are involved in the formation of polymer by the irradiation of solid methane, and they suggest that the ionic precursor to the polymer is CH_3^+. Similar suggestions for gas phase radiolysis of methane were made by Hummel.[18] The polymer formed by the solid irradiation is very similar in its properties to that formed in the gas phase irradiation. However, more recently it has been suggested that no polymer is produced in the irradiation of solid methane to very low conversions.[19]

The results of our mass spectrometric study provide support for the postulate of Sieck and Johnsen. The applicability of gas phase mass spectrometric studies to ionic processes in irradiated solids is not clearly established, although Libby[17b] implies that reactions in the two phases may be appreciably different. In any event, it is clear from our results (and those of Ausloos and co-worker[13]) that in the gas phase in pure methane (1) ionic reactions involving the major ions CH_4^+ and CH_3^+ do not proceed appreciably beyond the formation of CH_5^+ and $C_2H_5^+$, respectively; and (2) the small intensity of higher molecular weight product ions indicates that any ionic polymerization which is occurring involves initial reactant ions of small relative intensity. Several possibilities compatible with the present work come immediately to mind. While we think that the $C_3H_5^+$ ion formed in the sequence $CH_2^+ \rightarrow C_2H_3^+ \rightarrow C_3H_5^+$ is relatively

(18) R. W. Hummel, *Nature*, **192**, 1178 (1961).
(19) P. Ausloos, R. E. Rebbert, and S. G. Lias, *J. Chem. Phys.*, **42**, 540 (1965).

stable in methane, we have pointed out that some loss seems to be occurring, and this conceivably could involve further reaction culminating in the formation of polymer. The CH^+ and C^+ ions formed from methane are known[6,7] to react rapidly with methane, and the $C_2H_2^+$ ion formed as the first product from CH^+ reacts with methane at a very rapid rate. In fact, the subsequent reaction is so fast that the intensity of $C_2H_2^+$ becomes negligibly small at moderately high pressures. If the reactions of subsequent products also occur rapidly, one would expect that the product ions would not appear to a noticeable extent in the methane high pressure mass spectrum, which is in accordance with the experimental observation. Sieck and Johnsen[16] find that $G(\text{polymer}) = 2.0$, and they calculate that $G(CH^+) + G(C^+) = 0.14 + 0.04 = 0.18$. If one assumes that polymer is formed by the reaction of CH^+ and C^+, one calculates from the G values that about 11 methanes are involved in the formation of each polymer molecule. It is of considerable interest that Sieck and Johnsen report that between 12 and 20 carbons are incorporated in the polymeric chain, and that Davis and Libby[17a] report that 18 carbon atoms were involved in each polymer molecule.

Reactions of Gaseous Ions. XV. Methane + 1% Ethane and Methane + 1% Propane

M. S. B. Munson and F. H. Field

Contribution from the Esso Research and Engineering Company, Baytown Research and Development Division, Baytown, Texas. Received March 8, 1965

Mass spectrometric studies have been made of gaseous ionic reactions in mixtures of $CH_4 + 1\% C_2H_6$ and $CH_4 + 1\% C_3H_8$ at pressures up to 2 torr. The ionic distribution at high pressures is very different from that in pure CH_4. Both dissociative and nondissociative proton-transfer reactions are observed between CH_5^+ and C_2H_6 to give $C_2H_5^+$ and $C_2H_7^+$ in a ratio of 3 or 4 to 1. The proton affinity of ethane is therefore greater than the proton affinity of methane. From the formation of CH_5^+ in pure CH_4 and the dissociative proton-transfer reaction in $CH_4 + 1\% C_2H_6$, upper and lower limits for the proton affinity of methane can be determined: $115 \leq P(CH_4) \leq 121$ kcal./mole. Formation of $C_3H_9^+$ from proton transfer of CH_5^+ to C_3H_8 occurs to a very small extent, if at all; dissociative proton transfer to give both $C_3H_7^+$ and $C_2H_5^+$ was observed, however. Several plausible exothermic reactions which one might expect do not occur, and the nonreactivity of certain ions was established. These nonreactive ions illustrate the necessity for chemical considerations in discussing ionic reactions.

Introduction

In a recent paper[1] we have reported the ionic reactions occurring in pure methane (>99.9%) in a mass spectrometer at pressures as high as 2 torr. We observed that several of the product ions from reaction did not react further with methane and that extensive ionic polymerization involving methane did not occur. During the course of these experiments we observed that small amounts of impurities in the methane could produce major differences in the distribution of ions at high pressures. One may calculate that at 2 torr an ion will make roughly 50 collisions in passing out of the source of our mass spectrometer. If the collisions with these impurities have the usual efficiency for reaction which is characteristic of most gaseous ion–molecule reactions, one should then expect a major alteration in the distribution of ions at high pressures caused by reactions with these impurities even at concentrations of 1% or less. These findings

(1) F. H. Field and M. S. B. Munson, **87**, 3289 (1965).

suggest that we have here a technique for studying gaseous ionic reactions which are otherwise not easily accessible to investigation. There is, in addition, the hope that one can develop a systematic chemistry of gaseous ionic reactions.

