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Reactions of OH and OD with H_2O_2 and D_2O_2

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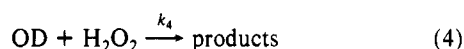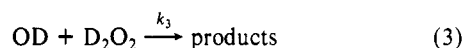(Received: March 13, 1989; In Final Form: May 31, 1989)*

The reactions OH + H_2O_2 → products (k_1) and OD + D_2O_2 → products (k_3) were studied in the temperature range 273-410 K. The obtained Arrhenius expressions are as follows: $k_1 = (2.76 \pm 0.80) \times 10^{-12} \exp((-110 \pm 60)/T)$ and $k_3 = (1.75 \pm 0.30) \times 10^{-12} \exp((-320 \pm 20)/T)$ cm^3 molecule^{-1} s^{-1}. The indicated errors are 2σ, including estimated systematic errors. The rate coefficients were independent of the buffer gas (He, N_2, or SF_6) used and the pressure (50-500 Torr) employed. The measured kinetic isotope effect, k_1/k_3, ranges from 2.7 at 410 K to 3.5 at 273 K. The values of the rate coefficients for OH + D_2O_2 → products (k_2) at 273 K and OD + H_2O_2 → products (k_4) at 298 K were the same as those of k_3 at 273 K and k_1 at 298 K, respectively. The possible exchange reaction such as OD + H_2O_2 → OH + HOOD is unimportant, with an upper limit of 2×10^{-15} cm^3 molecule^{-1} s^{-1} for the rate coefficient at 273 K. Bond energy-bond order (BEBO) calculations using a linear five-particle transition state for a H-abstraction reaction do not yield results that agree with experiments. Transition-state theory calculations using a five-particle nonlinear transition state, (HO)-O-H-O-H, yield results in reasonable agreement with the data.

Introduction

The rate coefficient, k_1, for the reaction of OH with H_2O_2

$$OH + H_2O_2 \xrightarrow{k_1} HO_2 + H_2O \qquad (1)$$
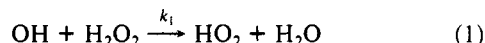
has been well studied in the temperature range 250-460 K by following the loss of OH in excess H_2O_2. The rate coefficient is quite large, $k(298 \text{ K}) = 1.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, and has a very small activation energy of ~400 cal mol^{-1}. These values are the average of four of the most recent studies and are recommended by the NASA/JPL evaluation panel.[1] There is a large body of evidence that suggests that the products of the reaction are HO_2 and H_2O, even though, to our knowledge, nobody has quantitatively measured the yield of HO_2 in reaction 1. Howard and Evenson[2] converted OH to HO_2 via reaction 1 and the HO_2 back to OH via the reaction $HO_2 + NO \rightarrow NO_2 + OH$ to set up a steady-state chain reaction and clearly showed that indeed reaction 1 proceeds as written above. Similar work has been carried out by Hack et al.[3] and Lovejoy et al.[4] The analogous reaction of OH with CH_3OOH, OH + $CH_3OOH \rightarrow CH_3O_2$ + H_2O, has a rate coefficient twice k_1 (4 times on a per H atom basis) and has a negative activation energy,[5] suggesting the possibility of a bound intermediate in the OH + peroxide reactions. So, is reaction 1 a simple H-abstraction reaction or does it proceed through a bound intermediate? In an attempt to shed some light on this question, we have carried out kinetic measurements on isotopically substituted species

$$OH + D_2O_2 \xrightarrow{k_2} \text{products} \qquad (2)$$

$$OD + D_2O_2 \xrightarrow{k_3} \text{products} \qquad (3)$$

$$OD + H_2O_2 \xrightarrow{k_4} \text{products} \qquad (4)$$

The second reason for investigating this set of reactions is to see what happens to the deuterium kinetic isotope effect (KIE) for the case when the energy barrier for the reaction is less than the differences in zero-point energies of the two isotopically labeled sets of reactants.

Reaction 1 is exothermic by 32.0 kcal mol^{-1} at 298 K. The measured activation energy of ≤0.5 kcal mol^{-1} is consistent with

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TABLE I: Possible Source Reactions That Take Place When Generating OH in the Presence of D_2O_2 during 248-nm Laser Photolysis of $O_3/H_2/D_2O$ Mixtures

$O_3 \xrightarrow{h\nu} O(^1D) + O_2$	(a)
$O_3 \xrightarrow{h\nu} O(^3P) + O_2$	(b)
$O(^1D) + H_2 \rightarrow OH(v''{\leq}4) + H$	(c)
$H + O_3 \rightarrow OH(v''{\leq}9) + O_2$	(d)
$OH(v''{\leq}9) + D_2O \rightarrow OH(v''{=}0) + D_2O$	(e)
$OH + O_3 \rightarrow HO_2 + O_2$	(f)
$HO_2 + O_3 \rightarrow OH + 2O_2$	(g)
$OH + H_2 \rightarrow H_2O + H$	(h)
$O(^1D) + D_2O \rightarrow OD + OD(v''{\leq}3)$	(i)
$OD(v''{\leq}3) + D_2O \rightarrow OD(v''{=}0) + D_2O$	(j)
$OD + H_2 \rightarrow HOD + H$	(k)
$OH + D_2O \rightarrow OD + HOD$	(l)

the exothermicity of a H atom abstraction reaction. This activation energy can be interpreted as yielding an energy barrier of reaction 1 that is much less than 0.5 kcal mol^{-1}, with a nonexistent barrier being likely. For a reaction with a small or zero barrier, the calculation of KIE is extremely difficult as shown in the case of Cl + C_2H_6,[6] which has near zero activation energy and is exothermic by only 2.6 kcal mol^{-1} at 298 K. Therefore, another data set on such low-barrier reactions would provide a testing ground for various theories of reaction rates.

