

## Detailed rate coefficients and the enthalpy change of the equilibrium reaction $\text{OH} + \text{C}_2\text{H}_4 = \text{MHOC}_2\text{H}_4$ over the temperature range 544–673 K

Eric WeiGuang Diao and YuanPern Lee

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# Detailed rate coefficients and the enthalpy change of the equilibrium reaction

## $\text{OH} + \text{C}_2\text{H}_4 \rightleftharpoons \text{HOC}_2\text{H}_4 + \text{M}$ over the temperature range 544–673 K

Eric Wei-Guang Diau and Yuan-Pern Lee<sup>a)</sup>

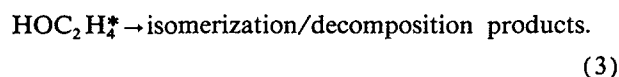
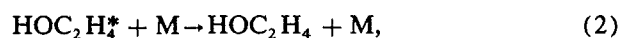
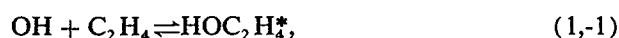
Department of Chemistry, National Tsing Hua University, 101, Sec. 2, Kuang Fu Road, Hsinchu, Taiwan 30043, Republic of China

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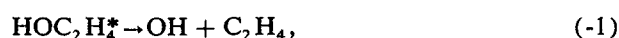
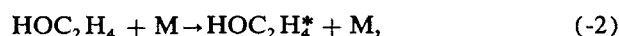
The reaction between OH and  $\text{C}_2\text{H}_4$  in He has been studied over the pressure range 278–616 Torr and the temperature range 544–673 K by means of the laser-photolysis/laser-induced-fluorescence technique. Analysis of the temporal profile of [OH] yielded the equilibrium constant for the reaction  $\text{OH} + \text{C}_2\text{H}_4 + \text{M} \rightleftharpoons \text{HOC}_2\text{H}_4 + \text{M}$ . The temperature dependence of the equilibrium constant led to the enthalpy of reaction  $\Delta H = -(30.3 \pm 0.8)$  kcal mol<sup>-1</sup> and the entropy of reaction  $\Delta S = -(30.9 \pm 1.0)$  cal K<sup>-1</sup> mol<sup>-1</sup> near 600 K, in agreement with previous predictions. Analysis of the detailed rate coefficients suggests that the H-atom abstraction reaction is relatively unimportant in the temperature range of our study; the rate coefficient determined previously for the H-atom abstraction near 673 K may have been overestimated. The temperature dependence of the rate coefficients for the forward, the reverse, and the adduct-loss reactions have been determined to be  $k_f = (4 \pm 3) \times 10^{-13} \exp[(1200 \pm 800)/T]$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,  $k_r = (6.2 \pm 1.0) \times 10^{11} \exp[-(11\,900 \pm 400)/T]$  s<sup>-1</sup>, and  $k_a = (8.8 \pm_{1.5}^{2.5}) \times 10^9 \exp[-(10\,400 \pm_{400}^{1600})/T]$  s<sup>-1</sup>, respectively.

### I. INTRODUCTION

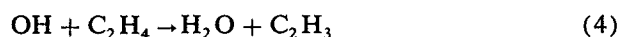
The reaction of OH with  $\text{C}_2\text{H}_4$  is important in the combustion of hydrocarbons<sup>1,2</sup> as well as in atmospheric chemistry.<sup>3,4</sup> There have been numerous experimental investigations of the rate coefficient and the mechanism of this reaction,<sup>5–30</sup> and reviews of the results.<sup>31–33</sup> At low temperatures ( $T < 500$  K), the initial step of the reaction is dominated by the electrophilic addition of OH to  $\text{C}_2\text{H}_4$  to form an adduct  $\text{HOC}_2\text{H}_4^*$ , followed by decomposition, stabilization, or isomerization of this adduct



The rate coefficient was generally determined by monitoring the consumption of OH. It depends on pressure and, at the high pressure limit, decreases slightly as temperature increases. In the temperature range 500–750 K, the rate coefficient decreases more rapidly as temperature increases; this is because the decomposition of the thermalized  $\text{HOC}_2\text{H}_4$  back to OH and  $\text{C}_2\text{H}_4$ ,



becomes important in this temperature range. At high temperatures ( $T > 750$  K), the abstraction of an H atom



becomes the major channel and the rate coefficient increases rapidly as the temperature increases.

Few spectroscopic studies of the  $\text{HOC}_2\text{H}_4$  adduct have been reported. The electron-spin resonance (ESR) spectrum of  $\text{HOC}_2\text{H}_4$  recorded in the photolysis of ethanol containing 1%  $\text{H}_2\text{O}_2$  at  $-70^\circ\text{C}$ <sup>34,35</sup> and in the reduction of  $\text{HOCH}_2\text{CH}_2\text{I}$ <sup>36</sup> suggested the nonequivalence of the  $\alpha$  and/or  $\beta$  protons. In a recent experiment using the pulse-radiolysis/kinetic-absorption technique, a structureless UV absorption in the range 210–265 nm was attributed to  $\text{HOC}_2\text{H}_4$ ; the self-reaction of  $\text{HOC}_2\text{H}_4$  was also studied.<sup>37</sup> No infrared spectrum of  $\text{HOC}_2\text{H}_4$  has been reported. Theoretical calculations have been performed to predict the structure of  $\text{HOC}_2\text{H}_4$  and the barrier heights and the structures of intermediates in various paths of the isomerization and decomposition of  $\text{HOC}_2\text{H}_4$ .<sup>38–40</sup> The enthalpy change for the title reaction has not been determined experimentally. According to empirical estimates,  $\Delta H^0$  is in the range  $-(29\text{--}35)$  kcal mol<sup>-1</sup>,<sup>17,24,29,41,42</sup> whereas *ab initio* calculations<sup>38–40</sup> gave values of  $-(24\text{--}29)$  kcal mol<sup>-1</sup>.

We have investigated the title reaction at temperatures ranging from 544 to 673 K by means of the laser-photolysis/laser-induced-fluorescence (LIF) technique. Through a careful control of experimental parameters to achieve equilibrium conditions suitable for an accurate determination of the double-exponential decay of [OH], we have been able to determine the equilibrium constant and the detailed rate coefficients of the title reaction. The temperature dependence of the equilibrium constant yields  $\Delta H$  and  $\Delta S$  of the reaction.

### II. EXPERIMENTAL

The technique and the experimental setup have been described in detail previously,<sup>43</sup> hence only a summary is

<sup>a)</sup> Also affiliated with the Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan, Republic of China.

given here. A few modifications have been made in order to carry out the reaction at high temperature.

The quartz reaction cell wrapped with the Nichrome heater and heat insulator was resistively heated to the desired temperature. A temperature controller (Omega model CN9000) monitored the output of a type *K* thermocouple (inserted slightly above the laser-probed reaction zone) and regulated the temperature of the cell to  $\pm 2^\circ\text{C}$ . The thermocouple was calibrated to  $\pm 1^\circ\text{C}$ . In a few experiments, the temperature of the reactants was also derived from the intensity distribution of various rotational lines in the laser excitation spectrum of OH; consistent results were obtained. The uniformity of the temperature in the reaction zone was checked by moving the thermocouple along the probed volume; the deviation was determined to be less than 1%.

Because  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  decompose at high temperature, an alternative source of OH was used. The OH radicals were generated by photolysis of  $\text{N}_2\text{O}$  with an ArF laser (193 nm, 3–10  $\text{mJ cm}^{-2}$ ) to give  $\text{O}(^1D)$  and  $\text{N}_2$ ,



followed by the rapid reaction of  $\text{O}(^1D)$  with  $\text{H}_2\text{O}$ ,



in which  $k_6 = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>32</sup> Because the temporal profile of  $[\text{OH}]$  was monitored normally in the reaction period 50  $\mu\text{s}$ –10 ms, a relatively large concentration of  $\text{H}_2\text{O}$  ( $\sim 5 \times 10^{15} \text{ molecules cm}^{-3}$ ) was added in order to convert most  $\text{O}(^1D)$  into OH within 5  $\mu\text{s}$  after photolysis.

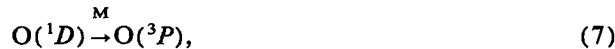
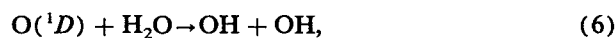
The relative concentration of OH was determined from the gated integrated fluorescence intensity of OH which was excited by a probe laser at a varied delay after the photolysis laser. The probe laser was a frequency-doubled dye laser pumped by the 532 nm emission of a Nd-YAG laser. The excitation wavelength of OH was 282.0 nm and the fluorescence near 310 nm was detected. The repetition rates of both lasers were set at 10 Hz and the fluorescence signal was typically averaged over 100 pulses at each delay.

All experiments were carried out under slow flow conditions so as to replenish the reactants. The diluent gas He (99.9995%) was used without further purification.  $\text{N}_2\text{O}$  (99%) was degassed at 165 K before used. A diluted gas sample of  $\text{C}_2\text{H}_4$  (1.75%  $\pm$  0.07% in He) prepared with standard gas-handling techniques was used in the experiments. The concentration of the  $\text{C}_2\text{H}_4/\text{He}$  mixture was determined by comparison of the integrated IR absorption (resolution 1  $\text{cm}^{-1}$ ) to those samples with known concentration.

