Reactions of the Carbonium Ions from the Decay of Propane-1,2-t_2 in Gaseous and Liquid Propane

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Abstract: The chemical fate of a tritiated propane molecule following the decay of the radioactive atom has been studied with a tracer technique involving the use of propane-1,2-t_2. The isotopically pure compound was allowed to decay in the presence of a large excess of inactive propane, both in the gas phase at 1 atm and in the liquid phase at $-130°$. The analysis of the labeled decay products was carried out by radio gas chromatography. The results obtained were compared with the low-pressure, decay-induced fragmentation pattern of propane-1-*t* and propane-2-*t*. The results are consistent with the view that the dissociation process, $C_3H_7^+ = C_3H_5^+ + H_2$, of the excited daughter ions observed at 10^{-5} torr is largely prevented in the gas phase at 1 atm by collisional deactivation processes, as suggested by the low yields of molecular hydrogen and propylene. The stabilized $C_3H_6T^+$ ions react with the inactive propane to give monotritiated propane and unlabeled propyl ions, indicating a thermoneutral hydride ion transfer process. Those $C_3H_6T^+$ ions (20%) that receive from the nuclear decay a larger excitation energy fragment into smaller ions and give tritiated products other than propane. The nature and the yields of the labeled products observed are in good agreement with those expected, if one takes into account the low-pressure fragmentation pattern and the ion–molecule reactions that are known to occur within the system. In the liquid phase, the only major product observed is propylene, along with a smaller amount of molecular hydrogen. The product distribution suggests that, when the decay takes place in liquid propane, most of the daughter $C_3H_6T^+$ ions are stabilized. Even in those cases when the nuclear transition leaves the organic ion in a highly excited state, its dissociation is limited to the first step, *i.e.*, to the process $C_3H_6T^+ = C_3H_4T^+ + H_2$. The $C_3H_4T^+$ ion, reacting with the inactive propane, eventually give rise to tritiated propylene.

A detailed investigation on the chemical reactions following the β decay of a tritium atom contained, respectively, in the molecules of methane and ethane has been carried out by means of a tracer technique involving the use of multilabeled alkanes.[1-3] The present paper describes the extension of the investigation to the chemical processes promoted by the decay of a radioactive atom contained in propane-1,2-t_2.

The choice of this molecule was suggested by the following considerations. In the first place, the necessary data on the low-pressure, decay-induced fragmentation of propane-1-*t* and propane-2-*t* had been determined by Wexler, Anderson, and Singer[4] with a specially designed mass spectrometer.

Secondly, the reactions of many organic ions in gaseous propane are well known, as a consequence of extensive investigations carried out with high-pressure mass spectrometric methods. Furthermore, the boiling point of propane makes it convenient to store, even for extended periods of time, samples of liquid $C_3H_6T_2$, thus allowing the study of the decay-promoted reactions not only in the gas but also in the liquid phase.

Finally, a study of the chemical reactions promoted by the decay of propane-1,2-t_2 is of special interest, in view of the unique fragmentation pattern determined by the low-pressure decay of propane-1-*t* and propane-2-*t*, which shows a significant deviation from those observed in the decay of all the other tritiated hydrocarbons so far investigated.[4-7]

In particular, the yields of the initial fragment, *i.e.*, the $C_3H_7^+$ ion, from the decay of propane-1-*t* and propane-2-*t* are 56 and 41%, respectively. This is to be compared with the much higher yields of the initial fragment from the decay of CH_3T, C_2H_5T, C_6H_5T, and the four monotritiated toluenes, all of which range from 83 to 72%. The relatively high percentage of daughter ions that dissociate, following the decay of both the monotritiated propanes at 10^{-5} torr, is not determined, according to Wexler,[4] by an unusually high amount of excitation energy imparted to the ion by the nuclear transition. The observed fragmentation is rather produced by the facile decomposition of the $C_3H_7^+$ ions into $C_3H_5^+$ ions, requiring only 4–10 kcal/mole for the primary and 30–40 kcal/mole for the secondary propyl ions.[4]