Experimental Section

The apparatus and the methodology used to carry out the experiments described here were the same as those used in previous OH reaction studies in our laboratory.[5] Briefly, the reactant OH

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(1) DeMore, W. B.; Molina, M. J.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*; JPL Publication No. 87-41; Jet Propulsion Laboratory: Pasadena, CA, 1987; Evaluation No. 8.

(2) Howard, C. J.; Evenson, K. M. *Geophys. Res. Lett.* **1977,** *4,* 437.

(3) Hack, W.; Hoyermann, K.; Wagner, H. Gg. *Int. J. Chem. Kinet. Suppl. 7* **1975,** 329.

(4) Lovejoy, E. R.; Murrells, T. P.; Ravishankara, A. R.; Howard, C. J. *J. Phys. Chem.*, submitted for publication.

(5) Vaghjiani, G. L.; Ravishankara, A. R. *J. Phys. Chem.* **1989,** *93,* 1948.

(6) Chiltz, G.; Eckling, R.; Goldfinger, P.; Huybrechts, G.; Johnston, H. S.; Meyers, L.; Verbeke, G. *J. Chem. Phys.* **1963,** *38,* 1053.

(OD) was generated by pulsed 248-nm KrF (or 266-nm, 4th harmonic of Nd:YAG) laser photolysis of either H_2O_2 (D_2O_2) or a mixture of O_3 and H_2O (D_2O) or H_2 (D_2). In the latter case, $O(^1D)$ produced in O_3 photodissociation reacts with H_2O (D_2O) or H_2 (D_2) to produce OH (OD). In order to make OH in D_2O_2 (and OD in H_2O_2), the reaction $O(^1D) + H_2$ (D_2) was used. The reactions that take place upon creation of $O(^1D)$ in the presence of H_2, D_2O, and D_2O_2 are listed in Table I for the generation of OH. The difficulties with this source are that reaction d should be run to completion within a few microseconds, the vibrationally excited OH should be rapidly quenched, and at the same time reactions h and k must be completely suppressed. To maximize quenching of $OH(v'' \leq 9)$, $[D_2O]$ has to be large but it must be smaller than $[H_2]$ such that most of the $O(^1D)$ reacts with H_2. If $[H_2]$ is large, reactions h and k will produce OH on a time scale similar to that being used for the measurement of k_2. Therefore, to suppress reactions h and k, we could carry out these experiments only at temperatures ≤ 273 K. Since the reaction of OH with D_2 is slower than the reaction of OH with H_2, we could study the reaction of OD with H_2O_2 at 298 K.

The temporal profiles of [OH] or [OD] in the presence of large excess of H_2O_2 or D_2O_2 were measured by detecting OH or OD via pulsed laser induced fluorescence in the A–X band. OH was pumped at ~ 281.1 nm and OD at ~ 287.6 nm. We have shown[5] that OH and OD can be detected with very high specificity and there is no chance of inadvertently detecting OD while monitoring OH or vice versa. The reaction mixture consisting of the peroxide, diluent gas, and when necessary, ozone and water were flowed through the reactor fast enough (2–15 cm s^{-1}) to replenish the mixture every few photolytic laser pulses that were 100-ms apart (10 Hz). The concentration of H_2O_2 in the mixture was directly measured via UV absorption at 213.9 nm (zinc atomic line) by taking the H_2O_2 cross section at this wavelength to be 3.30×10^{-19} cm^2 molecule^{-1}.[7] $[D_2O_2]$ was also measured at 213.9 nm. We have determined the UV absorption cross section for D_2O_2 to be 3.54×10^{-19} cm^2 molecule^{-1}.[7] These cross section values have an overall uncertainty of $\sim 5\%$ (1σ). Helium (99.9996%) was from Scientific Gas Products, and H_2 (>99.99%) and D_2 (>99.6%) were from U.S. Bureau of Mines. They were used as supplied. H_2O_2 (90%) and D_2O_2 (50% in D_2O and 98% D atoms) were from FMC Corp. and Icon Services, respectively. They were subjected to prolonged (~ 1 week) bubbling of the diluent gas through them to remove water. This procedure produces peroxides that were >97% pure with H_2O or D_2O being the major impurities. D_2O (99.8% D) was supplied by Merck, Sharp, and Dohme Canada and used as such. H_2O was distilled in the laboratory prior to use. Ozone was prepared by passing O_2 through a commercial ozonizer and stored over silica gel at 197 K. It was degassed at 77 K before use.

