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The isotope exchange reaction of fast hydrogen atoms with deuterated alkynes and alkenes

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The exchange reaction $H(1 \text{ eV}) + RD \rightarrow RH + D$, where RD was deuterated acetylene, methylacetylene, ethylene, and propylene was studied by laser induced fluorescence detection of the hydrogen and deuterium atoms. The reaction cross sections were 1.69 \pm 0.22, 0.50 ± 0.15 , 1.85 ± 0.20 , and 1.10 ± 0.14 Å², respectively. The fraction of the incident relative kinetic energy released as translation was 0.42, 0.34, 0.40, and 0.34. That the addition of a methyl group only slightly reduces the energy released as translation is regarded as proof that the reaction at this energy does not involve a long lived intermediate complex, but is a direct localized displacement. Further confirmation comes from the observation that the velocity of the D atom product of $H + C_2D_2$ is correlated with the velocity of the H atom reactant.

INTRODUCTION

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The addition of a radical to an unsaturated carbon-carbon bond is a fundamental reaction in organic chemistry. As the reactants approach each other they pass over a low barrier and then into a deep well. The origin of the barrier may be the change in bond angle caused by a change in hybridization; the well is the result of the replacement of the carboncarbon π bond with the stronger σ bond between one of the carbon atoms and the attacking radical. The reactants are not trapped in the well even temporarily unless there is a transfer of energy from the relative translation of the reactants to internal periodic modes of the radical-molecule complex.

What follows next depends on the lifetime of the complex compared to the mean free time between deactivating collisions. In a condensed phase or in a high pressure gas the complex is stabilized by the loss of energy to other molecules. In a very low pressure gas the initial addition must eventually be followed by the expulsion of the original radical or a new one. These processes are described by the equations

$$\mathbf{R}_1 + \mathbf{R}_2 \mathbf{R}_3 \rightleftharpoons \mathbf{R}_1 \mathbf{R}_2 \mathbf{R}_3^{\dagger}, \qquad (1, -1)$$

$$\mathbf{R}_1 \mathbf{R}_2 \mathbf{R}_3^{\dagger} \rightarrow \mathbf{R}_1 \mathbf{R}_2 + \mathbf{R}_3, \qquad (2)$$

$$\mathbf{R}_1 \mathbf{R}_2 \mathbf{R}_3^{\dagger} + \mathbf{M} \rightarrow \mathbf{R}_1 \mathbf{R}_2 \mathbf{R}_3 + \mathbf{M}. \tag{3}$$

The dagger superscript denotes a vibrationally excited species. M is an inert buffer gas. The attacking radical can be an alkyl radical, a halogen atom or a hydrogen atom. Perhaps, the simplest examples of these reactions are the cases when \mathbf{R}_1 and \mathbf{R}_3 are both hydrogen atoms and $\mathbf{R}_2\mathbf{R}_3$ is acetylene or ethylene. In order to follow the reaction one chooses R_1 to be a hydrogen atom and R₃ a deuterium atom. In other words the process is an isotope exchange:

$$\mathbf{H} + \mathbf{R}\mathbf{D} \to \mathbf{R}\mathbf{H} + \mathbf{D}.$$
 (4)

The kinetics of the addition of H atoms to acetylene and ethylene have been repeatedly studied and the results are

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encapsulated in the following rate constants expressed in units of cm³/molecules s.¹⁻⁴

$$k(H + C_2 H_2) = (9.2 \pm 2.6) \times 10^{-12} \exp[-(2410 \pm 140)/RT],$$
(5)
$$k(H + C_2 H_4)$$

=
$$(4.39 \pm 0.56) \times 10^{-11} \exp[-(2160 \pm 72)/RT],$$

(R = 1.987 cal/mol K). (6)

Rate constants of similar magnitude have been obtained for the addition of H atoms to propyne and propylene.^{5,6} Most of the past work on the H + alkene/alkyne reaction has been at high pressures whereby the addition product is stabilized. The rate constant for the $H + C_2D_2 = C_2DH + D$ exchange reaction has been determined by detecting H and D via ESR spectroscopy. In the temperature range of 300 to 470 K the rate constant is $2 \times 10^{-13} \exp(-5300/RT)$. At these low energies the intermediate vinyl radical has a lifetime of the order of a nanosecond so that collisional vibrational relaxation can compete with unimolecular dissociation.⁷ In the present high energy experiments very different results are found.

