$$CH_4(g) \qquad C_2H_8(g) \qquad C_3H_8(g)$$

$$C_4H_{10} \rightarrow C_4H_{10}(ads) \underset{slow}{\overset{fast}{\rightleftarrows}} CH_a + C_2H_b + C_3H_c$$

$$C_4H_m + (10-m)H$$

the kinetics of the cracking reaction may be controlled by the rate of hydrogenation of the $C_3$ species. The more rapid C–H bond rupture and the higher concentration of hydrogen on the surface accounts for the greater ease of cracking of butane than propane. The fact that the adsorbed hydrocarbon residue is more strongly held in the former case suggests that the relative rate of hydrogenation of surface species of this type increases with the molecular weight of the fragments. As the surface becomes progressively poisoned by residues, increasing proportions of $C_2$ and $C_3$ desorption products appear in the gas phase, as shown in Figure 6. From a study of the rate of forma-tion of methane by the hydrogenation of hydrocarbon radicals from nickel, Galwey[11] concludes that the attack of surface species by hydrogen atoms controls the kinetics of the decomposition of unsaturated hydrocarbons. In addition, the rate of methane formation was generally first order in hydrogen pressure. Similar investigations of the rates of hydrogenation of radicals formed from the dissociative adsorption of an homologous series of saturated hydrocarbons and of the kinetics of hydrocracking as a function of hydrogen pressure would shed further light on the mechanism of these complex hydrocarbon decomposition reactions.

(11) A. K. Galwey, *Proc. Roy. Soc.* (London), A271, 218 (1963).

# Ion–Molecule Reactions between Rare Gas Ions and Methane[1]

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*The reactions of $He^+$, $Ne^+$, $Ar^+$, $Kr^+$, and $Xe^+$ with methane have been studied over an energy range of 2–200 e.v. The yields of the fragment ions of methane correspond well to the findings of other investigators working at both thermal and higher energies and are found to vary only slightly with the energy of the incident ions. The relative cross sections show some deviations from the predictions of the theory of ion–molecule reactions. Exothermic reactions show an initially decreasing cross section as the kinetic energy of the encounter increases. At higher energies the cross sections level off and tend to increase. $E^{-1/2}$ energy dependence is followed only in the $He^+$–$CH_4$ reactions at energies below 10 e.v. Endothermic reaction cross sections are very low and show slight increases with energy over the entire range studied.*

## Introduction

For almost 40 years, methane has been subjected to irradiation by just about everything from $\gamma$-rays to low velocity heavy particles.[3] Experiments have progressed from the original $\alpha$-radiation study in which the pressure changes in a mixture of methane and radon were taken as evidence of reaction[4] to mass spectrometric analyses of the ionic fragments produced when methane was bombarded by various atomic and molecular ions.[5]

Mass spectrometric evidence has demonstrated that the polymerization observed in the radiolysis occurs to a large extent through ion–molecule reactions.[6,7] The irradiation of an argon–methane mixture by X-rays and 1.5 Mev. electrons yielded the same major products as the $\alpha$-radiation.[8] Mass spectrometric analysis revealed that the major contribution of the argon ions produced by the irradiation was $Ar^+ + CH_4 = Ar + CH_3^+ + H$. Additional work[9] using krypton indicated two almost equally probable charge-exchange reactions

$$Kr^+ + CH_4 = Kr + CH_4^+$$
$$Kr^+ + CH_4 = Kr + CH_3^+ + H$$
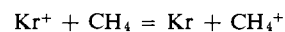
These same systems were studied in a "high" pressure mass spectrometer, and cross sections for the various reactions, including the production of $CH_4^+$ and $CH_2^+$ from the argon–methane mixture, were reported.[10]

Xenon–methane mixtures have also been studied in "high" pressure mass spectrometers[11,12] with interesting results. In addition to the usual $CH_n^+$ fragments, small amounts of ionic complexes, $XeH^+$ and $XeCH_n^+$

(1) This work was done under the auspices of the United States Atomic Energy Commission.

(2) Lever Brothers Foundation Fellow.

(3) For a review of methane radiolyses see S. C. Lind, "Radiation Chemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1961, p. 97.

(4) W. Mund and W. Koch, *Bull. Soc. Chim. Belges*, 34, 121 (1925).

(5) J. B. Homer, R. S. Lehrle, J. C. Robb, M. Takahasi, and D. W. Thomas, "Advances in Mass Spectrometry," Vol. 2, R. M. Elliot, Ed., Pergamon Press Inc., New York, N. Y., 1963, p. 503.

