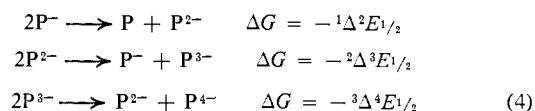


conclude from this that substitution either of the central protons or in the porphin skeleton can be regarded as a one-electron perturbation, having the effect of shifting the one-electron orbital levels without appreciably affecting the eigenfunctions. It is particularly interesting that the metal porphins fit into this scheme. It might have been thought, for example, that electron addition to a Cu^{II}-substituted porphin would result in the Cu^{II} being progressively reduced to Cu^I and Cu⁰. However, it is evident that the level being filled is essentially a porphin orbital, the Cu remaining in the +2 state. This confirms conclusions drawn from examination of the electronic spectra of the mono- and dinegative metal porphin anions. In fact, the presence of Cu²⁺ or Zn²⁺ in the system appears merely to raise the energy of the vacant orbital by 0.1 or 0.24 e.v., respectively. This is less than the effect of octaalkyl substitution, which raises the vacant level of etio-porphyrin I 0.30 e.v. above that of $\alpha,\beta,\gamma,\delta$ -tetraphenylporphin.

The potential intervals measure the disproportionation energies of the negative ions. Thus



All negative ions are thus stable to disproportionation, with roughly constant free energies for a given state of ionization. This was predicted¹⁰ and subsequently confirmed¹¹ for the mono- and dinegative ions of aromatic hydrocarbons. Presumably the positive and nearly constant disproportionation energies in the porphin series have a similar origin: namely, electron repulsion terms outweighing the drop in potential energy due to increased solvation, the two compensating effects running parallel with change in molecular size.

Acknowledgment. We are indebted to the Department of Scientific and Industrial Research for a special grant for the purchase of the Beckman spectrophotometer and for a maintenance award to D. C.

(10) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

(11) R. J. Hoijtink, E. de Boer, P. H. Van der Meij, and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956).

Reactions of Gaseous Ions. XVI. Effects of Additives on Ionic Reactions in Methane

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

Contribution from the Esso Research and Engineering Company, Baytown Research and Development Division, Baytown, Texas. Received May 21, 1965

Studies are reported on the ionic processes occurring in the source of a mass spectrometer at pressures up to 2 torr for mixtures of CH₄ + 1% X, where X = Kr, Xe, O₂, NO, H₂O, and ND₃. The proton affinities of Kr and Xe are less than 118 kcal./mole since proton transfer from CH₅⁺ does not occur. Kr, Xe, O₂, and NO have very little effect on the distribution of product ions in methane, and the proton affinities of both O₂ and NO are less than that of CH₄. Water and ammonia produce major changes in the ionic distribution at 2 torr, since about 90% of the total ionization is composed of hydrated or ammoniated protons. Proton transfer from CH₅⁺ and C₂H₅⁺ to water and ND₃ is rapid. Rapid hydrogen-deuterium exchange is observed between ND₃H⁺ and ND₃, but exchange is not observed between ND₄⁺ and CH₄.

Introduction

In the earlier papers in this sequence,^{1,2} we have discussed the ionic reactions which have been observed in a mass spectrometer at pressures up to 2 torr for methane and mixtures of methane with ethane and propane. The previous results showed that small concentrations of other compounds could have major effects on the distribution of ions in methane at high pressures.

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

(2) M. S. B. Munson and F. H. Field, *ibid.*, **87**, 3294 (1965).

It is the purpose of this paper to extend the series of additives to different types of compounds in an effort to develop a systematic ionic chemistry.

We studied mixtures containing 1% Kr and 1% Xe, which are effectively inert with respect to reaction with the secondary ions of pure CH₄, and we were able to obtain upper limits for the proton affinities of these rare gases. The radical scavengers, O₂ and NO, were also studied as additives, and these proved to be unreactive as well. These observations are of particular importance concerning the inhibition of radiolyses by NO. The radiation-induced polymerization of certain olefins is strongly inhibited by trace amounts of H₂O or NH₃, and this inhibition has been interpreted in terms of chain termination by proton transfer to these strong bases.^{3,4} Consequently, we studied H₂O and ND₃ as additives to determine their effectiveness as proton acceptors.

