Proton Transfer Reactions Occurring in Gas-Phase Radiolysis

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From the products formed in the gas-phase radiolysis of various reaction mixtures containing deuterium labelled compounds, it is inferred that: (*a*) H_3^+, ArH^+, KrH^+, and probably XeH^+ transfer a proton to n-pentane. In all cases, the protonated pentane ion decomposes to methane, ethane, propane, and the corresponding butyl, propyl, and ethyl ions. The relative probability of these three fragmentation processes does not vary with the nature of the proton donor, within experimental error. (*b*) H_3^+, ArH^+, KrH^+ and CH_5^+ effectively transfer a proton to cyclopropane. On the basis of isotopic labelling experiments, it is deduced that the protonated cyclopropane rearranges to the sec-propyl ion structure prior to or during reaction. Similarly, the protonated cyclobutane rearranges to the sec-butyl ion structure. (*c*) H_3^+, ArH^+ and KrH^+ transfer their proton to ethylene, propylene and butene, to form mainly ethyl, sec-propyl, sec-butyl ions, respectively. Carbonium ions such as $C_2H_5^+$ can also transfer a proton to olefins. In the latter case, however, alternative modes of reaction such as addition and hydride transfer reactions occur as well.

Gas-phase proton transfer reactions have been reported to occur in the mass spectrometer, but they have seldom been observed at atmospheric pressures under the action of ionizing radiation. The major reason for this has been that the presence of ionic reactants or intermediates in such systems can only be inferred from a product analysis after irradiation. However, in recent radiolytic studies which were carried out in the presence and in the absence of an electrical field, and in which extensive use was made of deuterium-labelled compounds, a distinction could be made between products of ion-molecule reactions and those of neutral excited molecule decompositions.[1] It has also been demonstrated that it is feasible to trace the course of ionic reactions in a radiolytic system in much the same way as free radical reactions are studied in photolytic or pyrolytic systems. Because one sees only the neutral product of the ion-molecule reaction in radiolysis, the information obtained from the radiolytic system is complementary to that gained from mass spectrometry where only the charged species are observed. Conventional analysis of the neutral products formed in the radiolysis of suitable deuterium-labelled compounds has the advantage that it is possible to establish, from the positioning of the deuterium atoms in any particular product, the structure of the reacting ion or of the intermediate complex. These techniques were applied in studies [2, 3] on proton-transfer reactions occurring in the gas-phase radiolysis of hydrocarbons. The results presented here are an extension of that work.

EXPERIMENTAL

MATERIALS

The deuterated compounds were obtained from Merck, Sharp and Dohme of Canada, Limited. All compounds were purified by means of gas chromatography. Mass-spectrometric analysis indicated that n-pentane-d_{12} contained 10 % $C_5D_{11}H$; cyclopropane-d_6

contained 7·4 % C_3D_5H; propylene-d_6 contained 4·3 % C_3D_5H; ethylene-d_4 contained 3·4 % C_2D_3H; propane-d_8 contained 3 % C_3D_7H; and isobutane-d_{10} contained 8 % C_4D_9H. Phillips reagent-grade CH_4 was purified by repeated slow distillation from −195 to −220°C. Assayed reagent-grade hydrogen, xenon, krypton, and argon were obtained from the Air Reduction Company. The deuterium gas, obtained from General Dynamics Corporation, contained 0·5 % HD.

IRRADIATION AND ANALYSIS

Pyrex reaction vessels of 500 ml provided with breakseals were used in all experiments. Prior to being filled, the cells were heated under vacuum close to the m.p. of Pyrex. The cells were irradiated at 40 ± 5°C in the National Bureau of Standards 50,000 Curie ^{60}Co source. Dosimetry was based on the measurement of the saturation current in a specially constructed reaction vessel.[1] Taking a W value for H_2 of 36·3 eV, the energy absorbed by hydrogen is $1{\cdot}35 \times 10^{18}$ eV/mole sec.

After irradiation, quantitative analysis of the products was carried out by expanding an aliquot of the irradiated material into an F and M fractometer provided with a silica gel or an alumina column, a flame ionization detector, and temperature programming. Subsequently, hydrogen was removed through a spiral trap immersed in liquid hydrogen as a refrigerant. Methane was then distilled and the remainder of the sample was introduced on to a Perkin-Elmer vapour fractometer (silica gel column) from which the product compounds were collected separately from the helium stream at the exit of the instrument. All fractions were introduced into a Consolidated 21-101 mass spectrometer in order to determine their isotopic compositions.

