

second-law value in the Knudsen study of Farber are errors in temperature measurement.

With the heat of formation of NiF_2^8 equal to -156 ± 2 kcal. mole $^{-1}$, the heat of sublimation of Ni^9 equal to 102.67 ± 1.40 kcal. mole $^{-1}$, and the atomization energy of fluorine 10 equal to 37.7 ± 0.1 kcal. mole $^{-1}$, one derives a dissociation energy of NiF_2 into atoms of

(8) K. S. Pitzer and L. Brewer, revision of G. N. Lewis and M. Randall, "Thermodynamics," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(9) R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley and Sons, Inc., New York, N. Y., 1963.

(10) J. G. Stamper and R. F. Barrow, *Trans. Faraday Soc.*, **54**, 1592 (1958);

217.0 kcal. mole $^{-1}$ and an average Ni-F bond energy of 108.5 kcal. mole $^{-1}$ (4.71 e.v.). The alternate heat of sublimation for Ni listed by Nesmeyanov, 11 which would seem to be incorrect in view of other values 9 listed in the literature, leads to an average Ni-F bond energy of 4.22 e.v. There are no optical spectroscopic data on $\text{NiF}(g)$ or $\text{NiF}_2(g)$ for comparison.

Acknowledgments.—This work was supported by the United States Atomic Energy Commission, by the National Science Foundation, and by the Advanced Research Projects Agency.

(11) A. N. Nesmeyanov, "Vapor Pressure of the Chemical Elements," Elsevier Publishing Co., New York, N. Y., 1963.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA]

The Photochemistry of Uranyl Oxalate 1

BY D. H. VOLMAN AND J. R. SEED

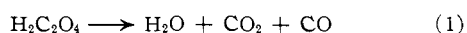
RECEIVED JULY 15, 1964

The photolysis of aqueous solutions of uranyl oxalate-oxalic acid was studied at various intensities, wave lengths, temperatures, concentrations, and acidities. The results are interpreted by the stoichiometrical relations: (1) $\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$; (2) $\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{CO}_2 + \text{HCOOH}$; and (3) $\text{U}^6 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{CO}_2 + 2\text{H}^+ + \text{U}^4$. The fraction of decomposition attributable to each pathway was found to be independent of intensity, wave length, and temperature and to depend on concentration and acidity. Quantum yields of gaseous product formation were evaluated for various experimental conditions. Mechanisms for (1) and (2) are given using the simplest uranyl complexes, $\text{UO}_2(\text{HC}_2\text{O}_4)^+$ and $\text{UO}_2(\text{C}_2\text{O}_4)$. For (3) a mechanism is given which accounts for the products by single electron-transfer steps and disproportionation of U^V to U^{IV} and U^{VI} .

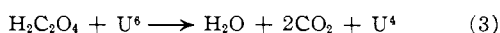
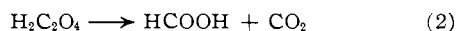
Introduction

For studies of photochemical reactions in aqueous solutions using volumes in the range of 1 to 10 $\mu\text{l.}$, it was necessary to have a suitable actinometric system. Consequently, we developed a simplified method of uranyl oxalate actinometry. 2 The actinometry is based on the determination of CO by flame-ionization gas chromatography after catalytic hydrogenation to methane. 3 The method was more sensitive than reported for any other chemical actinometer known to us.

The reaction usually given 4 for the photodecomposition of oxalic acid in uranyl oxalate actinometry is



From this equation, it appears that it should be possible to relate the CO yield to the oxalate decomposition and, hence, to the light absorbed. This reaction, however, does not represent the experimentally determined stoichiometry. Carter and Weiss 5 considered also the reactions



They observed that the relative proportions of reactions 1, 2, and 3 depend upon the acidity of the solution and the concentration of quenching ion present. Nevertheless, it seemed feasible to establish a relationship between the quantum yield of CO formation and that

of oxalate decomposition. In our earlier work, we established the relationship for a limited range of conditions.

The present work was initiated because of our interest in further development of the actinometric method. It soon became apparent, however, that the problem had inherent photochemical interest aside from actinometry. A major emphasis of this work, therefore, has been on the photochemistry of uranyl oxalate systems.