Experimental Section

The mass spectrometer and experimental procedure have been described elsewhere.^{1,2} One modification was made for pressure measurements in some of these experiments: the McLeod gauge, which had been used previously, was replaced by a quartz spiral bourdon

(3) T. H. Bates, J. F. V. Best, and F. Williams, *Nature*, **188**, 469 (1960).

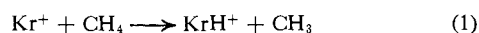
(4) M. A. Bonin, W. R. Busler, and F. Williams, *J. Am. Chem. Soc.*, **84**, 4355 (1962).

gauge (Texas Instruments, Inc.). Agreement between the pressures indicated by the two gauges was excellent. The additives which were used in these experiments were obtained from several commercial sources and were purified by distillations within the mass spectrometer gas handling system. The methane was Phillips Research Grade which was further purified in the manifold by distillation and absorption with molecular sieve. The mixtures were prepared volumetrically at approximately 1%, but the concentrations are not accurately known.

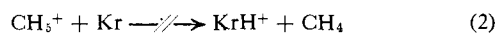
In all of these experiments the reactions of the primary ions of methane with the additives will produce only a trivial change of the concentrations of hydrocarbon product ions because the amount of additive is small compared with methane. Only the concentrations of the ions which do not react with methane, CH_5^+ , C_2H_5^+ , C_2H_4^+ , and C_3H_5^+ , can be drastically changed if reactions with the additives occur.

Results

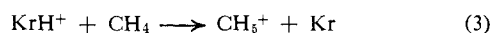
$\text{CH}_4 + 1\% \text{ Kr}$. The concentrations of the ions from methane at pressures up to 2 torr are essentially the same in this mixture as they are in pure methane; that is, the ions which do not react with methane do not react with Kr either. The relative concentration of Kr^+ decreases with increasing pressure as a result of the occurrence of charge-transfer reactions of Kr^+ with CH_4 .⁵ There is only a very small concentration of KrH^+ produced by reaction 1 which passes through a maximum and then



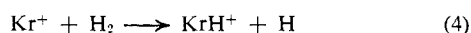
decreases. Since the relative concentration of CH_5^+ does not decrease and the relative concentration of KrH^+ does not increase monotonically over the entire pressure region, CH_5^+ does not transfer a proton to Kr (eq. 2). The small amount of KrH^+ formed



initially disappears, and we postulate that the reaction is as shown in eq. 3, because it is the lowest energy



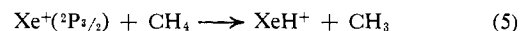
process for the consumption of KrH^+ . The relative concentration of KrH^+ is too small for (3) to cause any noticeable increase in the relative concentration of CH_5^+ . From (3) and the nonoccurrence of (2), we deduce that the proton affinity of Kr must be less than that of CH_4 : $P(\text{Kr}) < P(\text{CH}_4) = 118 \pm 3$ kcal./mole.² KrH^+ is also formed in the mixtures of Kr and H_2 ,⁶ presumably by (4), so $\Delta H_f(\text{KrH}^+) \leq 271$ kcal./mole



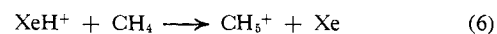
and $P(\text{Kr}) \geq 94$ kcal./mole. The wide limits, $94 \leq P(\text{Kr}) \leq 118$ kcal./mole, are the best which can be given at present for the proton affinity of krypton.

$\text{CH}_4 + 1\% \text{ Xe}$. The relative concentrations of the ions from CH_4 are essentially the same in this mixture as in pure methane at pressures as high as 2 torr; that is, the ions which do not react with methane do

not react with xenon either. It was suggested in previous work on $\text{CH}_4\text{-Xe}$ mixtures⁷ that reaction 5



occurred, which would imply that $\Delta H_f(\text{XeH}^+) \leq 230$ kcal./mole, assuming that the reaction is not endothermic and that $P(\text{Xe}) \geq 135$ kcal./mole. However, in these mixtures the relative concentration of Xe^+ does not decrease appreciably at pressures up to 2 torr so reaction 5 does not occur. In addition, proton transfer from CH_5^+ to Xe does not occur since the relative concentration of CH_5^+ does not decrease and XeH^+ does not increase monotonically over this pressure range (in contrast to Figure 2 for $\text{CH}_4 + 1\% \text{ H}_2\text{O}$ for which proton transfer does occur). The very small amount of XeH^+ which is formed passes through a maximum and then decreases as the pressure is increased. This behavior is probably the result of proton transfer from XeH^+ (eq. 6). These observa-



tions indicate that the proton affinity of xenon is less than the proton affinity of methane: $P(\text{Xe}) \leq P(\text{CH}_4) = 118$ kcal./mole.