While this suggestion is quite reasonable, from the low-pressure fragmentation data it can only be inferred that in the decay of propane-1-*t* and propane-2-*t* a considerable fraction of the $C_3H_7^+$ ions is formed in states of excitation energy comprised between 4–14 kcal/mole and, say, 100 kcal/mole. The lower limit is set by the energy required to form a $C_3H_5^+$ ion from a primary $C_3H_7^+$ ion, while the upper limit represents the energy required for the next step of unimolecular decomposition, involving a more extensive fragmentation, for instance, the formation of $C_3H_3^+$ or $C_2H_3^+$ ions.

It was hoped that the present experiments, involving the decay of propane-1,2-t_2 at 760 torr and in the liquid phase, *i.e.*, in systems where the stabilization of the excited ions becomes increasingly effective, could be useful, *inter alia*, to provide additional information on

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[1] F. Cacace, G. Ciranni, and A. Guarino, *J. Am. Chem. Soc.*, **88**, 2903 (1966).

[2] B. Aliprandi, F. Cacace, and A. Guarino, *J. Chem. Soc., Sect. B*, 519 (1967).

[3] F. Cacace, presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[4] S. Wexler, G. R. Anderson, and L. A. Singer, *J. Chem. Phys.*, **32**, 417 (1960).

[5] A. H. Snell and F. Pleasonton, *J. Phys. Chem.*, **62**, 1377 (1958).

[6] S. Wexler and D. C. Hess, *ibid.*, **62**, 1382 (1958).

[7] T. A. Carlson, *J. Chem. Phys.*, **32**, 1234 (1960).

the excitation level of those propyl ions that were found to dissociate into $C_3H_5^+$ ions at 10^{-5} torr.

Experimental Section

Materials. Propane-1,2-t_2 was obtained from propylene by reaction with tritium gas over a chromia–gel catalyst prepared and activated according to Burwell, *et al.*[8] Undesirable hydrogen exchange and double-bond migration reactions were found by these authors to be slow in comparison with the hydrogenation itself, as demonstrated by the high isotopic purity of the resulting deuterated hydrocarbons.

Propylene (0.033 mmole) and tritium gas (4 curies) were allowed to react in the presence of chromium oxide (40 mg) at −12° for a period of 36 hr. A large excess of inactive propane was immediately added to the reaction mixture, and most of the unreacted T_2 was eliminated by freezing and outgassing the sample.

The crude labeled propane was then purified twice by preparative gas chromatography, using a 4-m column, heated to 100° and packed with activated silica gel. After the second purification step, a radio gas chromatographic analysis of the propane failed to detect active impurities.

Unlike the tritiated methanes, the various propanes containing a different number of tritium atoms cannot be separated by gas chromatography. Therefore, a mass spectrometric analysis of the purified labeled propane was carried out. The percentage of monotritiated propane, the most likely impurity, was found to be below the detection limit, estimated to be around 10%. More significantly, the abundance of propane-1,2-t_2, *i.e.*, the ratio $C_3H_6T_2/C_3H_8$, was found to be in excellent agreement with the value calculated from a measurement of the specific activity of the sample.

The purified propane-1,2-t_2 was further diluted to the desired specific activity with inactive propane before being stored for the growth of the decay products.

The propylene, propane, and the other hydrocarbons used as carriers were commercial (Rivoira S.p.A., Torino) samples with a purity greater than 99.9%. The tritium gas was obtained from CEA (France) and its stated purity was greater than 95%, the main contaminant being ^3He. A gas chromatographic analysis carried out according to Smith and Carter[9] showed that the HT content in the sample was lower than 2%.

