A HIGH ENERGY CLASSICAL TRAJECTORY STUDY OF THE REACTIONS
O\(^{3}\)P + H\(_2\) → OH + H AND O\(^{3}\)P + H\(_2\) → O + H + H

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In this work the O\(^{3}\)P + H\(_2\) system was treated in the high energy range by applying the classical trajectory method. Cross sections and rate constants for both the exchange and the dissociative processes were calculated. The cross sections were obtained for the energy range (10–900) kcal mol\(^{-1}\) and rate constants for the temperature range (10\(^{3}\)–5 \times 10\(^{4}\)) K. An analytical model, which satisfactorily predicts correct cross sections in the high energy range, is also presented.

1. Introduction

The reaction of an atomic oxygen O\(^{3}\)P with a hydrogen molecule H\(_2\) is one of the most fundamental processes in combustion processes. This is one of the main reasons for the recent intensive experimental [1–6] and theoretical [7–11] research being carried out with respect to this system. Since it is accepted that in most combustion processes the temperature does not increase beyond 3000 K, all the numerical calculations of cross sections were done for energies below 30 kcal mol\(^{-1}\) [8, 9], a value which is far from the theoretical threshold for dissociation (≈103 kcal mol\(^{-1}\)). However, it is known that in certain regions of the combustion chamber, in particular in the vicinity of the ignition zone, the temperatures are much higher and can rise as high as 50000 K [12]. In order to study these cases the relevant rate constants are required for both the exchange and the dissociative processes. These magnitudes can be calculated if the corresponding cross sections for energies as high as 500 to 1000 kcal mol\(^{-1}\) are available. One of the aims of this paper is to determine these cross sections as well as the corresponding rate constants. In addition a classical model is presented which yields analytical expressions for the partial cross sections for both the exchange and the dissociative processes in the high energy region. The quantitative predictions of the model were confirmed reasonably well by the “exact” results.

To obtain the “exact” results the ordinary quasi-classical trajectory method was applied. The cross sections were obtained in the following way. For each energy a maximal impact parameter \(b_m\) was determined. (The largest value encountered was \(b_m = 1.65\ \text{Å}\).) Once \(b_m\) was found the corresponding cross sections were calculated employing 500 trajectories for most energies, however, for energies around thresholds (either for exchange or dissociation) more than 1000 trajectories were integrated. The potential energy surface used is the LEPS surface of Johnson and Winter [8], as calibrated by them to yield results which are as close as possible to the experimental measurement already.
known at that time [3, 4]. The usefulness of their potential was recently confirmed again by Schatz et al. [11] and also by us, as the reproduced rate constants were in good agreement with the experimental values for temperatures as high as 2000 K.

An important part of this study is devoted to the dissociation process. As far as we know, this system, in contrast to various others (e.g. Na⁺ + D₂ [13], Ar + H₂ [14], H + H₂ [15]), was never exposed to this kind of treatment. Results for both the cross sections and rate constants are given.

To decide whether the trajectory led to dissociation or not, the following checks were made. After the collision of the two reactive species, the program calculates the interatomic distances at each instant. Once one atom is far enough from the other two (~8 Å) a dissociation will occur if and only if the internal kinetic energy of the remaining pair is larger than their corresponding binding energy.

2. Theoretical studies – a model for the high energy region

In this section we present a model which yields analytical expressions for exchange and dissociative cross sections in the high energy region. The model is a simplified version of a hard sphere model devised more than a decade ago by Baer and Amiel [16–18] for studying high energy chemical reactions.

2.1. Dynamics

We consider the reactions:

\[ \text{A} + \text{BC} \rightarrow \text{AB} + \text{C}, \]

\[ \rightarrow \text{A} + \text{B} + \text{C}, \]  

(1)

where A, B and C are atoms which are approximated by rigid spheres of radii \( R_l \), \( l = A, B, C \). According to this model, the exchange or the dissociative reaction is considered as a two step process:

(a) A repulsive (hard sphere type) collision between A and C which causes C to leave the interaction region without affecting the position and/or the velocity of B.
(b) An interaction between B and A via a square-well potential.