In the previous work, the evidence for the occurrence of (5) was somewhat ambiguous. In Figure 2 of ref. 7 the ratio XeH^+/Xe^+ increases markedly with increasing energy of the ionizing electrons at constant pressure, although the appearance potentials of XeH^+ and Xe^+ were equal within experimental error. The fact that XeH^+/Xe^+ increases with increasing electron energy suggests that XeH^+ is formed from a higher energy process than reaction of Xe^+ in the ground state. The present results and those of ref. 7 are compatible if we assume that XeH^+ is formed from either $\text{Xe}^+(^2\text{P}_{1/2})$, $I = 13.4$ v., or CH_4^+ , $I = 13.1$ v., rather than from the ground state $\text{Xe}^+(^2\text{P}_{3/2})$. It is also of interest to note that Xe^+ does not react with H_2 to give XeH^+ ,⁸ a reaction of energy essentially equivalent to that of (5).

If $\text{Xe}^+(^2\text{P}_{1/2})$ is the reactant, then $\Delta H_f(\text{XeH}^+) \leq 260$ kcal./mole and $P(\text{Xe}) \geq 105$ kcal./mole. If CH_4^+ is the reactant, then $\Delta H_f(\text{XeH}^+) \leq 251$ kcal./mole and $P(\text{Xe}) \geq 114$ kcal./mole. The difference in energies of formation of these two ions is too small to allow us to distinguish between them as reactant ions. The best limits which can be established for the proton affinity of Xe at present are $105 \leq P(\text{Xe}) \leq 118$ kcal./mole.

Small amounts of XeCH_3^+ and XeCH_4^+ ions could readily be observed in this mixture, in confirmation of the earlier work,⁷ but the concentrations of these ions were too low to allow quantitative studies to be made.

$\text{CH}_4 + 1\% \text{ O}_2$. For mixtures of $\text{CH}_4 + 1\% \text{ O}_2$, it was startling to note that the distribution of hydrocarbon ions was essentially the same as for pure methane at pressures up to 2 torr; that is, the major product ions of methane, CH_5^+ , C_2H_5^+ , C_2H_4^+ , C_3H_5^+ , and C_3H_7^+ , do not react rapidly with O_2 . The non-reactivity of CH_5^+ is shown in Figure 1. The small difference between the values of the relative concen-

(5) F. H. Field, H. N. Head, and J. L. Franklin, *J. Am. Chem. Soc.*, **84**, 1118 (1962).

(6) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **29**, 282 (1958).

(7) F. H. Field and J. L. Franklin, *J. Am. Chem. Soc.*, **83**, 4509 (1961).

(8) D. P. Stevenson and D. O. Schissler in "The Chemical and Biological Action of Radiations, Vol. V, M. Haissinsky, Ed., Academic Press Inc., New York, N. Y., 1961, p. 249.

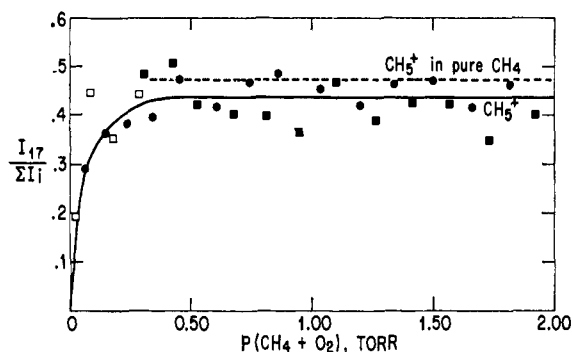
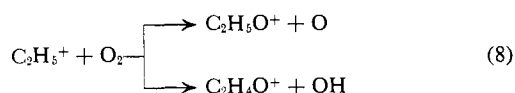
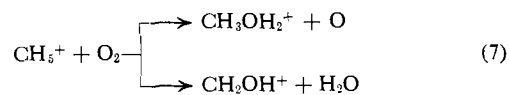


Figure 1. Relative concentration of CH_5^+ vs. P for CH_4 -1% O_2 mixtures; \square , \blacksquare , \bullet represent different experiments.

trations of CH_5^+ in this mixture and in pure CH_4 is probably less than the experimental error of both sets of measurements, but part of this difference may properly be attributed to reactions of CH_4^+ with O_2 . Since $\Delta H_f(\text{HO}_2^+) = 271$ kcal./mole⁹ or $P(\text{O}_2) = 94$ kcal./mole, proton transfer from CH_5^+ or any of the other hydrocarbon product ions to O_2 is endothermic and should not occur.