Results and Discussion

The rate coefficient for the reaction of OH with H_2O_2, k_1, has been previously measured with use of flow tube and pulsed photolysis techniques in the temperature range 250–460 K at pressures between 1 and 100 Torr. It is currently accepted[1] that k_1 at 298 K is 1.7×10^{-12} cm^3 molecule^{-1} s^{-1} and the activation energy is ~ 400 cal mol^{-1} in the temperature range 250–350 K. Measurements of k_1 were carried out in the present work to obtain a self-consistent data set for comparison with k_2, k_3, and k_4 measured with the same apparatus. All measurements of k_1 were carried out under pseudo-first-order conditions with respect to [OH] such that its temporal profile followed a simple exponential relationship

$$[OH]_t = [OH]_0 e^{-k_1't}$$

where $k_1' = (k_1[H_2O_2] + k_d^{OH})$ and is the pseudo-first-order rate coefficient for the decay of [OH], while k_d^{OH} is the first-order rate coefficient for the decay of [OH] in the absence of H_2O_2 due to reaction of OH with impurities and diffusion from the detection region. k_1' (which ranged from ~ 50 to 1×10^4 s^{-1}) was measured

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TABLE II: Rate Coefficients^a for Reactions 1–4 as a Function of Temperature Measured in This Work

temp, K	$k_1 \times 10^{12}$	$k_2 \times 10^{13}$	$k_3 \times 10^{13}$	$k_4 \times 10^{12}$
273	1.90 ± 0.12	5.3 ± 1.0	5.37 ± 0.26	
298	1.86 ± 0.18		5.91 ± 0.42	1.79 ± 0.26
323			6.32 ± 0.94	
348	2.01 ± 0.20		6.82 ± 0.28	
410	2.14 ± 0.40		8.01 ± 0.30	

^{a} The units are cm^3 molecule^{-1} s^{-1}, and the errors are 2σ.

at various concentrations of H_2O_2 to obtain k_1 from the slope of a k_1' versus $[H_2O_2]$ plot. The intercept of this plot yields k_d^{OH} (which typically was ~ 50 s^{-1}). The values of k_1 we obtained at various temperatures are listed in Table II. Our measured values of k_1 were invariant to changes in $[OH]_0$, the pressure (50–550 Torr) or the buffer gas used (He, N_2, or SF_6), the linear flow rate of the gas (2–15 cm s^{-1}), and the position of the absorption cell (placed at the entrance or at the exit of the reaction cell). A linear least-squares fit to our data points yields an Arrhenius expression

$$k_1 = (2.76 \pm 0.80) \times$$
$$10^{-12} \exp((-110 \pm 60)/T) \quad \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the errors are 2σ that include estimated systematic errors and $\sigma_A = A\sigma_{\ln A}$. Our results for k_1 are in excellent agreement with those from the previous four measurements.[1] When all the individual rate coefficients measured in the four previous investigations (scaled up using our UV absorption cross sections for H_2O_2) are used along with our values, we obtain

$$k_1 = (3.11 \pm 0.36) \times$$
$$10^{-12} \exp((-160 \pm 40)/T) \quad \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the errors are again 2σ and $\sigma_A = A\sigma_{\ln A}$.

The measurements of k_3 were similar to those of k_1. The observed first-order decay plots of [OD] were exponential, and the first-order rate coefficient, $k_3' = (k_3[D_2O_2] + k_d^{OD})$, was independent of the energy of the photolysis laser and residence time of the mixture in the reactor. k_3' varied linearly with $[D_2O_2]$ whose slope yielded a value for k_3. The values of k_3 obtained are listed in Table II. A fit of the k_3 data to an Arrhenius equation yields

$$k_3 = (1.75 \pm 0.30) \times$$
$$10^{-12} \exp((-320 \pm 20)/T) \quad \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The indicated errors are 2σ, including estimated systematic errors, with $\sigma_A = A\sigma_{\ln A}$.

To calculate the kinetic isotope effect in the OH + H_2O_2 reaction, the ideal set of reaction rate coefficients to be measured are for reactions 1 and 2. However, a measurement of k_2 is more difficult than that of k_3. To make OH in the presence of D_2O_2, we cannot use the common OH precursors since D_2O_2 would isotope scramble with the precursor very rapidly. Therefore, we carefully measured k_2 at 273 K using the $O_3/H_2/D_2O$ source since H_2 does not exchange with D_2O_2. As expected, k_2 was equal to k_3, and hence, k_2 was not measured at other temperatures. Instead, the ratio k_1/k_3 was used to assess the KIE. To ensure that OD and OH have the same rate coefficients for hydrogen-abstraction reactions such as in reaction 1, we also measured k_4 and k_5 at 298 K and found them to be the same as those for OH reactions with H_2O_2 and D_2, i.e., $k_4 = k_1$ and $k_5 = k_6$:

$$OD + D_2 \xrightarrow{k_5} D_2O + D \qquad (5)$$

$$OH + D_2 \xrightarrow{k_6} HOD + D \qquad (6)$$
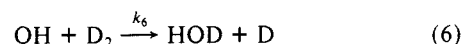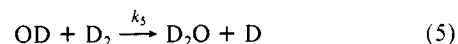
k_6 at 298 K has been previously measured to be $(1.83 \pm 0.12) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.[8] The value of k_5 at 298 K we determined was $(1.88 \pm 0.30) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, showing that $k_5 = k_6$.

