

two ANO basis sets employed herein significantly outperform the ISP basis in the F_2 case.

Conclusions

Several papers have reported very accurate ab initio force constants and spectroscopic quantities^{3,7,8} obtained with basis sets of TZ2P quality and higher. Our calculations presented herein and others^{14,15} show the sensitivity of gradients and therefore equilibrium geometries to basis sets of rather high quality. We have also shown that superposition errors (even with these high-quality basis sets) contribute significantly to the gradients and equilibrium geometries of these diatomics. Our results also show that the superposition error is magnified by the inclusion of core excitations, when employing basis sets that are not able to describe core correlation. From our experience it seems reasonable that in general (and without fortuitous error cancellation) the prediction of force constants to within 1% and equilibrium geometries to $\pm 0.002 \text{ \AA}$ is beyond the predictive ability of TZ2P (or TZ2P+f) basis sets for molecules composed of atoms in the first row. There are, of course, exceptions to this.

With the two ANO basis sets employed here the calculated force constants agree to within about 1%. At present the 5432+1100 ANO basis we employed herein is too large (50 basis functions per heavy atom) to be used in ab initio calculations on many chemically interesting systems. No systematic data is yet

available on the performance of smaller ANO-type basis sets. The ISP basis is small enough to allow calculations on larger systems, but contains a significant amount of superposition error. Such errors contribute primarily to the linear term in the stretching potentials of these diatomic molecules. Other remaining systematic errors that may influence the value of the equilibrium bond lengths, e.g., the neglect of core-valence correlation, will likely show a similar behavior. Hence accurate and reliable equilibrium structures, if available, can be used to remove such errors from force constant calculations. Correlation techniques employing localized MO basis sets²¹ can be used to remove some superposition error from the correlation energy. However, these techniques cannot address the problem of the superposition error that arises in bonded atom pair situations, and, the superposition error in these situations remains largely a property of the basis set.

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H/D Exchange Reaction between $CHCl_3$ and D_2O in Two-Liquid-Phase System

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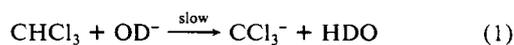
The kinetics of hydrogen isotope exchange between $CHCl_3$ and D_2O has been studied by using a system which is composed of two liquid phases, a chloroform phase and an aqueous phase. The area of the interface between these two phases was kept constant ($5.7 \times 10^{-3} \text{ m}^2$) during the reaction, where the reaction may be controlled by the interfacial transfer of chloroform. The isotopic content of chloroform in the chloroform phase was determined by an infrared absorption measurement. After the reaction, disappearance of deuterioxide ion was observed, which is caused by the chloroform hydrolysis reaction. The experimental results are reasonably explained on the basis of the model in which the reaction process is assumed to be composed of two steps: interfacial transfer of chloroform from the chloroform phase to the aqueous phase or vice versa, and the hydrogen isotope exchange reaction between $CHCl_3$ and D_2O in the aqueous phase. The rate constants for the interfacial transfer of chloroform and for the exchange reaction in the aqueous phase at $26.0 \text{ }^\circ\text{C}$ were $0.107 \pm 0.003 \text{ m}^{-2} \text{ s}^{-1}$ and $0.231 \pm 0.013 \text{ L mol}^{-1} \text{ s}^{-1}$, respectively.

1. Introduction

It has been reported that chloroform^{1,2} and other halocarbons^{3,4} are promising working materials for deuterium and tritium separation processes based on isotopically selective infrared multiple-photon-induced dissociation of these molecules. Chloroform seems to be especially suitable as the working material in the separation process of deuterium and tritium which exist as water, because the rate of the base-catalyzed hydrogen isotope exchange reaction between chloroform and water is far larger than that of other halocarbons which could possibly be used in an isotopic separation process.

The aim of this work is to evaluate the rate of hydrogen isotope exchange between chloroform and water, which form a two-liquid-phase system, and to clarify quantitatively the effect of the interfacial transfer of chloroform.

Some studies have been carried out on chloroform dissolved in alkaline aqueous solution⁵⁻⁷ and have demonstrated that the mechanism of the hydrogen isotope exchange reaction is the following:



where the first step is rate controlling.

