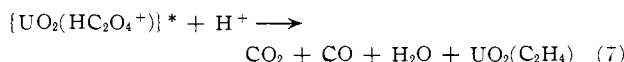


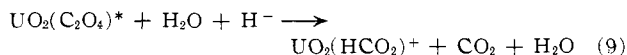
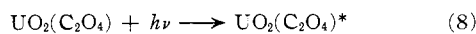
Tables II and V, as the quantum yield for oxalate decomposition is not known for the experimental conditions used. The values of Φ_d used are: 2537 Å., 0.62; 3660 Å., 0.49; 4350 Å., 0.58.⁸

The fraction of decomposition proceeding by each path is independent not only of intensity but also, as shown by the values in Table VI, of temperature and wave length; the fractions are, however, dependent on concentration and sulfuric acid concentration.

The concentration and acidity effects indicate that a uranyl complex with a protonated oxalate ion is involved in path 1. To the present time, little experimental work directed at the chemistry of uranyl oxalate complexes has been reported. Krishnamurty and Harris⁹ have reviewed the available studies and present evidence for complexing with both oxalate and mono-protonated oxalate ions. The following mechanism for path 1 is therefore proposed.



Similarly, the concentration and acidity effect indicate that a nonprotonated oxalate complex is involved in path 2. The following mechanism is therefore proposed.

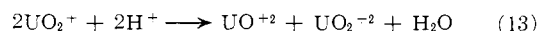
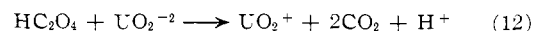
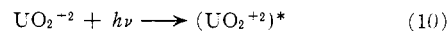


It would be expected that the formate complex would be replaced by an oxalate complex and that formic acid would be produced. Evidence that the oxalate complexes are indeed much stronger than the formate complexes was obtained in the present work by observing the effect on pH of adding uranyl oxalate to oxalic acid solutions and of adding uranyl formate to formic acid solutions. In the first case the pH decreased, while in the second case the pH increased.

(9) K. V. Krishnamurty and G. M. Harris, *Chem. Rev.*, **61**, 213 (1961).

The complexes indicated may, of course, not be the actual existing species as complexes containing more than one oxalate group or complexes containing both protonated and nonprotonated oxalate group on the same molecule are to be expected. The complexes chosen are the simplest possible ones.

For the third path, the following mechanism is proposed.



This scheme is similar to that proposed by Carter and Weiss.⁵ It accounts for the products, U^{IV} and CO_2 , by single electron-transfer steps. The specific uranium complexes have not been designated as they are not known. The free radical HC_2O_4 is kinetically equivalent to $\text{H}^+ + \text{CO}_2 + \text{CO}_2^-$. Adler and Noyes¹⁰ prefer CO_2^- , but for simplicity and in the absence of definite information, we have selected HC_2O_4 . Either radical, HC_2O_4 or CO_2^- , would be rapidly oxidized by U^{VI} . The rapid disproportionation of U^{V} to U^{VI} and U^{IV} has been well established.¹¹

In the last column of Table VI, the sums of the quantum yields for CO and CO_2 are given. These values may prove to be particularly useful in actinometry for microphotochemistry. The sensitivity may be enhanced by the simultaneous determination of these gases, and CO and CO_2 may be simultaneously determined by hydrogen flame ionization detectors after catalytic reduction to methane as described above. Thus the sensitivity we have previously reported, 2×10^{14} quanta,² may be increased by a factor of 3 to give a sensitivity of about 7.0×10^{13} quanta.

(10) S. J. Adler and R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2036 (1955).

(11) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," Methuen and Co. Ltd., London, 1957, p. 176.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND 21218]

The Argon-Deuterium Hydride Ion Reaction¹

BY M. A. BERTA² AND W. S. KOSKI

RECEIVED JULY 8, 1964

Reactions of HD^+ with argon (eq. 1-3) have been studied using a tandem mass spectrometer. In the first two reactions, attention was centered on the isotope effect, and the ratio $\text{ArH}^+/\text{ArD}^+$ between 2 and 25 e.v. varied from 1.3 to 1.9, respectively. In the charge-transfer reaction, the cross section was measured from 2 to 70 e.v., and indications were obtained that the reacting HD^+ ions were in vibrationally excited states.

