown in Table III. Under all conditions, isomerization to the *sec*-propyl structure (reaction 40) predominates over rearrangement to the protonated cyclopropane structure (reaction 39). As one goes from a lower to a higher energy (as from the xenon- to the krypton-sensitized radiolysis) the isomerization to the *sec*-propyl ion structure increases in importance; apparently, for the more excited $n\text{-}C_3H_7^+$ ions the lifetime of the ion is short enough that the assumption of the constrained geometry of the cyclic ion is unfavorable. Collisional deactivation of the excited precursor primary ion (Table III) leads to an increased importance of the isomerization to the protonated cyclopropane ion.

Table VII. Fraction of $C_3H_7^+$ Ions Reacting as Protonated Cyclopropane in the Radiolysis of Butanes

	$c\text{-}C_3H_7^+$, %	Reaction 44,[a] %
n-Butane, 20 Torr	18	
n-Butane, 200 Torr	21	
n-Butane, xenon sensitized, 200 Torr	26	
n-Butane, krypton sensitized, 200 Torr	8	
Isobutane, 20 Torr	~0.5	~2.6
Isobutane, xenon sensitized, 200 Torr	~0.4	~1.5
Isobutane, krypton sensitized, 200 Torr	~1.0	~12.5

[a] See Discussion.

D. Hydrogen Scrambling in the Propyl Ions. As mentioned above, the phenomenon of hydrogen scrambling in *sec*-propyl ions has been observed both in the gas phase[11] and in the nmr spectrum[14] of *sec*-propyl ions. The results given in Table I demonstrate that scrambling becomes more important as more energy is supplied to the ion, as suggested before.[11,14] Indeed, in an nmr study[14] of the *sec*-propyl ion, an activation energy for the hydrogen-scrambling process was measured. The value which was determined for E_{act} was 0.71 ± 0.017 eV (16.4 ± 0.4 kcal/mol), which, since it corresponds rather well with the 0.69-eV (16-kcal/mol) difference between the heat of formation of the *sec*-propyl ion and that of the *n*-propyl ion, seems to corroborate the suggestion made earlier[11] that hydrogen scrambling in the *sec*-propyl ion proceeds through a transition state resembling a *n*-propyl ion

$$CH_3\overset{+}{C}HCH_3 \rightleftarrows CH_3CH_2\overset{+}{C}H_2^* \qquad (44)$$

However, since we have shown that the *n*-propyl ion undergoes ring closure (reaction 39) in addition to going to the *sec*-propyl structure (reaction 40), one should observe some evidence of the protonated cyclopropane ion, even in isobutane, if indeed the mechanism of hydrogen shuffling is reaction 44. In the radiolysis of isobutane in the presence of 20% NH_3 a small amount of cyclopropane is indeed formed. Assuming that the cyclopropane is formed in the mechanism represented by reaction 44 followed by 39 and 35 we calculate the percentage of propyl ions which react from the protonated cyclopropane structure; these are given in Table VII, along with the corresponding percentages of ions which must have undergone reaction 44, assuming that the branching ratio for reactions 39 and 40 is the same as

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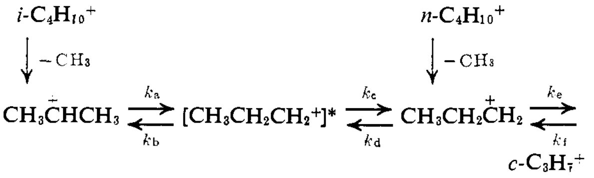
(21) M. Vestal, "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley-Interscience, New York, N. Y., 1968, p 59.