In our experiments the H atoms generated by dissociating H_2S molecules with a pulsed laser at 248 nm are roughly monoenergetic with about 1 eV of kinetic energy. The unsaturated molecules are deuterated. The essence of the experiment is the measurement of the ratio of the number densities of D atoms and H atoms in the system a short time tafter the generation of the H atoms. The ratio of the number densities is taken to be the ratio of the areas under the laser induced fluorescence (LIF) excitation curves. If k is the rate constant for Eq.(4), integration of its rate equation at short times gives

$$(\mathbf{D}) = k(\mathbf{H})(\mathbf{R}\mathbf{D})t. \tag{7}$$

Knowing t and the pressure of the deuterated gas RD a mea-

surement of (D)/(H) yields the desired rate constant. Because the time t is so short the product D atom does not on average have time to collide with any other species; its average nascent kinetic energy can be determined from the second moment of its Doppler broadened LIF excitation spectrum. The ratio measurement is accomplished with pulses of light from a second laser at 121.6 nm which excite fluorescence of the H and D atoms.

EXPERIMENTAL

The laser used to dissociate the H₂S was a Lumonics HyperEX 440 KrF excimer laser with fluence/pulse of 100 mJ/cm² operated at 10 Hz. In the experiments using polarized light the output of this laser was passed through a pile of quartz plates at Brewster's angle. Light thus produced is calculated to be 95% polarized. The second laser which was typically fired 100 ns after the first was a Lambda Physik FL2002E dye laser pumped by an MSC 201 XeC1 excimer laser. DMQ dye was used to produce 27 ns wide pulses at 364.8 nm. These pulses were focused in Kr at a typical pressure of 150 Torr. This method of generating hydrogen atom resonance radiation due to Wallenstein⁸ produces nanojoule VUV pulses. The resolution of the dye laser before tripling is 0.04 cm^{-1} . The pressures of the deuterated hydrocarbons were kept at or below 50 mTorr for two reasons. One was to ensure that only single collisions occurred and the other was because the hydrocarbons are strong absorbers of the fluorescent light emitted by the hydrogen atoms. The LIF is detected by a solar blind photomultiplier whose output pulse is fed to a boxcar averager where it is normalized by a pulse from another solar blind photomultiplier which monitors the VUV exciting light. The output of the boxcar averager is sent to a microcomputer. The perdeuterated hydrocarbons (99% D) were obtained from MSD isotopes.

RESULTS

The two results obtained for each hydrocarbon molecule were the cross section for the isotope exchange reaction and the average kinetic energy of the D atom product. The cross sections were calculated from the relation $k = v\sigma$ where v is the average relative speed of the H atom. When dissociated at 248 nm 90% of the SH radicals are in the v = 0 state and are rotationally cold.^{9,10} The calculation of the relative energy of the H atom and the deuterated molecule is given in the Appendix with the result that the relative energy is around 1 eV. The specific results for the cross sections and average kinetic energy of the products are given in Table I. The uncertainties listed there are the rms deviations from the mean of typically five measurements.

The average kinetic energy is obtained from the LIF excitation spectra shown in Figs. 1 and 2 as follows. The absorption frequency of a H atom moving toward the probe laser with a velocity v_z is shifted by v_0v_z/c where v_0 is the absorption frequency of a stationary H atom. Thus, the second moment of the symmetric absorption curve taken with respect to its center is $(v_0/c)^2 \langle v_z^2 \rangle$. If the velocity distribution is isotropic, then the average kinetic energy, $\langle E_T \rangle = m \langle v^2 \rangle / 2 = 3m \langle v_z^2 \rangle / 2$.