Introduction

The reaction of argon with the hydrogen molecule ion has been studied by several investigators³⁻⁶; however, a number of basic questions still remain unanswered. One of these is the isotope effect.

(1) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract AF 49(638)-1301.

(2) Air Force Institute of Technology Fellow.

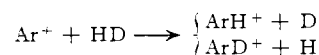
(3) J. B. H. Stedeford and J. B. Hasted, *Proc. Roy. Soc. (London)*, **A227**, 466 (1954-1955).

(4) F. Wolf, *Ann. Physik*, **28**, 361 (1937).

(5) C. F. Giese and W. B. Maier, *J. Chem. Phys.*, **39**, 739 (1963).

(6) J. B. Hasted, *Proc. Roy. Soc. (London)*, **A212**, 235 (1952).

The reaction



was investigated by Stevenson and Schissler.^{7,8} The ratio $\text{ArH}^+/\text{ArD}^+$ was found by them to be about 0.85. As pointed out by Stevenson, the then existing theory of ion-molecule reactions⁹ fails to account for the observed isotope effect found. This theory gives the

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

(8) D. P. Stevenson and D. O. Schissler, *ibid.*, **29**, 282 (1958).

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

cross section as

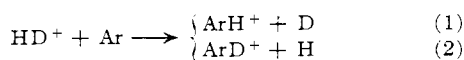
$$\sigma = \frac{\pi}{v_{\text{rel}}} \left(\frac{4e^2\alpha}{\mu} \right)^{1/2}$$

where v_{rel} is the relative velocity, α is the polarizability of the molecule, e is the charge of the ion, and μ is the reduced mass of the system. Recently, Rosenstock, *et al.*,¹⁰ wrote a review of ion-molecule reactions in which they discussed some of the shortcomings of the Gioumousis and Stevenson theory.⁹ They modified the theory by considering the necessity of conserving energy and angular momentum, thereby arriving at the following expression for the cross section

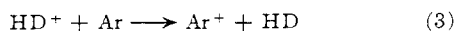
$$\frac{\sigma'}{\sigma} = \left(\frac{\alpha_P}{\alpha_R} \right)^{1/2} \left(\frac{m_{iP}m_{nP}}{m_{iR}m_{nR}} \right) \left(1 + \frac{\Delta H_R}{E_R} \right)^{1/2}$$

where the P and R subscripts stand for the products and reactants, respectively, i and n stand for ions and neutrals, respectively, α is the polarizability, m is the mass, ΔH_R is the heat of the reaction, and E_R is the energy of the bombarding ion. Thus, their treatment predicts the occurrence of an isotope effect. As this paper was being prepared, an article by Light¹¹ on the phase space theory of ion-molecule reactions appeared. The qualitative predictions of Light's approach seem to have similar dependences on the polarizability and mass as that of Rosenstock, *et al.* Preliminary applications to the $\text{He}^+ + \text{H}_2$ reactions are very encouraging. Very likely this treatment of the problems associated with simple ion-molecule reactions will give us a deeper insight into these types of reactions.

The object of this paper is to report the results of our studies on the isotope effect in the reactions



The cross sections of these reactions were studied as a function of the primary ion energy on a tandem mass spectrometer. Since this instrument is also suitable to the study of charge-exchange reaction, the reaction



is also included in this report.

Experimental

Apparatus.—The apparatus used in this work has been described elsewhere.¹² It consists of two mass spectrometers placed in tandem. The first stage is a modified commercial instrument made by Consolidated Electrodynamics Corp. It has a 180° sector, a 1-cm. radius of curvature, and a constant magnetic field of approximately 2500 gauss. The second stage has a 60° sector and a variable magnetic field. The resolution of the primary mass spectrometer (PMS) is about 12, while that of the secondary mass spectrometer (SMS) is about 120.