RESULTS AND DISCUSSION

Only a summary of the experimental observations is presented in this paper. Many of the results quoted are derived from detailed product analyses not given in their entirety here. Tables containing the isotopic compositions of the different products and the derivations of the ion pair yields and relative reaction rates discussed can be obtained from the authors upon request.

Nitric oxide was added as a free radical scavenger in most radiolysis experiments. Although removal of free radicals by NO usually simplifies the interpretation of the radiolysis mechanism, NO may also, to some extent, interact with some of the ions present in the system. In several cases, therefore, the concentration of NO was varied over a certain range in order to assess the effect of NO on the ionic reaction mechanism.

PROTON TRANSFER TO n-PENTANE

When hydrogen is irradiated in the presence of a small amount of alkane, RH, the following reaction mechanism will occur[2]:

$$H_2^+ + H_2 \rightarrow H_3^+ + H \quad (1)$$

$$H_3^+ + RH \rightarrow H_2 + RH_2^+ \quad (2)$$

The protonated hydrocarbon thus formed will eliminate H_2 or a smaller alkane, and the corresponding alkyl ion. For example, it was inferred that protonated n-pentane-d_{12} decomposes as follows:

$$C_5D_{12}H^+ \rightarrow CD_3H + \text{sec-}C_4D_9^+ \quad (3)$$

$$C_5D_{12}H^+ \rightarrow C_2D_5H + \text{sec-}C_3D_7^+ \quad (4)$$

$$C_5D_{12}H^+ \rightarrow C_3D_7H + C_2D_5^+ \quad (5)$$

The fragment carbonium ions ($C_nD^+_{2n+1}$) formed in reactions (3), (4) and (5) react with n-pentane in a hydride transfer reaction:

$$C_nD^+_{2n+1}+C_5D_{12}\rightarrow C_nD_{2n+2}+C_5D^+_{11} \qquad (6)$$

forming the corresponding fully-deuterated hydrocarbons as products (table 1).

TABLE 1.—PROTON TRANSFER TO n-PENTANE-d_{12}; MOLECULES FORMED PER ION PAIR

system	CD_3H	C_4D_{10}	C_2D_5H	C_3D_8	C_3D_7H	C_2D_6
n-C_5D_{12}+NO (1 : 0·05)	—	0·049	—	0·35	—	0 16
H_2+n-C_5D_{12}+NO (300 : 1 : 0·5)	0·56	0·44	0·14	0·14	0·069	0·065
Ar+H_2+n-C_5D_{12}+NO (1100 : 400 : 1 : 0·6)	0·34	0·29	0·050	0·058	0·029	0·024
Kr+H_2+n-C_5D_{12}+NO (500 : 300 : 1 : 0·5)	n.d.	0·29	0·053	0·058	0·029	0·026
Xe+H_2+n-C_5D_{12}+NO (300 : 300 : 1 : 0·5)	n.d.	0·099	—	0·39	—	0·12
H_2+Xe+n-C_5D_{12}+NO (300 : 1 : 1 : 0·5) *	0·60	0·48	0·11	0·13	0·054	0·065
H_2+Xe+n-C_5D_{12}+NO (300 : 10 : 1 : 0·5) *	0·77	0·67 (0·63)	0·12	0·40 (0·13)	0·065	0·15 (0·062)

* Values given are molecules formed per H_2^+ initially produced. Values in parentheses are values which may be attributed to proton tansfer reactions after correction for contributions from charge-transfer radiolysis. n.d., not determined; —, not formed.

No protonated alkanes except CH_5^+ and $C_2H_7^+$ have beed observed in the mass spectrometer, indicating that the higher homologues have a relatively short lifetime. This is corroborated with the protonated pentane by the fact that, even at a pressure of 25 cm, the ion pair yields ascribed to processes (3), (4) and (5) (0·56, 0·14, and 0·07, respectively) account for 0·77 of the H_3^+ ions formed. This is reasonably close to unity if one considers that other modes of decomposition may still be unaccounted for. For example, the decomposition of $C_5D_{12}H^+$ to give hydrogen and a pentyl ion would be difficult to detect by the analytical methods used in this study.