Although proton transfer to O_2 is endothermic, there are several exothermic reactions of these hydrocarbon ions with O_2 which can be written, but none of them apparently occur to any appreciable extent.



In previous work on CH_4 - O_2 mixtures at much lower pressures,¹⁰ it was noted that the major primary ions from CH_4 reacted only slowly with O_2 as well, but there is no ready explanation for the nonreactivity of any of these ions. CH_3O^+ and CH_3O_2^+ were major oxygenated product ions reported earlier, and these are observed as second-order product ions in this mixture as well.

The rate of reaction of O_2^+ with CH_4 is slow, about 4×10^{-11} cc./molecule sec. from the formation of product ions.¹⁰ In the present experiments we can observe the decrease in relative concentration of O_2^+ , and from a plot of $\log(I_{32}/\Sigma I_i)$ vs. P we can estimate the rate constant for disappearance of O_2^+ to be about 6×10^{-11} cc./molecule sec. This value is in good agreement with the earlier work and convincingly establishes the slowness of this reaction.

The major oxygenated product ion in these experiments is H_3O^+ , the concentration of which is a continuously increasing function of pressure and becomes approximately 7% of the total ionization at 2 torr. It is certain that all of the water is not removed from the methane and the walls of the system since we observed about 1% H_3O^+ in our most carefully purified methane at 2 torr. However, the value of 7% in these experiments seems too high to be attributed to water as an impurity and must come from some reaction in the

(9) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **36**, 2676 (1962).

(10) J. L. Franklin and M. S. B. Munson, Xth International Combustion Symposium, Cambridge, England, 1964.

system. Any neutral water which is formed in the gas phase by radical oxidation of methane would be converted by ionic reactions to H_3O^+ so it is not possible to decide whether or not the H_3O^+ comes directly from ionic reactions involving O_2 .

The effect of O_2 on the radiolysis of CH_4 in the presence of added alkanes (propane, butane, and pentane) has been studied by Ausloos, Lias, and Gorden.¹¹ They observe that for small values of the oxygen/alkane ratio (% $\text{CH}_4 = 99$; $\text{O}_2/\text{alkane} = 0-1$) there is only a small effect on the products of ionic processes, but that for a large value of this ratio (% $\text{CH}_4 = 90$; $\text{O}_2/\text{alkane} \cong 10$) the products of ionic processes are markedly reduced. They attribute these effects to reactions of C_2H_5^+ and CH_5^+ with O_2 . We wish to consider this suggestion in the light of our results.

In a previous work² we have determined that the rate constant for reaction of CH_5^+ with propane is approximately 10^{-9} cc./molecule sec. However, from the almost complete absence of third-order oxygenated product ions (except H_3O^+) in the present experiments, we can estimate that the rate constant for CH_5^+ with O_2 is probably less than 5×10^{-11} cc./molecule sec. The reaction of C_2H_5^+ with propane has a rate constant of approximately 6×10^{-10} cc./molecule sec.¹² The relative concentration of C_2H_5^+ is unaltered by oxygen, and from the virtual absence of products of reaction of C_2H_5^+ with O_2 (m/e 45 is less than 0.3% of the total ionization) we estimate that the rate constant for reaction of C_2H_5^+ with O_2 is probably less than 2×10^{-11} cc./molecule sec. Thus, at the same concentration oxygen cannot compete effectively with propane (and presumably with the higher alkanes) for C_2H_5^+ and CH_5^+ , and we estimate that the $\text{O}_2/\text{C}_3\text{H}_8$ ratio would have to be greater than 10-20 for oxygen to scavenge the methane product ions.

