Bimolecular Reactions of Trapped Ions. IV. Reactions in Gaseous Ethane and Mixtures with C_2H_2 and CD_4[1]

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Abstract: The ion–molecule reactions in pure gaseous ethane, C_2H_2–C_2H_6 mixtures, and CD_4–C_2H_6 mixtures have been studied using an ion-trapping technique. The reactions occurring in ethane have been identified and rate coefficients for reactions of the primary ions measured. For the C_2H_2–C_2H_6 mixtures the rates of reactions of the major ions have been measured. From studies of the CD_4–C_2H_6 mixtures we have established that CD_5^+ reacts rapidly with ethane, largely by D^+ transfer with possibly some direct H^- abstraction. $C_2D_5^+$ reacts more slowly, primarily by H^- abstraction.

Although the ionic reactions in ethane have been the subject of several mass spectrometric studies using the pressure variation technique,[2-6] there remain a number of disagreements concerning not only the rates of the reactions but also the identity of the reactions taking place. Recently, Wexler and Pobo,[7] using ion cyclotron resonance (icr) techniques, have mapped out the complex series of reactions occurring although no rate measurements were reported. Additional information concerning the ionic reactions in ethane has been provided by the recent radiolytic and photoionization mass spectrometric studies of Ausloos, et al.[8]

In this paper we report results obtained in a study of the ionic reactions in C_2H_6, C_2H_2–C_2H_6 mixtures, and CD_4–C_2H_6 mixtures using the ion-trapping technique developed recently.[9] The results obtained provide support, on the whole, for the reaction assignments made by Wexler and Pobo[7] and, in addition, provide quantitative rate data for the reaction of the major ions at an average reactant ion kinetic energy of $\sim$0.4 eV.

Experimental Section

The ion-trapping technique has been described in detail[9] and only a short summary need be given. Primary reactant ions are produced by an electron beam pulse of 1-μsec duration and variable electron energy and trapped in the negative space charge of a continuous electron beam of 5-eV energy (insufficient to cause ionization) and $\sim$8-μA trap current. A variable time after the ion production pulse a voltage pulse applied to the repeller electrode removes the ions for mass analysis. In the present work delay times between the ion formation and ion removal pulses of up to 3.2 msec were used. Source concentrations were approximately 1×10^{13} molecules cm^{-3}; these were not measured directly but were related to the sample inlet pressure through observation of the decay of CH_4^+ with reaction time in pure CH_4. All rate constants are therefore relative to the value of 1.20×10^{-9} cm^3 molecule^{-1} sec^{-1} established[10] for the $CH_4^+ + CH_4$ reaction. The

(1) For part III, see ref 18.

(2) (a) V. L. Tal'roze and E. L. Frankevich, *J. Amer. Chem. Soc.*, **80**, 2344 (1958); (b) F. H. Field and F. W. Lampe, *ibid.*, **80**, 5587 (1958); **81**, 3242 (1959).

(3) R. Fuchs, *Z. Naturforsch., A*, **16**, 1026 (1961).

(4) A. Henglein and G. A. Muccini, *ibid.*, **17**, 4521 (1962).

(5) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *J. Chem. Phys.*, **40**, 51 (1964).

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

(7) S. Wexler and L. G. Pobo, *J. Amer. Chem. Soc.*, **93**, 1327 (1971).

(8) P. Ausloos, R. E. Rebbert, and L. W. Sieck, *J. Chem. Phys.*, **54**, 2612 (1971).

(9) A. A. Herod and A. G. Harrison, *Int. Mass Spectrom. Ion Phys.*, **4**, 415 (1970).

results are presented in the accompanying figures as per cent total ionization *vs.* reaction time where the total ionization represents the sum of the collected ion currents at each time delay setting.

The ethane and acetylene were research grade gases which were carefully degassed before use. The CD_4 was obtained from Merck Sharp and Dohme, Montreal, and contained approximately 2% CD_3H.
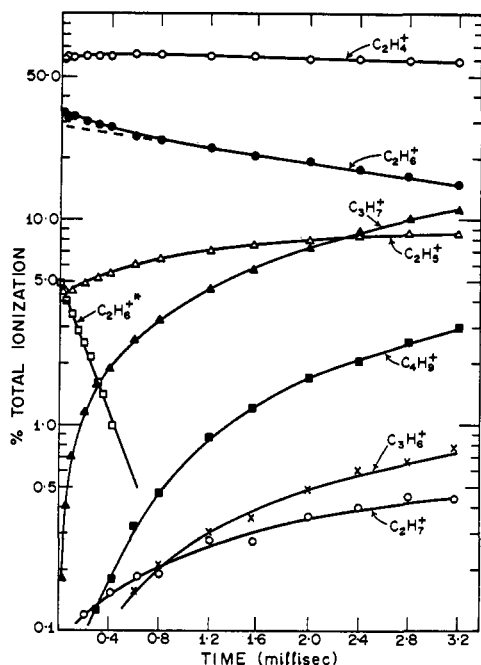
Results and Discussion