It is of interest to determine whether protonated pentane could be produced using other proton donors such as ArH^+, KrH^+ or XeH^+, and whether the relative probabilities of the modes of decomposition would vary with the ΔH of the reaction. Therefore, several H_2+inert gas+C_5D_{12}+NO mixtures were irradiated, in which the ratio inert gas/hydrogen was kept sufficiently large so that more than 95 % of the energy was absorbed by the inert gas. With argon and krypton,

$$Kr^++H_2\rightarrow KrH^++H \qquad (7)$$

$$Ar^++H_2\rightarrow ArH^++H \qquad (8)$$

are the major modes of reaction of Ar^+ and Kr^+ in such a system.[4] Charge transfer from krypton to hydrogen cannot occur because the krypton ionization potential is lower than that of hydrogen, while mass spectrometric studies[5] have shown that charge transfer from argon to hydrogen should be of minor importance compared to reaction (8).

If KrH^+ or ArH^+ formed in these mixtures does transfer its proton to n-C_5D_{12}, the major lower hydrocarbon products which should be observed would be the products resulting from decomposition processes (3), (4) and (5), followed by the hydride transfer reaction (6). The fact (table 1) that yields of CD_3H, C_2D_5H and C_3D_3H are comparable to those of C_4D_{10}, C_3D_8 and C_2D_6, respectively, shows that processes (3), (4) and (5) occur in these systems to the exclusion of charge transfer from the inert gas to pentane, which would lead to the formation of a large yield of C_3D_8 and smaller amounts of C_2D_6 and C_4D_{10}, all in the absence of partially deuterated products.[6] If the product yields are calculated relative to the energy absorbed by the inert gas (as in table 1), the sum of processes (3), (4) and (5) account for about 50 % of the Ar^+ and Kr^+ ions. On the other hand, the product yields account for more than 10 times the maximum number of H_3^+ ions which could be formed in the system by reaction (1), thus demonstrating conclusively that the proton donors were ArH^+ and KrH^+.

In contrast to the results obtained on the krypton and argon mixtures when a $Xe+H_2+C_5D_{12}+NO$ mixture is irradiated with more than 95 % of the energy absorbed by Xe, the observed product distribution is closely similar to that observed in the xenon-sensitized radiolysis of pentane[6] in the absence of hydrogen, clearly indicating that charge transfer from xenon to pentane is the major process taking place. On the basis of the product yields, at least 80 % of the Xe^+ ions can thus be accounted for.

These observations are not unexpected since there is no definite proof in the literature for the formation of XeH by reaction (9)

$$Xe^+ + H_2 \rightarrow XeH^+ + H. \tag{9}$$

Stevenson and Schissler[7] point out that this reaction has not been observed in the mass spectrum of xenon+hydrogen mixtures and hence the cross-section of this reaction must be less than 50 times that for the analogous formation of ArH^+.

In an attempt to form XeH^+, a mixture of hydrogen and xenon was irradiated in which the relative concentrations were adjusted so that at least 86 % of the energy was absorbed by hydrogen. When pentane was added to such a mixture in concentration equal to that of xenon (table 1, 6th experiment), the product distribution and yields were nearly identical to those observed in the radiolysis of $H_2+C_5D_{12}+NO$ mixtures in the absence of xenon. Because, according to Thompson and Schaeffer,[8, 9] reaction (10),

$$H_3^+ + Xe \rightarrow XeH^+ + H_2 \tag{10}$$

occurs with a rate comparable to the collision frequency, one would expect that a proton is transferred to xenon from H_3^+ at least as rapidly as to C_5D_{12}, thus, leading to diminution in product yields if XeH^+ does not, in turn, transfer its proton to pentane, but rather undergoes neutralization.[10] Such a drop in yield is not observed even when the concentration of xenon is increased to 10 times that of pentane, thus indicating that proton transfer from XeH^+ to pentane may be efficient.

The relative probabilities of the different modes of decomposition of the protonated pentane ion formed by proton transfer from H_3^+, ArH^+, KrH^+, XeH^+ and, as recently reported,[11] CH_5^+, do not change although the ΔH of the reaction differs with the different proton donors. Although a variation in the ion distribution with the ΔH of the proton transfer process has been observed in the mass spectrometer,[12] these changes are apparently not due to a change in the relative probability of the initial fragmentations, but rather to a lower or higher degree of decomposition of the fragment carbonium ion. No evidence for such fragmentation is seen at the much higher pressures at which the radiolytic experiments were carried out, indicating that these ions are apparently stabilized because of the higher collision frequency.

