



Detailed rate coefficients and the enthalpy change of the equilibrium reaction OH+C6H6↔MHOC6H6 over the temperature range 345–385 K

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Detailed rate coefficients and the enthalpy change of the equilibrium

reaction $OH+C_6H_6 \leftrightarrow HOC_6H_6$ over the temperature range 345–385 K

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The reaction between OH and C₆H₆ in He has been studied over the pressure range 250-500 Torr and the temperature range 345-385 K by means of the laser-photolysis/laser-induced-fluorescence technique. Analysis of the temporal profile of [OH] yielded the detailed rate coefficients and the equilibrium constant for the reaction $OH+C_6H_6+M\leftrightarrow HOC_6H_6+M$. The temperature dependence of the rate coefficients for the forward, the reverse, and the adduct-loss reactions have been determined to be $k_f = (2.0 \pm 0.1) \times 10^{-14} \exp[(1420 \pm 250)/T]$ cm³ molecule⁻¹ s⁻¹, determined to be $k_f = (2.0 \pm 0.1) \times 10^{-14} \exp[(1420 \pm 250)/T]$ cm³ molecule⁻¹ s⁻¹, $k_r = (3.0 \pm 0.2) \times 10^{12} \exp[-(8240 \pm 320)/T]$ s⁻¹, and $k_a = (1.7 \pm 0.3) \times 10^6 \exp[-(3500 \pm 360)/T]$ s⁻¹, respectively. The temperature dependence of the equilibrium constant led to the enthalpy of reaction $\Delta H(365\pm20 \text{ K}) = -(20.0\pm1.2) \text{ kcal mol}^{-1}$ and the entropy of reaction $\Delta S(365\pm20 \text{ K}) = -(33.6\pm2.5) \text{ cal K}^{-1} \text{ mol}^{-1}$, greater than previously reported values; after correction for temperature dependence, $\Delta H^0(298 \text{ K}) = -(19.9 \pm 1.2) \text{ kcal mol}^{-1}$ and $\Delta S^0(298 \text{ K}) = -(33.4 \pm 2.6)$ cal \overline{K}^{-1} mol⁻¹.

I. INTRODUCTION

Aromatic compounds are major pollutants in the atmosphere; their reactions with OH radicals are the initial oxidation steps.^{1,2} These reactions are also important in combustion chemistry.^{3,4} There are numerous reviews⁵⁻⁷ of experimental investigations of the rate coefficient and the mechanism of the reaction of OH with benzene (C_6H_6) .⁸⁻²³ The rate coefficient shows non-Arrhenius behavior over the temperature range 250-800 K, similar to those of the reactions of OH with unsaturated hydrocarbons.⁵ This behavior can be interpreted according to the following mechanism:

$$OH + C_6 H_6 \rightarrow HOC_6 H_6, \tag{1}$$

$$HOC_6H_6 \rightarrow OH + C_6H_6, \qquad (2)$$

$$OH + C_6H_6 \rightarrow H_2O + C_6H_5.$$
(3)

At low temperature (T < 325 K) the reaction is dominated by addition of OH to C₆H₆ to form an adduct hydroxycyclohexadienyl radical (HOC₆H₆), followed by decomposition, stabilization or isomerization of this adduct. The reported rate coefficients depend on pressure, and at the highpressure limit (above 200 Torr), increase slightly as temperature increases. In the temperature range 325-400 K, the apparent rate coefficient (determined by monitoring the consumption of OH during reaction) decreases rapidly as temperature increases; the reason is that the decomposition of thermalized HOC_6H_6 back to OH and C_6H_6 , reaction (2), becomes relatively more important at greater temperature. At temperatures greater than 400 K, abstraction of a H-atom by

OH, reaction (3), becomes the major channel and the rate coefficient shows an activation energy $\sim 5 \text{ kcal mol}^{-1}$.

A transient absorption attributed to HOC₆H₆ was previously observed in the pulse radiolysis of aqueous benzene solutions; the absorption in the range 270-340 nm peaked near 313 nm.^{24,25} Fritz et al. employed a long-path absorption cell with a cw-laser source and observed increased absorption ~308.3 nm after irradiation of a mixture of HNO₃/C₆H₆/N₂ with a 248 nm excimer laser; they attributed it to the absorption of the hydroxy-cyclohexadienyl radical.²⁶ This technique was later employed to study further oxidation reactions of HOC_6H_6 .²⁷ No detailed spectroscopic investigation of HOC₆H₆ is reported, nor theoretical calculation of the structure, vibrational frequencies, or the energy of HOC₆H₆.

In the intermediate range of temperature (325-400 K), nonexponential decay of OH radicals was observed in the kinetic measurements, consistent with the proposed mechanism. Based on such observation, Perry et al. estimated the lifetime of the adduct and consequently $k_2 \sim 100 \text{ s}^{-1}$ at 350 K.¹¹ By assuming a pre-exponential factor $A \sim 3 \times 10^{13}$ s⁻¹ for k_2 , they were able to estimate $\Delta H = -(18.6 \pm 3)$ kcal mol^{-1} for reaction (1) from the temperature dependence of reactions (1) and (2). Lorenz and Zellner estimated a rate coefficient $k_2 = 390 \text{ s}^{-1}$ at 375 K from the observed apparent rate coefficient of OH-consumption; a value $\Delta H = -(18.4)$ ± 1.4) kcal mol⁻¹ nearly identical to that by Perry *et al.* was estimated.¹⁵ These estimated values are slightly smaller but within uncertainty limits of the value $\Delta H^0 = -21 \pm 2$ kcal mol⁻¹ predicted by the bond-additivity rules of Benson.²⁸ However, the only direct measurement using the flash-photolysis/resonance-fluorescence technique by Witte et al. yielded a much smaller value;²¹ they determined the rate coefficients of reactions (1) and (2) from the slow and rapid components of the biexponential decay of OH over the

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temperature range 299-354 K; a value $\Delta H = -(16.5 \pm 1.4)$ kcal mol^{-1} was thereby derived.

