LADC-5865

SEP 12 1963

79665

MASTER

DEUTERIUM KINETIC ISOTOPE EFFECT IN THE HYDROGEN-IODINE REACTION *

John H. Sullivan

Los Alamos Scientific Laboratory
University of California
Los Alamos, New Mexico

ABSTRACT

Rates of reaction of deuterium with iodine were measured in the range 633 - 800° K. The elementary reactions are

$$I_2 = 2I$$

$$D_2 + I_2 \rightarrow 2DI \qquad (1)$$

$$2DI \rightarrow D_2 + I_2 \qquad (2)$$

$$I + D_2 \rightarrow DI + D \qquad (3)$$

$$D + DI \rightarrow D_2 + I \qquad (4)$$

$$D + I_2 \rightarrow DI + I \qquad (5)$$

$$I + DI \rightarrow I_2 + D \qquad (6)$$

The three independent constants, k_1, k_3, and k_4/k_5, in $(\text{mole/cc})^{-1}\text{sec.}^{-1}$ are given by $\log(k_1/T^{1/2}) = 12.50 - 40,790/4.575T$, $\log(k_3/T^{1/2}) = 12.41 - 33,770/4.575T$, $k_4/k_5 = 0.073$. From a comparison of these with previously obtained rates in the H_2 system, the kinetic isotope effects for reactions

(1) and (3) are: $\log({}_{H}k_1/{}_{D}k_1) = 1.68 + 150/4.575T$, $\log({}_{H}k_3/{}_{D}k_3) = 1.33 + 1020/4.575T$. The results for (3) were fitted to absolute rate theory including tunneling (unsymmetrical Eckart barriers) to obtain permissible ranges of tunneling factors and vibrational frequencies of the linear IH_2 complex. Internuclear distances in triangular IH_2 complexes were found to be only slightly greater than $r_e(HI) = 1.60$ Å and $r_e(H_2) = 0.74$ Å. Sato energy surfaces were calculated for a number of Sato parameters; tunneling for these surfaces was found to be negligible when computed from Eckart potentials fitted to the Sato surfaces. Agreement of theory with experiment could not be obtained for both the preexponential factor and the activation energy of $I + H_2$ for any value of the Sato parameter.

****

Isotope effects in the kinetics of simple gaseous chemical reactions have been shown by Bigeleisen[1] and by Johnston[2] to be important in comparing absolute rate theory with experimental results. Shavitt[3] and Weston[4] have compared values predicted by absolute rate theory with the experimental ratios of rate constants for isotopic exchanges in hydrogen. Sharp and Johnston[5] found theory in accord with the experimental results over a very long temperature range for the reactions $CF_3 + CHD_3 \rightarrow CF_3H, CF_3D + CD_3, CHD_2$. Bigeleisen[1] and coworkers measured the rate of reaction of chlorine atoms with HD and showed that a large body of experimental results[6,7,8] on the reactions of chlorine atoms with HD, H_2, D_2 and HT were in accord with Bigeleisen's absolute rate theory formulation of the effects of isotopic substitution on rates. A reaction with the simplicity of the chlorine atom reactions, and for which information on the transition state may be obtained from the kinetic isotope effect, is $I + H_2 \rightarrow HI + H$.

In this paper, the results are given of an experimental determination of the rates of the elementary reactions $I_2 + D_2 \rightarrow 2DI$ and $I + D_2 \rightarrow DI + D$. Structural parameters for the IH_2 transition state in accord with absolute rate theory are obtained from the ratios of the rates of $I + H_2, D_2 \rightarrow HI, DI + H, D$ and from the previously measured rate of the hydrogen reaction.

EXPERIMENTAL

The experimental method has been previously described in detail[9,10]. Rates of reactions in sealed fused silica vessels were determined from initial concentrations of deuterium and iodine and final concentrations of deuterium after the reaction was quenched. The deuterium (obtained from the Stuart Oxygen Co. and labelled >99.5% pure) was stored in the vacuum line as UD_3. To minimize contamination by H_2 the uranium and the vacuum line were previously conditioned (by sparking and flaming) with several samples of deuterium; also, before filling, each reaction vessel was conditioned with several samples of D_2 at a dull red heat. The purity of the D_2 was monitored by mass spectrometer analyses for HD of D_2 samples taken when filling the reaction vessels and samples taken from the reaction vessels after the reactions had been completed.

Corrections for the transient temperature lags at the start and end of the reaction were made as in reference 9. Corrections for diffusion were made at each temperature as described in footnote 8 of reference 10. The permeability of fused silica to deuterium was considered to be smaller than the permeability to hydrogen by a factor of $\sqrt{2}$.[11] The diffusion rate of deuterium through the walls of the reaction vessels, although varying with the temperature and the size of the vessel, was roughly 0.01% per hour.

METHOD OF CALCULATION

The stoichiometry of the reaction of D_2 with I_2 is given by $D_2 + I_2 \rightarrow 2DI$, $I_2 = 2I$. The elementary reactions which occur are [9,10,12]:

$$D_2 + I_2 \rightarrow 2DI \qquad (1)$$

$$2\,DI \rightarrow D_2 + I_2 \qquad (2)$$

$$I + D_2 \rightarrow DI + D \qquad (3)$$

$$D + DI \rightarrow D_2 + I \qquad (4)$$

$$D + I_2 \rightarrow DI + I \qquad (5)$$

$$I + DI \rightarrow I_2 + D \qquad (6)$$

The three independent rate parameters were taken to be k_1, k_3 and k_4/k_5, and rate measurements were made at 633.21, 666.79, 710.33, 737.93 and 799.77°K.

The rate equation for the production of DI from reactions (1) through (6) is Eq. 9 (written for D_2) of reference 10. Rate constants were calculated from this equation using $K \equiv (D_2)_{eq.}(I_2)_{eq.} / (DI)^2_{eq.} = 0.01771$, 0.01990, 0.02274, 0.02453, 0.02864 and $K_D \equiv (I)_{eq.} / (I_2)^{1/2}_{eq.} = 1.184$, 2.392, 5.383, 8.573, 21.53×10^{-6} $(\text{mole/cc})^{1/2}$ at 633, 667, 710, 738 and 800°K.[13]

The three rate parameters in Eq. 9 are k_1, k_3 and k_4/k_5. In the present experiments these were calculated by successive approximations using the following characteristics of the system which are analogous to the results obtained in the hydrogen reactions: 1) at 633, 667, 710 and 738°K and at low values of $(DI)/(I_2)$ the rates (and therefore calculated values of k_1 and k_3) are insensitive to k_4/k_5; 2) at 800°K the contribution of (1) to the overall rate is small and calculated values of k_3 and k_4/k_5 are only slightly dependent on k_1; 3) at 800°K k_4/k_5 can be determined with much greater precision than at the lower temperatures -- and, within the experimental errors of the low temperature runs, is independent of temperature.

A trial value $k_4/k_5 = 0.08$ was used in the rate equation, Eq. 9; as described in reference 9, least square or "best" values of k_1 and k_3 were then calculated from the experimental data of all runs at each temperature, 633, 667, 710 and 738°K. These "best" values were found to be only slightly dependent on the trial k_4/k_5; thus at 738° a + 15% change in k_4/k_5 produced a -0.1% change in k_1 and a + 1% change in k_3. The k_1's were extrapolated, $k_1 = AT^{1/2} \exp(-E/RT)$, to 800°K to give k_1 (800°K) = 659 $(\text{mole/cc})^{-1}\text{sec}^{-1}$.