Experiments were carried out to determine whether, if the H atom velocity distribution were anisotropic, the velocity distribution of the products would also be anisotropic. An anisotropic distribution of H atoms was created by photolyzing H₂S with polarized light. The LIF profiles of product D atoms were compared as the polarization of the incident light was rotated. For acetylene (but not for the ethylenes) there is indeed a certain amount, albeit small, of anisotropy in the D product distribution. Although the difference in the widths of the spectra (as shown in Fig. 3) are not large, the second moments differ by a reproducible amount. If we define $\langle E_T \rangle = 3m \langle v_z^2 \rangle/2$, then when the E vector of the dissociating light is parallel and perpendicular to the propagation vector of the probing laser $\langle E_{\rm REL} \rangle$ is 9.1 ± 1.5 and 10.4 ± 1.6 kcal/mol, respectively. The average kinetic energy for an isotropic distribution of H atoms is 1/3 of the parallel $\langle E_T \rangle$ plus 2/3 of the perpendicular $\langle E_T \rangle$ which gives an $\langle E_{\text{REL}} \rangle$ of 10.0 \pm 1.5 kcal/mol. The overall conclusion is that the reaction takes place in a time short

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FIG. 1. Fluorescence excitation spectra of D atoms from: (a) H + DCCD and (b) H + CH₃CCD. The smooth curves in Figs. 1 and 2 are the best Gaussian fits. The abscissa in all the figures is $v - v_0$ where v_0 is 82 259.1 cm⁻¹.



FIG. 2. Fluorescence excitation spectra of D atoms from (a) $H + C_2D_4$ and (b) $H + CD_3CDCD_2$.

compared to a rotation period, which is 0.8 ps for an average acetylene molecule at room temperature.

DISCUSSION

Cross sections

The rate constant for the isotope exchange reaction k is the rate constant for addition k_1 (assuming this is not mass dependent) times the fraction of the radical decompositions which yield D atoms. In other words, referring to Eqs. (1, -1) and (2):

$$k = k_1 k_2 / (k_{-1} + k_2).$$
(8)

This fraction is the fraction of hot CHD = CD radicals or CHD_2CD_2 radicals which decompose to D atoms. In the absence of isotope effects these fractions would be 1/2 and 2/3. It is difficult to compare the rate constants in Table I with those of Eqs. (5) and (6). The former were obtained at a single high energy, whereas the latter were obtained from thermal distributions at a much lower average energy. The activation energies of about 2 kcal/mol reduce the thermal rate constants considerably but play no role at incident energies of 24 kcal/mol.

Even though they cannot be compared with previous

experimental results, the high energy cross sections have an intuitive meaning. For acetylene and ethylene they are 1.68 and 1.85 Å², respectively, which indicate a high reaction probability on collision. For the smaller D_2 molecule the exchange cross section at a relative energy of 1 eV is 0.88 Å².¹¹ It would have been desirable to measure the cross sections as a function of relative energy; however, at 193 nm D atom signals were seen from deuteroacetylene and deuteroethylene in the absence of any H atom source. An intense intermediate energy laser, for example, at 222 nm was not available to us.

It should also be noted that the thermal rate constant for the $H + C_2H_4$ addition is more than five times that of the $H + C_2H_2$ addition. Our measurements show that the rate constants for the exchange reaction of 1 eV H atoms with C_2D_2 and C_2D_4 are about the same. Once again we see that a precise comparison between our high energy exchange rates and the thermal addition rates cannot be made. Clearly, energy barriers play a far more important role in the thermal reaction rates.