Furthermore, it has recently been suggested[2] that in the macroscopic radiation chemistry of methane the presence of small amounts of foreign substances (which may be radiation products) will extensively modify the ionic reactions and distributions in the system. Thus the phenomena which we can observe in our mass spectrometer at high pressure may be directly correlatable with radiation chemistry.

We have, therefore, begun a study of the ionic reactions in mixtures of methane with about 1% of several added compounds which will be reported in a series of papers. The problems of the formation of some of the ions by direct electron impact on the additives are eliminated by using a low concentration of the additive. At pressures above 1 torr reactions of the secondary ions become readily apparent. As additives we have studied several hydrocarbons, free-radical inhibitors such as O_2 and NO, ionic inhibitors such as NH_3 and H_2O, and effectively inert materials such as Kr and Xe. This paper will contain a report of mixtures of methane with 1% ethane and 1% propane, separately.

Experimental

The mass spectrometer and the experimental procedure for operation at pressures up to 2 torr have been described in the previous paper.[1] The experimental conditions for the present experiments with small concentrations of substances added to methane were as nearly the same as possible to the conditions of the previous experiments on pure methane (field strength = 6.25 v./cm.; ion path = 2.0 mm.; electron energy = 150 v.; 210 ± 10°). The hydrocarbons which were used as additives in these experiments were Phillips research grade which had been condensed from the cylinder into the gas manifold with liquid nitrogen, and then a center cut from this liquid was taken for use. The mixtures were prepared volumetrically at about 1% of the compound in the mixture, but the concentrations are not accurately known. Comparisons of the effectiveness of the different additives and the rates of reaction are, therefore, only approximate.

In an earlier paper[3] we have developed the kinetic rate equations which show that a maximum in a plot of relative concentration of an ion as a function of pressure is sufficient to establish that the ion is reacting to give other products. In this manner we may study reactions of secondary product ions which are not otherwise accessible. Appearance potentials were not measured for the ions because of the uncertainties in their measurement at pressures greater than 0.5 torr, and because for most of the processes we were interested in studying, the minimum energy of formation of the product ion was irrelevant. For the dominant reactions which we are considering in this paper, the relative concentrations of the reactant and product

(2) P. Ausloos, S. G. Lias, and R. Gorden, Jr., J. Chem. Phys., 39, 3341 (1963).
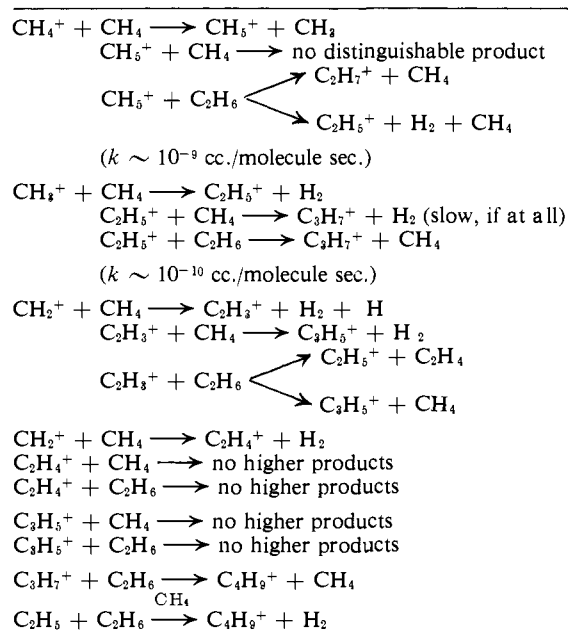(3) M. S. B. Munson, J. Am. Chem. Soc., 87, 2332 (1965).

ions are sufficient to establish the reaction sequence conclusively.

To simplify the discussion, the two additives, ethane and propane, will be considered separately.

Results for CH_4 + 1% C_2H_6

From knowledge of the rate constants obtained in previous studies on CH_4 and C_2H_6, it may be demonstrated that the presence of 1% C_2H_6 in CH_4 will result in only a trivial ($\sim$1%) change in the CH_4 primary ion distribution. Thus the addition of C_2H_6 will effect significant changes only in the concentrations of secondary and tertiary ions from CH_4 which are stable in CH_4. The identity of the reactions occurring between the ions from CH_4 and neutral C_2H_6 may be deduced from the observed changes in ion concentrations. The manner of making the deductions is described in subsequent paragraphs. Table I summarizes the reactions in CH_4 and CH_4-1% C_2H_6 mixtures.