Ethane. Figure 1 shows typical results obtained for pure ethane at 10.8-eV nominal ionizing electron energy while Figure 2 shows typical results obtained at 30-eV nominal electron energy. At the lowest electron energy, where only $C_2H_6^+$, $C_2H_5^+$, and $C_2H_4^+$ are present as primary ions, only $C_2H_6^+$ shows a significant decrease over the time range of 3.2 msec. The $C_2H_4^+$ abundance shows an initial small increase followed by a very small decrease at longer reaction times. At 30 eV (Figure 2), where the primary $C_2H_6^+$ abundance is lower, the $C_2H_4^+$ decrease is much more significant. Experiments at higher pressures, where the $C_2H_6^+$ disappears more rapidly, also showed a more pronounced decrease in $C_2H_4^+$. Thus we conclude that $C_2H_4^+$ is a reactive ion; the small decrease observed in Figure 1 indicates that it is also being formed, presumably by reaction 1

$$C_2H_6^+ + C_2H_6 \longrightarrow$$
$$C_2H_4^+ + H_2 + C_2H_6 \quad \Delta H = +8 \text{ kcal mol}^{-1} \quad (1)$$
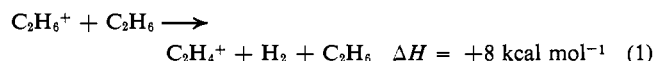
reported by Wexler and Pobo.[7]

At the lowest electron energies $C_2H_5^+$ also increases with reaction time indicating reaction 2 as a further

$$C_2H_6^+ + C_2H_6 \longrightarrow$$
$$C_2H_5^+ + H_2 + C_2H_5 \quad \Delta H = +19 \text{ kcal mol}^{-1} \quad (2)$$
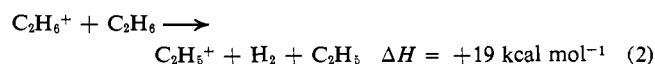
reaction of $C_2H_6^+$.

Reaction 2 may proceed through the intermediate formation of $C_2H_7^+$ and, in support of this proposal, we note that m/e 31 was above the expected contribution from $^{13}CCH_6^+$ and increased with reaction time.

Both reactions 1 and 2 are endothermic for ground state reactants and only $C_2H_6^+$ ions with excess internal energy or with sufficient translational energy will be able to overcome the energy barrier. The observed rate of reaction is quite small and increases with increasing excitation of the primary ion (see discussion of rate coefficients following).

(10) S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, **45**, 3107 (1967).

Figure 1. Ion intensities *vs.* reaction time for ethane: 10.8-eV nominal electron energy; $[C_2H_6] = 1.16 \times 10^{13}$ molecules cm^{-3} ($C_2H_6^+$ represents total molecular ion signal, $C_2H_6^{+*}$ represents component of higher reactivity).

The major higher mass products at low energies are $C_3H_7^+$ and $C_4H_9^+$ with a small amount of $C_3H_6^+$. In addition, low intensity ions were observed at m/e 44, 45, 46, and 49 (maximum intensities at 3.2 msec in 10.8-eV runs were 0.5, 0.2, 0.2, and 0.3%, respectively). It was observed that these ions were a smaller fraction of the total ionization in the runs at 30-eV nominal electron energy, suggesting that they might originate from reaction of $C_2H_6^+$. However, the identity and origin of these ions remains unknown.

The formation of $C_3H_6^+$ has been attributed to reaction 3 by Wexler and Pobo[7] and this is consistent with

$$C_2H_4^+ + C_2C_3H_6 \longrightarrow H_6^+ + CH_4 \quad \Delta H = -22 \text{ kcal mol}^{-1} \quad (3)$$

our results.