PROTON TRANSFER TO CYCLOALKANES

When a proton is transferred to a cycloalkane, the resulting protonated entity, $C_nH^+_{2n+1}$, is isomeric to a carbonium ion and, therefore, in contrast to the protonated alkanes such as $C_5D_{12}H^+$ discussed above, can be expected to have some stability. That is, the protonated cycloalkane may subsist for a sufficiently long time causing it to react as a carbonium ion instead of decomposing, in which case the structure of the ion can be determined. Proton transfer to cyclopropane was studied in detail. However, exploratory experiments indicate that analogous processes occur with other cycloalkanes such as methylcyclopropane and cyclobutane.

That fragmentation of the protonated cyclopropane formed in reaction (11)

$$H_3^+ + \text{c-}C_3H_6 \rightarrow C_3H_7^+ + H_2 \tag{11}$$

is not an important process is shown in the radiolysis of $H_2 + \text{c-}C_3H_6$ mixtures where the ion pair yields of the products up to C_3 account for only about 12 % of the H^+ in the system. The major products up to C_3 are methane and ethylene which are formed in equal amounts with ion pair yields of about 0·12 at an $H_2/\text{c-}C_3H_6$ ratio of 630. These yields vary little with the amount of NO added to the reaction mixture or a change of the ratio $H_2/\text{c-}C_3H_6$.

A plausible mechanism for the formation of methane would be reaction (11) followed by

$$C_3H_7^+ \rightarrow CH_4 + C_2H_3^+. \tag{12}$$

The vinyl ion, which would be formed in this decomposition, may react with cyclopropane,

$$C_2H_3^+ + \text{c-}C_3H_6 \rightarrow C_3H_5^+ + C_2H_4, \tag{13}$$

to form ethylene. This would account for the fact that, in the scavenged experiments, the ethylene yield is approximately equal to that of methane. The fact that the ethylene fraction observed in the radiolysis of $H_2 + \text{c-}C_3H_6 + \text{c-}C_3D_6$ mixtures consists entirely of C_2H_4 and C_2D_4 is consistent with the suggestion that the ethylene is formed as a result of a reaction such as (13).

Because only a fraction of the $C_3H_7^+$ ions formed in reaction (11) apparently decompose, it is of interest to determine the modes of reaction, as well as the structure of the stabilized entity, $C_3H_7^+$. A derivation of this structure is of particular interest in view of the suggestion of Meyerson *et al.*[13, 14] that $C_3H_7^+$ ions, originating from the fragmentation of alkane ions in the mass spectrometer, have a protonated cyclopropane ring structure. On the other hand, Stevenson [15] has postulated that these ions acquire the sec-propyl ion structure.

Since propane is a minor product (ion pair yield $<0·007$) in the scavenged H_2-cyclopropane radiolysis, it is evident that the protonated cyclopropane produced in reaction (11) does not undergo a hydride transfer reaction,

$$C_3H_7^+ + \text{c-}C_3H_6 \rightarrow C_3H_8 + C_3H_5^+ \tag{14}$$

with cyclopropane. If the protonated cyclopropane does acquire the sec-propyl ion structure, this observation would be expected since it was demonstrated in one experiment that sec-propyl ions, produced in the radiolysis of isobutane-d_{10},[16] did not react with additive cyclopropane to produce propane-d_7,

$$\text{sec-}C_3D_7^+ + \text{c-}C_3H_6 \rightarrow C_3D_7H + C_3H_5^+, \tag{15}$$

but reacted entirely with the isobutane to form propane-d_8,

$$\text{sec-}C_3D_7^+ + \text{iso-}C_4D_{10} \rightarrow C_3D_8 + C_4D_9^+. \tag{16}$$

However, from these results, it could be inferred that sec-propyl ions react with c-C_3H_6 at a rate which is 0·64 that of reaction (16), to form a more complex ion which is probably removed from the system by NO.

Thus sec-propyl ions, if produced, cannot be detected in the hydrogen-cyclopropane system unless some compound is added to the system with which the propyl ion undergoes a hydride-transfer reaction. Cyclohexane was chosen for this purpose, not only because sec-propyl ions react readily with cyclohexane [17]

$$\text{sec-}C_3H_7^+ + \text{c-}C_6D_{12} \rightarrow CH_3CHDCH_3 + C_6D_{11}^+, \qquad (17)$$

but also because an experiment in which cyclohexane was added to hydrogen in the absence of any other compound showed that proton transfer to cyclohexane produces essentially no product compounds below C_6.