Typical experimental conditions were as follows: total flow rate  $F_T = 7 - 16 \text{ STP cm}^3 \text{ s}^{-1}$  (STP = 1 atm and 273 K); total pressure  $P = 278 - 616 \text{ Torr}$ ; reaction temperature  $T = 544 - 673 \text{ K}$ ; flow velocity  $\bar{v} \approx 2 - 5 \text{ cm s}^{-1}$ ;  $[\text{H}_2\text{O}] \approx (4 - 7) \times 10^{15} \text{ molecules cm}^{-3}$ ;  $[\text{N}_2\text{O}] \approx (0.2 - 2.0) \times 10^{15} \text{ molecules cm}^{-3}$ ;  $[\text{C}_2\text{H}_4] \approx (2.4 - 199.8) \times 10^{14} \text{ molecules cm}^{-3}$ ;  $[\text{OH}]_0 \approx (1 - 4) \times 10^{11} \text{ molecules cm}^{-3}$ ; the interval between the photolysis laser and the probe laser is  $t = 20 \mu\text{s} - 30 \text{ ms}$ .

### III. RESULTS AND DISCUSSION

Photolysis of  $\text{N}_2\text{O}$  with the ArF laser produced  $\text{O}(^1D)$  almost instantly. However, the reaction of  $\text{O}(^1D)$  with  $\text{H}_2\text{O}$  required a few microseconds for completion. The OH radicals were produced rapidly, reached their maximum concentration in less than 5  $\mu\text{s}$ , and decayed slowly afterwards. A simplified mechanism consisting of the following reactions:



was used to model the production of OH. Reaction (7) includes all possible  $\text{O}(^1D)$ -depletion reactions other than reaction (6). The temporal profile of OH was derived by solution of the differential rate equations for reactions (6)–(8)

$$[\text{OH}] = 2k_6 [\text{H}_2\text{O}] [\text{O}(^1D)]_0 [\exp(-k_8 t) - \exp(-k_q t)] / (k_q - k_8), \quad (9)$$

in which

$$k_q = k_6 [\text{H}_2\text{O}] + k_7 \quad (10)$$

and  $[\text{O}(^1D)]_0$  is the initial concentration of  $\text{O}(^1D)$  after photolysis. Provided that  $k_q \gg k_8$ , the maximum concentration of OH is expressed by the equation

$$[\text{OH}]_{\text{max}} = 2k_6 [\text{H}_2\text{O}] [\text{O}(^1D)]_0 / k_q. \quad (11)$$

Typically  $k_q$  was adjusted to exceed  $1 \times 10^6 \text{ s}^{-1}$  so that  $[\text{OH}]_{\text{max}}$  was reached within 10  $\mu\text{s}$  after photolysis; hence  $[\text{OH}]_{\text{max}}$  was taken as  $[\text{OH}]_0$ , the 'initial'  $[\text{OH}]$  before its reaction with  $\text{C}_2\text{H}_4$ . The decay rate of OH,  $k_8$ , was normally in the range 20–80  $\text{s}^{-1}$ .

The title reaction was then carried out with  $[\text{C}_2\text{H}_4] \gg [\text{OH}]_0$  in the reaction cell. In Fig. 1, typical temporal profiles of  $[\text{OH}]$  at various concentrations of  $\text{C}_2\text{H}_4$  at 575 K are shown. The double-exponential character was not evident in the temporal profile of  $[\text{OH}]$  with smaller

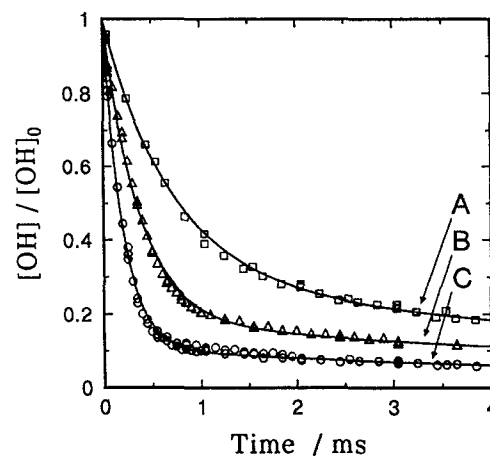
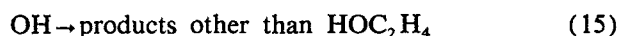
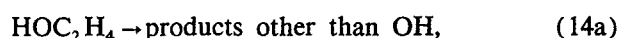
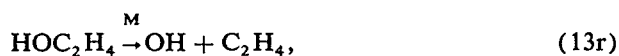
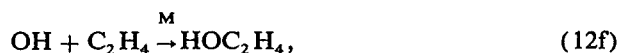


FIG. 1. Temporal profiles of  $[\text{OH}]$  at 286 Torr and 575 K.  $[\text{OH}]_0 \approx 1 \times 10^{11} \text{ molecules cm}^{-3}$ ,  $[\text{C}_2\text{H}_4]$  ( $10^{15} \text{ molecules cm}^{-3}$ ) = (A) 0.65; (B) 1.27; (C) 2.36. The solid curves represent the nonlinear least-squares fit.

[C<sub>2</sub>H<sub>4</sub>] (trace A); data of such decay characteristics were not used. Traces B and C, obtained with greater [C<sub>2</sub>H<sub>4</sub>], exhibited distinctly double-exponential decays with a rapid decay toward the equilibrium concentration within 1 ms of reaction period followed by a much slower decay in the milli-second range. An increase in [C<sub>2</sub>H<sub>4</sub>] decreased [OH] more rapidly and resulted in a smaller [OH]/[OH]<sub>0</sub> ratio throughout the entire decay.

A simplified mechanism consisting of reactions (6), (7), and



was used to model the reactions. For clarity, the rate coefficients of reactions (12)–(14) are expressed as  $k_f$  (the effective second-order rate coefficient for the forward reaction),  $k_r$  (the effective first-order rate coefficient for the reverse reaction), and  $k_a$  (the effective first-order rate coefficient for the reaction of the adduct), respectively. Reaction (14) includes the possible isomerization and decomposition processes of HOC<sub>2</sub>H<sub>4</sub> other than reaction (13), as well as the diffusion of HOC<sub>2</sub>H<sub>4</sub> from the probed volume. Reaction (15) is an extension of reaction (8); it takes into account reaction (4) (the H-atom abstraction channel), all possible reactions of OH with species other than C<sub>2</sub>H<sub>4</sub>, and the diffusion of OH away from the probed volume. To the first approximation,

$$k_{15} \simeq k_4 [\text{C}_2\text{H}_4] + k_8. \quad (16)$$

We derived the temporal profile of [OH] in the presence of C<sub>2</sub>H<sub>4</sub> by solving the differential rate equations for reactions (6), (7), and (12)–(15) to yield

$$[\text{OH}] = 2k_6 [\text{H}_2\text{O}] [\text{O}(^1D)]_0 \left[ \frac{(\gamma - k_q) \exp(-k_q t)}{(k_q - \lambda_1)(k_q - \lambda_2)} + \frac{(\gamma - \lambda_1) \exp(-\lambda_1 t)}{(k_q - \lambda_1)(\lambda_2 - \lambda_1)} - \frac{(\gamma - \lambda_2) \exp(-\lambda_2 t)}{(k_q - \lambda_2)(\lambda_2 - \lambda_1)} \right], \quad (17)$$

in which

$$\lambda_1 = [\alpha - (\alpha^2 - 4\beta)^{1/2}]/2 > 0, \quad (18)$$

$$\lambda_2 = [\alpha + (\alpha^2 - 4\beta)^{1/2}]/2 > \lambda_1 > 0, \quad (19)$$

$$\gamma = k_r + k_a, \quad (20)$$

$$\alpha = k_f [\text{C}_2\text{H}_4] + k_r + k_a + k_{15}, \quad (21)$$

$$\beta = k_f k_a [\text{C}_2\text{H}_4] + k_r k_{15} + k_a k_{15}. \quad (22)$$

Provided that  $k_q \gg \lambda_2 \gg \lambda_1$ , the initial rise of [OH] is taken as instantaneous and the expression for [OH] is simplified to

$$[\text{OH}] = [\text{OH}]_0 [(\gamma - \lambda_1) \exp(-\lambda_1 t) - (\gamma - \lambda_2) \exp(-\lambda_2 t)] / (\lambda_2 - \lambda_1). \quad (23)$$

Equation (23) is identical to that derived previously<sup>43</sup> from

a four-step mechanism for the reaction of OH + CS<sub>2</sub> in which OH was produced directly from photolysis of HNO<sub>3</sub> or H<sub>2</sub>O<sub>2</sub>. Because data points with a reaction period less than 50 μs were generally not used, the rise of [OH] did not interfere in the fitting of the temporal profile to a double-exponential decay of [OH].

