ductivity of the effluent water. It is pointed out, however,[14] that the accumulation of the contaminant on the resin does not interfere with the removal of inorganic substituents. In light of the present work, it may be concluded that in these instances the layer of contaminant which accumulates on the outside of the resin is not sufficiently thick or lipid-like to impede the desirable function of the resin, namely its ability to remove small inorganic ions. The work described in this contribution does indicate, however, that if the organic contaminant has the appropriate size and constitution, *e.g.*, an amphiphilic ion, then the resin's ability to remove small inorganic ions can also be impaired.

Implications in Biological Membrane Behavior. Mass transfer across lipid-like monolayers is of interest to biologists because of its obvious relevance to cell permeability. The influence of monolayers on gas transmission across the air–water interface is quite amenable to study, and considerable success has been realized in manipulating and studying this particular interface.[15] However, the construction of significant areas of stable lipid layers between contiguous aqueous phases is experimentally a much more demanding task. Resin solution systems afford a very convenient source of two aqueous phases capable of stable coexistence when in contact and possessing a well-defined interfacial area of considerable magnitude. Were it possible to interpose lipid layers between these phases, then this resin–lipid layer–solution system might afford a very convenient experimental means of studying lipid membrane transport. The model that has been proposed in this contribution to explain the inhibitory effects observed places a special emphasis on the lipid-like character of the interfacial region. If this is a legitimate representation of the mechanism, then this work demonstrates that ion-exchange resin systems may provide a useful additional tool in the study of transfer across lipid membranes.

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Reactions of He^3H^+ Ions with Gaseous Hydrocarbons. III. Cyclopropane, Propane, Isobutane, and *n*-Butane

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Abstract: The reactions of the He^3H^+ ions, formed from the decay of molecular tritium, with $c\text{-}C_3H_6$, C_3H_8, $n\text{-}C_4H_{10}$, and $i\text{-}C_4H_{10}$ were investigated at the pressures of 20 and 760 torr, under conditions excluding the interference of radiolytic processes. The nature and the yields of the tritiated reaction products, determined by radio gas chromatography, are consistent with the hypothesis that the He^3H^+ ions attack the gaseous hydrocarbons, giving excited protonated species, which dissociate into neutral fragments and simpler ions along energetically allowed pathways. The formation of the observed labeled products can be rationalized taking into account the various fragmentation processes and the consecutive reactions of the fragment ions with the inactive hydrocarbon. The reaction of He^3H^+ ion with $c\text{-}C_3H_6$ yields labeled C_3H_6 hydrocarbons, whose formation requires the stabilization of a fraction of the protonated ions. Furthermore, the high yield of tritiated $c\text{-}C_3H_6$ suggests a cyclic structure for the protonated ion and provides direct evidence for the existence of the cyclopropanium ion often postulated in different fields of chemistry. In the case of C_3H_8 and $n\text{-}C_4H_{10}$, on the other hand, the results can be interpreted without requiring the intervention of the stabilized protonated ions.

In the first paper of this series,[1] the β decay of molecular tritium was shown to provide a simple and convenient means to introduce an extremely reactive protonating agent, the He^3H^+ ion, into gaseous systems at atmospheric pressure, and to study its reactions by tracer techniques. The method was applied, under conditions excluding any interference from radiolytic processes, to the study of the ionic processes involved in the protonation of toluene,[1] and of methane and ethane,[2] by the He^3H^+ ions.

The present paper deals with the protonation of cyclopropane, propane, and the butanes with the same reagent.

The study of the reactions of the He^3H^+ ions with cyclopropane is of special interest, since the analysis of the tritiated reaction products provides some hope of establishing the cyclic structure of the protonated cyclopropane ion, which obviously cannot be demonstrated by mass spectrometric techniques. Such experimental evidence would represent a direct support for the existence of this cyclic $C_3H_7^+$ ion, often postulated to account for certain anomalies in the mass spectra of the alkanes,[3–5] and as intermediate in a variety of reactions occurring in solution.[6–8]

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Table I. Yields of Tritiated Products from the Reactions of He^3H^+ Ions with Cyclopropane, Propane, *n*-Butane, and Isobutane