It is seen (table 2) that, when c-C_6D_{12} is added in various concentrations to H_2+c-C_3H_6+NO mixtures, propane becomes the major product. More than 90 % of the propanes formed consist of CH_3CHDCH_3, thus demonstrating that reaction (17) occurs and that protonated cyclopropane rearranges to the sec-propyl ion structure prior to or during reaction. If $C_3H_7^+$, formed in a process such as (11), retained its ring structure, then, on statistical grounds, it would be expected that $CH_2DCH_2CH_3$ should be a major product. The above observations are also supported by the fact that, in the radiolysis of D_2+c-C_3D_6+c-C_6H_{12} mixtures, propane consists entirely of CD_3CDHCD_3.

From the observation that the propane-d_7 formed in the radiolysis of H_2+c-C_3D_6+c-C_6D_{12} mixtures contained approximately 80 % $CH_2HCD_2CD_3$, it may be concluded that the protonated c-C_3D_6 isomerizes mainly to the structure $CD_2HCDCD_3^+$ which is statistically favoured over the alternate configuration $CD_3CHCD_3^+$.

From earlier results [17] and those cited in this discussion, it is calculated that the rate of propyl ion addition to cyclopropane is 0·42 times as fast as reaction (17). Knowing this, it is possible to calculate, from the ion pair yields of CH_3CHDCH_3 given in table 2, the total ion pair yield which can be ascribed to propyl ions. In addition, if one assumes that a proton is transferred with the same probability to c-C_3H_6 as to c-C_6D_{12}, noting that process (12) occurs in this system with an ion pair yield of 0·08, an ion pair yield of 0·91 is obtained for H_3^+. Thus, it may be concluded that the proton-transfer reaction is highly efficient and that the majority of the protonated cyclopropane ions arrange to the stable sec-propyl ion structure and react further with either cyclopropane or the additive cyclohexane.

TABLE 2.—PROTON TRANSFER TO CYCLOPROPANE; MOLECULES FORMED PER ION PAIR

	CH_4	C_2H_4	CH_3CHDCH_3	$CH_2DCH_2CH_2D$	calc. $C_3H_7^+$
H_2+c-C_3H_6+c-C_6D_{12}+NO (176 : 1 : 0·2 : 0·1)	0·084	0·076	0·22	<0·002	0·65
H_2+c-C_3H_6+c-C_6D_{12}+NO (195 : 1 : 1 : 0·5)	n.d.	0·047	0·26	<0·002	0·36
Ar+H_2+c-C_3H_6+c-C_6D_{12}+NO (169 : 69 : 1 : 0·37 : 0·15)	0·032	0·04	0·25	<0·002	0·53
Kr+H_2+c-C_3H_6+c-C_6D_{12}+NO (99 : 67 : 1 : 0·37 : 0·15)	n.d.	0·07	0·17	0·005	0·37
Xe+H_2+c-C_3H_6+c-C_6D_{12}+NO (65 : 72 : 1 : 0·36 : 0·15)	0·021	0·17	0·040	0·086	0·086

A few H_2+c-C_3H_6+c-C_6D_{12}+inert gas mixtures were irradiated for which the ratio inert gas/hydrogen was kept sufficiently large so that more than 95 % of the total dose was absorbed by the inert gas. Processes (7) and (8) should again be the major modes of reaction of the Kr^+ or Ar^+ ions. It can be seen (table 2) that CH_3CHDCH_3 is the major product formed in these systems, indicating that processes (7) and (8) are followed by the proton-transfer reactions:

$$ArH^+ + c\text{-}C_3H_6 \rightarrow Ar + C_3H_7^+ \tag{18}$$

$$KrH^+ + c\text{-}C_3H_6 \rightarrow Kr + C_3H_7^+ \tag{19}$$

$C_3H_6D_2$ is not a product, clearly showing that charge transfer does not occur in these systems and direct radiolysis is unimportant, as it has been demonstrated [18] that the cyclopropane parent ion, if formed, would undergo the D_2^--transfer reaction

$$c\text{-}C_3H_6^+ + c\text{-}C_6D_{12} \rightarrow CH_2DCHDCH_3 + C_6D_{10}^+ \tag{20}$$

The yields of the observed products in these experiments calculated relative to the energy absorbed by the inert gases account for about 80 % of the Ar^+ and 50 % of the Kr^+ ions. The proton-transfer reaction is, therefore, a major process undergone by ArH^+ and KrH^+ in these mixtures. This finding, as well as the results of the pentane experiments discussed above, contradicts the assumption [19, 20] that the only fate of ArH^+ in the presence of hydrocarbons is the neutralization process

$$ArH^+ + e \rightarrow Ar + H. \tag{21}$$

Since processes other than (21) occur, the rate constants derived in those studies will be in error.