In order to obtain accurate values of the parameters  $\lambda_1$ ,  $\lambda_2$ , and  $\gamma$  from the least-squares fit of the [OH] temporal profile using Eq. (23), we adjusted the experimental conditions so that a distinctly double-exponential decay profile of [OH] was observed (i.e.,  $\alpha^2 \gg \beta$ , which also implies that  $\lambda_2 \simeq \alpha \gg \lambda_1 \simeq \beta/\alpha$ ). Under such conditions, the reactions may be taken as a two-step process—a rapid approach to equilibrium and a slow decay after the equilibrium is reached. The component of the slow decay is expressed as

$$[\text{OH}] = [\text{OH}]_0 (\gamma - \lambda_1) \exp(-\lambda_1 t) / (\lambda_2 - \lambda_1) = [\text{OH}]_{\text{eq}} \exp(-\lambda_1 t). \quad (24)$$

If the equilibrium concentration of OH, [OH]<sub>eq</sub>, was not too small,  $\lambda_1$  could be determined accurately. At lower temperatures, the forward reaction is much more rapid than the reverse reaction; hence the equilibrium constant  $K_c$  becomes greater

$$K_c = k_f/k_r = [\text{HOC}_2\text{H}_4]_{\text{eq}}/[\text{OH}]_{\text{eq}} [\text{C}_2\text{H}_4]_{\text{eq}}. \quad (25)$$

In order to maintain a suitable value of [OH]<sub>eq</sub> for accurate measurements of rate coefficients, we decreased the initial concentration of C<sub>2</sub>H<sub>4</sub>. However, the decrease in [C<sub>2</sub>H<sub>4</sub>] reduces  $\alpha^2$  more rapidly than  $\beta$ ; consequently, the condition  $\lambda_2 \gg \lambda_1$  does not hold for small [C<sub>2</sub>H<sub>4</sub>]. At higher temperatures, the rate of the reverse reaction becomes greater, hence large [C<sub>2</sub>H<sub>4</sub>] was used in order to maintain a reasonable [OH]<sub>eq</sub>. However, at  $T > 673$  K, we found it difficult to maintain the condition  $\lambda_2 \gg \lambda_1$  because the rate coefficients of the loss of HOC<sub>2</sub>H<sub>4</sub> and OH,  $k_r$ ,  $k_a$ , and  $k_{15}$  increased rapidly at higher temperature. Therefore, temporal profiles of [OH] with distinctly double-exponential decay could be obtained within only limited ranges of temperature, pressure, and [C<sub>2</sub>H<sub>4</sub>].

The observed temporal profiles of [OH] were fitted to Eq. (23) by means of a nonlinear least-squares method to determine  $\lambda_1$ ,  $\lambda_2$ , and  $\gamma$ . The values of  $\alpha$  and  $\beta$  were then derived from  $\lambda_1$  and  $\lambda_2$  according to Eqs. (18) and (19). The determined values of  $\alpha$ ,  $\beta$ ,  $\gamma$ , and the experimental conditions are all listed in Tables I and II.

It is difficult to derive individual rate coefficient accurately without the knowledge of either  $k_a$  or  $k_{15}$ . As described previously,<sup>43</sup> for the temporal profiles with distinctly double-exponential behavior, a simple method was used to determine the equilibrium constant without an explicit solution of  $k_f$  and  $k_r$ . If the fraction of unreacted OH when the equilibrium was reached is expressed as  $x_{\text{eq}}$ , from Eq. (24)

$$x_{\text{eq}} = [\text{OH}]_{\text{eq}}/[\text{OH}]_0 = (\gamma - \lambda_1)/(\lambda_2 - \lambda_1). \quad (26)$$

If one assumes that reactions (14) and (15) were negligible when the equilibrium was reached under our experimental conditions,

$$[\text{HOC}_2\text{H}_4]_{\text{eq}} = [\text{OH}]_0 - [\text{OH}]_{\text{eq}}. \quad (27)$$

Accordingly, the equilibrium constant  $K_c$  becomes

TABLE I. A summary of experimental conditions and fitted decay parameters of the temporal profile of [OH] at  $544 < T < 595$  K.<sup>a</sup>

Expt. no.	<i>T</i> (K)	<i>P</i> (Torr)	[C <sub>2</sub> H <sub>4</sub> ] (10 <sup>13</sup> ) <sup>b</sup>	[N <sub>2</sub> O] (10 <sup>13</sup> ) <sup>b</sup>	[H <sub>2</sub> O] (10 <sup>14</sup> ) <sup>b</sup>	$\alpha$ (10 <sup>3</sup> s <sup>-1</sup> )	$\beta$ (10 <sup>5</sup> s <sup>-2</sup> )	$\gamma$ (10 <sup>2</sup> s <sup>-1</sup> )	$x_{\text{eq}}$ (10 <sup>-2</sup> )	$K_p$ (10 <sup>4</sup> atm <sup>-1</sup> )
1	544	387	23.5	220	62	0.95 ± 0.02	0.34 ± 0.07	1.73 ± 0.16	15.5 ± 2.0	31.36 ± 5.14
2		384	36.8			1.50 ± 0.02	0.58 ± 0.11	1.93 ± 0.16	10.8 ± 1.2	30.13 ± 4.15
3	550	613	37.8	16	70	1.62 ± 0.02	1.02 ± 0.08	2.74 ± 0.13	14.0 ± 1.0	21.64 ± 2.07
4	558	384	29.8	215	60	1.27 ± 0.02	0.85 ± 0.05	3.67 ± 0.15	26.2 ± 1.5	12.40 ± 1.13
5		385	52.4			2.04 ± 0.03	1.44 ± 0.10	3.91 ± 0.16	16.8 ± 0.9	12.43 ± 1.00
6			100.7			3.61 ± 0.07	2.49 ± 0.57	4.21 ± 0.36	10.1 ± 1.1	11.59 ± 1.57
7	566	610	47.7	150	68	1.92 ± 0.04	1.80 ± 0.09	5.40 ± 0.22	25.6 ± 1.4	7.88 ± 0.69
8		612	75.0			3.11 ± 0.05	2.89 ± 0.25	5.49 ± 0.26	15.5 ± 1.0	9.39 ± 0.83
9		611	93.1			3.64 ± 0.04	3.57 ± 0.23	5.47 ± 0.20	13.0 ± 0.6	9.35 ± 0.71
10	573	537	40.5	83	53	1.78 ± 0.04	1.51 ± 0.05	7.19 ± 0.23	39.4 ± 1.7	4.88 ± 0.42
11		539	73.4			2.76 ± 0.05	2.57 ± 0.13	7.66 ± 0.29	26.1 ± 1.2	4.95 ± 0.40
12	572	539	107.2			4.18 ± 0.07	3.90 ± 0.23	7.87 ± 0.28	17.4 ± 0.8	5.70 ± 0.42
13	575	286	126.6			2.83 ± 0.05	3.22 ± 0.20	5.87 ± 0.26	18.0 ± 1.1	4.58 ± 0.40
14	575	290	163.3			3.73 ± 0.04	4.28 ± 0.26	6.15 ± 0.22	14.2 ± 0.7	4.72 ± 0.35
15	573	278	169.2			3.43 ± 0.10	4.39 ± 0.54	6.02 ± 0.48	14.8 ± 1.7	4.35 ± 0.61
16	575	286	236.2			5.17 ± 0.07	7.00 ± 0.68	6.61 ± 0.32	10.7 ± 0.7	4.52 ± 0.41
17	581	613	66.2	140	66	2.94 ± 0.06	3.98 ± 0.21	9.22 ± 0.38	29.3 ± 1.6	4.59 ± 0.42
18		614	101.3			4.38 ± 0.06	6.17 ± 0.30	9.56 ± 0.29	19.8 ± 0.8	5.04 ± 0.35
19	590	614	79.1	138	65	3.82 ± 0.06	6.09 ± 0.15	13.02 ± 0.30	32.6 ± 1.0	3.26 ± 0.22
20		615	123.6			4.54 ± 0.13	7.29 ± 0.59	11.45 ± 0.64	23.2 ± 1.7	3.33 ± 0.35
21			165.1			5.91 ± 0.14	9.43 ± 0.79	11.51 ± 0.59	17.7 ± 1.2	3.51 ± 0.33
22	593	380	71.6	202	62	2.83 ± 0.08	4.28 ± 0.20	12.60 ± 0.56	43.9 ± 2.6	2.21 ± 0.26
23	595	386	101.5			3.71 ± 0.07	5.34 ± 0.21	14.21 ± 0.43	37.2 ± 1.5	2.05 ± 0.16
24	594	382	128.8			4.82 ± 0.07	7.77 ± 0.28	14.18 ± 0.35	27.9 ± 0.9	2.48 ± 0.17
25	593	386	192.9			6.49 ± 0.11	9.97 ± 0.57	14.19 ± 0.45	20.4 ± 0.8	2.50 ± 0.18

<sup>a</sup>The uncertainties represent one standard deviation.<sup>b</sup>In units of molecules cm<sup>-3</sup>.TABLE II. A summary of experimental conditions and fitted decay parameters of the temporal profile of [OH] at  $603 < T < 673$  K.<sup>a</sup>