Thus our results tend to lead one to approximately the same conclusions as those of Ausloos, Gorden, and Lias concerning the effect of O_2 on methane ionic chemistry, although we think that they overestimate the magnitude of the effect. We believe that other factors may be involved in their actual experimental observation. Specifically, water, which can be produced by irradiation of CH_4 - O_2 mixtures, is an extremely effective inhibitor of ionic reactions, and even a very small amount would have a marked effect on the product distribution. We will show subsequently in this paper that proton transfer to H_2O from both CH_5^+ and C_2H_5^+ is very rapid and effectively removes these ions. Since the proton affinities of most of the simple oxygenated hydrocarbon derivatives are greater than the proton affinity of water,¹³ these probable products should also be very effective ionic scavengers.

$\text{CH}_4 + 1\% \text{NO}$. For mixtures of $\text{CH}_4 + 1\% \text{NO}$ it was also surprising to note that CH_5^+ , C_2H_5^+ , and C_3H_5^+ were unreactive; the relative concentrations of these ions remain essentially constant from 0.5 to 2 torr. If we assume that proton transfer from CH_5^+ to NO does not occur because the reaction is endothermic, then $P(\text{NO}) < P(\text{CH}_4) = 118$ kcal./mole or $\Delta H_f(\text{HNO}^+) \geq 270$ kcal./mole. This energy criterion

(11) P. Ausloos, S. G. Lias, and R. Gorden, Jr., *J. Chem. Phys.*, **39**, 3341 (1963).

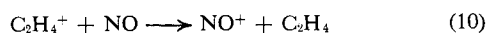
(12) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, **68**, 3098 (1964).

(13) M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 2332 (1965).

is not rigorous, and we should observe the reverse proton-transfer reaction to establish the limits, but a convenient source of HNO^+ is not readily available to establish this proton-transfer reaction to CH_4 . If the ion HNO^+ exists, one would expect the decomposition to NO^+ to be endothermic (eq. 9), so that $\Delta H_f(\text{HNO}^+) \leq 287$ kcal./mole. From these considerations we obtain limits for the proton affinity of NO, $100 \leq P(\text{NO}) \leq 118$ kcal./mole.



Although proton-transfer reactions to NO are endothermic, it is possible to write other reactions for these ions with NO which seem plausible, but which do not occur extensively. NO^+ , itself, does not give any indications of extensive reaction and its concentration increases from about 1 to about 5% of the total ionization. This increase is probably the result of charge exchange of C_2H_4^+ with NO, since this reaction is



exothermic and the increase in NO^+ is approximately the same as the decrease in C_2H_4^+ . The ions at m/e 30 are well resolved into a doublet, $\text{NO}^+ - {}^{12}\text{C}_2\text{H}_6^+ + {}^{13}\text{C}^{12}\text{CH}_5^+$, so there is no complication from isotope corrections. The ions at m/e 31 are also resolved into a doublet, but the low mass component, HNO^+ or CH_3O^+ , is never greater than 0.1% of the total ionization.

The most abundant ion which may contain C, H, N, and O is at m/e 45, probably CH_3NO^+ . The concentration of this ion increases continuously to approximately 1% of the total ionization at 2 torr. It is not possible to make an unambiguous determination of the source of this ion, but from stoichiometric and energetic considerations we guess it to come from a very slow reaction of CH_5^+ . H_3O^+ is formed in this mixture, as well, approximately 3% at 2 torr, but this concentration can readily be attributed to reactions with traces of water, so we can say little about ionic reactions giving this ion.

If we assume that all of the CH_3NO^+ is formed by reaction of CH_5^+ , then the rate constant for reaction of CH_5^+ with NO is of the order of 5×10^{-11} cc./molecule sec. A rate constant this small would not produce a noticeable decrease in the relative concentration of CH_5^+ . Any product ions which might be attributed to C_2H_5^+ are present only to the extent of a few tenths of a per cent of the total ionization, so the rate constant for reaction of C_2H_5^+ with NO is not greater than 1×10^{-11} cc./molecule sec. The reactions of these ions with NO are about as slow as the reactions with O_2 ; hence NO should also be relatively inefficient as an ion scavenger for the product ions of methane, except for C_2H_4^+ which is removed by charge transfer.

