

quadrupole resonance frequency) should be expected for a nonnegligible amount of charge transfer. It seems reasonable to expect that the increase in Br-Br distance might be approximately linear with  $F_{1N}$ . For the strong aliphatic amine- $X_2$  complexes ( $F_{1N} \approx 0.4$ ) the increase in the X-X bond length from that in the free halogen is about 0.25 Å. Hence, we might expect an increase in Br-Br length for benzene- $Br_2$  of about one-eighth to one-fourth of that value or from 0.03 to 0.06 Å ( $F_{1N}$  from 0.05 to 0.10). This increase is only slightly greater than the experimental uncertainty in the X-ray work, and we suspect that this argument can be made conclusive only if a very careful X-ray study is made. If there is nonnegligible CT in the benzene- $Br_2$  crystal, we also expect the benzene-Br distance to be less than the van der Waals distance. Experimentally, this distance is found to be 3.36 Å compared to 3.65 Å expected for the sum of van der Waals radii. Hence we believe the X-ray results are ambiguous but are also consistent with small but nonnegligible CT. A similar statement applies<sup>19b</sup> to the quadrupole resonance results.

**Complexes of  $n-\sigma$  Type.** There is no question that classical Coulomb and polarization forces can play only a minor part as compared with CT forces in accounting for the large observed  $-\Delta H$  and  $K$  values and dipole moments<sup>10</sup> of the strong  $n-\sigma$  complexes of iodine with the aliphatic amines. As a check on this conclusion, Dr. M. Itoh has very kindly computed the classical dipole-induced-dipole contributions to the stabilization energies and the dipole moments of  $NH_3-I_2$  and of  $(CH_3)_3N-I_2$ , following the procedure used by Hanna,<sup>2a</sup> and has obtained the results given in Table IV. Hence, there must indeed be considerable charge transfer in these stronger complexes; judging from the dipole

**Table IV.** Polarization Contributions to Stability and Dipole Moments of Amine-Iodine Complexes<sup>a</sup>

Complex	—Major computed polarization contributions—					
	—Approx 1—		—Approx 2—		—Observed—	
	$\mu$ , D	$W$ , kcal	$\mu$ , D	$W$ , kcal	$\mu$ , D	$-\Delta H$ , kcal
$H_3N-I_2$	0.91	0.34	1.96	1.58	~6.4	4.8
$(H_3C)_3N-I_2$	0.30	0.04	0.57	0.13	~6.0	10.2

<sup>a</sup> The approximations 1 and 2 are those of Hanna.<sup>2a</sup> The data used are:  $\mu$  of  $NH_3$ , 1.5 D,  $\mu$  of  $(CH_3)_3N$ , 0.63 D; dimensions of  $(CH_3)_3N-I_2$ , ref 20;  $I_2$  polarizability, ref 2a; observed  $\mu$ , see ref 10, Table 6-2.  $W$  = energy. In the computations, a point dipole located at the midpoint of the NH or CN bond was assumed.

moments,  $F_{1N} \approx 0.4$ . Moreover,  $K_z$ ,  $-\Delta H$ , and CT band intensity all increase together in these complexes with increasing donor strength, in agreement with the CT theory.

Because so many of the properties of the  $n-\sigma$  complexes appear to be correlated as logical extensions of the CT theory of weak complexes, it is clear that some CT also occurs in the weaker complexes. We concur with the conclusions of Hanna<sup>2a</sup> that the extent of CT action may have been overestimated for weak complexes in the past, but that it still involves forces whose magnitude is at least comparable to the electrostatic forces for most weak complexes. The predominance of CT forces in the  $n-\sigma$  iodine complexes make them a useful limiting test case. The rather smooth variation of CT-dependent properties of the complexes from the weak  $b\pi-a\pi$  or  $b\pi-a\sigma$  complexes to the strong  $n-\sigma$  complexes indicates that the extent of CT varies from very little ( $F_{1N} \approx 0.01$ ) to large ( $F_{1N} \approx 0.4$ ) in a similar way.

## Reactions of Gaseous Ions. XVII. Methane + Unsaturated Hydrocarbons

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*Contribution from Baytown Research and Development Division, Esso Research and Engineering Company, Baytown, Texas, and Corporate Research Laboratories, Esso Research and Engineering Company, Linden, New Jersey. Received December 23, 1968*

**Abstract:** Rapid proton transfer reactions are observed between  $CH_5^+$  and ethylene, propylene, and isobutylene. However,  $CH_5^+$  adds to acetylene to give mostly  $C_3H_5^+$  by a second-order process and  $C_3H_7^+$  by a collision-stabilized addition reaction.  $C_2H_5^+$  also reacts predominantly by proton transfer with propylene and isobutylene, but adds to ethylene and acetylene in collision-stabilized processes. Three-body alkylation reactions were observed for  $C_2H_5^+$  and  $C_2H_4$  and  $C_3H_7^+$  and  $C_3H_6$  to a much greater extent than for  $C_4H_9^+$  +  $i-C_4H_8$ . Estimates are made for lifetimes of collision complexes for several reactions.

In previous publications,<sup>2</sup> we studied the ionic reactions in methane at pressures as high as 2 Torr and the effects of several additives on the ionic distributions.

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(2) (a) F. H. Field and M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 3289 (1965); (b) M. S. B. Munson and F. H. Field, *ibid.*, **87**, 3294 (1965); (c) *ibid.*, **87**, 4242 (1965).

