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HTP kinetics studies of the reactions of O(2 ^3P_J) atoms with H$_2$ and D$_2$ over wide temperature ranges

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The O + H$_2$(1) and O + D$_2$(2) reactions have been investigated, using the high-temperature photochemistry (HTP) technique, over the 350 to 1420 and 390 to 1420 K temperature ranges, respectively. O(2 ^3P_J) atoms were generated from flash photolysis of CO$_2$ and monitored by time-resolved atomic resonance fluorescence with pulse counting. Above 430 K the rate coefficients are given by $k_1(T) = 7.3 \times 10^{-21} (T/\text{K})^{2.93} \exp(-2980 \text{ K}/T)$ cm^3 molecule^{-1} s^{-1} and $k_2(T) = 3.1 \times 10^{-16} (T/\text{K})^{1.65} \exp(-5260 \text{ K}/T)$ cm^3 molecule^{-1} s^{-1}. Combination of our data with those from other experiments which isolated the reactions from secondary processes yields our recommendations $k_1(T) = 1.5 \times 10^{-12} \exp(-3540 \text{ K}/T) + 3.7 \times 10^{-10} \exp(-7450 \text{ K}/T)$ cm^3 molecule^{-1} s^{-1} (300 K $\leqslant T \leqslant$ 2500 K) and $k_2(T) = 1.4 \times 10^{-12} \exp(-4260 \text{ K}/T) + 2.9 \times 10^{-10} \exp(-7780 \text{ K}/T)$ cm^3 molecule^{-1} s^{-1} (390 K $\leqslant T \leqslant$ 1420 K). Accuracy assessments are discussed in the text. $k_1(T)$, $k_2(T)$, and the kinetic isotope effect compare well with calculations based on recent ICVT/LAG and CEQB *ab initio* methods, which suggest that the first terms of the double exponential expressions approximate the tunneling contributions.

I. INTRODUCTION

The reaction

$$O(2\,^3P_J) + H_2 \rightarrow OH + H, \quad \Delta H^{\circ}_{298\,\text{K}} = +7.8 \text{ kJ mol}^{-1} \tag{1}$$
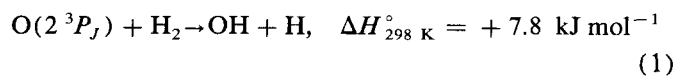
is an important chain-branching step in the combustion of hydrogen.[1] While there have been many measurements of the rate coefficient k_1, as reviewed, e.g., by Baulch *et al.*,[2] Cohen and Westberg,[3] and Warnatz,[4] these determinations were made in multireaction systems and the values of k_1 obtained depend on the kinetic model assumed. Only recently have isolated reaction measurements become available, which each cover a part of the range 300 to 2500 K.[5–7] We have now measured k_1 using a single isolated elementary reaction method, the high-temperature photochemistry (HTP) technique, over the range 350 to 1420 K.

Reaction (1) and its deuterium analog

$$O(2\,^3P_J) + D_2 \rightarrow OD + D, \quad \Delta H^{\circ}_{298\,\text{K}} = +9.4 \text{ kJ mol}^{-1} \tag{2}$$
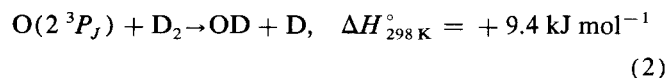
have been the subject of intense theoretical interest.[8–24] However, data for k_2 are sparse and, with the exception of three values in the range 420 to 470 K (Ref. 5), none were obtained under conditions where secondary reactions could be ignored. We have determined k_2 over the widest range to date, 390 to 1420 K, under isolated conditions in order to measure the kinetic isotope effect, $k_1(T)/k_2(T)$. This parameter, together with $k_1(T)$ and $k_2(T)$, serves as a sensitive test of theoretical models for (1) and (2).

Based on all the isolated reaction measurements, recommendations for k_1 and k_2 are given and the physical interpretation of individual parameters and the role of quantum mechanical tunneling are discussed.

II. TECHNICAL
A. Experimental method

The HTP apparatus, its operation, and the data reduction and error analysis procedures followed have been described already,[25–27] so a brief outline only is given here. The pseudostatic real time HTP method is similar in principle to conventional flash photolysis/resonance fluorescence (FP-RF). The metal and ceramic construction and the movable cooled inlet system allow higher temperatures to be reached. Ground state oxygen atoms are generated from flash photolysis of CO$_2$. O(^1D) formed initially is removed very rapidly on the time scale of our measurements through quenching by the Ar bath gas and by reaction with hydrogen (i.e., H$_2$ or D$_2$) (Ref. 28). O(^3P) reacts with excess hydrogen under pseudo-first-order conditions in a bath of heated Ar. The exponential decay of [O] is followed by time-resolved atomic resonance fluorescence at $\lambda = 130.2$ to 130.6 nm [O($3\,^3S$) → O(2 ^3P_J)] with pulse counting and signal averaging. Plots of typically six values of the pseudo-first-order decay coefficient k_{ps1} against hydrogen concentration are linear with slopes equal to the fundamental rate coefficient k_1 or k_2. The intercepts k_D reflect loss of O by diffusion out of the reaction zone. For H$_2$,

