Acknowledgment.—The authors gratefully acknowledge the support of this work by the United States Public Health Service, National Institutes of Health, Bethesda, Maryland. We are grateful to Miss Sue Feil for the standard methyl hydroperoxide preparation, Dr. L. C. Leitch for the $CD_3N_2CD_3$ sample and the Polychemicals Department, E. I. du Pont and Co. for the sample of C_2F_6.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, HUMBLE OIL AND REFINING COMPANY, BAYTOWN, TEXAS]

Reactions of Gaseous Ions. XI. Ionic Reactions in Krypton–Methane and Argon–Methane Mixtures

BY F. H. FIELD, HARLAN N. HEAD AND J. L. FRANKLIN

RECEIVED SEPTEMBER 8, 1961

In a study of the ionic reactions occurring in a mass spectrometer in argon–methane and krypton–methane mixtures, the ion–molecule reaction products ArH^+, ArC^+, $ArCH_2{}^+$, $ArCH_3{}^+$, KrH^+, KrC^+, $KrCH_2{}^+$ and $KrCH_3{}^+$ were observed. Charge exchange reactions between rare gas ions and methane were observed with Ar^+ producing $CH_2{}^+$ and $CH_3{}^+$, and Kr^+ producing $CH_3{}^+$ and $CH_4{}^+$. The ion-molecule reaction rates are in the order of 10^{-12} to 10^{-11} cc. molecule^{-1} sec.$^{-1}$ while the charge exchange reaction rates are in the order of 10^{-10} to 10^{-9} cc. molecule^{-1} sec.$^{-1}$. No reaction products were observed in a neon–methane mixture.

As an extension of the previously reported study of ion–molecule reactions at high pressure in the mass spectrometer in xenon–methane mixtures,[1] studies were made of the ion–molecule reactions in mixtures of other rare gases and methane. This paper is a report on the reactions observed in argon–methane and krypton–methane mixtures at ionization chamber pressures of 45×10^{-3} to 120×10^{-3} mm.

In the previous paper on xenon–methane mixtures the existence of the ions XeH^+ and $XeCH_n{}^+$, $n = 0$ to 4 was reported. However, in studies of argon–methane and krypton–methane mixtures only the ions ArH^+, KrH^+, $ArCH_n$ and $KrCH_n{}^+$, $n = 0$, 2 and 3, were observed. It is possible that a small amount of $KrCH_4{}^+$ was formed, but the large number of krypton isotopes made it impossible to be sure of its existence. In a study of a neon–methane mixture no ion–molecule reaction products were observed. No study was made of helium–methane mixtures as it would be expected that such a mixture would be less reactive than neon–methane.

Experimental

All measurements were made with the Humble chemical physics mass spectrometer which has been described previously.[2] It is a 12 in. radius of curvature 60° magnetic deflection instrument with conventional means of producing, analyzing and collecting the ions.

The ion source used for these studies comprises an ionization chamber 7.0 mm. in length, planar ion repeller electrodes separated by a 3 mm. gap, and a single drawout electrode between the electron gun filament and the entrance to the ionization chamber. This ion source is a compromise between the two different sources used in the xenon–methane studies.

The gas handling system consists of two reservoirs with gold foil leaks allowing the gases to mix and flow into the ionization chamber. Gas pressures in the ionization chamber (P_s) were determined from pressures (P_m) read on a McLeod gage attached to the gas inlet line to the ionization chamber. $P_s - P_m$ correlations were made by independent experiments as described previously.[1] Studies were made holding the P_s of methane constant and varying the rare gas pressure. In general the methane pressure was held at 60×10^{-3} mm. and rare gas pressure was varied at approximately 5×10^{-3} mm. internals between 0 and 60×10^{-3} mm.

The electron current was usually maintained at 1.0 microamp. Nominal electron voltage for all pressure studies was 70 volts. The field strength in the ionization chamber was 12.5 volts/cm. (ion repeller voltage = 5.0 volts), and the distance from the mid-line of the electron beam to the ion-exit electrode was 2.0 mm.