Expt. no.	<i>T</i> (K)	<i>P</i> (Torr)	[C <sub>2</sub> H <sub>4</sub> ] (10 <sup>13</sup> ) <sup>b</sup>	[N <sub>2</sub> O] (10 <sup>13</sup> ) <sup>b</sup>	[H <sub>2</sub> O] (10 <sup>14</sup> ) <sup>b</sup>	$\alpha$ (10 <sup>3</sup> s <sup>-1</sup> )	$\beta$ (10 <sup>5</sup> s <sup>-2</sup> )	$\gamma$ (10 <sup>2</sup> s <sup>-1</sup> )	$x_{\text{eq}}$ (10 <sup>-2</sup> )	$K_p$ (10 <sup>4</sup> atm <sup>-1</sup> )
26	603	616	191.5	140	63	6.62 ± 0.15	14.27 ± 0.52	24.35 ± 0.76	35.8 ± 1.5	1.14 ± 0.09
27		320	99.9	73	56	3.79 ± 0.10	8.10 ± 0.33	15.67 ± 0.63	40.2 ± 2.2	1.81 ± 0.19
28		322	166.7			5.36 ± 0.12	11.41 ± 0.64	16.16 ± 0.66	28.4 ± 1.5	1.85 ± 0.17
29		316	251.3			6.07 ± 0.11	12.89 ± 0.59	16.52 ± 0.53	25.4 ± 1.0	1.42 ± 0.11
30		320	517.3			11.29 ± 0.15	28.85 ± 1.65	18.12 ± 0.57	14.4 ± 0.6	1.40 ± 0.10
31	613	411	109.6	38	72	4.08 ± 0.14	8.66 ± 0.38	23.94 ± 0.97	54.2 ± 3.2	0.924 ± 0.129
32	612	410	758.9			16.66 ± 0.34	25.32 ± 1.06	20.26 ± 1.73	11.4 ± 1.2	1.22 ± 0.15
33	623	322	263.0	70	54	7.42 ± 0.24	23.98 ± 1.06	31.50 ± 1.37	41.7 ± 2.5	0.626 ± 0.070
34			495.8			11.46 ± 0.22	46.36 ± 2.59	30.99 ± 1.12	25.2 ± 1.2	0.704 ± 0.056
35		323	819.0			16.93 ± 0.26	71.28 ± 4.55	33.25 ± 1.16	18.0 ± 0.8	0.655 ± 0.048
36	633	519	419.4	49	47	11.32 ± 0.30	69.79 ± 4.72	40.30 ± 2.13	33.7 ± 2.3	0.543 ± 0.062
37	631	513	643.9			16.63 ± 0.34	101.12 ± 9.73	43.16 ± 2.23	24.0 ± 1.6	0.573 ± 0.057
38	634	528	787.8			25.00 ± 0.59	128.01 ± 21.63	48.39 ± 3.27	18.0 ± 1.5	0.669 ± 0.075
39	633	528	1026			24.96 ± 0.51	127.48 ± 25.71	38.86 ± 2.97	14.1 ± 1.4	0.690 ± 0.084
40	643	320	797.2	68	53	15.26 ± 0.49	111.4 ± 6.19	53.97 ± 2.74	33.7 ± 2.3	0.281 ± 0.032
41			893.0			17.69 ± 0.40	113.3 ± 4.53	57.53 ± 1.97	31.1 ± 1.4	0.283 ± 0.023
42			1097			20.31 ± 0.49	143.7 ± 9.14	59.52 ± 2.63	27.7 ± 1.6	0.272 ± 0.025
43	653	408	841.5	83	55	19.06 ± 0.41	172.0 ± 6.41	77.79 ± 2.60	39.8 ± 1.8	0.202 ± 0.018
44		410	1128			22.70 ± 0.61	201.7 ± 16.3	71.71 ± 3.70	30.0 ± 2.0	0.233 ± 0.025
45		408	1448			29.39 ± 0.59	298.6 ± 16.8	75.24 ± 2.87	23.7 ± 1.2	0.250 ± 0.020
46	663	321	1350	66	50	25.98 ± 0.72	333.4 ± 15.7	94.26 ± 4.05	34.7 ± 2.0	0.154 ± 0.016
47	662	322	1998			35.59 ± 0.87	467.5 ± 35.3	91.72 ± 4.63	23.8 ± 1.6	0.178 ± 0.018
48	673	508	1622	98	38	53.98 ± 2.93	1202 ± 136	180.6 ± 16.7	31.9 ± 3.8	0.144 ± 0.026

<sup>a</sup>The uncertainties represent one standard deviation.<sup>b</sup>In units of molecules cm<sup>-3</sup>.

$$K_c = k_f/k_r = (1 - x_{\text{eq}})/x_{\text{eq}} [\text{C}_2\text{H}_4]. \quad (28)$$

The equilibrium constant  $K_p$  (in units of  $\text{atm}^{-1}$ ) was calculated from

$$K_p = K_c/RT = 7.34 \times 10^{21} K_c/T, \quad (29)$$

in which  $K_c$  is expressed in units of  $\text{cm}^3 \text{ molecule}^{-1}$  and  $T$  in K. The values of  $x_{\text{eq}}$  and  $K_p$  derived from Eqs. (26)–(29) are also listed in Tables I and II. The condition  $\alpha^2 \gg \beta$  can be verified from the values listed in Tables I and II; generally  $\beta < 0.06 \alpha^2$ .

The error in the measurement of  $[\text{OH}]$  due to the error in the subtraction of the scattered light from the LIF signal is estimated to be  $\sim 2\%$  of  $[\text{OH}]_0$ . If the entire  $[\text{OH}]$  temporal profile is shifted upward by  $0.02 [\text{OH}]_0$ , the derived values of  $K_p$  decrease by  $\sim 6\%$ . Uncertainty in the  $[\text{OH}]_0$  measurement due to the instability of the LIF signal and the error in the timing of the two lasers is estimated to be approximately  $3\%$ . If the entire  $[\text{OH}]$  temporal profile is multiplied by  $1.03$ , the derived values of  $K_p$  decrease by  $\sim 4\%$ , respectively. The  $\sim 10 \mu\text{s}$  delay in the generation of OH after photolysis introduces  $\sim 2\%$  error in the  $K_p$  values. The  $[\text{OH}]_{\text{eq}}$  in Eq. (24) was overestimated because the equation ignored the period required for the equilibrium to be reached. The error in  $x_{\text{eq}}$  depends on  $\lambda_1$  and it is typically less than  $2\%$ . The standard error of  $K_p$  values determined from the derived  $x_{\text{eq}}$  in the nonlinear fitting were typically  $\pm 10\%$ . The systematic errors in the measurements of temperature and  $[\text{C}_2\text{H}_4]$  were about  $\pm 2\%$  and  $\pm 5\%$ , respectively. Therefore, the 95% confidence limits for the measurements of  $K_p$  are estimated to be approximately  $\pm 25\%$ .

### A. The enthalpy and the entropy changes of $\text{OH} + \text{C}_2\text{H}_4 \rightarrow \text{HOC}_2\text{H}_4$

The van't Hoff plot  $K_p$  vs  $T^{-1}$  is shown in Fig. 2. As illustrated in the figure, the values of  $K_p$  obtained at high pressure (symbol  $\square$  for  $513 < P < 616$  Torr) are within experimental uncertainties of those at low pressure (symbol  $\circ$  for  $278 < P < 411$  Torr). The values of  $K_p$  are also independent of  $[\text{C}_2\text{H}_4]$ . The excellent linearity in Fig. 2 indicates that within experimental uncertainties,  $\Delta H$  is independent of temperature; they were fitted well to the linear van't Hoff equation

$$\ln K_p = -(\Delta H/R)T^{-1} + \Delta S/R. \quad (30)$$

The fit yielded  $\Delta H = -(30.3 \pm 0.5) \text{ kcal mol}^{-1}$ ; the uncertainties represent one standard deviation. The values of  $\Delta S$  were then derived from  $\Delta H$  and values of  $K_p$  for each experiment by using Eq. (30); an average of  $\Delta S = -(30.9 \pm 0.3) \text{ cal K}^{-1} \text{ mol}^{-1}$  was obtained. Considering the errors in  $K_p$  and  $T$ , we report  $\Delta H = -(30.3 \pm 0.8) \text{ kcal mol}^{-1}$  and  $\Delta S = -(30.9 \pm 1.0) \text{ cal K}^{-1} \text{ mol}^{-1}$  at  $544 \leq T \leq 673 \text{ K}$ .