Two sets of runs were made at 800°K; in Set A, where $(DI)/(I_2) \ll 1$ (average concentrations over the reaction) in each run, the rates were insensitive to k_4/k_5; in Set B where $(DI)/(I_2) > 1$ in each run, the rates were sensitive to k_4/k_5. With the use of $k_1 = 659$ in Eq. 9, least square values of k_3 were calculated for each set of data for each of a number of trial k_4/k_5s. The results gave two curves, k_3 vs k_4/k_5, almost identical (see below) to the solid lines in Fig. 1. The intersection of the two curves gave values, $k_3 = 44.3$ $(\text{mole/cc})^{-1}\text{sec}^{-1}$, $k_4/k_5 = 0.073$ consistent with the "approximate" value $k_1 = 659$ and the data of both Set A and Set B.

The new value, $k_4/k_5 = 0.073$, was used in the 633-738°K data to obtain more accurate values of k_1 and k_3. The extrapolation of k_1 to

800°K and the determination of k_3 and k_4/k_5 at 800° were repeated as described above. The new value of k_1 at 800° was 660 $(\text{mole/cc})^{-1}\text{sec}^{-1}$. The results consistent with this k_1 and with both sets of 800° data are given by the intersection of the two solid lines in Fig. 2, $\langle k_3 \rangle = 44.3$ $(\text{mole/cc})^{-1}\text{sec}^{-1}$, and $\langle k_4/k_5 \rangle = 0.073$.

These values, unchanged from the previous approximate calculation, deomonstrate the very slight dependence of k_3 and k_4/k_5 on k_1 at 800°K and the very slight dependence of k_3 and k_1 on k_4/k_5 at the lower temperatures. To further demonstrate that in the 800° data $\langle k_3 \rangle$ and $\langle k_4/k_5 \rangle$ are only slightly affected by an error in k_1, calculations were made with $k_1 = 640$; the results (dotted lines in Fig. 1) indicate that a 3% error in k_1 affects $\langle k_3 \rangle$ by 0.2% and $\langle k_4/k_5 \rangle$ by about 1%.

In the H_2 experiments, reference 10, ${}_Hk_3(667°)$ was determined essentially independently of ${}_H(k_4/k_5)$ but in the present experiments ${}_Dk_3(667°)$ is slightly dependent on ${}_D(k_4/k_5)(667°)$ which is assumed to be equal to ${}_D(k_4/k_5)(800°)$. The possible error in ${}_Dk_3(667°)$ and therefore in ${}_Hk_3/{}_Dk_3$ introduced by this assumption is evaluated by considering the error in ${}_D(k_4/k_5)(667°)$ to be equal to the error in ${}_H(k_4/k_5)(667°)$. In reference 10, ${}_H(k_4/k_5)$ at 667° and 800° was determined from extensive measurements and a careful error analysis to be 0.07 ± 0.02 and 0.08 ± 0.01. With similar uncertainties (since the D_2 and H_2 runs are similar), ${}_D(k_4/k_5)$ would be 0.063 ± 0.018 and 0.073 ± 0.01 at 667° and 800°. The uncertainty in ${}_D(k_4/k_5)(800°)$ affects ${}_Dk_3$ (800°) by only a few-tenths percent. The uncertainty in ${}_D(k_4/k_5)(667°)$ leads to an uncertainty in ${}_Dk_3(667°)$ of 2.5% and an uncertainty in ${}_Hk_3/{}_Dk_3$ (667°) of 2.7% which should be considered as an extreme limit of error.

The uncertainties in ${}_{D}(k_4/k_5)$ indicate a possible temperature dependence which, if real, would have to be attributed to reaction (5); the activation energy corresponding to ${}_{H}k_4$ was shown to be zero[10] (from ΔH_3 and E_3) and therefore that for ${}_{D}k_4$ is very close to zero.

Corrections for HD impurity in the D_2 were made after the least square values of k_1 and k_3 were obtained. The average amount of HD in the D_2 was 1.1, 1.1, 1.2, 0.9, and 1.5% at 633, 667, 710, 738 and 800°K. With the assumption that $k_{HD} = 0.5(k_{H_2}+k_{D_2})$, the least square k_1s were corrected by -0.55, -0.55, -0.6, -0.45 and -0.75% -- and the least square k_3s were corrected by -0.75, -0.75, -0.75, -0.6 and -1.0%.

RESULTS

The least square values $\langle k_1 \rangle$ and $\langle k_3 \rangle$, after correction for HD impurity, are given in Table I. In Table II the experimental data are given together with rate constants (not corrected for HD impurity). The rate constants in Table II, which are included to give an indication of the experimental precision and to show that there is no trend with concentration, were calculated in the following way. For each run in the temperature range 633-738°K, k_1 was calculated using $\langle k_3 \rangle$ (uncorrected for HD) and $\langle k_4/k_5 \rangle = 0.073$ in Eq. 9; similarly k_3 was calculated for each run using $\langle k_1 \rangle$ (uncorrected for HD) and $k_4/k_5 = 0.073$. The averages of the individual values of k_1 and k_3 are roughly 0.5 to 1% higher than the corrected least square values given in Table I. For the runs at 800°K, $k_1 = 660$ $(\text{mole/cc})^{-1}\text{sec}^{-1}$ was used in Eq. 9; k_3 was calculated for each run of Set A using $k_4/k_5 = 0.073$ in Eq. 9; k_4/k_5 was calculated for each run of Set B using $\langle k_3 \rangle = 44.25$ (uncorrected for HD) in Eq. 9.

The ratios of isotopic rate constants are given in Table I. It should be noted that to obtain these ratios the 633°, 710°, and 737°K H_2 data in reference 9 were (in the light of the results of reference 10) recalculated using $k_4/k_5 = 0.08$ to give values of ${}_Hk_1$ and ${}_Hk_3$ slightly different from those given in reference 9. Values for ${}_Hk_1$ and ${}_Hk_3$ at 667° and 800° were taken from reference 10.[14]

A least square fit of k_1 and of k_3 gave the equations

$$\log (k_1/T^{1/2}) = 12.50 \pm 0.07 - (40,790 \pm 200)/RT$$

$$\log (k_3/T^{1/2}) = 12.41 \pm 0.1 - (33,770 \pm 300)/RT$$

A similar fit of the ratio of rate constants gave

$$\log ({}_Hk_3/{}_Dk_3) = 1.33 \pm 0.1 + (1020 \pm 140)/RT$$

$$\log ({}_Hk_1/{}_Dk_1) = 1.68 + 150/RT$$

Taylor and Crist[15] measured forward and reverse rates on the H_2 - I_2 - HI and D_2 - I_2 - DI systems at 667° and 698.6°K. Their data are not sufficiently extensive to determine k_1, k_3 and k_4/k_5 independently of other data. We compare our rates with theirs for the D_2 systems by calculating a least square k_1 from their data (four runs on the forward reaction and four runs on the reverse reaction were made at each temperature) using $k_4/k_5 = 0.07$ and ${}_Dk_3$ (667°) = 0.579, ${}_Dk_3$ (698.6°) = 1.81 $(\text{mole/cc})^{-1}\text{sec}^{-1}$ in Eq. 9. We corrected their reaction times by three minutes (see reference 10) and also corrected the least square k_1s by -1% for a 2% HD content as reported by TC. The results are in Table III where subscript "f" indicates the reaction of D_2 with I_2 and "r" the decomposition of DI. The agreement is good; only the value 3.83 is outside the combined limits of the experimental errors in their results and ours.