Appearance potential measurements were used to determine the identities of the reactions yelding the observed product ions. For these studies equal volume mixtures of the rare gas and methane components were maintained at a total P_s of 120×10^{-3} mm. The electron voltage scale was calibrated with the $^{36}Ar^+$ and $^{78}Kr^+$ ions.

The methane used in this work was Phillips Research Grade which has a stated purity of 99.9%. The argon (The Matheson Co.) and krypton (Air Reduction Co.) were found by mass spectroscopic analysis in our laboratories to have less than 1% impurities with the major impurity being H_2O. None of the impurities would offer serious interference in these studies.

Results

A. Observed Ion-molecule Reaction Products.—Tables I and II show portions of typical mass spectra for mixtures of equal parts of rare gas and methane at an ionization chamber pressure of 120×10^{-3} mm. The mass 41 peak in Table I is a combination of ArH^+ and $C_3H_5{}^+$ formed as a tertiary ion from methane. The intensity of ArH^+ can be obtained by subtracting an estimate of the $C_3H_5{}^+$ intensity from the measured mass 41 intensity.

Analysis of the spectra of krypton–methane mixtures was made complicated by the existence of the six isotopes of Kr. The observed mass spectra were reduced to monoisotopic spectra by application of the known abundances of Kr isotopes. For example, although I_{99} possibly could contain contributions from three different molecular ions, it was found that $^{83}KrCH_4{}^+$ and $^{86}KrCH^+$ could be taken as negligibly small in comparison with $^{84}KrCH_3{}^+$. Therefore, the monoisotopic intensity of $KrCH_3{}^+$ was obtained by dividing the intensity of the mass 99 peak by the relative percentage of ^{84}Kr isotope in pure krypton.

Partial monoisotopic mass spectra of equal volume rare gas and methane mixtures are given

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[1] F. H. Field and J. L. Franklin, *J. Am. Chem. Soc.*, to be published.

[2] F. H. Field, *ibid.*, **83**, 1523 (1961).

TABLE I

PARTIAL MASS SPECTRUM OF ARGON–METHANE MIXTURE

$P_s(CH_4) = 60 \times 10^{-3}$ mm.

Mass	Ion	Intensity (divisions)[a] $P_s(Ar) = 0$	$P_s(Ar) = 60 \times 10^{-3}$ mm.
12	C^+	589	343
13	CH^+	1,500	780
14	CH_2^+	4,200	4,900
15	CH_3^+	32,500	38,200
16	CH_4^+	30,000	13,500
17	CH_5^+	24,300	13,700
29	$C_2H_5^+$	17,200	16,500
40	Ar^+		7,560
41	ArH^+, $C_3H_5^+$	128	375
52	ArC^+		8.5
53	$ArCH^+$		0
54	$ArCH_2^+$		22
55	$ArCH_3^+$		6.5
56	$ArCH_4^+$		0.5
80	Ar_2^+		26

[a] 1 div = 1×10^{-15} amp.

TABLE II

PARTIAL MASS SPECTRUM OF KRYPTON–METHANE MIXTURE

$P_s(CH_4) = 60 \times 10^{-3}$ mm.

Mass	Ion	Intensity (divisions) P_s-(Kr) = 0	P_s-(Kr) = 60 × 10^{-3} mm.
12	C^+	298	161
13	CH^+	750	465
14	CH_2^+	2,230	1,500
15	CH_3^+	19,600	21,000
16	CH_4^+	18,600	19,500
17	CH_5^+	15,500	23,000
29	$C_2H_5^+$	10,600	12,600
84	$^{84}Kr^+$, $^{83}KrH^+$		1,850
85	$^{84}KrH^+$		225
96	$^{80}KrCH_4^+$, $^{82}KrCH_2^+$, $^{83}KrCH^+$, $^{84}KrC^+$		7
97	$^{82}KrCH_3^+$, $^{83}KrCH_2^+$, $^{84}KrCH^+$		16
98	$^{82}KrCH_4^+$, $^{83}KrCH_3^+$, $^{84}KrCH_2^+$, $^{85}KrCH^+$		31
99	$^{83}KrCH_4^+$, $^{84}KrCH_3^+$, $^{86}KrCH^+$		57
100	$^{84}KrCH_4^+$, $^{86}KrCH^+$		5
101	$^{86}KrCH_3^+$		24
168	$^{84}Kr_2^+$, $^{82}Kr\,^{86}Kr^+$		5