The present paper reports the ionic reactions in mixtures of methane with approximately 1% of a few unsaturated hydrocarbons. Since unsaturated hydrocarbons are produced in the irradiation of methane, we feel that these results will be pertinent to radiation chemistry. In addition, these experiments are part of a systematic study of the reactions of  $CH_5^+$ , and we had expectations

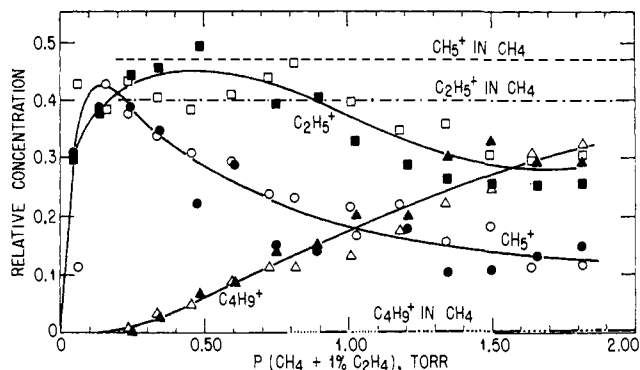


Figure 1. Relative concentrations of ions in  $\text{CH}_4 + 1\% \text{C}_2\text{H}_4$  mixtures as functions of total pressure. Open and filled points represent duplicate experiments.

of observing multiple-order processes at these pressures which cannot be observed at lower pressures.

### Experimental Section

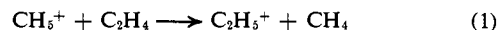
The instrument, experimental conditions, and experimental procedure have been adequately described previously,<sup>2</sup> and no further explanation will be given. The methane was Phillips Research Grade which was further purified within the gas-handling system by distillation and absorption with molecular sieve. The other hydrocarbons were greater than 99.5 mole % pure and were all distilled within the vacuum system. The other hydrocarbons were ethylene, propylene, isobutylene, and acetylene and were present as approximately 1% of the mixtures, although the actual concentrations are not known accurately.

### Results

The reactions of the primary ions produced by electron impact from methane are all rapid with methane and are now well established. There is also general agreement on the reactions of the major secondary product ions.<sup>2a,3,4</sup> In particular, it has been shown that  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ ,  $\text{C}_2\text{H}_4^+$ , and  $\text{C}_3\text{H}_5^+$  react only slowly, if at all, with methane. Consequently, it is possible to study the reactions with the added materials for those ions which do not react with methane. If the concentration of the added material is small (as it is in these experiments, about 1%), the added material will have essentially no effect on the ionic reactions of the primary ions of methane and only small amounts of ions of the additives will be produced by direct ionization. The predominant processes can be readily observed, but minor reactions cannot be identified. To simplify the discussion, we will consider each of the additives separately.

**Ethylene.** The ionic processes in mixtures of methane and 1% ethylene have been mentioned only briefly before,<sup>5</sup> so they will be discussed in detail here. Figure 1 shows the relative concentrations of the three major ions in this mixture of methane and ethylene. The open and filled points represent duplicate experiments. The agreement between the two experiments is sufficient to indicate the predominant processes. The maximum in the curve for  $\text{CH}_5^+$  indicates a reaction with ethylene since  $\text{CH}_5^+$  does not react with methane (as indicated

in this figure). The very broad maximum for  $\text{C}_2\text{H}_5^+$  in Figure 1 indicates that this ion is being both formed and consumed by reactions involving ethylene. The most likely reaction is proton transfer



From plots of the logarithm of the relative concentration of  $\text{CH}_5^+$  vs. pressure we estimate that the rate constant for reaction 1 is of the order of  $10^{-9}$  cc/(molecule sec).

An analysis of the relative intensities of the various reaction products shows that the predominant reaction of  $\text{CH}_5^+$  is the proton-transfer reaction indicated by reaction 1. Any intermediate complex,  $(\text{C}_3\text{H}_9^+)^*$ , which is formed in this reaction has a transitory existence since only traces of ions of  $m/e$  45 are detected in these experiments, 0.1% of the total ionization.

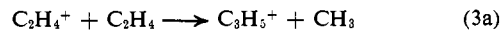
The gradual decrease in  $\text{C}_2\text{H}_5^+$  above 0.5 Torr indicates a reaction of  $\text{C}_2\text{H}_5^+$ , and the obvious product is the other major product ion,  $\text{C}_4\text{H}_9^+$ . As was mentioned earlier,  $\text{C}_3\text{H}_5^+$  is found in the high-pressure spectrum of pure  $\text{CH}_4$ , and it is formed by a process third order in pressure. In the  $\text{CH}_4$ - $\text{C}_2\text{H}_4$  mixture, the ratio  $(\text{C}_4\text{H}_9^+)/(\text{C}_3\text{H}_5^+)$  increases approximately linearly with increasing pressure, and the ratio,  $(\text{C}_4\text{H}_9^+)/[(\text{C}_4\text{H}_9^+) + (\text{C}_2\text{H}_5^+)]$ , increases roughly proportionally with  $P^2$  up to 1 Torr. Both of these observations indicate that the disappearance of  $\text{C}_2\text{H}_5^+$  is mainly from the collisional stabilized addition to ethylene



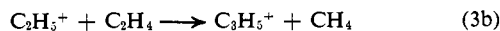
a process which would be fourth order in total pressure, rather than by simple addition without a stabilizing collision, a third-order process.