We have demonstrated that by careful control of experimental conditions accurate determination of the detailed rate coefficients of equilibrium reactions by means of the laserphotolysis/laser-induced-fluorescence (LIF) technique can be achieved.²⁹⁻³² We extended our method to investigate the reaction of OH with C₆H₆ to determine accurately the stabilization energy and the detailed rate coefficients.

II. EXPERIMENT

The technique and the experimental setup were described in detail;^{29,31} hence only a summary is given here. The reaction cell was made of quartz and has a jacket with silicone oil flowing through it to control the temperature of the reaction. The temperature of the silicone oil was regulated by a heated circulator (Neslab, EX-250XT) to <0.1 K. A thermocouple (type K) was inserted slightly above the laser-probed reaction zone to monitor the temperature of the reactants. The uniformity of the temperature in the reaction zone was regularly tested by moving the thermocouple along the probed volume; the deviation was less than 2 K.

An indirect source of OH was used because HNO3 and H₂O₂ decompose at high temperature. The OH radicals were generated by photolysis of N₂O with an ArF laser (193 nm, 2-3 mJ) to give $O(^{1}D)$ and N_{2} ,

$$N_2 O \rightarrow N_2 + O(^1 D)$$
(4)

followed by the rapid reaction $O(^{1}D)$ with H₂O,

$$O(^{1}D) + H_{2}O \rightarrow OH + OH$$
(5)

in which $k_5 = 2.2 \times 10^{-10} \text{ cm}^3$ molecule⁻¹ s⁻¹.³³ Because the temporal profile of [OH] was monitored in the reaction period 50 μ s-20 ms, H₂O with concentration ~5×10¹⁵ molecules cm^{-3} was added in order to convert most $O(^{1}D)$ into OH within 5 μ s after photolysis.

The relative concentration of OH at varied delay after the photolysis laser was determined from the integrated LIF intensity. The probe laser (Nd-YAG-pumped dye laser system) has a wavelength 282.0 nm and fluorescence of OH near 310 nm was detected. The repetition rates of both lasers were 10 Hz and the signal was typically averaged over 100 pulses at each delay. A typical temporal profile of OH decay consisted of 80-100 data points at varied delay.

The diluent gas He (99.9995%) was used without further purification. N₂O (99%) was degassed at 165 K before used. A diluted gas sample of C_6H_6 (2.10±0.07% in He), prepared with standard gas-handling techniques, was used in the experiments. The concentration of the C₆H₆/He mixture was determined by FTIR absorption.

Typical experimental conditions were as follows: total flow rate $F_T = 16-40$ STP cm³ s⁻¹ (STP=1 atm and 273 K); total pressure P = 250 - 500 Torr; reaction temperature T = 345 - 385 K; $[H_2O] \approx (4 - 8) \times 10^{15}$ molecules cm⁻³; $[N_2O] \approx (0.2 - 1.0) \times 10^{15}$ molecules cm⁻³; $[C_6H_6] \approx (0.9 - 3.4)$ ×10¹⁵ molecules cm⁻³; $[OH]_0 \approx (0.8 - 3.6) \times 10^{11}$ molecules cm^{-3} ; interval between the photolysis laser and the probe laser $t = 50 \ \mu s - 20 \ ms$.

III. RESULTS AND DISCUSSION

As demonstrated previously,^{31,32} under our experimental conditions the concentration of OH reached its maximum within 10 μ s after photolysis and the decay of OH in the absence of C_6H_6 was normally in the range 60-80 s⁻¹. Hence, [OH]₀ was derived by fitting the decay profile with 10 $\mu s < t < 100 \ \mu s$ to a single exponential decay; the error was estimated to be <2%.

The experiments were carried out with $[C_6H_6]/[OH]_0 > 2500$ in the temperature range at which the reaction rate of the thermal decomposition of the adduct HOC_6H_6 was comparable to that of the addition reaction. The concentration of C₆H₆ was also adjusted so that the double-exponential decay of OH was distinctly observed; only under such conditions could the decay coefficients of the rapid and the slow components be accurately determined.

A simplified mechanism, consisting of the following reactions:

$$OH + C_6 H_6 \rightarrow HOC_6 H_6, \tag{1,f}$$

$$HOC_6H_6 \rightarrow OH + C_6H_6, \qquad (2,r)$$

$$OH + C_6 H_6 \rightarrow H_2 O + C_6 H_5, \tag{3}$$

 $OH \rightarrow products$ other than HOC_6H_6 , (6,d)

 $HOC_6H_6 \rightarrow products$ other than OH, (7,a)

was used to model the quasiequilibrium. For clarity, the rate coefficients of reaction (1), (2), and (7) 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 (6) takes into account the diffusion of OH away from the probed volume and all possible reactions of OH with species other than C_6H_6 ; the rate coefficient is expressed as k_d . Reaction (7) includes the diffusion of HOC_6H_6 away from the probed volume and possible further reactions of HOC₆H₆ that do not regenerate OH as reaction (2) does.