Sample no.[a]	System composition, mole %	Pressure, torr	Yields[b]							
			Methane	Ethane	Ethylene	Propane	Propylene	Cyclopropane	*n*-Butane	Isobutane
1–4	c-C_3H_6 (100)	760	22.0[c]	4.0	15.2	2.0	7.1	18.8	...	..
5, 6	c-C_3H_6 (98) + O_2 (2)	760	23.0	3.7	12.1	2.2	6.7	19.2	...	..
7, 8	c-C_3H_6 (98) + O_2 (2)	20	23.0	4.2	9.5	1.8	6.9	20.0	...	..
9–12	C_3H_8 (100)	760	13.9	4.7	1.5	14.6	...	...	...	..
13–17	C_3H_8 (98) + O_2 (2)	760	12.8	5.1	...	12.3	...	...	...	..
18, 19	C_3H_8 (100)	20	18.0	5.9	~1	11.8	...	...	...	..
20–23	n-C_4H_{10} (100)	760	13.9	5.9	3.4	2.3	...	...	14.3	..
24–28	n-C_4H_{10} (98) + O_2 (2)	760	15.2	6.2	2.5	2.3	...	...	15.3	..
29–33	i-C_4H_{10} (100)	760	25.3	2.2	3.9	3.4	...	...	...	18.3
34–37	i-C_4H_{10} (98) + O_2 (2)	760	23.4	1.7	3.5	3.2	...	...	...	17.9

[a] Each sample represents a separately sealed vessel containing $^3H_2$ + RH. All the samples were stored at 25°, with a $^3H_2$ activity of 1.5 mCi in a volume of 250 ml, except for the low-pressure samples, when a 6-l. volume was employed. The radio gas chromatographic analysis involved a minimum of four runs for each sample. [b] Each yield represents the percentual fraction of the activity of the He^3H^+ ions found in a given product. The detection limit of the radio gas chromatography corresponded to a yield of *ca.* 1%. The standard deviation of the yields was *ca.* 5%; the accuracy of the absolute yield values is likely to be affected by a 10% uncertainty. The gas chromatographic columns employed would have allowed the detection of the following hydrocarbons: methane, ethane, ethylene, acetylene, propane, propylene, cyclopropane, methylacetylene, allene, *n*-butane, isobutane, butene-1, butene-2, isobutylene, pentanes, hexanes. [c] The yield is corrected for the small amount of tritiated methane contained in the molecular tritium.

The interaction of the He^3H^+ ions with propane, isobutane, and *n*-butane is also of interest. No definite evidence for the formation and stabilization of the corresponding protonated ions was obtained in the study of the "high-pressure" mass spectra[9,10] of the C_3 and C_4 alkanes, and of their reactions with a number of protonating agents,[11–14] in experiments carried out at pressures up to several torr, while recently Haynes and Kebarle[15] observed such ions in methane at pressures ranging from 1 to 160 torr. It was expected that the analysis of the products from the reaction of the He^3H^+ ions with propane and butanes could provide useful information on the decomposition pattern of the protonated ions, and perhaps on the possibility of a collisional stabilization of these excited species at the higher pressure of 760 torr. The reactions promoted by the decay of molecular tritium in a number of organic systems were the object of extensive investigation, in connection with the labeling technique introduced by Wilzbach.[16] The reader is directed to the first paper of the present series[1] for a short historical background on this line of research.

The results of early investigation on the specific systems related to the present study will be discussed in details in a following section.

Experimental Section

Full details on the reagents, the procedure, and the analytical techniques employed in the present investigation were given in the first papers of this series.

The propane, isobutane, and *n*-butane, used for the preparation of the samples and for the determination of the retention volumes in the radio gas chromatographic analyses, were Research Grade samples from Soc. Italiana Ossigeno (Milan, Italy). Their purity, checked by vpc, was found to exceed 99.9 mole %. The cyclopropane was a Research Grade product, from Matheson Co., with a purity greater than 99.5 mole %. The tritium was obtained from CEA (France). Its radio gas chromatographic analysis revealed that hydrogen tritide and tritiated methane were the only detectable impurities, their activity accounting respectively for 0.35 and 0.10% of the $^3H_2$ activity.

Results and Discussion

Reactions of He^3H^+ Ions with Cyclopropane. The yields of the tritiated products formed under different experimental conditions in the system $^3H_2$–cyclopropane, summarized in Table I, express the percentual ratio of the activity found in each labeled product the total activity of the He^3H^+ ions, that according to Wexler's mass spectrometric measurements[17] are formed in 94.5% of the $^3H_2$ decays. Under the conditions prevailing in the present investigation, the tritiated products observed can be expected, for reasons discussed in detail in the first paper of this series,[1] to arise exclusively from the reactions of the He^3H^+ ions, with no interference from the radiolytic processes promoted by the β particles of $^3H_2$. The tritiated methane, cyclopropane, and ethylene represent the major products observed, and their ratios appear to remain unaffected by a 40-fold decrease of the cyclopropane pressure in the system, from 760 to 20 torr. Smaller yields of tritiated ethane, propane, and propylene are also observed, the total yield of the labeled products accounting for *ca.* 70% of the activity contained in the He^3H^+ ions.

