TABLE III: Parameters Found by Fitting Eq 8 to Data for Four Reactions with $B_{\gamma} = 1$ and n = 2.5

Y	$\log A$, L mol ⁻¹ s ⁻¹ K ^{-2.5}	E _e , kJ mol⁻¹	<i>T</i> *, K	$\Delta S_{1/2}$, pm
C ₂ H ₆	3.6 ± 0.4	88 ± 9	813 ± 85	50
	2.9 ± 0.3^{a}	74 ± 6^{a}	688 ± 74^{a}	54ª
$C(CH_3)_4$	2.7 ± 0.1	66 ± 2	600 ± 28	59
H ₂ CO	2.0 ± 0.2	40 ± 5	546 ± 94	50
(H ₃ C) ₂ O	2.8 ± 0.2	65 ± 3	660 ± 37	52

^a Data of ref 17 deleted.

been argued⁴⁵ that the path of minimum potential energy is not the most appropriate path. Thus it is not surprising that the values of T above do not agree.

In the second to sixth lines of Table II the quantal equation for B_v is replaced by eq 15 and n is varied from -1.5 to +2.5, corresponding to changing vibrational partition functions from eq 9 to eq 11 or eq 12. As n increases the other three parameters decrease. Inserting a factor of T increases the rate, the activation energy (by RT), and the heat capacity of activation (by R), so the other parameters decrease to compensate. When n = 2.5 the value of T_* is similar to the value in the first line. Increase of n by 4 units has compensated for loss of the curvature associated with the explicit formula for B_{y} . This factor of T^{4} corresponds to treating the four new bending vibrations and the umbrella motions by eq 11. (See paragraph following eq 14 above.) The predicted values of log A and E_e from transition-state theory become 1.1 and 32 kJ mol⁻¹, respectively, both again lower than the fitted values in Table II. The fitted curve is shown in Figure 1

The entry with n = 0.5 corresponds to treating the four new bending degrees of freedom as free internal rotations (eq 12). Then log A is predicted to be 10.1. Since the fitted value is less than predicted for free rotation but, in the previous paragraph, the fitted value was greater than predicted for vibration, it could be useful to treat these degrees of freedom as hindered rotations. This cannot be done analytically. If the lower frequency bend is treated as a free rotation and the higher frequency bend as a vibration, the corresponding value of n is 1.5. The predicted value of log A is 5.2. It was shown in ref 41 that a hindered rotor partition

(45) Marcus, R. A.; Coltrin, M. E. J. Chem. Phys. 1977, 67, 2609.

function is approximately equal to the free rotor function (eq 12) multiplied by $\exp(-V_2/(3RT))$, where V_2 (= $2I_i(\pi c\omega_i)^2$) is the barrier to internal rotation. Calculating V_2 as above for the two low frequency bending modes, and adding $2V_2/3$ to the predicted barrier one obtains 35 kJ mol⁻¹ for E_e . Both E_e and log A from this model are similar to the values in Table II.

Parameters for the other reactions with n = 2.5 are compared in Table III. The corresponding fits are shown as solid curves in Figures 2 and 3.

The parameters for reaction 2 are the largest. Deleting the highest temperature point would reduce the parameters as shown by the entries marked with a superscript a. Based on the BEBO model of ref 4 the predicted values of these parameters would be 0.8, 23 kJ mol⁻¹, and 344 K for log A, E_e , and T_* , respectively.

Values of the effective barrier width at half height, from eq 17, are listed in the final column. The effective mass, m, was estimated¹ as $(M_{\ddagger} - M_{\rm H})M_{\rm H}/(2M_{\ddagger})$. The values of $\Delta S_{1/2}$ are remarkably consistent.

There is a correlation between the values of E_e in Table III and the values of C in Table I, as predicted in ref 43.

It should be emphasized that the present results are dependent on the model chosen. Variation of the position of the transition state or of the reaction path with temperature⁵ could also affect Arrhenius plot curvature.