The temporal profile of [OH] in the presence of C_6H_6 was derived by solving the differential rate equations for reactions (1)-(3), (6), and (7);

$$[OH] = [OH]_0[(\gamma - \lambda_1)exp(-\lambda_1 t) - (\gamma - \lambda_2) \\ \times exp(-\lambda_2 t)]/(\lambda_2 - \lambda_1),$$
(8)

in which

$$\lambda_1 = [\alpha - (\alpha^2 - 4\beta)^{1/2}]/2 > 0, \tag{9}$$

$$\lambda_2 = [\alpha + (\alpha^2 - 4\beta)^{1/2}]/2 > \lambda_1 > 0, \tag{10}$$

$$\mathbf{y} = k_r + k_a, \tag{11}$$

$$\alpha = k_f [C_6 H_6] + k_r + k_3 [C_6 H_6] + k_d + k_a, \qquad (12)$$

$$\beta = k_a k_f [C_6 H_6] + (k_r + k_a)(k_3 [C_6 H_6] + k_d).$$
(13)

Because data points with reaction period less than 50 μ s were not used, the rise of [OH] due to reactions (4) and (5) did not interfere in the fitting of the temporal profile to a double-exponential decay of [OH]. Values λ_1 , λ_2 , and γ were derived from the nonlinear least-squares fit of the [OH] temporal profile using Eq. (8). The values of α and β were then derived from λ_1 and λ_2 according to Eqs. (9) and (10). As discussed previously,³¹ we adjusted the experimental conditions to fulfill the criterion $\alpha^2 > 20\beta$ (i.e., $\lambda_2 > 20\lambda_1$) to assure a clear distinction between the rapid and the slow components of the double-exponential decay; accurate determinations of α and β were thus achieved from the nonlinear fit. As was also derived previously,³¹ under such conditions the fraction of [OH] at equilibrium was expressed as

$$x_{eq} = [OH]_{eq} / [OH]_0 = (\gamma - \lambda_1) / (\lambda_2 - \lambda_1); \qquad (14)$$

consequently the equilibrium constant K_p (in units of atm⁻¹) of reactions (1) and (2) was derived

$$K_p = K_c / RT = 7.34 \times 10^{21} (1 - x_{eq}) / x_{eq} [C_6 H_6] T$$
 (15)

without an explicit solution of k_f and k_r . The experimental conditions and the determined values of α , β , γ , x_{eq} , and K_p are listed in Table I. Following the same analysis as in previous work, we estimated the 95% confidence limits for the measurements of K_p from x_{eq} to be $\pm 25\%$.

To derive k_f , k_r , and k_a from Eqs. (11)–(13), we have to determine k_3 and k_d . Values of k_d were measured from the pseudo-first-order decay coefficient of OH in the absence of C₆H₆; previous work has demonstrated that such measurements provide reasonable values of k_d . Values of k_3 were derived by extrapolation of the reported rate coefficient of the H-abstraction reaction at higher temperature. An Arrhenius expression

$$k_3 = (3.8 \pm 0.1) \times 10^{-11} \exp[-(2560 \pm 180)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (16)

was derived by fitting the data of Tully *et al.* (for $1017 \ge T/K \ge 621$) (Ref. 13) and Madronich and Felder (for $1409 \ge T/K \ge 787$).²⁰ The values of k_f , k_r , k_a , and K_p derived by using Eq. (16) for k_3 are listed in Table II. As can be seen from the table, k_3 values predicted by Eq. (16) are probably slightly overestimated at T=385 K because consistent values of k_a were not obtained.

According to our experience with similar reactions, the activation energy of the H-abstraction reaction was typically overestimated because of the interference from the equilibrium reactions (1) and (2). Normally k_3 was relatively small in the temperature range of our study of equilibrium. Therefore, we also derived k_f , k_r , k_a , and K_p by assuming negligible k_3 ; the values are also listed in Table II. With such an assumption, more consistent values of k_a were derived at higher temperatures; hence we prefer the data derived by assuming negligible k_3 . At low temperatures, the rate coefficients derived from these two models of k_3 are almost identical because k_3 was negligibly small at low temperature.

A. The enthalpy and the entropy changes of $OH+C_6H_6 \rightarrow HOC_6H_6$

The van't Hoff plot K_p vs T^{-1} is shown in Fig. 1. The K_p values derived from x_{eq} (marked \triangle) and those derived from k_f/k_r by neglecting k_3 (marked \bigcirc) are within experi-

mental uncertainties of each other. The excellent linearity in Fig. 1 indicates that within experimental uncertainties ΔH is independent of temperature under our experimental conditions. The data were fitted to the linear equation

$$\ln K_p = -(\Delta H/R)T^{-1} + \Delta S/R.$$
(17)

The fit yielded $\Delta H = -(20.6 \pm 0.3)$, $-(20.0 \pm 0.4)$, and $-(20.6 \pm 0.4)$ kcal mol⁻¹ for models using x_{eq} , $k_3=0$, and Eq. (16), respectively; the uncertainties represent one standard deviation. The values of ΔS were also derived as $-(35.5 \pm 0.9)$, $-(33.6 \pm 0.9)$, and $-(35.6 \pm 0.9)$ cal K⁻¹ mol⁻¹ for models using x_{eq} , $k_3=0$, and Eq. (16), respectively. We prefer the data derived by assuming $k_3=0$; the other two sets of data provide an indication of possible errors. Considering the errors in K_p and T, we report ΔH (365±20 K)= $-(20.0\pm 1.2)$ kcal mol⁻¹ and ΔS (365±20 K) = $-(33.6\pm 2.5)$ cal K⁻¹ mol⁻¹; the uncertainties represent 95% confidence limits.