The effects of NO on the radiolysis of methane have been studied by Ausloos, Lias, and Gorden.¹¹ They found that the results with NO were very similar to the results observed for O_2 : little effect on the ionic products at low values of the nitric oxide/alkane ratio but marked effects of high values of this ratio in nitric oxide-alkane-methane mixtures. They attributed these effects to the scavenging ability of NO for C_2H_5^+ and CH_5^+ . The data presented in this paper show that the rate of reaction of these ions with NO is lower than

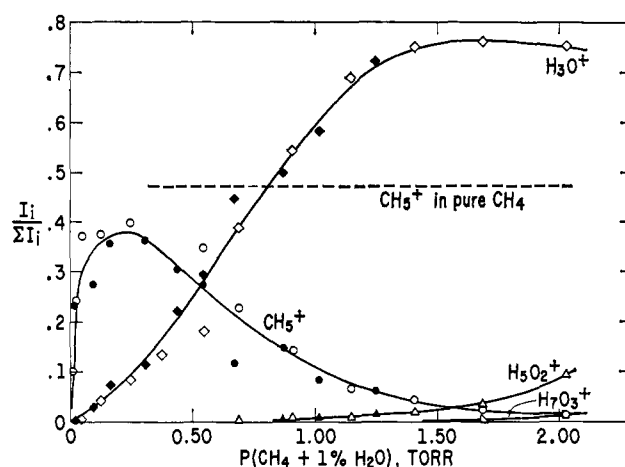
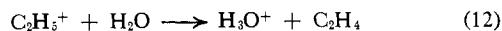
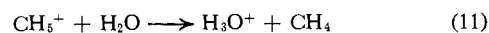


Figure 2. Relative concentrations of ions vs. P for mixtures of $\text{CH}_4 + 1\% \text{H}_2\text{O}$; filled and open points indicate duplicate experiments.

the rate of reaction with the alkanes and that large amounts of NO would be needed to scavenge the ions.

$\text{CH}_4 + 1\% \text{H}_2\text{O}$. Proton transfer is the dominant reaction in mixtures of $\text{CH}_4 + 1\% \text{H}_2\text{O}$ as shown in Figure 2, which demonstrates the effect of the proton-transfer reaction on CH_5^+ (eq. 11). Proton transfer from C_2H_5^+ also occurs (eq. 12), although it is not



represented in this figure. Essentially no oxygenated ions are produced other than the hydrated protons. This figure adequately shows the extreme sensitivity of the methane system to water, since 1% H_2O in the mixture is represented by 85% of the total ionization at 2 torr. This high sensitivity to water is also indicated by the fact that it is essentially impossible to eliminate H_3O^+ from the mass spectrum at high pressures. Water is, therefore, an extremely efficient ion scavenger for the two major ions of methane, and it is reasonable to assume that it will have a marked effect on methane radiolysis as we suggested in the discussion of methane-oxygen mixtures.

From plots of $\log(I_{17}/\Sigma I_i)$ and $\log(I_{29}/\Sigma I_i)$ vs. P we estimate that the rate constants for (11) and (12) are approximately 10^{-8} and 6×10^{-9} cc./molecule sec., respectively. As we have indicated in the previous papers,^{1,2} these rate constants are only approximate, but they are certainly indicative of very fast reactions.

There are two conflicting values for $\Delta H_f(\text{H}_3\text{O}^+)$: 157 ± 3 kcal./mole from electron impact measurements¹⁴ and 140 ± 4 from the occurrence and non-occurrence of certain ionic reactions.^{14,15} If $\Delta H_f(\text{C}_2\text{H}_5^+) = 224$ kcal./mole as seems to be very well established,¹⁶ then from (12), $\Delta H_f(\text{H}_3\text{O}^+) \leq 154$ kcal./mole or $P(\text{H}_2\text{O}) \geq 154$ kcal./mole. This value is just at the lower limit of the electron impact measurements and indicates that the determination is slightly high but is not incompatible with this value. No other

(14) D. Van Raalte and A. G. Harrison, *Can. J. Chem.*, **41**, 3118 (1963).

(15) See V. L. Talrose, *J. Pure Appl. Chem.*, **5**, 455 (1962).

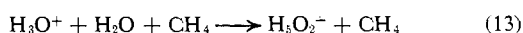
(16) Unless otherwise specified, heats of formation of gaseous ions are taken from F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, Table 45.