Table I. Reactions in CH_4 and CH_4 + 1% C_2H_6 Mixtures

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3$$
$$CH_5^+ + CH_4 \longrightarrow \text{no distinguishable product}$$
$$CH_5^+ + C_2H_6 \begin{cases} \longrightarrow C_2H_7^+ + CH_4 \\ \longrightarrow C_2H_5^+ + H_2 + CH_4 \end{cases}$$

($k \sim 10^{-9}$ cc./molecule sec.)

$$CH_4^+ + CH_4 \longrightarrow C_2H_5^+ + H_2$$
$$C_2H_5^+ + CH_4 \longrightarrow C_3H_7^+ + H_2 \text{ (slow, if at all)}$$
$$C_2H_5^+ + C_2H_6 \longrightarrow C_3H_7^+ + CH_4$$

($k \sim 10^{-10}$ cc./molecule sec.)

$$CH_2^+ + CH_4 \longrightarrow C_2H_3^+ + H_2 + H$$
$$C_2H_3^+ + CH_4 \longrightarrow C_3H_5^+ + H_2$$
$$C_2H_3^+ + C_2H_6 \begin{cases} \longrightarrow C_2H_5^+ + C_2H_4 \\ \longrightarrow C_3H_5^+ + CH_4 \end{cases}$$

$$CH_2^+ + CH_4 \longrightarrow C_2H_4^+ + H_2$$
$$C_2H_4^+ + CH_4 \longrightarrow \text{no higher products}$$
$$C_2H_4^+ + C_2H_6 \longrightarrow \text{no higher products}$$

$$C_3H_5^+ + CH_4 \longrightarrow \text{no higher products}$$
$$C_3H_5^+ + C_2H_6 \longrightarrow \text{no higher products}$$

$$C_3H_7^+ + C_2H_6 \xrightarrow{CH_4} C_4H_9^+ + CH_4$$
$$C_2H_5 + C_2H_6 \longrightarrow C_4H_9^+ + H_2$$

CH_5^+ + $C_2H_5^+$. Figure 1 shows the pressure dependence of the relative concentrations of CH_5^+ and $C_2H_5^+$ for these mixtures of ethane in methane. The contribution to the total concentration of $C_2H_5^+$ from primary ionization of C_2H_6 is negligible. The relative concentration of CH_5^+ passes through a maximum and then decreases to about 10% of its maximum value. The dotted lines in this figure indicate the relative concentrations of these ions in pure methane. Obviously CH_5^+ is reacting rapidly with ethane. From a plot of log $(I_{17}/\Sigma I_i)$ vs. P, one can obtain a value of kt of about 6 × 10^{-15} cc./molecule and a value of the rate constant, k, of about 6 × 10^{-9} cc./molecule sec. using the low pressure value for the residence time of the ion of mass 17 calculated from simple electrostatic considerations. The residence time of CH_5^+ under these experimental conditions is not well defined,[1] nor is the concentration of ethane accurately known, so this value for the rate constant
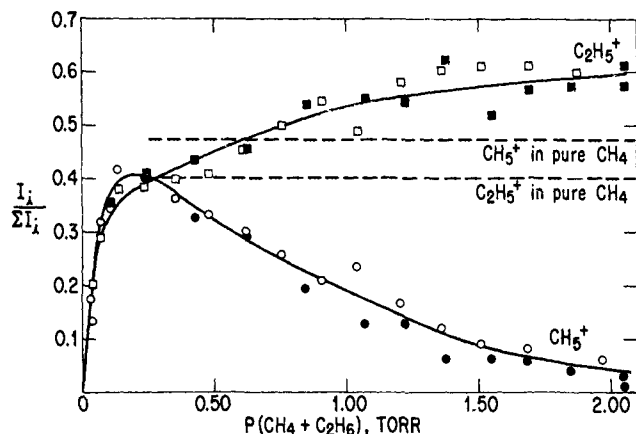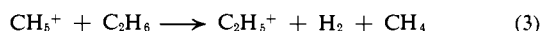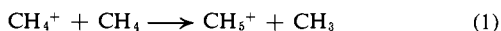
Figure 1. Relative concentration of $C_2H_5^+$ and CH_5^+ vs. total pressure of $CH_4 + 1\%$ C_2H_6. Solid and open points indicate duplicate experiments.

Figure 2. Relative concentrations of $C_2H_7^+$ and $C_4H_9^+$ vs. total pressure of $CH_4 + 1\%$ C_2H_6.

should be taken merely as an indication that the reaction is extremely fast.

It is apparent in Figure 1 that $C_2H_5^+$ is being formed from some process in addition to that producing it in pure methane, and from the relative concentrations of the species involved the other reactant must be CH_5^+. The sequence of reactions is, then

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \qquad (1)$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \qquad (2)$$

$$CH_5^+ + C_2H_6 \longrightarrow C_2H_5^+ + H_2 + CH_4 \qquad (3)$$

Reaction 3 is therefore the first directly observed reaction of the CH_5^+ ion and provides excellent support for the suggestion[2] that reactions of this type occur in the radiolysis of mixtures of methane with higher alkanes. This reaction may be considered as a proton-transfer reaction for which the resultant $C_2H_7^+$ ion has decomposed.