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(7) Vaghjiani, G. L.; Ravishankara, A. R. *J. Geophys. Res.* **1989**, *94*, 3487.

(8) Ravishankara, A. R.; Nicovich, J. M.; Thompson, R. L.; Tully, F. P. *J. Phys. Chem.* **1981**, *85*, 2498.

TABLE III: Reactions and the Values of Their Rate Coefficients at 273 K Used in the Numerical Simulations of [OH] Temporal Profiles in the Reaction of OD with H₂O₂

reaction	rate coeff,[a] cm³ molecule⁻¹ s⁻¹	ref
$OD + H_2O_2 \rightarrow HOD + HO_2$	variable (see text)	
$OD + H_2O_2 \rightarrow HOOD + OH$	variable (see text)	
$OD \rightarrow$ loss	~50	
$OH + H_2O_2 \rightarrow HOH + HO_2$	1.59×10^{-12}	1
$OH + H_2O_2 \rightarrow HOOH + OH$	variable (see text)	
$OH \rightarrow$ loss	~50	
$D_2 + OH \rightarrow DOH + D$	6.8×10^{-16}	8
$D_2 + OD \rightarrow DOD + D$	6.8×10^{-16} (same as $D_2 + OH$)	8
$D + O_3 \rightarrow OD + O_2$	2.5×10^{-11} (same as $H + O_3$)	1
$OH + O_3 \rightarrow HO_2 + O_2$	5.1×10^{-14}	1
$OD + O_3 \rightarrow DO_2 + O_2$	5.1×10^{-14} (same as $OH + O_3$)	1
$HO_2 + O_3 \rightarrow OH + 2O_2$	1.7×10^{-15}	1
$DO_2 + O_3 \rightarrow OD + 2O_2$	1.7×10^{-15} (same as $HO_2 + O_3$)	1
$OD + H_2O \rightarrow OH + HOD$	2×10^{-15}	6

[a] For first-order processes, the units are s⁻¹.

It is conceivable that reaction 1 proceeds via OH attack on one of the oxygen atoms in H₂O₂, leading to

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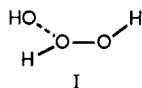
If the reaction were to take place by this path, it is very likely that an OH from the other end of H₂O₂ would be released. So, in reaction 4 for example, OD could react with H₂O₂ to give HOOD and OH. We looked for the appearance of OH in reaction 4 by generating OD in the presence of H₂O₂ at 273 K. Experimental conditions were chosen to maximize the possible contribution of reaction 4 to OH generation. [OH]₀/[OD]₀ was kept very low so that if a small fraction of reaction 4 proceeded by OH generation, the temporal profile of [OH] would deviate from an exponential. The [OH] temporal profile that decays exponentially for at least two lifetimes is shown in Figure 1. Also shown in the figure are the computed [OH] temporal profiles from numerical integration for various fractions of reaction 4 yielding OH. The appropriate reactions and their rate coefficients used in the simulations are shown in Table III. For curves a–d, the fraction of reaction 4 yielding OH is 10%, 5%, 2.5%, and 0%, respectively, with a rate coefficient of 2×10^{-15} cm³ molecule⁻¹ s⁻¹ for OD + H₂O → OH + HOD, which is another possible source of OH in this experiment. The above value for the rate coefficient for OD + H₂O is an upper limit determined in our recent study by observing loss of OD in excess H₂O.[5] Curve e shows the expected profile of [OH] for no exchange of OD with H₂O₂ or H₂O. The experimental data points indicate that exchange of OD in reactions with H₂O₂ and H₂O are unimportant. A rate coefficient much less than 2×10^{-15} cm³ molecule⁻¹ s⁻¹ is suggested for OD exchange reaction with H₂O₂. Of course, k_1 values measured by monitoring [OH] in the above experiments were the same as those measured in the absence of OD. If exchange was taking place, it should be expected that k_2 would be larger than k_3 and k_4 larger than k_1. The isotopically reversed system in which the appearance of OD in reaction 2 is monitored by generating OH in D₂O₂ is much more difficult to study since the rate coefficient for the reaction of OH with D₂O₂ is ~3 times smaller than that for the reaction of OH with H₂O₂, while the rate coefficient for the reaction of OD with H₂ is ~5 times larger than that for the reaction of OD with D₂. Quantum chemical calculations using the AMPAC (version 2.1) program[9] with AM1 and MINDO3/VHF Hamiltonians suggest that structure I is unstable with respect to the reactants and the exchange process should have a large activation energy. It is conceivable that the O atom in H₂O₂ is attacked by the H atom on the reactant OH. However, such a structure would require elaborate rearrangements to produce HO₂ and H₂O
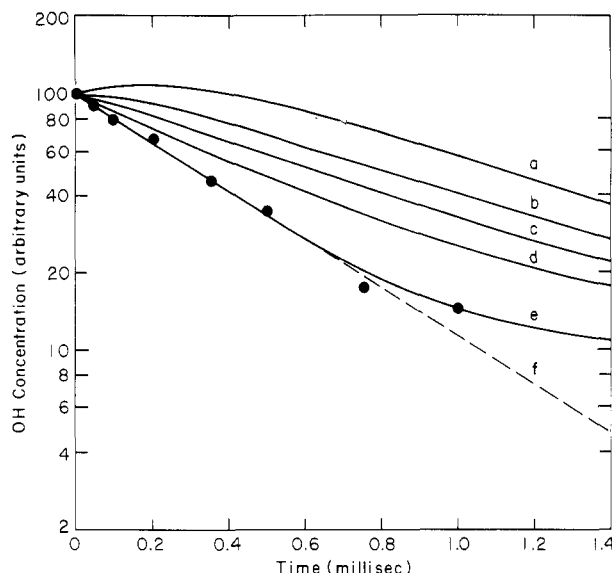