Formation of $C_3H_7^+$ was attributed to reaction 4 by Munson, *et al.*,[6] and to reaction 5 by Volpi, *et al.*,[5]

$$C_2H_5^+ + C_2H_6 \longrightarrow C_3H_7^+ + CH_4 \quad \Delta H = -9 \text{ kcal mol}^{-1} \quad (4)$$

$$C_2H_4^+ + C_2H_6 \longrightarrow C_3H_7^+ + CH_3 \quad \Delta H = -27 \text{ kcal mol}^{-1} \quad (5)$$

and by Fuchs.[3] The icr studies[7] indicated both reactions. Experiments with CD_4-C_2H_6 mixtures (see below) show that reaction 4 contributes only to a minor extent to formation of $C_3H_7^+$ and we attribute its formation primarily to reaction of $C_2H_4^+$.

Recently, Ausloos, *et al.*,[8] in photoionization experiments in C_2H_4-C_2D_6 mixtures have observed the reaction

$$C_2H_4^+ + C_2D_6 \longrightarrow C_2D_4^+ + C_2H_4D_2 \quad (6)$$
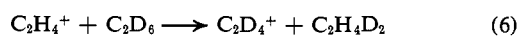
and measured a rate constant of 1.1×10^{-10} cm^3 molecule^{-1} sec^{-1}. Such a reaction would not be observable in our unlabeled system since the product would have the same m/e ratio as the reactant. They reported no products analogous to $C_3H_7^+$ formed in reaction 5; presumably the rate coefficient for this channel is too small to permit observation of these products in their system.
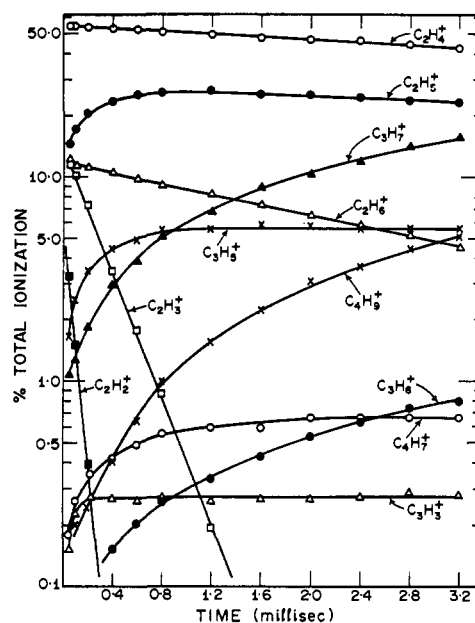

Figure 2. Ion intensities *vs.* reaction time for ethane: 30-eV nominal electron energy; $[C_2H_6] = 9.52 \times 10^{12}$ molecules cm^{-3}.

Formation of $C_4H_9^+$ was attributed to reaction of $C_3H_7^+$ by Munson, *et al.*,[6] and to reaction of $C_2H_5^+$ by Volpi, *et al.*,[5] and by Wexler and Pobo.[7] Our results both in pure ethane and in CD_4-C_2H_6 mixtures indicate that reaction 7 does indeed occur, although

$$C_2H_5^+ + C_2H_6 \longrightarrow C_4H_9^+ + H_2 \quad \Delta H = 7 \text{ kcal mol}^{-1} \quad (7)$$
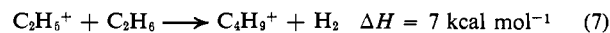
we cannot rule out the possibility that $C_3H_7^+$ also reacts to produce $C_4H_9^+$. The $C_4H_9^+$ product is more abundant in the 30-eV run (Figure 2) where the $C_2H_5^+$ precursor is also more abundant.

In the runs at 30-eV nominal electron energy $C_2H_3^+$ is a significant primary ion with $C_2H_2^+$ present in low yield. The new product ions observed are m/e 39 ($C_3H_3^+$), 41 ($C_3H_5^+$), and 55 ($C_4H_7^+$). The $C_3H_3^+$ intensity becomes constant after the $C_2H_2^+$ primary ion has disappeared indicating that $C_2H_2^+$ reacts in part by reaction 8 identified previously by icr measure-
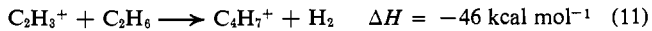
$$C_2H_2^+ + C_2H_6 \longrightarrow$$
$$C_3H_3^+ + CH_3 + H_2 \quad \Delta H = -8 \text{ kcal mol}^{-1} \quad (8)$$
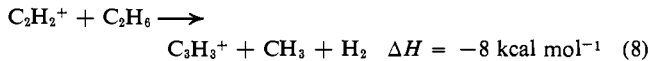
ments[7] and also indicating that $C_3H_3^+$ is not reactive toward ethane. The $C_3H_5^+$ product intensity becomes constant after the $C_2H_3^+$ reactant ion has disappeared thus indicating reaction 9. The $C_3H_5^+$ ion may also