The values of  $\Delta H$  and  $\Delta S$  determined at high temperatures can be corrected to give  $\Delta H^0$  and  $\Delta S^0$  by means of statistical thermodynamics. On the basis of the structure and vibrational frequencies of  $\text{HOC}_2\text{H}_4$  predicted by Sosa and Schlegel,<sup>38,39</sup> corrections of  $-0.4 \text{ kcal mol}^{-1}$  and  $-0.5$

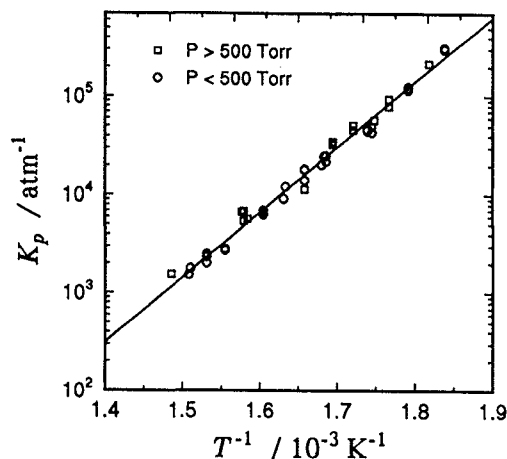
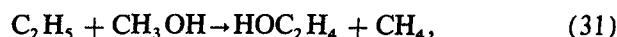


FIG. 2. A van't Hoff plot for the  $\text{OH} + \text{C}_2\text{H}_4 \rightleftharpoons \text{M}^{\text{HOC}_2\text{H}_4}$  equilibrium.  $\square$ — $513 < P < 616$  Torr;  $\circ$ — $278 < P < 411$  Torr.

$\text{cal K}^{-1} \text{ mol}^{-1}$  were derived for  $\Delta H$  and  $\Delta S$ , respectively, for the alternation of temperature from 600 to 298 K. The correction was not changed for  $\Delta H$ , but decreased to  $-0.4 \text{ cal K}^{-1} \text{ mol}^{-1}$  for  $\Delta S$  when the listed vibrational frequencies of  $\text{HOC}_2\text{H}_4$  were decreased by  $13\%$ ; the reduction ratio was determined by comparison of the observed vibrational frequencies of  $\text{C}_2\text{H}_4$  with the theoretical prediction at the same level of sophistication as that for  $\text{HOC}_2\text{H}_4$ . Thus,  $\Delta H^0 = -(30.7 \pm 0.9) \text{ kcal mol}^{-1}$  and  $\Delta S^0 = -(31.3 \pm 1.1) \text{ cal K}^{-1} \text{ mol}^{-1}$ .

To our knowledge, no experimental determination of  $\Delta H$  and  $\Delta S$  for the title reaction has been reported. Hinsta *et al.*<sup>44</sup> photodissociated a molecular beam containing 2-bromoethanol with 193 nm laser emission. They found that some  $\text{HOC}_2\text{H}_4$  containing up to  $43 \text{ kcal mol}^{-1}$  of internal energy survived from further dissociation to  $\text{OH} + \text{C}_2\text{H}_4$ ; the value was much greater than the expected  $\text{HO}-\text{C}_2\text{H}_4$  bond energy. They proposed that the internal energy in  $\text{HOC}_2\text{H}_4$  was probably mostly rotational and could not all be used to break the C–O bond, thus allowing the detection of metastable  $\text{HOC}_2\text{H}_4$ .

A few methods have been used to estimate  $\Delta H^0$  of reaction (12). Application of the additivity rule of Benson gave  $\Delta H_f^0(\text{HOC}_2\text{H}_4) = -10.2 \text{ kcal mol}^{-1}$ ; this result implies  $\Delta H^0 = -32.1 \text{ kcal mol}^{-1}$ .<sup>41</sup> Assuming that the C–H bond strength in  $\text{C}_2\text{H}_5\text{OH}$  is  $\sim 95.1 \text{ kcal mol}^{-1}$ ,<sup>45</sup>  $\Delta H_f^0(\text{HOC}_2\text{H}_4) = -13.1 \text{ kcal mol}^{-1}$  was derived by using  $\Delta H_f^0(\text{H}) = 52.1$ , and  $\Delta H_f^0(\text{C}_2\text{H}_5\text{OH}) = -56.1 \text{ kcal mol}^{-1}$ ,<sup>46</sup> hence  $\Delta H^0 = -35.0 \text{ kcal mol}^{-1}$ . However, when the C–H bond strength of  $\text{C}_2\text{H}_6$   $100.7 \pm 1.0 \text{ kcal mol}^{-1}$  (Ref. 47) was used for that of  $\text{H}-\text{C}_2\text{H}_4\text{OH}$ ,  $\Delta H_0 = -29.5 \text{ kcal mol}^{-1}$  was derived instead. Although previous *ab initio* calculations yielded smaller values of  $\Delta H \approx -24 \text{ kcal mol}^{-1}$ ,<sup>38,40</sup> Sosa and Schlegel recently used a larger basis set and corrected their value of  $\Delta H_f(\text{HOC}_2\text{H}_4)$  based on comparison of the theoretical calculation of the isodesmic reaction



with given experimental values of  $\Delta H_f^\circ$  for  $\text{C}_2\text{H}_5$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CH}_4$ ; the corrected value yielded  $\Delta H = -29$  kcal mol $^{-1}$ .<sup>39</sup> The values derived from *ab initio* calculation represent  $T = 0$  K; a correction of  $-1.1$  kcal mol $^{-1}$  should be employed to yield  $\Delta H^\circ$  at 298 K. Our experimental value  $\Delta H^\circ = -(30.7 \pm 0.9)$  kcal mol $^{-1}$  is consistent with most of these estimates.

The entropy of  $\text{HOC}_2\text{H}_4$  can be estimated from its structure and the vibrational frequencies predicted by theory. A value  $S^\circ(\text{HOC}_2\text{H}_4) = 66.8$  cal K $^{-1}$  mol $^{-1}$  was calculated when the vibrational frequencies listed by Sosa and Schlegel<sup>39</sup> were used; the value decreased to 65.8 cal K $^{-1}$  mol $^{-1}$  when the vibrational frequencies were decreased by 13%. With  $S^\circ(\text{OH}) = 43.9$  and  $S^\circ(\text{C}_2\text{H}_4) = 52.4$  cal K $^{-1}$  mol $^{-1}$ ,<sup>46</sup> our experimental result of  $\Delta S^\circ = -(31.3 \pm 1.1)$  cal K $^{-1}$  mol $^{-1}$  yielded  $S^\circ(\text{HOC}_2\text{H}_4) = 65.0 \pm 1.1$  cal K $^{-1}$  mol $^{-1}$ . Considering the possible uncertainties in the predicted structure and vibrational frequencies of  $\text{HOC}_2\text{H}_4$ , the agreement is excellent.

## B. Assumptions in the derivation of the individual rate coefficients

To derive  $k_f$ ,  $k_r$ ,  $k_a$ , and  $k_{15}$  from the measured  $\alpha$ ,  $\beta$ , and  $\gamma$  by using Eqs. (20)–(22) requires certain assumptions or approximations. If one assumes that reaction (4), the H-abstraction channel, is negligible, the values  $k_{15}$  are approxi-

mated by  $k_8$  which were determined by a fit of the  $[\text{OH}]$  temporal profiles recorded in the absence of  $\text{C}_2\text{H}_4$ ; hence the values of  $k_f$ ,  $k_r$ , and  $k_a$  were determined. This assumption is certainly valid at low temperature, but may not hold at temperatures above 600 K. Tables III and IV list the values of  $k_8$  determined from experiments and the rate coefficients  $k_f$ ,  $k_r$ , and  $k_a$  derived when  $k_{15} = k_8$  was assumed. The corresponding values of  $K_p$ , derived from  $k_f/k_rRT$ , are also listed. The  $K_p$  values thus obtained are slightly greater, but within experimental uncertainties of those listed in Tables I and II which were derived from values of  $x_{\text{eq}}$ . A fit of  $K_p$  to Eq. (30) yielded  $\Delta H = -(29.7 \pm 0.5)$  kcal mol $^{-1}$  and  $\Delta S = -(29.8 \pm 0.3)$  cal K $^{-1}$  mol $^{-1}$  within experimental uncertainties of those reported in the previous section.

If the rate expression for the H-atom abstraction channel reported by Tully<sup>18</sup>

$$k_4 = (3.36 \pm 0.64) \times 10^{-11} \exp[-(2997 \pm 144)/T] \times \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (32)$$

were used to derive  $k_{15}$  from Eq. (16), the  $k_a$  values determined by solving Eqs. (20)–(22) became negative for many experiments at higher temperature (nos. 32, 35, and 40–47 in Table II); therefore it is likely that Eq. (32) overestimated the rate coefficient  $k_4$ .

In order to estimate an upper limit of  $k_a$ , one could assume that the rate coefficient of the adduct loss  $k_a$  was

TABLE III. A summary of rate coefficients at  $544 < T < 595$  K derived from various assumptions.