In conclusion, transition-state theory with tunneling is capable of fitting the data points within experimental uncertainty. This method could be used for smoothing data or interpolating between experimental temperatures. Fitted preexponential factors and effective barrier heights are subject to uncertainty but should be more reliable than parameters from linear fits. There is a need for accurate experimental work at high temperatures to better define these parameters. Hindered internal rotations and asymmetric barriers should be incorporated in the fitted models. Further theoretical work and low temperature experimentation including studies of isotope effects could help in understanding the relationship between T_* , $\Delta S_{1/2}$, and the properties of the multidimensional potential surface.

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council of Canada for a grant in support of this work and R. Walsh for a valuable discussion.

Registry No. CH₃, 2229-07-4; H₂, 1333-74-0; C₂H₆, 74-84-0; C(C-H₃)₄, 463-82-1; H₂CO, 50-00-0; (H₃C)₂CO, 67-64-1.

Direct Evidence for the Tunneling Reaction HD + D \rightarrow H + D₂ in the Radiolysis of a D₂--HD Mixture at 4.2 K

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When a D₂-HD (15.6 mol %) mixture is γ -irradiated at 4.2 K, D and H atoms are produced and can be measured by ESR spectroscopy. ESR measurement has been performed at the very low microwave power level of $10^{-3} \mu$ W which does not result in saturation of the signals from the hydrogen atoms. The amounts of H atoms increase gradually upon storage of the irradiated samples at 4.2 K, while the amounts of D atoms decrease complementarily. The result indicates clearly the occurrence of the HD + D \rightarrow H + D₂ reaction, caused by quantum mechanical tunneling. Since the decrease in D-atom yields upon storage of the irradiated sample is larger than the increase in H-atom yields, some of the D atoms recombine with other D or H atoms.

Introduction

Basic to any theory of elementary chemical reactions is an understanding of the simplest atom-diatomic molecule exchange reaction. A number of experimental and theoretical studies on the reaction of H (or D) with H₂ (or HD or D₂) have been reported previously.¹ The role of the quantum mechanical tunneling effect

on the $H + H_2$ reaction has been one of the important problems in the theory of chemical kinetics. Previous studies, however, have been undertaken above room temperature. Thus it was difficult

⁽¹⁾ Truhlar, D. G.; Wyatt, R. E. Annu. Rev. Phys. Chem. 1976, 27, 1; related papers are cited therein.

Tunneling Reaction HD + D \rightarrow H + D₂

to discriminate between the reaction caused by the quantum mechanical tunneling effect and the reaction which proceeds by passing over a potential energy barrier.

In order to clarify the tunneling effect, the H_2 (HD, D_2) + D (H) reaction has been studied recently at ultralow temperatures, such as 4.2 and 1.9 K.^{2,3} A remarkable isotope effect on the formation of D and H atoms in the radiolysis of solid D_2-H_2 mixtures has been found at 4.2 K;² the ratio of the rate constant for the $H_2 + D$ reaction to that for the $D_2 + H$ reaction exceeds 2×10^4 . The results were explained in terms of a selective hydrogen atom abstraction reaction caused by quantum mechanical tunneling. The temperature effect on the decay of H (D) atoms in the radiolysis of solid H₂, D₂, and HD has been studied at 4.2 and 1.9 K.³ Since the decay rate of H atoms in solid H_2 does not depend upon the temperature,^{3,4} the fast decay of H atoms was explained by a model of tunneling migration³ in which the H atoms repeat a tunneling abstraction reaction with H_2 ($H_2 + H \rightarrow H$ + H₂) and migrate through solid H₂ to recombine with other H atoms. The fast decay of D atoms in the radiolysis of solid HD was explained by the HD + D \rightarrow H + D₂ reaction, also postulated to occur by a tunneling mechanism. In this reaction, however, an increase in the number of H atoms could not be observed upon the decay of D atoms. Since the ratio of initial yields of D atoms to those of H atoms in the radiolysis of solid HD is only 0.2, the increase of the H-atom yields was obscured by experimental errors. Therefore direct evidence for the tunneling reaction in the H $(D)-H_2$ (D_2, HD) system has not been obtained in the previous studies.