(22) (a) R. Liardon and T. Gaumann, *Helv. Chim. Acta*, **52**, 528 (1969); (b) R. Liardon and T. Gaumann, *ibid.*, **52**, 1042 (1969).

the ratios observed in *n*-butane under the same energy conditions. We see that, as would be expected if the formation of the protonated cyclopropane ion in isobutane proceeds through reaction 44, the yield of this ion increases as the energy of the precursor ion is increased (as in going from the xenon to the krypton sensitized radiolysis). This is in contrast to the results obtained in *n*-butane (Table VII) where the $CH_3CH_2\overset{+}{C}H_2$ species is formed directly; as discussed above, the importance of ring closure (reaction 39) as opposed to *sec*-$C_3H_7^+$ formation (reaction 40) is seen to decrease as the energy is increased.

The data given in Table VII indicate that about 1.5% of the propyl ions in the xenon-sensitized radiolysis and 12.5% in the krypton-sensitized radiolysis have undergone reaction 44. This would mean that, respectively, about 1 and 11% of the *sec*-propyl ions should show hydrogen scrambling in these systems. However, the results given in Table I show that the amount of hydrogen scrambling in the xenon- and krypton-sensitized radiolyses of isobutane is definitely much greater than these estimates. (The calculated percentages of rearrangement given in columns A and B of the table are based on assumed mechanisms consistent with reactions 44–39–35; column C gives minimum values for hydrogen scrambling, but even these are seen to be much higher than the estimated percentages of ions which have undergone reaction 44 as given in Table VII.) In view of this discrepancy, we must say that the transition state for hydrogen scrambling apparently does not always completely attain the structure of the *n*-propyl ion formed by fragmentation of a *n*-butane ion. That is



$$\begin{array}{ccccccc} i\text{-}C_4H_{10}^+ & & & & n\text{-}C_4H_{10}^+ & & \\ \downarrow -CH_3 & & & & \downarrow -CH_3 & & \\ CH_3\overset{+}{C}HCH_3 & \underset{k_b}{\overset{k_a}{\rightleftarrows}} & [CH_3CH_2CH_2^+]^* & \underset{k_d}{\overset{k_c}{\rightleftarrows}} & CH_3CH_2\overset{+}{C}H_2 & \underset{k_f}{\overset{k_e}{\rightleftarrows}} & \\ & & & & & & c\text{-}C_3H_7^+ \end{array} \quad (45)$$

where $[CH_3CH_2CH_2^+]^*$ represents a "*n*-propyl-ion-like" transition state for hydrogen reshuffling. The exact nature of this entity cannot be specified; actually the scheme as written is an artifical way of describing the relationship between this transition state and the *n*-propyl ion, since the transition state may actually have any of a number of structures intermediate between the *sec*-propyl and the *n*-propyl structures.

The mechanism for hydrogen reshuffling in the protonated cyclopropane ion has recently been discussed in detail.[6a] The results given in Table IV show the isotopic distribution of the cyclopropane formed in the proton (or deuteron) transfer reaction between ammonia and the *c*-$C_3D_3H_4^+$ ion formed in $CD_3CH_2CH_2CD_3$

$$c\text{-}C_3D_3H_4^+ + NH_3 \longrightarrow C_3D_2H_4 + NH_3D^+ \qquad (46)$$

$$c\text{-}C_3D_3H_4^+ + NH_3 \longrightarrow C_3D_3H_3 + NH_4^+ \qquad (47)$$

If no reshuffling occurred, one would expect to see primarily deuteron transfer (reaction 46). Actually the observed ratio of reaction 47 to 46 is 62:38, which is close to the statistical distribution of 57:43, and in fairly good agreement with the 57:43 ratio observed by Aboderin and Baird[23] for *c*-$C_3D_3H_3$:*c*-$C_3D_2H_4$ formed in the deamination of $CD_3CH_2CH_2NH_2$. This result confirms again that proton–deuteron scrambling in the protonated cyclopropane ion is a very rapid process.[5,6a,23]