DISCUSSION

Linear IH_2 Complex, Eckart Tunneling

The ratio of isotopic rate constants may be written as

$$k/k_D = (\Gamma/\Gamma_D)\ (\nu^*/\nu_D^*)\ (f/f^\ddagger)$$

where Γ's are tunneling factors, ν^*'s are imaginary frequencies in the complexes and f's are functions of the real vibrational frequencies for two isotopic molecules and are obtained from the ratio of partition functions[16]; the subscript D indicates quantities in the deuterium reaction. Bigeleisen et al.[1] evaluated $f(D_2/H_2)$

$$f(D_2/H_2) = 0.70738 \exp(889.93/T).$$

For a linear complex in the I + H_2 reaction,

$$f^\ddagger (ID_2/IH_2) = \prod_i^3 \frac{u_{Di} \sinh (u_i/2)}{u_i \sinh (u_{Di}/2)}$$

where $u = hc\omega/kT$.

The force field for the complex was taken to be

$$V = V_o + \tfrac{1}{2}f_1(\Delta r_1)^2 + \tfrac{1}{2}f_2(\Delta r_2)^2 + f_{12}\,(\Delta r_1)(\Delta r_2) + \tfrac{1}{2}f_\alpha(\Delta\alpha)^2$$

from which it can be shown that the vibrational frequencies in the ID_2 complex are lower than those in the IH_2 complex by a $\sqrt{2}$ factor for all values of the force constants[17]. The ratio of isotopic constants is then

$$k/k_D = 4\,\frac{\Gamma}{\Gamma_D}\ f(D_2/H_2)\ \frac{\sinh (0.707\ u_s/2)}{\sinh (u_s/2)} \left[\frac{\sinh (0.707\ u_b/2)}{\sinh (u_b/2)}\right]^2 \qquad \text{(E1)}$$

where u_s and u_b refer to the stretch and bending frequencies in the IH_2 complex.

Initially tunneling was taken to be negligible with Γ and Γ/Γ_D equal to one.[18] Pairs of frequencies were calculated for which E1 reproduced the experimental values of k/k_D at 700° and 800°K; these are given in Table IV. The two values of the bending frequency associated with each stretch agree within their uncertainties which reflect ±2% errors in the values of k/k_D at each temperature; the temperature interval is too small to determine a unique pair of frequencies from the data.

Similar pairs of frequencies in accord with the experimental values of k/k_D and with E1 were determined for $\Gamma/\Gamma_D = 0.90$, 0.95, 1.05, and 1.10. The bending frequencies ω_b are shown as functions of ω_s by the dashed and dotted curves in Fig. 2.

In the following section we use the rate of $I + H_2 \rightarrow HI + H$ and the ratio of isotopic rates to show that ω_s and ω_b can be restricted to a range of values if we make the reasonable requirement that the moment of inertia of IH_2, as calculated from absolute rate theory, be greater than 13×10^{-40} g cm^2. This minimum value of $I^{\ddagger}$ is obtained by considering that the internuclear distances in IH_2 cannot be less than those in the separated normal molecules, $r_e(HI) \doteq 1.60$ Å, $r_e(H_2) = 0.74$ Å. While the treatment does not give specific values for ω_s and ω_b it does provide a range of values as a criterion which must be met by any specific (e.g. Sato) potential surface. The results are independent of the detailed nature of the potential energy surface -- the restrictions on the surface being only that the reaction path near the saddle can be fitted to one of a very wide range of Eckart potentials.

The moment of inertia is obtained by setting Eyring's theoretical rate constant[19] $k_{th} = A_{th}(T)\exp(-E_o/RT)$ equal to $k = (1 \pm 0.3)\ 10^{12.55}\ T^{1/2}\exp(-E/RT)$.

Since

$$E = E_o + RT \times B(T, u_s, u_b, \tau) \qquad \text{(E2)}$$

where

$$B(T, u_s, u_b, \tau) = \frac{u_s}{e^{u_s}-1} + \frac{2u_b}{e^{u_b}-1} - \frac{u_{H_2}}{e^{u_{H_2}}-1} - 1 + \frac{d\ln \tau}{d\ln T}$$

the theoretical pre-exponential factor is, in terms of the experimental value,

$$A_{th}(T) = (1 \pm 0.3)\, 10^{12.55}\, T^{1/2} \exp\left[-B(T, u_s, u_b, \tau)\right]$$

When the electronic statistical weights of the iodine atom and the complex are taken to be equal and the numerical factors in A_{th} are evaluated for T = 700°K the moment of inertia of IH_2 is

$$I^{\ddagger} = (63 \pm 20) \times 10^{-40}\, f(u_s, u_b)\, \phi(\tau)\ \text{g cm}^2. \qquad \text{(E3)}$$

where

$$f(u_s, u_b) = (1-e^{-u_s})(1-e^{-u_b})^2 \exp\left[-\frac{u_s}{e^{u_s}-1} - \frac{2u_b}{e^{u_b}-1}\right] \qquad \text{(E4)}$$

and $\phi(\tau) = \frac{1}{\tau_{700}} \exp(-d \ln \tau / d \ln T)$ which can be evaluated by taking $\phi(\tau)$ to be

$$\phi(\tau) = \frac{1}{\tau_{700}} \exp\left[\frac{\ln \tau_{700}/\tau_{800}}{\ln 800/700}\right]$$

A maximum value of $\phi(\tau)$, rather insensitive to the exact shape of the potential barrier to reaction, can be computed if the barrier is taken to be an unsymmetrical Eckart potential. From this maximum value and the condition $I^{\ddagger} > 13 \times 10^{-40}$ g cm², equation E3 places a lower limit on u_b for any specified u_s.

The problem of calculating appreciable tunneling factors, (integrating the permeability of a one dimensional barrier over a Maxwell-Boltzmann distribution of incident particles,)

$$\Gamma = \frac{\text{quantum mechanical rate}}{\text{classical mechanical rate}} ,$$

has been solved by Bell[20] and Sharp and Johnston[5] for a truncated parabolic barrier; numerical computations of tunneling factors for symmetrical Eckart[21] barriers were made by Bell[22], Johnston and Rapp[23] and Shavitt[3], and for unsymmetrical Eckart barriers by Johnston and Heicklen[24].

Johnston and Heicklen computed Γ for a large range of the three parameters α_1, α_2 and u* which define the unsymmetrical Eckart barrier (see their Fig. 1),

$$\alpha_1 = 2\pi \Delta V_1 / h\nu^*$$

$$\alpha_2 = 2\pi \Delta V_2 / h\nu^*$$

$$u^* = h\nu^* / kT$$

$$\nu^* = \frac{1}{2\pi} (-F^* / m)^{1/2} .$$

As defined by Johnston[23,24] ΔV_1 and ΔV_2 are not activation energies but are the maximum energy changes (trough to saddle) along a straight line extension of the reaction path across the saddle; F* is the second derivative of the potential energy evaluated at the potential maximum. The barrier in the present calculations was taken to be this potential and, by using the Johnston and Heicklen formulation, Γ and also Γ_D for 700° and 800°K were computed for a range of parameters $\Delta V_1 < 35{,}000$ cal., $\Delta V_2 / \Delta V_1 < 0.1$ and $u^*_{700°} \leq 4$. Within this range, the computations show that $1 \leq \phi(\Gamma) \leq 1.3$.