The earlier studies on pure ethylene gave no second-order reactions for the disappearance of  $\text{C}_2\text{H}_5^+$ ,<sup>3b,6-8</sup> probably because  $\text{C}_2\text{H}_5^+$  is not one of the major product ions, even though it is reported and it does react. In other high-pressure studies of ionic reactions of ethylene, Kebarle, Haynes, and Searles<sup>9</sup> report the collision-stabilized addition of  $\text{C}_2\text{H}_5^+$  to  $\text{C}_2\text{H}_4$  in the presence of several Torr of Ar, reaction 2 with Ar rather than  $\text{CH}_4$  as the stabilizing species.

There is more  $\text{C}_3\text{H}_5^+$  in this mixture of methane and ethylene than in methane alone: a maximum of 13% of the total ionization in this mixture and only 6% in methane alone.<sup>2a</sup> In addition, the relative concentration of  $\text{C}_3\text{H}_5^+$  passes through a maximum at approximately 0.7 Torr and then decreases as the pressure is increased to 1.8 Torr for this mixture, but  $\text{C}_3\text{H}_5^+$  is essentially unreactive in methane. This increase in  $\text{C}_3\text{H}_5^+$  may come from the established reaction of  $\text{C}_2\text{H}_4^+$ <sup>6-8</sup>



and from



as reported recently by Tiernan and Futrell.<sup>10</sup>

$\text{C}_3\text{H}_5^+$  is formed (monotonically increasing with pressure up to 10% of the total ionization at 1.8 Torr)

(3) (a) S. Wexler and N. Jesse, *J. Am. Chem. Soc.*, **84**, 3425 (1962); (b) S. Wexler, A. Lifshitz, and A. Quattrochi, *Advances in Chemistry Series*, No. 58, American Chemical Society, Washington, D. C., 1966, p 193.

(4) (a) R. M. Haynes and P. Kebarle, *J. Chem. Phys.*, **45**, 3899 (1966); (b) F. P. Abramson and J. H. Futrell, *ibid.*, **45**, 1925 (1966).

(5) M. S. B. Munson and F. H. Field, *Proceedings of the API Division of Refining*, May 1966.

(6) C. E. Melton and P. S. Rudolph, *J. Chem. Phys.*, **32**, 1128 (1960).

(7) F. H. Field, *J. Am. Chem. Soc.*, **83**, 1523 (1961).

(8) S. Wexler and R. Marshall, *ibid.*, **86**, 781 (1964).

(9) P. Kebarle, R. M. Haynes, and S. Searles in ref 3b, p 210.

(10) T. O. Tiernan and J. H. Futrell, *J. Phys. Chem.*, **72**, 3080 (1968). We wish to acknowledge the help of the referee in calling this reaction to our attention.

by a process that is higher order in pressure than that forming  $C_3H_5^+$ . The data are too scattered for us to distinguish between a collision-stabilized addition of  $C_3H_5^+$  to ethylene analogous to (2), total pressure dependence of fifth order, and a simple addition which would be only fourth order. For pressures above 0.6 Torr the sum of the relative concentrations of  $C_3H_5^+$  and  $C_3H_9^+$  is substantially constant, as one would expect if  $C_3H_5^+$  reacted to give  $C_3H_9^+$ .

There is perhaps a small decrease in the sum of the relative concentrations of  $CH_5^+$ ,  $C_2H_5^+$ , and  $C_4H_9^+$  with increasing pressure and a corresponding increase in the sum of the relative concentrations of  $C_3H_5^+$  and  $C_3H_9^+$ . These observations indicate the possibility of small amounts of other reactions (possibly addition of  $CH_5^+$  to ethylene, etc.), but the dominant processes are those which have been given.

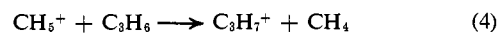
It is also of interest that  $C_4H_8^+$  is formed in this mixture by what appears to be a fourth-order process. Collisional stabilized addition of ethylene ion to ethylene was reported previously in pure ethylene at pressures of a few tenths of a Torr<sup>7,8</sup> and also for ethylene in the presence of a few Torr of Xe.<sup>9</sup> In our mixture of  $CH_4$  and  $C_2H_4$ ,  $C_2H_4^+$  is formed by two second-order processes, one involving the methane component of the mixture and the other charge exchange processes of unidentified ions with the added ethylene.

There are also indications in this mixture of further alkylation reactions since a small amount of  $C_6H_{13}^+$  is formed (approximately 1% of the total ionization at the highest pressures). However, this concentration is too small to warrant discussion.

**Propylene.** Figure 2 shows the relative concentrations of some of the major ions in a mixture of methane and 1% propylene. The points have been omitted for the sake of clarity. The agreement between duplicate experiments is approximately the same in these experiments as it was in the preceding experiments with ethylene. The sequence of the reactions is clearly indicated in this figure:  $CH_5^+$ ,  $C_2H_5^+$   $\rightarrow$   $C_3H_7^+$   $\rightarrow$   $C_6H_{13}^+$ .

No significance is attached to the indicated slight differences in the disappearance curves for  $CH_5^+$  and  $C_2H_5^+$ . Both of the ions react rapidly with propylene with rate constants of the order of  $10^{-9}$  cc/(molecule sec). The concentrations of the additives and the experimental conditions are not defined well enough to comment about possible differences in rates of reaction of these ions with ethylene or propylene (or isobutylene and acetylene). They are all approximately the same and there is no gross variation with molecular weight, less than a factor of 2.