(6) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, 23, 1353 (1955); 24, 926 (1956).

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(8) G. G. Meisels, W. H. Hamill, and R. R. Williams Jr., *J. Chem. Phys.*, 25, 790 (1956).

(9) G. G. Meisels W. H. Hamill, and R. R. Williams, Jr., *J. Phys. Chem.*, 61, 1456 (1957).

(10) C. E. Melton, *J. Chem. Phys.*, 33, 647 (1960).

(11) F. H. Field and J. L. Franklin, *J. Am. Chem. Soc.*, 83, 4509 (1961); see also ref. 5, p. 484.

(12) S. Wexler, *J. Am. Chem. Soc.*, 85, 272 (1963).

($n$ = 0, 1, . . ., 4), were observed. Field and Franklin,[11] from an analysis of their data, came to the surprising conclusion that none of the $CH_n^+$ fragments were formed by charge exchange between $Xe^+$ and $CH_4$. Meisels,[13] on the other hand, in a study of xenon sensitization of the radiolysis of methane, finds charge exchange between $Xe^+$ in the $^2P_{1/2}$ state and $CH_4$ the most probable explanation for the results. Talrose[14] has actually observed the reaction in his instrument, $Xe^+ + CH_4 = Xe + CH_4^+$, and reports evidence that it is due to the excited $Xe^+ (^2P_{1/2})$ ion.[15]

When Lindholm began operation of his tandem mass spectrometer in which he could study the charge exchange of positive ions and neutral species free from the obscuring and confusing effects of the electron beam, the reactions of 500-v. $Ne^+$, $Ar^+$, and $Kr^+$ ions with methane were included.[16] Cross sections for the formation of the various fragment ions of methane were measured and indicated a tendency toward greater fragmentation as the rare gas ion was varied from $Kr^+$ to $Ne^+$. A recent investigation, in which methane was bombarded by $Ar^+$ and $He^+$ ions at various energies up to 2000 e.v. using a time-of-flight spectrometer modified to permit positive-ion bombardment, indicates that no drastic changes occur in the yields of the various ions as the energy of the bombarding ion is varied from 35 to 2000 e.v.[5] The products observed, in order of decreasing yield, with $Ar^+$ were $CH_3^+$ > $CH_2^+$ > $CH^+$ ≈ $CH_4^+$ > $C^+$ and with $He^+$ were $CH_2^+$ > $CH^+$ > $CH_3^+$ ≈ $C^+$ > $CH_4^+$. The authors concluded that the relative importance of the various reactions is determined solely by the ionization potentials of the species involved. Translational energy is thought to be responsible for only minor changes in the fragmentation pattern of the methane.

It appears that at one time or another, various investigators have endeavored to study one or more of the reactions between rare gas ions and methane. The majority of the work reported has been carried out in conventional or "high" pressure mass spectrometers in which the excited and/or ionized rare gas is assumed to have essentially thermal energies. The technique of positive-ion bombardment has been used in two cases (He and Ar) over an energy range of 35–2000 v. and in three cases (Ne, Ar, and Kr) at an energy of 500 e.v. It was thought that it would be worthwhile to investigate the reactions of methane with the ions of all of the rare gases, with the exception of radon, in a two-stage mass spectrometer over the interesting energy range of 2 to 200 e.v. in order to obtain an organized and consistent picture of these reactions.

## Experimental

The two-stage mass spectrometer used in these investigations has been described elsewhere.[17] Briefly, it consists of a pair of mass spectrometers in tandem. A small, 180°, 1-cm. radius mass spectrometer (a modified Diatron manufactured by Consolidated Electrodynamics Corp.) ionizes and selects the primary ion

beam which is then focused, accelerated or decelerated to the desired energy, and refocused into the reaction chamber containing the target gas (methane in this experiment). Ionic reaction products are extracted at an angle of 90° to the primary ion beam and analyzed by the second mass spectrometer—an 8-in. radius of curvature, 60°-sector instrument.

This geometry permits detection of charge-exchange reactions while discriminating against reactions involving momentum transfer. However, in order to detect secondary ions from momentum transfer reactions, z-direction deflectors have been added to the secondary mass spectrometer, ion-accelerating lens. (The primary ion beam crosses the reaction chamber along the z-coordinate, i.e., parallel to the long dimension of the exit slit.) These deflectors can be adjusted to counteract the z-direction momentum transferred from primary ions to secondary products permitting the product ions to reach the detector. The ability of the z-deflectors to cancel the z-direction momentum is demonstrated by the fact that mass-transfer products from the reactions between nitrogen ions and carbon tetrachloride have been observed[17] and that the primary ion beam itself can be focused on the secondary mass spectrometer detector by using the z-deflectors along with higher-than-normal repeller voltages in the reaction chamber.