Experimental

Apparatus.—Experiments using 2537- \AA . radiation were carried out in the manner we have previously described, 6 using a helical mercury resonance arc. The reaction cell was a cylindrical quartz tube, 20-mm. diameter, in which stirring was accomplished by an induction method. For other wave lengths, a Pyrex cell, 42-mm. diameter and 35 mm. deep, with plane parallel windows was used. The light source for these experiments was a medium-pressure mercury arc, UA-3 GE 360-w. lamp. For 3660- \AA . radiation, Corning filter No. 7-39 was used. For 4350- \AA . radiation, an Optics Technology Monopass interference filter was used.

Materials.—Triply distilled water was used in all experiments. Oxalic acid, Mallinckrodt reagent, was recrystallized three times from water, centrifuged, and dried over calcium chloride. Uranyl oxalate was prepared by treating a hot solution of uranyl nitrate with excess oxalic acid. The solution was cooled, the resulting precipitate was centrifuged, washed, and dried, and the optical density at 2537 \AA . was measured. The uranyl oxalate was recrystallized from water and the optical density remeasured. After a third recrystallization, no change in optical density was observed. Some uranyl oxalate was also prepared from commercial uranous oxalate. The uranous salt was oxidized by hot concentrated nitric acid to uranyl and then treated in the manner described above. Uranyl formate was prepared by reacting formic acid with uranyl oxide.

Analysis.—Oxalate was determined by titration with potassium permanganate. Gaseous products, carbon monoxide and carbon

(1) Supported by the U. S. Army Research Office, Durham.

(2) K. Porter and D. H. Volman, *J. Am. Chem. Soc.*, **84**, 2011 (1962).

(3) K. Porter and D. H. Volman, *Anal. Chem.*, **34**, 748 (1962).

(4) C. M. Masson, V. Boekelheide, and W. A. Noyes, Jr., in "Catalytic Photochemical, Electrolytic Reactions" ("Technique of Organic Chemistry," Vol. 2), 2nd Ed., A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, pp. 294, 295.

(5) A. H. Carter and J. Weiss, *Proc. Roy. Soc. (London)*, **A174**, 351 (1940).

(6) D. H. Volman and L. W. Swanson, *J. Am. Chem. Soc.*, **82**, 4141 (1960).

dioxide, were removed from the reaction system by several freeze-pump-thaw cycles, fractionated, and measured in a gas buret. A liquid nitrogen trap retained all of the carbon dioxide and none of the carbon monoxide as determined by mass spectrographic analysis. Alternatively, carbon monoxide and carbon dioxide could be determined by flame-ionization gas chromatography. Following separation of the gases on an activated charcoal column, the individual gases were reduced to methane by catalytic hydrogenation using a nickel catalyst.³ It was found that hydrogenation of carbon dioxide required a longer catalytic column than we reported for carbon monoxide, and a 24-in. column was successfully employed for both gases.

Results

Variation of Intensity.—The absorbed intensity at 2537 Å. was varied over a sevenfold range by controlling the lamp current. The intensities were calculated from determinations of the rate of oxalate decomposition using the quantum yield value of 0.62.⁷ Within the experimental limits, the rate of decomposition was independent of time except for the very large conversions represented in expt. 8 and 9, Table I. At these high conversions, a precipitate identified as $U(C_2O_4)_2 \cdot H_2O$ was formed in the reaction vessel. Columns 4 and 5 give the ratios of CO and CO_2 formed to the oxalate decomposed. In this and subsequent tables, the average deviations are indicated by \pm following the average values.

TABLE I
PHOTOLYSIS OF URANYL OXALATE-OXALIC ACID SOLUTIONS
AT VARIOUS INTENSITIES
(2537 Å.; 30°; $[H_2C_2O_4]_0, 0.05 F$; $[UO_2C_2O_4]_0, 0.01 F$)

