

APPARENT AND TRUE THRESHOLD ENERGIES IN DEUTERIUM ABSTRACTION REACTIONS OF HOT HYDROGEN ATOMS

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Summary

The integral yield of a reaction involving hot hydrogen atoms has been evaluated as a function of the initial energy of the hot atom. On the assumption that the cross section for the reaction is given by the excitation function

$$S_R(E) = S_{R \max} \left(1 - \frac{E_0}{E} \right) \quad E > E_0$$

$$S_R(E) = 0 \quad E \leq E_0$$

or another function of similar general form, expressions for the integral product yield were derived from the kinetic theory of hot reactions.

Stochastic calculations, in which the thermal motion of the substrate was included, were also carried out. For the excitation functions considered, and for elastic collisions between the hydrogen atom and the substrate, the integral product yield is an approximately linear function of the initial energy of the hot atom over the range from 1.4 to 2.5 times the threshold energy. Simple extrapolation to zero of yields measured in this energy range would give an apparent threshold higher than the true value, and in general the true threshold is expected to be $90\% \pm 10\%$ of the apparent value obtained by extrapolation.

1. Introduction

Several reactions of hydrogen atoms, principally those involving the abstraction of deuterium from alkanes, have been studied by using atoms possessing excess translational energy ("hot" atoms) produced by photolysis of gaseous HBr or HI [1 - 5]. An advantage gained by using photochemically generated atoms rather than those produced by nuclear recoil is that the initial energy of the atoms is well defined. The threshold energy for a reaction is obtained by extrapolation to zero of the integral reaction yields

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measured at a series of initial hydrogen atom energies [3 - 5]. It has been pointed out [5] that simple extrapolation of yields at energies appreciably above the threshold usually leads to an apparent threshold energy significantly above the true value, and this observation is discussed more fully here.

2. Relation of integral yields to the excitation function

The excitation function for a reaction describes the relation between the reaction cross section and the relative translational energy of the reactants. The variation in the integral product yield with energy depends on the form of the excitation function, and in the following the energy dependence of integral yields is explored for particular excitation functions. In the functions considered, the reaction cross section rises from zero at the threshold with steadily decreasing slope to reach a maximum or limiting value at much higher energy, so that in the threshold region it can be represented by a function such as $1 - E_0/E$, $(1 - E_0/E)^{1/2}$ or $1 - (E_0/E)^2$, where E_0 is the threshold. The possible existence of a small low energy "tail" as suggested for the $H + H_2$ reaction [6] is ignored. Such a tail would not be detected experimentally from integral yield measurements of the type considered here.

A convenient way of relating the integral yield to the excitation function is by the use of the kinetic theory of Estrup and Wolfgang [7, 8]:

$$-\ln(1 - P) = \int_{E_{L_0}}^{E_{L_1}} \frac{p(E_L)}{\alpha E_L} dE_L \quad (1)$$

Here P is the integral reaction yield, $p(E_L)$ is the probability of reaction in a single collision at laboratory energy E_L of the hot atom, α is the average logarithmic energy loss of the hot atom in a non-reactive collision with the substrate and E_{L_0} is the threshold energy. This expression was originally developed for the yield of a reaction of atoms produced by nuclear recoil and in that case E_{L_1} is the upper bound of energy at which reaction can occur; E_{L_1} is taken here to be the initial energy of the hot atom. In the derivation of eqn. (1) thermal translational motion of the substrate is ignored. The assumptions and approximations involved in the kinetic theory have been discussed extensively [1, 9 - 15]. In particular, the atom is assumed to make a number of collisions at energies above the upper limit E_{L_1} for reaction so as to provide a statistically well-defined distribution of energies in the range from E_{L_1} to E_{L_0} . Although this assumption cannot be made in photochemical systems, where the first collision of the atom is within the reactive energy range, the theory still gives a reasonably good description of model photochemical systems, as can be seen in Fig. 2, which is discussed in more detail later.