A gas is ionized in the PMS. It then goes through deflector plates and a lens system that focuses the beam of ions into the reaction chamber which contains the target gas. The PMS lens system enables the kinetic energy of the primary ions to be varied from 2 to 200 e.v. The products of the reaction, or secondary ions, are pushed out of the reaction chamber by a repeller plate and are accelerated to 2 or 3 kev. These ions exit at right angles to the direction of the primary ion beam. The lens system for the SMS contains both a y- and z-focus lens. This arrangement

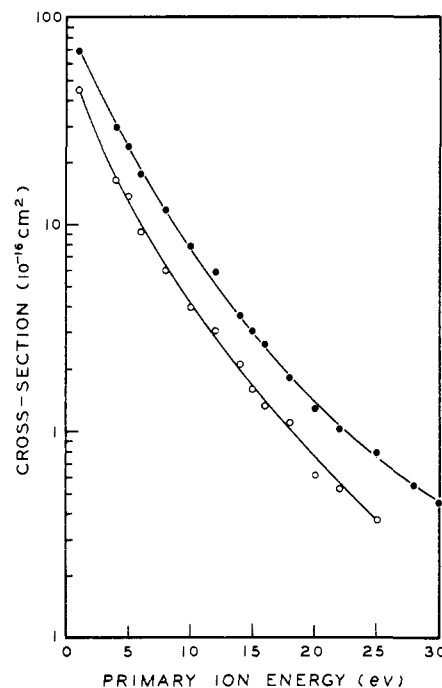


Fig. 1.—Cross-section curves of reactions 1 and 2 plotted as a function of the HD^+ ion energy.

facilitates the observation of both the charge-exchange and mass-transfer reaction products. The secondary ions are counted by using a 17-stage electron multiplier tube with copper-beryllium dynodes. The pulse from this multiplier is amplified by three Hewlett-Packard Type 460 wide-band amplifiers and counted with Baird-Atomic scalars. The present pulse-pair resolution of the counting system is 4 Mc. The peaks obtained are flat topped and saturated by the repeller.

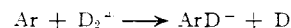
Procedure.—The HD was prepared using a modification of the technique described by Wender, *et al.*¹³ The prepared gas was 96.5% HD. The argon was research grade tank argon purchased from Linde and was 99.995% pure.

The deuterium hydride was introduced into the PMS until the manifold pressure reached about 1.5×10^{-6} torr from an "empty" pressure of about 4×10^{-7} torr. The argon was then introduced into the reaction chamber until a manifold pressure of about 4×10^{-6} torr was obtained. The manifold pressure is monitored using a Consolidated Type GIC-011 ionization gauge.

Results and Discussion

Figure 1 illustrates the cross-section curves for reactions 1 and 2. The cross sections are plotted as a function of the energy of the HD^+ ion. A recent calculation by Moran and Friedman¹⁴ gives a value for the bond energy of ArH^+ . Utilizing this information, the heat of reaction for the above reaction is calculated to be negative. This is consistent with the shapes of the cross-section curves; that is, they monotonically decrease with increasing primary ion energy.

At present we do not have an accurate method of measuring the pressure in the reaction chamber; consequently, the absolute value of the cross section for the reactions studied in this work was obtained by normalizing our results to those published by Giese and Maier⁵ for the reaction



Our other absolute cross sections were then obtained using the ArH^+ results as an internal standard. Although our curve for ArH^+ and the curves of Giese and Maier were not exactly the same shape, the fit

(10) H. M. Rosenstock, C. R. Mueller, M. B. Wallenstein, and M. L. Vestal, U. S. Atomic Energy Commission Report No. J. L. 1-650-3-7, UC-23, Isotopes-Industrial Technology TID-4500, 15th Ed., unpublished.

(11) J. C. Light, *J. Chem. Phys.*, **40**, 3221 (1964).

(12) E. R. Weiner, G. R. Hertel, and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 788 (1964).