E. Summary of the Isomerization Mechanisms. The composite isomerization mechanism (reaction 45) is capable of explaining all the results reported here, provided that $k_e \gg k_f$, $k_d \gg k_c$, $k_d > k_e$, and $k_b \gg k_c$. As mentioned above, the relative rates of the various possible reaction paths are strongly energy dependent. This scheme also explains the observation that *sec*-propyl ions formed in strongly acid solution slowly undergo carbon shuffling (reaction 1), since the *sec*-propyl ions indeed undergo a slow reversible ring closure reaction. This mechanism is not inconsistent with the results obtained in the study of the deamination of 1-propylamine,[6a] where no evidence was found for isomerization of the *sec*-propyl or protonated cyclopropane ions; in that study, the lifetime of the ions was much shorter, as evidenced by the fact that as much as 15% of the *n*-propyl ions were intercepted before undergoing any rearrangement at all. Therefore, it is probable that under the conditions of that study the *sec*-propyl and protonated cyclopropane ions undergo reaction before isomerization can occur, as pointed out by the authors.

F. Relative Stabilities of the *sec*-Propyl and Protonated Cyclopropane Ions. The fact that the nmr spectrum of the *sec*-propyl ion has been observed,[14] and no protonated cyclopropane ions were seen, indicates that the relative stabilities of these two ions are *sec*-propyl > protonated cyclopropane. A recent theoretical calculation[24] predicts, however, that the protonated cyclopropane ion is the more stable of the two ions (although the authors themselves feel that the results of their calculation are open to question). It is true (Table II) that the protonated cyclopropane ion reacts more slowly than the *sec*-propyl ion with *n*-butane, but the generalization that a more stable ion reacts more slowly[1] probably cannot be applied to a comparison between ions of such radically different geometries.

The Butyl Ion. A. Isomerization of the *sec*-Butyl Ion to the *tert*-Butyl Structure. The fact that *tert*-butyl ions are found in irradiated 3-methylpentane, where primary fragmentation processes lead only to *sec*-butyl ions, indicates that the isomerization process

$$CH_3\overset{+}{C}HCH_2CH_3 \longrightarrow (CH_3)_3C^+ \qquad (48)$$

occurs in the gas phase. It is known that the *tert*-butyl ion is not formed in a process involving rearrangement of the parent ion.[18] Process 48 has previously been demonstrated[3b,c] to occur in strong acid solution within 10^{-5} sec.

The effect of increased pressure on the isomerization reaction 48 can be derived from the results shown in Figure 4. In the irradiation of 3-methylpentane–rare gas mixtures, as the pressure is increased from 20 to 630 Torr, the total yield of butyl ions increases, demonstrating that secondary decompositions of the $C_4H_9^+$ ions are collisionally quenched to a greater and greater extent as the pressure is raised. Over this pressure range, however, the yield of *tert*-butyl ion actually decreases as the pressure is increased. This could mean

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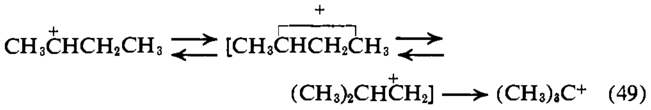
(23) A. A. Aboderin and R. L. Baird, *J. Amer. Chem. Soc.*, **86**, 2300 (1964).

(24) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *ibid.*, 91, 5350 (1969).

that collisional deactivation of the fragment *sec*-butyl ion quenches the isomerization reaction 48. Of course, as the pressure is raised, the time available to the ion before being intercepted is lowered. From the data in Figure 4, one can estimate that the isomerization reaction 48 occurs within 10^{-9}–10^{-8} sec, on the average, for butyl ions formed in the krypton-sensitized radiolysis of 3-methylpentane.