Expt. no.	Oxalate decomposed		Gaseous products, moles/mole of oxalate decomposed	
	Fraction	(Moles/min.) $\times 10^4$	CO	CO_2
		$I_a^a = 4.6 \times 10^{-6}$		
1	0.18	1.06	0.55	1.07
2	0.33	0.98	0.53	1.03
3	0.33	0.99	0.55	1.08
4	0.51	1.01	0.50	1.10
5	0.53	1.06	0.47	1.15
6	0.71	1.07
7	0.73	1.00
8	0.75	0.90	..	1.15
9	0.76	0.76	0.47	1.18
Av. 1-5		1.02 ± 0.03	0.52 ± 0.03	1.09 ± 0.03
		$I_a = 2.4 \times 10^{-6}$		
10	0.52	0.52	0.50	1.15
11	0.77	0.51	0.45	1.15
Av.		0.52 ± 0.01	0.48 ± 0.03	1.15 ± 0
		$I_a = 1.33 \times 10^{-6}$		
12	0.05	0.30	0.60	1.14
13	0.15	0.27	0.58	1.07
14	0.24	0.29	0.53	1.05
15	0.38	0.33	0.48	1.10
16	0.44	0.30	0.50	1.12
17	0.52	0.28	0.50	1.08
Av.		0.30 ± 0.02	0.53 ± 0.04	1.09 ± 0.03
		$I_a = 0.69 \times 10^{-6}$		
18	0.073	0.15	0.58	1.10
19	0.15	0.15	0.58	1.08
20	0.30	0.15	0.52	1.05
Av.		0.15 ± 0	0.53 ± 0.04	1.08 ± 0.02

^a In units of einstein/cc./min.

Variation of Temperature.—Table II gives the results of a series of experiments carried out at 50°. For these experiments the lamp intensity was main-

tained constant and about the same as for the highest intensity experiments of Table I. As the quantum yield at 50° is not known, the intensity has not been reported in the table. It is, however, almost certainly in the range $4-4.6 \times 10^{-6}$ einstein/cc./min.

TABLE II
PHOTOLYSES OF URANYL OXALATE-OXALIC ACID SOLUTIONS
AT 50°
(2537 Å.; $[H_2C_2O_4]_0, 0.05 F$; $[UO_2C_2O_4]_0, 0.01 F$; $I_a \sim 4.3 \times 10^{-6}$ einstein/cc./min.)

Expt. no.	Oxalate decomposed		Gaseous products, moles/mole of oxalate decomposed	
	Fraction	(Mole/min.) $\times 10^4$	CO	CO_2
21	0.17	1.02	0.55	1.06
22	0.34	1.03	0.49	1.06
23	0.39	0.99	0.49	1.06
24	0.68	1.02	0.43	1.08
Av.		1.02 ± 0.01	0.49 ± 0.03	1.07 ± 0.01

Variation of Concentration.—Table III gives the results of experiments in solutions in which the concentrations were different from those used in the experiments reported in Table I. The intensities were about equal to the lowest reported in Table I.

TABLE III
PHOTOLYSES OF URANYL OXALATE-OXALIC ACID SOLUTIONS
AT VARIOUS CONCENTRATIONS
(2537 Å.; 30°; $I_a \sim 7.0 \times 10^{-7}$ einstein/cc./min.)

Expt. no.	Initial concn., F		Oxalate decomposed		Gaseous products, moles/mole of oxalate decomposed	
	$UO_2C_2O_4$	$H_2C_2O_4$	Fraction	(Moles/min.) $\times 10^4$	CO	CO_2
25	0.001	0.005	0.11	0.17	0.27	1.33
26			0.21	0.16	0.27	1.31
27			0.36	0.17	0.27	1.20
28			0.49	0.18	0.30	1.21
29			0.63	0.18	0.28	1.24
			Av.	0.17 ± 0.01	0.28 ± 0.01	1.26 ± 0.05
30	0.001	0.01	0.13	0.15	0.44	1.00
31			0.24	0.15	0.40	1.01
32			0.39	0.15	0.31	1.06
			Av.	0.15 ± 0	0.38 ± 0.05	1.03 ± 0.03
33	0.002	0.01	0.14	0.16	0.34	1.27
34			0.17	0.16	0.32	1.16
35			0.41	0.16	0.31	1.14
			Av.	0.16 ± 0	0.32 ± 0.01	1.19 ± 0.05
36	0.006	0.03	0.13	0.16	0.46	1.17
37	0.005	0.05	0.16	0.16	0.52	1.03
			Av.	0.16 ± 0	0.48 ± 0.02	1.10 ± 0.07

Variations of Wave Length.—Table IV gives the results of experiments using 3660 and 4350 Å. light. These experiments were carried out in the Pyrex cell.

Variation of Acidity.—Table V gives the results of experiments carried out with added sulfuric acid in the Pyrex cell. The full light of the medium-pressure mercury lamp was used.