(13) I. Wender, R. A. Friedel, and M. Orchin, *ibid.*, **71**, 1140 (1949).

(14) T. F. Moran and L. Friedman, *J. Chem. Phys.*, **40**, 860 (1964).

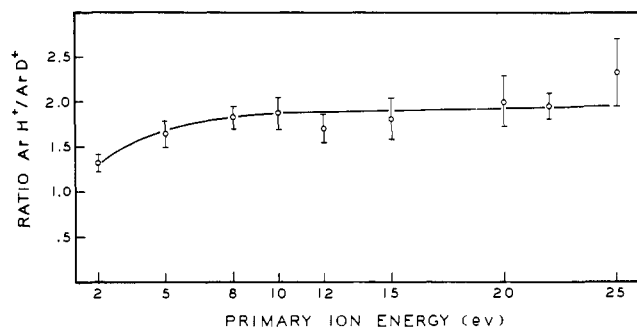


Fig. 2.—Ratio of $\text{ArH}^+/\text{ArD}^+$ as a function of the primary ion energy.

was good at the low energies. There was a divergence between the two curves of about 50% in some energy regions. The reason for this is not clear, but it may indicate that some instrumental discrimination with product ion energies exists in our spectrometer.

It is apparent from Fig. 1 that the cross section for ArH^+ is consistently higher than that for ArD^+ . Figure 2 illustrates the $\text{ArH}^+/\text{ArD}^+$ ratio as a function of the primary ion energy. A statistical analysis of the data was made taking into account the possible sources of error; this is indicated on the plot. The ratio has a value of 1.32 ± 0.095 at 2 e.v. and rises to a value of about 1.86 at the higher primary ion energies.

The dependence of the ratio $\text{ArH}^+/\text{ArD}^+$ on the primary ion energy can be rationalized by considering the possible action of two processes in competition. At low ion energies, there is probably complex formation. If we consider the breakup of any possible complex, the $\text{ArH}^+/\text{ArD}^+$ ratio would be expected to be less than unity. However, throughout the whole energy range we must consider the effect of the conservation of energy and angular momentum. The consequence of these variables can be predicted from the treatment of Rosenstock, *et al.*¹⁰ Here the isotope effect arises from the ratio $m_{iP}m_{nP}/m_{iR}m_{nR}$ and does not have a dependence of the primary ion energy. Rosenstock's approach gives an $\text{ArH}^+/\text{ArD}^+$ ratio of 1.905, interestingly close to our results. It seems possible, then, since these two effects operate in opposite directions, that at low incident ion energies the vibrational effect predominates; whereas at higher incident ion energies, the angular momentum effect predominates. The competition between the two could account for the change in the $\text{ArH}^+/\text{ArD}^+$ ratio with ion energy.

On the other hand, the theory of Light¹¹ indicates an energy dependence. However, since we have not as yet carried out the numerical analysis, it is not clear whether our observations either agree or disagree with his theory.

Our results for the $\text{ArH}^+/\text{ArD}^+$ ratio seem to be somewhat in disagreement with those of Stevenson and Schisler.⁸ They found this ratio to be about 0.85. If our energy variation is real, as it appears to be, an extrapolation of our curve to essentially zero energy could give an $\text{ArH}^+/\text{ArD}^+$ ratio of less than unity. This might tend to resolve the apparent conflict between us since their measurements correspond to much lower bombarding energies than used in this work.

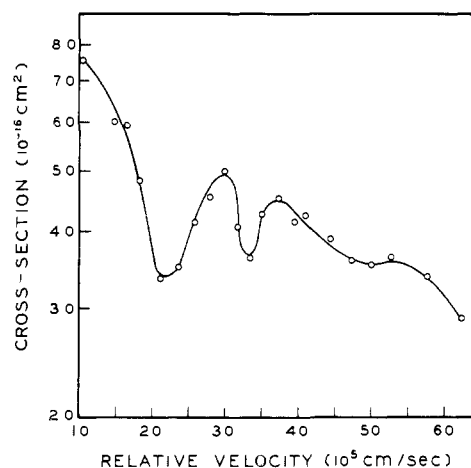


Fig. 3.—Cross section of reaction 3 plotted as a function of the relative velocity of the ion.

