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Molecular hydrogen exchange: A study of $\text{HD}(v=5) + \text{HD}(v=0) \rightarrow \text{H}_2 + \text{D}_2$ ^{a)}

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Many experimental and theoretical endeavors have tried to elucidate the reaction mechanism for molecular hydrogen exchange, $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$ (I). Early experiments¹ implied an atomic mechanism of heterogeneous atom production followed by $\text{D} + \text{H}_2 \rightarrow \text{H} + \text{HD}$, etc. (II). Shock tube studies by Bauer and co-workers² and others³⁻⁵ instead suggested a four-centered molecular mechanism involving translationally cool, vibrationally excited reactants, with an activation energy E_{act} for the elementary reactions (I) and (I_{rev}) of ~ 38 kcal/mole.⁵ After measuring the H atom concentration and HD yield in shock tube $\text{H}_2 + \text{D}_2$ mixtures, Lifshitz and Frenklach^{3(b)} concluded that there were too few H atoms to account for the product solely through the atomic route.⁶ Notably, Bauer *et al.*^{7,8} have excited room-temperature H_2 [or D_2], to $v=1$ by stimulated Raman scattering (SRS), and accounted for the observed HD product by the elementary reaction of $\text{D}_2(v=0)$ and V-V collisionally pumped $\text{H}_2(v \geq 3)$. Yet, several recent investigators^{9,10} maintain that only the atomic mechanism can sufficiently well explain all these observations. The present study experimentally addresses the importance of the molecular mechanism in hydrogen exchange.

The central focus in this controversy is that the ground electronic state $\text{H}_2 + \text{D}_2$ orbitals do not directly correlate with ground state 2HD for the expected square planar transition state.¹¹ Extensive calculations of reaction pathways for several bimolecular transition state geometries by Silver and Stevens¹² have shown that the reaction barrier lies above the $\text{H}_2 + 2\text{H}$ asymptote for each configuration. Wright¹³ has pointed out that a six-center, hexagonal transition state allows thermal reaction; calculations by Dixon *et al.*¹⁴ suggest $E_{\text{act}} \approx 60$ –67 kcal/mole for this trimolecular reaction, and that Bauer *et al.*'s SRS⁷ (though not the shock tube) findings can be explained using this mechanism. However, recent calculations by Goddard and Csizmadia¹⁵ indicate that the lowest H_4 singlet excimer state probably lies less than 54 kcal/mole above $\text{H}_2 + \text{H}_2$, and may thus serve as the transition state for concerted molecular $\text{H}_2 + \text{D}_2$ exchange. Bauer¹⁶ has reviewed in detail the previous experimental and theoretical research on hydrogen exchange.

This study investigates one likely elementary bimolecular pathway for the room temperature reverse reaction of I, $\text{HD}(v=5) + \text{HD}(v=0) \rightarrow \text{H}_2 + \text{D}_2$ (III), by excitation of the weak $\text{HD } v=5-0$ overtone [$\mu = 2.3 \times 10^{-24}$ esu-cm for $R(2)^{17-19}$] by cw intracavity dye laser excitation [6035.2 Å, $R(2)$], followed by measurement of the D_2 photoproduct. The energy deposited per molecule, 47 kcal/mole, is significantly larger than the ~ 38 kcal/mole⁵ that is supposedly required for the bimolecular reaction. The sensitivity of this experiment is high enough that the

expected reaction yield is $100\times$ the D_2 detection limit, though it is not high enough to monitor either any trimolecular mechanism product [$\text{HD}(v=5) + 2\text{HD}(v=0)$], or the reaction between laser- and collisionally pumped reactants, e.g., $\text{HD}(v=2) + \text{HD}(v=3)$ reactions which Poulsen⁵ has claimed are important in the shock tube studies. In contrast to Bauer *et al.*'s SRS technique,⁷ the present method is free from wall catalysis, possible H atom production due to collisions [such as $\text{H}_2(v=5) + \text{H}_2(v=5) \rightarrow$ dissociation,⁷ since excited state densities are very low here], and uncertainty as to the exact mechanism being examined.

The laser excitation setup has been detailed elsewhere.²⁰ The optoacoustic detection cell with ~ 500 Torr HD, and the cylindrical pyrex reaction cell (30 cm long, 6 mm i.d., quartz Brewster windows, sealed with an O-ring-Teflon stopcock) were inserted into a cw Rhodamine 6G dye laser with appropriate etalons. The HD (Merck; 98% HD, 0.5% D_2) reserve was immersed in liquid nitrogen for 2 days prior to use to freeze out any condensables. A typical run consisted of continuous irradiation by ~ 15 W at the center of the Doppler profile for ~ 4 h at room temperature. At the ~ 100 Torr HD pressures employed, the overtone transition is fully Doppler broadened (2.5 GHz FWHM) since collisional broadening is small (≤ 1 GHz/atm^{19,21}); also optoacoustic and reaction cell resonances coincide since pressure shifts are insignificant (0.36 GHz/atm^{17,19}). The $[\text{D}_2]/[\text{HD}]$ ratio of the reaction cell sample was measured using the mass spectrometer (Inficon 200) prior to, immediately after, and several hours after irradiation to check for Reaction (III). No heterogeneous D_2 conversion was observed in the reaction cell, though evidence for wall reactions was definitely observed in the stainless steel chamber of the mass analyzer; this last contribution led to a $\pm 0.15\%$ uncertainty in $[\text{D}_2]/[\text{HD}]$.