Since the activation energy of the reverse reaction is about zero the restriction on the range of ΔV_2 values seems realistic. The range of u* was initially restricted (see below) to those values for which $\Gamma < 1.5$ since for large u* and narrow barriers the usual Eyring formulation (i.e. E1, E2, E3, E4) becomes invalid and also tunneling can no longer be considered one dimensional. Johnston and Rapp[23], and Rapp[25] have pointed out that for large amounts of tunneling (narrow barriers, high u*) the reaction corrdinate cannot be treated as a one dimensional separable coordinate. Rapp emphasized that the usual formulation in absolute rate theory[26] is invalid in such cases: since the coordinates are not separable, the transition state vibration partition function cannot be written as a product of the separate partition functions. Johnston[2] considers the criterion of separability to be the ratio of the deBroglie wave length of the transferred atom to the linear dimensions of the quadratic region around the saddle point; when λ is large the reaction coordinate and vibrational modes are no longer separable. Our restriction to parameters for which $\Gamma < 1.5$ may be over-cautious. Sharp and Johnston[5] found agreement between experimental isotopic rate ratios and theoretical ratios calculated from an equation analogous to E1 with tunneling factors (two dimensional) as high as 17.

By using $I^{\ddagger} > 13 \times 10^{-40}$ g cm^2 and $\phi(\Gamma) \leq 1.3$ in E3, the minimum permissible bending frequency for each stretch was calculated and is shown by the solid curve in Fig. 2; all combinations of ω_s and ω_b below the line produce "unlikely" complexes in the sense that the internuclear distances in the complex would be less than r(HI) = 1.60 Å, $r(H_2)$ = 0.74 Å. Figure 2 also indicates that this condition places limits on $\mathcal{T}/\mathcal{T}_D$; i.e. if $\omega_s \geq 2000$ cm^{-1} then $\mathcal{T}/\mathcal{T}_D \geq 1.1$ — and for all ω_s, $\mathcal{T}/\mathcal{T}_D > 0.9$.

Tunneling computations were also made for very narrow barriers ($4 < u^* < 18$, $\Delta V_1 < 35{,}000$, $\Delta V_1/\Delta V_2 \leq 0.1$); although tunneling factors as high as $\mathcal{T} = 16$ were obtained, the maximum value of $\phi(\mathcal{T})$ for all barriers was about 2. Higher values of $\phi(\mathcal{T})$ used in E3 produce a slightly lower minimum ω_b for each ω_s; however, the tunneling computations showed that high values of $\phi(\mathcal{T})$ are correlated with high values $\mathcal{T}/\mathcal{T}_D > 1.2$; these latter values, as indicated by the dashed curves in Fig. 2 obtained from E1, restrict the permissible pairs ω_s ω_b to those above the full curve. Johnston and Rapp's calculations on the H + H_2 reaction indicate that $\phi(\mathcal{T})$ for two-dimensional tunneling is within 10-20% of $\phi(\mathcal{T})$ calculated for one dimensional tunneling. A similar change in $\phi(\mathcal{T})$ in the I + H_2 reaction would have only a negligible effect on the calculated minimum values of ω_b. The use of anharmonic vibrational partition functions and expressions for thermal vibrational energies in E3 <u>increases</u> the minimum value of ω_b calculated for each ω_s. The admissable pairs ω_s ω_b are therefore restricted to the area above the full curve in Fig. 2 even when very narrow barriers and anharmonicity are considered.

Triangular IH_2 Complex, Eckart Tunneling

Similar calculations were made for a triangular IH_2' complex with E1, E3, and E4 modified for the now non-degenerate bending frequency to give

$$k/k_D = 2\sqrt{2}\ \frac{\mathcal{T}}{\mathcal{T}_D}\ f(D_2/H_2) \prod^{2} \frac{\sinh\,(0.707\ u_i/2)}{\sinh\,(u_i/2)} \qquad \text{(E1')}$$

$$(ABC)^{1/2} = 5.2 \times 10^{-60}\, F(u_s, u_b)\, \phi(\tau)\ g^{3/2}\ cm^3 \qquad (E3')$$

$$F(u_s, u_b) = (1 - e^{-u_s})(1 - e^{-u_b}) \exp\left[- \frac{u_s}{e^{u_s}-1} - \frac{u_b}{e^{u_b}-1}\right] \qquad (E4')$$

where A, B, C, are the three moments of inertia.

The bending frequency was obtained from E1' as a function of τ/τ_D and the stretch frequency. The value of $(ABC)^{1/2}$ was then calculated using in E3' the maximum value of $\phi(\tau)$ found for the range of tunneling parameters considered.

When τ, τ_D and $\phi(\tau)$ were taken to be one (no tunneling), the maximum value of $(ABC)^{1/2}$ for any stretch frequency was $2.9 \times 10^{-60}\ g^{3/2}\ cm^3$. For parameters $\Delta V_1 < 35$ kcal, $\Delta V_1/\Delta V_2 < 0.1$, $u^* \leq 4.0$ which give moderate amounts of tunneling ($\tau \leq 1.5$, $\tau/\tau_D \leq 1.1$, $\phi(\tau) \leq 1.3$) the maximum value of $(ABC)^{1/2}$ was $4.5 \times 10^{-60}\ g^{3/2}\ cm^3$.

These numbers are of interest when compared to $(ABC)^{1/2}$ calculated for triangular complexes with r(H-I) = 1.60 Å and r(H-H) = 0.74 Å. For an isosceles triangle with ∠IHH = 76°, $(ABC)^{1/2} = 5.5 \times 10^{-60}$; for ∠IHH = 135°, the calculated $(ABC)^{1/2}$ was 4.7×10^{-60}. If these are considered to be minimal values of $(ABC)^{1/2}$ (since the interatomic distances are minimal), then complexes with IHH angles between 76° and 135° can be associated only with potential barriers which give $(ABC)^{1/2}$ values larger than 4.7×10^{-60} -- i.e. barriers which are narrower than the potential corresponding to $u^* = 4$, and for which $\tau > 1.5$.

From E3' the maximum value of $(ABC)^{1/2}$ for any combination of ω_s and ω_b (now neglecting the dependence of ω_b on ω_s through k/k_D) is seen to be $5.2 \times 10^{-60}\ \phi(\mathcal{T})$; since the maximum value of $\phi(\mathcal{T})$ is 2 over a very large range of barriers, the upper bound for $(ABC)^{1/2}$ when the tunneling effect is included is then 10.4×10^{-60}.

The assumption of harmonic vibrations and separability of coordinates may be invalid for narrow barriers. However if the vibrations are considered to be anharmonic, then since the partition function for anharmonic vibration is greater than that for the harmonic approximation, and since the thermal vibrational energy (given as the exponent in E4') increases with anharmonicity, the net result of these effects is to give an upper bound on $(ABC)^{1/2}$ still smaller than 10×10^{-60}.

In summary for the triangular IH_2 complex, transition state theory and the experimental preexponential factor $A = 10^{12.55}$ give an upper bound for $(ABC)^{1/2}$ of $10 \times 10^{-60}\ g^{3/2}\ cm^3$. This figure indicates that in complexes with IHH angles between 76° and 135° the internuclear distances are not more than 25% greater than 1.60 Å and 0.74 Å. Also, if $r(H\text{-}I) = 1.60$ Å and $r(H\text{-}H) = 0.74$ Å are considered to be minimum distances in such complexes, the experimental preexponential factor and the minimum $(ABC)^{1/2} = 4.7 \times 10^{-60}$ indicate that a minimum tunneling corresponding to $\mathcal{T} = 1.5$ must take place. The experiment results are consistent with no tunneling and the minimum distances of 1.60 Å and 0.74 Å only if the complex is taken to be essentially linear.

