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The inversion mechanism for the reaction $H + CD_4 \rightarrow CD_3H + D$

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The reaction $H + CD_4 \rightarrow CHD_3 + D$ is shown to take place by an inversion mechanism. The evidence is as follows. When the H atom has an anisotropic (perpendicular) velocity distribution, the D atom velocity distribution is also perpendicular. For a relative energy near 2 eV, the reaction cross section for $H + CD_4$ is $0.084 \pm 0.014 A^2$ and for $H + CH_3 D$ is $0.040 \pm 0.015 A^2$. At the same H atom energy, when CH_3CD_3 is substituted for CD_4 , no D atoms can be detected. Finally, around 80% of the initial H atom kinetic energy is released as kinetic energy of the D atom showing that the reaction is nearly vibrationally adiabatic.

An isotope exchange reaction can be written

$$\mathbf{X}_i + R \, \mathbf{X}_j \to \mathbf{X}_i R + \mathbf{X}_j,\tag{1}$$

where X_i and X_j are different isotopes of the element X. Depending on energetics the abstraction reaction

$$\mathbf{X}_i + R \, \mathbf{X}_i \to \mathbf{X}_i \mathbf{X}_i + R \tag{2}$$

can be as important or more important than the exchange. Theoretically the simplest exchange reactions are those involving hydrogen isotopes because the atom carries only one electron. The simplest of all the hydrogen atom exchange reactions are the isotopic versions of $H + H_2$ which have recently been extensively studied.¹⁻³ After this most important reaction one can envision a sequence of reactions with an increasing number of centers, i.e., H + DF, $H + D_2O$, $H + ND_3$, and $H + CD_4$. Because of experimental problems with chemical exchange we have chosen to investigate the most complex six atom reaction, $H + CD_4$. Thereby we can relate to an important question in organic chemistry, when is configuration retained about a tetrahedral carbon atom?

In 1938 Rice and Teller⁴ made a simple estimate of the threshold energy for the $H + CH_4$ exchange reaction. The inversion mechanism was assumed and the barrier was taken to be equal to the deformation energy of the methane molecule when one of its methyl groups is forced to be planar. By extrapolating a harmonic potential function of a bending vibration to a coordinate value corresponding to the planar configuration they found a barrier of 40 kcal/mole (1.74 eV). In 1939 Gorin *et al.*⁵ published a semiempirical valence bond calculation which yielded 37 kcal/mole (1.60 eV).

While the abstraction reaction with thermal H froms had been investigated previously, experimental work with fast hydrogen atoms did not begin until 1957 when $T + CH_4$ and $T + CD_4$ were studied.⁶⁻¹¹ Thermal T atoms were shown to be incapable of exchanging showing that there was a substantial barrier for this process. The fast T atoms required were produced either by neutron irradiation of ⁶Li or ³He or by photodissociation of TBr. The ratio of abstraction to exchange was measured at different energies; also the energy thresholds for abstraction and exchange were found to be 10 ± 2 and 35 ± 10 kcal/mole $(1.52 \pm 0.43 \text{ eV})$, respectively. For the last two decades there has been no reported experimental work on this reaction. Up to now there has been no proof or disproof of an inversion mechanism. Whereas in the exchange reaction

$$T + \operatorname{CH} R_1 R_2 R_3 \to \operatorname{CT} R_1 R_2 R_3 + \mathrm{H}, \tag{3}$$

where R_1 , R_2 , and R_3 are heavy groups, configuration was retained, nevertheless methane with its much smaller, lighter groups must have a lower barrier to exchange. As noted by Chou and Rowland¹¹ as far as proving the mechanism is concerned the experiments had "reached an impasse."

The way out of the impasse is to study the reaction as it occurs rather than to do product analysis after the fact. With the help of a pulsed dissociation laser H atoms can be generated on a nanosecond time scale. A pulsed Lyman $\alpha(121.6 \text{ nm})$ laser fired shortly afterwards probes the reactant H atoms and the product D atoms. This is done by measuring the Doppler broadened fluorescence excitation spectrum. From the spectrum one can determine the rate coefficient for the exchange reaction, the average kinetic energy of the product D atoms and the anisotropies of the angular distributions of the velocities of the H and D atoms with the use of polarized dissociating light. This last information as we will show leads to a proof that the reaction takes place by an inversion.

EXPERIMENT

The experiment is made possible by the development by a number of physicists of the four wave mixing technique¹² for generating VUV radiation. A gas is simultaneously subjected to three waves of frequencies ω_1 , ω_2 , and ω_3 which because of a small third-order susceptibility are combined with low efficiency to give a fourth wave. In terms of frequencies

$$\omega_4 = \omega_1 \pm \omega_2 \pm \omega_3, \tag{4}$$

where all combinations of signs are possible. Wallenstein was the first to show that Lyman α light could be generated by frequency tripling 364.8 nm light in Kr gas. $(\omega_1 = \omega_2 = \omega_3)$.¹³ The present experiments would not have been possible without the development of a much more intense Lyman α source. This was done by using an intermediate resonance with the $5p[1/2]_0$ state of Kr at 94 093 cm⁻¹, a $2\omega_1 - \omega_2$ process in which ω_1 was fixed at 47 046.5 cm⁻¹ and ω_2 was in the 845 nm region.

