

LETTERS TO THE EDITOR

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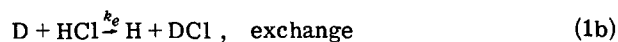
COMMUNICATIONS

Abstraction vs exchange in the reaction of D + HCl

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The branching ratio in the reaction of deuterium atoms with hydrogen chloride



has been studied for over 40 years.¹ Nevertheless, a controversy still exists regarding the Arrhenius parameters of the exchange rate constant k_e . In a static photochemical experiment, DeVries and Klein² determined that k_e is approximately equal to k_a at room temperature. This result was later confirmed by Klein and Veltman³ in a flow tube measurement. Wood,⁴ however, found in a similar photochemical study that $k_e = 0.05k_a$ at room temperature. All three experiments indicated that the activation energy for abstraction is larger than that for exchange, and that the pre-exponential factor for exchange is much smaller than gas kinetic. In contrast, McDonald and Herschbach⁵ determined in a molecular beam experiment that the steric factor for exchange is close to unity. Moreover, several *ab initio* quantum mechanical⁶⁻⁸ calculations revealed that the barrier for exchange is on the order of 20 kcal/mol, as compared with only 3.1 kcal/mol for abstraction.⁹⁻¹¹

In a real-time study¹¹ of the reaction $\text{H} + \text{HCl}$ we showed that previous investigations,¹²⁻¹⁴ which were conducted using flow tubes, had produced erroneous values of the rate constant. By using the flash photolysis-resonance fluorescence (FP-RF) method, we were able to completely eliminate surface effects, which had plagued the earlier studies. It is very likely that in Reaction (1) isotopic scrambling resulting from such reactions could similarly lead to incorrect values of the branching ratio.

In the present study we employed a variation of the FP-RF method. A gas mixture consisting of typically 7% D_2 , 0.3% SF_6 , and 1% HCl diluted with Ar was flowed slowly through a cubical monel cell. The experiment was carried out at room temperature, at total pressures ranging from 20 to 50 Torr. A mildly focused CO_2 TEA laser was used to dissociate <1% of the SF_6 molecules. The resulting F atoms reacted very rapidly with the D_2 producing deuterium atoms. Microwave powered atomic resonance lamps were used to excite selectively H, D, and Cl atoms in the reaction cell. A

solar-blind photomultiplier tube, mounted perpendicular to the plane of the laser beam and resonance lamps, was used to monitor the atomic fluorescence in real time. The H and D atoms were both excited with Lyman alpha radiation. The H atom radiation was produced from the residual impurities in ultrapure He, which was used as the discharge gas in the H lamp, whereas the D and Cl atom discharge gases were respectively 0.1% D_2 and 0.1% Cl_2 in ultrapure He. To assure that the D atom detector was insensitive to H atoms, a hydrogen atom filter was placed between the D resonance lamp and the cell. This filter consisted of a slowly flowing gas con-