When we submitted this paper for publication, a paper by Klein and Friedman¹⁵ on the isotope effect was called to our attention. We are indebted to the authors for a prepublication copy of their report. Although there is no actual duplication in the two studies, they are related and it may be of some interest to compare some of the results. Their work was done on a single-stage mass spectrometer and the primary ion energy attained an average maximum of about 8 e.v. The reaction of Ar^+ and Kr^+ with HD and He and Ne with HD^+ were studied by them.

Using the Eyring-Hirschfelder-Taylor theory,¹⁶ Klein and Friedman interpret the low energy region of their curves as due to complex formation. We are inclined to agree with them about the possibility of complex formation in this energy region. At the higher energies, their results are interpreted as being due to an atom-transfer process, and the lifetimes of any complexes formed would be short. Again, this is not too different, pictorially, from our proposal. However, we interpret the isotope effect in this region as arising mainly from the constraint of conserving angular momentum in the system. The approach of Klein and Friedman¹⁵ would not seem to be able to account for an effect as large as that observed by us.

It is also of interest to note that in the reactions of He and Ne with HD^+ , Klein and Friedman report maxima in the plot of the XH^+/XD^+ ratio as a function of energy. This is explained on the basis of a vibrationally excited HD^+ ion. No such maxima was observed in our reaction of Ar with the HD^+ ion, even though we also have vibrationally excited HD^+ ions present. This apparent difference in behavior may be due to various factors such as differences in the masses and energetics for the various reactions. Further discussion should be postponed until we have completed our studies of the Kr, Ne, and He reactions.

Figure 3 illustrates the cross section for the charge-transfer process (eq. 3). The cross section is plotted as a function of relative velocity of the ion. Reactions of this type are qualitatively governed by the Massey adiabatic hypothesis.¹⁷ The cross sections are expected to go through maxima when the following re-

(15) F. S. Klein and L. Friedman, *J. Chem. Phys.*, to be published.

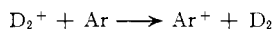
(16) H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *ibid.*, **4**, 479 (1936).

(17) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, New York, N. Y., 1952, p. 478.

lationship is satisfied

$$\frac{|\Delta E|a}{hv_{\text{rel}}} \approx 1$$

where $|\Delta E|$ is the energy defect, a is a parameter and is usually taken as about 7 Å., and v_{rel} is the relative velocity of the ion. As pointed out by Sluyters, *et al.*,¹⁸ this picture depends strongly on the value for $|\Delta E|$. Wolf⁴ examined the reaction



and found a maximum at 1.18 e.v. He assumed the D_2^+ was in the $v = 0$ state and used an energy defect of 0.3 e.v.

It can be seen from Fig. 3 that there are several maxima on the cross-section curve. This may be explained in the light of recent interpretations of the role of higher vibrational states of H_2^+ in ion-molecule reactions.¹⁹⁻²³ von Koch and Friedman¹⁹ calculated the population of the vibrational states of H_2^+ when it is formed by H_2 by the bombardment of 50-e.v. electrons. They found the upper states (to $v = 4$) to have a significant population. Kraus and Kopf²²

(18) Th. J. M. Sluyters, E. de Haas, and J. Kistemaker, *Physica*, **25**, 1376 (1959).

(19) H. von Koch and L. Friedman, *J. Chem. Phys.*, **38**, 1115 (1963).

(20) S. Kerwin, P. Marmet, and E. Clarke, *Can. J. Phys.*, **39**, 1240 (1961).

(21) P. Marmet and L. Kerwin, *ibid.*, **38**, 972 (1960).

(22) M. Kraus and A. Kopf, *J. Chem. Phys.*, **26**, 1776 (1957).