$$C_2H_3^+ + C_2H_6 \longrightarrow C_3H_5^+ + CH_4 \quad \Delta H = -51 \text{ kcal mol}^{-1} \quad (9)$$
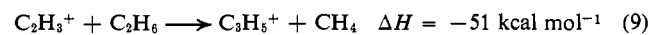
be produced by reaction 10 which has been previously

$$C_2H_2^+ + C_2H_6 \longrightarrow$$
$$C_3H_5^+ + CH_3 \quad \Delta H = -47 \text{ kcal mol}^{-1} \quad (10)$$

identified.[7] The $C_4H_7^+$ intensity also becomes constant after the $C_2H_3^+$ reactant has disappeared confirming the occurrence of reaction 11, previously identified by

$$C_2H_3^+ + C_2H_6 \longrightarrow C_4H_7^+ + H_2 \quad \Delta H = -46 \text{ kcal mol}^{-1} \quad (11)$$

Wexler and Pobo.[7] In addition, the increase in the $C_2H_5^+$ ion signal is much greater at the higher electron energy and this must be attributed to reactions 12 and
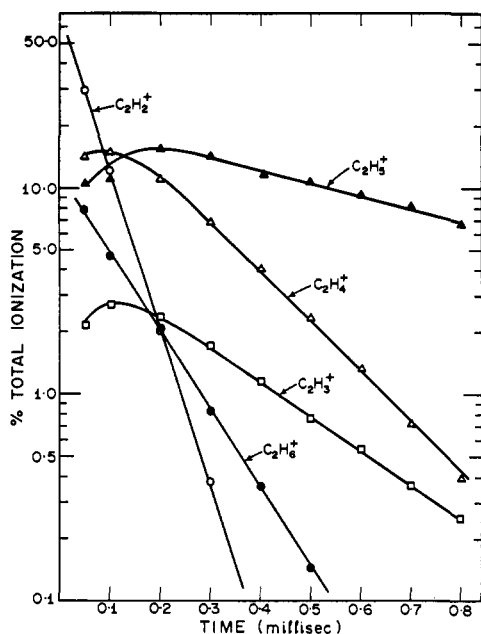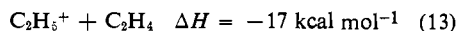
$$C_2H_2^+ + C_2H_6 \longrightarrow$$
$$C_2H_5^+ + C_2H_3 \quad \Delta H = -14 \text{ kcal mol}^{-1} \quad (12)$$
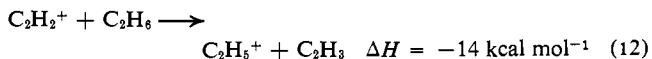
Figure 3. Reactant ion intensities vs. reaction time for C_2H_2–C_2H_6 mixture: $[C_2H_2] = 5.50 \times 10^{12}$ molecules cm^{-3}; $[C_2H_6] = 5.50 \times 10^{12}$ molecules cm^{-3}.

Figure 4. Product ion intensities vs. reaction time for C_2H_2–C_2H_6 mixture. Conditions as for Figure 3.

13, primarily (13), both of which have been reported

$$C_2H_3^+ + C_2H_6 \longrightarrow$$
$$C_2H_5^+ + C_2H_4 \quad \Delta H = -17 \text{ kcal mol}^{-1} \quad (13)$$

previously.[7] The conclusion that $C_2H_3^+$ reacts by reactions 9, 11, and 13 is in contrast to the observations by Ausloos, $et\ al.$,[8] that $C_2H_3^+$ disappeared in their system by the persistent complex formation (14). This

$$C_2H_3^+ + C_2H_6 \longrightarrow C_4H_9^+ \quad (14)$$

difference is undoubtedly explained by the different source pressures used in the two experiments. The $C_4H_9^+$ complex would not be stabilized by collision at the pressures (~ 0.3 mTorr) used in our experiments, and, indeed, the $C_2H_5^+$, $C_3H_5^+$, and $C_4H_7^+$ ions are those which would be expected from decomposition of the $C_4H_9^+$ collision complex.