$$k_{ps1} = k_D + k_1[\text{H}_2]. \tag{3}$$

The gases used were Linde 99.999% "Ultra High Purity" Ar from the liquid, Linde 99.8% "Bone Dry" CO$_2$, Linde 99.999% "UHP" H$_2$, Linde 1% H$_2$ in helium, Linde 99% isotopically pure D$_2$, and Linde 1% D$_2$ in helium. Many runs, especially at lower temperatures, were performed with H$_2$ or D$_2$ purified by passage through a 5A molecular sieve trap cooled in liquid nitrogen. Two types of covered thermocouples, both shielded to reduce radiation errors,[29] were employed: a chromel–alumel thermocouple at

$T < 1200$ K and a platinum–platinum/rhodium thermocouple over the entire range.

B. Isolation of the reaction

The secondary processes involving OH,

$$O + OH \rightarrow O_2 + H, \tag{4}$$

$$OH + H_2 \rightarrow H_2O + H, \tag{5}$$

$$OH + OH \rightarrow H_2O + O, \tag{6}$$

have to be considered if the magnitude of $k_4[OH]$ is a sizeable fraction of $k_1[H_2]$. At large initial [O] or low temperatures this has presented a problem in earlier work, because k_4 is large and temperature independent[4] while k_1 drops steeply with decreasing temperature. A key feature of the HTP technique is the use of small $[O]_{t=0}$ which eliminates the effects of (4). This can be seen in Fig. 1 where the results of numerical simulation of reactions (1) (Ref. 3) and (4) to (6) (Ref. 4) with $[H_2] = 5 \times 10^{16}$ cm^{-3} are shown. In our system, with $[O]_{t=0} \lesssim 2 \times 10^{11}$ cm^{-3} (Ref. 30), reaction (1) is well separated from secondary processes. Figure 1 may be contrasted to the modeling of Presser and Gordon.[5] They found that, even with a much higher $[H_2]$ of about 4×10^{18} cm^{-3}, k_1 would be overestimated by about 10% at 350 K and by a factor of 2.3 at 300 K for $[O]_{t=0} = 10^{11}$ cm^{-3}. These significant effects arise from their use of O_2 instead of inert CO_2 as the photolyte, because O_2 allows reactions such as $H + O_2 + M \rightarrow HO_2 + M$ and $O + HO_2 \rightarrow OH + O_2$. In our system, with no HO_2 chemistry, we predict errors for $[O]_{t=0} = 10^{11}$ cm^{-3} of less than 1% at 300 K, Fig. 1. Oxygen would, in any event, have been unsuitable in our high-temperature work because the rate of the reaction $H + O_2 \rightarrow OH + O$ would become appreciable.

This discussion applies as well to the analogous deuterium reactions, with greater emphasis since, as will be seen, $k_2(T) < k_1(T)$. To calculate the curve for reaction (2), shown on Fig. 1, we employ our determination of k_2 (see Sec. III B) and assume that the D analogs of the species in processes (4) to (6) have the same rate coefficients as the H species.

It is important that the contribution to k_{ps1} of k_D [see Eq. (3)] is constant while $[H_2]$ is altered. We calculate the ratio of the diffusion coefficients of O in H_2 and Ar to be 3.35:1 at 350 K, using Lennard-Jones parameters[31,32] for O, H_2, and Ar and following the procedure of Dixon-Lewis.[32] On the basis of the reciprocal mixing rule[33,34] the maximum change in k_D would be about 4%. This is small compared to the changes by at least a factor of 2 in k_{ps1} in the k_{ps1} vs $[H_2]$ or $[D_2]$ plots. At higher temperatures k_1 and k_2 are greater, therefore smaller mole fractions of hydrogen are required to give appreciable changes in k_{ps1} and any changes in k_D are reduced.

III. RESULTS

A total of 34 measurements of k_1 and 29 of k_2 have been made. These span the ranges 350 to 1420 and 390 to 1420 K, respectively. Extensive variation of the total concentration [M] (0.9 to 11×10^{-18} cm^{-3}), the distance from the cooled inlet to the reaction zone (5 to 45 cm) and the average gas velocity (2.6 to 40 cm s^{-1}) showed no influence on the rate coefficients, similarly as in our earlier HTP studies.[25,26,35–37] The variation in these parameters demonstrates that (i) gas flows are well mixed, (ii) thermal equilibrium of reactant and bath gases is attained, and (iii) no significant thermal decomposition of the reactants occurs. Independence from the flash energy (8.5 to 56 J) shows that the influence of photolysis and reaction products is negligible. The results were found to be consistent with or without molecular sieve purification or upon changing between pure and 1% mixtures, demonstrating that impurities have no influence. Changing between chromel–alumel and Pt–Pt/Rh thermocouples (below 1200 K) also has no effect.