Defining the velocities \( V_{l} \) and \( V_{i} \), \( l = A, B, C \) as the initial and final velocities of the \( l \)th atom before and after a collisional event, respectively, one obtains [18]

\[ V_{Af} = V_{Ai} - \frac{2}{|R_{AC}|^2} (V_{AC} \cdot R_{AC}) \frac{m_C}{m_A + m_C} R_{AC}, \]

(2)

where

\[ V_{AC} = V_{Ai} - V_{Ci}, \]

(3)

\[ |R_{AC}| = R_A + R_C, \]

(4)

\( R_{AC} \) is the vector along the line of centers during the collision between A and C, and \( m_C \) and \( m_A \) are the masses of atoms C and A, respectively.

Since, as assumed, the velocity \( V_{Bi} \) is not affected by the collision of A and C, we find from eq. (2) that the relative velocity \( V_{ABI} \) is given in the form:

\[ V_{ABI} = V_{ABI} - \frac{2}{|R_{AC}|^2} (V_{AC} \cdot R_{AC}) \frac{m_C}{m_A + m_C} R_{AC}. \]

(5)

Squaring and multiplying both sides by the reduced mass of A and B, i.e. \( \mu_{AB} \), one obtains

\[ E_{ABI} = E_{ABI} - 4 \left[ E_{ABI} E_{AC} \left( \frac{m_B m_C}{m_A + m_B} \right) \right]^{1/2} \]

\[ \times \cos \theta \cos \bar{\theta} + 4 \left( \frac{m_B^2}{m_A + m_B} \right) \frac{E_{AC} \cos^2 \theta}{E_{AC}} \]

(6)

where \( \theta \) and \( \bar{\theta} \) are angles between \( R_{AC} \) and \( V_{AC} \) and \( V_{ABI} \), respectively, at the instant A collides with C and \( m_B \) is the mass of the B atom. Since the model is applied only for high enough energies (>100 kcal mol⁻¹) we ignore the fact that the original molecule may vibrate or rotate. Therefore it can be assumed that

\[ V_{ABI} = V_{AC} = V_{i}, \]

(7)

where \( V_{i} \) is the relative velocity of A and BC. This outcome implies that \( \theta = \bar{\theta} \) as well.
Defining $E_t$ as the initial translational energy, one may show, following several algebraic manipulations, that:

$$E_{ABt} = \alpha E_t (1 - 4\beta \cos^2 \theta),$$

where:

$$\alpha = \frac{m_B (m_A + m_B + m_C)}{(m_A + m_C)(m_A + m_B)},$$

$$\beta = \frac{m_C m_A}{(m_A + m_C)(m_A + m_B)}.$$  \hfill (8)

The next step is to determine the conditions for a dissociative collision. If $\delta$ is defined as the angle between $\mathbf{V}_{ABt}$ and the line of centers of A and B, the condition for dissociation is \cite{18,19}:

$$F_{ABt} \cos^2 \delta > E_b,$$  \hfill (10)

where $E_b$ is the binding energy of A and B. Substitution of eq. (8) in eq. (10) leads finally to the condition for a dissociative collision to occur:

$$\alpha E_t \cos^2 \delta (1 - 4\beta \cos^2 \theta) > E_b.$$  \hfill (11)

2.2. Probability

The aim in this treatment is to calculate the probability of having a dissociative event once the relative energy $E_t$ is given. In order to do this we have to determine the probability $p(\theta, \delta)$ that the collision between A and C takes place in the interval $(\theta, \theta + d\theta)$ and the collision between A and B takes place in the interval $(\delta, \delta + d\delta)$ and to integrate over $\theta$ and $\delta$ so that the condition given in eq. (11) is always fulfilled. It can be shown that

$$p(\theta, \delta) d\theta d\delta = 4 \cos \theta \sin \theta d\theta \cos \delta \sin \delta d\delta$$

or:

$$p(\theta, \delta) d\theta d\delta = d(\cos^2 \theta) d(\cos^2 \delta).$$  \hfill (12)