Table I. Reactions of Methane Primary Ions with NH₃

Reaction	<i>k</i> , cc./molecule sec.	Comments
CH ₄ ⁺ + NH ₃ →	2.2 ± 0.7 × 10 ⁻⁹	NH ₃ ⁺ + CH ₄
		NH ₄ ⁺ + CH ₃
CH ₃ ⁺ + NH ₃ →	1.3 ± 0.2 × 10 ⁻⁹	NH ₄ ⁺ + CH ₂
		CH ₂ NH ₂ ⁺ + H ₂
CH ₂ ⁺ + NH ₃ →	2.0 ± 0.8 × 10 ⁻⁹	CH ₂ NH ₂ ⁺ + H
		NH ₄ ⁺ + CH

reactions occurring in this system provide any information about $\Delta H_f(\text{H}_3\text{O}^+)$.

The existence of the higher hydrated protons, H⁺·(H₂O)_{2,3}, has been established previously.^{13,17} In these experiments H₃O₂⁺ is formed by a three-body process, since the ratio I_{37}/I_{19} increases approximately



proportionally to P^2 .

No hydrates of hydrocarbon ions are formed; m/e 47, which could correspond to (C₂H₅⁺·H₂O), and m/e 35, which could correspond to (CH₅⁺·H₂O), are only 2 × 10⁻² and 4 × 10⁻²%, respectively, of the total ionization at 2 torr.

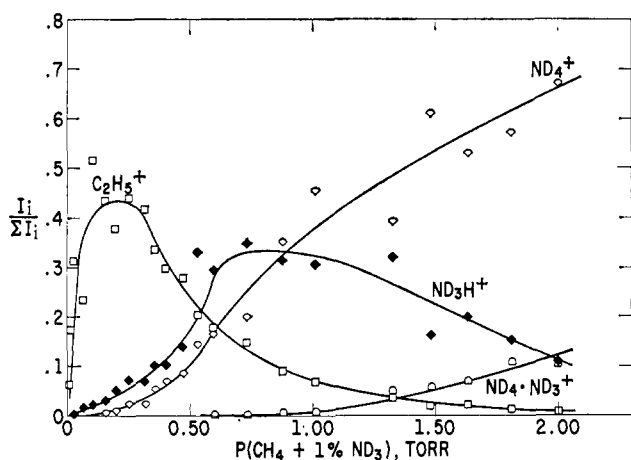


Figure 3. Relative concentrations of ions vs. P for mixtures of CH₄ + 1% ND₃.

C₂H₄⁺ and C₃H₅⁺ are nonreactive with water; there is no appreciable decrease in the relative concentrations of these ions up to 2 torr. Proton transfer from these two ions is endothermic if $\Delta H_f(\text{H}_3\text{O}^+) = 140$ kcal./mole and charge exchange for C₂H₄⁺ is also endothermic. The concentration of C₃H₇⁺ in this mixture is approximately one-half its value in pure CH₄. This decrease is probably caused by the reaction of a precursor with water which would decrease the rate of formation of this ion.

The extreme sensitivity of the ionic distribution in this system to small concentrations of water as the result of proton-transfer reactions is in excellent agree-

ment with the earlier suggestion⁴ that trace amounts of water served as very efficient chain-termination agents in the radiation-induced polymerization of α -methylstyrene and β -pinene in the liquid phase.

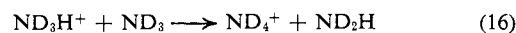
CH₄ + 1% ND₃. In a series of experiments at pressures not greater than 0.2 torr with NH₃/CH₄ ratios of the order of unity, it was possible to study the reactions of the primary ions of methane with ammonia. These data are summarized in Table I. A complete determination of the reaction products was not attempted and the rate constants which are reported are those obtained from the rate of decrease of the relative concentrations of the primary ions. It is of interest to note that the rate constants for reaction of these ions with NH₃ are all greater than the rate constants for reaction with CH₄¹⁸ even though the polarizability of CH₄ is greater than that of NH₃. However, 1% NH₃ or ND₃ will still have only a trivial effect on the reactions of the primary ions of methane.

Figure 3 shows the effect of 1% ND₃ on the ionic distribution in methane at pressures up to 2 torr.



The relative concentrations of the product ions of methane, CH₃⁺, C₂H₅⁺, C₃H₅⁺, and C₃H₇⁺, pass through maxima and then decrease with increasing pressure. Proton transfer is the dominant process since the ammoniated protons comprise 90% of the total ionization at 2 torr. We estimate that the rate constants for (14) and (15) are approximately 10⁻⁸ cc./molecule sec.