In order to confirm the tunneling reaction of $HD + D \rightarrow H$ + D₂, the radiolysis of a D₂-HD mixture has been undertaken at 4.2 K, and direct evidence for the HD + D \rightarrow H + D₂ reaction has now been obtained.

Experimental Section

The details of the experimental procedure were described in a previous paper.^{2,3} D_2 and HD were more than 99.5 and 98 mol % pure. A gaseous mixture of D_2 -HD (15.6 mol %) at 2.8 atm was sealed in a quartz sample tube. The sample of solid hydrogen was made by rapid cooling of the sample tube from room temperature to 4.2 K. The sample was irradiated at 4.2 K with γ -rays from Co-60 at a total dose of 0.1 Mrd. When the D_2 -HD mixture is γ -irradiated at 4.2 K, both D and H atoms are produced by γ -radiolysis of the mixture and trapped in the solid. The trapped hydrogen atoms were measured at 4.2 K by a JES-3BX ESR spectrometer. Since the ESR signals of the D and H atoms saturate at a microwave power level as low as 1 μ W, the ESR spectrometer was modified for the present work for measurements at extremely low microwave power levels. The amounts of D and H atoms were obtained by double integration of the signals, which was performed with a personal computer system.

Results and Discussion

Microwave Saturation Behavior of Trapped H(D) Atoms. In order to measure the concentration of H(D) atoms in solid hydrogen, the ESR spectra should be measured at a microwave power level which does not result in saturation of the signals. Previous measurements were performed at a microwave power level of 1 μ W and significant saturation of the signals occurred.^{2,3} Figure 1 shows the microwave power saturation behavior of the trapped H and D atoms produced by the γ -radiolysis of the D₂-HD (15.6 mol %) mixture at 4.2 K. The ESR spectra of the H and D atoms consist of two and three main lines, respectively. Each main line accompanies two satellite lines which were reported previously.⁵



Figure 1. Microwave power saturation behavior of trapped hydrogen atoms produced by γ -radiolysis of D₂-HD (15.6 mol %) at 4.2 K: (O) main peak of H atoms after γ -irradiation; (\bullet) main peak of H atoms after storage of γ -irradiated sample at 4.2 K for 555 min; (Δ) main peak of D atoms after γ -irradiation; (\bullet) main peak of D atoms after storage of γ -irradiated sample at 4.2 K for 555 min; (\Box) satellite peak of H atoms. The intensities of the main peaks of the H and D atoms of 0.1 μ W are normalized to 10.



Figure 2. Effect of storage of γ -irradiated solid D₂-HD (15.6 mol %) at 4.2 K on the amounts of D (0, 0; 0, 0) and H (ϕ , ϕ ; ϕ , ϕ) atoms. The different open and closed circles represent different experimental runs. (---) Decay of D atoms in neat solid HD at 4.2 K;⁷ (....) decay of D atoms in neat solid D₂ at 4.2 K.⁷

The satellite lines are very much weaker in intensity than the main line and are observed only when the microwave power level is high enough to heavily saturate the main lines. Figure 1 shows that the main H and D peaks begin to saturate at a microwave power of $5 \times 10^{-3} \mu$ W. The satellite lines, however, saturate at a microwave power of 0.8 μ W. The microwave saturation behavior of the H and D atoms just after γ -irradiation is the same as that after storage of the γ -irradiated sample for 555 min (Figure 1). Therefore the concentrations of H and D atoms were obtained here by measurement at $10^{-3} \mu$ W.