There are small relative concentrations of  $C_4H_7^+$  and  $C_4H_9^+$  ions (maximum concentration for either, 4% of the total ionization) which might result from reaction of  $CH_5^+$  with propylene, but it is readily apparent that the major reaction is proton transfer



We have no evidence for collisional stabilization of any excited intermediate,  $(C_4H_{11}^+)^*$ , for this reaction, since essentially no  $C_4H_{11}^+$  is produced in this mixture, even at the highest pressures.

The most abundant  $C_5$  ion in these experiments is  $C_5H_9^+$  (maximum relative concentration, 0.5% of the total ionization). Essentially no collisional stabilization

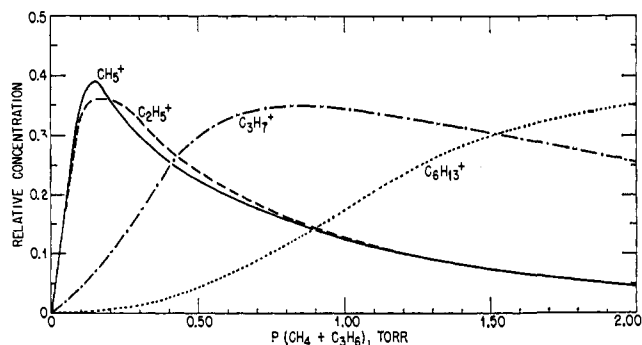
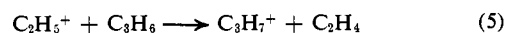
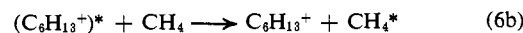
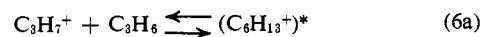


Figure 2. Relative concentrations of ions in  $CH_4 + 1\% C_3H_6$  as functions of pressure.

of any excited  $C_5H_{11}^+$  occurs, and no condensation products of ethyl ions with propylene are observed under the present conditions. In addition, a hydride-transfer reaction with the ethyl ion and propylene can be eliminated as a major reaction since the relative concentration of  $C_3H_5^+$  in this mixture of  $CH_4$  and  $C_3H_6$  does not become significantly larger than its value in pure methane. Hence,  $C_2H_5^+$  also reacts with propylene predominantly by proton transfer



The formation of  $C_6H_{13}^+$  appears to be caused by a three-body process



rather than by simple addition. Traces of  $C_9H_{19}^+$  ions were observed at the highest pressures, but the concentrations were too low to warrant discussion.

A small amount of information may be gleaned about some of the minor ions. We find that  $C_3H_5^+$  reacts with propylene (it does not react with methane). The reaction is presumably a collision-stabilized addition, since  $C_6H_{11}^+$  is formed in amounts approximately equal to the loss of  $C_3H_5^+$  at high pressures. Some  $C_6H_{11}^+$  may also be formed by elimination of  $H_2$  from  $C_6H_{13}^+$  produced in reaction 6a. The  $C_2H_4^+$  which is formed from methane in this mixture also reacts with propylene, although the reactions cannot be identified, but it does not react with methane.  $C_3H_6^+$  is formed as a product ion by charge exchange reactions in this mixture, perhaps from  $C_2H_4^+$ . At higher pressures the  $C_3H_5^+$  reacts rapidly and disappears. However, because of the established reactions of  $C_3H_6^+$  with propylene,<sup>11-13</sup> all of which are rapid, it is not possible to determine if  $C_3H_6^+$  reacts with methane.

**Isobutylene.** Figure 3 shows plots of relative concentrations of some of the major ions produced in  $CH_4 + 1\% i-C_4H_8$  as functions of pressure. The points for  $C_2H_5^+$  are not shown in this figure since they are very close to those for  $CH_5^+$ .  $CH_5^+$  and  $C_2H_5^+$  both react rapidly with isobutylene with rate constants of the order of  $10^{-9}$  cc/(molecule sec). It is obvious from this figure that the dominant reaction of both of these ions is proton transfer

(11) R. Fuchs, *Z. Naturforsch.*, **16a**, 1026 (1961).

(12) A. G. Harrison, *Can. J. Chem.*, **41**, 236 (1963).

(13) I. Koyano, I. Omura, and I. Tanaka, *J. Chem. Phys.*, **4**, 3850 (1966).

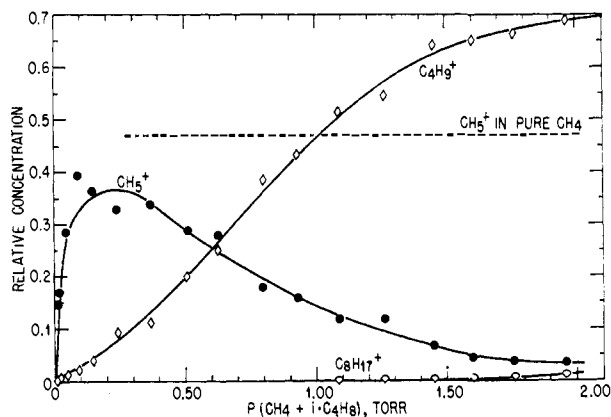
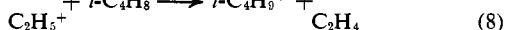


Figure 3. Relative concentrations of ions in  $\text{CH}_4 + 1\% i\text{-C}_4\text{H}_8$  as functions of pressure.

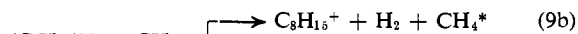
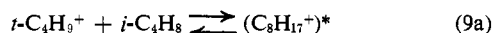


The kinetic order for the formation of  $\text{C}_4\text{H}_9^+$  is clearly third.