Growth and Analysis of the Decay Products. The propane-1,2-t_2 was allowed to decay in propane + 0.5% O_2 at room temperature and 1 atm for a period of 4 weeks. The samples were stored in 100-ml Pyrex ampoules and their specific activity was kept between 0.5 and 1 mcurie per mmole of gas. The propane-1,2-t_2 was also allowed to decay in liquid propane (both neat and containing 2% O_2) at −130° for the same period of time.

The analysis of the labeled decay products was carried out by radio gas chromatography, using a flow ionization chamber and a vibrating reed electrometer, according to a technique already described.[10] The following columns were employed for the analysis of the tritiated hydrocarbons: a 4-m column packed with activated silica gel and heated to 100° was used for the separation of (H_2 + CH_4), C_2H_6, C_2H_4, C_3H_8, and C_3H_6; a 3-m column packed with 5-A molecular sieves and heated to 100° was employed for the separation of H_2 from CH_4; a 2-m column of activated alumina, coated with 0.5% of silicone oil, purchased from the Burrell Co. (Pittsburgh, Pa.), was used for the separation of the C_3 and the C_4 hydrocarbons; a 12-m dimethylsulfolane column was chosen to separate (H_2 + CH_4), (C_2H_4 + C_2H_6), propylene, propane, and acetylene.

Results and Discussion

The yields of the tritiated products from the decay of propane-1,2-t_2 in the systems investigated are given in Table I. These yields represent the per cent of activity of the labeled fragments from the decay of $C_3H_6T_2$, *i.e.*, of the $C_3H_6T^3He^+$ ions, which is contained in each of the products identified.

Effects of the Radiation Damage to the System. The self-radiolysis of the sample, caused by the β particles associated with the decay of $C_3H_6T_2$, promotes the formation of labeled compounds, which could superimpose a product spectrum on the tritiated substances arising from the reactions of the $C_3H_6T^3He^+$ ions. The specific activity of the samples was therefore kept to the lowest level compatible with the requirements of the radiometric analysis. In the reasonable hypothesis that the G_{-M} value[11] is the same for propane and propane-t_2, one can calculate an upper limit for the yield of labeled products formed by radiolytic processes during the storage of samples having a specific activity below 0.5 mcurie/mmole. The results show that the activity of the radiolytic products is quite small when compared to the activity of the $C_3H_6T^3He^+$ ions formed in the same storage period. These estimates have been fully verified by blanks carried out with monotritiated methane and ethane in the study of the methane-t_4 and ethane-1,2-t_2 decay, respectively.[1-3]

Table I. Yields of Labeled Products from the Decay of Propane-1,2-t_2 in Propane

	Yields[a]		
Product	Propane + 2% O_2 gas phase at 25°	Propane + 2% O_2[b] liquid phase at −130°	Propane liquid phase at −130°
HT	9.3	4.4	5.3
CH_3T	7.9	2.2	2.4
C_2H_5T	1.9	1.0	1.1
C_2H_3T	4.9	1.8	1.8
C_2HT	0.7	2.7	2.7
C_3H_5T[c]	6.0	13.8	12.4
C_3H_3T[d]	~4.9[e]	1.8[e]	1.8[e]
C_4H_9T	...	...	...

[a] Percentage of the total activity of the $C_3H_6T^3He^+$ decay fragments found in each product. The standard deviation of the data is below 10%. [b] This value represents the percentage of oxygen added to propane before the condensation at −130°. [c] Propylene. [d] Allene + methylacetylene. [e] Approximate value owing to incomplete gas chromatographic separation.

These and other considerations, including the observation that the combined activity of the products identified is invariably smaller than the activity contained in the primary decay fragments and the minor effect of the radical scavengers on the product distribution, make it reasonable to assume that the tritiated products listed in Table I are formed by the reactions of the $C_3H_6T^3He^+$ ions with no significant contribution from radiolytic processes.