The experiment is carried out in a flowing cell with a mixture of H₂S(10 mtorr) and CD₄ (30 mtorr). An ArF laser at 193.3 nm irradiates the cell dissociating almost all the H_2 S in its path. 100 ns later a second perpendicular probing laser is fired whose wavelength is swept through the H and D atom absorptions by sweeping the 845 nm laser through the 21 cm⁻¹ which separates the H and D atom absorption frequencies. The necessary control experiments were performed; that is, no D atom fluorescence was observed when both lasers were fired with H₂S alone or with CD₄ alone. (At considerably higher pressures we have seen D signals generated from CD_4 by Lyman α light but not at these low pressures.) Most of the H atoms and a fortiori most of the D atoms suffer no collisions after they are formed. This is proven by the fact that the kinetic energy extracted from the LIF excitation spectrum of H atoms (Fig. 1) is consistent with the kinetic energy calculated from the state distribution of the SH radicals generated at even lower pressures.¹⁵ Experimental details have been given previously.¹⁴

RESULTS

The rate coefficient for the reaction is calculated from the equation

$$k = n_D / \{ n_{\rm H} n_{\rm CD4} t \}, \tag{5}$$

where n_i is the number density of species *i* and *t* is the time between peaks of the two laser pulses. The term rate coefficient is used because the term rate constant is commonly applied to reactants at thermal equilibrium. In the present case one of the reactants, CD_4 is at thermal equilibrium but the H atom has a 2 eV superthermal energy. The ratio n_D/n_H is taken to be the ratio of the areas under the LIF excitation spectra. The average kinetic energy associated with the velocity component v_z , where z is the direction of the probing laser, is given by

$$m\langle v_z^2 \rangle/2 = m\langle (v - v_0)^2 \rangle c^2/2v_0^2.$$
 (6)

 ν and ν_0 are the absorption frequencies of the moving atom and the atom at rest, respectively. When a gas is dissociated with polarized light, the angular dependence of the fragments' velocity distribution is given by

$$f(\theta) = 1/4\pi \{1 + \beta P_2 \ (\cos \theta)\},\tag{7}$$

where θ is the angle between the velocity and the *E* vector. The average squares of the component of the velocity parallel and perpendicular to the *E* vector are

$$\langle v_{\parallel}^2 \rangle = \langle v^2 \rangle \{ 1/3 + 2\beta/15 \}, \tag{8a}$$

$$\langle v_{\perp}^2 \rangle = \langle v^2 \rangle \{ 1/3 - \beta / 15 \}.$$
(8b)

Solving Eqs. (8) one finds that the average kinetic energy is

$$m\langle v^2 \rangle/2 = m\{\langle v_{\parallel}^2 \rangle + 2\langle v_{\parallel}^2 \rangle\}/2$$
(9a)

and the velocity anisotropy parameter is

$$\beta = 5\{\langle v_{\parallel}^2 \rangle - \langle v_{\perp}^2 \rangle\} / \langle v^2 \rangle.$$
^(9b)

The uncertainties in the following data are rms deviations over typically 6 individual D atom spectra and fewer for the much stronger H atom spectra. The rate coefficient is $1.53 \pm 0.25 \times 10^{-11}$ cm³/(molecule s). The corresponding rate coefficient for CH₃D is $0.74 \pm 0.27 \times 10^{-11}$ cm³/(molecule s). The average kinetic energies for the H and D atoms in the H + CD₄ reaction are 56.0 ± 0.6 and 48.2 ± 3.9 kcal/mole, respectively. Finally the parameter β is -0.77 ± 0.05 for the H atoms and -0.53 ± 0.28 for the



FIG. 1. H atom signals seen in mixture of H_2S and CD_4 irradiated with polarized 193 nm light. The solid (dotted) line is the spectrum obtained when the probing laser is perpendicular (parallel) to the *E* vector of the dissociating light.

D atoms. We note also a negative result. When CH_3CD_3 was substituted for CD₄ and the experiment carried out as before, no D atoms were observed.