in Table III. The intensities of the argon–methane reaction products are shown in Fig. 1 to increase linearly with argon pressure. The krypton–methane reaction products show the same linearity with krypton pressure although the data are more scattered.

TABLE III

PARTIAL MONIOSOTOPIC MASS SPECTRA OF RARE GAS–METHANE MIXTURES

P_s(rare gas) = $P_s(CH_4)$ P_s(total) = 120×10^{-3} mm.

Ar-CH_4 Mixture Ion	Ar-CH_4 Mixture Intensity (div.)	Kr-CH_4 Mixture Ion	Kr-CH_4 Mixture Intensity (div.)
Ar^+	7560	Kr^+	3170
ArH	330	KrH^+	395
ArC^+	8.5	KrC^+	5
$ArCH^+$	0	$KrCH^+$	0
$ArCH_2^+$	22	$KrCH_2^+$	32
$ArCH_3^+$	6.5	$KrCH_3^+$	100
$ArCH_4^+$	0.5	$KrCH_4$	<5
Ar_2^+	26	Kr_2^+	14

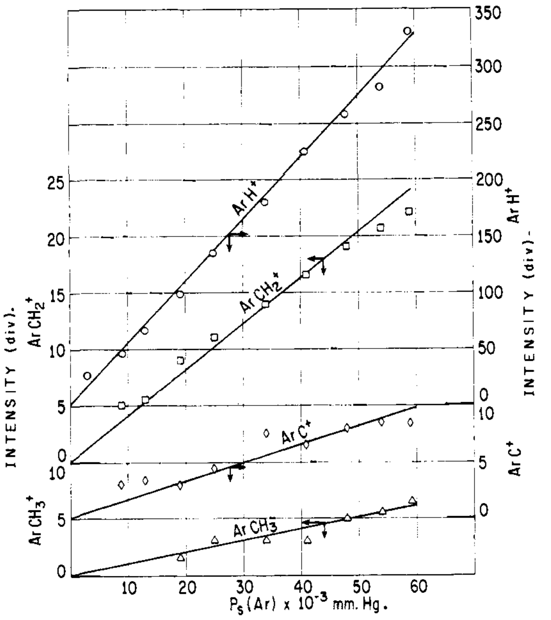

Fig. 1.—Argon–methane ion-molecule reaction product intensity plots: $P_s(CH_4) = 60 \times 10^{-3}$ mm.

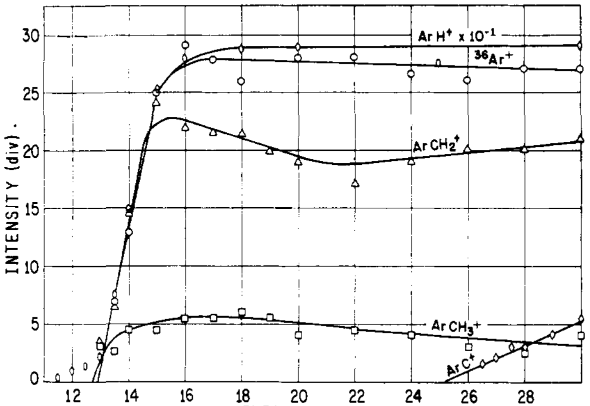

Fig. 2.—Ionization efficiency curves for argon–methane ion-molecule reaction products: $P_s(CH_4) = P_s(Ar)$ $P_s(\text{Total}) = 120 \times 10^{-3}$ mm.