Normal operating intensities of the primary rare gas ion beams were in the range of $10^{-12}$ to $10^{-11}$ amp. Secondary ion intensities were 1000 to over 200,000 c.p.m., depending upon the reaction cross sections involved. The pressure measured in the vacuum manifold surrounding the reaction chamber was 1–2 × $10^{-5}$ torr. From experiments involving reactions with known cross section, the pressure in the reaction chamber has been estimated to be roughly a factor of 10 to 100 greater, or $10^{-4}$ to $10^{-3}$ torr.

The gases used in this experiment were research grade purchased from the following companies: methane from Phillips Petroleum Co., argon from Linde Co., helium from Airco Co., and the other rare gases from The Matheson Co.

The general procedure for studying the reactions was the following. The rare gas was introduced into the primary mass spectrometer chamber. The gas flow rate and filament emission were adjusted so that the primary ion current, measured on the collector in the reaction chamber, was normally between $10^{-12}$ and $10^{-11}$ amp. Measurements of the primary ion current were made at several beam energies and the averaged results of several runs were plotted. Each rare gas gave its own characteristic curve which was reproducible.

The target gas was then admitted to the reaction chamber and the spectra of the reaction products were recorded for various beam energies over the 2–200-e.v. range. The intensities of the major product ions were obtained by focusing each secondary peak onto the electron multiplier detector and counting the amplified pulses.

Gas pressures in the inlet reservoirs were kept intentionally high to eliminate, as much as possible, any decay in the leak rates. Granville–Phillips adjustable leaks permitted accurate and sensitive control. The primary beam intensity was essentially constant during a run of several hours' duration. The secondary

(13) G. G. Meisels, *J. Chem. Phys.*, 31, 284 (199).
(14) V. L. Talrose, *Pure Appl. Chem.*, 5, 455 (1962).
(15) G. V. Karachevtsev, M. I. Markin, and V. L. Talrose, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1528 (1961).
(16) E. Lindholm, *Z. Naturforsch.*, 9a, 535 (1954).
(17) E. R. Weiner, G. R. Hertel, and W. S. Koski, *J. Am. Chem. Soc.*, 86, 788 (1964).

Table I

| No. | Reaction | $\Delta E^a$ | | |
|---|---|---|---|---|
| | | $^2P_{3/2}$ | $^2S$ | $^2P_{1/2}$ |
| 1 | $Xe^+ + CH_4 = Xe + CH_4^+$ | +0.97 | | -0.34 |
| 2 | $= Xe + H + CH_3^+$ | +2.27 | | +0.96 |
| 3 | $Kr^+ + CH_4 = Kr + CH_4^+$ | -0.90 | | -1.57 |
| 4 | $= Kr + H + CH_3^+$ | +0.40 | | -0.27 |
| 5 | $= Kr + H_2 + CH_2^+$ | +1.60 | | +0.93 |
| 6 | $Ar^+ + CH_4 = Ar + CH_4^+$ | -2.65 | | -2.84 |
| 7 | $= Ar + H + CH_3^+$ | -1.35 | | -1.54 |
| 8 | $= Ar + H_2 + CH_2^+$ | -0.15 | | -0.34 |
| 9 | $= Ar + 2H + CH_2^+$ | +4.35 | | +4.16 |
| 10 | $Ne^+ + CH_4 = Ne + H_2 + CH_2^+$ | -5.96 | | -6.06 |
| 11 | $= Ne + 2H + CH_2^+$ | -1.46 | | -1.56 |
| 12 | $= Ne + 3H(?) + CH^+$ | +1.44 | | +1.34 |
| 13 | $He^+ + CH_4 = He + H + CH_3^+$ | | -10.18 | |
| 14 | $= He + H_2 + CH_2^+$ | | -8.98 | |
| 15 | $= He + 2H + CH_2^+$ | | -4.48 | |
| 16 | $= He + 3H(?) + CH^+$ | | -1.58 | |
| 17 | $= He + 4H(?) + C^+$ | | +2.22 | |
| 18 | $Xe^+ + CH_4 = XeCH_3^+ + H$ | Only trace amounts | | |
| 19 | $Kr^+ + CH_4 = KrCH_2^+ + (2H, H_2)$ | of these ions | | |
| 20 | $He^+ + CH_4 = HeH^+ + CH_3$ | were observed | | |

$a$ Calculated from "preferred" appearance potentials as given by D. P. Stevenson and D. O. Schissler in "The Chemical and Biological Action of Radiation," Vol. 5, Academic Press Inc., New York, N. Y., 1961, p. 202, and from ionization potentials of the rare gases listed in ref. 22.

leak rate typically decreased at an approximate rate of 2%/hr. The effect of this decrease was minimized by reversing the order of collecting data on subsequent runs and averaging.