Decay-Induced Fragmentation of Propane-1,2-t_2. Since the probability of a decay event is independent of the position of the radioactive atom in the molecule, the propane-1,2-t_2 can be regarded, from the point of view of the fragmentation following the decay, as an equimolecular mixture of propane-1-t and propane-2-t. The resulting fragmentation pattern can be calculated from the data of Wexler and is given in Table II. The excess of inactive propane contained in the system intercepts any undissociated $C_3H_6T^+$ ion formed in the β decay, according to the thermoneutral hydride ion transfer reaction

$$C_3H_6T^+ + C_3H_8 \rightleftharpoons C_3H_7T + C_3H_7^+ \tag{1}$$

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[8] R. L. Burwell, Jr., *et al.*, *J. Am. Chem. Soc.*, **82**, 6272 (1960).

[9] H. A. Smith and E. H. Carter, "Tritium in the Physical and Biological Sciences," Vol. I, International Atomic Energy Agency, Vienna, 1962, p 121.

[10] F. Cacace, *Nucleonics*, **19**, 5, 45 (1961).

[11] A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, London, 1960, p 64.

The product of reaction 1, which has been established by Pettersson and Lindholm,[12] by Aquilanti and Volpi,[13] and by Sieck and Futrell[14] with deuterated reagents, is monotritiated propane, which cannot be detected in the presence of the excess of propane-1,2-t_2 necessary to produce the labeled decay fragments.

Table II. Low-Pressure Fragmentation of an Equimolecular Mixture of Propane-1-*t* and Propane-2-*t* Following β Decay[a]

m/e	Ionic fragment	Abundance, %
46	$(C_3H_7{}^3He)^+ + C_3H_7T^+$	<0.2
43	$C_3H_7^+$	48.50 ± 0.90
42	$C_3H_6^+$	2.80 ± 0.30
41	$C_3H_5^+$	18.00 ± 1.00
40	$C_3H_4^+$	0.90 ± 0.10
39	$C_3H_3^+$	4.60 ± 0.40
38	$C_3H_2^+$	3.50 ± 0.30
37	C_3H^+	3.60 ± 0.30
36	C_3^+	1.10 ± 0.10
29	$C_2H_5^+$	1.18 ± 0.30
28	$C_2H_4^+$	0.60 ± 0.10
27	$C_2H_3^+$	5.10 ± 0.70
26	$C_2H_2^+$	3.40 ± 0.30
25	C_2H^+	1.40 ± 0.20
24	C_2^+	0.60 ± 0.10
15	CH_3^+	1.40 ± 0.20
14	CH_2^+	0.80 ± 0.10
13	CH^+	0.55 ± 0.07
12	C^+	0.50 ± 0.07
3	$(^3He)^+$	<0.1
2	H^{2+}	<0.1
1	H^+	0.80 ± 0.10
20.5	$C_3H_5^{2+}$	0.15 ± 0.10
20.0	$C_3H_4^{2+}$	0.40 ± 0.10
19.5	$C_3H_3^{2+}$	0.20 ± 0.10
19.0	$C_3H_2^{2+}$	0.80 ± 0.20

[a] Calculated from ref 4; see text.

The over-all effect of reaction 1 would be simply to decrease the fraction of the activity contained in the observable labeled products. Therefore, it is possible to use the combined yields of the tritiated hydrocarbons identified as an indirect criterion to establish the abundance of the undissociated $C_3H_6T^+$ ions formed when the decay takes place in propane at 1 atm or in liquid propane.

Decay in the Gas Phase. In the gas phase, the total activity contained in products other than propane is 34.9%, in comparison with the value of 51.5% calculated from the data of Table II using the hypothesis that the decay-induced fragmentation processes are independent of pressure, as found in the decay of ethane-t_2 and methane-t_4.

This result, while hardly conclusive, suggests however that the fraction of $C_3H_6T^+$ ions escaping dissociation is higher than in the low-pressure experiments.

