# Reactions of Gaseous Ions. IX. Charge Exchange Reactions of Rare Gas Ions with Ethylene

BY J. L. FRANKLIN AND F. H. FIELD

Using a mass spectrometer ion source as a reactor, ions of all of the rare gases have been shown to undergo charge exchange reactions with ethylene. The rates of these reactions are in the order of 10^{-10} to 10^{-9} cc. molecule^{-1} sec.$^{-1}$ and thus are similar to those of other ion–molecule reactions. Xenon and argon ions, respectively, produce $C_2H_4^+$ and $C_2H_3^+$ predominantly. Krypton ions produce $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$ in approximately the ratio 1:2:1. Helium and neon ions react somewhat more slowly than the others and produce CH_2^+ predominantly.

Charge exchange has been the object of numerous investigations[1] and is known to occur wherever the ionization potential of the neutral species is less than the recombination energy of the positive ion with an electron. When $I = R$ resonance can exist, and, at these conditions, charge exchange occurs with extreme rapidity. Although some data are available on the cross section for (or rate of) charge exchange, such information is available primarily for reactions between monatomic or, at most, simple diatomic, species. Lindholm[2-5] has studied the decomposition of CH_4, H_2O, H_2S, NH_3 and several other small molecules brought about by charge exchange with monatomic ions but he did not measure reactions rates. Meisels, Hamill and Williams[6] report decomposition of light paraffins brought about by charge exchange with rare gas ions but they do not report cross sections. Field[7] observed the charge exchange reaction

$$C_2H_2^+ + C_2H_4 \longrightarrow C_2H_4^+ + C_2H_2$$
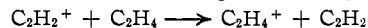
and found the rate constant to be 4.1×10^{-10} cc./molecule sec. Melton[8] has studied charge exchange of argon and methane and found rates of formation of CH_4^+, CH_3^+ and CH_2^+ comparable to those of other ion–molecule reactions.

In the absence of extensive data on the rate of charge exchange it seemed appropriate to undertake such studies. Accordingly, we have investigated several reactions of ethylene with ions of the noble gases and have measured the rates of the more important ones.

Experimental

Ethylene used in this study was Phillips Research grade, and the rare gases were Air Reduction Company spectroscopically pure quality.

The instrument was a 60° deflection, sector field type mass spectrometer having a 12 inch radius of curvature and designed for good differential pumping in the source and analyzer. The instrument has been described elsewhere.[7] The conditions maintained in the ionization chamber were: electron voltage = 70 v., electron current = 0.50 μamp., ion repeller voltage 5 v. corresponding to a field strength of 12.5 v./cm. Magnetic scanning was used to obtain the mass spectra.

To make the measurements ethylene was introduced into one of the gas handling reservoirs of the instrument in such a quantity as to give a pressure in the ionization chamber of 25 μ. This pressure was determined using the calibration techniques described previously.[7] The mass spectrum of ethylene then was determined. The rare gas under investigation was then introduced into the other gas handling reservoir in a quantity to give a desired ionization chamber pressure. The mass spectrum was measured again. From 8–10 pressures of rare gas were used, and after each addition of rare gas the ethylene pressure was readjusted to 25 μ. After all the measurements with rare gas were made, the rare gas was pumped out and the spectrum of ethylene again determined.

Results

Typical data obtained from the system argon–ethylene are given in Table I. The less important peaks are omitted. Unfortunately the spectrum behaves in an unusual manner as argon is added to ethylene: namely, it decreases steadily with increasing partial pressures of argon. All of the hydrocarbon peaks tended at first to decrease as the partial pressure of argon was increased, and only mass 27 (and its secondary product mass 29) later reversed the trend and increased at larger partial pressure. Further, the argon peak, even after correcting for charge exchange, does not increase in proportion to the partial pressure. In fact, if one sums all the peaks at each pressure one finds little change in total ionization with added argon. When the argon is pumped out of the instrument, the total ionization of the ethylene is only about two-thirds of its value before the addition of argon. After several hours with argon absent, the total ionization again attains its original value. This behavior was characteristic of all the rare gases. We do not understand it. It might be argued that the addition of the rare gas greatly changes the space charge in the ionization chamber, thus reducing the electron energy and so altering the fragmentation pattern of the ethylene. However, relative peak heights in the ethylene mass spectrum change little at electron energies in excess of about 20 volts. Although total ionization changes quite extensively, we do not think it possible that the energy of the electrons could be thus reduced from 70 to 20 v. or less, and so we do not think that this could be responsible for the behavior of the ethylene spectrum with the addition of rare gas. Certainly this would not explain the persistence of the reduced total ionization after the rate gas is removed from the source. Rather, we think the phenomenon is instrumental in origin and perhaps is attributable to some change in the surface of the ionization chamber brought about by the simultaneous presence of ethylene and rare gas.