(23) A. Weingartshofer and E. Clarke, *Phys. Rev. Letters*, **13**, 591 (1964).

calculated the transition probabilities from the molecular ground state to various vibrational levels in the molecule ion and found them to be: 0.44, 0.87, 1.00, 0.91, and 0.72. Kerwin, *et al.*,²⁰ measured these transition probabilities and generally corroborated the results. Various investigators have also used vibrationally excited states in charge-transfer reactions.^{18, 24}

The lifetime of some vibrational states of HD^+ have been measured at around 200 μsec .²⁵ Thus, it is almost certain that the HD^+ is formed in vibrationally excited states and that these states live long enough to allow the molecule ion to react in excited states. This makes several values available for $|\Delta E|$ in the charge-transfer process. Thus, although there may be some ambiguity in assigning the observed peaks to particular vibrational states, the observed structure in the cross-section curve suggests that HD^+ ions in the $v = 0, 1, 2, 3$, and perhaps $v = 4$ states are reacting with argon in the charge-exchange process.

In conclusion, therefore, this study reveals an isotope effect in the reaction $\text{HD}^+ + \text{Ar} \rightarrow \text{argon hydrides}$ which is compatible with deductions obtained by considering the conservation of energy and angular momentum in this reaction. In the charge-exchange reaction, the measurements support the idea that vibrationally excited states are involved in the process.

(24) E. Gustafson and E. Lindholm, *Arkiv Fysik*, **18**, 219 (1960).

(25) J. R. Hiskes, *Phys. Rev.*, **122**, 1207 (1961).

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Mechanisms of the Reaction of Vanadium(IV) and Chromium(VI) and of the Induced Oxidation of Iodide Ion¹

BY JAMES H. ESPENSON

RECEIVED JUNE 19, 1964

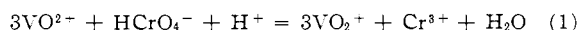
The 3-equiv. reaction between vanadium(IV) and chromium(VI) in acidic perchlorate solution follows the rate equation

$$-d[\text{HCrO}_4^-]/dt = [\text{VO}_2^+]^2[\text{VO}_2^+]^{-1}\{k[\text{HCrO}_4^-] + k'[\text{H}^+][\text{HCrO}_4^-]^2\}$$

at 25° and ionic strength 1.00 F , $k = 0.563 M^{-1} \text{sec}^{-1}$ and $k' = 5.4 \times 10^4 M^{-3} \text{sec}^{-1}$. A mechanism consistent with the first term involves a sequence of three 1-equiv. reactions, in which chromium(V) is an unstable intermediate. The k' pathway presumably involves reaction of dichromate ion along a similar reaction sequence. These postulated mechanisms are compared with results on related systems. The oxidation of iodide ion induced by this reaction is interpreted in terms of its competition for the intermediate chromium(V), and ratios of rate constants are obtained by the study of apparent stoichiometry of the induced reaction. Combination of these results and data from earlier studies on related systems allows some conclusions to be drawn concerning the role of hydrogen ion in several reaction steps.

Introduction

The over-all oxidation-reduction reaction in which chromium(VI) oxidizes vanadium(IV) to vanadium(V) is not expected to occur in a single step, since chromium undergoes a change of three units in oxidation number.



For this reason, the mechanism involves a sequence of less complex elementary reaction steps. Intermediate oxidation states of chromium are expected to play an important role in the mechanism. A preliminary

communication of portions of this work has already appeared.²

With regard to stoichiometry, this reaction is similar to two previously studied reactions, iron(II)-chromium(VI)³ and cerium(IV)-chromium(III).⁴ Both these latter reactions follow essentially the same pattern: reduction of chromium(V) to chromium(IV), or the reverse, is the slowest step in a reaction sequence made up of three 1-equiv. changes.

A thorough study of the kinetic behavior of the vanadium(IV)-chromium(VI) reaction was under-

(1) This work was performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission; contribution No. 1528.

(2) J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 1883 (1964).

(3) J. H. Espenson and E. L. King, *ibid.*, **85**, 3328 (1963).

(4) J. Y.-P. Tong and E. L. King, *ibid.*, **82**, 3805 (1960).