The first step in the formation of the tritiated products is likely to be the protonation of cyclopropane by the He^3H^+ ions, according to eq 1, where, as in the following equations, the asterisk indicates a tritiated species.

$$c\text{-}C_3H_6 + He^3H^+ \longrightarrow (C_3H_7{}^*)^+_{exc} + He \qquad (1)$$

Processes similar to reaction 1 were observed by mass spectrometric techniques, using other protonating reagents such as H_3^+ and D_3^+.[18] Reaction 1 is strongly exothermic, and part of the excited protonated ions can be expected to dissociate, while the remaining ions are stabilized by collision.

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$$(C_3H_7^*)^+_{exc} \xrightarrow{+M} C_3H_7^{*+} \qquad (2)$$

The stabilized ions can react with the inactive cyclopropane according to a thermoneutral proton transfer

$$C_3H_7^{*+} + c\text{-}C_3H_6 \longrightarrow C_3H_6^* + C_3H_7^+ \quad \Delta H_3 \simeq 0 \qquad (3)$$

to form the observed tritiated C_3H_6 hydrocarbons. Proton-transfer processes analogous to reaction 3 have already been observed between such ions as protonated methane and ethane and the corresponding alkanes.[2,11]

Owing to the large excess of inactive cyclopropane present in the system, reaction 3 causes the whole activity initially contained in the stabilized $C_3H_7^{*+}$ ions to be transferred into the $C_3H_6^*$ hydrocarbons, whose combined yield (19.2% cyclopropane + 6.7% propylene) may be therefore taken as an indication that about 26% of the excited protonated ions formed in reaction 1 are stabilized by collision. Moreover, the relative yields of tritiated cyclopropane and propylene provide strong evidence for a cyclic structure of the $C_3H_7^{*+}$ ions from reaction 1, with only a relatively minor rearrangement to a linear structure.

The decomposition pathways of the excited $C_3H_7^{*+}$ ions that dissociate may be deduced, to a certain extent, from the pattern of labeled products isolated. The observed formation of tritiated methane suggests that a large fraction of the protonated ions fragment according to the scheme[18]

$$(C_3H_7^*)^+_{exc} \longrightarrow CH_4^* + C_2H_3^{*+} \qquad (4)$$

The measured yield of tritiated methane was found to reach 22–23%. One can roughly estimate, assuming a statistical distribution of tritium between the products of process 4, that the $C_2H_3^{*+}$ ions contain *ca.* 17% of the He^3H^+ ions activity. This value, combined with the observed yield of tritiated methane, indicates that approximately 40% of the excited protonated ions, formed in reaction 1, dissociate according to eq 4.

The remaining excited $C_3H_7^{*+}$ ions that escape stabilization fragment[18] to form one hydrogen molecule and a $C_3H_5^{*+}$ ion, according to the equation

$$(C_3H_7^*)^+_{exc} \longrightarrow C_3H_5^{*+} + H_2^* \qquad (5)$$

The $C_3H_5^{*+}$ ions could conceivably react with the inactive cyclopropane, according to the thermoneutral hydride-ion transfer process

$$C_3H_5^{*+} + c\text{-}C_3H_6 \longrightarrow C_3H_6^* + C_3H_5^+ \quad \Delta H_6 \simeq 0 \qquad (6)$$

analogous to the reaction of labeled ethyl[18–20] and propyl ions,[12,18,21,22] respectively, with ethane and propane. However, the $C_3H_5^{*+}$ was recently shown to undergo efficient exothermic reactions with cyclopropane,[23] which are probably much faster than process 6. One of such reactions

$$C_3H_5^{*+} + c\text{-}C_3H_6 \longrightarrow C_2H_4^* + C_4H_7^{*+} \quad \Delta H_7{}^{24} \simeq -27 \text{ kcal/mole} \qquad (7)$$

provides a direct route to the formation of the labeled ethylene, observed in this system with a yield of 12–15%.