Linear Complex, Sato Potential

The potential energy of a linear complex is usually calculated from the London equation as a function of the internuclear distances by the semi-empirical method of Eyring[26] or by a modification of this proposed by Sato[27]. The reaction I + H_2 was treated using Sato's equations; energy surfaces were calculated for each of the following values of Sato's parameter, k_s = 0.14, 0.15, 0.16, 0.175, 0.18, 0.19, 0.20. Electronic dissociation energies, internuclear distances and Morse potential parameters used in Sato's equations were, $D_e(H\text{-}H) = 109.51$, $D_e(H\text{-}I) = 73.78$ kcal., $r_e(H_2) = 0.7416$ Å, $r_e(HI) = 1.604$ Å, $\beta(H_2) = 1.942$ Å^{-1}, $\beta(HI) = 1.750$ Å^{-1}.[28]

One such surface, Fig. 3, shows characteristics common to all the calculated surfaces. As expected in an endothermic reaction, the H-I distance in the complex is, very closely, 1.60 Å and the H-H distance is considerably extended over that in the normal H_2 molecule. The real stretch frequency corresponds closely to the vibrational frequency, 2310 cm^{-1} of HI. For all values of k_s the reaction path has very slight curvature in the region near the saddle point and, within ±0.3 Å of the saddle point, the surface is well represented by $V = V_0 + \frac{1}{2}f_1(\Delta r_1)^2 + \frac{1}{2}f_2(\Delta r_2)^2$. According to Johnston's criterion for separability the theoretical rate can be formulated in terms of separable modes of vibration and one dimensional tunneling (see below) since the deBroglie wave length of a hydrogen atom at 750° is .6 Å.

Table V gives the properties of the complex for k_s = 0.14, 0.175 and 0.20, and, calculated from these properties, the theoretical values A_{th} and E_{th} (to be compared to $(3.5 \pm 1) \times 10^{12}$ and 32,800 ± 250 cal.). E_{th} was calculated from equation E2 and A_{th} from the formulation given in reference 19. Bending force constants were obtained from $\partial^2 V(\text{Sato})/\partial\alpha^2$ and bending frequencies were then calculated from

$$\lambda_b = \frac{f_\alpha}{r_1 r_2}\left[\frac{r_1}{r_2}\,\mu_H + \frac{r_2}{r_1}\,\mu_I + \frac{r_1 + r_2}{r_1 r_2}\,\mu_H\right]$$

where μs are reciprocal masses.[29]

In determining tunneling quantities to be used in the equations for A_{th} and E_{th}, tunneling was taken to be one dimensional and the reaction path across the saddle was fitted to an Eckart potential; for $k_s = 0.175$ and 0.20, tunneling was negligible, $\Gamma = 1$, $d\ln\Gamma/d\ln T = 0$; for $k_s = 0.14$, tunneling was small, $\Gamma = 1.07$, $d\ln\Gamma/d\ln T = 0.15$. It should be noted that if tunneling through the saddle is negligible then tunneling along any other path is also negligible.

The theoretical values E_{th} and A_{th} determined by the Sato surfaces agree moderately well with the experimental results. Precise agreement cannot be obtained for both E and A when k_s is varied further; when k_s is decreased below $k_s = 0.14$, then A_{th} can be brought into agreement with 3.5×10^{12} but E_{th} becomes larger than 35.4 kcal.

ACKNOWLEDGEMENTS

It is with great pleasure that I thank Wesley Jones for many helpful discussions. All programming and machine computations was the work of members of the Theoretical Division and is gratefully acknowledged; I am indebted to Ivan Cherry and Carroll Reed for the determination of rate constants, to Kenneth Crandall for the Eckart potential computations, to James Smith for the Sato potential computations and to Keith Zeigler for least square computations of Arrhenius parameters.

Table I. Experimental Results and Ratios of Rate Constants

T	$\langle k_1 \rangle$ $(\text{mole/cc})^{-1}\text{sec}^{-1}$	$10^{-3}\langle k_3 \rangle$ $(\text{mole/cc})^{-1}\text{sec}^{-1}$	k_4/k_5	${}_Hk_1/{}_Dk_1$	${}_Hk_3/{}_Dk_3$
633.21°K	0.681	0.110	----	1.936	3.56
666.79	3.47	0.579	----	1.903	2.88
710.33	24.44	2.72	----	1.909	2.69
737.93	72.4	6.87	----	1.882	2.646
799.77	(660)	43.8	0.073	(1.886)[a]	2.534

[a] from the extrapolated values of ${}_Hk_1$ and ${}_Dk_1$

Table III. Comparison with Taylor and Crist's Data

	$k_1(JS)$	$k_1(TC)_f$	$k_1(TC)_r$
T	$(\text{mole/cc})^{-1}\text{sec}^{-1}$		
667°K	3.47	3.51	3.83
698°	14.8	14.4	15.3

Table II. Experimental Data

$(D_2)_o$	$(I_2)_o$	$(I_2)_f$	Time	k_1	$10^{-3}k_3$	k_4/k_5
------ 10^6 x mole/cc ---------			sec	$(\text{mole/cc})^{-1}\text{sec}^{-1}$		
T = 622.21°K						
29.244	26.485	16.152	30064	0.685	0.112	
29.710	25.210	14.906	31242	0.686	0.117	
29.693	24.932	14.749	31242	0.683	0.106	
30.035	28.216	17.411	28613	0.688	0.126	
30.035	23.886	14.489	28613	0.685	0.111	
26.187	17.612	9.613	39502	0.683	0.107	
26.187	17.132	9.300	39502	0.686	0.115	
5.370	6.0515	4.626	79337	0.684	0.111	
5.370	6.3907	4.903	79337	0.682	0.105	
7.086	23.393	21.57	18771	0.681	0.097	
2.0125	3.980	3.457	108440	0.684	0.110	
1.9546	4.3403	3.792	108440	0.687	0.116	
1.3950	3.5560	3.2197	108440	0.684	0.110	
T = 666.79°K						
11.935	8.507	5.706	9737	3.46	0.548	
11.976	5.950	3.883	9737	3.45	0.541	
15.785	9.107	3.388	20484	3.50	0.596	
15.821	14.430	6.270	20484	3.52	0.637	
15.049	8.690	3.775	17331	3.50	0.600	
15.044	11.867	5.586	17331	3.49	0.592	

Table II. Experimental Data (Contd.)

$(D_2)_o$	$(I_2)_o$	$(I_2)_f$	Time	k_1	$10^{-3}k_3$	k_4/k_5
------- 10^8 x mole/cc --------			sec	$(mole/cc)^{-1}sec^{-1}$		
T = 666.79°K						
15.581	12.101	6.467	13157	3.49	0.584	
15.585	13.160	7.137	13157	3.49	0.594	
4.8566	1.6925	0.5303	60489	3.45	0.560	
4.782	1.6037	0.5015	60489	3.46	0.565	
0.6793	1.3344	1.1263	64075	3.46	0.564	
0.7237	1.4695	1.2330	64075	3.45	0.559	
0.2599	1.0634	1.0138	42162	3.48	0.582	
0.3163	1.2253	1.1573	42162	3.54	0.616	
0.3001	1.1790	1.1161	42162	3.55	0.624	
T = 710.33°K						
11.269	11.568	5.905	3010	24.6	2.76	
11.274	10.732	5.358	3010	24.6	2.75	
11.209	10.265	5.072	3013	24.7	2.79	
11.216	11.797	6.073	3013	24.6	2.77	
10.342	8.344	3.900	3382	24.5	2.66	
10.356	9.108	4.353	3382	24.6	2.75	
0.8131	0.7802	0.5453	12583	24.4	2.69	
0.4862	0.9325	0.7356	15831	24.4	2.68	
0.5089	0.8829	0.6856	15823	24.2	2.64	
2.6983	0.8746	0.1860	15895	24.9	2.83	
2.4679	0.9444	0.2431	15895	24.9	2.82	

Table II. Experimental Data (Contd.)

