Rate Constants and Cross Sections for the Production of OH^- from O^- and H^- in Water[1]

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Abstract: Rate constants and cross sections for the reactions $H^- + H_2O \rightarrow OH^- + H_2$ and $O^- + H_2O \rightarrow OH^- + OH$ have been measured as a function of energy in the energy range from 0 to 10 eV. The results show a $V^{-1/2}$ energy dependence for the cross section in the energy range from 0 to 5 eV for both reactions. At higher energies the cross section is about constant with increasing energy. The change in the function is interpreted as a contribution to the abundance of OH^- from the reactions $H^- + H_2O \rightarrow OH^- + 2H$ and $O^- + H_2O \rightarrow OH^- + O + H$. The experimental value for the rate constant for the reaction of H^- with H_2O was found to be $k = 3.8 \times 10^{-9}$ cm^3 molecule^{-1} sec^{-1} compared to a theoretical value of $k = 3.1 \times 10^{-9}$ cm^3 molecule^{-1} sec^{-1}. These values are about an order of magnitude lower than those previously reported for this reaction in the literature. The value of the rate constant for the reaction of O^- with H_2O was $k = 1.35 \times 10^{-9}$ compared to the theoretical value of $k = 1.0 \times 10^{-9}$ cm^3 molecule^{-1} sec^{-1}. No previous value of this rate constant is available for comparison with the present results. Results from this study show that the theory of ion–molecule reactions can be used to estimate rate constants for reactions of anions and neutral molecules.

Despite the theoretical and experimental interest in phenomena associated with the interaction of ionizing radiation with matter, few reliable rate constants and cross sections for negative ion–molecule reactions at low energies are available. A research mass spectrometer provides an environment especially suited to investigate such reactions, since the pressure and temperature are easily controlled. Furthermore, the comparative simplicity of negatively charged species found in the mass spectrometer makes possible the interpretation of the dynamics in terms of the fundamental properties of the individual molecules and ions. The exact nature of the elementary reactions which produce ionic species in a gas controls such factors as ion mobility, emission of electromagnetic radiation, and production of neutral chemical products. It is therefore of great importance not only to learn the identity of the terminal negative ions but also to identify the elementary reactions which lead from a primary product to a specific negative ion and a specific neutral product.

In the low-energy region, 0–20 eV, two main processes substantially determine the composition of the terminal ions. They are simple charge transfer and ion–molecule reactions. In a pure system, such as water, in which the electron affinity of the parent neutral molecule is low, simple charge transfer is relatively unimportant. Ion–molecule reactions in water vapor have been studied rather extensively. Yet, even the simplest negative ion–molecule reactions in water are not completely characterized. This is true because of the reatively low cross section for the production of negative ions by low-energy electrons. Hence the abundance of ions produced by a secondary reaction is quite low even in the relatively high 10^{-3}-Torr pressure range.

In addition to the identification of specific reaction products, the energy dependence of the reaction cross section, σ, is of great importance. Theory predicts[2] an $E^{-1/2}$ dependence for an interaction potential of $\phi = -2e^2\alpha r^{-4}$ where e is the charge on the electron, α is the polarizability of the neutral molecule, and r is the internuclear distance. For this interaction potential, the rate constant k is equal to σv and is independent of energy. Thus, a rate constant determined at any energy can be extrapolated to thermal energy. In short, if the energy dependence of σ is known, results obtained at higher energy can be extrapolated to thermal energies.

The purpose of the present work was to measure the absolute value for reaction cross sections for negative ion–molecule reactions in H_2O as a function of translational energy. The results could be used to test the various theoretical models which have previously been applied mainly to positive ion–molecule reactions.[3–6] Briefly, the models show either an E^{-1} or an $E^{-1/2}$ energy dependence.

The classical theory[3a] uses as a model the interaction of a point charge and a polarizable molecule at rest. Calculations based on this model show the $E^{-1/2}$ energy dependence for σ. To correct for the point-charge concept, Hamill and Theard[3b] introduced a "geometrical cross section" correction term to the classical theory. At high energies the "geometrical cross section" term dominates and the energy dependence changes from $E^{-1/2}$ to E^{-1}. Light and Horrocks[4] have also used the hard-sphere collision concept to deduce an E^{-1} energy dependence for relatively high-energy collisions. Dugan and Magee[5] also predict from a quantum mechanical model an E^{-1} energy dependence for σ in the high-energy region. Because of limited experimental data, these models have not been tested for even very simple negative ion–molecule reactions. Thus, our present results were to be used to either support or modify the theories from the negative ion–neutral molecule aspect.