Direct Evidence for the $HD + D \rightarrow H + D_2$ Reaction at 4.2 K. When the D₂-HD (15.6 mol %) mixture is γ -irradiated at 4.2 K, the yield of D atoms is about twice as large as that of H atoms. Thus, if reaction 1 occurs at 4.2 K, it is expected that the

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⁽⁴⁾ Katunin, A. Ya.; Lukashevich, I. I.; Orozmamatov, S. T.; Sklyarevskii, V. V.; Suraev, V. V.; Filippov, V. V.; Shevtsov, V. A. Pis'ma Zh. Eksp. Teor. Fiz. 1981, 34, 375.

⁽⁵⁾ Jen, C. K.; Foner, S. N.; Cochran, E. L.; Bowers, V. A. Phys. Rev. 1958, 112, 1169.

concentration of H atoms should increase and that of D atoms should decrease. Figure 2 shows the concentrations of H and D atoms upon storage of the irradiated D₂-HD (15.6 mol %) mixture at 4.2 K. The results of four independent runs, indicated by different filled and open circles, are shown there. The concentration of H atoms, denoted by filled circles, increases gradually upon storage at 4.2 K, while the concentration of D atoms, denoted by open circles, decreases complementarily. This result indicates clearly the occurrence of reaction 1 at 4.2 K. Since the threshold energy for reaction 1 is about 10 kcal mol^{-1,6} the reaction cannot proceed thermally at 4.2 K by passing over a potential energy barrier. In fact, for a 10 kcal mol⁻¹ barrier, the reaction time for reaction 1 would exceed 10400 years if it occurred thermally at 4.2 K. According to a theoretical calculation of the rate constant,³ reaction 1 takes place by quantum tunneling at 4.2 K in a time period from several minutes to hours. Therefore reaction 1 proceeds at 4.2 K by quantum mechanical tunneling.

It is interesting to compare the increment of the H-atom yield with the decrement of the D-atom yield upon storage of the irradiated sample at 4.2 K. The concentration of H atoms increases from 0.33 to 0.52, in arbitrary units, upon storage for 555 min, whereas the concentration of D atoms changes from 0.68 to 0.38 (in the same units) upon storage for the same time period. The decrement of D atoms is 1.6 times larger than the increment of H atoms. Thus some of the D atoms decay by recombination with other D and H atoms.

According to the previous study on the decay of H and D atoms in solid D_2 ,³ D atoms repeat a tunneling abstraction reaction with D_2 ($D_2 + D \rightarrow D + D_2$) and migrate slowly through the solid. H atoms, however, cannot react with D_2 at 4.2 K because the reaction is endothermic, and thus they cannot migrate through the solid D_2 . Therefore the mobile atoms in the D_2 -HD (15.6 mol %) mixture are probably D atoms.

(6) Kuppermann, A.; White, J. M. J. Chem. Phys. 1966, 44, 4352.

We can roughly estimate the behavior of D atoms upon storage for 555 min at 4.2 K from the results of Figure 2. The fraction of the D atoms that migrate to solute HD is $(0.19/0.68) \times 100\%$ = 28% of the initial D atoms. Another fraction of D atoms recombine with other H and D atoms during the migration. This fraction is $\{(0.30 - 0.19)/0.68\} \times 100\% = 16\%$ of the initial D atoms. The rest (56% of the initial D atoms) neither migrate to HD molecules nor to other D (H) atoms in a time less than 555 min. The dashed line⁷ in Figure 2 represents the decay of D atoms in the neat HD solid where D atoms decay mainly by the reaction of D atoms with HD molecules (reaction 1). The dotted line⁷ represents the decay of D atoms in the neat D_2 solid where D atoms decay by recombination with other D atoms. The D atoms in the D_2 -HD (15.6 mol %) mixture decay slower than in neat HD, but they decay faster than in neat D_2 . The D atoms in the D₂-HD mixture must migrate to HD molecules and then react with them, while the D atoms in the neat HD solid are always in contact with the HD molecules. Thus the decay rate of D atoms in the D_2 -HD mixture is slower than that in the neat HD solid. The D atoms in the neat D_2 solid migrate a long distance for recombination with other D(H) atoms whose concentration is much lower than that of 15.6 mol % HD. Thus the D atoms in the D_2 -HD mixture decay faster than in the neat D_2 solid.