Discussion

The concentrations for which the most accurate quantum yield determinations of uranyl oxalate decomposition have been made are $H_2C_2O_4, 0.05 F$, and $UO_2C_2O_4, 0.01 F$.⁸ These were the concentrations used for the experiments reported in Tables I and II and part of Table IV. Although these are the concentration conditions for which the stoichiometry of eq. 1 might be assumed to hold, our results show that this is not the case; the yield of CO is less than half that of CO_2 and about half of the oxalate decomposition yield.

(8) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 82.

(7) W. G. Leighton and G. S. Forbes, *J. Am. Chem. Soc.*, **52**, 3193 (1930).

TABLE IV
 PHOTOLYSES OF URANYL OXALATE-OXALIC ACID SOLUTIONS AT 3660 AND 4350 Å.

Expt. no.	Conditions	Oxalate decomposed		Gaseous products, moles/mole of oxalate decomposed	
		Fraction	(Moles/min.) × 10 ⁴	CO	CO ₂
38	3660 Å.	0.10	0.021	0.26	1.42
39	UO ₂ C ₂ O ₄] ₀ , 0.001 <i>F</i>	0.40	0.029	0.26	1.21
40	[H ₂ C ₂ O ₄] ₀ , 0.005 <i>F</i>	0.57	0.028	0.24	1.27
41		0.96	0.016	0.24	1.28
		Av. 38-40	0.026 ± 0.003	0.26 ± 0.01	1.30 ± 0.08
42	3660 Å.	0.11	0.63	0.56	1.06
43	[UO ₂ C ₂ O ₄] ₀ , 0.01 <i>F</i>	0.23	0.63	0.55	1.07
44	[H ₂ C ₂ O ₄] ₀ , 0.05 <i>F</i>	0.46	0.59	0.52	1.05
		Av.	0.61 ± 0.02	0.54 ± 0.02	1.06 ± 0.01
45	4350 Å.	0.066	0.33	0.60	1.15
46	[UO ₂ C ₂ O ₄] ₀ , 0.01 <i>F</i>	0.12	0.25	0.57	1.08
47	[H ₂ C ₂ O ₄] ₀ , 0.05 <i>F</i>	0.27	0.18	0.53	1.06
48		0.45	0.23	0.51	1.04
49		0.55	0.23	0.50	1.04
		Av.	0.24 ± 0.04	0.54 ± 0.04	1.08 ± 0.03

 TABLE V
 PHOTOLYSES OF URANYL OXALATE-OXALIC ACID
 IN H₂SO₄ SOLUTIONS

(>2800 Å.; 25°; [H₂C₂O₄]₀, 0.05 *F*; [UO₂C₂O₄]₀, 0.01 *F*)

Expt. no.	H ₂ SO ₄ <i>F</i>	Oxalate decomposed		Gaseous products, moles/mole of oxalate decomposed	
		Fraction	(Moles/min.) × 10 ⁴	CO	CO ₂
50	1.0	0.027	0.20	0.75	1.25
51		0.065	0.19	0.66	1.27
52		0.16	0.16	0.89	1.21
53		0.24	0.12	0.87	1.15
		Av.	0.17 ± 0.03	0.79 ± 0.09	1.22 ± 0.04
54	0.1	0.050	0.75	0.67	1.14
55		0.11	0.68	0.73	1.03
56		0.22	0.67	0.73	1.01
57		0.40	0.60	0.78	1.04
		Av.	0.68 ± 0.04	0.73 ± 0.03	1.03 ± 0.01
58	0.01	0.050	0.75	0.60	1.13
59		0.12	0.74	0.59	1.18
60		0.23	0.68	0.60	1.06
61		0.42	0.64	0.58	1.09
		Av.	0.70 ± 0.04	0.59 ± 0.01	1.11 ± 0.04

ing relations

$$\left. \begin{aligned}
 f_1 &= \frac{(\text{CO})_t}{(\text{H}_2\text{C}_2\text{O}_4)_d} \\
 f_2 &= 2 - \frac{(\text{CO}_2)_t + (\text{CO})_t}{(\text{H}_2\text{C}_2\text{O}_4)_d} \\
 f_3 &= \frac{(\text{CO}_2)_t}{(\text{H}_2\text{C}_2\text{O}_4)_d} - 1
 \end{aligned} \right\} \quad (4)$$

where *t* and *d* refer to total mole amounts formed and decomposed, respectively. From the known quantum yields of oxalate decomposition, the quantum yields attributable to each path may be calculated from the relationship

$$\Phi = f\Phi_d \quad (5)$$

In Table VI, the fraction of decomposition attributable to each pathway, and, where possible, the