The occurrence of reaction 3 provides some useful information about the heat of formation of CH_5^+ and the proton affinity of methane. From reaction 1 and the assumption that rapid gaseous ionic reactions are exothermic or thermoneutral, we calculate that $\Delta H_f(CH_5^+) \leqslant 232$ kcal./mole, using $I(CH_4) = 12.98$ v.,[4] $\Delta H_f(CH_3) = 32$ kcal./mole,[5] and $\Delta H_f(CH_4) = -18$ kcal./mole.[6] From reaction 3 and the same assumption about the heat of reaction, we may calculate that $\Delta H_f(CH_5^+) \geqslant 226$ kcal./mole, using $\Delta H_f(C_2H_5^+) = 224$ kcal./mole[7] and $\Delta H_f(C_2H_6) = -20$ kcal./mole.[6] These limits for the heat of formation of CH_5^+, $226 \leqslant \Delta H_f(CH_5^+) \leqslant 232$ kcal./mole, are as close as one can reasonably expect to achieve. From the definition of proton affinity

$$CH_4^+ + H^+ \longrightarrow CH_5^+ \quad P(CH_4) \equiv -\Delta H_r \qquad (4)$$
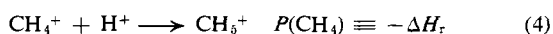
we can calculate the proton affinity of methane, $P(CH_4) = 118 \pm 3$ kcal./mole, taking $\Delta H_f(CH_5^+)$ to be the average of the upper and lower limits. Several quan-

(4) K. Watanabe, T. Nakayama, and J. Mottl, "Final Report on Ionization Potentials of Molecules by a Photoionization Method," Army Project No. 5B 99-01-004, Dec. 1959.

(5) B. E. Knox and H. B. Palmer, Chem. Rev., 61, 247 (1961).

(6) A.P.I. Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds," Chemical Thermodynamic Properties Center, Texas A & M, College Station, Texas.

(7) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, Table 45.
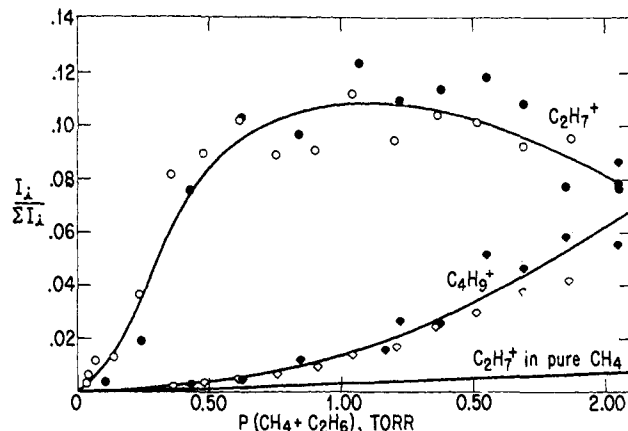
tum mechanical calculations of the proton affinity of methane have been made,[8–10] and the results of these calculations are all in the range of 7.0–7.5 v. or 160–170 kcal./mole. We cannot explain the difference between the experimental and calculated values, but we feel that the experimental values are correct.

The increase in the relative concentration of $C_2H_5^+$ in Figure 1 is not equal to the decrease in relative concentration of CH_5^+ so that either there is another product formed from reaction of CH_5^+ with ethane, or $C_2H_5^+$ reacts with ethane to give other products. Both of these alternatives occur and will be considered in turn.

$C_2H_7^+$. The first is a simple proton-transfer reaction which forms protonated ethane, $C_2H_7^+$. The

$$CH_5^+ + C_2H_6 \longrightarrow C_2H_7^+ + CH_4 \qquad (5)$$
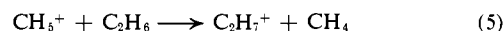
formation of this ion by a third-order process to the extent of 10–12% of the total ion concentration is indicated in Figure 2, together with a curve which we feel represents the best data for the formation of $C_2H_7^+$ in pure methane. It was mentioned in the earlier work on pure methane that it is always possible that the $C_2H_7^+$ could be formed from reaction with a trace impurity of ethane. This figure lends credibility to the earlier assumption. From the relative amount of $C_2H_7^+$ formed and CH_5^+ lost, we can estimate that about one-third to one-fourth of the CH_5^+ gives simple proton transfer, and the remainder gives the dissociative proton-transfer reaction to produce $C_2H_5^+$.

The proton affinity of ethane is therefore greater than the proton affinity of methane: $P(C_2H_6) > P(CH_4) = 118 \pm 3$ kcal./mole. In our previous work on ionic reactions in ethane,[11] we suggested that the proton affinity of ethane was about 120 kcal./mole. The agreement between these two values is satisfactory; however, no upper limit to the proton affinity of ethane can be obtained from these data.

It is possible that $C_2H_7^+$ might react to some extent, but the scatter of the data is such that no great confidence can be attached to the slight decrease in rela-

(8) J. Higuchi, J. Chem. Phys., 31, 563 (1959).

(9) J. R. Hoyland and F. W. Lampe, ibid., 37, 1066 (1962).

(10) F. W. Lampe and J. H. Futrell, Trans. Faraday Soc., 59, 1957 (1963).

(11) M. S. B. Munson, J. L. Franklin, and F. H. Field, J. Phys. Chem., 68, 3098 (1964).

tive concentration of $C_2H_7^+$ at the highest pressures. The reaction, if any, is not very fast.