3. Line-of-centres function

A simple excitation function which is often used is the line-of-centres function [16]

$$\begin{aligned} S_R(E) &= S_{R \max} \left(1 - \frac{E_0}{E}\right) & E > E_0 \\ S_R(E) &= 0 & E \leq E_0 \end{aligned} \quad (2)$$

where $S_R(E)$ is the reaction cross section and $S_{R \max}$ is the value of $S_R(E)$ at very high energy. The function is expressed in terms of relative transitional energy E and the threshold E_0 is also in relative energy. In the symbolism of the kinetic theory, $p(E) = S_R(E)/S(E)$ where $S(E)$ is the collision cross section, and (2) becomes

$$\begin{aligned} p(E) &= p_\infty \left(1 - \frac{E_0}{E}\right) & E > E_0 \\ p(E) &= 0 & E \leq E_0 \end{aligned} \quad (3)$$

If thermal substrate motion is ignored, as in the derivation of eqn. (1), the laboratory energy of the hot atom and the relative energy are related by $E = E_L M_S / (M_S + M_H)$ and $E_0 = E_{L_0} M_S / (M_S + M_H)$, where M_H and M_S are the masses of the hot atom and the substrate. The integral yield for a reaction following the line-of-centres excitation function is then obtained from eqn. (1):

$$-\ln\{1 - P(E_{L_1})\} = \int_{E_{L_0}}^{E_{L_1}} \frac{p_\infty}{\alpha} \left(\frac{1}{E_L} - \frac{E_{L_0}}{E_L^2} \right) dE_L \quad (4)$$

If α is assumed to be independent of energy, as would be the case for elastic rigid sphere interaction between atom and substrate, then the integral yield varies with the initial energy E_{L_1} of the atom according to

$$-\ln\{1 - P(E_{L_1})\} = \frac{p_\infty}{\alpha} \left\{ \ln\left(\frac{E_{L_1}}{E_{L_0}}\right) + \frac{E_{L_0}}{E_{L_1}} - 1 \right\} \quad (5)$$

For small values of P , $-\ln(1 - P)$ is approximately equal to P .

Figure 1 shows the integral product yield as a function of the initial laboratory energy of the hot atom, calculated from eqn. (5) with $p_\infty/\alpha = 0.082$. The relationship between P and E_{L_1} shows pronounced upward curvature from the threshold to $E_{L_1}/E_{L_0} = 1.4$, and is then almost linear in the range $E_{L_1}/E_{L_0} = 1.5 - 3.0$.

In a typical experimental case, the apparent threshold might be obtained by using a linear or almost linear extrapolation of measured yields in the range $E_{L_1}/E_{L_0} = 1.4 - 2.5$. Such a procedure applied to the yield curve in Fig. 1 would lead to an apparent threshold well above the true value.