Other processes, which are possible routes to the tritiated ethylene, *i.e.*, the fragmentation process of the excited protonated ions

$$(C_3H_7^*)^+_{exc} \longrightarrow CH_3^{*+} + C_2H_4^* \qquad (8)$$

and the hydride-ion transfer from the inactive cyclopropane to the $C_2H_3^{*+}$ ions formed in reaction 4

$$C_2H_3^{*+} + c\text{-}C_3H_6 \longrightarrow C_2H_4^* + C_3H_5^+ \quad \Delta H_9{}^{24} \simeq -58 \text{ kcal/mole} \qquad (9)$$

cannot be ruled out on the grounds of purely energetic considerations. The failure to observe reaction 8 in the mass spectrometric study of the protonation of cyclopropane with H_3^+ ions suggests, however, that its rate is low in comparison with the competitive processes 4 and 5, while the $C_2H_3^+$ ions were found to react rapidly with c-C_3H_6 to form $C_5H_9^+$ ions.[18] Figure 1 illustrates the scheme proposed for the reactions following the attack of cyclopropane by the He^3H^+ ions and for the formation of the tritiated products.

A final remark stems from a comparison between the present results, obtained in cyclopropane at 1 atm, and the mass spectrometric investigation by Aquilanti and Volpi[18] on the protonation of cyclopropane with H_3^+ ions, at a maximum H_2 pressure of 0.3 torr. It appears that the fraction of the excited $C_3H_7^+$ ions surviving fragmentation is surprisingly similar in both cases, despite the much higher efficiency of the stabilization processes to be expected at 760 torr. One should consider, however, that the protonation of cyclopropane by the H_3^+ is considerably less exothermic than process 1 and therefore can be expected to produce $C_3H_7^+$ ions in states of lower excitation. Furthermore, the results of a very recent mass spectrometric study suggest that the excited protonated ions from the reaction of D_3^+ with a number of alkanes are formed either in a state that undergoes a fast, pressure-independent dissociation or in a state long lived enough to allow collisional stabilization; the exothermicity of the reaction being an important factor in determining the relative population of the two states.[25] If such an interpretation could be applied to the protonation of cyclopropane by the He^3H^+ ions, and extended to the higher pressure prevailing in the present investigation, it would explain the experimental observation that the yields of tritiated products, expecially the cyclopropane/methane ratio, appear to be insensitive to an increase of cyclopropane pressure from 20 to 760 torr.

The reactions initiated by the decay of molecular tritium in the tritium–cyclopropane system were investigated by Gant and Yang.[26] Owing to the high activity of $^3H_2$ employed, 1000–10,000 times higher than in the present investigation, the sample was subjected to extensive radiolytic decomposition, as demonstrated, *inter alia*, by the formation of *unlabeled* ethylene, ethane, propylene, and propane, in amounts detectable by the thermal conductivity cell of a gas chromatograph from the radiolysis of the inactive cyclopropane. For this reason, a comparison with the present results is difficult. The major tritiated products observed by Gant and Yang were propane, propylene, cyclopropane, and ethylene, whose yields were markedly affected by the addition of a radical scavenger. It ap-

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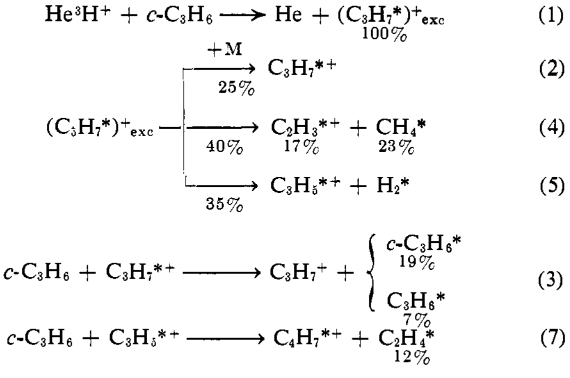

Figure 1. Protonation of cyclopropane by the He^3H^+ decay ions.

pears that the investigation was primarily directed to determine the relative contribution of the different mechanisms to the formation of the tritiated products in the Wilzbach method, while the superimposition of predominant radiolytic processes made difficult a detailed study of the reactions of the decay ions with cyclopropane.

Reactions of He^3H^+ Ions with Propane. The major products formed from the reactions of He^3H^+ ions with propane are tritiated methane and propane, in nearly equivalent yields, with smaller amounts of ethane and ethylene, and only traces of butanes. The yields are insensitive to the addition of 2 mole % of oxygen as a radical scavenger, and the decrease of the C_3H_8 pressure from 760 to 20 torr has only a minor effect on the tritiated product distribution, except for a slight increase of the labeled methane yield, from 14 to 18%.