In each of the experiments, the secondary leak rate was adjusted so that the pressure increase owing to the methane was approximately the same. In this way, it was possible to compare the relative cross sections of the various reactions studied without the need of applying large and uncertain correction factors. These relative cross sections, calculated as the intensity of the secondary beam divided by the intensity of the primary beam measured at the same primary beam energy, are plotted as functions of the energy. Each cross section was measured at least four times and the results were averaged. Deviations ranged up to 15% for most reactions—slightly higher for the Ne curves.

## Discussion of Results

Table I is a list of the reactions observed and the energy defects of these reactions assuming that ground states of the methane ion fragments are involved and that only the $^2S$ state of $He^+$ and the $^2P_{3/2}$ and $^2P_{1/2}$ states of $Ne^+$, $Ar^+$, $Kr^+$, and $Xe^+$ are present in the primary bombarding beams. The appearance potentials (AP) for the fragment ions from methane have been measured many times and are compiled by Krauss, et al.,[18] and Field and Franklin.[19] For the purpose of calculating the $\Delta E$ values of the reactions in Table I, the "preferred value," as given by Field and Franklin,[19] of the AP values of the methane ion fragments and the IP (ionization potentials) values of the rare gases were used.

The relative cross sections are plotted as functions of the incident ion energy in Figures 1–5. Variation with energy is quite apparent, and, for each of the exo-

thermic reactions in Table I, with the exception of those involving $Ne^+$ ions, the cross section initially decreases as the energy increases. The curves of all endothermic reactions increase slowly with energy over the entire range studied.

$Xe^+$–$CH_4$ Reactions. The only exothermic reaction that can be written for this system is reaction 1 between $Xe^+$ ions in the $^2P_{1/2}$ state and methane. Endothermic reaction 2 requires at least 0.96 e.v. of energy which corresponds to a $Xe^+$ ion with about 9 e.v. of kinetic energy in the laboratory coordinate system. However, $CH_3^+$ ions were observed when the bombarding $Xe^+$ beam had an energy as low as 2 e.v. Although there is a 1- or 2-v. uncertainty at the low primary ion energies,[17] it is not enough to account for the 7-v. discrepancy observed. It is possible that there are excited $Xe^+$ ions present in the primary beam which could supply the necessary energy and could account for the small amounts of $CH_3^+$ present below the expected threshold of 9 e.v. A trace of a complex ion, $XeCH_3^+$, was observed. This ion is the most abundant $XeCH_n^+$ ion reported by investigators using "high" pressure spectrometers to study xenon–methane mixtures.[11,12] Greater sensitivity would undoubtedly have permitted detection of the other complex ions in our instrument.

$Kr^+$–$CH_4$ Reactions. Cross sections for the production of both $CH_4^+$ and $CH_3^+$ are large and display the behavior of exothermic reactions (Figure 2). Previous investigators[9,10] have observed reactions 3 and 4 in conventional or "high" pressure instruments but did not report any evidence of complex ion formation.[19a] An ion peak was observed in this experiment at mass 98, corresponding to $KrCH_2^+$ (reaction 19), indicating that complexes similar to those seen in the $Xe^+$–$CH_4$ reactions are formed. Again, the limit of our sensitivity prevented more detailed study of the complex, and

(18) M. Krauss, A. L. Wahrhaftig, and H. Eyring, Ann. Rev. Nucl. Sci., 5, 241 (1955).

(19) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press Inc., New York, N. Y., 1957, pp. 247–251.