Since ND₃H⁺ is the dominant ammonium ion, the reactions involved must be essentially proton-transfer reactions without scrambling of protons in the complex. Some mass 20, ND₃⁺ + ND₂H₂⁺, is formed, but in the pressure region above 0.3 torr where proton transfer from the product ions occurs, ND₃H⁺ is present in larger relative abundance. Furthermore, since ND₃H⁺ passes through a maximum and then decreases with increasing pressure and ND₄⁺ increases continuously over this pressure range, hydrogen-deuterium exchange must occur. The rate constant for reaction 16 must



be of the order of 10⁻⁹ cc./molecule sec. This reaction is the first exchange reaction which we have observed between a protonated molecule ion and the

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neutral molecule, but the reaction should be one of general occurrence.

In addition to this reaction the transformation of ND_3H^+ to ND_4^+ means that exchange between the protonated molecule ion, ND_4^+ , and the neutral molecule of another species, CH_4 , is very slow; that is, reaction 17 does not occur.



The ions at m/e 41 and 42 were doublets for which the lower components, C_3H_5^+ and $\text{C}_3\text{H}_6^+ + {}^{13}\text{C}^{12}\text{C}_2\text{H}_5^+$, passed through maxima in relative concentrations and then decreased with increasing pressure; the higher components, $\text{N}_2\text{D}_6\text{H}^+$ and N_2D_7^+ , became appreciable only at the highest pressures. Thus, the reaction of C_3H_5^+ and the existence of the higher ammoniated protons are both clearly established.

The relative concentration of C_3H_7^+ is much lower in this mixture than in pure methane: maximum abundance of 0.4% compared with 2–3%. Since, in addition, this small relative concentration of C_3H_7^+ passes

through a maximum with increasing pressure, proton transfer occurs for this ion as well.

There were two product ions of reasonable abundance which probably are C,N species: m/e 49, $\text{C}_2\text{H}_5\text{ND}_3^+$, and m/e 61, $\text{C}_3\text{H}_5\text{ND}_3^+$. Both ions are present to the extent of 3–4% of the total ionization at the highest pressures, but their structure and origin cannot be established conclusively.

Ammonia is, therefore, a very efficient proton-transfer agent and should have marked effects on ionic processes with little effect on radical processes. The present observation that small concentrations of ammonia have a major effect on the ionic distribution in methane at 2 torr is very good support for the suggestion³ that the very large inhibitory effect of traces of ammonia on the radiation-induced polymerization of cyclopentadiene in the liquid phase was the result of proton transfer from the hydrocarbon ions.

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Equilibrium and Kinetic Studies of the Deprotonation of the Monoanion of Several Dicarboxylic Acids in Water and in Deuterium Oxide¹

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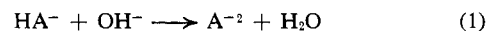
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The rate constant for the rapid abstraction by hydroxide ion of a proton from the monoanion of three alkyl-substituted succinic acids varies inversely as the ratio of the acid dissociation constants K_{a1}/K_{a2} . These data confirm the generality of this result found previously for a series of 2,2-disubstituted malonic acids and for three cis-3,3-disubstituted cyclopropane-1,2-dicarboxylic acids. Acid dissociation constants and rate constants for the proton abstraction have also been determined in D_2O for the three cyclopropane acids as well as for the three succinic acids. These isotopic data as well as acid dissociation constants for the monomethyl esters of these acids are consistent with the interpretation that the breaking of an intramolecular hydrogen bond in the monoanion is rate determining although these data cannot conclusively establish the presence of such an intramolecular hydrogen bond.

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Introduction

Recent temperature-jump kinetic studies^{2–5} have shown that the rate constant in aqueous solution for the reaction



where HA^- denotes the monoanion of three different cis-cyclopropane-1,2-dicarboxylic acids and also of a series of 2,2-dialkylmalonic acids, is inversely proportional to the ratio of the acid dissociation constants, K_{a1}/K_{a2} , for these acids. The dependence of the measured relaxation times on pH, sample acid concentration, and ionic strength have established beyond doubt the identity of the reaction being observed. However, these kinetic data do not permit a description of bonding of the acid hydrogen in the HA^- ion.

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