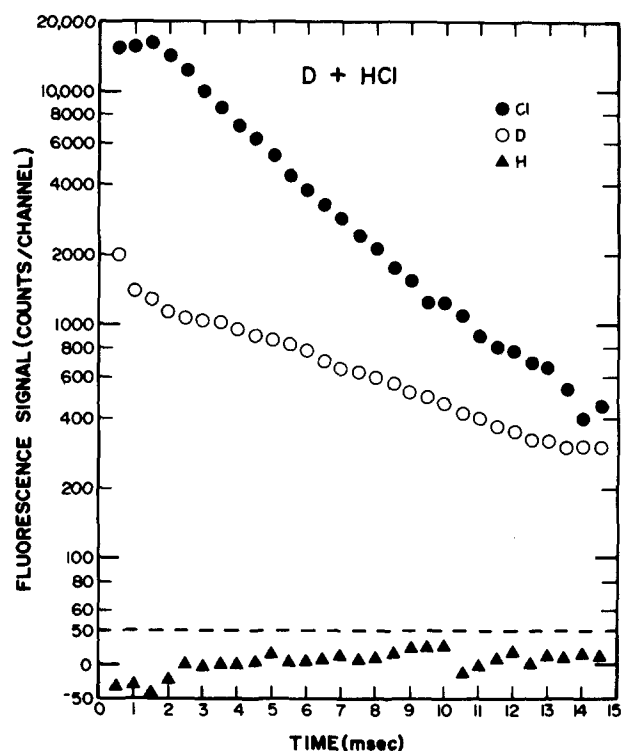


FIG. 1. Typical fluorescence signal produced with Cl, D, and H atomic resonance lamps. A total gas pressure of 20 Torr was used. The Cl, D, and H signals were accumulated over 30, 100, and 120 flashes, respectively, and then scaled with reference to the total D signal. The residual background due to light scattering has been subtracted from each fluorescent signal. Note the break from semilog to Cartesian coordinates at 50 counts/channel.

taining H atoms, which were produced in an auxiliary microwave discharge of pure H₂. Likewise, a D atom filter was inserted between the H lamp and the cell to assure H atom selectivity. Further details of the apparatus and experimental conditions will be presented in a future publication.¹⁵

Typical time-resolved fluorescence signals generated with the three resonance lamps are shown in Fig. 1. The D and Cl signals were found to decay exponentially, whereas no H atom signal was observed above the background. Calibrations were carried out to determine the sensitivity of the H atom detector. Gas mixtures consisting of SF₆, D₂, and variable amounts of H₂ in Ar were irradiated with the CO₂ laser. Hydrogen atom concentrations as low as 0.2% of the D concentration were clearly detectable with the H atom resonance lamp and the D filter. Upon replacement of the D filter with the H filter, the H-Lyman alpha signal completely disappeared. A kinetic simulation¹⁵ for the reactive mixture shows that the H to D ratio is approximately equal to k_e/k_a . Extrapolating the H atom detection sensitive to a signal-to-noise ratio of two, we obtain a conservative upper estimate of k_e to be $1.1 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 325 K. If the pre-exponential factors for the two channels are assumed to be equal, then a lower bound for the exchange barrier is 7.2 kcal/mol.

Initiation of the reaction by IR multiphoton excitation^{16,17} produces several side effects which need to be examined. Energy absorbed by SF₆ is rapidly thermalized, causing a temperature jump. From optoacoustic measurements of the energy absorbed, we estimate that the temperature jump is 25 ± 5 K. Another effect is that multiphoton dissociation of polyatomic molecules can produce electronically excited fragments, which could affect the present experiment in two ways. First, such fragments could emit at wavelengths detected by the photomultiplier ($115 < \lambda < 190 \text{ nm}$).^{18,19} We in fact observed a rapidly decaying UV signal when the resonance lamps were off. In Fig. 1 this "background" effect has been subtracted from the total signal measured with the resonance lamps on. Second, the excited photofragments could react with deuterium and chlorine atoms, thereby increasing their decay rates. In the absence of such reactions, the principal sink for these atoms is diffusion out of the viewing zone, which occurs at a rate that is typically 20% of the observed decay rates.¹⁵ Still another possible effect is radiation trapping of D-Lyman alpha produced by the high initial concentrations ($\sim 10^{13} \text{ cm}^{-3}$) of D atoms.²⁰

The key point is that, despite these artifacts, the detection method employed is highly sensitive to H atoms.

The absence of an H-Lyman alpha signal in Fig. 1 establishes an upper bound for k_e/k_a , and a lower estimate of the exchange barrier, thus resolving the paradox posed by Thompson *et al.*²¹ Our results disagree with the early photochemical studies,²⁻⁴ but are consistent with the more recent room temperature measurement of Endo and Glass²² and with the molecular beam study of McDonald and Herschbach.⁵ Our lower estimate of the exchange barrier is also consistent with the much higher values of the *ab initio* calculations.⁶⁻⁸ We plan to measure $k_e(T)$ at high temperatures in order to determine its Arrhenius parameters.

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