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(1) Supported by the U. S. Atomic Energy Commission under Contract No. At-(40-1) 3729 with the University of Georgia.

(2) C. E. Melton, "Principles of Mass Spectrometry and Negative Ions," Marcel Dekker, New York, N. Y., 1970, p 273.

(3) (a) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958); (b) L. P. Theard and W. H. Hamill, *J. Amer. Chem. Soc.*, **84**, 1134 (1962).

(4) J. C. Light and J. Horrocks, *Proc. Phys. Soc., London*, **84**, 527 (1964).

(5) J. V. Dugan and L. J. Magee, NASA TN-D 3229, Feb 1966.

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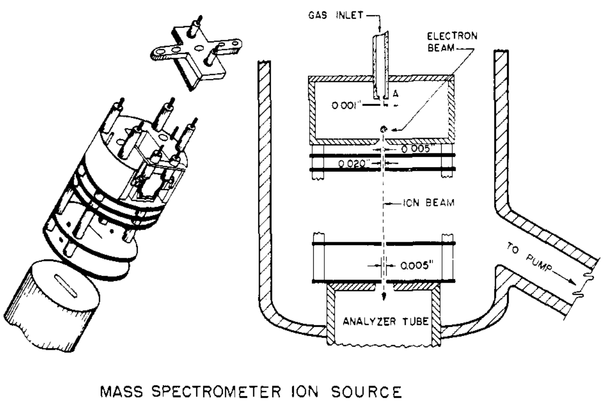

Figure 1. High-pressure ion source for the mass spectrometer.

Experimental Section

Results were obtained with a 6-in. radius, 90° sector type of research mass spectrometer constructed at this laboratory. The instrument, experimental procedures, and necessary calibration have been described elsewhere.[7,8] Therefore, only a brief recount will be given here.

For the experiments, a triply distilled sample of water was expanded into a 5-l. borosilicate glass-expansion reservoir. The reservoir was connected to the ionization chamber by a molecular leak 0.001 in. in diameter. Gas flowed through the leak and into a "tight" ionization chamber. (See Figure 1. The ion exit slit is 0.005 × 0.250 in.) Pressures as high as 0.6 Torr could be maintained in the ionization chamber. The sample was ionized by electrons of controlled energy and intensity emitted from a thoria iridium filament. Reaction mechanisms were deduced by the usual method of studying the intensity of primary and secondary ions as a function of electron energy and pressure in the ionization chamber. The pressure in the ionization chamber was determined by methods previously discussed.[7,8] Because of adsorption on surfaces, the pressure of the water vapor was difficult to measure directly in the ionization chamber. A method was used in which water vapor was maintained at the normal vapor pressure in the expansion volume for suitable constant-temperature baths. Thus, the pressure behind the leak could be measured and calculated. The density of water vapor effusing from the leak was assumed to be equal to that for argon, with equal pressures for the two gases behind the leak. The pressure of argon in the ionization chamber was calculated from a knowledge of the experimental parameters and the relationship

$$N^+ = \sigma N_0 N_e l \qquad (1)$$

where N^+ is the ion current, N_0 is the density of neutral species, N_e is the electron current, and l is the path length for the electrons.

A value of $\sigma = 2.79 \times 10^{-16}$ cm^2 was used for the cross section for production of $^{40}Ar^+$ with 100-eV electrons.[7-9] As tests of the apparatus and of the pressure determination, the ionization cross section for O^- from O_2 was measured at an electron energy of 6.6 eV. A measured value of 1.32×10^{-18} cm^2 was obtained. The value is in good agreement with some recent experimental values of 1.3×10^{-18} cm^2. The energy scale was calibrated with O^- from CO, AP(O^-/CO) = 9.5 eV,[10] and O^- from O_2, AP(O^-/O_2) = 4.4 eV.[10] The appearance potential (AP) of an ion is defined as the minimum energy required to produce that ion from a given neutral molecule.

Ions were detected by means of either a Faraday cup attached to vibrating capacitor amplifier, which activated a strip-chart recorder, or a 14-stage electron multiplier amplifier. A 10^{10}-ohm Victoreen glass-encased input resistor was used with the Faraday cage. The trace of the actual intensity of a given ion beam was measured by a millimeter scale. The detector circuit was calibrated for linearity by measuring the isotopic abundance of neon on three different scales and comparing the experimental results with the known value. The linearity was better than 0.25% over all ranges.