Figure 2 compares the k_1 and k_2 data on an Arrhenius plot. A fit for $k_1(T)$ to the form $k = A (T/K)^n \exp(-B K/T)$ cm^3 molecule^{-1} s^{-1}, which has frequently been applied to this reaction,[3–6] yielded

$$k_1(T) = 7.3 \times 10^{-21} (T/K)^{2.93}$$

$$\times \exp(-2980 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \tag{7}$$

The variances[38–40] of the parameters A, n, and B are $\sigma_A^2 = 2.4 \times 10^{-39}$, $\sigma_n^2 = 7.8 \times 10^{-1}$, and $\sigma_B^2 = 4.3 \times 10^5$. Coupling between these correlated parameters is reflected by the covariances (Refs. 38–40): $\sigma_{An} = -4.4 \times 10^{-20}$, $\sigma_{AB} = 3.2 \times 10^{-17}$, and $\sigma_{nB} = -5.7 \times 10^2$. This coupling causes some individual parameters to be far less certain than the final fitted $k_1(T)$. The curve defined by Eq. (7) is drawn
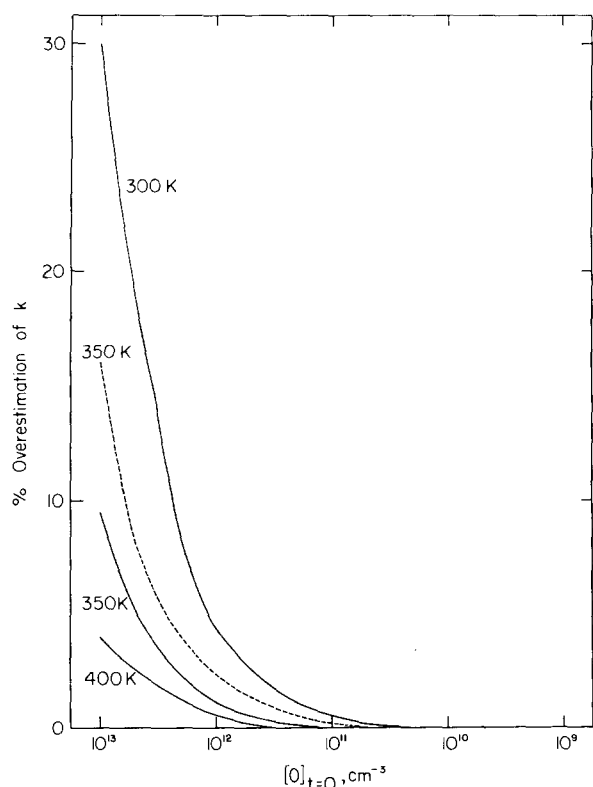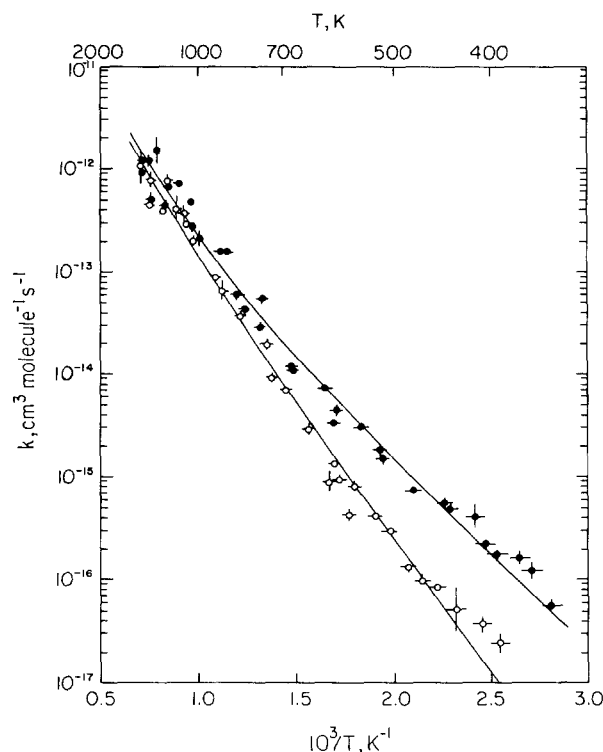

FIG. 1. Results of kinetic modeling (see the text) showing errors caused by secondary reactions as a function of initial O-atom concentration. (—) $O + H_2$; (---) $O + D_2$.