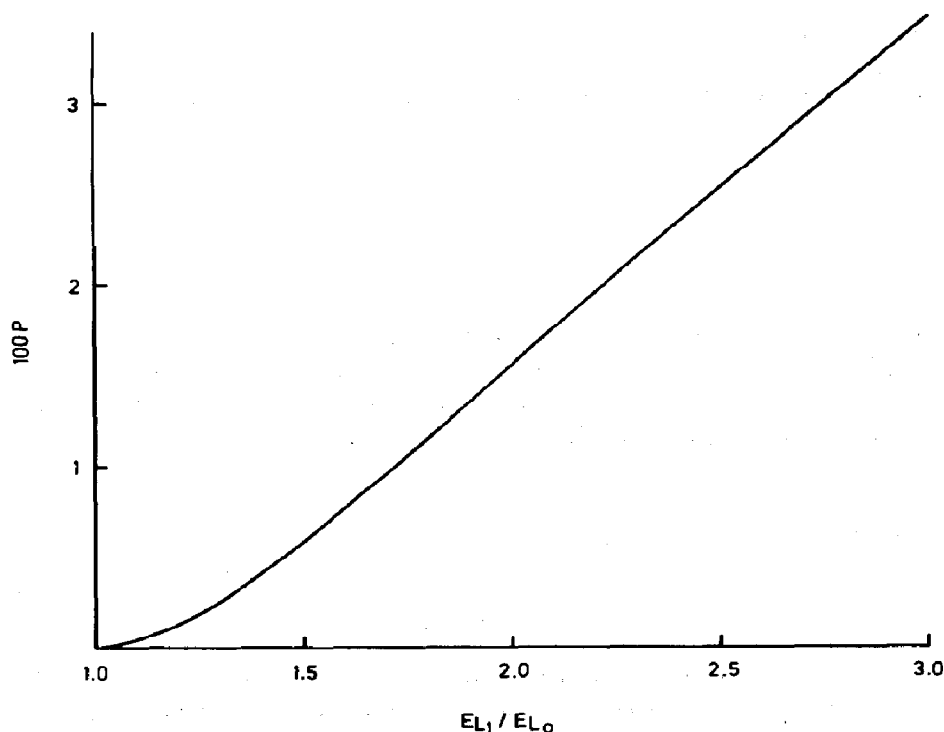


Fig. 1. Integral product yield for reaction with line-of-centres excitation function calculated from eqn. (5) with $p_{\infty}/\alpha = 0.082$.

Linear extrapolation of the points at $E_{L1}/E_{L0} = 1.4$ and $E_{L1}/E_{L0} = 2.5$ gives an apparent threshold $E_L = 1.19E_{L0}$.

4. Other excitation functions

The functions

$$S_R(E) = S_{R\max} \left\{ 1 - \left(\frac{E_0}{E} \right)^2 \right\} \quad E > E_0$$

$$S_R(E) = 0 \quad E \leq E_0$$
(6)

and

$$S_R(E) = S_{R\max} \left(1 - \frac{E_0}{E} \right)^{1/2} \quad E > E_0$$

$$S_R(E) = 0 \quad E \leq E_0$$
(7)

discussed by Eu and Liu [17] are qualitatively similar to the line-of-centres function.

In both cases $p(E_L)/E_L$ rises rapidly from zero at the threshold to reach a value which remains roughly constant (within 20% of its maximum

value) in the range $E_L/E_{L_0} = 1.4 - 2.5$. Reference to eqn. (1) shows that the yield curves are expected to be qualitatively similar to Fig. 1, with upward curvature immediately above the threshold followed by an extended almost linear region. Extrapolation of yields well above the threshold again would lead to an apparent threshold well above the true value. Application of the simple treatment given earlier to function (6) gives the yield curve

$$-\ln\{1 - P(E_{L_1})\} = \frac{P_\infty}{\alpha} \left\{ \ln\left(\frac{E_{L_1}}{E_{L_0}}\right) + \frac{1}{2} \left(\frac{E_{L_0}}{E_{L_1}}\right)^2 - \frac{1}{2} \right\} \quad (8)$$

and the apparent threshold obtained by linear extrapolation of the yields at $E_{L_1}/E_{L_0} = 1.4$ and $E_{L_1}/E_{L_0} = 2.0$ is 15% above the true value. This illustrates the fact that the low energy tail on the yield curve is expected to be smaller, and the apparent threshold lower, for those functions for which $p(E_L)/E_L$ approaches its maximum value more rapidly above the threshold.

By contrast with functions (2), (6) and (7), an excitation function having a constant or even increasing slope above the threshold, such as $S_R(E) \propto E - E_0$, might be considered. The yield curve for such a function displays upward curvature at all energies above the threshold. Linear extrapolation of yields at energies well above the threshold would be inappropriate, but if carried out would lead to an apparent threshold well above the true value.