It is difficult to correct accurately for the temperature dependence of ΔH and ΔS to give ΔH^0 and ΔS^0 without knowledge of the structure and vibrational frequencies of HOC₆H₆. However, by comparison with similar systems and taking advantage of a relatively small deviation in temperature from 298 K, we were able to estimate a correction of 0.1 kcal mol⁻¹ and 0.2 cal K⁻¹ mol⁻¹ for ΔH^0 and ΔS^0 , respectively. Thus, ΔH^0 (298 K)=-(19.9±1.2) kcal mol⁻¹ and ΔS^0 (298 K)=-(33.4±2.6) cal K⁻¹ mol⁻¹. With ΔH_f^0 =(9.32±0.29) and 19.8 kcal mol⁻¹ for OH and C₆H₆, ^{34,35} respectively, ΔH_f^0 =(9.2±1.5) kcal mol⁻¹ for HOC₆H₆ is derived.

The value of ΔH derived in this study is 3.5 kcal mol⁻¹ more negative than that reported by Witte et al., 21 -16.5 ± 1.4 kcal mol⁻¹. Witte *et al.* did not fit their doubleexponential decay curve with Eq. (8); they derived rate coefficients k_f and k_r by fitting the data at both ends, respectively, to a single-exponential decay equation, and by assuming negligible k_3 , k_d , and k_a . Values of K_p derived from values of k_f and k_r reported by Witte *et al.* are also shown in Fig. 1 (marked by \times and + for P = 100 and 150 Torr, respectively); the data points at higher pressure (P=150 Torr) and higher temperature (T>331 K) agree well with our measurements. At temperatures below 325 K, the reported values of k, are less than 30 s⁻¹. Considering the errors in their measurements and the assumption of $k_3 = k_d = k_a = 0$, their values of K_p should have much greater uncertainties at low temperature; the values were most likely underestimated because k_d and k_a were not negligible. Our experiments were carried out at greater temperatures with $k_r > 100 \text{ s}^{-1}$, hence our values of ΔH and ΔS should be more accurate. The ΔH value reported by Witte *et al.* implies ΔS =-23.4 cal K⁻¹ mol⁻¹, much smaller than what one normally expects for an association reaction.

Benson estimated ΔH_f^0 of HOC₆H₆ from that of cyclohexadienyl (C₆H₇, ΔH_f^0 =49.9 kcal mol⁻¹);³⁶ a value ΔH^0 =-21 kcal mol⁻¹ for reaction (1) was estimated.²⁸ Value of ΔH_f^0 for HOC₆H₆ was also estimated from 6-hydroxy cyclohexadiene-1,3 which in turn was estimated from cyclohexadiene-1,3; values ΔH_f^0 (HOC₆H₆)=10±1 kcal mol⁻¹ and ΔH^0 =-19±1 kcal mol⁻¹ for reaction (1)

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TABLE I. A summary of experimental conditions and fitted decay parameters of the temporal profiles of [OH] at 345≤T≤385 K.ª