In independent experiments we have found that when H_2S is photodissociated with 193 nm light in the presence of CD_4 no D atom LIF signal is seen, confirming that the barrier for isotope exchange with a methyl group is very high. Thus, in going from deuteroethylene to deuteropropylene, we would expect that the cross section would diminish by 25% and be further reduced by steric hindrance. Similarly, the cross section for 1-methyl, 2-deuteroacetylene would be expected to be less than half that of dideuteroacetylene.

The cross-section data tell us that at high energies translational energy is very efficiently transformed into internal energy of a radical complex. The product translational energy tells us about the nature of this complex. At thermal energies it is known¹⁻⁴ that 200–500 Torr of a buffer gas such as H_2 or He are required to prevent reversion of the newly formed vinyl or ethyl radical into their initial constituents, H atoms and C_2H_2 or C_2H_4 . In other words, the lifetime of the radical complex is of the order of a nanosecond. The exothermicities of the addition reactions are

$$C_2H_2 + H \rightarrow C_2H_3$$
, $\Delta H = -47$ kcal/mol, (9)

$$C_2H_4 + H \rightarrow C_2H_5$$
, $\Delta H = -38$ kcal/mol. (10)

Thus, the observations are that a vinyl or an ethyl radical with about 47 or 38 kcal/mol, respectively, of internal energy will decompose in about a nanosecond. When a high energy, 24 kcal/mol, H atom attacks acetylene or ethylene, there may not be time to form a complex. More precisely, internal vibrational energy redistribution (IVR) may be slower than dissociation.

D atom translational energies

Looking at the translational energy of the D atom products shown in Table I one sees that about 40% of the available energy is released in translation. This suggests an incomplete IVR in the complex which in turn suggests a very short lifetime. A striking and convincing proof is furnished by the data on the methylated derivatives. Each of these molecules has three more atoms and, therefore, nine more vibra-



FIG. 3. Spectra of H atoms dissociated from H_2S by 248 nm light whose E vector is parallel (a) and perpendicular (b) to the probing beam direction. (c) and (d) are the spectra of the D atom products of H + DCCD when the H atom reactants have the spectra shown in (a) and (b), respectively.

tional modes than the unsubstituted molecule. Nevertheless, the translational energy release is diminished only slightly.

Figures 1 and 2 show that the fluorescence excitation curves can be fitted by Gaussian distributions, which means that the curve can be fitted by a single parameter conveniently chosen to be the second moment. A thermalized system is characterized by a temperature which in turn implies a Gaussian distribution of velocity component along any axis. However, the converse is not true. That is, a Gaussian distribution of velocity components does not necessarily imply that the system is thermalized. If the available energy were equally partitioned over the n vibrational modes of the product molecule and its rotational states, the kinetic energy distribution would be given by $f(E_T) = AE_T^{1/2}(E_{AVL} - E_T)^n$. Using this distribution function the average fraction of the available energy released as translation is calculated to be 3/(2n + 5). These quantities, listed in Table I, are much less than the observed fractions which emphasizes the lack of internal energy equilibration in these reactive collisions. We ascribe the Gaussian line shape to the operation of the central limit theorem; though the energy is fairly well known, there are many other parameters of the collision such as impact parameter and initial orientation which are randomly distributed.

TABLE I. Results for cross sections and average kinetic energy.

Reaction	E _{AVL} (kcal/mol)	k (cm ³ /molecules)	σ (Å ²)	E' _{REI} (kcal/mol)	f_T	3/(2n+5)
$\overline{H + C_2 D_2}$	24.0	$(2.42 \pm 0.31) \times 10^{-10}$	1.69 ± 0.22	10.0 ± 1.5	0.42	0.16
$H + CH_3CCD$	24.3	$(7.2 \pm 2.1) \times 10^{-11}$	0.50 ± 0.15	8.3 ± 1.0	0.34	0.09
$H + C_2 D_4$	24.1	$(2.7 \pm 0.3) \times 10^{-10}$	1.85 ± 0.20	9.6 ± 1.5	0.40	0.10
$H + C_3 D_6$	24.4	$(1.61 \pm 0.20) \times 10^{-10}$	1.10 ± 0.14	8.2 ± 0.8	0.34	0.05