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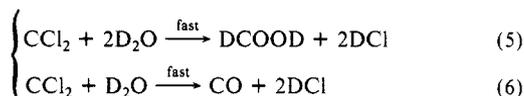
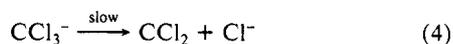
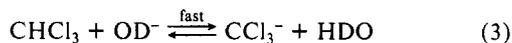
(4) Makide, Y.; Hagiwara, S.; Tominaga, T.; Takeuchi, K.; Nakane, R. *Chem. Phys. Lett.* **1981**, *82*, 18.

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Besides the exchange reaction, chloroform undergoes alkaline hydrolysis⁸⁻¹⁴ by the mechanism



In this case reaction 3, which is the same as reaction 1, is the fast step, because step 4 is much slower than (3).

The rate of the base-catalyzed hydrogen isotope exchange between chloroform and water in the aqueous phase and the rate of alkaline hydrolysis of chloroform have been determined by Hine et al.^{5,8} It is seen from their work that the rate of the hydrolysis reaction is lower than that of the exchange reaction by a factor of more than 1000. In this case consumption of base by the hydrolysis reaction is negligible and the hydrolysis reaction will have little effect upon the exchange reaction.

Some studies of the rate of the hydrogen exchange reaction between chloroform and water in a two-liquid-phase system have been reported. Symons and Bonnett¹⁵ have reported exchange rate constants which are in good agreement with Hine's data under the condition of homogeneous mixing of the liquid phases. Maienschein and Barry¹⁶ have found that the mass transfer between the two phases is rate controlling under the condition that the hydroxide concentration is large or the stirring speed of the two liquid phases is small. They also reported exchange rate constants as a function of temperature.

In the present study the interfacial area between the two liquid phases is kept constant and relatively small. For the kinetic description of the reaction in this system, we considered a model in which the interfacial transfer is taken into account. The reaction behavior is reasonably explained on the basis of this model and kinetic parameters are obtained. A quantitative evaluation of the effect of the interfacial transfer of chloroform upon the rate of the whole exchange reaction was made.

The decrease in concentration of OD^- caused by the hydrolysis of chloroform, which arises because the isotope exchange reaction required many hours, and the associated decrease in the rate of the exchange reaction were also observed in this system. It will be discussed quantitatively in the Appendix.

2. Experimental Procedure and Results

Chloroform was purchased from Nakarai Ltd. It contains 1% ethanol as a stabilizer which was removed by extraction using distilled water. After the extraction, ethanol was not detected in the chloroform by infrared absorption measurement. A solution of $\text{NaOD}/\text{D}_2\text{O}$ was prepared by dissolving NaOH pellets in D_2O which has an isotopic purity of 99.8%. The concentration of OD^- in the solution was determined by titration using HCl standard solution.

A schematic diagram of the stirred reactor employed for the experimental runs is shown in Figure 1. After the reactor was filled with N_2 gas, 100 mL of CHCl_3 and 90 mL of D_2O were admitted. The temperature of the reactor was controlled at 26.0 °C by a thermostat. Ten milliliters of $\text{NaOD}/\text{D}_2\text{O}$ solution of a given NaOD concentration was then added to the reactor. The

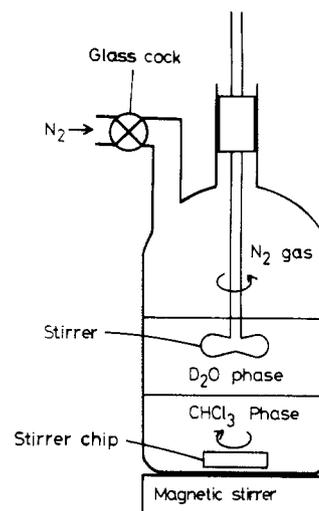


Figure 1. Experimental setup for the measurement of the rate of hydrogen isotope exchange between D_2O and CHCl_3 in a two-phase system.