(19a) Note Added in Proof. F. H. Field, H. N. Head, and J. L. Franklin, J. Am. Chem. Soc., 84, 1118 (1962), have studied the $Kr^+$–$CH_4$ and $Ar^+$–$CH_4$ reactions and reported observation of the complexes $KrCH_n^+$ and $ArCH_n^+$.
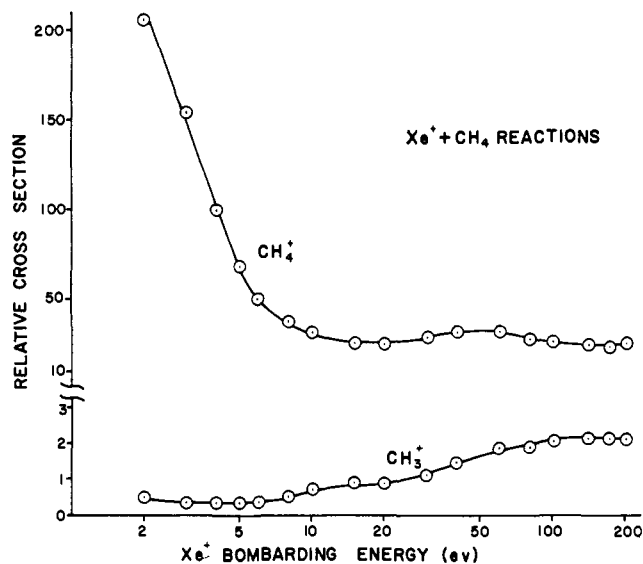
Figure 1. Relative cross sections of reactions between $Xe^+$ ions and methane as a function of $Xe^+$ energy.
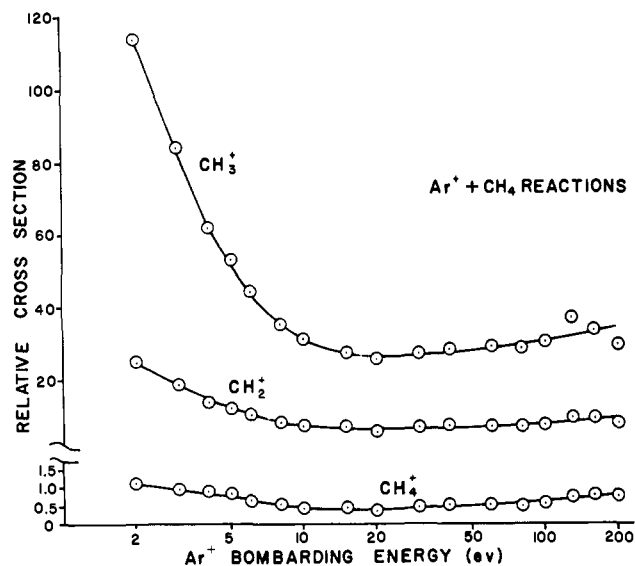


Figure 3. Relative cross sections of reactions between $Ar^+$ ions and methane as a function of $Ar^+$ energy.
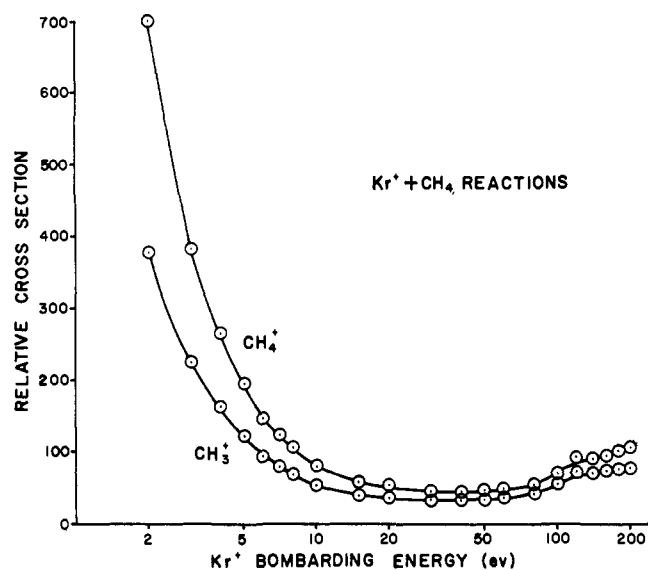


Figure 2. Relative cross sections of reactions between $Kr^+$ ions and methane as a function of $Kr^+$ energy.
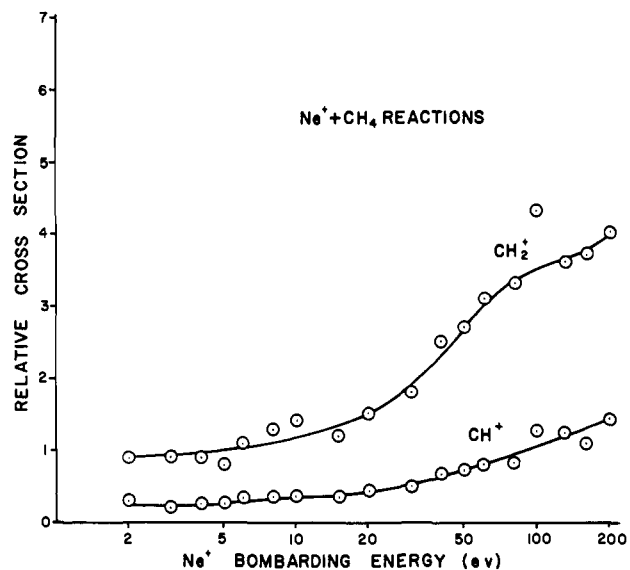


Figure 4. Relative cross sections of reactions between $Ne^+$ ions and methane as a function of $Ne^+$ energy.

there is a good possibility that $KrCH_2^+$ is only the most abundant of the entire $KrCH_n^+$ group.