$(D_2)_o$	$(I_2)_o$	$(I_2)_f$	Time	k_1	$10^{-3}k_3$	k_4/k_5
------- 10^6 x mole/cc --------			sec	$(\text{mole/cc})^{-1}\text{sec}^{-1}$		
			T = 737.93°K			
12.629	7.277	1.9501	1544	72.7	6.92	
11.475	9.405	3.496	1441	72.3	6.74	
7.818	7.549	3.568	1510	72.1	6.68	
7.817	6.598	2.956	1510	72.6	6.87	
7.974	6.833	3.205	1365	73.4	7.16	
7.979	8.702	4.444	1365	72.8	6.96	
7.963	7.085	3.621	1200	72.6	6.87	
7.963	8.949	4.887	1200	72.5	6.83	
6.708	6.472	3.389	1380	73.1	7.03	
7.788	6.719	3.434	1210	72.2	6.71	
7.794	8.263	4.452	1210	72.8	6.94	
8.414	8.880	3.941	1730	72.2	6.71	
10.191	12.020	5.550	1479	73.4	7.22	
0.8835	0.6909	0.4549	3754	72.8	6.92	
0.8853	0.7784	0.5218	3754	72.8	6.94	
1.2266	0.7191	0.2150	9045	72.4	6.85	
1.0992	0.6918	0.2323	9047	72.4	6.85	
0.3671	0.7003	0.5039	8952	73.2	7.00	
0.3666	0.7078	0.5109	8955	72.9	6.95	

Table II. Experimental Data (Contd.)

$(D_2)_o$	$(I_2)_o$	$(I_2)_f$	Time sec	k_1	$10^{-3}k_3$ (mole/cc)$^{-1}$sec^{-1}	k_4/k_5
			T = 799.77°K Set A			
--------10^8 x mole/cc		--------				
1.8863	4.4017	3.1506	5948		440	
1.6059	3.1662	2.0966	7520		445	
1.3621	3.2826	2.4967	5341		436	
1.2430	2.4166	1.7936	5033		447	
1.2138	3.3666	2.7141	4475		446	
1.4457	4.6264	3.7793	4344		436	
--------10^8 x mole/cc		--------	T = 799.77°K Set B			
2.9650	1.0981	0.2322	6404			0.072
2.2788	0.8518	0.1678	8051			0.076
3.3077	0.9664	0.0857	9490			0.071
2.7419	1.0448	0.2298	6539			0.060
3.9781	1.1252	0.2086	4974			0.079
3.8542	1.2492	0.1937	6323			0.076

Table IV. Bending Frequencies and Moments of Inertia for the Linear IH_2 Complex: No Tunneling

ω_s cm^{-1}	ω_b[a] cm^{-1}	ω_b[b] cm^{-1}	10^{40} $I^{\ddagger}$
200	1250 ± 50	1200 ± 80	5.3 ± 2
600	1170 ± 50	1120 ± 80	14 ± 4
800	1110 ± 50	1040 ± 80	16 ± 5
1000	1020 ± 60	950 ± 90	17 ± 5
1200	910 ± 70	850 ± 70	17 ± 5
1400	760 ± 90	680 ± 100	14 ± 4
1600	560 ± 100	430 ± 200	9 ± 3
1800	260 ± 150	---	2 ± 1

a) calculated from ${}_Hk_3/{}_Dk_3 = 2.75 \pm .05$ at 700°K

b) calculated from ${}_Hk_3/{}_Dk_3 = 2.53 \pm .05$ at 800°K

Table V. Parameters for the Linear IH_2 Complex and Theoretical Values of the Preexponential Factor and Activation Energy as Determined by Sato Energy Surfaces

k_s	r(H-I) Å	r(H-H) Å	ω_s cm^{-1}	ω_b cm^{-1}	10^{12} A_{th} (mole/cc)$^{-1}$sec^{-1}	E_{th} kcal.
0.14	1.60	1.54	~2300	335	25	35.4
0.175	1.60	1.84	~2300	195	60.4	34.5
0.20	1.60	2.74	2300	74	685	34.3

* This work was sponsored by the U. S. Atomic Energy Commission

1. Bigeleisen, Klein, Weston and Wolfsberg, J. Chem. Phys. 30, 1340 (1959). References to previous work by Bigeleisen and coworkers are given in this paper.
2. H. S. Johnston in *Advances in Chemical Physics*, I. Prigogine, editor (Interscience Publishers, Inc., New York 1961) Vol. III, pp. 131-170.
3. I. Shavitt, J. Chem. Phys. 31, 1359 (1959).
4. R. Weston, Jr., J. Chem. Phys. 31, 892 (1959).
5. T. E. Sharp and H. S. Johnston, J. Chem. Phys. 37, 1541 (1962).
6. H_2, P. G. Ashmore and J. Chanmugan, Trans. Faraday Soc. 49, 254 (1953).
7. D_2, G. K. Rollefson, J. Chem. Phys. 2, 144 (1934).
8. HT, W. M. Jones, J. Chem. Phys. 19, 78 (1951).
9. J. H. Sullivan, J. Chem. Phys. 30, 1292 (1959). References to previous work on the H_2-I_2 and D_2-I_2 systems are given in this paper.
10. J. H. Sullivan, J. Chem. Phys. 36, 1925 (1962).
11. In our temperature range the permeability of fused silica to H_2 is actually 1.29 times the permeability to D_2 [Lee, Frank, and Swets, J. Chem. Phys. 36, 1062 (1962)], but this slight difference affects our results negligibly.
12. S. W. Benson and R. Srinivasan, J. Chem. Phys. 23, 200 (1955).
13. The DI equilibrium constants were calculated from K_{HI} and the theoretical values for the equilibrium $D_2(HI)^2/(H_2)(DI)^2$ given by J. Bigeleisen and M. G. Mayer, J. Chem. Phys. 15, 261 (1947).
14. The results for the *hydrogen* reactions are summarized here. At 633, 667, 710, 738 and 800°K, k_1 = 1.318, 6.60, 46.65, 136.2, (1245)$(\text{mole/cc})^{-1}\text{sec}^{-1}$

and $10^{-3}k_3$ = 0.392, 1.67, 7.32, 18.18, 111.0 $(\text{mole/cc})^{-1}\text{sec}^{-1}$. Also, $\log (k_3/T^{1/2}) = 12.55 \pm 0.07 - (32{,}800 \pm 250)/RT$.