Figure 1. Simulated and measured temporal profiles of [OH] during 248-nm photolysis of O₃/D₂/H₂O/H₂O₂ mixture at 273 K. The 2σ error bars on the measured points are smaller than the diameter of the points. The [OH] profiles resulting from different fractions of reaction 4 that yield in the exchange products are shown as curves a (10%), b (5%), c (2.5%), and d (0%) for the case when OD + H₂O → OH + HOD has a rate coefficient of 2×10^{-15} cm³ molecule⁻¹ s⁻¹. Curve e is that expected from no exchange of OD with H₂O and H₂O₂. The observed [OH] profile therefore indicates that exchange of OD in H₂O₂ (or H₂O) is unimportant with an upper limit for the rate coefficient of ~2 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹. Curve f is a linear least-squares fit to data points, showing the exponential decay for two 1/e times.

products and hence was not considered here.

Some illustrative comparisons of the results for reaction 1 with those for H abstraction from C–H and O–H bonds can be made. When the C–H bond is as weak as ~90 kcal mol⁻¹, as is the case in diethyl ether's CH₂ groups, the rate coefficient for their reaction with OH is large and there is no measurable activation energy for the reaction.[10] The measured isotope effect is ~2.0, independent of temperature.[11] In the case of OH reactions with hydrogen and deuterium peroxides, the rate coefficients are a factor of 5–8 times smaller than in the ether case, while the HOO–H bond energy is less than those in the ether. Also, the observed kinetic isotope effects are larger, ranging from 2.7 to 3.5. Comparison of the measured k_1 value to the rate coefficient for OH reaction with methylhydroperoxide, for the channel with CH₃O₂ and H₂O as the products

$$OH + CH_3OOH \xrightarrow{k_7} CH_3O_2 + H_2O \qquad (7)$$

shows that k_7 is approximately $2k_1$.[5] Considering that there are two abstractable H atoms in H₂O₂, it appears that k_7 is 4 times larger compared to the rate coefficient for reaction 1. Furthermore, reaction 7 exhibits a negative temperature dependence and a KIE of 2.0 at 298 K. The bond energy for CH₃OO–H is, within 2 kcal mol⁻¹, the same as that for HOO–H.

H₂O₂ is a polar species (dipole moment, μ = 2.26 D) as is OH (μ = 1.65 D). Therefore, long-range dipole–dipole interactions should be important. A simple collision frequency calculation using these dipole moments suggests a value of ~8 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for the collision rate. Adding other terms such as dipole-induced–dipole interactions will only increase this frequency. This large collision frequency shows the attractive nature of the encounter. Quantum structural calculations suggest that short-lived intermediates such as H–O–O–H–O–H (with various angles and bond lengths) are not very stable. In fact, no reasonable structure (that could lead to HO₂ and H₂O products) was found

(9) QCPE Program 506, Ampac, version 2.1. A general molecular orbital package. Department of Chemistry, Indiana University, Bloomington, IN 47405.

(10) (a) Tully, F. P.; Droege, A. T. *Int. J. Chem. Kinet.* **1987**, *19*, 251. (b) Wallington, T. J.; Liu, R.; Dagaut, P.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1988**, *20*, 41.

(11) Tully, F. P. Private communications.

that was stable with respect to the reactants. This suggests that long-range attractions and hydrogen-bonded structures are not very likely in this case. Electrostatic forces could, of course, lead to an attractive surface for the encounter of OH with H_2O_2.

On the basis of the data and arguments presented above, we can not prove whether reaction 1 is a simple H atom abstraction reaction or not. Therefore, transition-state theory calculations for a H-abstraction pathway were carried out to see if the experimental data would agree with the calculated rate coefficients.