B. Ionization Efficiency Curves and Reaction Mechanism Determinations.—The ion efficiency curves in Fig. 2 show that the products ArH^+, $ArCH_2^+$ and $ArCH_3^+$ all appear at about the same voltage as Ar^+, indicating the occurrence of the set

$$Ar^+ + CH_4 \longrightarrow (ArCH_4)^+ \longrightarrow ArH^+ + CH_3 \quad (1)$$

$$\longrightarrow ArCH_2^+ + H_2 \quad (2)$$

$$\longrightarrow ArCH_3^+ + H \quad (3)$$

of reactions in which $(ArCH_4)^+$ is a transient intermediate which is not observable. The analogous reactions were found with krypton–methane mixtures. We have no direct evidence for postulating in equation 2 the formation of H_2 rather than 2H, but H_2 would require significantly less energy and is more likely. The reaction for the formation of $ArCH_3^+$ is subject to some doubt as the intensity of this peak was quite low. We have no explanation for the tail on the foot of the ArH^+ curve except to note that the mass 41 peak is a combination of ArH^+ and $C_3H_5^+$ from methane. However, the $C_3H_5^+$ will not fully account for the tail as appearance potential measurements of pure methane indi-

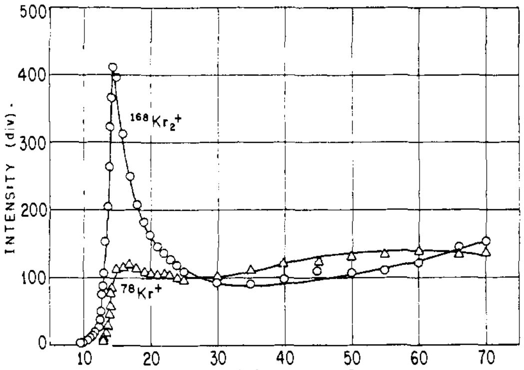

Fig. 3.—Krypton ionization efficiency curves: monoisotopic $I_{\mathrm{Kr}_2} = 282\ I_{^{78}\mathrm{Kr}^+}$, monoisotopic $I_{\mathrm{Kr}_{22}} = 2.75\ I_{^{168}\mathrm{Kr}_2^+}$.

cate that $C_3H_5^+$ probably comes from the primary ion, CH_2^+, which has an appearance potential only 0.2 volt below that of Ar^+.

As seen in Fig. 2 the appearance potential of ArC^+ is about 12 volts above the ionization potential of Ar^+. KrC^+ was found to be about 9 volts above Kr^+. The intensities of these ions were low, making the appearance potential measurements accurate to no more than ± 4 or 5 volts. However, the appearance potential measurements are in such a range as to suggest two possible reaction mechanisms: (1) reaction between CH^+ ion from methane and rare gas atoms or (2) reaction between an excited state rare gas ion and methane. We have no data that would determine which mechanism might be correct.

In conjunction with the rare gas–methane studies ionization efficiency curves were determined for the pure rare gases. The curve for krypton is shown in Fig. 3. Depending upon the treatment of the tailing, the appearance potential of Kr_2^+ is 0.6 to 1.5 volts below the ionization potential of Kr^+. We have no explanation for the tailing. Similar curves were obtained with argon except there was less tailing. The appearance potential of Ar_2^+ was about 1.7 volts below that of Ar^+. These data support the conclusion of Hornbeck and Molnar[3] that the diatomic ion is formed from a reaction between an excited state atom and a grouns state atom. However, our data differ from those of Hornbeck and Molnar in that we found the ratio of diatomic to atomic ions to increase with atomic weight whereas they found the opposite trend. We feel our data are the more reliable because our mass spectrometer allows a full resolution of the higher mass peaks while the resolution of the mass spectrometer used by Hornbeck and Molnar is such that the peaks of the diatomic ions are superimposed upon those of the monatomic ions. This low resolution makes it difficult to determine the intensities of the small diatomic peaks.