Expt. No.	Т (К)	P (Torr)	[C ₆ H ₆] (10 ¹⁴) ^b	α (s ⁻¹)	β $(10^3)^c$	γ (s ⁻¹)	(10^{-2})	$\frac{K_p}{(10^2 \text{ atm}^{-1})}$
1	245	250	12.0	1670+ 30	112 + 22	167 + 22	62+10	2440+ 760
2	345	300	13.7	1070 ± 30 1740 ± 40	113 ± 23 147 ± 39	107 ± 23 188 ± 36	6.3 ± 1.8	2290 ± 1100
3	345	300	14.8	1920± 30	135± 33	167 ± 28	5.3±1.9	2560± 960
4	345	250	15.8	2010 ± 40	127± 36	169± 30	5.5±1.9	2300 ± 840
5	345	300	16.3	2010 ± 40	191± 41	222 ± 35	6.7 ± 2.2	1800 ± 650
6	345	250	17.5	2110 ± 40	147 ± 39	179 ± 31	5.4 ± 1.9	2120 ± 770
2 2	345	300	18.5	2420 ± 70 2320 \pm 40	211 ± 64 149 ± 43	209 ± 59 176 + 31	5.3 ± 3.1 5.1 ± 1.7	2050 ± 1300 2090 + 740
° 9	345	300	19.9	2320 ± 40 2420 \pm 50	148 ± 43 195+ 62	212 + 44	57+23	1770+ 760
10	345	300	21.3	2640 ± 30	157 ± 37	169 ± 23	4.3 ± 1.1	2220 ± 600
11	351	300	11.1	1490± 30	111± 19	244± 29	12.4 ± 2.4	1330 ± 300
12	351	300	12.6	1720 ± 40	124 ± 20	256± 29	12.1 ± 2.0	1210 ± 240
13	351	290	12.7	1950 ± 30	151 ± 16	323 ± 22	13.6 ± 1.3	1050 ± 130
14	351	300	14.7	2100 ± 40	168 ± 23	300 ± 26	11.2 ± 1.5 10.8 ± 1.2	1120 ± 180
15	351	305	14.9	2330 ± 40 2290 + 40	210 ± 23 150+17	350 ± 23 351 ± 22	10.0 ± 1.3 13.0 ± 1.1	931 + 100
17	351	300	15.1	1890 ± 40	139 ± 17 122 ± 21	249 ± 27	10.4 ± 1.7	1190 ± 220
18	351	300	18.9	2300 ± 40	132 ± 29	245 ± 30	8.5 ± 1.5	1190 ± 240
19	355	300	13.8	1770± 30	144± 16	319± 26	14.6±1.7	878± 130
20	355	250	14.0	1850 ± 40	142 ± 22	295 ± 30	12.7±1.9	1010 ± 180
21	355	300	14.7	1780 ± 30	139 ± 17	305 ± 27	13.8 ± 1.8	876± 140
22	355	300	15.2	1950 ± 40	153 ± 18	324 ± 25	13.5 ± 1.5	872 ± 120
23	355	300	15.0	2030 ± 30 2140 + 40	180 ± 23 206 + 18	339 ± 33 383 ± 25	13.4 ± 1.9 14.6 ± 1.4	746 ± 02
25	355	300	17.6	2330 ± 30	199 + 14	399+19	14.0 ± 1.4 14.4 ± 1.0	698+ 64
26	355	250	17.6	2340 ± 40	198 ± 20	365 ± 24	12.8 ± 1.2	799± 94
27	355	300	19.6	2430 ± 40	178 ± 22	351 ± 27	12.1 ± 1.3	768± 99
28	355	300	21.4	2800 ± 50	234± 29	369± 28	10.8 ± 1.2	801± 110
29	361	300	11.8	1920 ± 50	170 ± 15	501 ± 34	23.5 ± 2.1	559± 71
30	361	300	12.9	1960 ± 50	167 ± 18	440 ± 35	19.7 ± 2.1	643± 92
31	361	250	14.0	2120 ± 50 2100 \pm 70	103 ± 13 181 ± 26	480± 31	20.4 ± 1.7	564 ± 100
32	361	300	14.0	2100 ± 70 2220 ± 60	181 ± 20 188 + 23	400 ± 49 452 ± 30	17.0 ± 2.7 17.8 ± 2.0	588+ 86
34	361	250	16.3	2560 ± 60	229 ± 24	489 ± 37	16.7 ± 1.7	625 ± 81
35	361	500	16.3	2560± 80	237 ± 26	598± 51	21.2 ± 2.3	465± 68
36	361	300	16.9	2380± 50	214 ± 21	485± 34	17.8±1.6	555± 68
37	361	250	19.0	2770 ± 40	211 ± 18	450± 25	14.2 ± 1.0	646± 62
38	361	300	19.1	2830 ± 70	253 ± 300 232 ± 24	534± 43 507+ 24	16.7 ± 1.7 15.7 ± 1.4	532 ± 72
40	361	500	22.5	3350 ± 100	232 ± 24 283 ± 38	507 ± 54	15.7 ± 1.4 16.2 ± 1.8	468 ± 66
41	361	300	23.7	3330 ± 100	219 ± 48	465± 56	12.5 ± 1.8	603 ± 110
42	367	300	9.2	1450± 30	140± 6	575± 24	30.8 ± 2.2	355± 37
43	367	300	13.4	1930± 40	161± 7	608± 23	29.6±1.4	355± 30
44	367	300	19.0	2400 ± 60	210 ± 12	693± 33	27.1 ± 1.7	282± 27
45 46	372	301	1/./	2470± 80 2870±110	300 ± 20	860± 34	33.3 ± 2.7	223 ± 29 255 ± 42
40	372	301	22.8	2870 ± 110 3180 + 100	313 ± 30 389 ± 26	1030 ± 61	30.9 ± 2.3	194 + 23
48	372	301	26.6	3320 ± 100	357 ± 34	806± 58	22.4 ± 2.0	256 ± 32
49	375	306	15.2	2500± 80	265 ± 12	1080 ± 50	42.7±2.5	173± 20
50	375	306	17.9	2670 ± 110	365 ± 41	958± 84	34.1 ± 3.9	211± 38
51	375	500	19.5	3160 ± 100	322 ± 20	1110 ± 63	34.0±2.4	195 ± 23
52	375	306	21.5	2970 ± 70	390 ± 21	990 ± 44	31.6 ± 1.8	197 ± 19
55 54	375	306	23.3	3410 ± 120 3660 ± 110	379 ± 34 477 ± 77	1080 ± 78 1230 \pm 65	30.4 ± 2.7 32.3 ± 2.1	193 ± 20 148 ± 16
55	375	306	34.2	4040 ± 120	496 ± 41	1250 ± 0.000 1060 ± 67	24.6 ± 1.9	175 ± 20
56	381	300	11.5	2520 ± 110	340± 18	1430± 83	57.9±4.5	122 ± 23
57	381	300	13.3	2430 ± 120	303± 19	1290± 91	53.4±4.9	127 ± 26
58	381	300	21.3	2860 ± 100	363 ± 18	1300 ± 69	45.1 ± 3.1	110± 15
59	381	300	27.5	3710 ± 130	469 ± 31	1380 ± 87	36.2 ± 2.8	123 ± 16
61	385	300	13.4	3310 ± 100 2430 ± 100	401 ± 42 321 ± 17	1210- 98	50.4±5.0	109 ± 21 96+10
62	385	300	16.9	2620 ± 100	361 ± 19	1370 ± 80	52.6 ± 4.1	101 ± 17
63	385	300	22.8	2990±100	391± 17	1510± 72	50.7±3.1	81± 11
64	385	300	24.7	3700 ± 120	497 ± 21	1880 ± 85	50.9 ± 3.0	75± 10
65	385	300	29.2	4010 ± 180	580± 37	1810 ± 120	44.6±3.8	81± 13
66	385	300	33.1	4720 ± 140	649± 33	1870 ± 92	38.9±2.4	90± 10

The uncertainties represent one standard deviation.