For a given value of $\delta$ the range of $\cos^2 \theta$ values for which eq. (11) is fulfilled is

$$0 \leq \cos^2 \theta \leq \min \left[ 1, \frac{\alpha E_t \cos^2 \delta - E_b}{4\alpha \beta E_t \cos^2 \delta} \right].$$  \hfill (13)

In what follows we assume $4\beta < 1$. If $D_e$ is defined as

$$D_e = E_b/\alpha E_t (1 - 4\beta)$$  \hfill (14)

and $D_m$ as

$$D_m = E_b/\alpha E_t,$$  \hfill (15)

then the probability $P_d$ for having a dissociation is given in the form:

$$P_d = \int_{D_m}^{D_e} d(\cos^2 \delta) \int_{0}^{1} d(\cos^2 \theta),$$  \hfill (16)

where:

$$T_c = (\alpha E_t \cos^2 \delta - E_b)/4\alpha \beta E_t \cos^2 \delta.$$  \hfill (17)

Solving these integrals leads to:

$$P_d = 1 + (E_b/4\alpha \beta E_t) \ln (1 - 4\beta).$$  \hfill (18)

The model can be extended also to include exchange reactions and inelastic (elastic) collisions. We assume that the probability for having an inelastic (elastic) collision is independent of energy and equal to $P_i$ and that $P_e$ is the probability for having an exchange reaction. Since

$$P_o + P_c + P_i = 1$$  \hfill (19)

and recalling eq. (18), we obtain

$$P_e = -(E_b/4\alpha \beta E_t) \ln (1 - 4\beta) - P_i.$$  \hfill (20)

Eqs. (18) and (20) simplify significantly assuming $m_A > m_C$. In this case the dependence on $\beta$ disappears and $\alpha$ becomes

$$\alpha = m_B/(m_B + m_C)$$

so that

$$P_d = 1 - \frac{m_C + m_B E_b}{m_B E_t}$$  \hfill (21)

and

$$P_e = \frac{m_C + m_B E_b}{m_B} E_t - P_i.$$  \hfill (22)
It should be mentioned that a primitive treatment of a hard sphere model yields for \( P_d \) for any mass combination [19],

\[
P_d = 1 - \frac{E_b}{E_t},
\]

(21')

which according to our model is valid only when both conditions, namely \( m_A \gg m_C \) and \( m_B \gg m_C \), are fulfilled.

3. Results

This section is divided into two main subsections, the first dealing with general results, such as total cross sections as a function of energy and rate constants as a function of temperature, and the other treating results related to the model presented in the previous section.

3.1. Cross sections and rate constants

In this section we give the results associated with both exchange collisions and dissociative collisions. It should be emphasized that all rate constants to be presented here are for the (initial) ground state \((\nu_i = 0; j_i = 0)\) only and not the usual thermally averaged rate constants.

3.1.1. The reactive exchange process

In fig. 1a the reactive cross section \( \sigma_e \) from ground state \((\nu = 0; j = 0)\) is shown as a function of the total (kinetic) energy \( E_t \) for the entire energy range \( 10 \leq E_t \leq 900 \text{ kcal mol}^{-1} \) studied. The reactive cross section is seen to become maximal in the region \( 100 \leq E_t \leq 200 \text{ kcal mol}^{-1} \), after which it monotonically drops to become practically zero around \( 1000 \text{ kcal mol}^{-1} \). As we shall see later the main reason for \( \sigma_e \) to decrease above \( E_t = 200 \text{ kcal mol}^{-1} \) is connected with the opening of the dissociative channel.

In fig. 1b \( \sigma_e \) is presented as a function of \( E_t \), but only for energies much below dissociation. The results, as far as we can tell, are identical to those of Johnson and Winter [8].