Endothermic reaction 5 was observed, but the yield of $CH_2^+$ was very low.

*$Ar^+-CH_4$ Reactions.* Reactions 6–8 are all exothermic and were observed. From the energy defects, it can be seen that the $CH_4^+$ ion is produced with more than enough excess energy to undergo decomposition to $CH_3^+$ and H. According to Langer, *et al.*,[20] the bond strength of $CH_3^+$ is rather large ($D(CH_2^+-H) = 5.54$ e.v.), and thus one would not expect decomposition of the $CH_3^+$ formed in reaction 7 since the excess energy is less than 2 e.v. This is compatible with the observation that $CH_3^+$ is the most abundant ion present.

(20) A. Langer, J. A. Hipple, and D. P. Stevenson, *J. Chem. Phys.*, **22**, 1836 (1954).
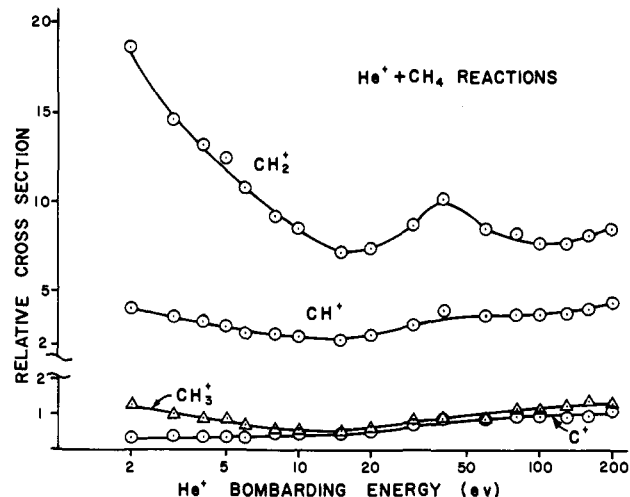


Figure 5. Relative cross sections of reactions between $He^+$ ions and methane as a function of $He^+$ energy.

No evidence of any complex ions ($ArCH_n^+$) was found.

*Ne$^+$–CH$_4$ Reactions.* The cross sections of all reactions between neon ions and methane appear to be very low. Only two ions, $CH_2^+$ and $CH^+$, were detected. The cross sections for both ions followed the typical behavior of endothermic reactions. According to the energy defects, however, $CH_2^+$ should be produced in an exothermic process. The same behavior in the Ne$^+$ ion reactions with ammonia was observed by us previously.[21] Lindholm's values for the cross sections of these same reactions of Ne$^+$, Ar$^+$, and Kr$^+$ ions at 500-e.v. energy with both ammonia and methane reflect the same behavior.[16] On the other hand, our work on bombardment of pentaborane-9[22] and of carbon tetrachloride[23] did not reveal any anomalously low cross sections of the Ne$^+$ reactions.

It is possible that the $CH_2^+$ ion can be formed only in an excited state, and thus the energy requirements are quite different from those listed in Table I. This would mean that comparable requirements restrict NH$^+$ formation in the ammonia reaction. Such a coincidence seems improbable. Also, if $CH_2^+$ could only be formed in an excited state, one would expect very little of it in the Ar$^+$ reactions where the energy available is much less. Another possibility is that Ne$^+$ ions cannot form an intimate collision complex and thus the ions we observe arise solely from dissociative charge-exchange reactions which are expected to have very low cross sections in this energy region. This implies that collision complexes are formed in the reactions of methane with the other rare gases. That this is decidedly possible is evident from the observation of such ions as $XeCH_3^+$ and $KrCH_2^+$.

*He$^+$–CH$_4$ Reactions.* The recombination energy of the helium ion is so high that only the reaction producing C$^+$ is endothermic. The source of the small maximum in the $CH_2^+$ cross section curve at 40 e.v. is unknown. It may be attributable to a near-resonant condition of He$^+$ with some excited state of the $CH_2^+$ ion and thus a high charge-exchange cross section in this region.