The fact that the relative importance of process 48 increases as the energy imparted to the ion increases, as in going from the xenon- to the krypton-sensitized radiolysis (Figure 4), however, clearly indicates that there is an activation energy for reaction 48. This activation energy has been estimated to be 0.78 eV (18 kcal/mol) from the results obtained in an nmr study;[3b] the energy difference between the *sec*-$C_4H_9^+$ ion and the *i*-$C_4H_9^+$ ion is 0.69 eV (16 kcal/mole).[18] Therefore, one possible and plausible mechanism for this rearrangement would be



$$\mathrm{CH_3\overset{+}{C}HCH_2CH_3 \rightleftarrows [\overset{+}{\overline{CH_3CHCH_2CH_3}} \rightleftarrows (CH_3)_2CH\overset{+}{C}H_2] \longrightarrow (CH_3)_3C^+} \quad (49)$$

(where $\overset{+}{\overline{\mathrm{CH_3CHCH_2CH_3}}}$ may be a protonated methylcyclopropane ion or simply a transitory three-membered ring structure in which the terminal $-CH_3$ has not lost its identity as a methyl group).[6c]

In the results reported here there is no positive evidence for this particular mechanism; no products were observed in any experiment which could be attributed to reaction of the protonated methylcyclopropane ion, *i.e.*

$$c\text{-}\mathrm{C_3H_5(CH_3)^+ + NH_3 \longrightarrow} c\text{-}\mathrm{C_3H_5(CH_3) + NH_4^+} \quad (50)$$

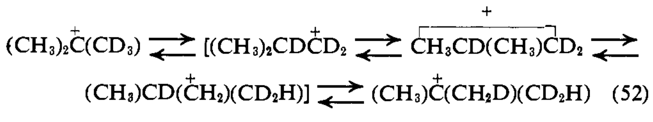
or the isobutyl ion, *i.e.*

$$\mathrm{(CH_3)_2\overset{+}{C}HCH_2 + RD \longrightarrow (CH_3)_2CHCH_2D + R^+} \quad (51)$$

so that, if formed, the lifetime of these intermediate ions in our system is very short.

Evidence for process 49 was, however, found recently in a study of the deamination of isobutylamine,[6c] where the $\mathrm{(CH_3)_2CH\overset{+}{C}H_2}$ ions were seen to rearrange to *tert*-butyl ions and to *sec*-butyl ions *via* a methyl-branched three-membered ring intermediate. In that study, a small fraction (~0.6%) of the ions was seen to form protonated methylcyclopropane ions. If these ions were present in such extremely small yields, their presence would have gone undetected in our experiments.

B. Hydrogen Scrambling in the Butyl Ions. The *tert*-butyl ion undergoes an energy-dependent hydrogen reshuffling process, as demonstrated by the results given in Table VI. An activation energy of more than 1.21 eV (28 kcal/mol) has been estimated[4d] for this process. This lower limit for the energy barrier is not inconsistent with the activation energy of ~1.39 eV (~32 kcal/mol) which would be observed[18] if the transition state for the process went through an "isobutyl-ion-like" structure. For example



$$\mathrm{(CH_3)_2\overset{+}{C}(CD_3) \rightleftarrows [(CH_3)_2CD\overset{+}{C}D_2 \rightleftarrows \overset{+}{\overline{CH_3CD(CH_3)CD_2}} \rightleftarrows (CH_3)CD(\overset{+}{C}H_2)(CD_2H)] \rightleftarrows (CH_3)\overset{+}{C}(CH_2D)(CD_2H)} \quad (52)$$

where $\overset{+}{\overline{\mathrm{CH_3CD(CH_3)CD_2}}}$ may again be a protonated methylcyclopropane ion or simply a transitory three-membered ring structure in which an internal hydride (deuteride) transfer from a methyl group occurs.[6c] However, as in the case of hydrogen reshuffling in the *sec*-propyl ion, we must say that the ion in the transition state does not completely attain the isobutyl structure, since that ion is known to isomerize to the *sec*-butyl ion as well as to the *tert*-butyl ion, but the *tert*-butyl ions formed in the radiolysis of neopentane isomerize to the *sec*-butyl ion structure to a negligible extent.[10, 19]

The nmr spectrum of the *sec*-butyl ion[3b] shows effects traceable to the occurrence of the thermoneutral 2–3 hydride shift

$$\mathrm{CH_3\overset{+}{C}HCH_2CH_3 \rightleftarrows CH_3CH_2\overset{+}{C}HCH_3} \quad (53)$$