(1) For an extensive discussion see H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952.

(2) E. Lindholm, Proc. Phys. Soc., **A66**, 1068 (1953).

(3) E. Lindholm, Ark. Fys., **8**, 257, 433 (1954).

(4) E. Lindholm, Z. Naturforschg., **9a**, 535 (1954).

(5) E. Lindholm, Institute of Petroleum, "Conference on Applied Mass Spectrometry," London, 1953.

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

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

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

TABLE I

TYPICAL DATA, ARGON–ETHYLENE MIXTURE

Argon source pressure, μ	Abundance at indicated m/e								$\frac{28}{28°}$	Σ26ᵃ	Σ27ᵇ	Δ26ᶜ	Δ27ᵈ	(Arₚ⁺)ᵉ	ln $\frac{(Ar_0{}^+)}{(Ar^+)}$
	25	26	27	28	29	39	41	40							
0	605	4450	7450	14300	2070	600	2770	0	1	5410	9530	0	0	0	...
6	560	4120	7470	11800	1900	530	2370	2180	0.825	4980	9370	520	1540	4240	0.667
10	470	3630	7350	11500	1960	540	2450	2760	.805	4520	9310	270	1640	4670	.523
21	437	3630	7950	9500	1940	470	2050	5160	.665	4425	9890	825	3560	9545	.615
28	386	3720	8850	10000	2200	501	2190	5460	.700	4560	11500	760	4830	11050	.700
39	360	3550	9420	9000	2260	483	2050	6780	.630	4390	11680	980	5680	13440	.683
46	338	3470	9660	9210	2320	470	1950	7310	.645	4290	11980	800	5840	13950	.646
49	319	3470	9800	8560	2170	456	1850	7550	.600	4280	11970	1030	6250	14830	.672
56	315	3380	9730	7940	2050	417	1600	7990	.555	4100	11780	1100	6500	15590	.668
66	294	3340	9800	7600	2170	436	1600	9030	.530	4100	11970	1230	6910	17170	.642
0	415	2680	5130	9130	1190	374	1670	0	1	3295	6320	..	..	Av. =	.646

ᵃ Σ26 = sum of peaks at mass 26, 39 and 53 (not shown in table). ᵇ Σ27 = sum of peaks at mass 27 and 29. ᶜ Δ26 = $26_p - (28/28_0)(26_0)$ where 26_p and 26_0 are the 26 peak at pressures p and 0, respectively. ᵈ Δ27 = $27_p - (28/28_0)(27_0)$ where 27_p and 27_0 are the 27 peak at pressures p and 0, respectively. ᵉ (Ar⁺) = peak at mass 40. (Ar₀⁺) = Ar⁺ + Δ26 + Δ27.

The rate at which charge is passed from a rare gas ion, X^+, to ethylene is given by

$$-\frac{d(X^+)}{dt} = k(X^+)(C_2H_4) \qquad (1)$$

which integrates to

$$\ln\frac{(X_0{}^+)}{(X^+)} = k(C_2H_4)\tau \qquad (2)$$

when (C_2H_4) is large compared to (X^+).

In these experiments ethylene concentration and repeller voltage were held constant. $(X_0{}^+)$ is the initial concentration of rare gas ions before reaction with ethylene. This, of course, is not directly observable, but can be estimated by adding to (X^+) the amount of hydrocarbon ions in excess of that measured in the absence of rare gas. If the hydrocarbon ion intensities (except those increased by charge exchange) had remained constant, the calculation would be simple and straightforward. In view of the unusual behavior of the mixture it was necessary to estimate the value of the hydrocarbon peak before exchange. We observe that the intensities of the ions of mass 25 and 28 drop at about the same rate; i.e., their ratio remains constant, as argon is added. These cannot be losing charge by exchange with argon because both C_2H and C_2H_4 have smaller ionization potentials than argon. Similarly, C_2H^+ cannot be formed by dissociative charge exchange of C_2H_4 with Ar^+ because its appearance potential is higher than $I(Ar)$. We conclude then that these ions are not specifically affected by the argon, and thus the intensity of either ion may be used to estimate the extent of ionization of ethylene before charge exchange with argon. Thus, in Table I, $C_2H_4{}^+$ was employed in this capacity.