^bIn units of molecules cm^{-3} . ^cIn units of s^{-2} .

					M	
l in	Kuo	and	1 66.	Reaction	OH+C_H_	OC.H
L,		unu	200.	1100000	OLL OBLIG	0060

TABLE II. A summary of rate coefficients at 345≤T≤385 K derived from various assumptions.

					k ₃ =0				Eq. (16), $k_3 = 3.8 \times 10^{-11} \exp[-2560/T]$				
Expt. No.	Т (К)	P (Torr)	[C ₆ H ₆] (10 ¹⁴) ^a	(s^{-1})	$(10^{-13})^{b}$	k_r (s ⁻¹)	k_a (s ⁻¹)	$\frac{K_p}{(10^2)^c}$	$\frac{k_3}{(10^{-14})^{b}}$	$k_{f} (10^{-13})^{b}$	$\begin{pmatrix} k_r \\ (s^{-1}) \end{pmatrix}$	k_a (s ⁻¹)	$\frac{K_p}{(10^2)^c}$
1	345	250	13.0	69.5	11.0	96	71	2440	2.28	10.8	98	69	2340
2	345	300	13.7	109	10.5	100	88	2230	2.28	10.3	103	85	2130
3 4	345 345	250	14.8	737	11.4	105	73 65	2280	2.28	10.9	106	63	2480
5	345	300	16.3	66.1	10.6	120	102	1880	2.28	10.3	122	100	1790
6	345	250	17.5	71.5	10.7	107	72	2120	2.28	10.4	109	70	2030
7	345	300	18.5	68.7	11.6	118	92	2090	2.28	11.4	120	89	2020
8 Q	345	300	19.1 10.0	59.8	10.8	110	00 85	2090	2.28	10.6	113	63 82	2010
10	345	300	21.3	66.7	11.3	109	61	2210	2.28	11.1	111	58	2130
11	351	300	11.1	67.5	10.7	165	80	1360	2.58	10.4	168	76	1300
12	351	300	12.6	68.2	11.0	188	77	1220	2.58	10.7	193	72	1160
13	351	290	12.7	67.2	12.3	240	83	1070	2.58	12.1	245	78	1030
14	351	305	14.7	66 1	13.1	215	100	1190	2.58	12.8	219	96	1150
16	351	305	15.0	58.8	12.5	278	73	944	2.58	12.3	283	68	906
17	351	300	15.1	71.0	10.4	183	67	1190	2.58	10.1	187	62	1130
18	351	300	18.9	67.4	10.5	186	58	1180	2.58	10.2	192	53	1120
20	355	250	13.8	67.3	10.0	231	87	895	2.81	9.7	238	81 76	843
20	355	300	14.0	90.6	9.4	213	81	865	2.81	9.2	231	74	818
22	355	300	15.2	68.2	10.3	240	84	887	2.81	10.0	247	77	838
23	355	250	15.6	71.8	10.4	242	97	883	2.81	10.1	250	89	837
24	355	300	16.3	75.8	10.3	278	105	769	2.81	10.1	285	98	728
25 26	355	250	17.6	69.7	10.6	274	92 91	71Z 814	2.81	10.5	282	83 83	074 774
27	355	300	19.6	69.7	10.0	274	77	773	2.81	10.0	282	69	730
28	355	300	21.4	71.4	11.0	281	88	811	2.81	10.8	288	81	771
29	361	300	11.8	67.5	11.5	401	100	581	3.16	11.1	412	89	548
30	361	300	12.9	67.4	11.3	345	95	664 556	3.16	10.9	355	85	627 524
32	361	250	14.0	69.6	10.8	371	95	579	3.16	10.5	382	84	544
33	361	300	16.0	64.9	10.7	358	93	605	3.16	10.3	370	82	560
34	361	250	16.3	65.8	12.3	391	98	642	3.16	12.0	401	88	608
35	361	500	16.3	72.2	11.6	495	102	477	3.16	11.3	509	89	451
37	361	250	10.9	73.9	10.8	371	99 79	509 648	3.10	10.5	398 381	87 69	535
38	361	300	19.1	70.0	11.0	438	97	543	3.16	11.4	449	85	514
39	361	300	21.2	71.7	10.7	421	86	518	3.16	10.4	434	73	488
40	361	500	22.5	76.2	11.9	511	89	472	3.16	11.6	525	75	447
41	361	300	23.7	67.3	11.8	398	122	603	3.10	11.5	409	56	572
43	367	300	9.2 13.4	72.0	8.7 9.4	514	94	364	3.55	8.4 9.0	535	74	336
44	367	300	19.0	72.2	8.6	595	98	289	3.55	8.2	621	72	266
45	372	301	17.7	70.5	8.7	711	155	240	3.90	8.3	744	122	219
46	372	301	19.6	70.5	9.9	731	131	267	3.90	9.5	761	101	247
47	372	301	22.8	70.5	9.1	684	122	205	3.90	8.8 8.8	713	113	188
49	375	306	15.2	69.7	8.9	951	134	183	4.12	8.5	992	88	167
50	375	306	17.9	69.7	9.2	777	181	232	4.12	8.8	813	145	211
51	375	500	19.5	72.0	10.1	985	123	201	4.12	9.7	1030	81	185
52 53	375	306	21.5	69.7	8.9	821	168	212	4.12	8.5	862	128	193
54	375	306	23.3	69.7	9.7 8.5	1080	144	154	4.12	9.5	1140	89	139
55	375	306	34.2	69.7	8.5	913	145	182	4.12	8.1	960	99	165
56	381	303	11.5	72.0	8.8	1200	234	141	4.59	8.4	1260	167	128
57	381	306	13.3	72.0	8.1	1090	197	142	4.59	7.6	1160	131	126
50 50	381 381	302	21.5	72.0	7.U 8.2	120	161	120	4.39 4 50	כ.ס 7 פ	1200	102	105
60	381	301	31.9	71.0	8.0	1050	156	145	4.59	7.5	1120	92	129
61	385	301	13.4	70.6	7.0	1190	235	112	4.92	6.4	1280	145	95
62	385	300	16.9	72.8	7.0	1150	222	115	4.92	6.5	1240	135	100
03 64	285 385	302 302	22.8 24 7	71.0 72.8	0.2	1510	202	90 81	4.92 1 02	5.7	1420	88 81	76
65	385	302	29.2	71.0	7.3	1590	212	87	4.92	6.8	1710	96	76
66	385	302	33.2	73.0	8.4	1690	184	95	4.92	7.9	1790	79	84