$C_3H_7^+$ *and* $C_4H_9^+$. In .pure ethane reaction 6 was reported,[11] and this reaction also occurs in these mix-

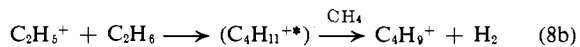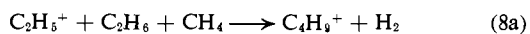$$C_2H_5^+ + C_2H_6 \longrightarrow C_3H_7^+ + CH_4 \qquad (6)$$
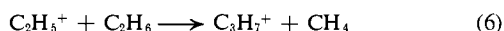
tures since the relative concentration of $C_3H_7^+$ is about 5 % at 2 torr in contrast to about 2 % at 2 torr in pure CH_4. From $\Delta I_{43}/I_{29}$ one can calculate that kt for reaction 6 is about 8×10^{-17} cc./molecule, and that k is about 6×10^{-11} cc./molecule sec. This value for k is of the same order as the value of 5×10^{-11} cc./ molecule sec., which can be obtained from the formation of $C_3H_7^+$ in pure ethane.[11] Reaction 6 is notably slower than reaction 3 and also slower than the reaction of the C_1^+ ions with ethane.

Another product ion whose formation is much greater in the mixture containing 1 % C_2H_6 than in pure CH_4 is $C_4H_9^+$, whose relative concentration as a function of pressure is also shown in Figure 2. In pure methane at 2 torr, the relative concentration of $C_4H_9^+$ is 0.4 %. From Figure 2 it is apparent that $C_4H_9^+$ is formed by a process that is higher order in pressure than the one forming $C_2H_7^+$. Further, the ratio I_{57}/I_{43} increases approximately linearly with pressure so $C_4H_9^+$ is not formed from $C_2H_5^+$ reacting with ethane in a reaction analogous to reaction 6. This observation of a higher kinetic order for the formation of $C_4H_9^+$ than for $C_3H_7^+$ from reaction with ethane is in agreement with the earlier observations made in pure ethane. Although $C_4H_9^+$ can be formed from a second-order reaction of $C_2H_5^+$ with ethane by an exothermal process, the reaction does not occur to any appreciable extent.

In ethane it was suggested that these differences in kinetic order could be explained by the sequence

$$C_2H_5^+ \xrightarrow{C_2H_6} C_3H_7^+ \xrightarrow{C_2H_6} C_4H_9^+ \qquad (7)$$
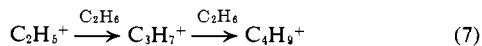
an explanation which is possible in these mixtures as well. However, in the present experiments the relative concentration of $C_4H_9^+$ at 2 torr is larger than the relative concentration of $C_3H_7^+$, both are monotonically increasing functions in this pressure range, and the maximum partial pressure of C_2H_6 is only 0.02 torr. An alternative explanation of these data which seems more plausible to us is a three-body reaction or the equivalent reaction of a collision complex

$$C_2H_5^+ + C_2H_6 + CH_4 \longrightarrow C_4H_9^+ + H_2 \qquad (8a)$$

$$C_2H_5^+ + C_2H_6 \longrightarrow (C_4H_{11}^{+*}) \xrightarrow{CH_4} C_4H_9^+ + H_2 \qquad (8b)$$

This process requires a high pressure of the third body and will not be observed at the lower pressures of the previous experiments. In the subsequent presentation of the other additives, we will give further examples of this process; in addition, a somewhat similar situation has been reported previously in acetylene for the formation of $C_6H_5^+$ and $C_6H_4^+$ by fourth-order processes.[12]

$C_2H_3^+$, $C_3H_5^+$, *and* $C_2H_4^+$. These ions show essentially the same behavior in this mixture as they do in pure methane. $C_2H_3^+$ reacts and does so with the same rate constant as that observed in pure CH_4.[1] There is essentially no decrease in relative concentration of $C_3H_5^+$ so this ion does not react rapidly with

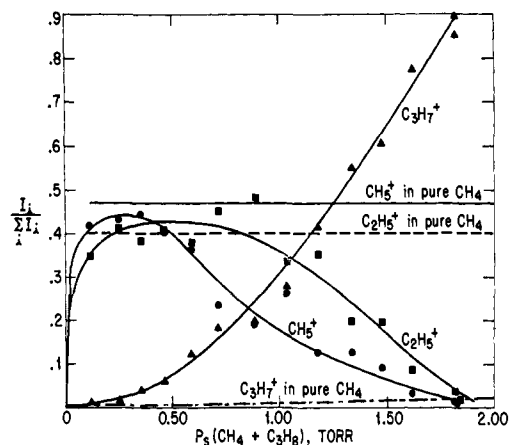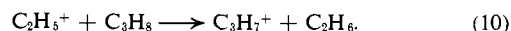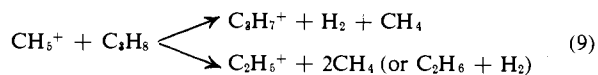(12) M. S. B. Munson, *J. Phys. Chem.*, **69**, 572 (1965).

Figure 3. Relative concentration of CH_5^+, $C_2H_5^+$, and $C_3H_7^+$ vs. total pressure of $CH_4 + 1 \% C_3H_8$.

ethane, either. With regard to $C_2H_4^+$, one of the surprising observations in the earlier work on methane and ethane separately was that the $C_2H_4^+$ ion did not react with either, although exothermic reactions with both can be written. It is observed in these experiments that the relative concentration of $C_2H_4^+$ does not decrease with increasing pressure. This observation confirms the previously reported nonreactivity with ethane.