5. Effect of variation of α

The derivation of (5) and (8) assumes that α is constant over the relevant energy range, as would be the case for elastic hard sphere collisions. It is more realistic to assume that collisions are inelastic and that α might increase with increasing energy. The qualitative effect of such a variation would be to reduce the values of P at energies well above the threshold relative to those at energies near the threshold, thus lowering the apparent threshold obtained by extrapolation. This was not extensively examined because of the lack of information about the energy dependence of α , but a few calculations were carried out using eqn. (1) with an energy-dependent α , and the apparent threshold was estimated by linear extrapolation through the points at $E_{L_1}/E_{L_0} = 1.4$ and $E_{L_1}/E_{L_0} = 2.0$. Both the line-of-centres function and a function proportional to $1 - (E_0/E)^3$ were used in the calculations. It was found that unless α increased very sharply with energy (by more than 80% between E_{L_0} and $2E_{L_0}$) the apparent threshold still lay above the true threshold.

6. Stochastic calculations of reaction yields

The model used for the calculation of the yield curve in Fig. 1 is unrealistic in that it neglects thermal motion of the substrate and assumes a

rigid sphere interaction between the collision partners. In order to investigate the effect of thermal motion of the substrate stochastic calculations of yields for different forms of the excitation function have been carried out. The calculations are limited to elastic collisions between the hydrogen atom and the substrate, but have been performed using a soft interaction potential (ninth power repulsive) as well as the rigid sphere interaction. The method used is outlined below.

It is imagined that a hydrogen atom at an initial laboratory translational energy E_L , is injected into a thermal substrate medium. The hydrogen atom is then allowed to make successive collisions with the substrate until either it meets a criterion for reaction in one of the collisions or its energy falls below a predetermined threshold. If, in one of the collisions, the reaction criterion is met the hydrogen atom is removed from the reaction system and the fact is recorded as a reaction and referenced to the particular initial energy of the hydrogen atom concerned. Another hydrogen atom is then injected. In practice many hydrogen atoms are introduced (500), their fates followed and at the end of the run the integral yield P is calculated using

$$P(E_{L_i}) = \frac{\text{number of atoms reacted}}{\text{number of atoms injected}}$$

The whole procedure is then repeated for a sufficient number of initial hydrogen atom energies to enable the yield curve over the photochemical energy range to be obtained.

Whether reaction occurred in any particular collision was determined randomly using the probability of reaction at the relative collisional energy E given by the excitation function. If reaction did not occur, the atom suffered a change in translational energy and a new value of the energy was calculated.

For each collision, the laboratory energy E_L of the hydrogen atom was transformed to an energy E relative to that of the substrate. This was achieved by a random selection of both the collision angle γ and the laboratory velocity V_S of the substrate from appropriately weighted distributions [18, 19] and the calculation of E from E_L , V_S and γ .

The probability $p(E)$ of reaction in a single collision at the relative energy E was then calculated from

$$p(E) = \frac{S_R(E)}{S(E)} = \frac{S_{R \max}}{S(E)} \left(1 - \frac{E_0}{E}\right)^z \quad E > E_0$$

$$p(E) = 0 \quad E \leq E_0$$
(9)

This equation involves the reaction cross section $S_R(E)$, the total collision cross section $S(E)$ and the maximum reaction cross section $S_{R \max}$.

Calculations were carried out both for the line-of-centres function (2) ($z = 1$) and for the Eu and Liu function (7) ($z = 1/2$). In using eqn. (9) to calculate the single collision probability, the laboratory energy threshold

E_{L_0} was transformed to a relative energy threshold E_0 by application of the mass factor.