C. Charge Exchange Reactions.—Charge exchange reactions between rare gas ions and hydrocarbons have been observed previously. The decomposition of light paraffins by charge exchange with rare gas ions has been reported by Meisels, Hamill and Williams.[4] Rare gas ion reactions with ethylene were studied by Franklin and Field.[5] Melton[6] has studied the charge exchange reactions of argon and krypton ions with methane.

Since Melton already has studied the charge exchange reactions in argon–methane and krypton–methane mixtures and the primary purpose of this report was to study the ion-molecule reactions, no attempt was made to operate under conditions favorable for the study of charge exchange. The high pressures required to obtain sufficient intensities of ion-molecule reaction products for adequate study reduced the efficiency of collection and made it difficult to determine accurately which portion of the primary mass intensities from methane could be attributed to electron bombardment and which to charge exchange. However, sufficient data were obtained to allow a comparison with the reactions which Melton reported.

Charge exchange would be expected in the systems studied because the ionization potentials of both Kr (14.0 e.v.) and Ar (15.8 e.v.) are higher than that of CH_4 (13.12 e.v.)[7] but not so much higher as to make the required energy dissipation in such a reaction prohibitive. In all experiments with rare gas–methane mixtures the absolute intensities of the ions from methane declined markedly, smoothly and reproducibly as the pressure of rare gas was increased. We believe that this is an instrumental effect of unknown origin. Charge exchange reactions were indicated experimentally by an increase of intensity of some of the primary ions from methane with increased rare gas pressure. As shown in Tables I and II such an increase is noted in the mass 14 and 15 ions with the argon–methane mixtures and in the mass 15 and 16 ions in the krypton–methane mixtures indicating the charge exchange reactions

$$Ar^+ + CH_4 \longrightarrow Ar + H_2 + CH_2^+ \qquad (4)$$
$$\Delta H = -13 \text{ kcal./mole}$$

$$Ar^+ + CH_4 \longrightarrow Ar + H + CH_3^+ \qquad (5)$$
$$\Delta H = -32 \text{ kcal./mole}$$

$$Kr^+(^2P_{1/2}) + CH_4 \longrightarrow Kr + H + CH_3^+ \qquad (6)$$
$$\Delta H = -6 \text{ kcal./mole}$$

$$Kr^+ + CH_4 \longrightarrow Kr + CH_4^+ \qquad (7)$$
$$\Delta H = -20 \text{ kcal./mole}$$

A plot showing the increase of these charge exchange products with increase in rare gas pressure will be shown and discussed later. The formation of H_2 in equation 4 is indicated because the formation of 2H would require that the reaction be endothermic.

Melton[6] reports the observation of the reaction

$$Ar^+ + CH_4 \longrightarrow Ar + CH_4^+ \qquad (8)$$

in addition to the reactions which we observed. He states that the probability of this reaction is about the same as for reaction 4. We found no evidence of this reaction. Instead, as seen in Table I, our data show that mass 16 has about the

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[3] J. A. Hornbeck and J. P. Molnar, *Phys. Rev.*, **84**, 621 (1951).

[4] G. G. Meisels, W. H. Hamill and R. R. Williams, *J. Chem. Phys.*, **25**, 790 (1956); *J. Phys. Chem.*, **61**, 1456 (1957).

[5] J. L. Franklin and F. H. Field, *J. Am. Chem. Soc.* **83**, 3555 (1961).

[6] C. E. Melton, *J. Chem. Phys.*, **33**, 1594 (1960).

[7] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

same depression with added argon as masses 12 and 13, which we know for energetic reasons are not formed by charge exchange.

D. Rate Constant Determinations.—The reactions involving Ar^+ and CH_4 are given in equations 1–5. For these reactions the rate expression for the consumption of Ar^+ is

$$\ln (Ar^+/Ar_0^+) = -k(CH_4)\tau_{Ar^+} \qquad (9)$$

A similar expression may be written for krypton. τ_{Ar^+} is the ion chamber residence time of the reactant Ar^+ ions. Residence time can be calculated from the relation $\tau = (2dM/eE)^{1/2}$, d = distance from electron beam to ion exit electrode, M = mass and E = ionization chamber field strength. The bimolecular rate constant, k, is the sum of the rate constants of the individual reactions. Ar_0^+ is the intensity of argon ions that would have been measured had no reactions taken place and is equal to the sum of the measured intensities of Ar^+ and all the reaction product ions coming from Ar^+.