Expt. no.	$T$ (K)	$[\text{C}_2\text{H}_4]$ ( $10^{13}$ ) <sup>a</sup>	$k_8$ ( $\text{s}^{-1}$ )	Assuming $k_{15} = k_8$				Assuming $k_a = 40 \text{ s}^{-1}$				Assuming Eq. (33) for $k_a$				
				$k_a$ ( $\text{s}^{-1}$ )	$k_f^b$	$k_r$ ( $\text{s}^{-1}$ )	$K_p$ ( $10^4 \text{ atm}^{-1}$ )	$k_{15}$ ( $\text{s}^{-1}$ )	$k_4^c$	$k_f^b$	$k_r$ ( $\text{s}^{-1}$ )	$K_p$ ( $10^4 \text{ atm}^{-1}$ )	$k_a$ ( $\text{s}^{-1}$ )	$k_f^b$	$k_r$ ( $\text{s}^{-1}$ )	$K_p$ ( $10^4 \text{ atm}^{-1}$ )
1	544	23.5	22	40	3.21	132	32.70	22	0	3.15	133	31.92	39	3.19	133	32.27
2		36.8		42	3.48	152	30.99	37	0.41	3.43	153	30.26	40	3.49	152	30.83
3	550	37.8	20	73	3.50	201	23.21	206	4.92	3.00	234	17.11	71	3.49	202	22.92
4	558	29.8	68	71	2.81	296	12.47	150	2.75	2.51	327	10.10	68	2.78	298	12.27
5		52.4		74	3.02	317	12.51	222	2.94	2.74	351	10.28	71	3.00	320	12.31
6		100.7		71	3.10	351	11.61	314	2.49	2.84	381	9.81	67	3.07	353	11.44
7	566	47.7	20	125	2.85	415	8.88	250	4.82	2.35	500	6.11	120	2.82	419	8.72
8		75.0		110	3.38	439	9.98	363	4.57	2.93	509	7.47	105	3.36	443	9.83
9		93.1		113	3.30	434	9.86	460	4.73	2.83	507	7.24	108	3.27	437	9.67
10	573	40.5	20	132	2.57	587	5.60	160	3.46	2.25	679	4.25	124	2.54	594	5.48
11		73.4		122	2.69	644	5.35	244	3.05	2.40	726	4.23	114	2.67	651	5.25
12		107.1		111	3.14	676	5.97	340	2.99	2.85	747	4.90	104	3.12	682	5.86
13	575	126.6	100	123	1.69	464	4.66	425	2.57	1.43	547	3.34	113	1.67	472	4.50
14		163.3		122	1.85	493	4.78	528	2.62	1.59	575	3.52	112	1.82	501	4.63
15	573	169.2	86	141	1.62	460	4.50	580	2.92	1.33	562	3.03	131	1.59	469	4.34
16	575	236.2	100	144	1.86	517	4.60	837	3.12	1.56	621	3.20	134	1.84	526	4.46
17	581	66.2	20	190	3.02	733	5.21	360	5.14	2.51	882	3.60	181	2.99	741	5.10
18		101.3		176	3.36	780	5.43	524	4.98	2.87	916	3.96	167	3.33	788	5.34
19	590	79.1	20	233	3.16	1069	3.67	403	4.84	2.68	1262	2.64	220	3.13	1081	3.60
20		123.6		209	2.73	936	3.63	537	4.18	2.30	1105	2.60	196	2.70	948	3.54
21		165.1		194	2.87	957	3.73	677	3.98	2.47	1111	2.77	181	2.84	969	3.64
22	593	71.6	68	229	2.09	1031	2.51	299	3.23	1.76	1220	1.79	209	2.06	1050	2.43
23	595	101.5		196	2.19	1225	2.21	320	2.48	1.93	1381	1.72	175	2.16	1245	2.14
24	594	128.8		203	2.59	1215	2.63	465	3.08	2.28	1378	2.04	185	2.55	1232	2.56
25	593	192.9		180	2.59	1239	2.59	576	2.63	2.33	1379	2.09	162	2.56	1256	2.52

<sup>a</sup> In units of molecules cm $^{-3}$ .

<sup>b</sup> In units of  $10^{-12}$  cm $^3$  molecule $^{-1}$  s $^{-1}$ .

<sup>c</sup> In units of  $10^{-13}$  cm $^3$  molecule $^{-1}$  s $^{-1}$ .

TABLE IV. A summary of rate coefficients at 603 &lt;math&gt;T &lt; 673&lt;/math&gt; K derived from various assumptions.

Expt. no.	$T$ (K)	$[C_2H_4]$ ( $10^{13}$ ) <sup>a</sup>	$k_8$ ( $s^{-1}$ )	Assuming $k_{15} = k_8$				Assuming $k_a = 40 s^{-1}$				Assuming Eq. (33) for $k_4$					
				$k_a$ ( $s^{-1}$ )	$k_f^b$	$k_r$ ( $s^{-1}$ )	$K_p$ ( $10^4 atm^{-1}$ )	$k_{15}$ ( $s^{-1}$ )	$k_4^c$	$k_f^b$	$k_r$ ( $s^{-1}$ )	$K_p$ ( $10^4 atm^{-1}$ )	$k_a$ ( $s^{-1}$ )	$k_f^b$	$k_r$ ( $s^{-1}$ )	$K_p$ ( $10^4 atm^{-1}$ )	
26	603	191.5	20	331	2.18	2 104	1.26	526	2.64	1.91	2395	0.969	291	2.14	2 143	1.22	
27		99.9	36	345	2.19	1 222	2.18	472	4.36	1.75	1527	1.40	319	2.15	1 247	2.10	
28		166.7		292	2.23	1 324	2.05	629	3.56	1.87	1576	1.44	266	2.19	1 349	1.97	
29		251.3		280	1.75	1 372	1.55	690	2.60	1.49	1612	1.12	246	1.71	1 405	1.48	
30		517.3		299	1.83	1 514	1.47	1414	2.66	1.56	1772	1.07	263	1.79	1 548	1.41	
31	613	109.6	20	440	1.71	1 754	1.16	367	3.17	1.38	2154	0.768	389	1.67	1 804	1.11	
32	612	758.9		171	1.93	1 855	1.24	980	1.26	1.80	1986	1.09	129	1.89	1 896	1.19	
33	623	263.0	36	540	1.61	2 610	0.726	716	2.59	1.35	3110	0.512	454	1.57	2 695	0.685	
34		495.8		544	1.68	2 555	0.774	1406	2.76	1.40	3059	0.540	463	1.63	2 635	0.731	
35		819.0		517	1.66	2 808	0.695	2004	2.40	1.42	3285	0.508	429	1.61	2 895	0.656	
36	633	419.4	60	932	1.72	3 098	0.645	1676	3.85	1.34	3990	0.389	820	1.68	3 209	0.606	
37	631	643.9	50	807	1.90	3 508	0.631	2250	3.42	1.56	4276	0.425	701	1.86	3 614	0.598	
38	634	787.8	80	618	2.55	4 220	0.699	2499	3.07	2.24	4799	0.541	526	2.50	4 312	0.672	
39	633	1026		593	2.05	3 294	0.720	3095	2.94	1.75	3846	0.528	502	2.00	3 383	0.685	
40	643	797.2	36	1114	1.23	4 283	0.328	2006	2.47	0.99	5357	0.210	885	1.18	4 511	0.299	
41		893.0		935	1.33	4 818	0.316	1900	2.09	1.12	5713	0.225	708	1.28	5 044	0.290	
42		1097		989	1.31	4 964	0.300	2334	2.09	1.10	5912	0.212	749	1.25	5 202	0.275	
43	653	841.5	20	1514	1.34	6 266	0.240	2164	2.55	1.08	7739	0.157	1179	1.28	6 599	0.218	
44		1128		1292	1.37	5 880	0.263	2714	2.41	1.13	7131	0.179	991	1.32	6 179	0.240	
45		1448		1360	1.51	6 164	0.275	3873	2.66	1.24	7484	0.187	1073	1.45	6 450	0.253	
46	663	1350	36	1998	1.22	7 428	0.182	3482	2.55	0.97	9386	0.114	1513	1.16	7 912	0.162	
47	662	1998		1706	1.32	7 413	0.197	5004	2.49	1.07	9132	0.130	1326	1.26	7 845	0.178	
48	673	1622	50	3325	2.21	14 740	0.164	6591	4.03	1.81	18020	0.109	2763	2.14	15 296	0.153	
$E_a$ (kcal mol <sup>-1</sup> )				22.1 <sup>d</sup>	- 2.2 <sup>e</sup>	23.2				- 2.5 <sup>e</sup>	23.9			20.6 <sup>d</sup>	- 2.3 <sup>e</sup>	23.5	

<sup>a</sup>In units of molecules cm<sup>-3</sup>.<sup>b</sup>In units of 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>c</sup>In units of 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>d</sup>The value will increase by ~2.4 kcal mol<sup>-1</sup> when the rate of diffusion of C<sub>2</sub>H<sub>4</sub>OH away from the probed volume (~20 s<sup>-1</sup>) was subtracted from  $k_a$ .<sup>e</sup>Derived from fitting the data with  $P > 500$  Torr and  $T < 590$  K.

small. The value  $k_a = 40 s^{-1}$  derived previously at 544 K (experiments 1 and 2) should be a realistic estimate of  $k_a$  because  $k_{15}$  was small at that temperature; it is also consistent with the rate of diffusion away from the detection region for the adduct. This value was used for all temperatures to solve  $k_{15}$ ,  $k_f$ , and  $k_r$  by Eqs. (20)–(22). The results are also summarized in Tables III and IV. The values of  $K_p$ , calculated from the derived values of  $k_f$  and  $k_r$ , are also listed; they are approximately 25% smaller than those listed in Tables I and II and also showed greater variations, indicating that the assumption of a constant  $k_a$  was not adequate. Furthermore, the values of  $k_4$  calculated from Eq. (16) with the derived  $k_{15}$  values are also listed in Tables III and IV. They do not correlate well with  $T^{-1}$  and are within the range (2–5) × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for most experiments performed at 550 <math>T < 673</math> K, inconsistent with a large activation energy expected for the abstraction reaction. However, a fit of  $K_p$  to Eq. (30) yielded  $\Delta H = -(31.0 \pm 0.6)$  kcal mol<sup>-1</sup> and  $\Delta S = -(32.6 \pm 0.4)$  cal K<sup>-1</sup> mol<sup>-1</sup>, still close to our reported values; this result indicates that the  $\Delta H$  and  $\Delta S$  values are insensitive to the values of  $k_a$  and  $k_{15}$  under our experimental conditions.