This process has been shown[3b] to have an activation energy of 0.26 eV (6 kcal/mol). Such shifts have also been observed in a recent study of the deamination of partially deuterated butylamines.[6d] The results given in Table V show that the $\mathrm{CH_3CH_2C^+HCD_3}$ ion formed in $\mathrm{(CH_3)_2CHCH_2CD_3}$ also undergoes hydrogen reshuffling processes involving the terminal methyl groups, since the D atoms are scrambled in this ion. It is not really possible to speculate on the mechanism of this scrambling process without further information, but by analogy with the scrambling mechanisms in the *sec*-propyl and *tert*-butyl ions, one might expect that it proceeds through a "*n*-butyl-ion-like" transition state.

C. Isomerization of the *n*-Butyl Ion. Since a major fraction of the butyl ions in *n*-hexane originate[22b] in reaction 54, the structures of the butyl ions observed in

$$\mathrm{CH_3CH_2CH_2CH_2CH_2CH_3^+ \longrightarrow CH_3CH_2CH_2CH_2^+ + C_2H_5} \quad (54)$$

this system may give some information about the rearrangement processes of the $\mathrm{CH_3CH_2CH_2CH_2^+}$ ion. Indeed, in the radiolysis of *n*-hexane, at least three butyl ions can be detected: the *sec*-butyl ion, the *tert*-butyl ion (formed most likely in rearrangement process 48), and an ion we have designated as $C_4H_9^+$ (or $C_4D_9^+$) which undergoes hydride transfer reactions to yield a product labeled at the primary position (reaction 21). Since the protonated cyclopropane ion undergoes a hydride transfer reaction to yield a product labeled at the primary position, the possibility must be considered that the $C_4H_9^+$ ion which reacts in *n*-hexane has a cyclic structure. Unfortunately, little can be said on this point, since neither cyclobutane nor methylcyclopropane was observed as a proton transfer product from $C_4H_9^+$ to ammonia (although it is possible that small amounts of these products may have been formed).

D. Isomerization of the Protonated Cyclobutane Ion. There is evidence that[25] the protonated cyclobutane ion does exist. If this is the case, it is probable that the ion initially formed by proton transfer to cyclobutane (reaction 33) is the protonated cyclobutane ion. By analogy with the protonated cyclopropane ion, one would expect that if this ion, itself, underwent a hydride (deuteride) transfer reaction, the product would be labeled at the primary rather than the secondary position. Therefore, the fact that the butane formed in the reaction sequence

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(25) F. Cacace, A. Guarino, and E. Passagno, *J. Amer. Chem. Soc.*, 91, 3131 (1969).

$$CD_5^+ + c\text{-}C_4D_8 \longrightarrow C_4D_9^+ + CD_4 \quad (55)$$

$$C_4D_9^+ + i\text{-}C_5H_{12} \longrightarrow CD_3CDHCD_2CD_3 + C_5H_{11}^+ \quad (56)$$

is labeled in the secondary position indicates that the protonated cyclobutane ion isomerizes to the *sec*-butyl ion prior to or during reaction. The most probable route for this rearrangement is

$$c\text{-}C_4H_9^+ \longrightarrow [CH_3CH_2CH_2CH_2^+]^* \longrightarrow CH_3CH_2\overset{+}{C}HCH_3 \quad (57)$$

From the results given above (see Results section), it can be seen that when a proton is transferred to c-C_4D_8, the proton has approximately a statistical chance of ending up on a given carbon atom in the final reaction product. This indicates that a rapid shuffling of H (D) atoms in the protonated cyclobutane ion must have occurred, since according to the mechanism depicted above, and what is known about hydrogen shuffling in the *sec*-butyl ion (*i.e.*, 2–3 shifts should be strongly favored over 1–2 or 3–4 shifts), the proton would be expected to have a greater than statistical chance of ending up on a methyl group.