The fraction 3/(2n + 5) is calculated on the assumption that the vibrational quanta are all small compared to the total energies; in other words, that quantum numbers are large. This is not the case for all seven modes of the product DCCH, for example. Instead let us calculate a vibrational temperature by assuming that the seven modes comprise a microcanonical ensemble with a fixed total energy of 14 kcal/mol, the average vibrational energy of DCCH. The result is 1700 K. On the other hand, because the translational distribution is close to Gaussian (see Fig. 1) it can be parametrized by a temperature which turns out to be 3400 K. The DCCH product is comparatively cold vibrationally, which is an alternate argument that the intermediate does not live long enough for complete equilibration of the available energy.

Anisotropy of product velocities

The experiment using polarized light was intended to create an anisotropic distribution of reactant H atom velocities to see if the corresponding D atom velocity distribution would also be anisotropic. The observable which can actually be extracted from the experiment is $\langle P_2 (\cos \theta_{v,v'}) \rangle$ where the average is over all reactive collisions and $\theta_{v,v'}$ is the angle between the H and D atom velocity vectors. Because the H and D atoms are so light compared to the hydrocarbon molecules, this angle is approximately the angle between the relative velocity vectors of the reactants and products.

To prove this result, first we write the expression for the anisotropic velocity distribution produced by photodissociation with polarized light:

$$f(\theta_{v,E}) = (1/4 \pi) \left[1 + \beta P_2(\cos \theta_{v,E}) \right]$$
(11)

where $\theta_{v,E}$ is the angle between the electric vector of the light wave and the velocity of the fragment, the H atom. When we calculate the distribution of velocity directions, v' of the product D atoms, we must integrate over all initial directions of the reactant H atom using the addition theorem for Legendre polynomials, obtaining

$$\langle P_2(\cos\theta_{v,E})\rangle = \langle P_2(\cos\theta_{v,v'})\rangle P_2(\cos\theta_{v',E}). \quad (12)$$

Thus the distribution function for the direction of the D atom velocity is

$$F(\theta_{v',E}) = (1/4 \pi) \{ 1 + \gamma P_2(\cos \theta_{v',E}) \}, \qquad (13)$$

where

$$\gamma = \beta \langle P_2(\cos \theta_{v,v'}) \rangle. \tag{14}$$

In other words the product angular distribution will be anisotropic only if both the reactant angular distribution and the differential cross section are anisotropic. If we assume that the distribution over speeds is factorable from the distribution over angle, we find that

$$\beta/5 = \left[\langle v_z^2 \rangle - \langle v_x^2 \rangle \right] / \left[\langle v_z^2 \rangle + 2 \langle v_x^2 \rangle \right], \tag{15}$$

where z is the direction of the E vector and x is any perpendicular direction.

Using the data given at the end of the Results section, we find that $\gamma = -0.23 \pm 0.06$. The value of β found⁶ for H atoms dissociated from H₂S at 248 nm is -0.66 and therefore $\langle P_2(\cos \theta_{v,v'}) \rangle$ is 0.35. If we equate $P_2(\cos \theta_{v,v'})$ to

0.35, the root is an angle of 41°, which is a typical angle between the product and reactant. No anisotropy was seen for the deuteroalkenes possibly because the typical scattering angles were closer to 54.7° for which P_2 is zero.

A molecular beam experiment, in principle, measures the full angular dependence of the differential reactive scattering cross section. In the bulb we are only measuring the average of P_2 . The particular reactant used here, the H atom if generated by the thermal dissociation of H_2 , cannot easily be accelerated to energies of 1 eV so that the use of polarized light in a bulb offers a relatively quick method for detecting anisotropy.

Comparison with theory

A theoretical study of these reactions would involve (a) the construction by *ab initio* calculations or otherwise of a suitable potential surface and (b) the integration of a large number of random trajectories on this surface or the use of a statistical theory. Considerable progress has been made along these lines.

