

Reaction of O^+ , CO^+ , and CH^+ Ions with Atomic Hydrogen

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Rate coefficients for reactions of the ions O^+ , CO^+ , and CH^+ with atomic hydrogen have been measured for the first time at 300 K. This provides basic data for the ion chemistry of planetary atmospheres, cometary atmospheres, and interstellar molecular clouds. The $O^+ + H$ measurement supports quantal calculations of this reaction. The $CO^+ + H$ reaction provides an example of partial spin nonconservation in a charge-transfer reaction occurring in a deep potential well. Reactions of the same ions with H_2 that have been measured elsewhere are also reported.

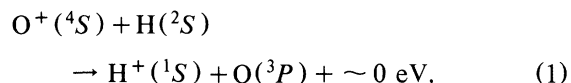
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Reactions of ions with atomic hydrogen may be important in interstellar molecular clouds and in planetary and cometary atmospheres where atomic hydrogen is abundant. They may also be important in laboratory discharges, plasmas, and combustion systems. Atomic hydrogen reactions are particularly important at the boundaries of fusion reactors. The relative simplicity of the atomic hydrogen reactant allows theoretical determination of rate coefficients in some cases. For these reasons we have measured the previously unmeasured reactions of O^+ , CO^+ , and CH^+ ions with atomic hydrogen. Measurements with molecular hydrogen, which have previously been carried out, were also a consequence of the experiment.

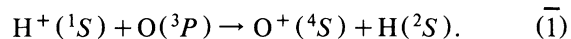
The measurements were carried out at 300 K in selected-ion-flow drift tubes in Trento and in Innsbruck. The measurements involving H_2 as a reactant were straightforward, just as described by McFarland *et al.*¹ For the atomic hydrogen reactions, H_2 was dissociated in a high-frequency discharge (Trento) and, alternatively, by surface dissociation (Innsbruck) and the mixture of H_2 and H introduced into the drift tube. The problem of competition between the reactions of the above ions with H and with H_2 was solved in two steps. (a) The degree of dissociation of hydrogen was determined in each case by applying a recently developed method² involving the reaction of CO_2^+ with H and H_2 . The CO_2^+ reaction with H_2 produces $CO_2H^+ + H$ but no COH^+ product ions,

while CO_2^+ reacting with H results in COH^+ product ions but no CO_2H^+ . The known rate coefficients for these reactions allow us to determine the degree of dissociation from the differences in the respective CO_2^+ ion decreases and CO_2H^+ ion increases when the dissociation source is on and off. (b) With knowledge of the degree of hydrogen dissociation, the same method² is then applied (observation of the decrease of the ion signals of O^+ , CO^+ , and CH^+ with the source on and off) to obtain the rate coefficients for the reactions of the above ions with H_2 and H, respectively. The values obtained for the rate coefficients were the same with the two atomic hydrogen sources used and the accuracy of measurement is believed to be better than $\pm 30\%$.

The results are given in Table I. For the reaction



the measured rate coefficient is $k_1 = 6.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ over the experimental range of mean average kinetic energies (\bar{E}_{KE}) from 0.05 to 0.15 eV. This measurement confirms the theoretical value of k_1 as well as the value of k_1 that has been deduced from measurements of the reverse reaction ($\bar{1}$),



The measured value⁶ of $k_{\bar{1}} = 3.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \pm 50\%$ yields a value of $k_1 = 6.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$

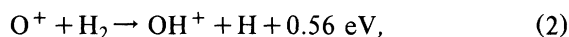
TABLE I. Measured reaction-rate coefficients.

Reaction	$k(\bar{E}_{KE})$ ($\text{cm}^3 \text{s}^{-1}$)	E_{KE} (eV)	k_L ($\text{cm}^3 \text{s}^{-1}$)	Other values (300 K)	
(1) $\text{O}^+ + \text{H} \rightarrow \text{H}^+ + \text{O}$	6.0×10^{-10}	0.06	2.0×10^{-9}		
(2) $\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}$	1.2×10^{-9}	0.07	1.6×10^{-9}	1.7×10^{-9a}	2.0×10^{-9b}
(3) $\text{CO}^+ + \text{H} \rightarrow \text{H}^+ + \text{CO}$	7.5×10^{-10}	0.06	1.9×10^{-9}		
(4) $\text{CO}^+ + \text{H}_2 \rightarrow \text{HCO}^+ + \text{H}$	1.3×10^{-9}	0.06	1.5×10^{-9}	1.8×10^{-9c}	2.0×10^{-9b}
(5) $\text{CH}^+ + \text{H} \rightarrow \text{C}^+ + \text{H}_2$	7.5×10^{-10}	0.05	2.0×10^{-9}		
(6) $\text{CH}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + \text{H}$	1.2×10^{-9}	0.065	1.6×10^{-9}		1.2×10^{-9d}

^aRef. 3.^bRef. 4.^cN. G. Adams, D. Smith, and D. Grief, *Int. J. Mass Spectrom. Ion Phys.* **26**, 405 (1978).^dRef. 5.