Excited State Donor–Acceptor Complexes. Olefin Isomerization as a Probe to Monitor Decay Processes[1]

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Abstract: The formation and reactions of excited state complexes (exciplexes) between excited states of metalloporphyrins or aromatic hydrocarbons and electron-deficient aromatic nitro compounds have been investigated. Various nitrostilbenes have been used as acceptors so that photoinduced geometric isomerization of the olefinic bond can provide information regarding possible fates of exciplex excitation energy. For zinc and magnesium porphyrins it is found that both excited singlets and triplets can form exciplexes with nitro compounds. The singlet and triplet exciplexes do not interconvert; in fact they have quite different reactivities. Exciplexes formed with the porphyrins do not decay *via* other excited states of porphyrin or acceptor; formation of ions from these exciplexes is evidently unimportant in nonpolar solvents. Triplet exciplexes are much more active in producing isomerization in the acceptor; evidence exists for a chain mechanism involving exchange of acceptor during the triplet exciplex lifetime. Excited singlets of tetracene and perylene form exciplexes with the nitrostilbenes that lead to isomerization of the acceptor with low efficiency. The triplet of tetracene is unreactive under the same conditions. Small changes in solvent or structure of the donor can produce large changes in exciplex formation constants as well as in the reactivity of the exciplex.

Photoassociation of electronically excited molecules in solution with ground states of the same species or other molecules is a well-established phenomenon.[4] Particularly well studied have been reactions of excited states with electron donors or acceptors.[5] Complexes between excited singlet states and electron donors or acceptors have been detected by the appearance of fluorescence from the complex concurrent with quenching of fluorescence from the free excited state.[5] Although singlet complexes have been perhaps better characterized due to their emission phenomena, triplet donor–acceptor complexes have also been detected.[6,7] In several cases excited complexes (exciplexes) of this sort have been suggested as intermediates in the course of chemical reactions.[8,9] It is probable that exciplexes involving photoexcited porphyrins and related compounds are involved in photosynthesis and related photobiological processes.

Despite the widespread occurrence of exciplexes, relatively little is known regarding mechanisms of exciplex decay. Often exciplex formation results simply in return of both partners to the ground state even in systems where one or both partners show distinctive emission or photochemistry in the absence of the other. Evidently in these cases exciplex formation provides a path for nonradiative decay, but the details of the mechanism are not clear.[10] In a recent review, Stevens[4] has discussed the possible fates of exciplexes formed by photoassociation. Chart I summarizes the several possibilities suggested by Stevens.

We have previously investigated the formation of exciplexes between excited states of metalloporphyrins and electron-deficient aromatic nitro compounds.[11] These complexes are nonfluorescent and in most cases

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(2) (a) National Science Foundation Predoctoral Fellow, 1965–1969; (b) National Science Foundation Undergraduate Research Participant, 1969–1970; (c) National Defense Education Act Predoctoral Fellow, 1969–present.

(3) Alfred P. Sloan Foundation Fellow, 1970–1972; author to whom correspondence should be directed.

(4) B. Stevens, *Advan. Photochem.*, in press.

(5) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968); H. Knibbe, K. Rollig, F. P. Schaffer, and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967); H. Beens, H. Knibbe, and A. Weller, *ibid.*, **47**, 1184 (1967), and references therein.

(6) H. Beens and A. Weller, Loyola International Conference on Molecular Luminescence, Chicago, Ill., 1968; reprinted in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 203.

(7) N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, **91**, 7113 (1969).

(8) P. J. Wagner and A. E. Kemppainen, *ibid.*, **91**, 3085 (1969).

(9) S. G. Cohen and N. Stein, *ibid.*, **91**, 3690 (1969), and references therein.

(10) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

(11) D. G. Whitten, I. G. Lopp, and P. D. Wildes, *J. Amer. Chem. Soc.*, 90, 7196 (1968).