C_2H_2–C_2H_6 Mixtures. In an attempt to delineate more clearly the products of the reaction of $C_2H_2^+$ with ethane, several runs were carried out using a 1:1 C_2H_2–C_2H_6 mixture at low electron energy where $C_2H_2^+$ was the major primary ion. Typical results are shown in Figures 3 and 4. Quantitative interpretation of the results is complicated by the high reactivity of the $C_2H_6^+$, $C_2H_5^+$, $C_2H_4^+$, and $C_2H_3^+$ ions from ethane with the acetylene neutral. However, from the initial rise in the $C_2H_3^+$, $C_2H_4^+$, and $C_2H_5^+$ ion signals it is obvious that these ions are produced by reaction of $C_2H_2^+$ with ethane. In addition, $C_3H_3^+$, $C_3H_5^+$, $C_4H_7^+$, and possibly $C_4H_5^+$ appear to be products of reaction of $C_2H_2^+$. Thus the reactions of $C_2H_2^+$ with ethane are extremely complex and include reactions
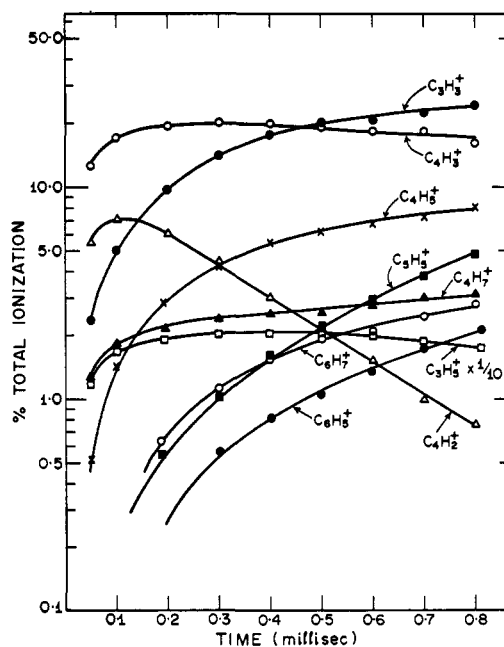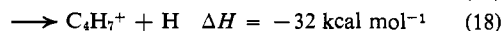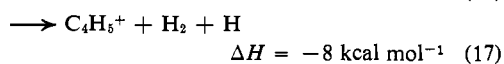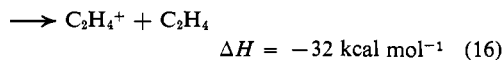
$$C_2H_2^+ + C_2H_6 \longrightarrow C_2H_3^+ + C_2H_5$$
$$\Delta H = -3 \text{ kcal mol}^{-1} \quad (15)$$
$$\longrightarrow C_2H_4^+ + C_2H_4$$
$$\Delta H = -32 \text{ kcal mol}^{-1} \quad (16)$$
$$\longrightarrow C_4H_5^+ + H_2 + H$$
$$\Delta H = -8 \text{ kcal mol}^{-1} \quad (17)$$
$$\longrightarrow C_4H_7^+ + H \quad \Delta H = -32 \text{ kcal mol}^{-1} \quad (18)$$
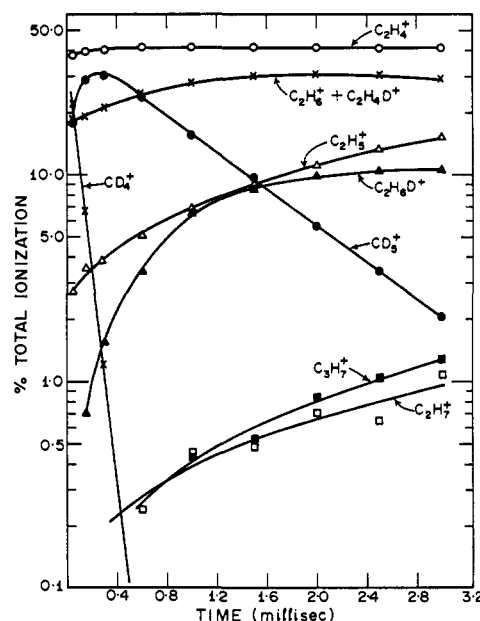

Figure 5. Ion intensities vs. reaction time for CD_4–C_2H_6 mixture: low electron energy; $[CD_4] = 9.9_6 \times 10^{12}$ molecules cm^{-3}; $[C_2H_6] = 9.6_9 \times 10^{11}$ molecules cm^{-3}.

8, 10, 12, and 15–18. All of these reactions, with the exception of (17), only tentatively identified in the present work, have been reported previously from icr experiments.[7] The alternative of dissociative charge transfer from $C_2H_2^+$ to C_2H_6 yielding the products $C_2H_3^+$, $C_2H_4^+$, and $C_2H_5^+$ is unlikely since the reactions are endothermic in each case. The relative importance of the various reaction channels is impossible to assess because the ions derived from ethane are themselves reactive and yield the same higher mass products.