As in the case of cyclopropane, the first step in the formation of the tritiated products appears to be the protonation of C_3H_8 by the decay ions

$$C_3H_8 + He^3H^+ \longrightarrow (C_3H_9^*)^+_{exc} + He \quad (10)$$

The protonated ions are formed in a state of high excitation, owing to the large exothermicity of reaction 10. Therefore, if not stabilized by collision

$$(C_3H_9^*)^+_{exc} \xrightarrow{+M} C_3H_9^{*+} \quad (11)$$

they dissociate along the energetically allowed fragmentation pathways

$$(C_3H_9^*)^+_{exc} \longrightarrow C_2H_5^{*+} + CH_4^* \quad (12)$$

$$(C_3H_9^*)^+_{exc} \longrightarrow C_3H_7^{*+} + H_2^* \quad (13)$$

The observed tritiated propane could conceivably arise from the stabilized $C_3H_9^{*+}$ ions, *via* a thermoneutral proton transfer, similar to those observed between CH_5^+ and $C_2H_7^+$ ions and, respectively, methane and ethane.[1,11]

$$C_3H_9^{*+} + C_3H_8 \longrightarrow C_3H_8^* + C_3H_9^+ \quad \Delta H_{14} \simeq 0 \quad (14)$$

On the other hand, tritiated propane can also be formed from the labeled propyl ions, through the thermoneutral hydride-ion transfer.[11,12,21,22]

$$C_3H_7^{*+} + C_3H_8 \longrightarrow C_3H_8^* + C_3H_7^+ \quad \Delta H_{15} \simeq 0 \quad (15)$$

There are several reasons which make the second mechanism for the formation of tritiated propane more attractive. First, it does not require the intervention of stabilized $C_3H_9^+$ ions, whose existence was never unequivocally established in the mass spectrometric investigations on the protonation of C_3H_8 with relatively mild reagents such as H_3^+,[11] CHO^+,[12] and CH_5^+,[13] carried out at pressures up to 2 torr. Even at pressures of 5–40 torr, the experiments of Haynes and Kebarle[15] showed that most of the excited $C_3D_8H^+$ ions from the protonation of deuterated propane with the CH_5^+ ions dissociated into ethyl and propyl ions. In the second place, the production of tritiated methane indicates that fragmentation of the excited $C_3H_9^+$ ions does actually occur, and it would be difficult to explain why only one, and the less endothermic, of the two possible fragmentation processes (12 and 13), demonstrated in the mass spectrometric study of similar protonation reactions, is prevented by collisional stabilization.

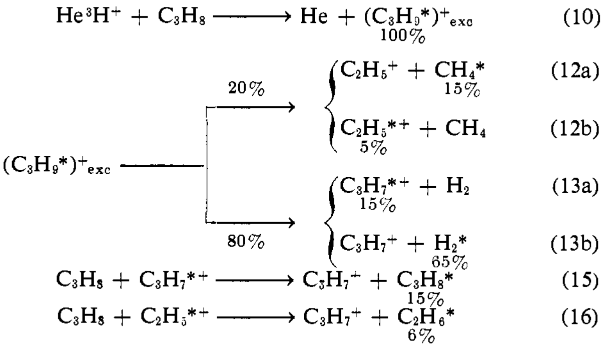

Figure 2. Protonation of propane by the He^3H^+ decay ions.

Finally, the data of Table I indicate that the combined yield of all the tritiated products identified accounts only for 30–40% of the activity of the protonating reagent, the He^3H^+ ion. While it is certainly possible that the lack of a satisfactory activity balance involves the formation of labeled organic products undetectable by radio gas chromatography, it appears that the most likely explanation can be traced to the formation of relatively large amounts of hydrogen tritide, which cannot be determined in the present experiments, owing to its presence, as a relatively abundant impurity, in the molecular tritium. The necessity of assigning 65% of the activity originally contained in the He^3H^+ ions to H_2^*, and only 15% to the $C_3H_7^{*+}$ ions, suggests that a long-lived $C_3H_9^{*+}$ intermediate is not formed in the initial protonation step. Whether this is caused by the fast dissociation of the protonated intermediate (12), or by a direct hydride-ion transfer from the C_3H_8 to the He^3H^+ ion, cannot be deduced from the present results. A scheme for the reactions promoted by the attack of the He^3H^+ ions on C_3H_8, where the relative rates of the fragmentation processes and the tritium distribution among the reaction products are adjusted to account for the observed features of the products spectrum, is illustrated in Figure 2. It is interesting to note that the relative rates of processes 12 and 13 given in the figure, *ca.* 1:4, approaches the ratio of the abundance, *ca.* 1:5, of the ethyl and propyl ions observed in the protonation of C_3D_8 by CH_5^+ ions in methane at 5–40 torr.[15] Furthermore, the distribution of tritium between the products of reaction 13 approaches the value to be expected from the observation by Haynes and Kebarle[15] that only roughly 10% of the propyl ions from the protonation of C_3D_8 with CH_5^+ ions contain a protium atom, which represents, in their experiments, the counterpart of a tritium atom.