Nagase and Kern¹² determined the potential energy of the $H + C_2H_2$ system at some 30 points and obtained a potential barrier of 6.2 kcal/mol and a well depth of (40.1 + 6.2) kcal/mol from minimum to maximum. The hand waving explanation of the low barrier given in the first paragraph of this paper is subject to the criticism that rehybridization accompanies bond formation rather than preceding it. Assuming that the barrier can be identified with the experimental activation energy, which is about 2 kcal/ mol, the existence of the barrier is not theoretically obvious; a term this small may be fortuitous. The calculations of Nagase and Kern do show that during the addition both the hydrogen atoms bound to the acetylene move through large angles to accommodate the attacking hydrogen atom. This prediction is at least consistent with the typical angle of 41° found previously.

Hase and co-workers¹³⁻¹⁶ have carried out particularly extensive calculations on the $H + C_2H_4$ and the prototype $H + C_2$ reactions. Potential functions were chosen for the $H + C_2 H_4$ reaction which fit spectroscopic and thermodynamic observables as well as an ab initio calculated structure and energy of the transition state. A barrier of 2.5 and a 38.0 kcal/mol well depth were found. By running a large number of trajectories on these potential functions the addition cross section was calculated as a function of energy and a value of 3.34 ± 0.74 Å² was found at a relative energy of 20 kcal/ mol. This cross section cannot be directly compared with our cross section of 1.85 \pm 0.20 Å² because the trajectories were run across the transition state but not to completion, that is, separation of a hydrogen atom originally bound in the ethylene. Also the rate may be somewhat dependent on the fact that a heavier D rather than a lighter H atom is being released. At thermal energies RRKM calculations of the rate constant have been successful.¹³ Trajectory calculations on the reactions discussed here producing results on the total cross section, the kinetic energy release and the differential cross section all as a function of relative translational energy are now feasible.

Ab initio calculations have also been performed on the reaction of H with acetylene leading to abstraction¹²:

$$H + C_2 H_2 \rightarrow C_2 H + H_2, \quad \Delta H = +21.7 \text{ kcal/mol.}$$
(16)

The barrier to abstraction has been calculated to be 32.4 kcal/mol and therefore this channel is predicted not to occur with our available energy of only 24 kcal/mol. Similarly, the reaction producing H_2 from $H + C_2H_4$ is considered unimportant under our conditions.

The exothermic reaction

$$\mathbf{F} + \mathbf{C}_2 \mathbf{H}_4 \to \mathbf{C}_2 \mathbf{H}_3 \mathbf{F} + \mathbf{H},\tag{17}$$

which seems at first sight to be analogous to

$$\mathbf{H} + \mathbf{C}_2 \mathbf{D}_4 \rightarrow \mathbf{C}_2 \mathbf{D}_3 \mathbf{H} + \mathbf{D},\tag{18}$$

has been extensively studied by molecular beam scattering (Lee and co-workers¹⁷⁻²⁰) and infrared emission (Mc-Donald and co-workers).^{21,22} About 50% of the available energy was released into translation which is not a statistical expectation. However, Hase and Bhalla²³ deduced from trajectory studies that there is a statistical internal energy distribution at the transition state. The centrifugal potential and the potential energy release in the exit channel account for the large amount of energy released into translation. Hase and Bhalla calculated an exit channel barrier of 5 kcal/mol for reaction (17) which is distinctly greater than the 2 kcal/ mol activation energy of reaction (18). The fact that propylene and ethylene have nearly the same translational energy release is the strongest argument that the fast H atom exchange reaction is direct in contrast to the F atom displacement reaction which appears to involve a long lived intermediate complex.