CD_4–C_2H_6 Mixtures. To obtain information on the products and rate of reaction of ethyl ions with C_2H_6,
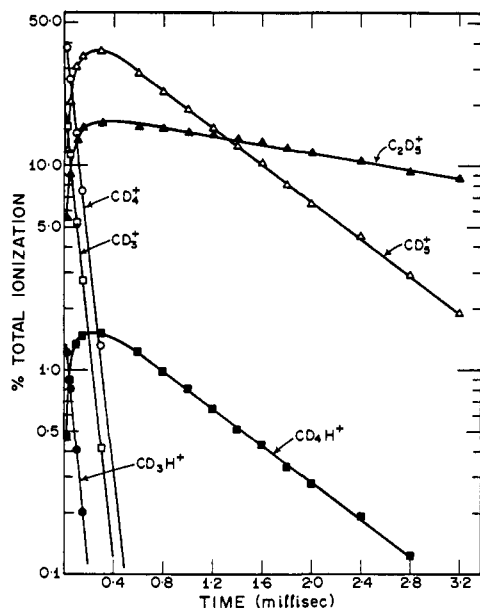
Figure 6. CD_4 ion intensities vs. reaction time for CD_4–C_2H_6 mixture: $[CD_4] = 1.0_0 \times 10^{13}$ molecules cm^{-3}; $[C_2H_6] = 9.9_0 \times 10^{11}$ molecules cm^{-3}.

Figure 7. Ethane and product ion intensities for CD_4–C_2H_6 mixture. Conditions as for Figure 6.

the reactions in CD_4–C_2H_6 mixtures (approximately 10:1 CD_4:C_2H_6) were studied.

Figure 5 shows typical results obtained at low electron energies where only CD_4^+ is formed by electron impact on CD_4. The CD_4^+ primary ion reacts rapidly with neutral CD_4 to produce CD_5^+ which, in the absence of additives, is unreactive.[9,11] The decrease in CD_5^+ intensity at reaction times greater than 0.4 msec therefore must be attributed to reaction with C_2H_6. The products of this reaction are m/e 32 ($C_2H_6D^+$), 29 ($C_2H_5^+$), and 30 ($C_2H_4D^+$) which all increase as the CD_5^+ decreases. That the increase in m/e 30 is attributable to formation of $C_2H_4D^+$ and not $C_2H_6^+$ was shown by separate experiments in CH_4–C_2H_6 mixtures where only m/e 31 ($C_2H_7^+$) and 29 ($C_2H_5^+$) increased as CH_5^+ reacted.

These results indicate the deuteron-transfer reaction

$$CD_5^+ + C_2H_6 \longrightarrow C_2D_6D^+ + CD_4 \qquad (19)$$
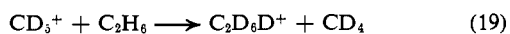
followed by decomposition of some of the $C_2H_6D^+$ ions. The relative yields under our experimental conditions were found to be $C_2H_6D^+$:$C_2H_4D^+$:$C_2H_5^+$ = 0.37:0.40:0.23. The decomposition reactions 20 and 21

$$C_2H_6D^+ \longrightarrow C_2H_5^+ + HD \qquad (20)$$

$$\longrightarrow C_2H_4D^+ + H_2 \qquad (21)$$
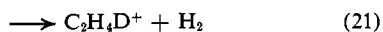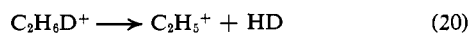
would be expected to yield $C_2H_4D^+$ and $C_2H_5^+$ in the ratio 2.5:1 if the hydrogens and the deuterium have become completely randomized. The observed ratio 1.7:1 is considerably lower than this calculated ratio and is close to the ratio 1.3:1 observed for the same ions in the reaction of D_3^+ with C_2H_6.[12] In this latter work the result was attributed to a scrambling reaction involving only the hydrogens of one methyl group (H_3C–C^+H_3D) with operation of an isotope effect favoring H_2 loss. In contrast to these results Abramson and Futrell[13] have found, using a variety of deu-

terium-labeled methyl ions and methane molecules, that the $C_2X_7^+$ complex formed in the reaction of CX_3^+ with CX_4 decomposes to $C_2X_5^+$ with essentially complete hydrogen–deuterium randomization. This apparent discrepancy may be reconciled if we assume that in the reaction of both CD_5^+ and D_3^+ with ethane the reaction occurs in part by direct H^- abstraction. The H^- abstraction reaction would lead to $C_2H_5^+$ only and a lowered $C_2H_4D^+$/$C_2H_5^+$ ratio. Assuming complete scrambling in decomposition of $C_2H_6D^+$ and no isotope effect, we calculate that approximately 7% of the total reaction of CD_5^+ with C_2H_6 occurs by the direct H^- transfer step.