There were small relative concentrations of ions of mass greater than $C_4H_9^+$, but the concentrations of these ions were too small to warrant discussion.

Results for $CH_4 + 1 \% C_3H_8$

CH_5^+, $C_2H_5^+$, *and* $C_3H_7^+$. As was the case with the CH_4–C_2H_6 mixture, the addition of 1 % C_3H_8 to CH_4 does not produce a significant change in the reactions of the primary ions from CH_4. Figure 3 shows the relative concentrations of the dominant ions in this mixture together with curves indicating the relative concentrations of these ions, CH_5^+, $C_2H_5^+$, and $C_3H_7^+$, in pure methane. Both $C_2H_5^+$ and CH_5^+ react rapidly with propane to give $C_3H_7^+$. From the decrease in CH_5^+ with increasing pressure, we estimate that the rate constant for reaction 9 is on the order of 10^{-9} cc./molecule sec. The reaction of $C_2H_5^+$ with propane (reaction 10), with a rate constant of 6×10^{-10} cc./ molecule sec., has already been established in propane. $C_3H_7^+$ is not formed by simple third-order processes, since the shape of this curve is very different from that for the third-order ion, $C_2H_7^+$, in Figure 2. The curve for the disappearance of $C_2H_5^+$ is sufficiently different from that for CH_5^+ in Figures 1 and 3 to indicate that in the range 0.5–1.0 torr the ion is formed by a process in addition to reaction 2, but above 1 torr it is consumed by a subsequent reaction. These curves are compatible with reactions 9 and 10; that is, CH_5^+

$$CH_5^+ + C_3H_8 \left\langle \begin{array}{l} \nearrow C_3H_7^+ + H_2 + CH_4 \\ \searrow C_2H_5^+ + 2CH_4 \text{ (or } C_2H_6 + H_2) \end{array} \right. \qquad (9)$$

$$C_2H_5^+ + C_3H_8 \longrightarrow C_3H_7^+ + C_2H_6. \qquad (10)$$

reacts with propane to give dissociative proton transfer, but to two different sets of products. The heats of reaction to the two sets of products in reaction 9 are nearly the same. We cannot make a reliable estimate of the relative amounts of the two types of dissociative

proton-transfer reactions, except that they are roughly comparable, certainly differing from each other by less than a factor of ten. Reaction 9 is consistent with but does not narrow the limits for $\Delta H_f(CH_5^+)$. In studies on the dissociation of propane by ion impact,[13] it was considered that $C_2H_5^+$ and $C_3H_7^+$ were formed by collision with some hydrogen-containing ions as the result of dissociative proton-transfer reactions.

$C_3H_9^+$. The question of simple proton transfer from CH_5^+ to propane to give $C_3H_9^+$ is somewhat unsettled. There is always slightly more mass 45 than can be accounted for by the ^{13}C isotopes of the C_3^+ species. However, mass 45 is a common background ion and also one which can easily be attributed to reasonable oxygenated impurities. Further, since the relative concentration of the mass 45 species was never greater than 0.1%, a small error in the correction for the ^{13}C isotope could easily account for the residual ion current for m/e 45. Consequently we do not feel that the existence of $C_3H_9^+$ is unequivocally established. If $C_3H_9^+$ be formed by proton-transfer reactions from CH_5^+ to propane with sufficient lifetime to be detected in our apparatus, it is formed to about 1% of the extent that $C_2H_7^+$ is formed from proton transfer to ethane under comparable conditions. The relative concentration of the small amount of $C_2H_7^+$ formed in this mixture of methane and propane passes through a maximum and then decreases rapidly; consequently, it must react with propane. The reaction is probably dissociative proton transfer, but it is not possible to be certain. If $C_3H_9^+$ exists so that the proton affinity of propane be a meaningful concept, then reaction of $C_2H_7^+$ suggests that $P(C_2H_6) < P(C_3H_8)$, whatever the fate of $C_3H_9^+$.

Other Ions. $C_3H_5^+$ and $C_2H_4^+$, which do not react with methane or ethane, react with propane since the concentrations of these ions pass through maxima and then decrease as the pressure is increased. The decrease in $C_2H_4^+$ is accompanied by an equal increase in $C_3H_6^+$, which suggests a reactant–product relationship between the two ions. No ion of increasing intensity other than $C_3H_7^+$ is present in sufficiently large concentration to account for the decrease in $C_3H_5^+$. These observations suggest the following reactions.

$$C_3H_5^+ + C_3H_8 \longrightarrow C_3H_7^+ + C_3H_6 \qquad (11)$$

$$C_2H_4^+ + C_3H \longrightarrow C_3H_6^+ + C_2H_6 \qquad (12)$$
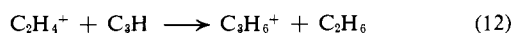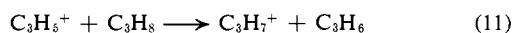
These are the same reactions postulated in the previous experiments on propane.[11] From the decrease in $C_3H_5^+$ in this mixture and the known rate constant for reaction with C_3H_8 and the nonreactivity in pure CH_4, we estimate that the rate constant for reaction of $C_3H_5^+$ with CH_4 is less than 10^{-12} cc./molecule sec.