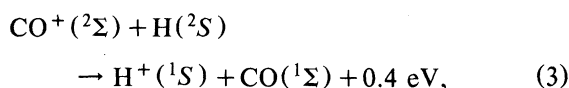
$\pm 50\%$. Theoretical quantal calculations⁷ yield a value of $k_1 = 5.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \pm 15\%$ at 300 K, increasing to $7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 1000 K. The calculations show that the charge transfer is due to strong radial coupling between the $B^3\Sigma^- \text{ O}^+ + \text{H}$ and the $X^3\Sigma^- \text{ O} + \text{H}^+$ potential curves at large internuclear distances, $(8-12)a_0$. The calculated value of k_1 is then close to the spin-weighted fraction ($\frac{3}{8}$) of the Langevin collision rate constant for the $^3\Sigma^-$ state, $k_L = 2\pi e[\alpha(\text{H})/\mu]^{1/2}$, $7.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, where $\alpha(\text{H}) = 0.667 \text{ \AA}^3$ is the polarizability of H and μ is the $\text{O}^+ + \text{H}$ reduced mass. Thus the present measurement confirms both theory and the previous measurement of the reverse reaction (1). Reaction (1) is the major source of H^+ ions in the Earth's upper ionosphere.⁶

For the reaction



the measured value of $k_2 = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ is $\frac{3}{4}$ of the Langevin value, $k_L = 1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The early measurements⁴ which gave $k_2 = 2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \pm 30\%$ are now known to have been systematically too high. Later measurements³ yielding $k_2 = 1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \pm 20\%$ are also apparently slightly too high. No case of a rate coefficient which exceeds the collision rate constant for a thermal energy reaction has yet been established. The lower limits of the earlier measurements are almost within the present experimental error.

For the reaction



the measured value for k_3 is $7.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The Langevin collision rate coefficient $k_L = 1.9$

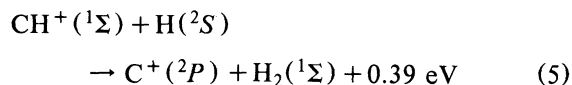
$\times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Since only the singlet products of (3) are energetically accessible, one might expect $k_3 \leq \frac{1}{4} k_L = 4.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, where $\frac{1}{4}$ is the statistical-weight ratio of singlet products to total products. The measured value clearly exceeds that, implying some "spin conversion" in the reactive collision. Recently, five examples of such spin conversion in thermal-energy charge-transfer reactions have been reported.⁸ The charge transfer $\text{CO}^+ (^2\Sigma) + \text{NO} (^2\Sigma) \rightarrow \text{NO}^+ (^1\Sigma) + \text{CO} (^1\Sigma)$ also indicates spin nonconservation,⁷ coincidentally by the same ratio as Reaction (3). The most extreme spin nonconservation case, $\text{H}_2\text{O}^+ (^2B) + \text{NO}_2 (^2A) \rightarrow \text{H}_2\text{O} (^1A) + \text{NO}_2^+ (^1\Sigma)$ occurs on essentially every collision. The $\text{CO}^+ + \text{H}$ reactants enter a very deep potential well (6.6 eV), much deeper even than the $\text{H}_2\text{O}^+ - \text{NO}_2$ potential well depth which is ~ 3.6 eV. A deep well facilitates the occurrence of the curve crossings which are presumably necessary for the spin conversion to occur.

For the reaction



the rate coefficient $k_4 = 1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ is close to $k_L = 1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, as expected. The earlier measurements are somewhat too high just as in the case of the $\text{O}^+ + \text{H}_2$ reaction.

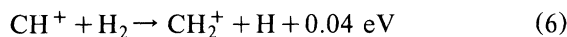
The reaction



has a rate coefficient $k_5 = 7.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which is large although substantially less than $k_L = 2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The value k_5 decreases as $\sim (\bar{E}_{KE})^{-1.1}$ from 0.05 to 0.12 eV. The measured value of k_5 allows no greater than a 0.03-eV barrier

height on the reaction surface and the decrease with \bar{E}_{KE} suggests no barrier at all. Calculations^{9,10} of the potential surface show that a barrier exists on the collinear $^2\Sigma^+$ potential surface but that deviations from collinear geometry suffice to remove the barrier. The CH^+ ion has been observed in diffuse interstellar molecular clouds and accounting for its production has been a problem. Low-temperature ion chemistry cannot occur, since the reverse reaction to (5), which would produce CH^+ , is endothermic. It is now believed¹¹ that CH^+ is probably produced in high-temperature shocked gas by this endothermic reaction. In any case the loss process (5) must be included in any attempt to model CH^+ concentrations in interstellar molecular clouds. In view of the present measurement it appears that a value near the collision rate constant will be appropriate to low temperatures, but a smaller value at the high shock temperatures. The value in the Prasad and Huntress model,¹² $k_5 = 9.4 \times 10^{-12} (T/300 \text{ K})^{1.25} \text{ cm}^3 \text{ s}^{-1}$ is too small by about three orders of magnitude at $\sim 50 \text{ K}$.

Finally, the reaction



has a rate coefficient $k_6 = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, which agrees precisely with a measurement of Smith and Adams.⁵ The value of k_L is $1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

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