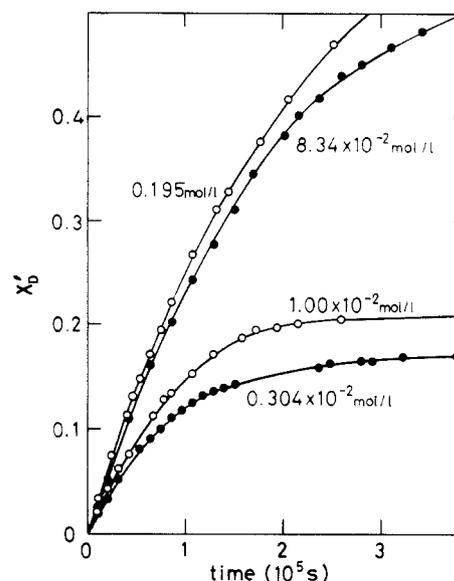


Figure 2. Examples of the time dependence of the molar fraction of CDCl_3 in chloroform phase, X'_D . Initial concentrations of OD^- are indicated at each curve. The theoretical limit for X'_D in the absence of hydrolysis reaction is 0.90.

time of the addition of this solution is the starting time of the reaction.

A magnetic stirrer and mechanical stirrer were used to stir the chloroform phase and the aqueous phase, respectively. The interface was kept undisturbed by rotating the stirrers in opposite directions. The area of the interface was taken as the area of the cross section of the reactor, $5.7 \times 10^{-3} \text{ m}^2$ (Figure 1).

After an appropriate interval, 0.01 mL of chloroform was removed by a syringe and injected into a degassed IR gas cell. The deuterium isotope mole fraction of chloroform, $[\text{CDCl}_3]/([\text{CDCl}_3] + [\text{CHCl}_3]) \equiv X'_D$, was determined from the infrared absorption measurement. The gas cell, 40 mm in diameter, 100 mm in length, with NaCl windows was used for the infrared measurement. Memory effect of the cell due to desorption of chloroform from window seal material, such as Viton O-rings, was avoided by the use of a Torr Seal. For quantitative analysis of the concentration of CDCl_3 , absorption bands accompanying deformation vibrations of C-H and C-D (1120 and 914 cm^{-1} , respectively) were used.

Some examples of the experimental results for the time dependence of the deuterium isotope mole fraction of chloroform in the chloroform phase are shown in Figure 2. It is noted that both the initial rate of increase in the fraction of CDCl_3 and final

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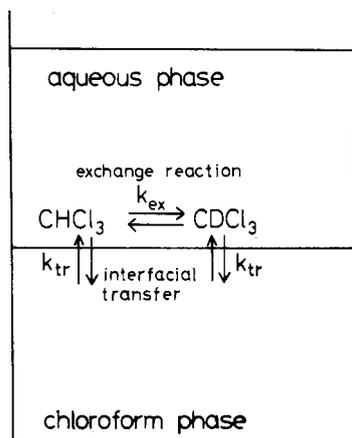


Figure 3. Illustration of the model proposed in this work.

values of the fraction of CDCl₃ depend on the initial concentration of OD⁻. For the blank run where no NaOD was added, no CDCl₃ was detected by IR measurement. This means the reaction cannot occur without addition of OD⁻ to this system.

The final values of the fraction of CDCl₃ seems to be far smaller than the value, 0.90, calculated for the case when no hydrolysis reaction occurs. At the end of each reaction, OD⁻ and OH⁻ could not be detected by phenolphthalein. Moreover, chloride ion was detected by adding 1 N AgNO₃. Clearly, chloroform has undergone alkaline hydrolysis.

3. Process of the Reaction

For the quantitative understanding of the process of the exchange reaction in the two-liquid-phase system, a simple model which is composed of two main steps is proposed: chloroform transfer from the chloroform phase to the aqueous phase or vice versa, and hydrogen isotope exchange in the aqueous phase. The outline of the model is illustrated in Figure 3. The model is based on the following assumptions: (1) the exchange reaction occurs only in the aqueous phase, (2) the concentrations of CHCl₃ and CDCl₃ are homogeneous in each phase, (3) the isotope effect for the interfacial transfer of chloroform is negligible, (4) concentration of chloroform in the aqueous phase will be constant throughout the reaction, and (5) the reaction under the present nonturbulent conditions is controlled by the interfacial transfer of chloroform.

Assumption 1 seems to be accepted, because another experiment showed that the concentration of NaOH in the chloroform phase, which was determined by atomic absorption spectroscopy analysis, was on the order of ppb after 13 h of shaking with 0.5 mol L⁻¹ NaOH aqueous solution. Assumption 1 is also confirmed by the fact that the tritium exchange rate between water and chloroform is independent of the ratio between the volume of the chloroform phase and that of the aqueous phase.¹⁷ Assumption 2 is supported by the sufficient stirring of each phase. Assumption 3 is based on the small mass ratio of CHCl₃ and CDCl₃. Assumption 4 means that the reaction is in a stationary state. Assumption 5 is supported by the work of Maienschein and Barry where the reaction was controlled by the interfacial transfer when the mixing rate is slow, even if the two liquids are homogeneously mixed, where the interfacial area may have been much larger than that in the present study.