Small concentrations of ions of mass greater than $C_3H_7^+$ were observed, as high as m/e 99. The most abundant of these ions were $C_4H_9^+$ (0.6% at 2 torr), $C_5H_{11}^+$ (0.2% at 2 torr), and $C_6H_{13}^+$ (0.4% at 2 torr). The relative abundance of $C_4H_9^+$ is slightly greater than the 0.4% at 2 torr in methane, but, unlike the experiments with $1\% C_2H_6$, it is not one of the major product ions. From these data it is apparent that $C_3H_7^+$ does not react rapidly with methane, since the higher concentration of $C_3H_7^+$ in the CH_4–C_3H_8 mixture does not significantly increase the $C_4H_9^+$ concentration.

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

Since $C_6H_{13}^+$ is found only in very small concentrations the reaction

$$C_3H_7^+ + C_3H_8 \xrightarrow{CH_4} C_6H_{13}^- + H_2 \qquad (13)$$
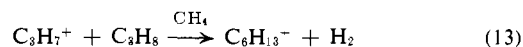
is not of much consequence, in contrast to the appreciable amount of $C_4H_9^+$ which was presumed to be formed from the analogous reaction with ethane (8).
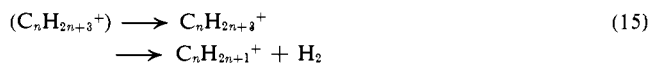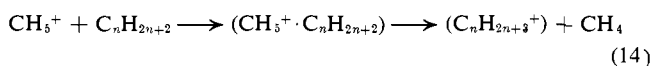
Table II summarizes the observations which we have been able to make for these mixtures.
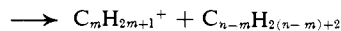
Table II. Reactions in $CH_4 + 1\% C_3H_8$ Mixtures

$$CH_5^+ + C_3H_8 \left\langle \begin{array}{l} C_3H_7^+ + H_2 + CH_4 \\ C_2H_5^+ + 2CH_4 \end{array} \right. \quad (k \sim 10^{-9} \text{ cc.}/\text{molecule sec.})$$

$C_2H_5^- + C_3H_8 \longrightarrow C_3H_7^+ + C_2H_6$
$C_2H_4^+ + C_3H_8 \longrightarrow C_3H_6^+ + C_2H_6$
$C_3H_5^+ + C_3H_8 \longrightarrow C_3H_7^+ + C_3H_6$
$C_3H_5^+ + CH_4 \longrightarrow$ no products $\quad (k < 10^{-12}$ cc./molecule sec.)
$C_3H_7^+ + CH_4 \longrightarrow$ no reaction
$C_3H_7^+ + C_3H_8 \longrightarrow$ no net reaction (or at least very slow)

Discussion

Proton-transfer reactions have been observed from CH_5^+ to ethane and propane. The existence of the protonated ions of the alkanes above C_2H_6 has not yet been convincingly established, however. These data suggest that if these ions do exist so that the term "proton affinity" is meaningful for the higher alkanes, then it should increase with increasing numbers of C atoms in the alkanes. The reactions of CH_5^+ with the higher alkanes should have rate constants of the order of 10^{-9} cc./molecule sec. The present data suggest that the reactions between CH_5^+ and propane or ethane are ones in which the collision complexes, $(CH_5^+ \cdot C_2H_6)$ and $(CH_5^+ \cdot C_3H_8)$, are very loosely bound with no new C–C bonds being formed. One can consider that complexes of this type will always dissociate to give the protonated alkane, which may or may not decompose.

$$CH_5^+ + C_nH_{2n+2} \longrightarrow (CH_5^+ \cdot C_nH_{2n+2}) \longrightarrow (C_nH_{2n+3}^+) + CH_4 \qquad (14)$$

$$(C_nH_{2n+3}^+) \longrightarrow C_nH_{2n+3}^+ \qquad (15)$$
$$\longrightarrow C_nH_{2n+1}^+ + H_2$$

or

$$\longrightarrow C_mH_{2m+1}^+ + C_{n-m}H_{2(n-m)+2}$$

There exist several agents for proton transfer other than CH_5^+, such as H_3^+, $C_2H_7^+$, XeH^+, etc., which should react in the same matter. The decomposition pattern of the $C_nH_{2n+3}^+$ ion should depend upon the energy with which it is formed, which should be related to the strength of the Brønsted acid. Nothing is known at present about this subject of the effect of acid strength on the decomposition pattern.