FIG. 2. Summary of the rate coefficients obtained for the reactions of O with H_2 (●) and D_2 (○), showing three-parameter fits (see the text). Error bars represent $\pm \sigma_T$ and $\pm \sigma_k$.

on Fig. 2, which additionally shows the measured k_2 values and the fit

$$k_2(T) = 3.1 \times 10^{-16}(T/K)^{1.65}$$

$$\times \exp(-5260 \ K/T) \ cm^3 \ molecule^{-1} \ s^{-1}. \quad (8)$$

The variances for Eq. (8) are $\sigma_A^2 = 1.2 \times 10^{-29}$, $\sigma_n^2 = 2.0 \times 10^0$, and $\sigma_B^2 = 1.3 \times 10^6$ with associated covariances $\sigma_{An} = -4.7 \times 10^{-15}$, $\sigma_{AB} = 3.8 \times 10^{-12}$, and $\sigma_{nB} = -1.6 \times 10^3$. We note that Eq. (7) gives k_1 values which are slightly lower than the observed data for $T < 430$ K and that the underestimation of k_2 by Eq. (8) at $T < 430$ K is more pronounced. This is further considered in Sec. V.

IV. COMPARISON WITH EARLIER MEASUREMENTS
A. Reaction with H_2

In Fig. 3 we compare our data for $k_1(T)$ with those studies where reaction (1) was isolated from other processes and the derived k_1 values were independent of the kinetic model assumed. The flash photolysis/shock tube (FP-ST) experiments of Sutherland et al.[6] cover the range 880 to 2500 K, their FP-RF measurements cover 500 to 920 K and the FP-RF determinations by Presser and Gordon[5] cover 300 to 470 K. Many discharge/flow experiments were performed under conditions where reactions involving OH were important, see, e.g., Refs. 41–45. These are therefore not considered. We have, however, included those measurements of Dubinsky and McKenney[7] from 510 to 740 K, where the correction factor is less than 1.15. Those k_1 values are thus only marginally dependent on the rates assumed for pro-
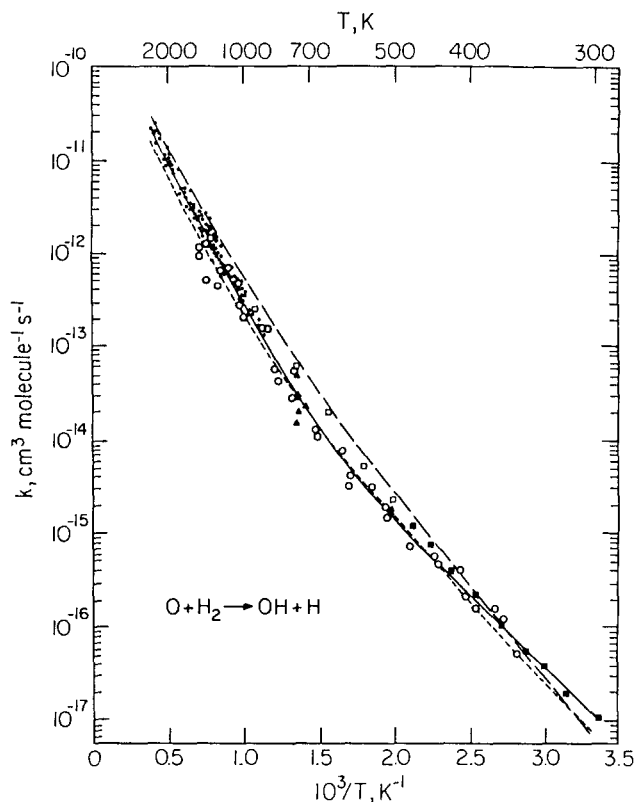

FIG. 3. Comparison of present k_1 values to earlier recommendations and isolated reaction measurements. (○) Present study; (■) Presser and Gordon (Ref. 5); (▲) Dubinsky and McKinney (Ref. 7); (□) Sutherland et al. FP-RF (Ref. 6); (·) Sutherland et al. FP-ST (Ref. 6); (—) best fit to all data shown; (---) Cohen and Westberg recommendation (Ref. 3); (– – –) Warnatz recommendation (Ref. 4).

cesses such as (4) and (5). Comparison with our results (see Fig. 3) shows generally satisfactory agreement. The FP-ST points of Sutherland et al.[6] overlap ours, as do the data of Presser and Gordon[5] and Dubinsky and McKenney.[7] However the FP-RF results of Sutherland et al.[6] lie systematically somewhat above ours, with the largest differences in the range 500 K $\lesssim T \lesssim 800$ K. We see no obvious error in any of the earlier work. Secondary reactions would cause derived k_1 values to fall too *high* rather than too *low*, cf. Sec. II B. Similarly, impurities would increase observed values.