Bond energy–bond order (BEBO) calculations were carried out for all four reactions in order to compare the predicted results with experiments. The program used was a modified version of that written by Brown.[12] The formalism treats the reaction as a linear encounter involving five masses; thus, the nonreacting OH end of the HOOH molecule is treated as a single mass:

$$HOOH + OH \rightarrow (HO)-O\cdots H\cdots O-H \rightarrow HOO + HOH$$
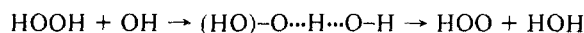
The required input includes the atomic masses of the five "particles", the four normal bond lengths between them (i.e., the bond lengths in stable molecules), bond energies of the HOO–H, H–OH, and O–O bonds as defined by Brown,[12] frequencies of the (HO)–O–H and H–O–H bending modes and the O–H, O–O, and H–O stretches, and electronic degeneracy and symmetry of the reagents and activated complex. Most of these parameters are readily obtained, except for the bending modes. For example, in HOOH, there are bending modes of 1266 and 1393 cm^{-1} that could be used; the effect of using one rather than the other is an insignificant change in the results. (However, the difference is not insignificant in the KIE calculations described below.) It was further assumed that the activated complex is an electronic doublet state. With these input parameters, BEBO calculates the properties of the activated complex (bond lengths, vibrational frequencies, etc.) and the height of the potential energy barrier. From the energy barrier, an activation energy is calculated, as described by Brown.[12] Since the activated complex is assumed to be linear, there are no internal rotations. The calculated values for the HOO$\cdots$HOH and HOOH$\cdots$OH bonds are reasonable, i.e., 1.02 and 1.88 Å, respectively. Less reasonable are the very low frequencies that BEBO predicts: stretches of 74i and 3340 cm^{-1} and bends of 872, 48, and 168 cm^{-1} for HO–O$\cdots$H, O$\cdots$H$\cdots$O, and H$\cdots$O–H, respectively. (The frequencies for the isotopic reactions differ only slightly: for example, for OD + DOOD, the corresponding values are 70i, 2383, 868, 43, and 130 cm^{-1}.) The rate coefficients computed with these frequencies are fitted by a three-parameter expression $k_1 = 3.5 \times 10^{-18}T^{2.45} \exp(-50/T)$ cm^3 molecule^{-1} s^{-1}, which gives 3.5×10^{-12} and 7.8×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 and 410 K, respectively. The predicted temperature dependence is much larger than that observed. Furthermore, the calculated rate coefficient at 298 K is a factor of 2 higher than the experimental result. This is not surprising since BEBO is unrealistically simple and is restricted to a linear transition state. A better method is to use transition-state theory (TST) with a nonlinear transition state and vibrational frequencies close to those predicted by the BEBO model. Using a nonlinear transition state allowed us to take into account the effects of internal rotations in the complex and provided a more realistic model of the reaction. However, as anticipated, the low bending frequencies taken from BEBO calculations still resulted in much stronger temperature dependences than the experimental results justified.

We therefore tried changing some of the vibrational frequencies to decrease the temperature dependences. We used the same bending frequencies (with a small estimated correction for mass change) that were used in the TST calculations for the OH + CH$_3$F reaction,[13] which is structurally similar to the OH + H$_2O_2$ reaction: H$_2$F–C$\cdots$H$\cdots$O–H as compared with HO–O$\cdots$H$\cdots$O–H. The two bending frequencies that gave good agreement with experiments for OH + CH$_3$F were 400 and 700 cm^{-1}; we used 350 and 650 cm^{-1} for OH + HOOH.

There are also three internal rotors in the activated complex to consider: (1) rotation about the O–O bond (this rotor is present in the reagent HOOH also); (2) rotation about the breaking O$\cdots$H bond; and (3) rotation about the newly forming H$\cdots$OH bond. HOOH is not planar, but symmetric, possessing two nonsuperimposable optical isomers. As the molecule undergoes internal rotation around the O–O bond, two different potential barriers are encountered; the cis barrier is only about 1.1 kcal mol^{-1}, while the trans barrier is about 7.0 kcal mol^{-1}. In the activated complex, presumably both of these barriers will be altered. The accurate accounting for the effects of two unequal barriers in calculating thermodynamic functions, whether in stable molecules or in an activated complex, is a difficult task. In our TST calculations, we assumed a single rotational barrier, with potential energy equal to the "calorimetric" barrier of 3.5 kcal mol^{-1} deduced by Giguere et al.[14] from heat capacity measurements. (With a rotational barrier height of 3.5 kcal mol^{-1}, we calculate the value of $S(298$ K) for HOOH to be 55.62 cal mol^{-1} K^{-1}, in excellent agreement with the NBS published value.[15]) We assumed further that in the activated complex the rotational barrier is lowered by ~1.0 kcal mol^{-1}. Any further lowering of the barrier in the activated complex increases the entropy of activation and therefore increases the reaction barrier height (for a fixed value of $k(298$ K)) and hence the temperature dependence of k. Since we are already calculating too much temperature dependence compared to the experimental results, we conclude that the barrier should not be lowered further. This rules out an alternative assumption that has been made in some similar calculations,[16] namely, that the hindered rotation becomes free in the activated complex. We ignored the vibrational anharmonicity resulting from the rotational asymmetry in both the reagents and the activated complexes.[17] Presumably they would be similar in both cases and thus cancel out of the calculations. We also ignored the very small difference in rotational barrier heights between HOOH and DOOD; the resultant error is inconsequential. These assumptions are mooted in the BEBO calculation because there is no internal rotation (or optical isomerism) in a linear molecule. We assumed the HO–O$\cdots$HOH and HOOH$\cdots$OH bonds to be 0.4 Å longer than the normal OH bond, or 1.4 Å. These values are different from the BEBO-calculated bond lengths, but they put O atoms the same distance apart and hence give approximately the same moment of inertia, the parameter that most affects the TST calculations. Assuming longer bonds (such as one would expect if the long-range attractive forces increase the effective collision cross section) would increase the entropy of activation and, as with lowering the internal rotational barrier, increase the temperature dependence of k to an undesirable value.