We constructed the rate equation in terms of the deuterium isotope mole fraction of chloroform in the aqueous phase, X_D , and that in the chloroform phase, X'_D . The time derivatives of X_D and X'_D can be written as follows:

$$dX_D/dt = v_{ex} + v_{tr} \quad (7)$$

$$dX'_D/dt = v'_{tr} \quad (8)$$

where v_{ex} , v_{tr} , and v'_{tr} are the rate of increase of X_D by the exchange

TABLE I: Rate of Interfacial Transfer R_{tr} and That of Exchange Reaction R_{ex} at 26 °C

$[\text{OD}^-]_0,^a$ $10^{-2} \text{ mol L}^{-1}$	$R_{tr},^b$ 10^{-5} s^{-1}	$R_{ex},^c$ 10^{-5} s^{-1}
0.304	61 ± 2	70.2 ± 4.0
0.307	61 ± 2	70.9 ± 4.0
0.491	61 ± 2	113 ± 6
0.915	61 ± 2	211 ± 12
1.00	61 ± 2	231 ± 13
8.34	61 ± 2	1930 ± 110
8.54	61 ± 2	1970 ± 110
18.5	61 ± 2	4270 ± 240
19.5	61 ± 2	4500 ± 250

^a Alkali concentration. ^b Rate of interfacial transfer. ^c Initial rate of exchange reaction.

reaction in aqueous phase, rate of increase of X_D by interfacial transfer of CDCl₃, and the rate of increase of X'_D by the interfacial transfer of CDCl₃, respectively.

By assuming a steady state of $[\text{CCl}_3^-]$, the rate equation for reactions 1 and 2 is written as follows:

$$v_{ex} = k_{ex}[\text{OD}^-](1 - X_D)Y_D - pk_{ex}[\text{OD}^-]X_D(1 - Y_D) \\ = k_{ex}[\text{OD}^-][Y_D - pX_D + (p - 1)X_DY_D] \quad (9)$$

where k_{ex} is the rate constant of the forward reaction of eq 1 and 2, p is the isotope effect on the reaction rate which is defined as the ratio of the rate constant of the backward reaction to that of the forward reaction, and Y_D is a deuterium isotope mole fraction of water:

$$Y_D \equiv (2[\text{D}_2\text{O}] + [\text{HDO}])/2([\text{D}_2\text{O}] + [\text{HDO}] + [\text{H}_2\text{O}])$$

The increase of X_D and X'_D caused by the interfacial transfer of chloroform is written as follows:

$$v_{tr} = k_{tr}S(X'_D - X_D) \quad (10)$$

$$v'_{tr} = [k_{tr}Sa_0/(b/V_0)](X_D - X'_D) \quad (11)$$

where S is an interfacial area between the chloroform phase and the aqueous phase, b is the amount of chloroform in the chloroform phase, V_0 is the volume of the chloroform phase, k_{tr} is a rate constant of interfacial transfer of chloroform, and a_0 is a concentration of chloroform in the aqueous phase and assumed to be constant according to assumption 4 made previously. From eq 7-11 we obtain

$$dX_D/dt = k_{ex}[\text{OD}^-][Y_D - pX_D + (p - 1)X_DY_D] + k_{tr}S(X'_D - X_D) \quad (12)$$

$$dX'_D/dt = [k_{tr}Sa_0/(b/V_0)](X_D - X'_D) \quad (13)$$

We paid attention to the initial reaction rate r

$$r = (dX'_D/dt)_{t=0}$$

because the whole solution of eq 12 and 13 can be obtained only if the time dependence of $[\text{OD}^-]$ accompanying the alkaline hydrolysis is given, as will be discussed in Appendix. At the beginning of the reaction

$$[\text{OD}^-] = [\text{OD}^-]_0 \quad (14)$$

$$Y_D = 1 \quad (15)$$

$$X'_D \ll X_D \quad (16)$$

where $[\text{OD}^-]_0$ is the initial concentration of OD⁻ in the aqueous phase. By considering assumption 5 we assumed a stationary state of X_D :

$$dX_D/dt = 0 \quad (17)$$

By the use of eq 14-17, eq 12 and 13 become a single equation:

$$1/br = (1/k_{ex})(1/a_0V_0[\text{OD}^-]_0) + 1/k_{tr}Sa_0V_0 \quad (18)$$

The initial rate of the exchange reaction, r , is obtained from figures

(17) Yokoyama, A.; Suzuki, K.; Fujisawa, G.; Ishikawa, N.; Iwasaki, M. *Radiochim. Acta* 1986, 40, 107.