We have combined the data of Fig. 3 to derive a $k_1(T)$ expression for the 300 to 2500 K range. Because the various authors did not all report estimates of σ_{k1} and σ_T we have performed a weighted fit assuming equal proportional uncertainties in all the data. Fitting to the forms of Eqs. (7) and (8) gives $k_1(T) = 5.5 \times 10^{-23} (T/K)^{3.59} \exp(-2570 \ K/T) \ cm^3 \ molecule^{-1} \ s^{-1}$, but this systematically underestimates the combined data set at $T \approx 1000$ K and $T < 400$ K and is therefore unsatisfactory. A number of other fits were attempted and the best empirical agreement was obtained with the form $k = A \exp(-B \ K/T) + C \exp(-D \ K/T) \ cm^3 \ molecule^{-1} \ s^{-1}$:

$$k_1(T) = 1.5 \times 10^{-12} \exp(-3540 \ K/T)$$

$$+ 3.7 \times 10^{-10}$$

$$\times \exp(-7450 \ K/T) \ cm^3 \ molecule^{-1} \ s^{-1}. \quad (9)$$

The curve of this equation ($300\,\text{K} \leqslant T \leqslant 2500\,\text{K}$) is plotted in Fig. 3. A physical interpretation of the parameters will be discussed in Sec. V. Using variances ($\sigma_A^2 = 2.8 \times 10^{-20}$, $\sigma_B^2 = 2.1 \times 10^4$, $\sigma_C^2 = 2.8 \times 10^{-21}$, $\sigma_D^2 = 4.2 \times 10^4$) and covariances ($\sigma_{AB} = 7.5 \times 10^{-11}$, $\sigma_{AC} = 1.6 \times 10^{-23}$, $\sigma_{AD} = 7.6 \times 10^{-11}$, $\sigma_{BC} = 4.1 \times 10^{-9}$, $\sigma_{BD} = 1.9 \times 10^4$, $\sigma_{CD} = 1.1 \times 10^{-8}$) we arrive at 2σ confidence levels for $k_1(T)$. These intervals are, e.g., $\pm 29\%$ at 300 K, $\pm 12\%$ at 390 K, $\pm 6\%$ at 1400 K, and $\pm 13\%$ at 2500 K. For $T < 350\,\text{K}$ and $T > 1420\,\text{K}$, where the data are derived from one method only and any unsuspected systematic errors will not be apparent from the scatter of Fig. 3, we allow for possible systematic errors of 15% by increasing the 2σ limits to $\pm 33\%$ at 300 K and $\pm 20\%$ at 2500 K.

Figure 3 also shows the recommendations of Cohen and Westberg[3] and Warnatz,[4] which both cover the temperature range 300 to 2500 K and summarize earlier data for k_1. Suggested uncertainties for Cohen and Westberg's expression are a factor of 1.6 ($350\,\text{K} < T < 900\,\text{K}$), rising to a factor of 2 for $T \approx 300\,\text{K}$ and $T > 1600\,\text{K}$.[3] Warnatz[4] gives an uncertainty factor of 1.4. The expression of Warnatz[4] falls significantly above ours for $T > 400\,\text{K}$, especially at $T \approx 700\,\text{K}$, where it gives $k_1(T)$ greater by more than a factor of 2 than observed here. It lies close to the FP-RF data of Sutherland et al.[6] but, like the expression of Cohen and Westberg,[3] underestimates k_1 at $T \approx 300\,\text{K}$. The line of Cohen and Westberg,[3] who took more data sets into account, is closer to ours, particularly for $400\,\text{K} < T < 800\,\text{K}$. It underestimates $k_1(T)$ for $T > 800\,\text{K}$, while lying within their quoted uncertainty. At these high temperatures our line, dominated by the FP-ST results,[6] falls between the two recommendations.

B. Reaction with D$_2$

For reaction (2) the only previous isolated reaction measurements are those by Presser and Gordon over the range 420 to 470 K (Ref. 5); these are shown together with our results in Fig. 4. Again we choose a fit of the form $k = A \exp(-B\,\text{K}/T) + C \exp(-D\,\text{K}/T)$ cm^3 molecule^{-1} s^{-1}, using weighting which incorporates their quoted σ_{k2} and σ_T. Because the temperature range studied is narrower than for reaction (1) the individual parameters A to D are less well defined than for the H$_2$ reaction. We have therefore set A equal to 1.4×10^{-12}, similar to the value obtained for $k_1(T)$ and in accord with theoretical predictions (see Sec. V). The resulting recommendation for k_2 ($390\,\text{K} \leqslant T \leqslant 1420\,\text{K}$) is

$$k_2(T) = 1.4 \times 10^{-12} \exp(-4260\,\text{K}/T)$$
$$+ 2.9 \times 10^{-10}$$
$$\times \exp(-7780\,\text{K}/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}. \tag{10}$$