We treated the two new hindered rotors in the activated complex as we did in the OH + haloalkane model: namely, that the rotation about the HOO$\cdots$HOH bond has a 1.0 kcal mol^{-1} barrier (and $Q_f = 5.9$) and that about the HOOH$\cdots$OH bond a 2.0 kcal mol^{-1} barrier (and $Q_f = 6.2$). The barrier heights are assumed to be the same in DOOD, but the partition functions will be different because of mass effects.

The assumed vibrational frequencies in the activated complexes (in order of HO–OHOH stretch, HOO$\cdots$HOH stretch, HOO–H$\cdots$OH stretch, HO–O$\cdots$HOH bend, HOO$\cdots$H$\cdots$OH bend, and HOOH$\cdots$O–H bend, or corresponding isotopic analogue) are as follows:

(1)	OH + HOOH	1000, 73i, 3340, 850, 350, 650
(2)	OH + DOOD	1000, 73i, 2525, 850, 350, 650
(3)	OD + DOOD	1000, 73i, 2525, 850, 350, 550
(4)	OD + HOOH	1000, 73i, 3340, 850, 350, 550

(14) Giguere, P. A.; Liu, I. D.; Dugdale, J. S.; Morrison, J. A. *Can. J. Chem.* **1954**, *32*, 117.

(15) Wagman, D. D., et al. The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C$_1$ and C$_2$ Organic Substances in SI Units. *J. Phys. Chem. Ref. Data, Suppl. 2* **1982**, *11*.

(16) Jeong, K. M.; Kaufman, F. *J. Phys. Chem.* **1982**, *86*, 1816; *J. Phys. Chem.* **1984**, *88*, 1222.

(17) See, for example: Redington, R. L.; Olson, W. B.; Cross, P. C. *J. Chem. Phys.* **1962**, *36*, 1311.

(12) Brown, R. L. *J. Res. Natl. Bur. Stand. (U.S.)* **1981**, *86*, 605.

(13) Cohen, N.; Benson, S. W. *J. Phys. Chem.* **1987**, *91*, 162.

The imaginary frequency, the reaction coordinate, plays no role in the calculations except for determining the magnitude of the Wigner tunneling correction. Because this frequency is so low, the Wigner correction is near unity. This is consistent with the very low barrier for this reaction. Our assumed properties for the activated complex (which determine the entropy of activation at 298 K), together with the experimental k(298 K) for OH + HOOH, imply a barrier height of 650 cal mol^{-1}. The experiments suggest an even lower barrier.

The vibrational frequencies of HOOH and DOOD are known, but there is one ambiguity regarding which of the bending modes, 1393 or 1266 cm^{-1} in HOOH and 1028 or 947 cm^{-1} in DOOD, to use as the mode that "becomes" the HO–O···HOX (or DO–O···DOX) bend (where X is either H or D, depending on whether the attacking radical is OH or OD). With no other differences, changing from the higher to the lower of each of these reagent bending frequencies changes the ratio of k_3/k_1 over the temperature range of 273–410 K by about 10%.

The temperature dependence of k_1 was extrapolated from the experimental value of k(298 K) by a procedure described previously.[18] The isotopic rate coefficients were calculated from relationship 8, where $u = 1.439\omega/T$ and $f(u) = u/(e^u - 1)$.

$$\frac{k_i(T)}{k(T)} = \frac{\exp[\Delta S(T)_i/R]}{\exp[\Delta S(T)/R]} \times$$
$$\frac{\exp[\sum f(u_{\mathrm{rgt},i})_n - \sum f(u_{\mathrm{ts},i})_n] \exp[1/2(\sum u_{\mathrm{rgt},i,n} - \sum u_{\mathrm{ts},i,n})]}{\exp[\sum f(u_{\mathrm{rgt}})_n - \sum f(u_{\mathrm{ts}})_n] \exp[1/2(\sum u_{\mathrm{rgt},n} - \sum u_{\mathrm{ts},n})]} \quad (8)$$

The summations are over all the vibrational frequencies in the reference reagent, reference reagent transition state, isotope, and isotope transition state that change values. The frequencies (ω) are in units of cm^{-1}. $\Delta S(T)$ and $\Delta S(T)_i$ are the entropies of activation at temperature T for the reference reaction and isotopic reaction, respectively. The subscripts "rgt" and "ts" refer to the reactants and the transition state, respectively.

The results of the TST calculations for OH + HOOH can be described by the expression $k_1 = 5.1 \times 10^{-16}T^{1.4} \exp (55/T)$ cm^3 molecule^{-1} s^{-1}. Extrapolating to 1000 K, we obtain 8.5×10^{-12} cm^3 molecule^{-1} s^{-1}, in good agreement with earlier experiments.[19] Over the temperature range 273–410 K, k_1 is adequately fitted by the two-parameter expression $7.6 \times 10^{-12} \exp(-420/T)$ cm^3 molecule^{-1} s^{-1}. The calculated values are shown in Figure 2. The agreement between the calculated and experimental values is reasonable. The calculated temperature dependence is stronger than that observed. The results are "normalized" to the value at 298 K.