Small amounts of other processes may be occurring since about 3%  $\text{C}_4\text{H}_7^+$ , 5%  $\text{C}_3\text{H}_7^+$ , and 2%  $\text{C}_3\text{H}_9^+$  are produced, but it is not possible to sort them out. For example,  $(\text{C}_5\text{H}_9^+)/(\text{C}_4\text{H}_9^+)$  and  $(\text{C}_5\text{H}_{11}^+)/(\text{C}_4\text{H}_9^+)$  are substantially independent of pressure with values of 0.025 and 0.005, respectively. These observations suggest that  $\text{C}_5\text{H}_9^+$  and  $\text{C}_5\text{H}_{11}^+$  may be formed from the same reactants as  $\text{C}_4\text{H}_9^+$ . The small concentrations of  $\text{C}_3\text{H}_7^+$ ,  $\text{C}_5\text{H}_9^+$ , and  $\text{C}_5\text{H}_{11}^+$  reflect the small extent of condensation reactions. The low concentration of  $\text{C}_4\text{-H}_7^+$  relative to  $\text{C}_4\text{H}_9^+$  is a measure of less favored hydride-transfer reactions.

Very little collisional stabilization of possible excited intermediates for (7) or (8),  $(\text{C}_5\text{H}_{13}^+)^*$  or  $(\text{C}_6\text{-H}_{13}^+)^*$ , occurs, since ions at  $m/e$  73 were less than 0.05% of the total ionization and ions at  $m/e$  85 were less than 0.2%.

The relative concentration of octyl ions in this mixture is very low, much lower than the concentration of butyl ions in the mixture with ethylene or hexyl ions in the mixture with propylene. The ratio  $(\text{C}_8\text{H}_{17}^+)/(\text{C}_4\text{-H}_9^+)$  and also  $(\text{C}_8\text{H}_{15}^+)/(\text{C}_4\text{H}_9^+)$  increase linearly with  $P^2$  in these experiments, observations which strongly suggest the collisional stabilized alkylation reaction in preference to bimolecular addition. The invariance of the  $(\text{C}_8\text{H}_{17}^+)/(\text{C}_8\text{H}_{15}^+)$  ratio, 0.40, as a function of pressure suggests that both are formed by the same reactions



With ethylene,  $\text{C}_4\text{H}_7^+$  was less than 1% of  $\text{C}_4\text{H}_9^+$  and with propylene  $\text{C}_6\text{H}_{11}^+$  is less than 10% of  $\text{C}_6\text{H}_{13}^+$  and the  $\text{C}_6\text{H}_{11}^+$  is probably formed from  $\text{C}_3\text{H}_5^+$ , not  $\text{C}_3\text{H}_7^+$ .

This much lower extent of alkylation for isobutylene is surprising. The alkylation of isobutylene in solution has been used commercially for years and recently experiments have been done in which octanes are produced in liquid isobutylene from  $t$ -butyl ions generated in the gas phase.<sup>14,15</sup> It has also been reported from these

(14) E. W. Schlag and J. J. Sparapany, *J. Am. Chem. Soc.*, **86**, 1875 (1964).

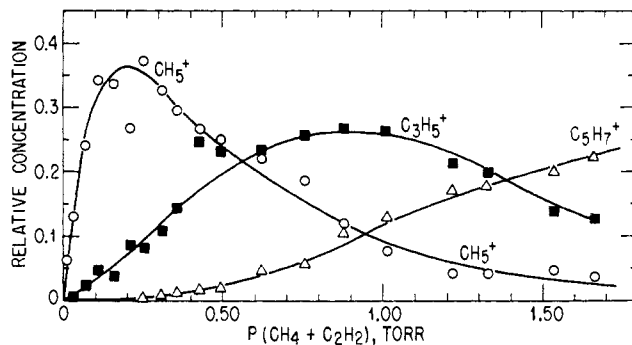


Figure 4. Relative concentrations of ions in  $\text{CH}_4 + 1\% \text{C}_2\text{H}_2$  as functions of pressure.

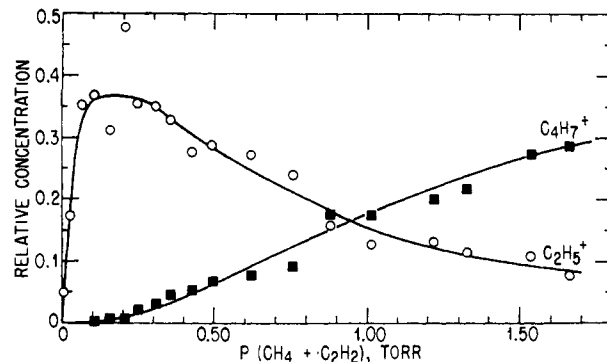


Figure 5. Relative concentrations of ions in  $\text{CH}_4 + 1\% \text{C}_2\text{H}_2$  as functions of pressure.

laboratories that alkylation by  $\text{sec-C}_4\text{H}_9^+$  of isobutylene at 1–1.5 Torr is less extensive than analogous reactions of propylene, 1-butene, and 1-pentene.<sup>16</sup>

A couple of rationalizations can be offered for this unexpected difference. The butyl ions produced in these experiments may have appreciable amounts of extra internal energy: proton transfer is 65–70 kcal/mole exothermic from  $\text{CH}_3^+$  and 30–35 kcal/mole exothermic from  $\text{C}_2\text{H}_5^+$ . It is likely, then, that this extra energy favors the reversible dissociation of the  $(\text{C}_8\text{H}_{17}^+)^*$  complex in (9a) and would require many more collisions (higher density) for stabilization. In addition, we must recall that the present experiments are performed at approximately 200°, much hotter than the other alkylation experiments, and it may be that the highly branched octyl ions are unstable at the temperatures of our experiments. A compatible temperature dependence of chemical ionization spectra has been reported previously.<sup>17</sup>

**Acetylene.** Figures 4 and 5 show plots of relative abundances of major ions in a mixture of methane and 1% acetylene. We have grouped the ions according to what we feel are the reactant-product sequences.