Let $[C_2H_4{}^+]_0$ and $[C_2H_4{}^+]_p$ be, respectively, the intensity of ethylene ion at 0 and p pressure of argon. Further, let $(I_i)_0$ and $(I_i)_p$ be the intensity of the ith ionic species at 0 and p μ of argon, respectively. Were charge exchange not to occur, we could write that for each argon pressure, p

$$\frac{(I_i)_p}{(I_i)_0} = a \text{ constant} = \frac{[C_2H_4{}^+]_p}{[C_2H_4{}^+]_0} \qquad (3)$$

We know $(I_i)_0$, $[C_2H_4{}^+]_p$ and $[C_2H_4{}^+]_0$ so we can compute $(I_i)_p$ for each pressure. Then the excess of the measured intensity $(I_i)_m$ of the ion at that

pressure over $(I_i)_p$ may be attributed to charge exchange. Such computations are made for all ions and the total charge exchange at any pressure is obtained by summing the charge exchange for all the hydrocarbon ions, i.e.
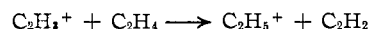
$$(I_i)_m - (I_i)_p = \Delta I_i, \text{ and}$$
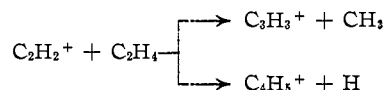
$$\Sigma\Delta I_i = \text{total charge exchange}$$

This excess $\Sigma\Delta I_i$ when added to $(Ar^+)_m$ gives the intensity $(Ar^+)_0$ of the argon ion before charge exchange. Thus

$$(Ar^+)_0 = (Ar^+)_m + \Sigma\Delta I_i = (Ar^+)_m + \Delta_p27 + \Delta_p26$$

where Δ_p27 and Δ_p26 are the enhancement of the $C_2H_3{}^+$ and $C_2H_2{}^+$ ions by charge exchange at the argon pressure, p. It is known[7] that vinyl ion undergoes the reaction

$$C_2H_3{}^+ + C_2H_4 \longrightarrow C_2H_5{}^+ + C_2H_2$$

and acetylene ion, the reactions

$$C_2H_2{}^+ + C_2H_4 \begin{cases} \longrightarrow C_3H_3{}^+ + CH_3 \\ \longrightarrow C_4H_5{}^+ + H \end{cases}$$

Consequently, the vinyl ion intensity at each pressure is taken as the sum of the measured intensities of mass 27 and 29, and the acetylene ion as the sum of the intensities of the ions of mass 26, 39 and 53. The intensities before charge exchange were, of course, corrected for secondary ions also.

In the above we have treated the exchange reaction as involving only singly charged rare gas ions. Actually, doubly charged ions of argon, krypton and xenon are present to the extent of 7–8%[9] and, conceivably, may undergo some charge exchange reactions with ethylene. However, the second ionization potentials of the rare gases are quite high (54.4 v. for He to 21.2 v. for Xe) and exchanges yielding ground state rare gas ions $(X^{++} \rightarrow X^+ \; (^2P_0))$ involve so much energy that the ethylene will undergo extensive decomposition; that is, the $C_2H_4{}^+$, $C_2H_3{}^+$ and $C_2H_2{}^+$ ions in which we are here interested will not be formed.[10] Transitions to excited states of X^+

(9) V. H. Dibeler, F. L. Mohler and R. M. Reese, J. Research Natl. Bur. Standards, 38, 617 (1947).
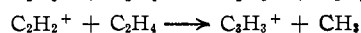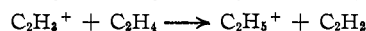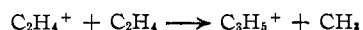
(10) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

can be found[11] for certain rare gas ions which can produce $C_2H_4^+$, $C_2H_3^+$ and $C_2H_2^+$, singly or in combination, but the energetic restrictions are such that the extent of such reactions will not be great. Taking into account these considerations and also the fact of the relatively small abundances of the doubly charged ions initially formed, we believe that any error made in of necessity neglecting the reactions of the doubly charged ions will not diminish seriously the worth of our results.

