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## Dynamics of the ion-molecule reaction $\text{Kr}^+(\text{H}_2, \text{H})\text{KrH}^+$

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The ion-molecule reaction



has recently aroused considerable interest for several reasons. Although the reaction is exoergic by 0.3 eV (see below), an energy barrier of 0.44 to 1.2 eV was predicted by Kuntz and Roach,<sup>1</sup> who employed a semi-empirical diatomics-in-molecules technique to calculate a potential energy surface for the ground state of linear  $\text{KrH}_2^+$ . This prediction, at odds with the long established maxim that exoergic reactions of positive ions have no activation energy,<sup>2</sup> was seemingly supported by an analysis<sup>3</sup> of the differential cross section for scattering of  $\text{H}_2^+$  on Kr. However, the thermal energy rate coefficient for the reaction of  $\text{Kr}^+(^2P_{3/2})$  with  $\text{H}_2$  has recently been measured by a variety of techniques.<sup>4-6</sup> The values obtained, although nearly an order of magnitude smaller than the thermal energy rate coefficient for the analogous reaction of  $\text{Ar}^+$ , have indicated that the activation energy for Reaction (1) can be no larger than 0.05 eV.

Ion beam studies<sup>7</sup> of the reaction  $\text{Kr}^+(\text{D}_2, \text{D})\text{KrD}^+$  gave the unexpected result that the product ion is isotropically distributed about the center of mass (c.m.) at 0.87 eV initial relative energy, although at higher energy (2.7 eV) the product distribution does more nearly resemble what one would expect on the basis of the now familiar spectator stripping model.<sup>8</sup>

A third unusual feature of this reaction is the observation<sup>6,9</sup> that the  $^2P_{1/2}$  excited state of  $\text{Kr}^+$  reacts with  $\text{H}_2$  only half as rapidly as does the  $^2P_{3/2}$  ground state. This fact has been attributed<sup>6</sup> to an avoided crossing which causes the  $^2P_{3/2}$  state to correlate with ground state products and the  $^2P_{1/2}$  state to correlate with excited state products.

We report here the results of a study in which velocity vector distributions and integral cross sections for Reaction (1) were measured over the range 0.036–3.0 eV initial relative energy. The beam instrument used in this study is a single beam-collision chamber type of chemical accelerator with product velocity and angular analysis.<sup>10,11</sup>

Because the reactant ions are produced by impact of

35 eV electrons, nearly all (98.5%) of the  $\text{Kr}^+$  ions are in the  $^2P$  state.<sup>12</sup> These ions are presumably distributed statistically in a 2:1 ratio between the  $J=3/2$  and the  $J=1/2$  levels,<sup>13</sup> which differ in energy by 0.66 eV.<sup>14</sup>

The value of 0.3 eV for the exoergicity of Reaction (1) is calculated from the dissociation energy  $D_0(\text{KrH}^+) = 4.38$  eV, derived from a flowing afterglow study of the equilibrium between  $\text{KrH}^+$  and  $\text{H}_3^+$  in Kr- $\text{H}_2$  mixtures.<sup>15</sup> This bond energy is in good agreement with values calculated from data on the elastic scattering of protons on krypton.<sup>16,17</sup>

Product velocity vector distributions<sup>18</sup> for Reaction (1) show that the  $\text{KrH}^+$  ions are scattered in a nearly isotropic manner about the c.m. at relative collision energies less than about 1 eV. Such symmetry about the c.m. would necessarily be produced if the reaction proceeded via the formation of a collision complex whose lifetime exceeded several rotational periods; there is, however, no reason to suppose that the potential energy hypersurface for Reaction (1) contains a basin of the depth necessary for the formation of such a complex. The most plausible explanation, therefore, for the observed isotropic product velocity vector distributions is that, at these low energies, Reaction (1) occurs directly in rather intimate (i.e., small impact parameter) collisions which lead to hard-spherelike scattering of the ionic product and concomitant momentum transfer to the freed atom.