Equation 9 was used to calculate k, and individual rate constants were obtained by assuming that the ratio of an individual rate constant to the bimolecular rate constant is equal to the ratio of the intensity of an individual product ion to the sum of the product ions from Ar^+; *i.e.*

$$k_i = k(P_i^+/\Sigma P_i^+) \qquad (10)$$

The calculation of Ar_0^+ proved to be a difficult task for, in summing the intensities of the reaction products, estimates of the charge exchange products CH_2^+ and CH_3^+ had to be made. These charge exchange reactions were the predominant reactions for the consumption of argon ions representing about 80% of the total Ar^+ formed. Since it was possible that the CH_2^+ and CH_3^+ ions produced by charge exchange could undergo further ion–molecule reactions, it was necessary to include these ion–molecule product intensities in the calculation. In our calculations the following were chosen as representing the ion–molecule reactions of methane

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \qquad (11)$$
$$CH^+ + CH_4 \longrightarrow C_2H_2^+ + H_2 + H \qquad (12)$$
$$CH_2^+ + CH_4 \longrightarrow C_2H_3^+ + H_2 + H \qquad (13)$$
$$CH_2^+ + CH_4 \longrightarrow C_2H_4^+ + H_2 \qquad (14)$$
$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \qquad (15)$$

Reactions 11 and 15 had been reported previously.[8,9] Reactions 12, 13 and 14 were based on appearance potential measurements made on methane in these Laboratories. These are difficult measurements and the reactions postulated from them are open to some question, especially for reactions 12 and 13, for the ionization efficiency curves of $C_2H_2^+$ and $C_2H_3^+$ indicated that these ions are probably products of more than one reaction. All higher order reactions in methane were assumed to be negligible.

By assuming the reactions of equations 11–15, the original intensities of CH_2^+ and CH_3^+ may be obtained as

$$I_{14}^0 = I_{14} + I_{27} + I_{28} \qquad (16)$$

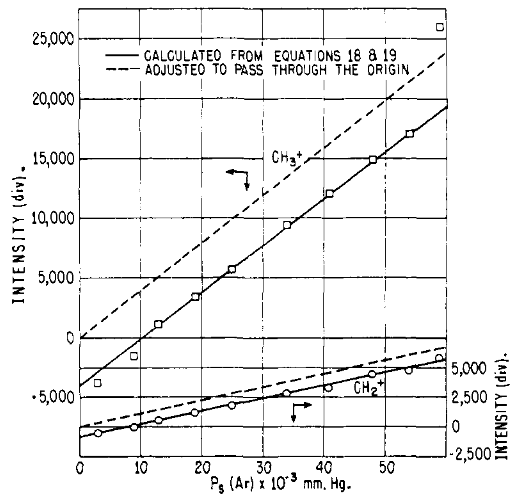

Fig. 4.—Argon–methane charge exchange reaction product intensity plots: $P_s(CH_4) = 60 \times 10^{-3}$ mm.

and

$$I_{15}^0 = I_{15} + I_{29} \qquad (17)$$

The separation of I_{14}^0 and I_{15}^0 into those portions formed by electron bombardment of methane and those due to Ar^+–CH_4 charge exchange could not be done in a straightforward manner because the methane primary ion intensities were depressed as rare gas was added. Estimates of the contributions from electron bombardment of methane to I_{14}^0 and I_{15}^0 were made using I_{12} as a measure of the amount of CH_4 primary ions formed by electron bombardment. Mass 12 was used for this purpose because it may be demonstrated from energetic arguments that C^+ is not involved in charge exchange. Thus those portions of I_{14}^0 and I_{15}^0 due to charge exchange were calculated by

$$I_{14}^0 \text{ (charge exchange)} = I_{14}^0 \text{ (measured)}$$
$$- I_{12} \text{ (measured)} \left(\frac{I_{14}^0}{I_{12}}\right) \text{ (pure methane)} \qquad (18)$$
$$I_{15}^0 \text{ (charge exchange)} = I_{15}^0 \text{ (measured)}$$
$$- I_{12} \text{ (measured)} \left(\frac{I_{15}^0}{I_{12}}\right) \text{ pure methane)} \qquad (19)$$