In order to compute the rate constant by (2) we must know the concentration of ethylene and the ionization chamber residence time. The former is obtained by calibration.[7] The average residence time, τ, is taken as $(2dm/Ve)^{1/2}$ where d is the distance from the center of the electron beam to the ion exit slit; V is the field strength in the source; e is the charge on the electron; and m is the mass of the rare gas ion. In our source

$$\tau = 1.82 \times 10^{-7} M^{1/2} \qquad (4)$$

It is a matter of some concern whether the average residence time may be obtained correctly by use of equation 4. At the relatively high pressures employed surface and space charge effects might alter the residence times sufficiently to give rate constants that are in error. Similarly, ion–electron recombination might be thought to occur to a sufficient extent at these relatively high pressures to affect adversely the accuracy. In an effort to ascertain whether our rate constants are trustworthy, we have calculated the rate constants for the ethylene reactions

$$C_2H_4^+ + C_2H_4 \longrightarrow C_3H_5^+ + CH_3$$
$$C_2H_3^+ + C_2H_4 \longrightarrow C_2H_5^+ + C_2H_2$$
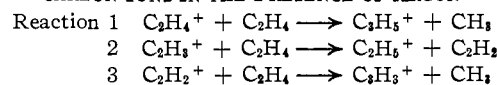$$C_2H_2^+ + C_2H_4 \longrightarrow C_3H_3^+ + CH_3$$

at each of the pressures of rare gas employed. In Table II the results (calculated from data in Table I) for three of the ions with argon are given. These are typical of the results obtained with all of the rare gases. It is evident that none of the reactions shows serious variations with pressure of added argon. Table III gives average rate constants obtained for these reactions with the various rare gases studied. Although there is some variation in the rate constants determined in these studies, the variation does not seem to be systematic and no doubt represents the reproducibility of our measurements. Table III also includes values for the various rate constants determined in other studies. One of these studies[12] was made at source pressures of 2–20 μ and the other[7] at source pressures of 5–100 μ. The studies reported in reference 12 employed a CEC model 21–620 cycloidal focusing mass spectrometer. The present results and those reported by Field[7] employed the same instrument, a 60°, 12 in. radius of curvature, sector field mass spectrometer. In view of the differences in instruments and conditions employed, we think that the data given in Table III show satisfactory agreement and justify our use of the average time τ calculated by equation 4. These concordant results also suggest that conditions in the

ion source are sufficiently like those at lower pressures so that we need not have serious doubts about the validity of the results.

TABLE II

RATE CONSTANTS FOR SECONDARY REACTIONS OF HYDRO-CARBON IONS IN THE PRESENCE OF ARGON

Reaction 1 $C_2H_4^+ + C_2H_4 \longrightarrow C_3H_5^+ + CH_3$

2   $C_2H_3^+ + C_2H_4 \longrightarrow C_2H_5^+ + C_2H_2$

3   $C_2H_2^+ + C_2H_4 \longrightarrow C_3H_3^+ + CH_3$

Argon source pres., μ	Rate constants (cc./molecule sec.) for reaction $\times 10^{10}$		
	1	2	3
0	3.4	4.3	2.5
6	3.5	4.2	2.4
10	3.6	4.4	2.7
21	3.7	4.1	2.4
28	3.7	4.2	2.5
39	3.8	4.0	2.5
46	3.5	4.0	2.5
49	3.7	3.8	2.5
56	3.5	3.6	2.3
66	3.6	3.8	2.3
0	3.3	3.9	2.6
	$3.6 \pm 0.1 \times 10^{-11}$	$4.0 \pm 0.2 \times 10^{-10}$	$2.5 \pm 0.1 \times 10^{-10}$

From data calculated as discussed above, overall second-order rate constants have been calculated and the results are given in Table IV. Duplicate determinations were made for each of the rare gases and the replicate values are given in column 2 of Table IV. Attempts were made, without success, to observe the complexes $XeC_2H_4^+$ and $HeC_2H_4^+$. In no study have we been able to observe the addition product of an ion and a neutral molecule, and we conclude that the complexes involved in these charge exchange reactions decompose with the large rate generally observed in ion–molecule reactions. The rate constant that we report then is in all cases for the reaction $X^+ + C_2H_4 \longrightarrow XC_2H_4^+$. With each of the rare gases two or more secondary ions were formed by charge exchange. The fraction of each observed is given in column 3 of Table IV.