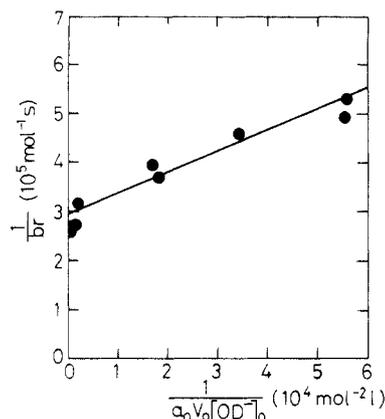


Figure 4. Plot of $1/br$ vs $1/a_0V_0[OD^-]_0$. By this plot some kinetic parameters are determined and the model proposed in this work is examined.

like Figure 2. The values of k_{tr} and k_{ex} determined by the plot of $1/br$ vs $1/a_0V_0[OD^-]_0$ (Figure 4) are $0.107 \pm 0.003 \text{ m}^{-2} \text{ s}^{-1}$ and $0.231 \pm 0.013 \text{ L mol}^{-1} \text{ s}^{-1}$, respectively, at 26.0°C . Here we used $a_0 = 0.059 \text{ mol L}^{-1}$.

For the comparison of the rate of the exchange reaction and the rate of the interfacial transfer, it is obvious from eq 12 that the comparison of parameters

$$R_{ex} = k_{ex} [OD^-]_0 \quad (19)$$

$$R_{tr} = k_{tr}S \quad (20)$$

is suitable. The values of R_{ex} and R_{tr} are listed in Table I.

4. Discussion

The model of the exchange process seems to be successful in explaining the results of the experiments, because of the linearity between $1/br$ and $1/a_0V_0[OD^-]_0$ as indicated in Figure 4. Furthermore, the value, $0.231 \pm 0.013 \text{ L mol}^{-1} \text{ s}^{-1}$ at 26°C , obtained for the rate constant k_{ex} shows good agreement with the literature values, $0.207 \text{ L mol}^{-1} \text{ s}^{-1}$ at 20.0°C (Hine et al.⁵), $0.22 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25°C (Maienschein and Barry¹⁶), and $0.21 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25°C (Symons and Bonnett¹⁵). The kinetic parameters obtained by fitting the model with the experimental results are consistent with the presumption that the rate of interfacial transfer of chloroform is much lower than that of the exchange reaction (Table I).

In section 3, we made assumptions based on the homogeneity of the aqueous phase. Stirring of the aqueous phase may support these assumptions. In detailed discussions, however, we should construct a model which will include a concentration distribution of species in the system, such as CHCl_3 , OD^- , and D_2O , especially near the interfacial region. In the present model these detailed effects are included in the macroscopic parameter for interfacial transfer, k_{tr} .

To evaluate the value of dX'_D/dt throughout the reaction, the consumption of OD^- caused by the hydrolysis reaction must be taken into account. The time dependence of X'_D can be calculated by assuming

$$[OD^-] = [OD^-]_0 \exp(-t/T) \quad (21)$$

where T is a parameter characterizing the rate of the hydrolysis reaction. This simple decay of $[OD^-]$ is consistent with chemical eq 3–6.¹⁷ The whole calculation is shown in the Appendix. The values of k_{ex} , k_{tr} , and T are obtained (Table II) by fitting this model with each experimental run (Figure 2). The average values of k_{ex} , k_{tr} , and T , obtained by this method over the experimental runs using various initial OD^- concentrations are $0.254 \text{ L mol}^{-1} \text{ s}^{-1}$, $0.116 \text{ m}^{-2} \text{ s}^{-1}$, and $1.45 \times 10^{-5} \text{ s}^{-1}$, respectively. The value of k_{ex} agrees with our value determined in section 3 and also with literature values (see section 3). The values obtained from each run, however, deviate from each other and the fitting of the model