Despite such remarkable agreement with the most recent data obtained by high-pressure mass spectrom-

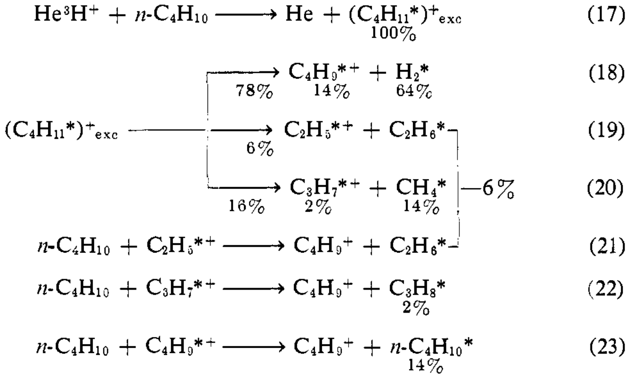

Figure 3. Protonation of *n*-butane by the He^3H^+ decay ions.

etry, there is no doubt that considerable caution must be exercised when comparing experiments carried out with different protonating agents under different pressures. For instance, while Volpi and Aquilanti, in their study on the protonation of C_3H_8 and C_3D_8 with H_3^+ and D_3^+ ions, observed reactions analogous to processes 10, 12, 13, 15, and 16, the relative rates of the fragmentation reactions were different from those reported in Figure 2, the excited protonated ions being found to dissociate predominantly (2:1) to form ethyl ions. On the other hand, the tritium distribution between the products of reaction 12 given in Figure 2 approaches the value to be expected from the data obtained by the same authors in the protonation of C_3D_8 with $^3H^+$ ions.[11]

It is interesting to compare the present results with those reported by Yang and Gant[27] in their study of the Wilzbach labeling of propane. Despite the occurrence of extensive radiolytic labeling, promoted by the high concentration of $^3H_2$, about 2 Ci in a 150-ml sample, the ingenious techniques employed, including the use of radical scavengers, the replacement of tritium with hydrogen tritide, the irradiation of the system with an external γ-ray source, etc., enabled these authors to estimate the contribution of the various labeling mechanisms to the formation of the tritiated products. The yields given by Yang and Gant for the "decay labeling," *i.e.*, for the processes initiated by the He^3H^+ ions, methane (12%), ethane (2.7%), propane (15%), isobutane (2%), and *n*-butane (2%), are in good agreement with the data of Table I, obtained in the absence of radiolytic labeling processes. Owing to the specific purpose of the work, no information on the mechanisms responsible for the formation of the labeled products is given by Yang and Gant.

Reactions of He^3H^+ Ions with *n*-Butane. The major tritiated products from the reactions of He^3H^+ ions with *n*-butane at 760 torr are methane and *n*-butane in almost equivalent yields (15%), ethane (6%), and smaller amounts of ethylene and propylene. These yields are not significantly affected by the addition of 2 mole % of oxygen to the butane. As in the case of propane and cyclopropane, the attack of *n*-butane by the He^3H^+ ions

$$n\text{-}C_4H_{10} + He^3H^+ \longrightarrow (C_4H_{11}^*)^+_{exc} + He \qquad (17)$$

forms excited protonated ions that fragment along three different energetically allowed pathways.