Acknowledgment. The authors thank to Professor Kenji Fueki of Nagoya University for his encouragement throughout the work. This work was supported in part by a Grant-in Aid for Special Project Research on Properties of Matter in Quantum Condensed Phase at Ultralow Temperatures from the Ministry of Education, Science and Culture, Japan.

Registry No. D₂, 7782-39-0; HD, 13983-20-5; D atomic, 16873-17-9; H atomic, 12385-13-6.

(7) The decay curves for the D atoms are quoted from the results of ref 3.

Study of the Thermochemistry of the $C_2H_5 + O_2 \Leftrightarrow C_2H_5O_2$ and $t-C_4H_9 + O_2 \Leftrightarrow t-C_4H_9O_2$ Reactions and of the Trend in the Alkylperoxy Bond Strengths

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The gas-phase equilibria involving the reactions of ethyl and *tert*-butyl radicals with molecular oxygen to form the corresponding alkylperoxy radicals have been studied over limited temperature ranges: 336–381 °C for the $C_2H_5 + O_2$ system and 277–307 °C for the $t-C_4H_9 + O_2$ reaction. The radicals were generated homogeneously in a tubular reactor by the pulsed 248-nm photolysis of C_2H_5Br (C_2H_5) or the 193-nm photolysis of 4,4-dimethyl-1-pentene ($t-C_4H_9$). The relaxation of the alkyl radical to equilibrium in the presence of O_2 was monitored in real-time experiments using photoionization mass spectrometry. The experiments yielded at least one value of the equilibrium constant at each temperature studied. The enthalpy changes for both $R + O_2 \Leftrightarrow RO_2$ equilibria were obtained by using a third law procedure combining the measured equilibrium constants with calculated or estimated entropy changes for the same reactions. For $R = C_2H_5$, we obtained $\Delta H^0_{298} = -35.2 \pm 1.5$ kcal mol⁻¹ (using the calculated value of $\Delta S^0_{298} = -35.8 \pm 0.7$ cal mol⁻¹ K⁻¹) and for $R = t-C_4H_9 \Delta H^0_{298} = -36.7 \pm 1.9$ kcal mol⁻¹ (using the estimated value of $\Delta S^0_{298} = -41 \pm 2$ cal mol K⁻¹). The thermochemical information obtained on these equilibria, combined with that determined earlier for $R = CH_3$ and $t-C_3H_7$, indicates that the $R-O_2$ bond strength ($-\Delta H^0_{298}$) increases from 32 to 37 kcal mol⁻¹ as the size of the alkyl group increases from CH₃ to $t-C_4H_9$. This trend in RO₂ bond strengths can be reproduced by using group additivity estimates for the heats of formation of RO₂ and heats of formation of the larger alkyl radicals (C₂H₅ to $t-C_4H_9$) from recent data evaluations. The magnitudes of the four $R-O_2$ bond strengths can also be reproduced if the O-(C)(\dot{O}) group enthalpy (used to calculate RO₂ heats of formation) is lowered 1.9 kcal mol⁻¹ (to 12.3 kcal mol⁻¹).

Introduction

The reactions of alkyl free radicals (R) with molecular oxygen are important elementary kinetic steps in the mechanisms of all gaseous hydrocarbon oxidation processes.^{1–6} Up to 300 °C (at

modest oxygen pressures) these reactions proceed primarily by a reversible addition process: $^{1\!-\!8}$

$$\mathbf{R} + \mathbf{O}_2 \Leftrightarrow \mathbf{RO}_2 \tag{1}$$

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