TABLE II: Values of Fitting Parameters Obtained in the Appendix

run no.	$[OD^-]_0$, $10^{-2} \text{ mol L}^{-1}$	k_{tr} , $\text{m}^{-2} \text{ s}^{-1}$	k_{ex} , $\text{L mol}^{-1} \text{ s}^{-1}$	$1/T$, 10^{-5} s^{-1}
1	0.304	0.147 ± 0.043	0.346 ± 0.093	1.35 ± 0.14
2	1.00	0.092 ± 0.007	0.265 ± 0.060	1.84 ± 0.13
3	8.34	0.109 ± 0.003	0.153 ± 0.050	1.16 ± 0.12
av		0.116	0.254	1.45

to the experimental result is not necessarily satisfactory. This seems to originate in the assumption for the simple decay of $[OD^-]$ in the two-phase system, as indicated by eq 21, as well as the assumption of no isotope effect in the rate of the exchange reaction (Appendix).

5. Summary

The rate of the hydrogen isotope exchange reaction between CHCl_3 and D_2O was studied for the two-liquid-phase system in which the interfacial area was kept constant. In this system the interfacial transfer of chloroform is regarded as rate controlling. The transfer rate constant determined from initial reaction rates was $0.107 \pm 0.003 \text{ m}^{-2} \text{ s}^{-1}$ at 26.0°C .

The decrease in concentration of OD^- is observed in this system. This is caused by the hydrolysis of chloroform, which becomes significant because the reaction takes a long time.

Acknowledgment. We thank Mr. Koukichi Hotta and Mr. Seido Ogura for their assistance in the experiments and Prof. Ichiro Fujiwara (Otemon Gakuin University), Dr. Nobutsugu Imanishi (Faculty of Engineering, Kyoto University), and Dr. Tsutomu Sakurai (Japan Atomic Energy Research Institute) for their valuable discussions.

Appendix

We solved the differential eq 12 and 13 under the condition of eq 21. Equation 21 is a reasonable simplification of the decrease in OD^- caused by the hydrolysis reaction, because the reactions 3–6 are represented by the rate equation

$$-d[OD^-]/dt = k_{hy}a_0(3 + f)[OD^-]$$

where k_{hy} is a rate constant and f is the fraction of the chloroform which produces formate upon hydrolysis.¹⁷ In this case

$$1/T = k_{hy}a_0(3 + f) \quad (A1)$$

For convenience we assumed that there is no isotope effect on the rate constant of the exchange reaction, i.e., $p = 1$. Although this seems to be a rough approximation,^{5,6} we believe that the characteristics of the formula 21 will not be disturbed qualitatively by this approximation.

Using the relation

$$Y_D = 1 - 10(a_0V_aX_D + bX'_D)/V_a d \quad (A2)$$

and the assumption

$$dX_D/dt = 0 \quad (A3)$$

as mentioned in section 3, eq 12 and 13 are written as follows

$$dX'_D/dt + (f(t)/\beta)X'_D = f(t) \quad (A4)$$

$$1/\beta \equiv 1 + 10(b + a_0V_a)/V_a d$$

$$f(t) \equiv \frac{(a_0V_o/b)k_{tr}Sk_{ex}[OD^-]_0 \exp(-t/T)}{(1 + 10a_0/d)k_{ex}[OD^-]_0 \exp(-t/T) + k_{tr}S}$$

where V_a is the volume of the aqueous phase and d is the density of deuterium oxide. Solving the differential eq A4 under the condition that $X'_D = 0$ at $t = 0$, and using the relation $a_0V_a \ll b$ and $a_0 \ll d/10$, we obtain

$$X'_D \approx \beta \left\{ 1 - \left[\frac{k_{ex}[OD^-]_0 \exp(-t/T) + k_{tr}S}{k_{ex}[OD^-]_0 + k_{tr}S} \right]^{(a_0V_o/b)Tk_{tr}S/\beta} \right\} \quad (A5)$$

$$\beta \approx V_a d / (V_a d + 10b)$$

Parameters k_{tr} , $k_{ex}[\text{OD}]_0$, and T are determined by the least-squares fitting of eq A4 with the experimental result shown in Figure 2. The values of these parameters are listed in Table II. From the value of $1/T$ in Table II, the rate of the hydrolysis reaction, k_{hy} , can be estimated by (A1), using $f = 0.2$ as indicated

in ref 17. The average value is $7.7 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$, which is in fairly good agreement with $6 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ obtained from Figure 5 in ref 17 and $6 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ obtained by interpolating the values tabulated in Table I of ref 8.