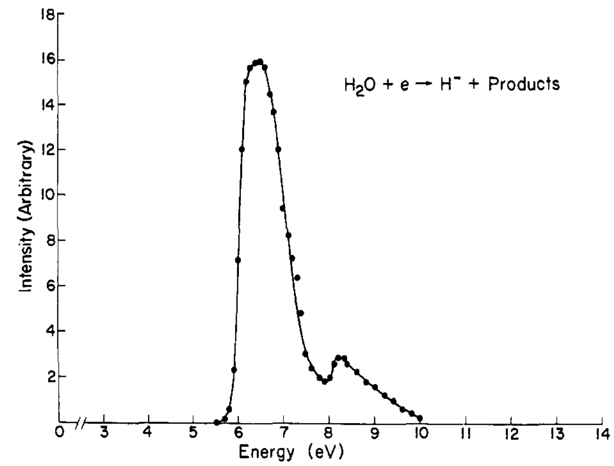

Figure 2. Ionization efficiency curve for the production of H^- from H_2O by electron impact.

Results and Discussion

The measured value for rate constants and cross sections for the reactions

$$H^- + H_2O \longrightarrow OH^- + H_2 \qquad (I)$$

and

$$O^- + H_2O \longrightarrow OH^- + OH \qquad (II)$$

are given in Table I. The values were measured with the ionizing electron beam adjusted to produce the maximum intensity of reactant ions. For example, reaction I was studied for an electron energy of 6.5 eV (see Figure 2) and reaction II was studied for an electron energy of 11 eV (see Figure 3). These two values of electron energy were selected to minimize interference of reaction I with reaction II. For example, reaction I does not occur at 11 eV because the abundance of H^- is essentially zero, as shown in Figure 2. Although reaction II can interfere with the interpretation of reaction I at 6.5 eV (see Figure 3), the abundance of O^- formed at 6.5 eV is only 3% of that of H^- formed at this energy.

Table I. Rate Constants and Cross Sections[a]

$H^- + H_2O \rightarrow OH^- + H_2$			$O^- + H_2O \rightarrow OH^- + OH$		
Energy,[b] eV	k	σ	Energy, eV	k	σ
0.5	3.83	3.85	0.5	1.35	5.40
1.0	3.79	2.72	1.0	1.32	3.78
1.5	3.82	2.22	1.5	1.39	3.23
2.0	3.81	1.92	2.0	1.36	2.74
2.5	3.86	1.75	2.5	1.35	2.45
3.0	3.85	1.60	3.0	1.32	2.18
3.5	3.87	1.48	3.5	1.37	2.10
4.0	3.84	1.37	4.0	1.35	1.93
4.5	3.86	1.30	4.5	1.38	1.84
5.0	3.90	1.25	5.0	1.42	1.82

[a] k is in cm^3 molecule^{-1} sec^{-1} and σ is in 10^{-15} cm^2 molecule^{-1}.
[b] In the laboratory system.

The abundance of OH^- as a function of energy is given in Figure 4. Because of the high abundance of H^- relative to O^-, the abundance of OH^- found by reaction I is much higher than that formed by reaction II.

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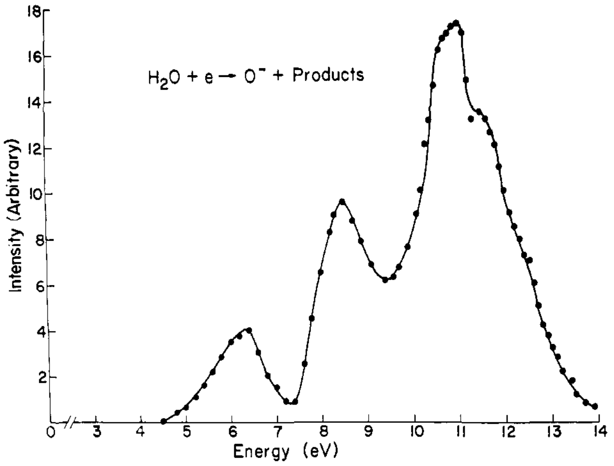

Figure 3. Ionization efficiency curve for the production of O^- from H_2O by electron impact.