A smaller value of  $k_4$  derived from a calculation using the bond-energy-bond-order (BEBO) method was recommended by Tsang and Hampson,<sup>48</sup>

$$k_4 = 2.6 \times 10^{-20} T^{2.75} \exp(-2100/T) \times \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (33)$$

Equation (33) predicts the  $k_4$  value of  $6.87 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 673 K, approximately 17% of that predicted by Eq. (32). When the predicted values of  $k_4$  were used to derive  $k_{15}$ , excellent results for  $k_f$ ,  $k_r$ ,  $k_a$ , and  $K_p$  were obtained, as also listed in Tables III and IV. The temperature dependence of  $K_p$  gave  $\Delta H = -(30.2 \pm 0.5)$  kcal mol<sup>-1</sup> and  $\Delta S = -(30.8 \pm 0.3)$  cal K<sup>-1</sup> mol<sup>-1</sup> almost identical to the values reported in the previous section.

In conclusion, although accurate rate coefficients for the H-atom abstraction reaction could not be determined from our experiment, under our experimental conditions, the models which use a smaller rate coefficient for the H-atom abstraction reaction (Eq. 33) are preferred. At low temperatures, the derived rate coefficients are independent of the model because the H-abstraction channel is negligible in all cases.

### C. The rate coefficients $k_f$ and $k_r$

As listed in Tables III and IV, the rate coefficient of the reverse reaction  $k_r$  depends less on pressure than that of the forward reaction  $k_f$ . Figure 3 is the Arrhenius plot of  $k_r$ ,



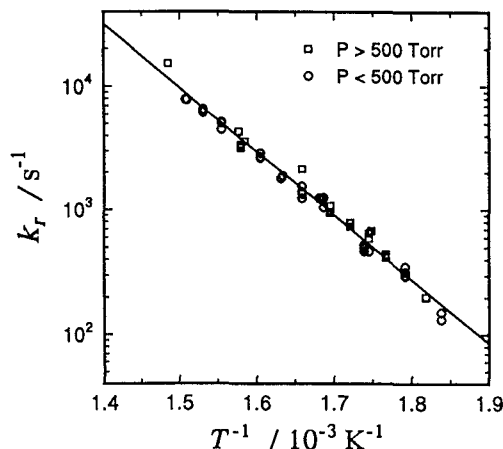


FIG. 3. An Arrhenius plot of  $k_r$  derived by using Eq. (33) for  $k_4$ .  $\square$ — $513 < P < 616$  Torr;  $\circ$ — $278 < P < 411$  Torr.

[derived by using Eq. (33) for  $k_4$ ] with symbols  $\square$  for  $513 < P < 616$  Torr and  $\circ$  for  $278 < P < 411$  Torr. The least-squares fit of the entire set of data yielded an activation energy of  $23.5 \pm 0.4$  kcal mol $^{-1}$ , whereas the fit of only the data at  $P > 500$  Torr gave  $E_a = 23.7 \pm 0.8$  kcal mol $^{-1}$ . The values of  $k_r$  derived with neglect of the H-atom abstraction reaction are slightly smaller than those shown in Fig. 3; the data at  $P > 500$  Torr yielded  $E_a = 23.5 \pm 0.8$  kcal mol $^{-1}$ . The values of  $k_r$  derived with the assumption that  $k_a = 40$  s $^{-1}$  also yielded  $E_a = 23.9 \pm 0.4$  kcal mol $^{-1}$ ; as before, these values are insensitive to the models employed. Hence, we report here

$$k_r = (6.2 \pm 1.0) \times 10^{11} \exp[-(11\,900 \pm 400)/T] \text{ s}^{-1}. \quad (34)$$

The uncertainties in  $k_f$  are greater than those in  $k_r$ . The Arrhenius plot of  $k_f$  is shown in Fig. 4 with symbols  $\square$  for  $513 < P < 616$  Torr and  $\circ$  for  $278 < P < 411$  Torr. Evidently

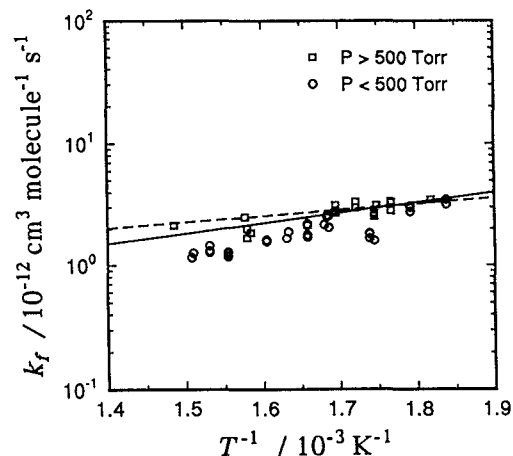


FIG. 4. An Arrhenius plot of  $k_f$  derived by using Eq. (33) for  $k_4$ .  $\square$ — $513 < P < 616$  Torr;  $\circ$ — $278 < P < 411$  Torr. The solid line represents the least-squares fit of the data with  $P > 500$  Torr. The dashed line represents the least-squares fit of the data with  $P > 500$  Torr and  $T < 590$  K.

at higher temperature, the high-pressure limit has not been reached even at  $P = 400$  Torr. A least-squares fit of the data with  $P > 500$  Torr yielded  $E_a = -(3.9 \pm 0.7)$  kcal mol $^{-1}$ . Values of  $E_a = -(3.8 \pm 0.7)$  and  $-(4.1 \pm 0.8)$  kcal mol $^{-1}$  were derived from models with the assumption that  $k_{15} = k_8$  and  $k_a = 40$  s $^{-1}$ , respectively. However, because at high temperature the  $k_f$  values are more sensitive to the values of  $k_a$  and  $k_{15}$  and their high-pressure limit requires higher pressure to reach, it is likely that the activation energy of  $E_a = -(2.3 \pm 1.6)$  kcal mol $^{-1}$  derived from fitting the data with  $P > 500$  Torr and  $T < 590$  K is more accurate. Therefore, we report

$$k_f = (4 \pm 3) \times 10^{-13} \exp[(1200 \pm 800)/T] \times \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (35)$$

The activation energy is slightly greater than, but within experimental uncertainties of the  $0.9$  kcal mol $^{-1}$  value reported in previous kinetic measurements at low temperature.

#### D. The rate coefficient $k_a$

The  $k_a$  values listed in Tables III and IV [assuming Eq. (33) for  $k_4$ ] are plotted against  $T^{-1}$  in Fig. 5. All data except one [experiment (32)] showed an excellent linear correlation between  $\ln k_a$  and  $T^{-1}$ . The large deviation of  $k_a$  in experiment (32) was due to a relatively small value of  $x_{\text{eq}}$  and a small kink in the slow component of the temporal profile of [OH]; hence this data point was not included in the least-squares fit. The activation energy was determined to be  $20.6 \pm 0.5$  and  $20.7 \pm 0.8$  kcal mol $^{-1}$  when the entire data set and the data at  $P > 500$  Torr were used, respectively.