A trace of HeH$^+$ was observed, which was surprising in view of the fact that none of the other rare gas hydride ions were seen. von Koch and Friedman[24] have studied the formation of HeH$^+$ from He–H$_2$ and He–CH$_4$ mixtures. They find HeH$^+$ from a He–CH$_4$ mixture is about 1% as abundant as that from a He–H$_2$ mixture. The main reactions proposed involve proton exchange from methane fragment ions to helium atoms. In our experiment, this would require a secondary reaction between a product of an initial He$^+$–CH$_4$ reaction and a neutral helium atom in the reaction chamber. This would suggest that the cross section of such a reaction was relatively high in contradiction to the findings mentioned above. An alternative reaction path would be direct formation of the HeH$^+$ from an encounter of a He$^+$ ion and a methane molecule, either through a hydrogen atom transfer or a transient complex of He$^+$ and CH$_4$ which decomposed

to give the observed HeH$^+$. The cross section for this process would be very low since only a trace of HeH$^+$ was observed. This is more compatible with the previous observations.[24]

The question of the type of encounter taking place in these reactions (charge exchange *vs.* ion–molecule complex formation) requires comment. According to the charge-exchange theory as developed by Rapp and Fracis,[25] the Massey–Burhop criterion[26] is valid for asymmetric charge-exchange reactions in what is termed the "intermediate velocity" region. The region of transition from this intermediate velocity region to the low velocity region is found to be $10^5 < \mu^{1/2}v < 10^6$, where $\mu$ is the reduced mass of the colliding species in a.m.u. and $v$ is the relative velocity in cm./sec. The procedure for extrapolation to the low velocity region, in the case of symmetrical charge exchange, by Rapp and Fracis uses the Gioumousis and Stevenson approach[27] and results in an expression for the cross section which differs from the Gioumousis and Stevenson expression for the microscopic cross section by a probability factor only. They appear to be saying that in the low velocity region the important collisions are those involving intimate encounters between the two reacting species since the Gioumousis and Stevenson theory of ion–molecule reactions assumes collision complex formation. For the case of asymmetric, nonresonant charge exchange in the low velocity region, Rapp and Fracis state that the main unknown is the probability of charge exchange for impact collisions and that the behavior of such cross section curves "remains unsettled."

Rosenstock[28] has reviewed the theoretical treatment of ion–molecule reactions and included a consideration of angular momentum. The assumptions made are those of a collision complex and an $r^{-4}$ interaction potential. The predicted macroscopic cross sections have an $E^{-1/2}$ dependence where $E$ is the kinetic energy of the incident ion.

A recent paper by Light[29] attacks the problem using "phase space" terminology but appears to contain the same basic assumptions incorporated by Rosenstock. Calculation of a model system illustrates the effect on the cross section of changes in exothermicity, polarizability, and the reduced mass of the system.

A few simple calculations show that the energy range studied in this experiment lies within the "intermediate velocity" region, as defined by Rapp and Fracis, except for a very small overlap into the "transition" region in the cases of Xe and Kr. Thus, the Massey–Burhop criterion is expected to be valid. A glance at the curves in Figures 1–5 is enough to indicate that a multitude of electronically and vibrationally excited states of the product ions must be invoked to account for the "resonance" shapes of many of the curves.

While this explanation is certainly a possibility, the alternative of assuming that the dominant reactions

(21) G. R. Hertel and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 1683 (1964).
(22) G. R. Hertel and W. S. Koski, *ibid.*, **87**, 404 (1965).
(23) Unpublished data.
(24) H. von Koch and L. Friedman, *J. Chem. Phys.*, **38**, 1115 (1963).

(25) D. Rapp and W. E. Fracis, *ibid.*, **37**, 2631 (1962).
(26) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952, p. 514.
(27) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).
(28) H. M. Rosenstock, "Ion–Molecule Reactions," A.E.C. Report No. JLI-650-3-7, UC-23, Isotopes—Industrial Technology TID-4500, 1959, unpublished.
(29) J. C. Light, *J. Chem. Phys.*, **40**, 3221 (1964).

(in the region below 10 e.v.) involve intermediate complex formation is equally valid and much more attractive.