DISCUSSION

Δ

3

Approximate cross sections can be derived from the rate coefficients by dividing by an average relative velocity of the reactants. Welge has recently shown¹⁵ that only 62.6% of the SH radicals formed in the photodissociation at 193 nm of H_2S are in the v = 0 state. The balance are in various vibrational states up to v = 6. However if we assume that the 13.5% of radicals having v > 3 leaving maximum H atom kinetic energies of 1.3 eV or less can not react, we find an average kinetic energy of the reacting atoms of 2.28 eV or an average speed of 2.10×10^6 cm/s. The average relative kinetic energy for the $H + CD_4$ reaction will be reduced by a factor of 20/21 and is therefore 2.17 eV. However to be consistent we must reduce the number density of the H atoms in Eq. (5) by a factor of 0.865 because the remaining H atoms have been assumed to be too slow to react. The cross sections obtained with these corrections are for $H + CD_4$, $0.084 \pm 0.014 \text{ A}^2$ and for H + CH₃D, $0.040 \pm 0.015 \text{ A}^2$. This fact supports the inversion mechanism. A direct three center process in which an H atom collided with a D atom and displaced it would imply that the reaction cross section would be proportional to the number of deuterons in the target molecule. The cross section for $H + CH_3D$ would have been 1/4 and not about 1/2 of the cross section for CD₄. The implication is that the other three hydrogen atoms do play a role in the exchange process. During a collision the three light H atoms can move faster into a configuration

coplanar with the carbon atom than can the three heavier D atoms. With CH₃D, a greater fraction of collisions (relatively) will be reactive. The statistical factor of 4 nevertheless causes the exchange cross section to be larger for CD_4 .

In an ideal perpendicular transition, with the transition dipole perpendicular to the velocity of the departing fragments which depart before the parent molecule can rotate at all, the anisotropy parameter β would be -1. In the present experiment on H_2S where the transition dipole of the $\pi \rightarrow \sigma^*$ transition is perpendicular to the molecular plane a value of -0.77 ± 0.05 was measured. Much of this difference is due to the fact that the pile of eight quartz plates used to polarize the 193.3 nm light is calculated to be only 95% polarized. Also when so many plates are inserted in front of the light beam the signal strength is strongly degraded and the experimental error is greater than in the other experiments. Nevertheless it is clear that when the E vector of the dissociating light is rotated not only does the spectrum of the H atom change which is to be expected but also the D atom spectrum is anisotropic as shown in Figs. 1 and 2. As shown elsewhere, ¹⁶ an average over the scattering angle Θ between the H and D atom velocities can be derived which we will call the reaction anisotropy,

$$\langle P_2 (\cos \Theta) \rangle = \beta_{\rm D} / \beta_{\rm H}.$$
 (10)

Substituting the observed β 's in Eq. (10) one finds a reaction anisotropy of 0.69 implying a typical scattering angle of either 25° or 155°. Before interpreting this quantity we note the surprising fact that the exchange reaction is very nearly elastic, i.e., the D atom takes away $86 \pm 7\%$ of the incident H atom kinetic energy. A very strong repulsion is implied in a

> D-par. D-perp.



FIG. 2. D atom signals seen in the same system. Same notation as in

direction closely parallel or antiparallel to the incident H atom velocity. If the departing D atom were to be repelled on the same side as the entering H atom thus retaining configuration, there would have to be a strong attraction for the H atom and a strong repulsion for the D atom although both would be in equivalent positions. Therefore in any mechanism the very fast H atom would generate a fast D atom also moving in the forward direction. However a front side replacement would give rise to larger scattering angles. If the velocity of the exiting D atom were almost parallel to the initial velocity of the H atom it would collide with the remaining three bound hydrogen atoms. Thus either it collides or flies off at a larger angle. In any case the reaction anisotropy would be less. The fact that when even one of the D atoms of CD_4 is substituted with a methyl group, the reaction does not go is a further support for the inversion mechanism at this 2 eV energy.

Our final picture of the mechanism of reactions of fast hydrogen atoms with methane is as follows. Reactions of small impact parameter in which the incident hydrogen atom is directed almost at the C atom are of two types. In one the H atom is incident close to the direction of the C-H bond and abstraction results. In the other the H atom is incident close to a threefold axis but opposite to a C-H bond which will be broken by the inversion process. As the impact parameter increases more of the incident relative energy will not be available for surmounting the energy barriers for the reaction. This effect will be more pronounced for the exchange reaction which has the higher barrier and will therefore have a smaller cross section. At still larger impact parameters inelastic nonreactive collisions will occur, exciting bending vibrations and rotations.

Some years ago the late Don Bunker and coworkers^{17,18} performed trajectory calculations on a reasonably chosen potential surface for the CH₅ system. They found that at low energies such as used in the present experiments exchange takes place by means of an inversion but that at higher energies a direct replacement becomes the dominant mechanism. We have recently performed the same experiments on SiD₄ and SiH₃D and have obtained results remarkably close to those obtained here on CD₄ and CH₃D except that the cross sections were about five times larger.¹⁹ The implication is that elasticity or equivalently vibrational adiabaticity is a characteristic of the inversion not sensitive to the details of the potential. In classical language, during the inversion some of the kinetic energy of the fast H atom is converted to potential energy but not kinetic energy of the transition state. This potential energy is largely recovered in the symmetrical separation of the product D atom.

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