The observation of the relatively large yield of $C_2H_6D^+$ at our low pressures ($\sim$0.3 mTorr) is surprising. Munson and Field[14] have observed $C_2H_7^+$ previously in CH_4–1% C_2H_6 mixtures at high pressures, formed by the reaction analogous to 19, and estimated the proton affinity (PA) of C_2H_6 to be approximately 120 kcal mol^{-1}, corresponding to ΔH_f ($C_2H_7^+$) $\approx$ 225 kcal mol^{-1}. This value when combined with ΔH_f ($C_2H_5^+$) = 219 kcal mol^{-1} [15] indicates that reactions 20 and 21 are probably exothermic. Despite this, $C_2H_7^+$ has a significant lifetime; under our experimental conditions the ions must survive, on the average, for $\sim$10^{-4} sec before undergoing collision with a neutral molecule. If the fragmentation reaction is indeed exothermic such a long lifetime appears unreasonable. This suggests either that ΔH_f ($C_2H_7^+$) is considerably less than 225 kcal mol^{-1} (PA(C_2H_6) greater than 220 kcal mol^{-1}) or that there is a significant activation energy for loss of H_2 from $C_2H_7^+$.

Figures 6 and 7 show typical results obtained at higher electron energies where both CD_3^+ and CD_4^+ are formed by electron impact on methane-d_4. The

(11) F. H. Field and M. S. B. Munson, J. Amer. Chem. Soc., 87, 3289 (1965).

(12) V. Aquilanti, A. Galli, and G. G. Volpi, J. Chem. Phys., 47, 831 (1967).

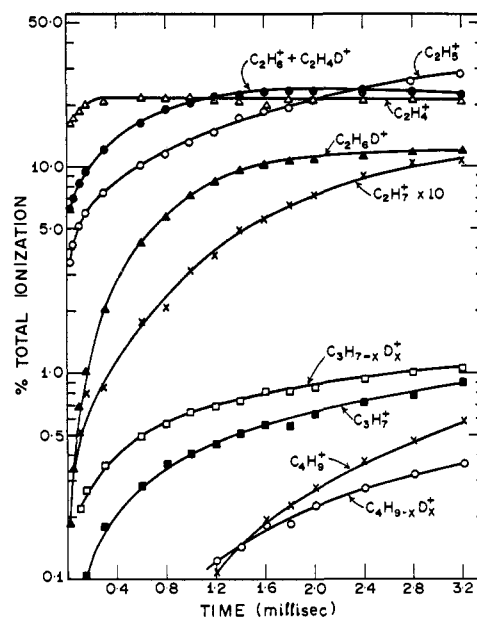(13) F. P. Abramson and J. H. Futrell, ibid., 45, 195 (1966).

(14) M. S. B. Munson and F. H. Field, J. Amer. Chem. Soc., 87, 3294 (1965).

(15) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS, U. S. Government Printing Office, Washington, D. C., 1969, p 26.

Table I. Disappearance Rate Coefficients

Reaction	k (exptl),^{a} this work	Lit. (ref)	k (calcd)^a
$C_2H_2^+ + C_2H_6$	$1.3 \pm 0.2 \times 10^{-9}$	2.1×10^{-9} (6)	1.34×10^{-9}
$C_2H_3^+ + C_2H_6$	$3.7 \pm 0.1 \times 10^{-10}$	$4.8 \pm 0.9 \times 10^{-10}$ (6)	1.33×10^{-9}
$C_2H_4^+ + C_2H_6$	$>5 \times 10^{-12}$ ^{b}	$<1 \times 10^{-11}$ (6)	1.32×10^{-9}
$C_2H_6^+ + C_2H_6$	$1.85 \pm 0.05 \times 10^{-11}$ (low energy)		1.30×10^{-9}
	$3.2 \pm 0.2 \times 10^{-11}$ (30 eV)	0.7–1.8×10^{-11} (6)	
$C_2H_3^+ + C_2H_2$	$3.1 \pm 0.2 \times 10^{-10}$		1.19×10^{-9}
$C_2H_4^+ + C_2H_2$	$8.3 \pm 0.2 \times 10^{-10}$		1.18×10^{-9}
$C_2H_5^+ + C_2H_2$	$1.0 \pm 0.1 \times 10^{-10}$		1.17×10^{-9}
$C_2H_6^+ + C_2H_2$	$1.4 \pm 0.1 \times 10^{-9}$		1.16×10^{-9}
$CD_5^+ + C_2H_6$	$1.07 \pm 0.04 \times 10^{-9}$	$\sim 1 \times 10^{-9}$ (14)	1.41×10^{-9}
$C_2D_5^+ + C_2H_6$	$2.8 \pm 0.1 \times 10^{-10}$		1.25×10^{-9}