15. A. H. Taylor and R. H. Crist, J. Am. Chem. Soc. 65, 1377 (1941).
16. J. Bigeleisen and M. Wolfsberg, J. Chem. Phys. 21, 1972 (1953); ibid 23, 1535 (1955).
17. Except if either of the conditions, $f_1 - f_{12} = -\frac{1}{2}f_2$, $f_1 = \frac{1}{2}f_2 = f_{12}$ is approximated. The first condition is equivalent to the real stretch frequency being equal to ν*i; in the second condition the stretch frequencies are either both real or both imaginary.
18. The sufficient condition for no quantum mechanical effect is that the barrier be sufficiently broad -- not that $\Upsilon = 1$, $\Upsilon/\Upsilon_D = 1$. For some Eckart barriers, appreciable reflection and tunneling cancel to give $\Upsilon \cong 1$, $\Upsilon/\Upsilon_D = 1$. For other barriers, $\Upsilon/\Upsilon_D = 1$ even when the net tunneling effect is as large as $\Upsilon = 3$.
19. Glasstone, Laidler and Eyring, Theory of Rate Processes (McGraw-Hill Book Company, Inc., New York, 1941) p 193.
20. R. P. Bell, Trans. Faraday Soc. 55, 1 (1959).
21. C. Eckart, Phys. Rev. 35, 1303 (1930).
22. R. P. Bell, Proc. Roy. Soc. (London) A 139, 466 (1933).
23. H. S. Johnston and D. Rapp, J. Phys. Chem. 83, 1 (1961).
24. H. S. Johnston and J. Heicklein, J. Phys. Chem. 66, 532 (1962).
25. D. Rapp, Thesis. University of California, Berkeley, (1960).
26. Reference 16.
27. S. Sato, J. Chem. Phys. 23, 592, 2465 (1955). See also references 4 and 5.

28. $D_e = D_o^o + \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e$. Values of D_o^o, ω_e, $\omega_e x_e$ and r are from G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Co., Inc. 1950) 2nd ed.; β was obtained from Eq. (III, 100), p. 101.

29. H. S. Johnston and P. Goldfinger [J. Chem. Phys. 37, 700 (1962)] have pointed out that if bending force constants in a complex are less than 10^{-13}erg./rad^2, the angular vibrational amplitude is large, and the use of activated complex theory based on small vibrations and separability of energy is invalid. For k = 0.20 our calculated value of f_α in IH_2 is 0.3×10^{-13} erg./rad^2.

Fig. 1. Determination of k_3 and k_4/k_5 at 800°K. The dashed lines show that a small uncertainty in k_1 has a negligible effect on k_3 and k_4/k_5.

Fig. 2. Bending frequency in linear IH_2 as a function of stretching frequency and τ/τ_D: —— minimum bending frequency as a function of ω_s; — — — ω_b as a function of ω_s where $I^{\ddagger} > 13 \times 10^{-40}$ g cm^2; ----- ω_b as a function of ω_s for "unlikely" complexes, since for these cases $I^{\ddagger} < 13 \times 10^{-40}$.

Fig. 3 Sato potential energy surface for $k_s = 0.175$.

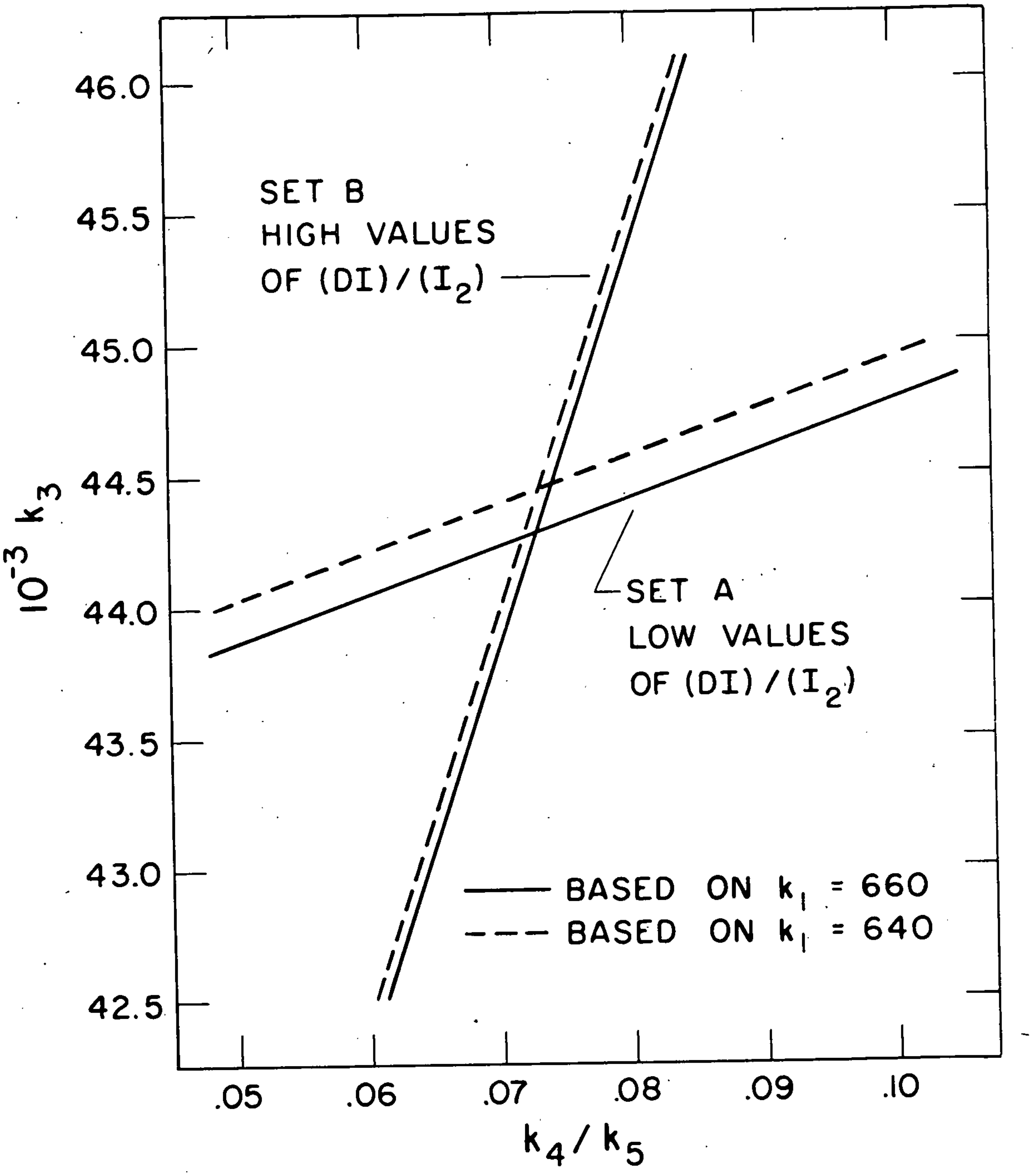
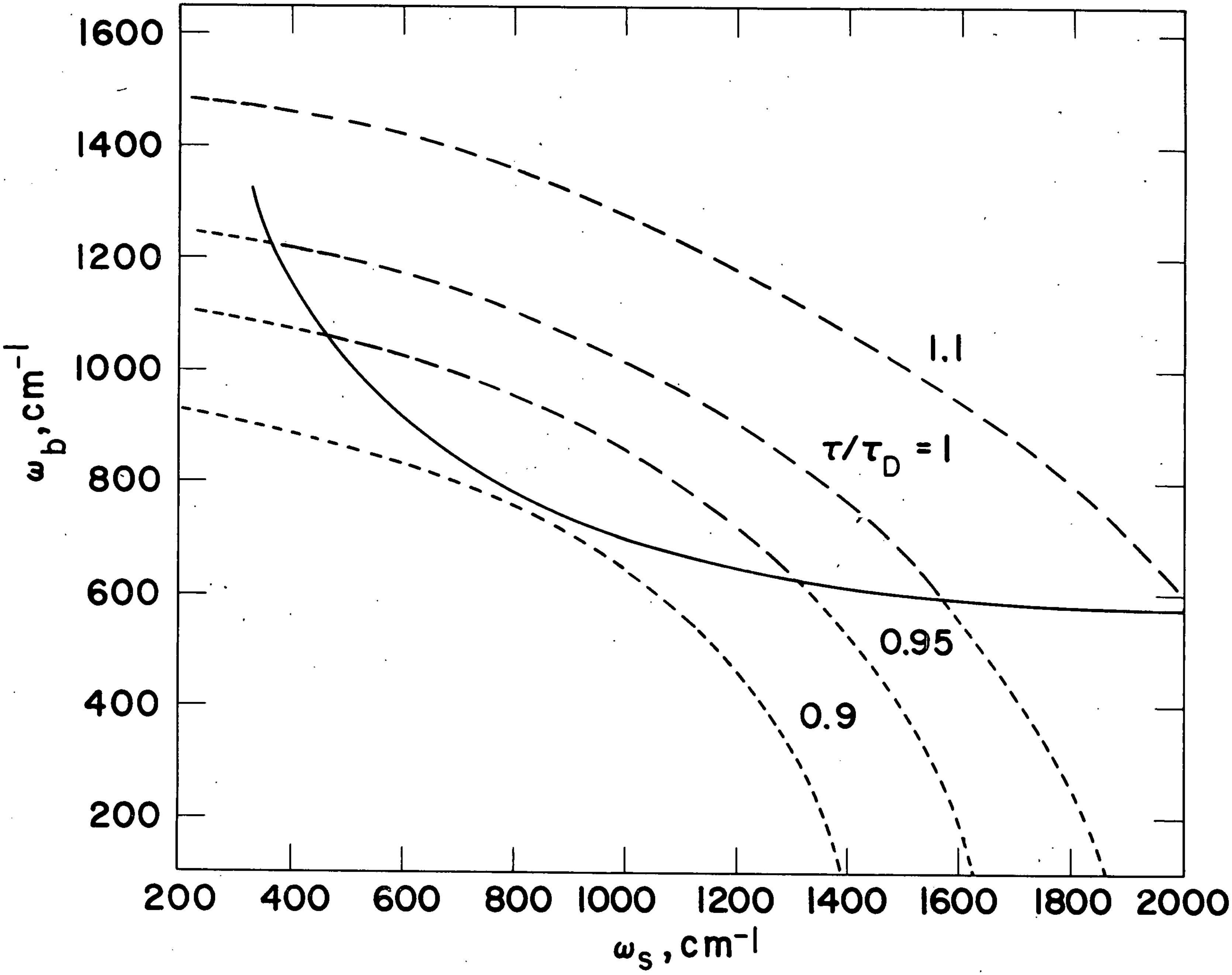