When xenon is added to the $H_2 + c\text{-}C_3H_6 + c\text{-}C_6D_{12} + NO$ system, CH_3CHDCH_3 is only a minor product, and $CH_2DCHDCH_3$ is formed in appreciable yield, demonstrating that parent cyclopropane ions are formed by the charge-transfer mechanism:

$$Xe^+ + c\text{-}C_3H_6 \rightarrow Xe + C_3H_6^+ \tag{22}$$

followed by reaction of $C_3H_6^+$ with $c\text{-}C_6D_{12}$ (reaction (20)). Thus, again the H^+-transfer reaction (9) occurs at a much lower rate than the analogous processes (7) and (8).

It may be expected that CH_5^+, which is formed in the radiolysis of methane [11] by the process

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \tag{23}$$

would effectively transfer a proton to $c\text{-}C_3H_6$,

$$CH_5^+ + c\text{-}C_3H_6 \rightarrow CH_4 + C_3H_7^+. \tag{24}$$

This process is exothermic by about 65 kcal if one accepts [21] a value of 234 kcal of $\Delta H_f(CH_5^+)$, and a sec-propyl ion structure for $C_3H_7^+$. The formation of CH_3CHDCH_3 in the radiolysis of a $CH_4 + c\text{-}C_3H_6 + c\text{-}C_6D_{12}$ mixture (table 2) confirms the occurrence of process (24). Also, the fact that the value of 0·69, which can be calculated for the ion pair yield of sec-$C_3H_5^+$, agrees closely with the estimated value of 0·68 for the ion pair yield of CH_7^+,[11] indicating that reaction (24) occurs with a high efficiency.

In the radiolysis of $H_2 + C_4H_8$ (600 : 1) mixtures, fragmentation of the $C_4H_9^+$, which may be expected to be formed by the proton-transfer reaction

$$H_3^+ + c\text{-}C_4H_8 \rightarrow C_4H_9^+ + H_2 \tag{25}$$

is of minor importance. Ethane and ethylene are the major lower hydrocarbon products, but they account for only 10 % of the H_3^+ ions. On the other hand, $CH_3CH_2CHDCH_3$ is a product in the radiolysis of a $H_2 + c\text{-}C_4H_8 + c\text{-}C_6D_{12} + NO$

(400 : 1 : 0·4 : 0·2) mixture, indicating that a fraction of the $C_4H_9^+$ ions formed in process (25) are stabilized and rearrange to the sec-butyl ion structure prior to, or during reaction.

PROTON TRANSFER TO OLEFINS

Proton transfer to an olefin gives a protonated entity which, as with the protonated cycloalkanes, is isomeric to a carbonium ion and, in view of the results presented above, may be expected to react as such. Unlike the protonated cycloalkane, however, the protonated olefin can assume a carbonium ion structure without ring opening or rearrangement.

Hydrogen or deuterium was irradiated in the presence of small amounts of ethylene, propylene, 1-butene, cis-2-butene, and trans-2-butene. Only those experiments with propylene additives will be discussed in detail.

When hydrogen is irradiated in the presence of a small amount of added propylene, the formation of H_3^+ by reaction (1) should be followed by