The fact that the reactive cross sections were calculated for such high energies permits the calculation of rate constants for temperatures as high as \( 50000 \text{ K} \) (see fig. 2a). Although such high temperatures are not usual, they are still encountered in certain regions of the combustion chamber [12].

Rate constants for the low temperature range in the interval \((1000-3000) \text{ K}\) are shown in fig. 2b together with the experimental results of Baulch et al. [3] and the numerical results of Johnson and Winter [8]. The fit among the different types of results is rather good.
3.1.2. The dissociation process

The cross section for dissociation $\sigma_d$ from the ground state ($v_i = 0, j_i = 0$) is shown in fig. 3a as a function of the kinetic energy. The cross section increases monotonically from the threshold around 125 kcal mol$^{-1}$ until $E_t = 600$ kcal mol$^{-1}$ where it seems to approach a plateau region. Any further increase in energy (from 600 to 900 kcal mol$^{-1}$) hardly changes $\sigma_d$. It is interesting to note that the threshold is at $\approx 125$ kcal mol (where we found one dissociative collision out of 350 trajectories), a value which is relatively far from 103 kcal mol$^{-1}$, the minimal (kinetic) energy required to dissociate the H$_2$ molecule. Although we considered results for $v = 0$ and $j = 0$ only, we also performed a few calculations for other values of $j$, namely $j = 3, 6$. Except for the threshold region, all the results were found to be, within the statistical error, independent of $j$.

The calculated cross sections were used to obtain the corresponding rate constants for dissociation. The results are shown in fig. 4 for the temperature range (2000–50000) K. Even though the rate constants change by 15 orders of magnitude in this range the Arrhenius plot still yields a straight line. The fact that this plot remains linear over such a large temperature range...
range indicates that the cross section for dissociation is of a very simple form. That indeed was found to be the case, as will be discussed in the next section.

The linear Arrhenius plot permits the calculation of the corresponding Arrhenius parameters $A$ and $E_0$:

$$A = 4.42 \times 10^{-19} \text{ molecule cm}^2 \text{ sec}^{-1},$$

$$E_0 = 6.1 \text{ eV} \approx 141 \text{ kcal/mol}.$$

The value of the activation energy $E_0$ is about 40% higher than the threshold for dissociation which is the binding energy of H$_2$, i.e. 103 kcal/mol. However, $E_0$ is rather close to the threshold energy for dissociation ($\approx 125$ kcal/mol) as was determined from the trajectory calculation.

3.2. The numerical results and the model predictions

We now consider results which are above the threshold for dissociation. In figs. 5 and 6 $\sigma_d$ and $\sigma_e$ are plotted as a function of $E_t^{-1}$, while the sum $(\sigma_d + \sigma_e)$ is shown as a function of $E_t$ in fig. 7. The straight lines in figs. 5 and 6 are the least square fit lines derived using the results for $E_t \geq 200$ kcal mol$^{-1}$. If we write the cross sections $\sigma_d$ and $\sigma_e$ for the considered energy range as [see eqs. (18) and (20)]:

$$\sigma_d = \sigma_d(1 - A_dE_t^{-1})$$  \hspace{1cm} (23)

and

$$\sigma_e = \sigma_e(-P_i + A_eE_t^{-1})$$  \hspace{1cm} (24)

the least square fit yields:

$$\sigma_d = 2.80 \text{ Å}^2, \quad P_i = 0.23,$$

$$A_d = 159 \text{ kcal mole}^{-1}, \quad A_e = 232 \text{ kcal mole}^{-1}.$$

Fig. 4. The Arrhenius plot of the rate constants for the dissociative reaction $O + H_2(v_i = 0, j = 0) \rightarrow O + 2H$.

Fig. 5. A linear plot of the cross section for the dissociative reaction $O + H_2(v_i = 0, j = 0) \rightarrow O + 2H$ as a function of the reciprocal energy in kcal mol$^{-1}$. The line is a least squares fit of the data (see text).