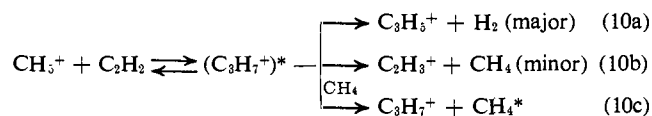
Figure 4 shows the fate of  $\text{CH}_3^+$ . With acetylene, in a striking contrast to the previously mentioned olefins, the dominant process is not proton transfer, but a condensation reaction to give  $\text{C}_3\text{H}_5^+$ . The data for  $\text{C}_2\text{H}_3^+$  are not shown in this figure, but the maximum concentration of  $\text{C}_2\text{H}_3^+$  in this mixture is about the same as the value in pure methane and the maximum concentration occurs at 0.2–0.3 Torr (essentially the same as that for

(15) N. S. Viswanathan and L. Kevan, *ibid.*, **89**, 2842 (1967).

(16) M. S. B. Munson, *ibid.*, **90**, 83 (1968).

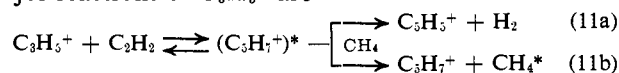
(17) (a) M. S. B. Munson and F. H. Field, *ibid.*, **88**, 4337 (1966); (b) F. H. Field, M. S. B. Munson, and D. A. Becker in ref 3b, p 167.

$\text{CH}_5^+$ ). Both of these observations indicate that the reaction is predominantly not proton transfer, although some is probably occurring. Proton transfer from  $\text{C}_2\text{H}_5^+$  is endothermic and consequently may be neglected. In addition to these ions, a maximum of 6%  $\text{C}_3\text{H}_7^+$  is formed and the ratio  $(\text{C}_3\text{H}_7^+)/(\text{C}_3\text{H}_5^+)$  increases linearly with pressure up to about 1 Torr. Consequently, the reactions of  $\text{CH}_5^+$  with acetylene are

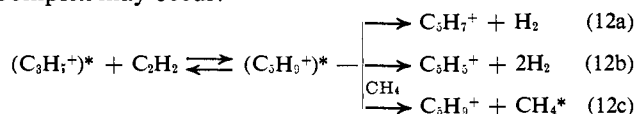


$\text{C}_2\text{H}_3^+$  reacts with methane to give  $\text{C}_3\text{H}_5^+$ , but this is only 6% of the total ionization.

It is also apparent from Figure 4 that  $\text{C}_3\text{H}_5^+$  reacts, necessarily with acetylene since it does not react with methane. In addition to the large amount of  $\text{C}_3\text{H}_7^+$  which is formed, there is also about 1.5%  $\text{C}_5\text{H}_5^+$  formed and the ratio  $(\text{C}_5\text{H}_7^+)/(\text{C}_5\text{H}_5^+)$  increases linearly with increasing pressure. Consequently, we feel that the major reactions of  $\text{C}_3\text{H}_5^+$  are



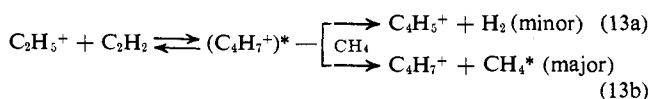
There are, however, complications which may occur. If the lifetime of the excited complex,  $(\text{C}_3\text{H}_7^+)^*$ , is long enough, collisions with acetylene must also be considered. Therefore, reactions of this excited intermediate complex may occur.



Similar reactions may occur with the stabilized  $\text{C}_3\text{H}_7^+$  produced in (10c), but we shall neglect those for the moment because  $\text{C}_3\text{H}_7^+$  is only 6% of the total ionization. The observation that  $(\text{C}_5\text{H}_7^+)/(\text{C}_5\text{H}_5^+)$  increases about linearly with pressure suggests that reaction 11b is the predominant process in these experiments and not (12a). This result is expected since  $(\text{C}_2\text{H}_2)/(\text{CH}_4)$  is about 0.01 and reactions 12 and 10c should be in approximately this ratio. About 2%  $\text{C}_5\text{H}_9^+$  is formed at the highest pressures by a process of a higher order in pressure than that for  $\text{C}_5\text{H}_5^+$  and  $\text{C}_5\text{H}_7^+$ , so it is possible that some  $\text{C}_3\text{H}_7^+$  reacts.

Only very small amounts of  $\text{C}_7$  ions are formed in these experiments, <0.2% of the total ionization, so we cannot follow the polymerization further.