The most abundant fragment at low pressure is the $C_3H_4T^+$ ion, produced in 18% of the nuclear transitions. Such an ion reacts with propane according to the well-established[15] hydride ion transfer process 2, to produce labeled propylene. The observed propylene yield,

$$C_3H_4T^+ + C_3H_8 \longrightarrow C_3H_5T + C_3H_7^+ \qquad (2)$$

including the contributions from the reactions of the other ions, is only one-third of the value expected from the data of Table II. This may be taken as strong evidence that a substantially smaller fraction of the decay-formed, excited $C_3H_6T^+$ ions dissociate at atmospheric pressure to give $C_3H_4T^+$ ions.

On the other hand, the formation of tritiated products other than C_3H_7T, including HT, CH_3T, C_2H_5T, etc., with a total yield of about 30%, indicates that a corresponding aliquot of the $C_3H_6T^+$ ions fragmentate, even when the decay occurs at atmospheric pressure. For instance, the yield of C_2H_3T, formed from the $C_2H_2T^+$ ions *via* a hydride ion transfer from propane, approaches the value expected on the basis of the low-pressure fragmentation data.

The high efficiency of the stabilization process which prevents, at 760 torr, the fragmentation of that fraction of $C_3H_6T^+$ ions that would dissociate into $C_3H_4T^+$ ions at 10^{-5} torr is to be compared with the lack of a measurable stabilization for those $C_3H_6T^+$ ions that undergo a more extensive fragmentation at low pressure.

The comparison suggests that the excitation level of those $C_3H_7^+$ ions that have been found to produce $C_3H_5^+$ ions at 10^{-5} torr is low indeed, as suggested by Wexler,[4,16] and actually approaches the inferior limit of the large energy interval allowed by his mass spectrometric experiments.

We shall therefore assume, in agreement with the theoretical model on the molecular excitation following the β decay, that the excitation energy of 70 to 80% of the organic ions produced by the nuclear transition is sufficiently low and distributed in such a way as to make their collisional stabilization possible at 760 torr. The remaining 20% or so of the organic ions is formed in higher excited states (up to 20 ev), and the distribution of excitation energy is such as to make their stabilization impossible even at 1 atm pressure.

Therefore, the data of Wexler[4] on the abundance of the fragments from the highly excited $C_3H_7^+$ ions from the nuclear decay will be directly employed to evaluate the nature and the yields of the labeled products other than propane.

Table III summarizes the yields of the tritiated products (HT, CH_3T, etc.) from the primary dissociation of the highly excited $C_3H_6T^+$ ions, calculated by making reasonable hypotheses on the nature of the neutral fragments arising from any dissociation process. In view of the lack of more detailed information, it has been assumed that the tritium activity is distributed in a statistical way among the reaction products.

In addition to the stable products from reactions 3 to 18 (Table III), other products arise from the reactions of the tritiated ions with propane. The reactions of several ions ($C_3H_5T^+$, $C_3H_3T^+$, C_3HT^+, C_3T^+, etc.) are not known. The other ions react according to the well-established processes 19 to 25, to give products whose calculated yields are summarized in Table IV.

In order to calculate the over-all yield of a given product, the contributions from the pertinent processes listed in Tables III and IV are combined. The calculated product distribution shows a satisfactory agreement with the experimental yields (Table V), with the exception of the propylene and the C_3H_4 hydrocarbons.

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(12) E. Pettersson and E. Lindholm, *Arkiv Fysik*, 24, 49 (1963).

(13) V. Aquilanti and G. G. Volpi, *J. Chem. Phys.*, 44, 2307 (1966).

(14) L. W. Sieck and J. H. Futrell, *ibid.*, 45, 560 (1966).

(15) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *ibid.*, 41, 2998 (1964).

(16) S. Wexler, "Actions Chimiques et Biologiques des Radiations," Vol. 8, M. Haissinsky, Ed., Masson et Cie, Paris, 1965, p 143.