Fig. 6. A linear plot of the cross section for the exchange reaction $O + H_2(v_i = 0, j = 0) \rightarrow H + OH$ as a function of the reciprocal energy for energies above 125 kcal mol$^{-1}$. The line is a least squares fit of the data (see text).
Fig. 7. The dependence of the sum of the cross sections for dissociation and exchange on the kinetic energy.

In constructing the model one of the assumptions was that both the total cross sections and the partial cross sections for elastic and inelastic collisions are energy independent. These two assumptions are not directly associated with the hard-sphere model but are necessary if the model is to be examined quantitatively. In order to examine the range of validity of this assumption we plotted

\[ \sigma_e + \sigma_d = \sigma_t - \sigma_i, \]  

(26)

as a function of \( E \) in fig. 7. A slight energy dependence was encountered. Our hope is that this energy dependence is not so strong as to prevent the testing of the hard-sphere model.

It should, however, be emphasized that the assumptions concerning the lack of dependence of \( \sigma_t \) and \( P_e \) on the energy can be employed for a limited energy range only. In general, of course, both are expected to be energy dependent. Eq. (24), for instance, will lead to negative exchange cross sections if \( P_e \) is assumed to be energy independent throughout the entire energy range of interest.

The model predicts that both \( \sigma_d \) and \( \sigma_e \) behave linearly with \( E_t^{-1} \). This prediction, within the statistical error, is confirmed, as can be seen from figs. 5 and 6. The model also predicts that \( A_d \) and \( A_e \) are equal, which was only partly confirmed as the two differ by 33%. According to the model the binding energy and \( A_d \) (or \( A_e \)) are related by the equation:

\[ A = \frac{\ln (1 - \beta)}{4 \beta \alpha} E_b; \quad A = A_d, A_e, \]  

(27)

where \( \alpha \) and \( \beta \) are given by eqs. (9). Substituting the relevant numerical values, one finds that \( E_b \) is 72 kcal mol\(^{-1}\) calculated from the dissociation results, and 107 kcal mol\(^{-1}\) calculated from the reaction results. The correct value of \( E_b \) is 103 kcal mol\(^{-1}\). Thus we notice that both predictions for \( E_b \) are fairly close and reasonably close to the correct value. It is of particular interest that the model prediction for \( E_b \) based on the reaction results is only 4% off from the correct value. Taking the average value we obtain \( E_b = 90 \text{ kcal mol}^{-1} \).

One important point remains to be clarified. According to the model no dissociation is expected unless \( E > 220 \text{ kcal mol}^{-1} \); (i.e. about twice the binding energy), yet according to the exact treatment the true threshold is around 125 kcal mol\(^{-1}\). This difference has to be attributed to the range of validity of the model. The model is not expected to be relevant around the threshold of dissociation because not only more than one collision occurs between each pair of interacting atoms before dissociation takes place, but also the assumption concerning the separability of the interactions is invalid. These limitations, however, become less severe as the energy increases, consequently the relevance of the model is enhanced.

Analysis of the trajectory results using the model also yields information on the total cross section \( \sigma_t \) as well as on the sum of the cross sections \( \sigma_i \) for the inelastic and elastic collision. For \( \sigma_t \) we obtained the value 2.68 \( \text{Å}^2 \), which is about half the estimated geometrical value of \( \sigma_t \). For \( \sigma_i \) we obtained 0.41 \( \text{Å}^2 \) which is a reasonably small number.

4. Conclusion

In this work we studied the \( \text{O}^3\text{P} + \text{H}_2 \) reactions. Although results are given for the whole
energy range $10 < E_t < 900 \text{ kcal mol}^{-1}$, the emphasis in this study was mainly on the high energy region starting at the threshold for dissociation. We calculated exchange and dissociative cross sections that were later used to calculate the relevant rate constants as a function of temperature. The calculations were performed for the temperature range $10^3 \leq T \leq 5 \times 10^5 \text{ K}$. In those cases where either experimental values are known or other calculated results are available good agreement was obtained. This refers to temperatures below 3000 K. In addition, for the high energy region a hard sphere type model was devised which was found to yield results in reasonable agreement with the exact results.

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References