With increasing collision energy, however, the peak in the  $\text{KrH}^+$  velocity vector distribution shifts to the forward direction, approaching the velocity expected on the basis of the spectator stripping model<sup>8</sup> at collision energies of 2–3 eV (c.m.). These results, therefore, essentially confirm those previously reported by Henglein and co-workers<sup>7</sup> for the reaction  $\text{Kr}^+(\text{D}_2, \text{D})\text{KrD}^+$ .

Integral reaction cross sections  $\sigma_R$  are calculated from the thin-target approximation

$$\sigma_R = \frac{I_C(0^\circ)K_C/K_A}{I_A(0^\circ)n_B L}, \quad (2)$$

where  $I_C(0^\circ)$  and  $I_A(0^\circ)$  are, respectively, the product and reactant ion intensities measured at the angle of

TABLE I. Integral cross sections for the reaction  $\text{Kr}^+(\text{H}_2, \text{H})\text{KrH}^+$ .

Most probable relative energy	Collection efficiency	Integral cross section
$E(\text{eV})$	$K_C/K_A$	$R(\text{\AA}^2)$
0.036	1.32	9.77
0.056	2.29	10.5
0.058	2.16	9.62
0.113	1.62	7.65
0.141	1.42	6.36
0.174	1.70	6.44
0.233	1.51	5.27
0.280	1.17	3.23
0.282	1.47	4.07
0.316	1.39	4.21
0.387	1.41	3.81
0.458	1.51	3.23
0.482	1.21	3.33
0.581	1.01	1.96
0.699	1.34	1.82
0.940	1.27	0.73
1.17	1.15	0.98
1.19	1.47	0.47
1.42	1.21	0.50
2.13	1.10	0.59
2.37	1.20	0.56
2.96	1.16	0.49

The  $\text{Kr}^+$  reactant, produced by impact of 35 eV electrons, is presumably a 2:1 mixture of  $\text{Kr}^+(^2P_{3/2})$  and  $\text{Kr}^+(^2P_{1/2})$ .

maximum intensity,  $n_B$  is the number density of  $\text{H}_2$  molecules in the collision chamber, and  $L$  is the collision path length. The factor  $K_C/K_A$ , which accounts for differences in collection efficiency caused by differences in angular distributions, is obtained directly by appropriate integration of the measured angular distributions at each collision energy.<sup>11</sup> The values obtained and the integral cross sections for Reaction (1) are listed in Table I. The experimental uncertainty in  $\sigma_R$  is estimated to be  $\pm 50\%$ .

At the lowest collision energies, the cross sections reported here for Reaction (1) are only about 1/5 the size of those for the corresponding reaction of  $\text{Ar}^+$ , in agreement with the thermal energy rate coefficients measured for Reaction (1).<sup>4-6</sup> At higher collision energies, the ratio is more nearly 1/10, as first reported by Henglein and co-workers.<sup>7</sup> Over the energy range 0.05–1.0 eV (c. m.), the absolute values measured in the present study are consistently smaller (by about 30%) than the values determined by Henchman and co-workers,<sup>19</sup> although both sets of data indicate that the cross section varies with collision energy approximately as  $E^{-1/2}$ . A similar energy dependence was observed in an ion cyclotron resonance study of

this reaction from thermal energies up to 0.25 eV (c. m.).<sup>6</sup>

The magnitude of the cross sections reported here and the monotonic increase in  $\sigma_R$  with decreasing collision energy essentially confirm the conclusion reached in the earlier, thermal energy studies of this reaction; namely, there is no detectable energy barrier to Reaction (1). Additionally, the observation that the integral cross section for Reaction (1) is much smaller (approximately 1/10) than that predicted by the Langevin ion-induced dipole cross section is consistent with the conclusion, inferred from the isotropy of the product velocity vector distributions at low collision energies, that Reaction (1) only occurs in small impact parameter collisions.

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