Discussion

The rate constants for a large number of ion–molecule reactions have been determined,[14,15] and with few exceptions they fall within the range 10^{-10} to 10^{-9} cc./molecule sec. The rate constants that we have determined for charge exchange reactions fall within this range and so are comparable in this respect to other ion–molecule reactions. The rate constant for all such reactions is given approximately by the equation[13–16]

$$k = 2\pi e \left(\frac{\alpha}{\mu}\right)^{1/2} \qquad (5)$$

where e is the charge on the electron, α is the polarizability of the neutral molecule and μ is the reduced mass. Equation 5 also predicts approximately (within an order of magnitude) the rate constants for the charge exchange reactions in Table IV, and this further supports the conclusion

(11) C. E. Moore, Natl. Bureau of Standards Circ. No. 467 (1949).

(12) F. H. Field, J. L. Franklin and F. W. Lampe. *J. Am. Chem. Soc.*, **79**, 2419 (1957).

(13) F. W. Lampe and F. H. Field, *Tetrahedron*, **7**, 189 (1959).

(14) F. W. Lampe, J. L. Franklin and F. H. Field. "Kinetics of the Reactions of Ions with Molecules," in "Advances in Kinetics," Vol. I, Pergamon Press (to appear soon).

(15) H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).

(16) G. Gioumousis and D. P. Stevenson, *ibid.*, **29**, 294 (1958).

<div align="center">TABLE III</div>

<div align="center">RATE CONSTANTS FOR SECONDARY REACTIONS OF HYDROCARBON IONS IN THE PRESENCE OF VARIOUS RARE GASES</div>

Reactions	Xe	Kr	Ar	Ne	He	10^{10} k, Lit. None
			10^{10} k in presence of noble gas			
$C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3$	2.8,2.8	2.9,3.5	3.6,3.4	3.6		3.3-4.6[12]
$C_2H_2^+ + C_2H_4 \rightarrow C_3H_3^+ + CH_3$	1.9,2.3	1.8,2.5	2.6,2.5	2.8		2.3[7]
						2.4[12]
$C_2H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_2$	5.0,5.3	3.8,4.4	4.0,4.0	4.3,4.7	4.7,3.5	3.0[12]
						3.6[7]

<div align="center">TABLE IV</div>

<div align="center">CHARGE EXCHANGE REACTIONS, RATES AND ENERGETICS</div>

		10^{10} k, cc. molec. $^{-1}$ sec. $^{-1}$	Fraction of reaction	$\Delta E_0,$[a] v.	$\Delta E_1,$[a] v.
$Xe^+ + C_2H_4 \rightarrow XeC_2H_4^+$—	→ $C_2H_4^+ + Xe$	7.25, 6.25	0.85, 0.84	−1.57	−2.9
	→ $C_2H_2^+ + H_2 + Xe$		.15, .16	+2.07	+0.04 or −0.26
$Kr^+ + C_2H_4 \rightarrow KrC_2H_4^+$—	→ $C_2H_4^+ + Kr$	11.8,10.8	.25, .22	−3.44	−4.1
	→ $C_2H_3^+ + H + Kr$		.45, .49	+0.64 or −0.06	−0.6
	→ $C_2H_2^+ + H_2 + Kr$		.30, .29	−0.8	−1.46
$Ar^+ + C_2H_4 \rightarrow ArC_2H_4^+$—	→ $C_2H_2^+ + H_2 + Ar$	11.3,10.4	.14, .12	−2.5	−2.7
	→ $C_2H_3^+ + H + Ar$		.86, .88	−1.7	−1.9
$Ne^+ + C_2H_4 \rightarrow NeC_2H_4^+$—	→ $C^+ + Ne + ---$	1.9, 1.3	.10, .15	~−0.9 (?)	
	→ $CH^+ + Ne + ---$		.10, .14	−3.5 or ~−0.1 (?)	
	→ $CH_2^+ + Ne + CH$?		.70, .63	−2.3 or −5.0 or −0.2 (?)	
	→ $CH_3^+ + Ne + CH$?		.10, .08	−4.6 or −1.1 (?)	
$He^+ + C_2H_4 \rightarrow HeC_2H_4^+$—	→ $CH_2^+ + He + ---$	2.15,3.25	.85, .88	??	
	→ $CH_3^+ + He +$		.15, .12	??	