Qualitatively, the curves in Figures 1–5 show the general pattern expected from the ion–molecule theory with respect to the effects of polarizability, reduced mass, and exothermicity vs. endothermicity (with the exception of the $Ne^+$ reactions). Considering that the one exothermic $Xe^+-CH_4$ reaction requires $Xe^+$ ions in the $^2P_{1/2}$ state and that the reaction is not as exothermic as the corresponding $Kr^+-CH_4$ reaction, the relative cross sections are compatible with the predictions. The effects of lower polarizability of the neutral products and of lower reduced mass are more obvious in the $Ar^+-CH_4$ and $He^+-CH_4$ reactions. Additional support for the ion–molecule interpretation is the presence of the complex ions $XeCH_3^+$ and $KrCH_2^+$ at low primary beam energies.

As the kinetic energy of the incident ion surpasses roughly 10 e.v., the cross sections become less dependent upon the energy and in most cases begin to increase slowly with energy. The cause of this behavior is attributed to a change in the basic type of the dominant encounters occurring. At the higher energies, and thus velocities, of the ions there is less chance of complex formation and a corresponding increase in the importance of charge-exchange encounters.

No matter which theoretical treatment one accepts (ion–molecule complex intermediates or symmetrical charge exchange involving excited states), the energy dependence of the low energy portions of the cross section curves should approach an $E^{-1/2}$ dependence. Considering symmetrical charge exchange in the intermediate velocity region, the energy dependence should be even less.[25]

Table II shows the approximate energy dependence found experimentally for the low energy portions of the cross section curves of the exothermic reactions. Only

**Table II.** Energy Dependence of Cross Section over Low Energy Range (2–10 e.v.) for $\sigma \sim E^{-x}$

| Prim. ion | Value of $x$ for reaction producing | | | |
|---|---|---|---|---|
| | $CH_4^+$ | $CH_3^+$ | $CH_2^+$ | $CH^+$ |
| $Xe^+$ | 1.5 | .. | .. | .. |
| $Kr^+$ | 1.33 | 1.33 | .. | .. |
| $Ar^+$ | 0.7 | 0.9 | 0.8 | .. |
| $Ne^+$ | .. | .. | .. | .. |
| $He^+$ | .. | 0.5 | 0.5 | 0.3 |

the helium reactions apparently follow the predicted $E^{-1/2}$ behavior. Excluding the $Ne^+$ reaction which behaved anomalously, the dependence appears to vary systematically. Theoretical considerations have assumed an $r^{-4}$ interaction potential, implying a point

charge interacting with a polarizable molecule. This situation is more closely approximated by helium ions than the other rare gas ions, and it is only reasonable to expect deviations from the predicted behavior as the size and polarizability of the ion increases. Gioumousis and Stevenson[27] point out that, although many reactions involving simple species (e.g., those involving hydrocarbons) follow an $E^{-1/2}$ dependence, indicating that the view of an ion as a structureless point charge is an oversimplification.

The matter of cross section dependence on energy of ion–molecule reactions has also been investigated by Hamill and co-workers, and the failure of the $E^{-1/2}$ dependence in a number of reactions, some including rare gas ions, has been reported in several publications.[30]

## Conclusions

The reactions of rare gas ions and methane, studied over an energy range of 2–200 e.v., yield the same fragment ions previously observed in experiments at both thermal and higher energies (up to 2000 e.v.).

It is possible to interpret the results in terms of either charge-exchange or ion–molecule theory. To explain the data strictly in terms of charge exchange would require consideration of a variety of excited states in order to minimize the energy defects of the reactions which display resonance behavior. One could then explain the low, nonresonant behavior of the $Ne^+$ reactions as owing to the absence of suitable excited states of any of the methane fragment ions. This interpretation ignores completely the complex ions observed.

In terms of the ion–molecule picture, the complex ions are immediately accounted for, the general shapes of the low energy portions of the curves correctly reflect the exothermicity or endothermicity of the reactions, and the effects of polarizability and reduced mass can account for the variations in the relative magnitudes of the cross sections. The anomalous $Ne^+$ results can be explained by assuming that a collision complex between $Ne^+$ and methane does not form.

Neither approach predicts the energy dependence found experimentally. The true picture is probably a combination of the two processes with complex formation dominant at the lower incident ion energies (<10 e.v.) and charge exchange increasing in importance as the energy increases.

In view of the assumptions made in the current theories, the failure of the cross sections to obey the predicted $E^{-1/2}$ energy dependence in all cases but the helium reactions is not surprising. The assumption of the $r^{-4}$ interaction potential is not necessarily valid in cases involving large, polarizable molecules.

(30) L. P. Theard and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 1134 (1962); N. Boelrijk and W. H. Hamill, *ibid.*, **84**, 730 (1962); R. F. Pottie, A. J. Lorquet, and W. H. Hamill, *ibid.*, **84**, 529 (1962).