The ion energy given in Table I is the maximum energy of the ion, *eEd*, where *e* is the charge of the ion, *E* is the electric field strength, and *d* is the ion path length in the ionization chamber. Thus, the cross sections represent average values rather than discrete values for an exact energy. In the low-energy region, however, the value of the rate constant is independent of energy.

At higher energies the rate constant increases with increasing ion energy. This behavior may be caused by the occurrence of the reaction

$$O^- + H_2O \longrightarrow OH^- + O + H \qquad \text{(III)}$$

The onset for reaction III is at about 5 eV ion energy. The cross section for reaction II also changes from a $V^{-1/2}$ dependence in this energy range as shown in Figure 5.

The cross sections and rate constants for reaction I differ by about an order of magnitude from those reported by Stockdale, *et al.*[10] No ready explanation for this large discrepancy can be given. The pressure measurement is most suspect, but this source of error is unlikely in view of the fact that the absolute values of the cross section for production of H^- from H_2O reported by these workers[11] are in good agreement with those reported by this laboratory.[6] An error in the measurement of the pressure for either group would give disagreement in the value of the absolute cross section. Unfortunately, no values for rate constants and cross sections for reaction II are available for comparison with this investigation. The reaction has been studied by other workers, but values of the rate constants and cross sections were not reported.

If one assumes that the theory for positive ion-molecule reactions can be applied to negative ions, rate constants can be calculated for comparison with experiment. The rate constant is given by the relationship

$$k = (eEd/M)^{1/2}Q \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \qquad (2)$$

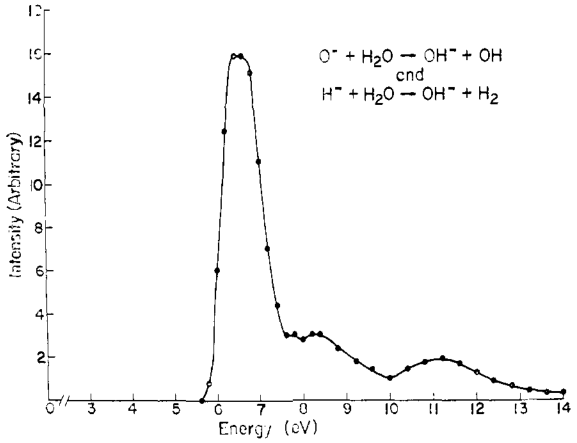

Figure 4. Ionization efficiency curve for the production of the secondary ion, OH^-, from H_2O by electron impact.

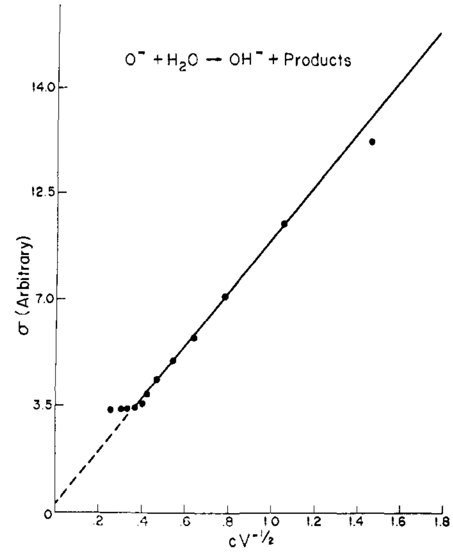

Figure 5. Energy dependence of the cross section for the production of OH^- by an ion-molecule reaction of O^- with H_2O.

where *e* is the charge of the electron, *E* is the electric field strength, *M* is the mass of the ion, *d* is the distance the ion travels, and

$$Q = 2\pi\left(\frac{2Me^2\alpha}{M_r}\right)^{1/2}\frac{1}{(eEd)^{1/2}} \text{ cm}^2 \text{ molecule}^{-1} \qquad (3)$$

where α is the polarizability of the neutral and M_r is the reduced mass. Substituting appropriate values in eq 2, we obtain, for the reaction of H^- with H_2O, $k = 3.1 \times 10^{-9}$ cm^3 molecule^{-1} sec^{-1} and, for the reaction of O^- with H_2O, $k = 1.0 \times 10^{-9}$ cm^3 molecule^{-1} sec^{-1}. The theoretical values for each reaction are about 30% lower than our experimental values. On the other hand, the theoretical values are an order of magnitude lower than the previously reported[10] experimental values.

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[11] R. N. Compton and L. G. Christophorou, *Phys. Rev.*, **154**, 110 (1967).