Table III. Labeled Products Formed from the Primary Fragmentation Following the Decay of Propane-1,2-t_2 in Gaseous Propane

Dissociation reaction[a]	Calculated yield[b] of tritiated products, %			
(3) $C_3H_6T^+ \rightarrow C_3H_4{}^{*+} + H_2{}^* + H^*$	HT	0.3		
(4) $C_3H_6T^+ \rightarrow C_3H_3{}^{*+} + 2H_2{}^*$	HT	2.6		
(5) $C_3H_6T^+ \rightarrow C_3H_2{}^{*+} + 2H_2{}^* + H^*$	HT	2.0		
(6) $C_3H_6T^+ \rightarrow C_3H^{*+} + 3H_2{}^*$	HT	3.1		
(7) $C_3H_6T^+ \rightarrow C_3{}^+ + 3H_2{}^* + H^*$	HT	0.9		
(8) $C_3H_6T^+ \rightarrow C_2H_5{}^{*+} + CH_2{}^*$	...	...		
(9) $C_3H_6T^+ \rightarrow C_2H_4{}^{*+} + CH_3{}^*$	...	...		
(10) $C_3H_6T^+ \rightarrow C_2H_3{}^{*+} + CH_4{}^*$	CH_3T	2.9		
(11) $C_3H_6T^+ \rightarrow C_2H_2{}^{*+} + CH_4{}^* + H^*$	CH_3T	1.9		
(12) $C_3H_6T^+ \rightarrow C_2H^{*+} + CH_4{}^* + H_2{}^*$	HT	0.4	CH_3T	0.8
(13) $C_3H_6T^+ \rightarrow C_2{}^+ + CH_4{}^* + H_2{}^* + H^*$	HT	0.2	CH_3T	0.3
(14) $C_3H_6T^+ \rightarrow CH_3{}^{*+} + C_2H_4{}^*$	C_2H_3T	0.8		
(15) $C_3H_6T^+ \rightarrow CH_2{}^{*+} + C_2H_4{}^* + H^*$	C_2H_3T	0.5		
(16) $C_3H_6T^+ \rightarrow CH^{*+} + C_2H_4{}^* + H_2{}^*$	C_2H_3T	0.3	HT	0.2
(17) $C_3H_6T^+ \rightarrow C^+ + C_2H_4{}^+ + H_2{}^* {}^+ H^*$	C_2H_3T	0.3	HT	0.1
(18) $C_3H_6T^+ \rightarrow H^+ + C_3H_6{}^*$	C_3H_5T[c]	0.7		

[a] The asterisk indicates a tritiated species, containing a statistical fraction of the activity initially present in the $C_3H_6T^+$ ion. [b] See footnote *a* of Table I. [c] Propylene.

Table IV. Labeled Products from the Reactions of Tritiated Primary Ions with Propane

Reaction	Calculated yield of the tritiated product, %	
(19) $C_3H_2T^+ + C_3H_8 \rightarrow C_3H_3T + C_3H_7{}^+$ [a]	C_3H_3T[d]	2.0
(20) $C_2H_4T^+ + C_3H_8 \rightarrow C_2H_5T + C_3H_7{}^+$ [b]	C_2H_5T	1.3
(21) $C_2H_3T^+ + C_3H_8 \rightarrow C_2H_5T + C_3H_6{}^+$ [b]	C_2H_5T	0.3
(22) $C_2H_2T^+ + C_3H_8 \rightarrow C_2H_3T + C_3H_7{}^+$ [a–c]	C_2H_3T	2.2
(23) $C_2HT^+ + C_3H_8 \rightarrow C_2HT + C_3H_8{}^+$ [a]	C_2HT	1.0
(24) $CH_2T^+ + C_3H_8 \rightarrow CH_3T + C_3H_7{}^+$ [c]	CH_3T	0.6
(25) $C_3H_3T^+ + C_3H_8 \rightarrow C_3H_5T + C_3H_6{}^+$	C_3H_5T[e]	0.5

[a] Reference 15. [b] M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **87**, 3294 (1965). [c] Reference 12. [d] Allene + methylacetylene. [e] Propylene.