[a] $\Delta E_0 = Ap$ (hydrocarbon ion) $- I(^2P_{1^1/_2})$ of rare gas. $\Delta E_1 = Ap$(hydrocarbon ion) $I(^2P_{1/_2})$ of rare gas.   All hydrocarbon appearance potentials taken from Field and Franklin.[10]   All ionization potentials of rare gases taken from Moore[11] except $I(^2P_{1/_2})Xe$ which was taken from Fox.[17]

that these are kinetically similar to ion–molecule reactions.

The measured rate constants for charge exchange with neon and helium are considerably smaller than those of the other rare gases. The reason for this discrepancy is not apparent. It may be due to the large difference in ionization potential between ethylene and these rare gases which would tend to reduce the probability of forming the complex $XC_2H_4^+$.

It is of interest to consider the energetics of the charge exchange reactions of rare gas ions and ethylene. In columns 4 and 5 of Table IV are listed ΔE values for the reactions in question. ΔE_0 is for reaction with the lower $(^2P_{1^1/_2})$ state and ΔE_1 is for reaction with the upper $(^2P_{1/_2})$ state of the ground state doublet of the rare gas ion. The nature of the reactions of Ne^+ and He^+ to form small fragments is quite uncertain and the ΔE values are at best approximate.

The formation of $C_2H_4^+$ by charge exchange with any of the rare gas ions is quite exothermic. In fact, the reaction is so exothermic with Ar^+, Ne^+ and He^+ that, presumably, all of the ethylene ions break down to smaller fragments.

The formation of $C_2H_2^+$ by Kr^+ and Ar^+ is exothermic with either state of the doublet. With xenon, the ground state does not possess enough energy to bring about the reaction. The appearance potential of $C_2H_2^+$ from ethylene is

(17) R. E. Fox, J. Chem. Phys., 32, 385 (1960).

13.5 v.[10] However, if one calculates the appearance potential from known heats of formation,[10] a value of 13.2 v. is obtained. This probably more nearly approximates true value, and if it is employed one finds that the charge exchange with the upper state of the doublet is exothermic by 0.26 v.

Both $C_2H_2^+$ and $C_2H_4^+$ are produced exothermically by both states of Kr^+. The upper state of Kr^+ also has enough energy to produce $C_2H_3^+$. However, the ground state of the doublet is very close to the known ground state appearance potential of $C_2H_3^+$ from ethylene. Several values have been determined, and if the lowest one is employed or if the appearance potential is calculated from the recommended value of $\Delta H_f(C_2H_3^+)$ = 280 kcal./mole, we find the reaction to be slightly exothermic. Presumably, the lowest value is the more nearly correct one.

With both He and Ne there are several exothermic reactions that could have produced the ions observed, and so it is not possible to identify the effective one from the available data. It is rather surprising that C^+ and CH^+ were not observed with He. In fact, one of the helium runs gave some indication of an increase in these ions, but the data were rather uncertain and were not supported by the repeat run.

It is also surprising that neither helium nor neon brought about any enhancement of C_2^+ or C_2H^+. The appearance potential of C_2H^+ is

known to be below the ionization potential of Ne, and indeed it is not far different from that of CH_2^+. Also C_2H^+ is present in the primary spectrum in greater abundance than CH_2^+. We cannot explain its absence.