Intensities of the charge exchange reaction products as calculated in equations 18 and 19 are shown in Fig. 4 to be remarkably linear with argon pressure. Despite this excellent linearity, the defined line did not pass through the origin but instead indicated negative intensities at low argon pressures. As it was felt that the slopes of these lines were more meaningful than the absolute intensities of the calculated values, constants were added to equations 18 and 19 to force the lines through the origin. Values for the charge exchange intensities of CH_2^+ and CH_3^+ were taken from the dotted lines of Fig. 4 for use in the calculation of Ar_0^+.

For the krypton–methane mixtures the results as calculated for the charge exchange products CH_3^+ and CH_4^+ from equations analogous to 18 and 19 passed through the origin in a plot similar to Fig. 4 making the addition of constants to these equations unnecessary.

Individual rate constants are given in Table IV for ion–molecule reactions and Table V for charge exchange reactions. Each value reported is an

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(8) V. L. Tal'roze and A. K. Lyubimova, *Doklady Akad. Nauk S.S.S.R.*, **86**, 909 (1952).

(9) D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **23**, 1353 (1955).

TABLE IV

AVERAGE RATE CONSTANTS FOR ION-MOLECULE REACTIONS AT E = 12.5 VOLT/CM.

Reactions	k (cc./mol. sec.)
$Ar^+ + CH_4 \longrightarrow ArH^+ + CH_3$	0.20×10^{-10}
$Ar^+ + CH_4 \longrightarrow ArCH_2^+ + H_2$	$.008 \times 10^{-10}$
$Ar^+ + CH_4 \longrightarrow ArCH_3^+ + H$	$.003 \times 10^{-10}$
$Kr^+ + CH_4 \longrightarrow KrH^+ + CH_3$	$.122 \times 10^{-10}$
$Kr^+ + CH_4 \longrightarrow KrCH_2^+ + H_2$	$.010 \times 10^{-10}$
$Kr^+ + CH_4 \longrightarrow KrCH_3^+ + H$	$.030 \times 10^{-10}$
[a]$Xe^+ + CH_4 \longrightarrow XeH^+ + CH_3$	$.38 \times 10^{-10}$
$Xe^+ + CH_4 \longrightarrow XeCH_2^+ + H_2$	$.0045 \times 10^{-10}$
$Xe^+ + CH_4 \longrightarrow XeCH_3^+ + H$	$.022 \times 10^{-10}$

[a] Taken from ref. 1.

TABLE V

AVERAGE RATE CONSTANTS FOR CHARGE EXCHANGE REACTIONS AT E = 12.5 VOLT/CM.

Reaction	k (cc./mole sec.)
$Ar^+ + CH_4 \longrightarrow Ar + H_2 + CH_2^+$	2.3×10^{-10}
$Ar^+ + CH_4 \longrightarrow Ar + H + CH_3^+$	9.1×10^{-10}
$Kr^+ + CH_4 \longrightarrow Kr + H + CH_3^+$	4.9×10^{-10}
$Kr^+ + CH_4 \longrightarrow Kr + CH_4^+$	7.4×10^{-10}

average of 14 readings at different rare gas pressures. Agreements among replicate results were easily within a factor of 2. Previously obtained xenon–methane ion–molecule reaction rate constants are included in Table IV for comparative purposes.