Figure 5 shows the fate of  $\text{C}_2\text{H}_5^+$ . In these experiments the rate constants for reaction of both  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  are of the order of  $10^{-9}$  cc/(molecule sec), but the disappearance of  $\text{C}_2\text{H}_5^+$  appears to be about a factor of 2 slower than the disappearance of  $\text{CH}_5^+$ . As mentioned previously, proton transfer from  $\text{C}_2\text{H}_5^+$  to  $\text{C}_2\text{H}_2$  is endothermic and should be negligible. It is not possible to determine the second-order reactions of  $\text{C}_2\text{H}_5^+$ , but under the present conditions, the major product is the collision-stabilized  $\text{C}_4\text{H}_7^+$  ion. A smaller amount of  $\text{C}_4\text{H}_5^+$  is produced (about 2%) and the ratio  $(\text{C}_4\text{H}_7^+)/(\text{C}_4\text{H}_5^+)$  increases approximately linearly with pressure. Consequently, we feel that the reactions of  $\text{C}_2\text{H}_5^+$  are



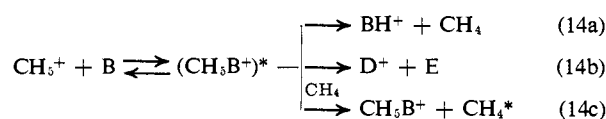
Only very small amounts of  $\text{C}_6\text{H}_9^+$  (<0.3%) or  $\text{C}_6\text{H}_7^+$  (<0.2%) were observed, so the polymerization cannot be followed further.

Only very small amounts of  $\text{C}_4\text{H}_3^+$  and  $\text{C}_4\text{H}_2^+$  are formed from reactions of acetylene ions with acetylene (<0.2% of the total ionization). Our earlier study showed a rapid reaction of acetylene ions with methane,<sup>2a</sup> and the acetylene/methane ratio is 0.01 to 0.02. In the present experiments the rate constant for the reaction of  $\text{C}_2\text{H}_2^+$  with methane was  $4.7 \pm 0.7 \times 10^{-10}$  cc/(molecule sec.) This value was determined for pressures in the range of 0.05–0.3 Torr and is independent of the acetylene concentration. This result agrees very well with our earlier value of  $4.6 \pm 0.7 \times 10^{-10}$  cc/(molecule sec), obtained in methane.<sup>2a</sup>

## Discussion

The importance of unsaturated molecules in the radiolysis of methane has been noted previously.<sup>18</sup> Ethylene and propylene, for example, are formed at low conversions but they rapidly react. Our results show quite readily that the ethylene and propylene which are formed in the radiolysis can readily be removed by ionic reactions as well as free-radical processes. Indeed, since the major secondary ions of methane are unreactive with methane, they will react with any of the radiolysis products. The addition of ethylene to methane causes an increase in butane formation,<sup>18</sup> as we would expect from our experiments. A direct explanation for the observed propane enhancement by ethylene through an ionic process is not readily available. The addition of ethylene causes a marked increase in the amount of polymer formation, and the polymerization is unaffected by NO.<sup>18</sup> We have shown the rapid initial steps to ionic polymerization in these experiments, and previous experiments indicate that these reactions would not be inhibited by NO.<sup>2c</sup>

The present experiments enable us to make some qualitative observations about the intermediate complexes involved in these reactions. If we consider the reactions



to a first approximation

$$\frac{(\text{CH}_5\text{B}^+)}{(\text{D}^+) + (\text{BH}^+)} \simeq \frac{k_{14c}(\text{CH}_4)}{k_{14a} + k_{14b}} = \frac{k_b(\text{CH}_4)}{\Sigma k_u}$$

We are forced to neglect the reversible dissociation of  $(\text{CH}_5\text{B}^+)^*$  because we have no way of measuring the reaction. We can, therefore, obtain from the intensity ratios a rough measure of the ratios of rate constants for collision stabilization ( $k_b$ , bimolecular) and unimolecular decomposition of the complex ( $k_u$ , unimolecular). Table I shows these results.

In addition, if we assume that the excited complexes have rate constants for stabilization (or other bimolecular reactions) of the order of  $10^{-10}$  cc/(molecule sec), then we will obtain the values in the last column of Table I for the approximate lifetimes of these intermediate complexes. Field<sup>7</sup> estimated the rate constants for dis-

(18) See, for example, (a) L. W. Sieck and R. H. Johnson, *J. Phys. Chem.*, **67**, 2281 (1963); (b) R. W. Hummel, *Discussions Faraday Soc.*, **36**, 75 (1963).

**Table I.** Lifetimes of Intermediate Complexes

Ion	Neutral	Inter- mediate complex	$k_b/\Sigma k_u$ , cc/molecule ( $\sim$ )	$\tau = 1/k_u$ , sec ( $\sim$ )
$\text{CH}_5^+$	$\text{C}_2\text{H}_4$	$\text{C}_3\text{H}_9^{+*}$	$<5 \times 10^{-19}$	$<5 \times 10^{-9}$
	$\text{C}_3\text{H}_6$	$\text{C}_4\text{H}_{11}^{+*}$	$<5 \times 10^{-19}$	$<5 \times 10^{-9}$
	<i>i</i> - $\text{C}_4\text{H}_8$	$\text{C}_5\text{H}_{13}^{+*}$	$<5 \times 10^{-19}$	$<5 \times 10^{-9}$
	$\text{C}_2\text{H}_2$	$\text{C}_3\text{H}_7^{+*}$	$1 \times 10^{-17}$	$1 \times 10^{-7}$
$\text{C}_2\text{H}_5^+$	$\text{C}_3\text{H}_6$	$\text{C}_5\text{H}_{11}^{+*}$	$1 \times 10^{-18}$	$1 \times 10^{-8}$
	<i>i</i> - $\text{C}_4\text{H}_8$	$\text{C}_6\text{H}_{13}^{+*}$	$1 \times 10^{-18}$	$1 \times 10^{-8}$
	$\text{C}_2\text{H}_2$	$\text{C}_4\text{H}_7^{+*}$	$4 \times 10^{-16}$	$4 \times 10^{-6}$
$\text{C}_3\text{H}_5^+$	$\text{C}_2\text{H}_2$	$\text{C}_5\text{H}_7^{+*}$	$5 \times 10^{-16}$	$5 \times 10^{-6}$

sociations of intermediate complexes in ethylene and obtained values for  $1/k$  of the order of  $10^{-7}$  sec.