^aIn units of molecules cm^{-3} . ^bIn units of cm^3 molecule⁻¹ s⁻¹. ^cIn units of atm^{-1} .

2

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FIG. 1. A van't Hoff plot of the $OH+C_6H_6+M \leftrightarrow HOC_6H_6+M$ over equilibrium. O, derived by assuming $k_3=0$; Δ , derived from x_{eq} ; ×, from Witte *et al.* (100 Torr) (Ref. 21); +, from Witte *et al.* (150 Torr). The solid and the dashed lines represent least-squares fitted equations of data marked O and +, respectively.

were derived.³⁷ Our value of ΔH is in excellent agreement with those predicted by Bensen.

The value of ΔS for reaction (1) may be estimated by comparison of HOC₆H₆ and C₆H₆. Values of 0.6, 1.3, 3.4, 4.9, and 1.4 cal K⁻¹ mol⁻¹ were estimated for corrections of S_{trans} , S_{rot} , S_{vib} , S_{symmetry} , and S_{spin} , respectively, in going from C₆H₆ to HOC₆H₆; hence a value $\Delta S = -32.3$ cal K⁻¹ mol⁻¹ for reaction (1) was estimated when $S^0(\text{OH})=43.9$ cal K⁻¹ mol⁻¹ was used. A similar estimate of ΔS from cyclohexadienyl ($S^0=72.1$ cal K⁻¹ mol⁻¹) (Ref. 36) yielded S^0 (HOC₆H₆)=77 cal K⁻¹ mol⁻¹; consequently $\Delta S^0 = -31.4$ cal K⁻¹ mol⁻¹ was estimated for reaction (1). Our experimental value $\Delta S^0 = -(33.4\pm2.5)$ cal K⁻¹ mol⁻¹ is consistent with the prediction. It should be noted that even when the low value of $\Delta S^0 = -31.4$ cal K⁻¹ mol⁻¹ was used, a value $\Delta H^0 = -(19.3\pm0.1)$ kcal mol⁻¹ was derived from the third-law method; this value is within experimental uncertainties of that determined from the van't Hoff plot.

B. The rate coefficients k_f and k_r

Under our experimental conditions, the rate coefficients of the forward and the reverse reaction $(k_f \text{ and } k_r)$ do not alter appreciably with pressure. Previous reports indicated that at pressures above 100 Torr k_f is near the high-pressure limit and is essentially independent of total pressure.⁵

Figure 2 shows the Arrhenius plot of k_f ; the data derived by using $k_3=0$ and Eq. (16) are marked by \bigcirc and \diamondsuit , respectively; the error bars which represent one standard deviation of data marked \bigcirc are also illustrated. Our values of $(1.09\pm0.04)\times10^{-12}$ cm³ molecule⁻¹ s⁻¹ at $345 \le T \le 361$ K are in excellent agreement with previous work, $k_f = (1.0-1.3)\times10^{-12}$ cm³ molecule⁻¹ s⁻¹.^{5,11,13,15,21} However, a slightly negative temperature dependence of k_f was observed, contrary to the previously reported activation en-



FIG. 2. An Arrhenius plot of k_f derived by assuming $k_3=0$ (symbol \bigcirc , the error bars represent one standard deviation) and by using Eq. (16) for k_3 (symbol \diamondsuit). The solid and the dashed lines represent least-squares fitted equations of data marked \bigcirc and \diamondsuit , respectively.