Experimental runs were performed with reactant pressures of 65, 94, 98, and 187 Torr neat HD (Runs 1–4, respectively). In each case no production of D_2 was measured within the stated precision. The sensitivity of this experiment is presently discussed.

The expected fractional conversion to photoproduct via Reaction (III), assuming small reaction yields, is²⁰

$$\frac{[\text{D}_2]}{[\text{HD}]} = \frac{\alpha P}{\hbar\omega a} \frac{k_R}{\Gamma} t, \quad (1)$$

where α is the $R(2)$ absorption coefficient at Doppler center (2.4×10^{-9} /cm-Torr, based on the integrated α in Ref. 17), P is the intracavity laser power at Doppler center, $\hbar\omega$ is the photon energy, a is the cell cross-sectional area (including compensation for "dead volume"), k_R is the rate constant for Reaction (III), Γ is the rate constant

for collisional quenching from $\text{HD}(v=5)$, and t is the irradiation duration. Based on the model in Bauer *et al.*'s SRS study⁷ $k_R \approx 3 \times 10^{-11}$ cc/molecule-sec (~ 20 collisions); whereas in Poulsen's model⁵ $k_R \approx 6 \times 10^{-10}$ cc/molecule-sec, a nearly gas kinetic rate.

The collisional quenching rate, Γ , has contributions due to reaction (k_R) and collisional quenching; loss due to diffusion is small. Based on V - TR relaxation of $\text{HD}(v=1)$ by $\text{HD}^{22,23}$ and the harmonic model, V - TR loss is slow, $\sim 7 \times 10^{-16}$ cc/molecule-sec. V - TR and V - V transfer to nonresonant impurities (O_2 , N_2 , etc.) should be insignificant. The rate for HD V - V relaxation is uncertain. The most nearly thermoneutral transfer, $\text{HD}(v=5) + \text{HD}(0) \rightarrow \text{HD}(4) + \text{HD}(1)$, is 690 cm^{-1} endoergic; however, with sufficient rotational compensation it is nearly thermoneutral, e.g., $\text{HD}(v=5, J=2) + \text{HD}(0, 3) \rightarrow \text{HD}(4, 0) + \text{HD}(1, 0) - 50 \text{ cm}^{-1}$, and may be quite fast. Note that even with possible partial rotational compensation the exoergic V - V transfers: $\text{HD}(v=1) + \text{D}_2(0) \rightarrow \text{HD}(0) + \text{D}_2(1) + 640 \text{ cm}^{-1}$ (1.5×10^{-15} cc/molecule-sec; 350 000 collisions²³) and $\text{H}_2(1) + \text{D}_2(0) \rightarrow \text{H}_2(0) + \text{D}_2(1) + 1170 \text{ cm}^{-1}$ (1.0×10^{-14} cc/molecule-sec; 45 000 collisions²⁴) are quite slow. Also the transfer $\text{HCl}(1) + \text{HD}(0) \rightarrow \text{HCl}(0) + \text{HD}(1) - 740 \text{ cm}^{-1}$ is as endoergic as $\text{HD } 5+0 \rightarrow 4+1$ and its energy deficit may also be partially compensated by rotational state changes. Its slow rate, (2.9×10^{-15} cc/molecule-sec; 150 000 collisions²²), may nearly equal that for $\text{HD } 5+0 \rightarrow 4+1$.²⁴ The vibrationally nearly resonant $\text{HCl}(1) + \text{D}_2(0) \rightarrow \text{HCl}(0) + \text{D}_2(1) + 108 \text{ cm}^{-1}$ (1.6×10^{-13} cc/molecule-sec; 2400 collisions²⁵) is somewhat faster. In addition, recent calculations²⁶ suggest that 10^4 collisions are required for the nearly resonant transfer $\text{H}_2 1+1 \rightarrow 2+0$. Based on all this evidence the rate constant for $\text{HD } 5+0 \rightarrow 4+1$ is probably $< 10^{-13}$ cc/molecule-sec.

If the bimolecular mechanism is correct, only reactive quenching is most important and then $k_R/\Gamma = 1$ in Eq. (1). The expected linear conversions are then 17%, 8%, 15%, and 9% for Runs 1-4, respectively, which are each much greater than the stated 0.3% sensitivity range. Evidently $k_R \lesssim \Gamma/50$, and even if V - V quenching requires only 1 collision (corresponding to a rate which is over $1000 \times$ faster than any V - V rate described above), the upper limit for k_R would still be much too small to be consistent with the values employed in Bauer's and Poulsen's models. Apparently, within the stated limits $\text{HD} + \text{HD}$ (and similarly $\text{H}_2 + \text{D}_2$) four-centered exchange does not occur with only one vibrationally excited reactant. The possibility still exists that either both reactants must be vibrationally excited for a four-center reaction to occur or that the energy barrier is much greater than previously thought.

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