Using the variances ($\sigma_B^2 = 3.0 \times 10^3$, $\sigma_C^2 = 1.3 \times 10^{-20}$, $\sigma_D^2 = 1.6 \times 10^5$) and covariances ($\sigma_{BC} = -2.9 \times 10^{-9}$, $\sigma_{BD} = -1.2 \times 10^4$, $\sigma_{CD} = 4.3 \times 10^{-8}$) we would arrive at 2σ confidence levels for $k_2(T)$ of $\pm 25\%$ at 390 K, $\pm 19\%$ at 1000 K, and $\pm 27\%$ at 1420 K. However, since the data are dominated by a single experiment (the present work),

we allow for possible unrecognized systematic errors of 15% to obtain final 2σ limits for $k_2(T)$ of $\pm 29\%$ at 390 K, $\pm 24\%$ at 1000 K, and $\pm 31\%$ at 1420 K.

$k_2(T)$ resulting from Eq. (10) is drawn in Fig. 4. We also show earlier data for k_2 derived from systems where processes (4)–(6) could not be neglected. These are the discharge/flow experiments of Clyne and Thrush[41] (490 to 670 K) and Westenberg and deHaas[46] (420 to 970 K), and the shock tube work of Pamidimukkala and Skinner[47] (2100 to 2480 K). The apparently good agreement between extrapolations of the shock tube and our work, Fig. 4, suggests that $k_2(T)$ now may be well characterized from 390 to 2480 K. Therefore, we propose for that whole region

$$k_2(T) = 1.4 \times 10^{-12} \exp(-4250\,\text{K}/T)$$
$$+ 3.6 \times 10^{-10}$$
$$\times \exp(-7980\,\text{K}/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}. \tag{11}$$

C. The kinetic isotope effect $x = k_1/k_2$

In order to obtain a convenient expression for the kinetic isotope effect x we evaluate the ratio $k_1(T)/k_2(T)$ from Eqs. (9) and (10) at 50 points equally spaced in T^{-1} over the 390 to 1420 K range and fit the results to yield

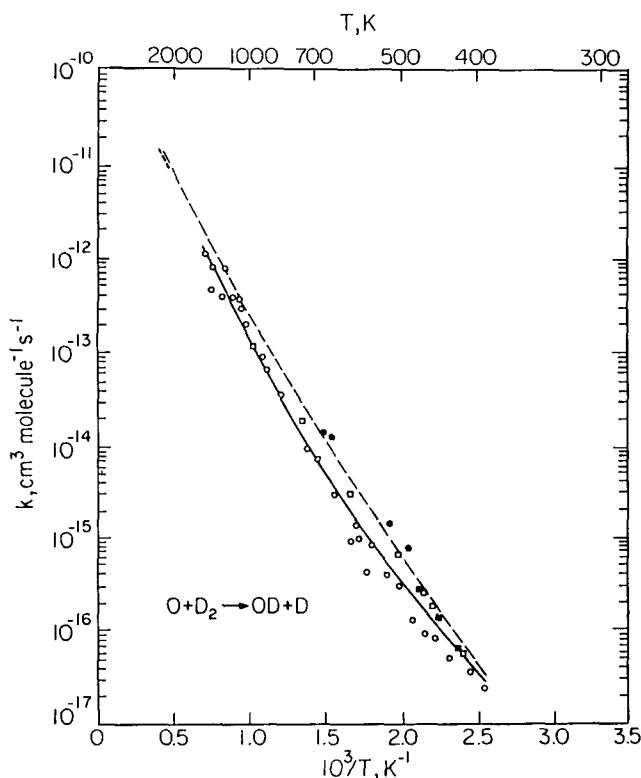$$x(T) = 6.5 \times 10^{-3}\ (T/\text{K})^{0.64} \exp(+1230\,\text{K}/T). \tag{12}$$

FIG. 4. Comparison of present k_2 values to earlier measurements. (O) Present study; (□) Westenberg and deHaas (Ref. 42); (■) Presser and Gordon (Ref. 5); (●) Clyne and Thrush (Ref. 37); (—) best fit to present data and those of Ref. 5; (---) Pamidimukkala and Skinner (Ref. 43); (– – –) results from *ab initio* calculations (Refs. 15, 21, and 44), as discussed in Sec. V.

This reproduces x to within 5%. By combining the confidence intervals for $k_1(T)$ and $k_2(T)$ the 2σ confidence intervals for $x(T)$ are estimated at $\pm$ 32% at 1000 K, rising to $\pm$ 41% at 390 K and $\pm$ 37% at 1420 K.