$$(C_4H_{11}^*)^+_{exc} \longrightarrow C_4H_9^{*+} + H_2^* \qquad (18)$$

$$(C_4H_{11}^*)^+_{exc} \longrightarrow C_2H_5^{*+} + C_2H_6^* \qquad (19)$$

$$(C_4H_{11}^*)^+_{exc} \longrightarrow C_3H_7^{*+} + CH_4^* \qquad (20)$$

Methane is directly formed from reaction 20, while the labeled ethyl, propyl, and *n*-butyl ions react further with the inactive butane, according to the exothermic or thermoneutral hydride-ion transfer processes

$$C_2H_5^{*+} + C_4H_{10} \longrightarrow C_2H_6^* + sec\text{-}C_4H_9^+ \qquad \Delta H_{21}{}^{28} \simeq -19 \text{ kcal/mole} \qquad (21)$$

$$C_3H_7^{*+} + C_4H_{10} \longrightarrow C_3H_8^* + sec\text{-}C_4H_9^+ \qquad \Delta H_{22}{}^{28} \leqslant 0 \qquad (22)$$

$$C_4H_9^{*+} + C_4H_{10} \longrightarrow C_4H_{10}^* + C_4H_9^+ \qquad \Delta H_{23} \simeq 0 \qquad (23)$$

that yield the observed tritiated ethane, propane, and butane. The scheme illustrated in Figure 3 gives the relative probability of the various fragmentation processes and the distribution of tritium among the different species, which are consistent with the observed spectrum of the tritiated products. It may be pointed out that the scheme proposed in Figure 3 includes only processes which are not only energetically allowed, but were also well established by mass spectrometric investigations.[11,15,29] Even the postulated attack of the He^3H^+ ion on the *n*-butane is similar, except for the higher exothermicity, to the protonation by other reagents, such as CH_5^+ and H_3^+ ions.

Reactions of He^3H^+ Ions with Isobutane. The spectrum of labeled products formed in this system is qualitatively similar to that observed in *n*-butane, the major differences arising from the much higher yield of methane (25% *vs.* 15%) and the much lower yield of ethane (2% *vs.* 6%). This trend is entirely to be expected, owing to the different structure of the excited ion resulting from the exothermic protonation

$$i\text{-}C_4H_{10} + He^3H^+ \longrightarrow (i\text{-}C_4H_{11}^*)^+_{exc} + He \qquad (24)$$

The fragmentation of the branched i-$C_4H_{11}^{*+}$ ion occurs predominantly along two different pathways.

$$(i\text{-}C_4H_{11}^*)^+_{exc} \longrightarrow C_3H_7^{*+} + CH_4^* \qquad (25)$$

$$(i\text{-}C_4H_{11}^*)^+_{exc} \longrightarrow i\text{-}C_4H_9^{*+} + H_2^* \qquad (26)$$

Methane is formed directly from reaction 25, while the propyl and isobutyl ion yield the observed propane and isobutane through a hydride-ion transfer with the inactive isobutane.

$$C_3H_7^{*+} + i\text{-}C_4H_{10} \longrightarrow C_3H_8^* + t\text{-}C_4H_9^+ \qquad \Delta H_{27}{}^{28} \leqslant 14 \text{ kcal/mole} \qquad (27)$$

$$i\text{-}C_4H_9^{*+} + i\text{-}C_4H_{10} \longrightarrow i\text{-}C_4H_{10}^* + i\text{-}C_4H_9^+ \qquad \Delta H_{28} \simeq 0 \qquad (28)$$

The relative rates of the two fragmentation processes and the distribution of tritium among the various labeled species, deduced from the analysis of the tritiated products, are illustrated in Figure 4.

In the case of isobutane a clue to the initial site of attack by the He^3H^+ ions leading to the formation of tritiated isobutane can be obtained from the isotopic composition of the final product. In fact, the different

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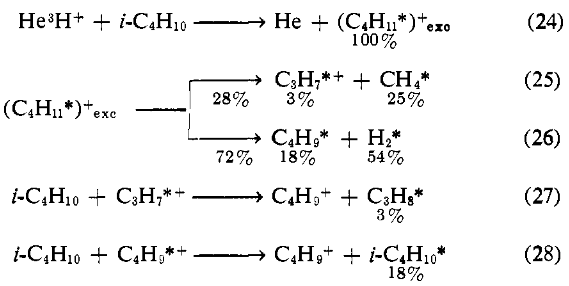
[27] K. Yang and P. L. Gant, *J. Phys. Chem.*, **66**, 1619 (1962).

[28] F. P. Lossing, P. Kebarle, and J. B. De Sousa, "Advances in Mass Spectrometry," J. D. Waldron Ed., Pergamon Press, London, 1959, p 431; F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, p 243.