For the hard sphere interaction $S(E)$ was taken as 0.32 nm^2 . For calculations involving the repulsive potential $V(r) = dr^{-9}$, $S(E)$ was arbitrarily defined so as to exclude collisions with energy loss of the hydrogen atom of less than 1% of the maximum possible; this procedure led to a slow variation in $S(E)$ with energy [4]:

$$S(E) = \pi b_{\max}^2 = \pi y_{0\max}^2 \left(\frac{9d}{E} \right)^{2/9} \quad (10)$$

where b is the impact parameter and y_0 is a function of b and E which determines the deflection angle χ [20]. The value of $y_{0\max}$ used was 1.1 and the repulsive potential employed was that appropriate for H-Xe interaction [4], with $d = 0.329 \text{ J mol}^{-1} \text{ nm}^9$.

If the value of $p(E)$ was less than a number selected at random from a linearly weighted distribution between zero and unity, then this corresponded to no reaction. Alternatively, when the value of $p(E)$ was greater than the value of the random number the reaction criterion was met. In this case, the hydrogen atom was removed from the substrate medium and the next hydrogen atom injected at the source energy. If, however, no reaction occurred, the laboratory energy of the hydrogen atom was changed from E_L' to E_L'' after collision. This new laboratory energy was calculated using [4]

$$E_L'' = E_L' - \frac{\mu}{M} \left\{ 2E_L' - M_S V_S^2 + (M_S - M_H) \left(\frac{2E_L'}{M_H} \right)^{1/2} V_S \cos \gamma \right\} (1 - \cos \chi) + \left\{ \mu \left(\frac{2E_L'}{M_H} \right)^{1/2} V_S \sin \gamma \cos \eta \sin \chi \right\} \quad (11)$$

where η (azimuthal angle) and χ (deflection angle) are the scattering angles, $M = M_S + M_H$ and μ is the reduced mass of the substrate and the hydrogen atom.

In addition to V_S and γ , the azimuthal angle η and impact parameter b were selected randomly from suitable weighted distributions [19]. For the rigid sphere potential χ is determined by b and for the ninth power repulsive potential χ is determined by y_0 , *i.e.* by both b and E .

The value of E_L'' was once again transformed to a relative energy, and the single collision reaction probability was calculated. The whole procedure was then repeated until the laboratory energy of the hydrogen atom fell below a predetermined threshold or the hydrogen atom was removed in reaction. In this way the fate of each of the injected hydrogen atoms was followed, the reactive events were recorded and the integral reaction yield for a particular source energy was calculated. The whole procedure was then repeated for several different values of the initial laboratory translational energy of the hydrogen atom.

7. Comparison with eqn. (5)

In order to compare the results of the above procedure with those predicted by the explicit function in eqn. (5), stochastic calculations were carried out for a rigid sphere interaction potential and a line-of-centres excitation function. To keep the substrate stationary, fulfilling the condition for which eqn. (5) was derived, the temperature, which determines the distribution of V_S , was set at 0 K. The substrate mass used was $0.018 \text{ kg mol}^{-1}$ and the cross sections were $S_{R \max} = 0.025 \text{ nm}^2$ and $S(E) = 0.32 \text{ nm}^2$. The threshold energy chosen was $E_{L_0} = 55 \text{ kJ mol}^{-1}$ and the integral yield was computed for several values of E_{L_i} between 65 and 195 kJ mol^{-1} .

The quantities needed to calculate P from eqn. (5) were obtained from the masses and cross sections. $p_\infty = S_{R \max}/S(E) = 0.0781$. For rigid spheres, $\alpha = 1 + \beta \ln \beta / (1 - \beta)$, with $\beta = (M_S - M_H)^2 / (M_S + M_H)^2$; hence $\alpha = 0.108$.

Figure 2 shows both the stochastically calculated values of $-\ln(1-P)$ and the yield curve obtained from the explicit function (5). Some statistical fluctuations are evident, but there is excellent agreement between the two sets of results. In both cases the higher energy yields extrapolate to an energy well above the threshold of 55 kJ mol^{-1} .