Figure 5 shows $x(T)$ with four other measurements of x and their associated 2σ confidence intervals. There is agreement between the present estimates of $x(T)$ and the results of Presser and Gordon,[5] Westenberg and deHaas[44] (as calculated by Bowman et al.[15]) and Pamidimukkala and Skinner[47] (error limits quoted by Bowman et al.[15]). However, the data of Clyne and Thrush[41] are inconsistent with the other results, which shows that systematic errors do not necessarily cancel.

V. DISCUSSION

There has been much investigation of reactions (1) and (2) at the theoretical level to model thermal rate coefficients, rate coefficients for vibrationally excited hydrogen, and the branching ratio for the reaction of O(^3P_J) with HD.[8-24] Recently extensive calculations have been made based on the Mod Pol CI RMOS ("modified polarization configuration interaction rotated Morse oscillator spline") surface.[12] One approach, that of Garrett and Truhlar, applied "improved canonical variational TST" (ICVT) with a "least-action ground state" (LAG) estimation of quantum mechanical tunneling.[20,21,23] The other approach is to couple a three-dimensional TST rate coefficient with a transmission coefficient Γ^{CEQB} ("collinear exact quantum incorporating adiabatic bending") to account for tunneling, nonadiabaticity, and recrossing effects.[14-17,20,23] We use results from both methods to interpret the observations.

Both ICVT/LAG and CEQB calculations indicate that tunneling is very important at lower temperatures, accounting for more than 90% of reaction (1) at 300 K.[15,21] We have derived rates due to tunneling alone for reactions (1) and (2), k_1^t and k_2^t, from the ICVT/LAG theoretical calculations of the overall rates $k_1(T)$ and $k_2(T)$.[21] We obtain the tunneling rate coefficients as the difference $k_{ICVT/LAG} - k_{ICVT}$. CEQB results are not employed because Γ^{CEQB} also reflects contributions from nonadiabaticity and recrossing which are difficult to separate from tunneling effects (Refs. 15 and 48). k_1^t and k_2^t are plotted in Fig. 6, clearly showing that they follow simple Arrhenius-type behavior over the temperature range indicated. Thus we obtain

$$k_1^t(T) = 2.0 \times 10^{-12}$$

$$\times \exp(-3650 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1}\text{ s}^{-1},$$
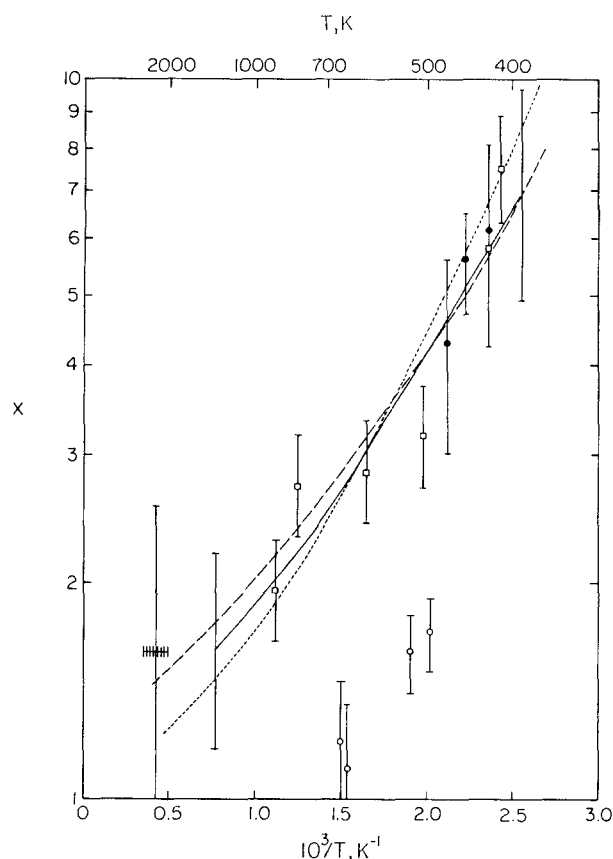
$$(13)$$