 TABLE VI
 DECOMPOSITION PATH AND QUANTUM YIELDS

Wave length, Å.	Initial concn., <i>F</i>		<i>f</i>	<i>f</i> ₁	<i>f</i> ₂	<i>f</i> ₃	Φ(Φ _{CO})	Φ ₁	Φ ₂	Φ _{CO₂}	Φ _{CO} + Φ _{CO₂}
	UO ₂ C ₂ O ₄	H ₂ C ₂ O ₄									
2537	0.01	0.05	0.52	0.39	0.09	0.33	0.24	0.05	0.68	1.01	
2537	0.006	0.03	0.46	0.37	0.17	0.28	0.23	0.11	0.72	1.00	
2537	0.005	0.005	0.05	0.52	0.52	0.03	0.32	0.28	0.02	0.96	
2537	0.002	0.01	0.32	0.49	0.19	0.20	0.30	0.12	0.74	0.94	
2537	0.001	0.01	0.38	0.59	0.03	0.24	0.37	0.02	0.64	0.88	
2537	0.001	0.005	0.28	0.45	0.26	0.17	0.28	0.16	0.78	0.95	
2537 ^a	0.01	0.05	0.49	0.44	0.07						
3660	0.01	0.05	0.54	0.40	0.06	0.26	0.20	0.03	0.52	0.78	
3660	0.001	0.005	0.26	0.44	0.30	0.13	0.22	0.15	0.64	0.77	
4350	0.01	0.05	0.54	0.38	0.08	0.31	0.22	0.05	0.62	0.93	
>2800 ^b	0.01	0.05	0.79	-0.01	0.22						
>2800 ^c	0.01	0.05	0.73	0.24	0.03						
>2800 ^d	0.01	0.05	0.59	0.30	0.11						

^a 50°. ^b [H₂SO₄], 1.0 *F*. ^c [H₂SO₄], 0.1 *F*. ^d [H₂SO₄], 0.01 *F*.

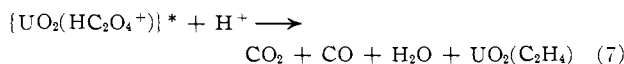
At the present time it is not possible to definitively state the stoichiometrical equations which will account for the relative quantities of CO and CO₂ formed and oxalate decomposed. It, therefore, seems wisest to use the simplest possible set, 1, 2, and 3, suggested by Carter and Weiss.⁵ On this basis, the fraction of reaction by the various pathways is given by the follow-

quantum yields for each pathway and for gaseous product formation are given. For the data of Table I, there is only a single entry in Table VI, as the yields of CO and CO₂ were found to be independent of intensity. The values in the first row of Table VI are, therefore, averages calculated from all of the data in Table I. Quantum yields are not given for values calculated from

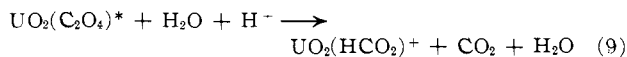
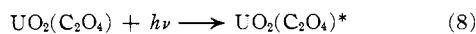
Tables II and V, as the quantum yield for oxalate decomposition is not known for the experimental conditions used. The values of Φ_d used are: 2537 Å., 0.62; 3660 Å., 0.49; 4350 Å., 0.58.⁸

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.

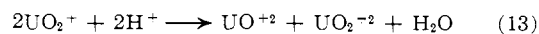
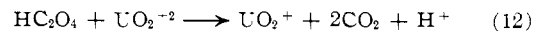
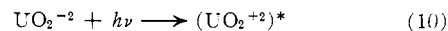


It would be expected that the formate complex would be replaced by an oxalate complex and that formic acid would be produced. Evidence that the oxalate complexes are indeed much stronger than the formate complexes was obtained in the present work by observing the effect on pH of adding uranyl oxalate 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.

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The Argon-Deuterium Hydride Ion Reaction¹

BY M. A. BERTA² AND W. S. KOSKI

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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.

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(2) Air Force Institute of Technology Fellow.

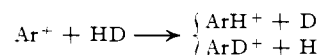
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The reaction



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

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