CONCLUSION

The reactions of hydrogen atoms with acetylene and ethylene which have been much investigated at thermal energies have now been studied at 1 eV relative energy. At thermal energies an intermediate vinyl or ethyl radical complex is formed which can either dissociate or be stabilized by collisions. At high energies the isotope exchange process becomes a direct displacement reaction. Evidence for this conclusion is twofold. First, the fraction of available energy channeled into translation is much higher than what one would expect if internal equilibration of the energy had taken place. Moreover, if a long lived intermediate were indeed being formed, one would expect the translational energy release to decrease as the number of vibrational modes of the system is increased. This is not the case as shown by comparison of acetylene and methylacetylene as well as ethylene and propylene.

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APPENDIX

Here we calculate the uncertainty in the relative kinetic energy of photofragments which react with other molecules which are at thermal equilibrium. The discussion is specialized to an H atom dissociated from H_2S reacting with a molecule M but the equations are quite general.

If the parent molecule H_2S has a momentum p_{H_2S} , after dissociation the fragments H and SH have momenta given by

$$\mathbf{p}_{\mathrm{H}} = (m_H/m_{\mathrm{H}_2\mathrm{S}})\mathbf{p}_{\mathrm{H}_2\mathrm{S}} + \mathbf{P}, \tag{A1}$$

$$\mathbf{p}_{\rm SH} = (m_{\rm SH}/m_{\rm H,S})\mathbf{p}_{\rm H,S} - \mathbf{P}, \qquad (A2)$$

where \mathbf{P} is the momentum generated by the photodissociation which is equal and opposite for the two fragments. The relative velocity of the H atoms and the molecule M is

$$\mathbf{v}_{\mathrm{H}r} = \mathbf{v}_{\mathrm{H}} - \mathbf{v}_{\mathrm{M}} = \mathbf{p}_{\mathrm{H}} / m_{\mathrm{H}} - \mathbf{v}_{\mathrm{M}}$$
(A3)

$$= \mathbf{P}/m_{\mathrm{H}} + \mathbf{v}_{\mathrm{H},\mathrm{S}} - \mathbf{v}_{\mathrm{M}}.$$
 (A4)

The relative translational energy is

$$E_{\rm REL} = \mu_{\rm H,M} v_{\rm Hr}^2 /2$$
(A5)
= $\mu_{\rm H,M} \left[{\bf P}^2 / m_{\rm H}^2 + 2 {\bf P} \cdot ({\bf v}_{\rm H_2 \rm S} - {\bf v}_{\rm M}) / m_{\rm H} \right]$

$$+ v_{H_2S}^2 + v_M^2 - 2v_{H_2S} \cdot v_M]/2,$$
 (A6)

where $\mu_{i,i}$ is the reduced mass of species *i* and *j*.

When E_{REL} is averaged over the Maxwell-Boltzmann distributions for $v_{H,S}$ and v_M , one obtains

$$\langle E_{\rm REL} \rangle = \mu_{\rm H,M} \left[P^2 / m_{\rm H}^2 + 3kT / \mu_{\rm M,H_2S} \right] / 2.$$
 (A7)

The mean square fluctuation in E_{REL} is

$$\langle E_{\text{REL}}^2 \rangle - \langle E_{\text{REL}} \rangle^2 = \mu_{\text{H,M}}^2 \left[P^2 k T / (m_{\text{H}}^2 \mu_{\text{M,H}_2\text{S}}) + 3(kT)^2 / 2\mu_{\text{M,H}_2\text{S}}^2 \right] / 2.$$
(A8)

If we insert the mass of the C_2D_4 molecule and use T = 300 K in Eq. (A8), we find that the rms uncertainty in the relative energy, i.e., the square root of Eq. (A8) is 1.3 kcal/mol. The actual uncertainty in the relative energy is greater because the KrF laser emission covers the 248.1 to 248.7 nm range and the H₂S bond energy is somewhat uncertain. The overall uncertainty may be as high as 2–3 kcal/mol. Nevertheless when a light fragment such as H collides with a heavy reactant such as C_2D_4 , the relative energy is fairly well defined.

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