Table V. Comparison of Calculated and Experimental Yields of Labeled Products from the Decay of Gaseous Propane

Product	Yield, %	
	Calcd[a]	Found
HT	9.8	9.3
CH_3T	6.5	7.9
C_2H_5T	1.6	1.9
C_2H_3T	4.1	4.9
C_2HT	1.0	0.7
C_3H_5T[b]	1.2	6.0
C_3H_3T[c]	2.0	4.9
C_4H_9T	...	...
Total activity in products other than C_3H_7T	33.5[d]	35.6

[a] See text. [b] Propylene. [c] Allene + methylacetylene. [d] Calculated from the abundance of propyl + propylene ions given in Table I.

It should be pointed out, however, that the calculated yields represent at best *a lower limit*, since the reactions of several tritiated ions, *i.e.*, the $C_3H_5T^+$, $C_3H_3T^+$, C_3HT^+, C_3T^+, CHT^+, and CT^+ ions, whose combined activity reaches about 5%, are not known and have not been considered. In addition, the isotope effects and the possibility of a nonstatistical tritium distribution can effect, to some extent, the calculated distribution.

Decay in the Liquid Phase. The yields of the tritiated products show a dramatic change when the decay takes place in liquid propane at −130°. First, the HT yield, which provides a rough indication of the extent of the primary fragmentation processes, drops to less than one-half of the value found in gas-phase decay, while the tritiated propylene yield is more than doubled, in contrast with the sharply reduced yields of all the other products. Both these findings can be rationalized if one assumes that the much shorter time required for collision in the liquid phase tends to stabilize all the $C_3H_6T^+$ ions formed in lower excitation states, including part of those ions that would dissociate in the gas phase at 760 torr. The stabilized ions react with the inactive propane to give monotritiated propane according to reaction 1.

In addition, even in those cases where the fast dissociation of highly excited $C_3H_6T^+$ ions takes place, the chain of unimolecular fragmentation processes that could lead to extensively "degraded" ions is limited to the first step, *i.e.*, the formation of the $C_3H_4T^+$ ion. Such a species, stabilized by collision, eventually reacts with the inactive propane to form C_3H_5T through the hydride ion transfer process (eq 2).

Only a minor fraction of the β transitions, where the daughter ions are formed with an extremely high excitation energy, lead to such products as labeled methane, acetylene, and ethylene. The yield of these latter products in the liquid propane is, in any case, much lower than in the gas phase.

Conclusions

The analysis of the tritiated products from the decay of propane-1,2-t_2 in gaseous propane at 760 torr indicates that even in the case of propane, as for the other alkanes so far investigated, 70 to 80% of the nuclear transitions produce daughter ions in states of low excitation energy. All these ions survive fragmentation when the decay occurs at atmospheric pressure and react with the inactive propane forming C_3H_7T. The remaining 20–30% of the β transitions produces highly excited ions, which are not stabilized even at atmospheric pressure and fragment into smaller ions. Such dissociation and the reactions of the fragment ions are responsible for the formation of the labeled products other than C_3H_7T.

The general interpretation of the product distribution from the decay in the gas phase is confirmed by the results obtained from the decay in liquid propane.

Here the dissociation of the daughter $C_3H_5T^+$ ions is largely prevented. When the dissociation takes place, it is limited to its first step involving the formation of $C_3H_4T^+$ ions, which react with inactive propane to give C_3H_5T, the major product observed.