^{a} Units, cm^3 molecule^{-1} sec^{-1}. ^{b} Does not include reaction analogous to that observed by Ausloos, et al.:^{8} $C_2D_4^+ + C_2H_6 \rightarrow C_2H_4^+ + C_2D_4H_2$, $k \approx 1 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}.

CD_3^+ and CD_4^+ ions react rapidly to produce $C_2D_5^+$ and CD_5^+, respectively (Figure 6). In addition a small amount of CD_4H^+ is observed because of the CD_3H impurity. The $C_2D_5^+$ ion is unreactive in pure $CD_4^{9,11}$ and the decrease in yield at longer reaction times must be due to reaction with C_2H_6. The $C_2D_5^+$ reacts in part to give $C_3H_{7-x}D_x^+$ ($x = 1$–3) (reaction 4) and $C_4H_{9-x}D_x^+$ ($x = 1$–3) (reaction 7) in low yields; however, the major reaction yields $C_2H_5^+$ by the hydride-transfer reaction. This reaction is definitely a hydride-transfer

$$C_2D_5^+ + C_2H_6 \longrightarrow C_2D_5H + C_2H_5^+ \qquad (22)$$

reaction and not D^+ transfer followed by fragmentation since the yields of $C_2H_6D^+$ and $C_2H_4D^+$ are entirely accounted for by the reaction of CD_5^+. The relative yields for reaction of $C_2D_5^+$ are approximately $C_3X_7^+$: $C_4X_9^+$:$C_2H_5^+ = 0.10$:0.05:0.85. Hydride abstraction from higher hydrocarbons by $C_2D_5^+$ is well established, primarily from radiolytic studies;^{16} however, the present work is the first evidence for the reaction with ethane.

Disappearance Rate Coefficients. The rate coefficients for disappearance of the various reactant ions as determined from the slopes of the linear semilogarithmic plots are recorded in Table I and compared with previous experimental values and values calculated on the basis of ion-induced dipole interactions.^{17} The limits of error quoted represent the mean deviation of repeat determinations. Several aspects deserve comment.

The rate coefficient for reaction of $C_2H_4^+$ does not include reaction 6, which is unobservable in our system, and is a lower limit to the rate of reaction to form identifiable products, since $C_2H_4^+$ is formed by ion–molecule reactions. The rate constant for reaction of $C_2H_2^+$ is very close to the calculated collision rate coefficient and therefore appears more reasonable than

the considerably higher value reported by Munson, et al.^{6} On the other hand, our value for reaction of $C_2H_3^+$ is in satisfactory agreement with that reported by the same workers.

The semilogarithmic plots for the $C_2H_6^+$ ion (Figures 1 and 2) consistently showed curvature in the initial region both at low and high electron energy, although the extent of the curvature appeared to decrease with increasing electron energy. Such a curvature has been observed previously^{18} for the reaction $H_2S^+ + H_2S$ and was attributed to reaction of an excited ion. Substraction of the linear portion of the plot from the composite curve leads to the straight line labeled $C_2H_6^{+*}$ in Figure 1 and a rate coefficient of approximately 3×10^{-10} cm^3 molecule^{-1} sec^{-1} for the excited species. The rate coefficients reported in Table I were obtained from the linear portion of the plot at longer reaction times and show a definite increase with increasing electron energy. This is consistent with the fact that the reactions of $C_2H_6^+$ are endothermic for ground state reactants.

The rate coefficient for reaction of CD_5^+ with C_2H_6, 1.07×10^{-9} cm^3 molecule^{-1} sec^{-1}, is in excellent agreement with the rough estimate of 1×10^{-9} reported by Munson and Field^{14} some years ago and is only slightly lower than the calculated collision rate coefficient, indicating that reaction occurs on practically every collision. In contrast, the rate coefficient for reaction of $C_2D_5^+$ is approximately a factor of 5 lower than the collision rate coefficient, indicating that many of the collisions do not lead to detectable reaction. With the exception of the reaction of $C_2H_6^+$ the rate coefficients for reactions of ions with acetylene are lower than the calculated collision rates by factors ranging from approximately 10 to 1.4.

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