46.0
45.5
45.0
44.5
44.0
43.5
43.0
42.5
$10^{-3}\ k_3$
.05
.06
.07
.08
.09
.10
k_4 / k_5
SET B
HIGH VALUES
OF (DI)/(I_2)
SET A
LOW VALUES
OF (DI)/(I_2)
BASED ON k_1 = 660
BASED ON k_1 = 640

Fig 2

Fig 2


1600
1400
1200
1000
800
600
400
200
ω_b, cm^{-1}
200
400
600
800
1000
1200
1400
1600
1800
2000
ω_s, cm^{-1}
1.1
$\tau/\tau_D = 1$
0.95
0.9

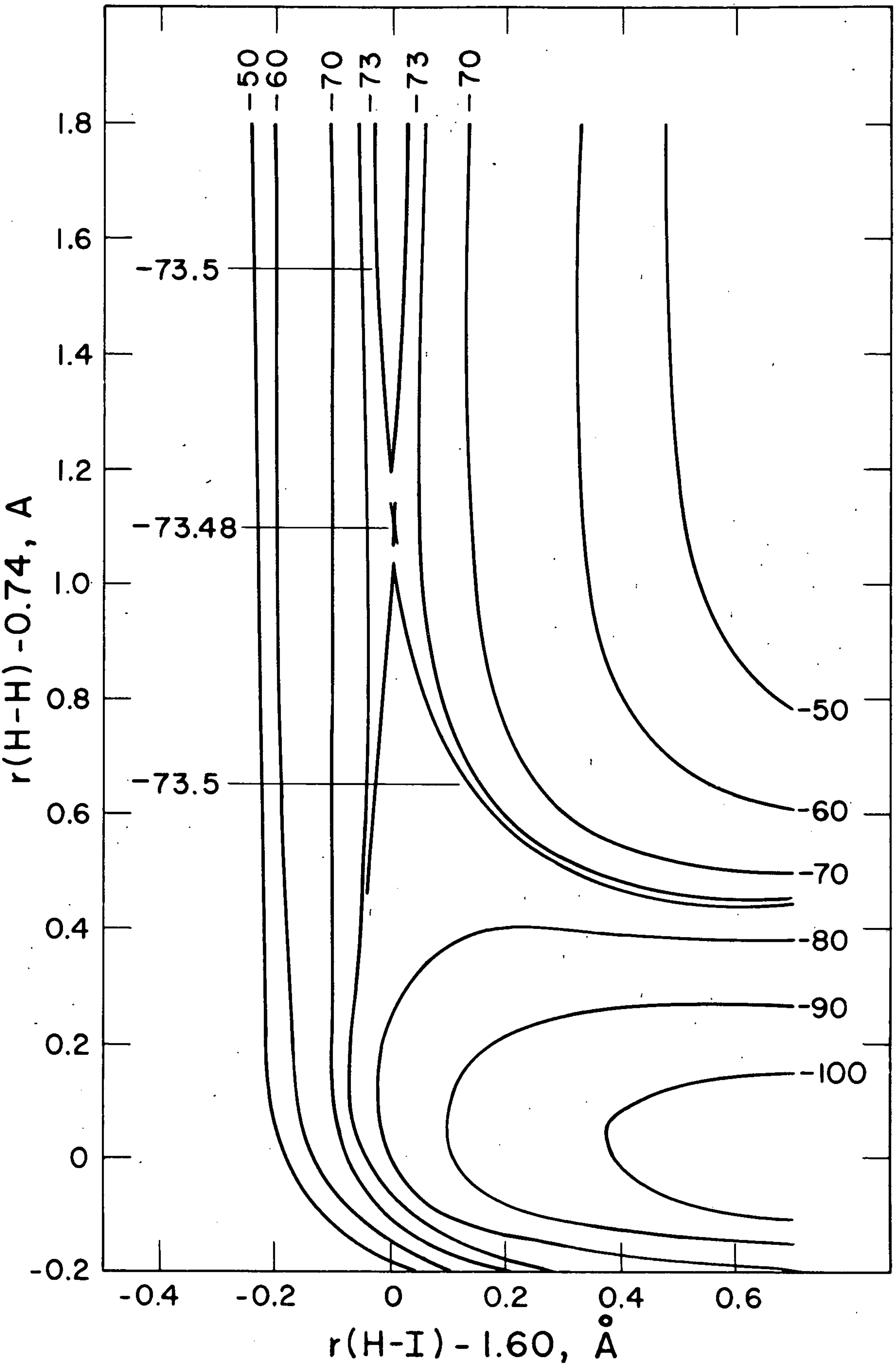

-50
-60
-70
-73
-73
-70
-73.5
-73.48
-73.5
-50
-60
-70
-80
-90
-100
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.2
0
0.2
0.4
0.6
r(H-H) -0.74, Å
r(H-I) - 1.60, Å

Fig 3