Dissociative proton-transfer reactions similar to these reported in this paper may be occurring in acid-catalyzed isomerization and cracking of hydrocarbons. The literature in these fields is tremendous and cannot be summarized in a few sentences, but some of the observations can also be explained in terms of Brønsted acids donating a proton to the alkanes which then

dissociate to give carbonium ions.[14] A suggestion that this type of reaction might occur has been made in connection with the cracking of paraffins.[15] The differences in product distribution which have been reported for different acids with the same hydrocarbon may perhaps be attributed to different decomposition patterns of the protonated alkanes resulting from proton transfer from acids of different strengths. Generally, the very strong acids which are used are also either oxidizing agents or Lewis acids as well, and we can only speculate at present about the frequency of occurrence of these dissociative proton transfer reactions in acid chemistry, but these reactions should be considered in interpreting data from proton-donating systems.

The data reported in this paper confirm the previous suggestions of Ausloos, Lias, and Gorden[2] from studies on methane radiolysis that dissociative proton transfer CH_5^+ to alkanes is a very rapid process. Since the higher alkanes are products of the radiolysis of methane, the existence of these reactions means that the disappearance of CH_5^+ will occur through different processes as a function of the extent of conversion. If one considers that CH_5^+ has reacted to virtual completion with 1% ethane or propane within approximately 1 μsec. at 2 torr, then at pressures in the neighborhood of 1 atm. only trace amounts of alkanes would be required for essentially quantitative reaction with CH_5^+. Since CH_5^+ donates a proton to the alkanes and $C_2H_5^+$ also reacts with the alkanes and both are nonreactive with methane, the mechanism of the radiolysis of methane must be carefully reconsidered since the reactions of the two predominant ions, CH_5^+ and $C_2H_5^+$, will be with the products of radiolysis.

In the mass spectrometric study of gaseous ionic reactions in methane by Wexler and Jesse,[16] it was reported that CH_5^+ passed through a slight maximum and then decreased and $C_2H_5^+$ increased continuously as the pressure was increased to about 0.4 torr. They interpreted this in terms of a reaction forming $C_2H_5^+$ from CH_5^+ and CH_4, which is endothermic and shown by our data not to occur in pure methane. Our present data present a plausible explanation for this observation in terms of a dissociative proton-transfer reaction from CH_5^+ to a small amount of ethane present as an impurity.

Table III shows ions which do not react in the reaction medium and one exothermic second-order reaction which can be written for each pair. The reactions in this table all seem plausible, and many might be expected on the basis of known ionic chemistry, but none of them occurs to any appreciable extent.

We have no explanation for these observations and know of no theoretical developments capable of explaining them.

Table III. Nonreactive Ions

Reaction	ΔH, kcal./mole
$C_2H_5^+ + CH_4 \longrightarrow C_3H_7^+ + H_2$	-16
$C_2H_4^+ + CH_4 \longrightarrow C_3H_6^+ + H_2$	-6
$C_2H_4^+ + C_2H_6 \longrightarrow C_4H_8^+ + H_2$	-25
$C_3H_5^+ + C_2H_6 \longrightarrow C_4H_7^+ + CH_4$	-20
$C_3H_7^+ + CH_4 \longrightarrow C_4H_9^+ + H_2$	-6
$C_3H_7^+ + C_3H_8 \longrightarrow C_4H_9^+ + C_2H_6$	-20

Since one would always expect a collision complex of finite lifetime, although perhaps very short, from the reaction

$$I^+ + M \longrightarrow (IM^+) \begin{cases} I^+ + M \\ S^+ + R \end{cases} \quad (16)$$
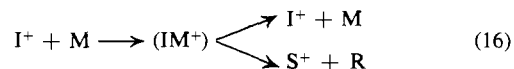
the question is essentially why the complex dissociates to give only the original reactants. It is possible that the decompositions to these nonobserved products have an activation energy and do not compete favorably with the reversible decomposition to reactants. For the simple gaseous ionic reactions which have been studied over a sufficiently wide temperature range to determine an activation energy, no activation energy has been observed.[12,17,18] However, none of these reactions involve complexes containing as many atoms as the ones we are considering. Perhaps the most nearly comparable analogy would be with the electron impact mass spectrum of the higher molecular weight alkanes. For these molecules the parent and high mass ions are formed to a very small extent of the total ionization[19] and these higher mass ions, particularly the parent ions, have pronounced negative temperature coefficients.[18] It is possible, then, that the higher molecular weight bimolecular product ions will be formed to a larger extent at lower temperatures, an effective negative activation energy. At present, however, there is no evidence about any temperature coefficients for these reactions. It would be most desirable for studies of this sort to be carried out.

(14) P. H. Emmett, Ed., "Catalysis," Vol. VI, Reinhold Publishing Corp., New York, N. Y., 1958: (a) F. E. Condon, Chapter 2; (b) H. H. Voge, Chapter 5.
(15) Reference 14, p. 452.
(16) S. Wexler and N. Jesse, *J. Am. Chem. Soc.*, **84**, 3425 (1962).

(17) A. Cassuto in "Advances in Mass Spectrometry," Vol. 2, R. M. Elliott, Ed., The MacMillan Co., New York, N. Y., 1963, p. 296.
(18) D. P. Stevenson and D. O. Schissler, in "The Chemical and Biological Action of Radiations," Academic Press Inc., New York, N. Y., 1961, p. 167.
(19) "Tables of Mass Spectral Data," A.P.I. Research Project 44, ref. 7.