Rate constants for the ion–molecule reactions forming RH^+ and RCH_2^+, where R represents a rare gas atom, do not vary significantly with rare gas species, but the rate constant for the formation of $ArCH_3^+$ is an order of magnitude smaller than those for the formation of $KrCH_3^+$ and $XeCH_3^+$. Our values of 2.3×10^{-10} and 9.1×10^{-10} cc./mole sec. for rate constants for the formation of CH_2^+ and CH_3^+, respectively, by charge exchange in argon–methane mixtures compare with the values obtained by Melton of 3×10^{-10} and 16×10^{-10}.

Acknowledgment.—We wish to acknowledge the able assistance of Mr. W. C. Gieger who performed the experimental work reported in this paper.

[CONTRIBUTION NO. 293, RESEARCH AND DEVELOPMENT DIVISION, JACKSON LABORATORY, ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

Preparation, Trapping, Identification and Chemistry of Captive Perfluoroalkyl Radicals. I

BY S. V. R. MASTRANGELO

RECEIVED SEPTEMBER 11, 1961

Perfluoroalkyl radicals were produced by passage of a radio frequency discharge through C_2F_6 and $C-C_4F_8$ gas and were trapped on a liquid nitrogen finger. They were identified by chlorination and bromination of the deposits followed by analysis of the products with gas chromatographic and mass spectrometric techniques. Warm-up products of the captive radicals and reaction products with tetrafluoroethylene also were identified. Identification of the products of reaction of the captive radicals with Cl_2, Br_2 and TFE, as well as with themselves on warming, showed that the radicals present in the blue deposit were CF_2: while those in the red deposit were CF_3.

Introduction

The stabilization of free radicals by trapping them at low temperatures[1] provides the opportunity to study at leisure the chemistry and physics of these normally transient and highly reactive intermediates. Several recent articles[2–4] present excellent reviews of this rapidly growing field. Progress in the study of the chemistry of these species also has been made in recent years. For example, Milligan and Pimentel[5] reported that the CH_2 radical produced by photolysis of diazomethane in solid argon and nitrogen at 20°K. reacts at 35°K. to form methane, ethylene, propylene, cyclopropane and polyethylene. A more complete survey of low temperature chemistry is given by Ralph Klein.[6]

In the present publication, a report is given of the method of preparation, trapping and identification of captive CF_2: and $CF_3\cdot$ radicals. Some physical and chemical properties of the trapped species are described. Included are halogen and fluoroölefin addition and radical transformation reactions which are accompanied by striking color changes.

Apparatus and Procedure

I. **Apparatus.**—The apparatus used for production of fluorocarbon radicals is shown schematically in Fig. 1. Gas from the cylinder marked "parent" was bled from two Hoke needle valves through a 3-inch diameter coil of 1/8-inch copper tubing (to restrict the flow) preceded by a Maxisafe vacuum gauge. The rate of flow was calibrated against the pressure reading on this gauge. The pressures downstream from the copper coil were read on a McLeod gauge. These ranged from 0.1 to several mm.

The radical trap was 160 mm. in length from the top of the 45/50 standard joint and had an outside diameter of 55 mm. The cold finger o.d. was 25 mm. On some occasions, a rectangular finger was used for obtaining visible spectra. The use of vertical inlet and outlet tubes with stopcocks

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[1] See, for example, F. O. Rice and M. Freamo, *J. Am. Chem. Soc.*, **73**, 5529 (1951); **75**, 548 (1953); F. O. Rice and C. J. Grelecki, *ibid.*, **79**, 1880; 2679 (1957); *J. Phys. Chem.*, **61**, 824, 830 (1957).

[2] H. P. Broida, *Ann. N. Y. Acad. Sci.*, **67**, 530 (1957).

[3] H. P. Broida, "Endeavour," XVII, No. 68, 208 (1958).

[4] Arnold M. Bass and H. P. Broida, "Formation and Trapping of Free Radicals," Academic Press, Inc., New York, N. Y., 1960.

[5] D. E. Milligan and G. C. Pimentel, *J. Chem. Phys.*, **29**, 1405 (1955).

[6] Arnold M. Bass and H. P. Broida, "Stabilization of Free Radicals at Low Temperatures," U. S. Department of Commerce, N.B.S. Monograph 12 (1960).