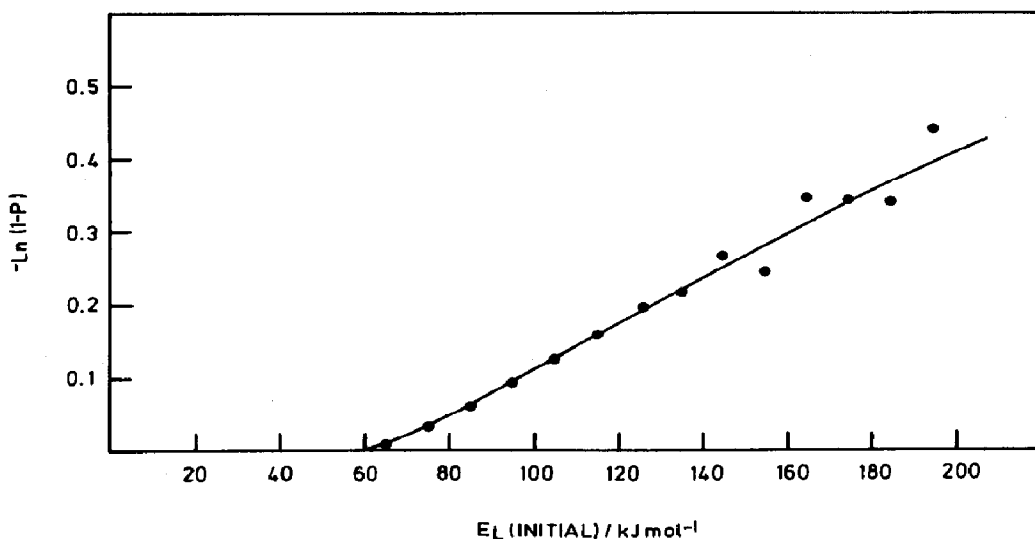


Fig. 2. Dependence of integral product yield on initial laboratory energy for reaction with line-of-centres excitation function (rigid sphere potential; $T = 0 \text{ K}$; $S_{R \max} = 0.025 \text{ nm}^2$; $S(E) = 0.32 \text{ nm}^2$; $E_{L_0} = 55 \text{ kJ mol}^{-1}$; $M_S = 0.018 \text{ kg mol}^{-1}$): ●, stochastic results; —, calculated from eqn. (5).

8. Calculations with thermal substrate motion

For a substrate undergoing thermal motion there is a distribution of relative energies E corresponding to any particular laboratory energy E_L of

the hydrogen atom. Subsequent calculations of integral yields were carried out with the substrate having a velocity distribution corresponding to a temperature of 293 K and calculated yields were used to examine the relationship between the true threshold and the apparent value obtained by extrapolation. As in the case of a stationary substrate, it was found that the apparent threshold lies above the true value, and the effects of changes in some of the quantities used in the calculation, the type of interaction potential, the mass of the substrate, the form of the excitation function and the value of $S_{R\max}$ were explored. In all cases the threshold used was $E_{L_0} = 55 \text{ kJ mol}^{-1}$.

The effect of the substrate mass on the apparent threshold was examined by computing yields for a line-of-centres function with $S_{R\max} = 0.04 \text{ nm}^2$, the ninth power repulsive interaction potential and substrate masses of 0.002, 0.018, 0.050 and 0.100 kg mol^{-1} . It was found that increases in the substrate mass substantially increased the integral yields, as would be anticipated, since the average energy loss of a hydrogen atom in a collision is reduced by increasing the substrate mass. Despite this marked change in yields, the apparent extrapolated threshold was insensitive to the value of the substrate mass used in the calculations. The other factor which controls energy loss in a collision is the interaction potential between the hydrogen atom and the substrate, the energy loss being smaller for the ninth power repulsive potential than for the rigid sphere potential. Computed yields assuming the excitation function (7) were substantially higher when a ninth power repulsive potential was used than for a rigid sphere potential, but little change in the apparent threshold was evident. Thus for elastic collisions the apparent threshold is not strongly influenced by factors affecting the average energy loss in collision. By contrast, the form of the excitation function has an important effect on the position of the apparent threshold. This can be seen by reference to Fig. 3, which shows a comparison of computed integral yields for two reactions, one of which follows the line-of-centres function (2) and the other the steeper function (7). Apart from the difference in the form of the excitation function the conditions used in the calculation were the same in both cases; the value of $S_{R\max}$ was 0.008 nm^2 , the substrate mass was $0.018 \text{ kg mol}^{-1}$, the ninth power repulsive potential was used and the temperature was 293 K. In both cases extrapolation of the yields well above the threshold gives an apparent threshold higher than the true value, but the apparent threshold obtained for function (7) is closer to the true value.