The isotope effect calculation for k_3/k_1 at the five temperatures of the experiments, 273, 298, 323, 348, and 410 K, with use of the higher pair of bending frequencies in the reagents, gave the ratios 0.31, 0.34, 0.36, 0.39, and 0.44, respectively, which can be fitted by $k_3/k_1 = 1.29T^{-0.058} \exp(-300/T)$ or $0.87 \exp(-280/T)$, whence $k_3 = 6.6 \times 10^{-12} \exp (-700/T)$ cm^3 molecule^{-1} s^{-1}, which is shown in Figure 2. The lower pair of bending frequencies gave 0.35, 0.38, 0.41, 0.43, and 0.48, respectively. The agreement between the calculated and measured values of k_3 are reasonable. Again, the observed temperature dependence is smaller than that calculated. The increase in the calculated activation energy in reaction 3 over reaction 1 is also seen in the experimental data.

The calculations for k_4/k_1 gave 1.15 at 298 K, whence k_4 (298 K) $= 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; those for k_2/k_1 gave 0.27 (0.30 with the lower reagent bending frequencies) at 273 K, whence k_2 (273 K) $= 5.0 \times 10^{-13}$ (5.6×10^{-13}) cm^3 molecule^{-1} s^{-1}. The agreement between experiment and calculation is fair. In the case of k_2, k_3, and k_4, contrary to the case of k_1, there were no parameters that were adjusted to better fit the data. All the
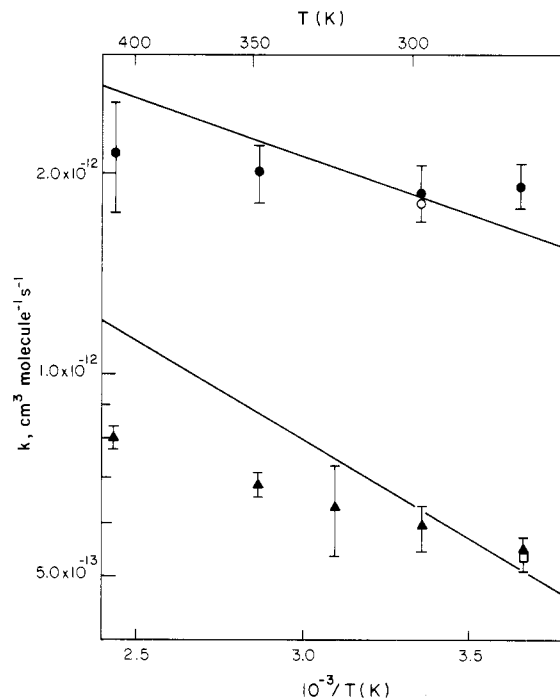

Figure 2. Arrhenius plot of the rate coefficients k_1 (●) and k_3 (▲) determined in this work, in the temperature range 273–410 K. Also shown are the values of k_4 (298 K) (O) and k_2 (273 K) (□). The straight lines show the calculated dependences of k_1 (top line) and k_3 (bottom line), from the TST calculations described in the text.

parameters were taken from those for reaction 1 with the appropriate changes for the isotopic substitution.

The agreement between calculations and experimental results is thus well within the uncertainties of the former. The measured temperature dependence in k_1 and k_3 are more accurate than the values k_1 through k_4 that require the knowledge of the absolute concentration of the peroxides. Therefore, the A factors and the KIEs are less accurate than E_a for each reaction. Two noteworthy conclusions emerge from a theoretical perspective: (1) the linear BEBO model predicts bending frequencies in the activated complex that are surely too low; and (2) the barrier to internal rotation in the HO–OH (DO–OD) molecule does not vanish in the activated complex.

Conclusions

We have experimentally shown that reaction 1 does not proceed via formation of an adduct that can lead to an exchange reaction between OH reactant and the OH (OD) moiety in the peroxide. The TST calculations using realistic frequencies can predict the observed small temperature dependence of k_1 and the observed kinetic isotope effects in the OH + hydrogen peroxide reaction. It is therefore likely that reaction 1 is a simple H-abstraction reaction. The observation of kinetic isotope effects in the range 2.7–3.5 need not imply a large potential energy barrier for the reaction, and the KIE can appear in reactions with no potential energy barrier because of zero-point energy differences and mass effects. Any role played by long-range attraction due to dipole–induced-dipole and other dispersion forces in the encounter between OH and H_2O_2 cannot be ruled out, but the agreement between the TST calculations and the experimental data does not require any such attractions.

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(19) Baulch, D. L.; Drysdale, D. D.; Horne, D. G.; Lloyd, A. C. *Evaluated Kinetic Data for High Temperature Reactions: Homogeneous Gas Phase Reactions of the H_2-O_2 System*; Butterworths: London, 1972; Vol. 1, p 193.