In the model with  $k_{15} = k_8$ , the values of  $k_a$  at 673 K are approximately 30% greater than those shown in Fig. 5 because all the observed rate of loss was attributed to  $k_a$ . A value  $E_a = 21.6 \pm 0.8$  kcal mol $^{-1}$  was obtained from the

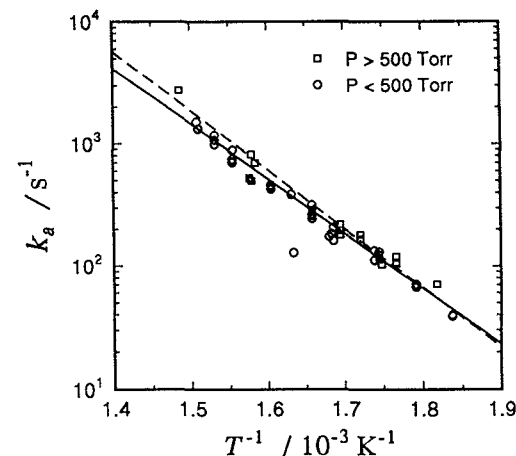
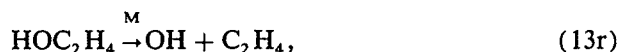


FIG. 5. An Arrhenius plot of  $k_a$  derived by using Eq. (33) for  $k_4$ .  $\square$ — $513 < P < 616$  Torr;  $\circ$ — $278 < P < 411$  Torr. The solid line represents the least-squares fit of the data [except for one point (see the text)]. The dashed line represents the least-squares fit of the data derived by neglecting the H-abstraction channel (data not shown).

data at  $P > 500$  Torr. When the rate of diffusion of  $\text{HOCC}_2\text{H}_4$  away from the probed volume ( $\sim 20 \text{ s}^{-1}$ ) was subtracted from  $k_a$ , an activation energy of  $(23.0 \pm 0.7) \text{ kcal mol}^{-1}$  was derived. Hence, we report

$$k_a = (8.8_{-1.5}^{+2.5}) \times 10^9 \exp\left[-(10400_{-400}^{+1600})/T\right] \text{ s}^{-1}. \quad (36)$$

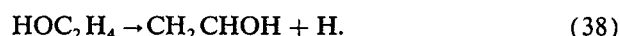
Sosa and Schlegel calculated various reaction potential surfaces of  $\text{OH} + \text{C}_2\text{H}_4$  and the predicted barrier heights of 29, 32 and 34  $\text{kcal mol}^{-1}$ , respectively, for the reverse reaction



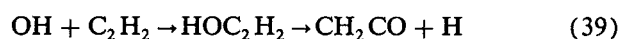
the [1,3]-hydrogen shift



and the  $\beta$ -hydrogen dissociation



Although the predicted barriers for reactions (37) and (38) are higher than that of reaction (13), the tunneling effect of the H atom is expected to decrease substantially the activation energies of the former reactions. The tunneling effect in the similar reactions



has been investigated theoretically by Miller and Melius.<sup>49</sup> Our  $E_a$  values of  $(20.6_{-0.8}^{+3.2})$  and  $(23.7 \pm 0.8) \text{ kcal mol}^{-1}$  for  $k_a$  and  $k_r$  are consistent with this prediction, although we cannot specify which reaction path(s) is responsible for the loss of  $\text{HOCC}_2\text{H}_4$ .

### E. Simulation of the rate measurement at 673 K

Typically, in a rate measurement, a pseudo-first-order condition was employed and the logarithmic decay of the concentration of the reactant with respect to reaction time was followed. If a complex reaction mechanism is involved, the measurement is susceptible to interference, especially when the concentration of the reactant was probed within only a limited period of reaction.

In our experiments at high temperature, a large concentration of  $\text{C}_2\text{H}_4$  ( $\sim 10^{16} \text{ molecules cm}^{-3}$ ) was employed in order to obtain a distinctly double-exponential temporal profile of  $[\text{OH}]$  in the reaction period  $50 \mu\text{s} - 2 \text{ ms}$ . In contrast,  $[\text{C}_2\text{H}_4] \sim 10^{14} \text{ molecules cm}^{-3}$  was used in a typical determination of the rate of the title reaction and  $[\text{OH}]$  was

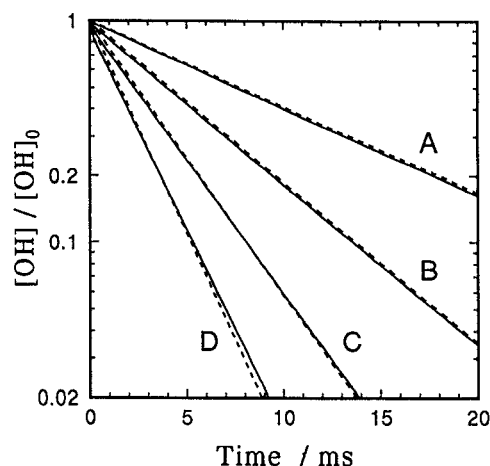


FIG. 6. A simulation of decay plots of  $[\text{OH}]$  at 508 Torr and 673 K.  $[\text{C}_2\text{H}_4]$  ( $10^{14} \text{ molecules cm}^{-3}$ ) = (A) 1.0; (B) 3.0; (C) 6.0; (D) 10. The solid lines represent temporal profiles predicted by our model. The dashed lines represent pseudo-first-order decays predicted from Tully's data for  $k_4$  [Eq. (32)]. The parameters are listed in Table V.

monitored in the later period of reaction, typically 1–20 ms. The small  $[\text{C}_2\text{H}_4]$  used in the experiments implies a large value of  $x_{\text{eq}}$ ; therefore only the slow component of the original double-exponential decay was observed under such experimental conditions.

Under the condition  $\alpha^2 \gg \beta$ , the decay rate of the slow component of the  $[\text{OH}]$  temporal profile  $\lambda_1$  is approximated by  $\beta/\alpha$ . At small concentrations of  $\text{C}_2\text{H}_4$ , the value of  $\alpha$  was dominated by  $\gamma + k_{15}$ . If the rate of the H-abstraction reaction is small,  $\alpha \approx \gamma$ ; hence

$$\lambda_1 \approx \beta/\alpha \approx k_8 + (k_f k_a/\gamma) [\text{C}_2\text{H}_4]. \quad (41)$$

Therefore, the dependence of the decay rate of the slow component on  $[\text{C}_2\text{H}_4]$  yielded  $k_f k_a/\gamma$ . A value of  $k_f k_a/\gamma = 4.07 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was derived for  $T = 673 \text{ K}$  and  $P = 508 \text{ Torr}$ , this value is close to  $k_4 = 3.91 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  derived from Tully's work.

With the rate coefficients  $k_f$ ,  $k_r$ , and  $k_a$  determined at 673 K and 508 Torr in the model assuming  $k_{15} = k_8$ , the values  $\alpha$ ,  $\beta$ ,  $\lambda_1$ , and  $\lambda_2$  were calculated for each  $[\text{C}_2\text{H}_4]$ . Table V lists the values of  $\alpha$  and  $\beta$ , the expression for the

TABLE V. Parameters for the simulation of decay rate at 673 K.

$[\text{C}_2\text{H}_4]$ ( $10^{14}$ ) <sup>a</sup>	From our mechanism with $k_{15} = k_8 = 50 \text{ s}^{-1}$			From Eq. (32)	
	$\alpha$ ( $10^4 \text{ s}^{-1}$ )	$\beta$ ( $10^6 \text{ s}^{-1}$ )	$[\text{OH}]/[\text{OH}]_0$	$k_4 [\text{C}_2\text{H}_4]$ ( $\text{s}^{-1}$ )	$k_{15}^b$ ( $\text{s}^{-1}$ )
1.0	1.83	1.64	$0.990 \exp(-90t) + 0.010 \exp(-18246t)$	39	89
3.0	1.88	3.11	$0.970 \exp(-167t) + 0.030 \exp(-18611t)$	117	167
6.0	1.94	5.31	$0.942 \exp(-277t) + 0.058 \exp(-19164t)$	235	285
10.0	2.03	8.22	$0.905 \exp(-413t) + 0.095 \exp(-19912t)$	391	441

<sup>a</sup> In units of  $\text{molecules cm}^{-3}$ .

<sup>b</sup>  $k_{15} = k_4 [\text{C}_2\text{H}_4] + k_8$  with  $k_8 = 50 \text{ s}^{-1}$ .

temporal profile of  $[\text{OH}]$  [Eq. (23)], and the expected pseudo-first-order decay rate coefficient ( $k_{15}$ ) using the values of  $k_4$  reported by Tully<sup>18</sup> [Eq. (32)], for various concentrations of  $[\text{C}_2\text{H}_4]$ . The decay rates of the slow component of the double-exponential temporal profile are in excellent agreement with the anticipated pseudo-first-order decay rates, as demonstrated in Fig. 6. The solid lines are the predicted temporal profiles of  $[\text{OH}]$  based on the rate coefficients determined in this work, and the dashed lines are the predicted pseudo-first-order decays based on the reported  $k_4$  by Tully. It is clear that the observed decay rates for the "abstraction channel" can also be simulated by our model which assumes a negligible rate for the abstraction of H. The model with low values of  $k_4$  [Eq. (33)] also gave similar results.

#### IV. CONCLUSION

By analysis of the temporal profile of  $[\text{OH}]$  in the reaction of OH with  $\text{C}_2\text{H}_4$ , we determined the equilibrium constant of the title reaction. The temperature dependence of the equilibrium constant leads to  $\Delta H^\circ = -(30.7 \pm 0.9)$  kcal mol<sup>-1</sup> and  $\Delta S^\circ = -(31.3 \pm 1.1)$  cal K<sup>-1</sup> mol<sup>-1</sup>. On the basis of analysis of the individual rate coefficients in the reaction mechanism, we think that previous studies may have overestimated the rate coefficient for the H-abstraction reaction near 673 K. The temperature dependence of the rate coefficients for the forward, the reverse, and the adduct-loss reactions have also been determined.

#### ACKNOWLEDGMENT

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