The effect of an increase in $S_{R\max}$ was examined by comparing yields for the function (7) with $S_{R\max} = 0.008 \text{ nm}^2$, $S_{R\max} = 0.025 \text{ nm}^2$ and $S_{R\max} = 0.040 \text{ nm}^2$. As well as producing a substantial increase in yields, the increase in $S_{R\max}$ from 0.008 to 0.040 nm^2 resulted in a small lowering of the apparent threshold, from $1.11E_0$ to about $1.08E_0$.

The main factor affecting the apparent threshold is thus the form of the excitation function, with the value of $S_{R\max}$ having a minor effect. On average, for several runs carried out under a variety of conditions, the

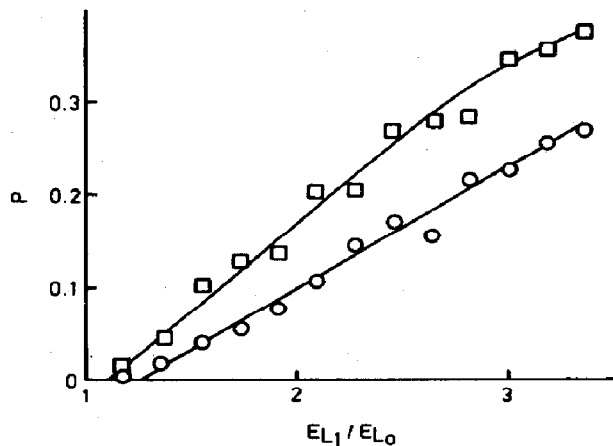


Fig. 3. Integral yields for reactions (ninth power repulsive potential; $M_S = 0.018 \text{ kg mol}^{-1}$; $T = 293 \text{ K}$; $S_{R \max} = 0.008 \text{ nm}^2$): \square , following excitation function (7); \circ , following excitation function (2).

apparent threshold obtained by extrapolation is about $1.2E_{L_0}$ for the line-of-centres function (2) and about $1.1E_{L_0}$ for the function (7).

9. Relation between apparent and true thresholds

There is a broad agreement between calculations carried out using expressions based on the kinetic theory of hot reactions and those using stochastic methods. The calculations show that for an excitation function of the general type (2), (6) or (7), and for energy transfer in elastic collisions between the hydrogen atom and the substrate, the integral reaction yield is an approximately linear function of the initial energy of the hydrogen atom over the range from $E_{L_1} = 1.4$ to $E_{L_1} = 2.5E_{L_0}$. Extrapolation of yields in this energy range to zero gives an apparent threshold energy above the true value. As a rough generalization, the true threshold is expected to be $90\% \pm 10\%$ of the apparent threshold. If the excitation function is steep, with $S_R(E)/E$ approaching its maximum value rapidly, the apparent threshold is closer to the true value than if the excitation function is shallow.

An example of the relationship between the true and apparent thresholds is provided by the work of Gann *et al.* [21] on the abstraction by hot hydrogen atoms of the secondary deuterium atoms in $n\text{-C}_4\text{D}_{10}$. The true threshold, estimated by a method based on the temperature variation of the HD yield, is 0.35 eV , whereas the apparent threshold, determined by extrapolation of integral reaction yields over the range from 0.48 to 0.92 eV , is about 0.38 eV .

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