$$CH_3CHCH_2 + H_3^+ \rightarrow C_3H_7^+ + H_2 \tag{26}$$

The only products up to C_4 which are observed in such an experiment are methane and ethylene (ion pair yield = 0·023), thus demonstrating that fragmentation of the protonated propylene occurs only to a minor extent. Because propane is not observed, the $C_3H_7^+$ produced in reaction (25) must undergo a hydride-ion transfer reaction with propylene to a limited extent, if at all. On the other hand, in an independent experiment, propyl ions formed in the radiolysis of isobutane were observed to add to propylene, probably to form a heavier ion which can be removed from the system by NO. Therefore, in order to measure the yield of the propyl ions, varying amounts of cyclohexane were added as interceptor to hydrogen + propylene mixtures in a series of experiments. As with the analogous cyclopropane experiments discussed above, CH_3CHDCH_3 is the major product produced in the irradiation of a $H_2 + CH_3CHCH_2 + c\text{-}C_6H_{12} + NO$ mixture, thus showing that reaction (26) is followed by reaction (17) in this system and, therefore, that the protonated propylene, $C_3H_7^+$, has the sec-propyl ion structure prior to, or during reaction. That some rearrangement occurs in the protonated intermediate is shown by the irradiation of $H_2 + CD_3CDCD_2 + c\text{-}C_6D_{12}$ mixtures, where the product propanes consist of $CD_3CD_2CD_2H$ and CD_3CDHCD_3 in a ratio of about 3·5 to 1.

Knowing that the rate of propyl ion addition to propylene is 1·53 times faster than hydride transfer with cyclohexane [17] (reaction (17)), we may deduce from the yields of propane attributed to reaction (17) a total propyl ion yield of about 0·44. Further, assuming that a proton is transferred from H_3^+ to cyclohexane at the same rate as to propylene, it is calculated that the average yield of H_3^+ accounted for by the observed products is 0·80, indicating that the proton-transfer reaction to propylene occurs with a high efficiency.

In similar experiments with ethylene as the added olefin, CH_3CH_2D appeared as the major product with an ion pair yield of 0·19 when the $C_2H_4/c\text{-}C_6D_{12}$ ratio was 2·0. From relative reaction rates determined in separate experiments (ethyl ion addition to ethylene occurs with a rate which is 1·2 times as fast as hydride transfer with cyclohexane), it is calculated that about 98 % of the H^+ ions have been accounted for, thus demonstrating that proton transfer from H_3^+ to ethylene is highly efficient.

Again, in similar experiments with 1-butene, cis-2-butene, and trans-2-butene as the olefins added to H_2 with $c\text{-}C_6D_{12}$ as the butyl ion interceptor, n-butane-d_1 having the structure $CH_3CHDCH_2CH_3$ appeared as a product in all three cases, thus demonstrating that the protonated butene reacts as a sec-butyl ion. Isobutane was not a product, indicating that $C_4H_9^+$ does not always rearrange to the thermodynamically more stable t-butyl ion.

Proton transfer reactions from carbonium ions to larger olefins

$$C_mH_{2m+1}^+ + C_nH_{2n} \rightarrow C_mH_{2m} + C_nH_{2n+1}^+ \qquad (27)$$

are usually exothermic, but may occur with low probability because addition to the double bond, as well as hydride-transfer reactions, may constitute alternative modes of reaction of the $C_mH_{2m+1}^+$ ion. From the radiolysis of $C_3D_8 + C_3H_6$—NO mixtures, it could be deduced that all three reactions occur. In these mixtures, C_3D_8 is the source of the $C_2D_5^+$ ions [22] which can either react with C_3D_8

$$C_2D_5^+ + C_3D_8 \rightarrow C_2D_6 + C_3D_7^+, \qquad (28)$$

or with C_3H_6,

$$C_2D_5^+ + C_3H_6 \rightarrow C_2D_4 + C_3H_6D^+ \qquad (29)$$

$$C_2D_5^+ + C_3H_6 \rightarrow C_2D_5H + C_3H_5^+ \qquad (30)$$

$$C_2D_5^+ + C_3H_6 \rightarrow C_5D_5H_6^+. \qquad (31)$$

On the basis of the above mechanism, approximate values of the relative rates of the different processes can be obtained from the yields of C_2D_6, C_2D_5H, and C_2D_4 and their variations with C_3H_6 concentration. However, because a fraction of C_2D_6 and C_2D_4 is also formed by reactions [23] other than (28) and (29), more accurate determination was based on the isotopic analysis of the ethane and ethylene formed in the radiolysis of $C_3D_8 + C_3H_8$ (1 : 1) mixtures in the presence of various amounts of C_3H_{36} From these results it is calculated that the relative probabilities of reactions (28), (29), (30) and (31) are 1·00, 1·07, 0·16 and 0·93, respectively. Radiolytic studies [3, 17] have shown that $C_2H_5^+$ and n-$C_3H_7^+$ can also transfer a proton to other organic compounds such as CH_3OH and CH_3COCH_3.

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