It is interesting that, with both neon and helium, the ratio of CH_2^+ to CH_3^+ is the same as it is in the primary mass spectrum of ethylene. Indeed, the proportions of C^+, CH^+, CH_2^+ and CH_3^+ produced by charge exchange with neon are rather similar to those in the primary spectrum of ethylene. This may, of course, be merely a coincidence, since similar relations to the primary spectrum are not observed with the other rare gases. However, it suggests the possibility that a different mechanism is involved, i.e., that the reaction may be

$$He^+ + C_2H_4 \longrightarrow C_2H_4He^+ \longrightarrow C_2H_4^{+*} + He$$

$$C_2H_4^{+*} \longrightarrow Products$$
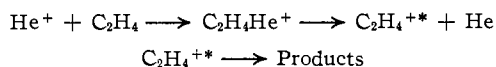
Under these circumstances one would expect the products to occur in the same proportion as in the primary spectrum for similar amounts of excitation.

No clear relation between ΔE and relative abundance is observable. It does appear that charge exchange reactions can occur only if they are exothermic (or at least not endothermic). Also, we do not note any reactions in Table II where $-\Delta E$ is as great as five volts. We do not know, however, whether reactions having this much excess energy are not favored or whether, with so much excess energy, other preferred modes of reactions are induced. It does appear that considerations other than energy are of importance. Thus, the formation of $C_2H_2^+$, which occurs via a four-center reaction, is less favored than either $C_2H_3^+$ or $C_2H_4^+$. Further, where enough energy is available it appears that the formation of $C_2H_3^+$ is favored above that of $C_2H_4^+$. Although one cannot be certain, these results may be attributed to differences in entropy in the activated complex.
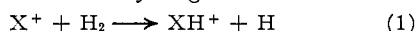

Hydrogen Inhibition of the Rare Gas Sensitized Radiolysis of Cyclopropane

BY C. F. SMITH, B. G. CORMAN AND F. W. LAMPE[1]

Argon, krypton and xenon sensitize the gas-phase radiolysis of cyclopropane. Hydrogen also acts as a sensitizer but in moderate quantities inhibits the rare gas sensitization; in larger quantities, it inhibits its own sensitization. A sensitization and inhibition mechanism is proposed from which specific reaction rates for the radiolysis sensitization by argon and hydrogen are derived.

The fact that the rare gases will sensitize the gas-phase radiolysis of various compounds such as acetylene,[2] butadiene,[2b] ethylene[3] and several inorganic gases,[2b] by some energy transfer process or processes, is well known in radiation chemistry. In addition, it has been shown recently that irradiated rare gases will sensitize the formation of hydrogen atoms and consequently the hydrogenation of ethylene.[4] Moreover, it was strongly suggested that this hydrogen atom sensitization occurred by means of the known reaction of the rare gas ions with molecular hydrogen,[5] viz.

$$X^+ + H_2 \longrightarrow XH^+ + H \qquad (1)$$

If we consider for simplicity that the rare gas sensitized radiolysis of some hydrocarbon, RH, also occurs via reaction with X^+, viz.

$$X^+ + RH \longrightarrow disappearance\ of\ RH \qquad (2)$$
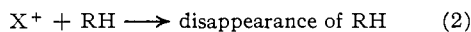
then addition of hydrogen to a constant composition radiolysis mixture of X and RH would result in a competition for X^+ between H_2 and RH and would

retard the rate of reaction of RH, provided that the hydrogen atoms produced in (1) do not react appreciably with it. Reaction 2 might be thought of as a simple charge transfer, (2a)

$$X^+ + RH \longrightarrow RH^+ + X \qquad (2a)$$
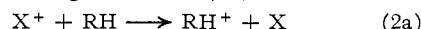
or as a dissociative charge transfer reaction,[6] (2b); (2b) can be considered as being related to the hydride transfer processes recently shown to be important in gas-phase radiation chemistry.[7-9]

$$X^+ + RH \longrightarrow R^+ + X + H \qquad (2b)$$
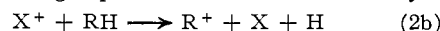
For the purpose of this paper it is sufficient to know only that RH is consumed in (2). Since (1) and (2) are in direct competition (as long as H-atoms do not react with RH) a study of the retardation effect of hydrogen on the rare gas sensitized radiolysis of RH should yield the ratio of rate constants k_1/k_2. As k_1 is known from mass spectrometric measurements,[5] such studies should in principle permit calculation of k_2, the over-all specific reaction rate for the sensitized radiolysis.

Cyclopropane seemed a good choice for RH as its inertness to hydrogen atom attack at room temperature has been demonstrated.[10]

(1) Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania.

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