[29] F. H. Field and F. W. Lampe, *J. Am. Chem. Soc.*, **80**, 5587 (1958).

lability of the primary and tertiary H atoms makes it possible to evaluate, by a method introduced by Otvos, *et al.*,[30] and improved by Wolfgang, *et al.*,[31] the distribution of the activity in the tritiated i-C_4H_{10}. The result obtained, showing that most (>90%) of the ^3H activity is contained in the methyl groups, suggests that, unless an extensive reshuffling of the H atom follows the protonation, the attack which causes the tritium atom to remain bound in the isobutyl ion must take place on the methyl groups, while the attack on the tertiary carbon is likely to be followed by the elimination of tritium as hydrogen tritide,[32] according to eq 26.



$$He^3H^+ + i\text{-}C_4H_{10} \longrightarrow He + \underset{100\%}{(C_4H_{11}^*)^+_{exo}} \quad (24)$$

$$(C_4H_{11}^*)^+_{exc} \xrightarrow[28\%]{} \underset{3\%}{C_3H_7^{*+}} + \underset{25\%}{CH_4^*} \quad (25)$$

$$(C_4H_{11}^*)^+_{exc} \xrightarrow[72\%]{} \underset{18\%}{C_4H_9^*} + \underset{54\%}{H_2^*} \quad (26)$$

$$i\text{-}C_4H_{10} + C_3H_7^{*+} \longrightarrow C_4H_9^+ + \underset{3\%}{C_3H_8^*} \quad (27)$$

$$i\text{-}C_4H_{10} + C_4H_9^{*+} \longrightarrow C_4H_9^+ + \underset{18\%}{i\text{-}C_4H_{10}^*} \quad (28)$$

Figure 4. Protonation of isobutane by the He^3H^+ decay ions.

Finally, the difference in CH_4^* and $C_2H_6^*$ yields from the interaction of the He^3H^+ ions with n-C_4H_{10} and i-C_4H_{10} is again evidence for the absence of a long-lived protonated intermediate capable of undergoing rearrangement and qualitatively reflects the trend reported by Aquilanti and Volpi[11] for the abundances of the propyl and ethyl ions in the protonation of n-C_4H_{10} and i-C_4H_{10} with H_3^+.

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(32) This interpretation is supported by a most recent mass spectrometric observation (G. G. Volpi, private communication) that both $C_4H_8D^+$ and $C_4H_9^+$ ions are formed in the protonation of $(CH_3)_3CD$ with $^3H^+$ ions.

Ab Initio Bond-Orbital Calculations. I. Application to Methane, Ethane, Propane, and Propylene

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Abstract: A bond-orbital approach to *ab initio* calculations using a basis set of spherical Gaussians is developed and applied to methane, ethane, propane, and propylene. The method places emphasis on the transferability of nonorthogonalized bond orbitals from molecule to molecule. Several properties of methane and ethane are calculated using two different basis sets. Barriers to internal rotation in ethane, propane, and propylene are also calculated. The results for propane show that there is considerable interaction between the two methyl groups. The correct stable geometry is predicted for propylene, but the computed barrier is too small.

Quantum mechanical calculations, *ab initio*, on rather large molecules of chemical interest are now being carried out by means of the Roothaan LCAO–SCF technique.[1] Thus such molecules as benzene,[2] pyrrole,[3] pyridine,[4] and pyrazine[5] have been treated.

An interpretive disadvantage of the LCAO–SCF procedure is that the molecular orbitals (MO's) do not in general correspond to the chemist's intuitive picture of molecules in terms of localized chemical bonds, lone-pair electrons, and the like. This can be overcome by subjecting the MO's to a unitary transformation utilizing the method suggested by Lennard-Jones and Pople[6] and further developed by Edmiston and Ruedenberg.[7] This procedure yields a set of localized orbitals which correspond in many cases to bond orbitals or lone pairs.

In this paper we begin by assuming that molecules such as CH_4 or C_2H_6 can be described in terms of 1s core, C–H bond, and C–C bond orbitals, and that these functions, after Löwdin orthogonalization,[8] are at least a fair description of the localized orbitals which would result from a transformation of the SCF–MO's obtained utilizing the same basis set. We further assume that the nonorthogonalized C–H bond functions in CH_4, C_2H_6, C_3H_8, etc., are identical and can be carried over from molecule to molecule without change.

Atomic Orbitals

The carbon core and the bond orbitals are written as linear combinations of a minimal set of 1s, 2s, and 2p orbitals centered at the carbon atoms and 1s orbitals centered at the hydrogens. Ideally Slater orbitals would be used to represent these functions but the

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