Registry No. CHCl_3 , 67-66-3; H_2O , 7732-18-5; H_2 , 1333-74-0.

A Shock Tube and Modeling Study of the $\text{CH}_3 + \text{CH}_2\text{O}$ Reaction at High Temperatures[†]

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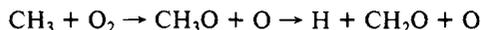
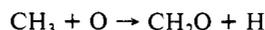
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The reaction $\text{CH}_3 + \text{CH}_2\text{O} \rightarrow \text{CH}_4 + \text{CHO}$ has been studied in a shock tube in the temperature range 1170–1630 K, and its rate constant has been determined by kinetic modeling of the observed CO formation: $k_1 = 10^{15.0 \pm 0.4} \exp(-11600 \pm 1260/T)$. The results confirm earlier observations that the Arrhenius plot curves upward rather sharply at temperatures above 1000 K, although the effect appears less dramatic than reported previously. This nonlinearity cannot be rationalized by a standard transition-state model. However, the inclusion of a correction for quantum mechanical tunneling leads to an acceptable fit of the observed data over the entire experimental range (300–1700 K). A nonlinear least-squares fit to the calculated values covering 300–2000 K gives rise to $k_1 = 10^{-12.05} T^{7.4} \exp(483/T) \text{ cm}^3/\text{mol}\cdot\text{s}$.

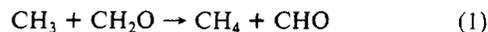
Introduction

The rate constant for the reaction of the CH_3 radical with CH_2O , an important intermediate in high-temperature hydrocarbon oxidation reactions, has not been determined reliably above 1000 K.¹⁻⁶ This reaction is not only relevant to the thermal decomposition and oxidation of ethers (such as CH_3OCH_3 ²⁻⁵ and $\text{CH}_3\text{O}-t\text{-C}_4\text{H}_9$) but is also important to the chemistry of hydrocarbon combustion processes at high temperatures. Since the CH_3 radical is the most stable alkyl radical which can be directly converted to CH_2O by its facile reactions with O, O_2 , and OH, viz.



the $\text{CH}_3 + \text{CH}_2\text{O}$ reaction is therefore inherently coupled and becomes an important process to be incorporated into the complex mechanisms of ether and hydrocarbon combustion reactions.

The $\text{CH}_3 + \text{CH}_2\text{O}$ reaction was also shown to be pivotal in our recent modeling of CO formation in the decomposition of CH_3NO_2 at high temperatures.⁶ In order to model quantitatively the yields of CO in the temperature range 940–1520 K, Hsu and Lin⁶ found it necessary to increase the well-established low-temperature rate constant for the reaction^{7,8}



by more than 2 orders of magnitude. This conclusion seemed to be in line with the high-temperature results of Pacey et al.^{2,3} and, especially, those of Aronowitz and Naegeli⁴ from their studies of the dimethyl ether decomposition reaction above 1000 K.

The apparent drastic increase in the rate constant (k_1) at high temperatures,^{4,6} apart from possible uncertainties in kinetic

modeling due to assumed mechanisms and to compounded errors in the values of rate constants used for other reactions, was attributed to the following two possibilities:⁶ (1) the presence of the quantum mechanical tunneling effect, which is known to cause a nonlinear Arrhenius behavior,⁹ and (2) the appearance of an additional reaction channel, $\text{CH}_3 + \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{CHO} + \text{H}$, which is endothermic by only 17 kJ/mol. An analogue of the second possibility, $\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}$, was shown to occur sometime ago by Liu and Laidler.¹⁰

The objective of the present study was to measure reliably the rate constant of the subject reaction, as well as to determine the origin of the sharp increase in the observed rate constant values above 1000 K.

Experimental Section

The shock tube and CW CO laser setups used for this experiment have been described in earlier papers from our laboratory.^{6,11,12} The stainless steel shock tube has an i.d. of 6.35 cm and is equipped with piezoelectric pin gauges for the measurement

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