Treating the other data qualitatively, we know that the lifetimes of the  $(\text{C}_4\text{H}_9^+)^*$  complex from  $\text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_4$  and the  $(\text{C}_6\text{H}_{13}^+)^*$  complex from  $\text{C}_3\text{H}_7^+ + \text{C}_3\text{H}_6$  must be roughly  $10^{-6}$  sec because of the large concentrations of the stabilized ions. On the other hand, the lifetime of the  $(\text{C}_3\text{H}_7^+)^*$  complex from  $\text{C}_4\text{H}_9^+ + \text{C}_4\text{H}_8$  must be lower, perhaps  $10^{-8}$  sec, and this small lifetime is probably due to the rapid reversible decomposition of any complex since no other products were detected.

It is of interest to note in Table I that the more unsaturated the complex intermediate, the longer its lifetime or the greater the extent of collisional stabilization. This difference in lifetimes does not appear to be solely the result of differences in energy of the excited intermediate complexes above the ground states of the ions.  $(\text{C}_3\text{H}_9^+)^*$ , which is not appreciably stabilized by collision, has about 241 kcal/mole energy if formed by addition of  $\text{CH}_5^+$  to  $\text{C}_2\text{H}_4$ .  $\Delta H_f(\text{C}_3\text{H}_9^+)$  is not known, but if the molecule is stable, we would estimate it at

215–220 kcal/mole.<sup>1b,3</sup> Consequently, the excitation energy is 20–25 kcal/mole. On the other hand,  $(\text{C}_3\text{H}_7^+)^*$  formed from  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_2$  has about 283 kcal/mole, roughly 90 kcal/mole above the *sec*- $\text{C}_3\text{H}_7^+$  ion, and it is stabilized to a much greater extent.

There appears to be a fundamental difference in the nature of the intermediate complexes.  $\text{CH}_5^+$  probably reacts with olefins predominantly through a loose complex involving no new C–C bond formation, perhaps something like the stripping model.<sup>19</sup> This is the same type of complex which we suggested for reactions with the paraffins.<sup>1b</sup> We feel it likely that there would be no scrambling of hydrogens in this complex. The complex with acetylene obviously involves C–C bond formation and the resultant allyl ion would probably show appreciable H–D mixing if appropriate deuterated compounds were used.

Similarly,  $\text{C}_2\text{H}_5^+$  reacts with the higher olefins predominantly by a loose complex, but perhaps there are small amounts of strongly bound species. The absence of appreciable H–transfer reactions suggests that the attack is primarily at the olefinic bond. We are at a loss for good explanation for the long-lived complexes with  $\text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_7^+ + \text{C}_3\text{H}_6$  and the short-lived complex for  $\text{C}_4\text{H}_9^+ + i\text{-C}_4\text{H}_8$ . Obviously, much further work needs to be done to determine the patterns of reactivities of hydrocarbon ions.

**Acknowledgment.** We are grateful to Mr. W. C. Gieger for performing these experiments with his accustomed skill. We wish to express our deep appreciation for his continued and very able assistance in our research for the past several years.

(19) A. Henglein in ref 3b, p 63.

## Photolysis of Condensed Allyl Chloride<sup>1</sup>

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Contribution from the Department of Chemistry, University of California, Davis, California 95616. Received December 12, 1968

**Abstract:** The photolysis at 254 nm of liquid allyl chloride at 27° and of solid allyl chloride at 77°K has been studied by microphotochemistry. By the use of aqueous acetone as an actinometer, quantum yields for 18 products containing six or fewer carbon atoms were determined. The primary process proposed is cleavage of the carbon–chlorine bond to give allyl radical. Mechanisms for the formation of the products are given.

Few studies of the photochemistry of halogenated olefins have been reported. The results on several haloethylenes are summarized in a review article,<sup>2</sup> and results on vinyl chloride have been recently reported.<sup>3</sup> The uv photolysis of allyl iodide<sup>4</sup> was found to yield iodine with a quantum yield of 0.07, and allyl chloride–

mercury mixtures<sup>5</sup> gave mercurous chloride and polymer under uv irradiation.

We have recently reported some results on the photolysis of condensed allyl chloride, solid and liquid.<sup>6</sup> The study was primarily directed at the possible formation of hydrochloric acid and various  $\text{C}_3$  hydrocarbons in order to gain information on the primary process. In the present paper, we have extended the investigation to

(1) This investigation was supported by a grant from the National Science Foundation.

(2) J. R. Majer and J. P. Simons, *Advan. Photochem.*, **2**, 137 (1964).

(3) T. Fujimoto, A. M. Rennert, and M. H. J. Wijnen, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Paper PHYS-135.

(4) W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

(5) O. A. Reutov and M. A. Besprozvannyi, *Dokl. Akad. Nauk SSSR*, **80**, 765 (1951).

(6) D. H. Volman and R. W. Phillips, *Ber. Bunsenges. Phys. Chem.*, **72**, 242 (1968).