FIG. 5. Summary of the results for the kinetic isotope effect $x = k_1/k_2$. Error bars on the experimental data represent 2σ confidence intervals. (—) Present study. Error bars shown only at each end of the plot. (□) Westenberg and deHaas (Refs. 15 and 40); (●) Presser and Gordon (Ref. 5); (○) Clyne and Thrush (Ref. 37); (+ + +) Pamidimukkala and Skinner (Refs. 15 and 43); (– – –) ICVT/LAG calculations (Ref. 21), as discussed in Sec. V; (---) CEQB calculations (Refs. 15 and 44), as discussed in Sec. V.
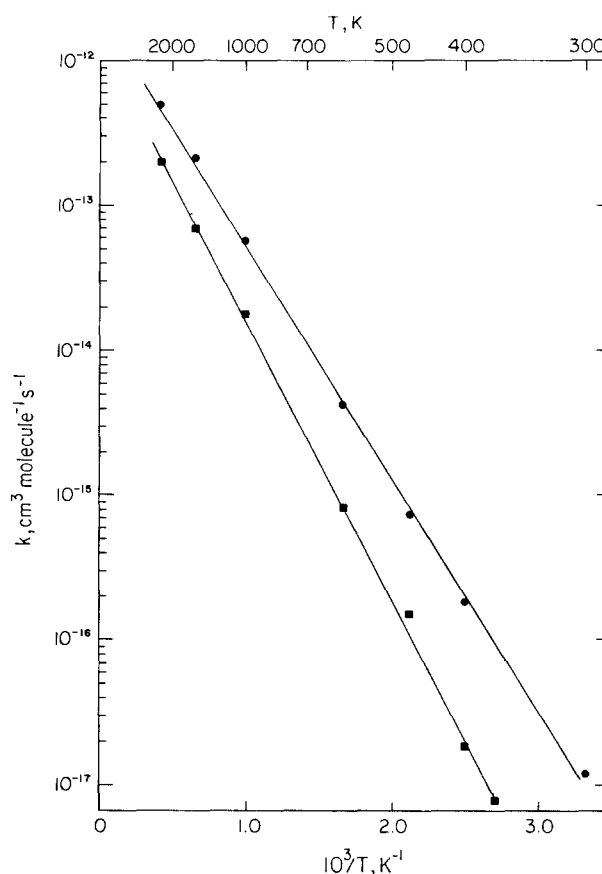

FIG. 6. Rate coefficients due to tunneling alone, as calculated by subtracting ICVT from ICVT/LAG results (Ref. 21), showing Arrhenius fits. (●) O + H$_2$; (■) O + D$_2$.

$$k_2^i(T) = 1.4 \times 10^{-12}$$

$$\times \exp(-4480 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \tag{14}$$

These relations are grounds for empirically treating tunneling as a second reaction channel. Indeed, the term of Eq. (9) dominant at lower temperatures is in good accord with $k_1^i(T)$. For reaction (2) the "preexponential factor" for the lower temperature channel was fixed (see earlier) to agree with $k_2^i(T)$, and the resulting "activation energy" is in fair agreement with that of Eq. (14). We conclude that representing $k_1(T)$ and $k_2(T)$ as sums of two channels has physical meaning since the first terms approximate the tunneling contributions at the lower temperatures, where that factor is significant. This may account for the poor fits of the three-parameter expressions of Fig. 2 at the lowest temperatures. Similar situations occurred in our studies of the reactions of $H(1\ ^2S)$ with NH_3 and N_2O, where tunneling is also important.[25,35]

Further evidence of significant tunneling in the reaction of O with hydrogen below 500 K lies in the OH/OD branching ratio for O + HD, where Robie et al.[49] have experimentally confirmed the results from ICVT/LAG and CEQB calculations which predict that this ratio would be strongly temperature dependent because of tunneling.[16,17,23]

The ICVT/LAG and CEQB data[15,21,48] for $k_1(T)$ and $k_2(T)$ can now be compared with the experimental equations (9) and (10). The theoretical $k_2(T)$ line is shown in Fig. 4; because on the scale of the figure the two ab initio methods give very similar results, a single averaged curve is drawn. The theoretical $k_1(T)$ line falls too close to the Warnatz recommendation[4] (above 370 K) and ours (below 370 K) to be clearly distinguishable and is therefore not shown separately. The overall agreement is good although for reaction (1) the theoretical results lie closer to Warnatz's recommendation[4] and the FP-RF data of Sutherland et al.[6] than to our recommendation and the other experimental data.

We can also compare theoretical and observed kinetic isotope effects, which amplify small differences between calculated rate coefficients. From Eq. (9) and (10) and the associated variances the limit of $x(T)$ as T tends to infinity is 1.27 ± 0.53 (1σ level), which compares well with the value of 1.34 calculated from relative hard-sphere collision rates of O with H_2 and D_2. Kinetic isotope effects derived from ICVT/LAG and CEQB data are plotted in Fig. 5. While the ICVT/LAG results are slightly closer to the $x(T)$ data and show a shallower temperature dependence than the CEQB results, both calculations are in satisfactory accord with $x(T)$ given the experimental uncertainties.

In conclusion, the present measurements for k_1 over the 350 to 1420 K range generally confirm the other isolated measurements which each cover part of this range. Combined with the other data we have obtained an expression for 300 to 2500 K, although resolution of discrepancies at 500 K $\lesssim T \lesssim$ 800 K is desirable. We have considerably extended the range of isolated measurements for k_2. Our recommended double exponential rate expressions are in reasonable accord with detailed theoretical treatments where tunneling is

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