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Flash Photolysis Studies of 1,3,5-Cyclooctatriene. A Reversible Ring Opening[1a,b]

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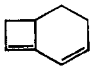
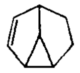
Abstract: Studies of 1,3,5-cyclooctatriene in cyclohexane and *n*-hexane by flash photolysis have resulted in the detection of two transient species, both of which decay by first-order processes with lifetimes (at 25° in *n*-hexane) of 91 msec and 23 sec. Both transients are formed during the flash. A fivefold increase in the concentration of the long-lived species occurs simultaneously with the disappearance of the short-lived species. From spectroscopic and kinetic evidence the long-lived species is identified as *cis,cis*-1,3,5,7-octatetraene, the instability of which results from a low activation energy (17 kcal/mole) for recyclization to 1,3,5-cyclooctatriene. Arguments are presented for the identification of the short-lived transient as a strained, cyclic stereoisomer of 1,3,5-cyclooctatriene. The opening of this cyclic transient to form octatetraene has an Arrhenius activation energy of 16 kcal/mole. The formation of stable 1,3,5,7-octatetraene (*cis,trans* and/or *trans,trans*) has been observed and has been found to occur *via* the photoisomerization of the unstable *cis,cis* stereoisomer, thus providing an example of a biphotonic process.

There has been much recent interest in the photochemistry of cyclic polyenes. Numerous rearrangement reactions have been investigated yielding results of considerable importance from a mechanistic point of view.[3] Although one would expect that transient as well as stable photoisomers might be involved in the photochemical rearrangements of these molecules, previous work has been directed almost exclusively toward observing the stable products. In an attempt to detect and characterize transient species, we have applied the flash photolysis technique to the study of a representative compound, 1,3,5-cyclooctatriene (I). Previous photochemical studies[4-6] have shown that prolonged photolysis of I in a variety of solvents produces a bicyclic isomer (II) as well as a tricyclic isomer (III). These results differ markedly from those reported for 1,3-cyclohexadiene for which the primary photochemical process in solution[7a] is ring opening to 1,3,5-hexatriene. As suggested by Barton,[7b] a ring with $2n$ members containing $n - 1$ conjugated double bonds should undergo facile photochemical conversion to an open chain compound with n conjugated double bonds. The failure of previous workers[4-6] to isolate 1,3,5,7-octatetraene as a major photolysis product of I is shown by the present results to be due to the unexpected rapidity with which the *cis,cis* isomer of this conjugated polyene recyclizes to I. Evidence will also be presented for the identification of a second important transient as a photochemically produced stereoisomer of I.


II


III

Experimental Section

The flash photolysis apparatus consists of six oxygen-filled quartz discharge tubes, each 20 cm long, capable of producing flashes with a total discharge energy of 3750 joules and a duration of 4 μsec.[8] Solutions to be studied were contained in a jacketed 20-cm quartz cell. The filter jacket was filled with distilled water during all runs except for one experiment using a glacial acetic acid filter as described below.

Transient changes in optical density following a flash were followed by employing a d.c. xenon lamp (Osram XBO 150 W/1), a grating monochromator (Bausch and Lomb f/4.4 0.5M) adjusted for 1-mμ band width, a photomultiplier tube (EMI 955 8 BQ), and an oscilloscope (Tektronix 535) fitted with a Polaroid camera in the standard manner.

I was synthesized, purified, and separated from its thermal bicyclic isomer according to the procedure described by Cope, *et al.*[9]

Transient optical density changes were measured over the 250–500-mμ wavelength range at intervals of 20 mμ after flashing solutions of I in Spectrograde cyclohexane ($1\text{–}30 \times 10^{-6}$ *M*). The region where a positive result was obtained was reinvestigated at intervals of 2–3 mμ.

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[3] See, for example, the recent article by R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966).

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[5] J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).

[6] W. R. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964).

[7] (a) The results of these studies are summarized in the recent review article by R. Srinivasan, *Advan. Photochem.*, 4, 128 (1966); (b) D. H. R. Barton, *Helv. Chim. Acta*, 42, 2604 (1959).

[8] A detailed description of this apparatus is presently being prepared for publication by L. L.

[9] A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbal, *J. Am. Chem. Soc.*, 74, 4867 (1952).