ergy 0.4–1.0 kcal mol⁻¹. The observed negative temperature dependence of k_f is consistent with that of similar reactions of OH with toluene, *p*-xylene, phenol, and *m*-cresol.⁵ Recently, Knispel *et al.* employed an improved method of analysis of the OH-decay profile to find a slightly negative temperature dependence of k_f .³⁸ The greater values of k_f observed previously at higher temperature may be due to interference from the reverse reaction. When only the initial rapid decay was measured, the decay rate is represented as

$$\lambda_2 \approx \alpha = k_f [C_6 H_6] + k_r + k_3 [C_6 H_6] + k_d + k_a; \qquad (18)$$

consequently k_f may have been overestimated. Our values of k_f (derived by assuming $k_3=0$) are expressed in Arrhenius form as

$$k_f = (2.0 \pm 0.1) \times 10^{-14} \exp[(1420 \pm 250)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$
 (19)

in which the error limits represent one standard deviation. A similar result with

$$k_f = (1.3 \pm 0.1) \times 10^{-14} \exp[(1570 \pm 270)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$
 (20)

was obtined for k_f derived by using Eq. (16) for k_3 . However, it is also possible that k_f approaches to a constant value 1.1×10^{-12} cm³ molecule⁻¹ s⁻¹ at low temperature.

The Arrhenius plot of k_r is shown in Fig. 3; the data derived by using $k_3=0$ and Eq. (16) are marked by \bigcirc and \diamondsuit , respectively. The k_r values determined by Knispel *et al.*³⁸ (symbol + in Fig. 3) using an improved method of analysis are in excellent agreement with ours. The values of k_r (symbol \times) derived by Witte *et al.*²¹ from a simplified analysis are slightly greater than ours, with error limits overlapping each other. The rate coefficients k_r (derived by assuming $k_3=0$) are expressed in Arrhenius form as





$$k_r = (3.0 \pm 0.2) \times 10^{12} \exp[-(8240 \pm 320)/T] \text{ s}^{-1}$$
(21)

in which the uncertainties represent one standard deviation. A similar result with

$$k_r = (4.9 \pm 0.4) \times 10^{12} \exp[-(8420 \pm 310)/T] \text{ s}^{-1}$$
(22)

was obtained for k_r derived by using Eq. (16) for k_3 . The values reported by Knispel *et al.*,³⁸

$$k_r = (9.0 \pm 4.2) \times 10^{12} \exp[-(8570 \pm 200)/T] \text{ s}^{-1},$$
(23)

and by Witte et al.,²¹

$$k_r = 3 \times 10^{12} \exp[-(8200 \pm 700)/T] \text{ s}^{-1},$$
 (24)



FIG. 4. An Arrhenius plot of k_a derived by assuming $k_3=0$ (symbol \bigcirc) and by using Eq. (16) for k_3 (symbol \diamondsuit). The error bars represent one standard deviation. The solid and the dashed lines represent least-squares fitted equations of data marked \bigcirc and \diamondsuit , respectively.

are similar to our results. The values k_r (350 K)=100 s⁻¹ and k_r (375 K)=390 s⁻¹ estimated by Perry *et al.*¹¹ and Lorenz and Zellner,¹⁵ respectively, are approximately 50% of our values; this error contribute to an underestimate ~0.5 kcal mol⁻¹ for ΔH .

C. The rate coefficient k_a

The rate coefficient k_a represents the decrease in [HOC₆H₆] due to processes other than the reverse reaction. The k_a values listed in Table III are plotted against T^{-1} in Fig. 4; symbols \bigcirc and \diamondsuit represent data derived from the assumption $k_3=0$ and Eq. (16), respectively. The values de-

TABLE III. A summary of rate coefficients k_f, k_r, k_a , and equilibrium constant K_p at $345 \le T \le 385$ K.^a

			Assuming	k ₃ =0			From x_{eq}			
Т (К)	No. expts.	$(10^{-13})^{b}$	$\frac{k_r}{(s^{-1})}$	k_a (s ⁻¹)	$\frac{K_p}{(10^3 \text{ atm}^{-1})}$	$(10^{-13})^{b}$	k_r (s ⁻¹)	k_a (s ⁻¹)	K_p (10 ³ atm ⁻¹)	$\frac{K_p}{(10^3 \text{ atm}^{-1})}$
345	10	11.0±0.4	109±10	78±13	217±23	10.8±0.4	111±11	75±13	209±23	216±25
351	8	11.5 ± 1.0	211±37	78±13	116±12	11.3 ± 1.1	215±38	73±13	111 ± 11	115 ± 12
355	10	10.4±0.5	256±30	88±8	84.4±8.9	10.1 ± 0.4	264±31	81±8	79.9±8.4	83.1±8.8
361	13	11.3±0.6	406±50	91±10	57.4±6.1	11.0±0.6	418±51	80±10	54.1±5.9	56.2±5.9
367	3	9.0±0.4	520 ± 72	105±16	34.6±5.1	8.6±0.4	542±75	83±17	31.9±4.7	33.1±4.2
372	4	9.2±0.5	751±87	140±16	24.4±2.9	8.9±0.5	784±91	107±13	22.4 ± 2.7	23.2 ± 3.0
375	7	9.1±0.6	925±101	147±21	19.5±2.5	8.7±0.6	969±108	103±24	17.8±2.3	18.5±2.1
381	5	8.0±0.7	1140±70	186±31	13.6±1.0	7.6±0.7	1210±70	117±32	12.1 ± 1.0	12.4 ± 1.0
385	6	7.2±0.7	1440±250	210±17	9.7±1.4	6.7±0.7	1540±260	104±29	8.4±1.2	8.7 ± 1.0
E_{a}/R (K)		$-(1420\pm250)$	8240±320	3500±360		-(1570±270)	8420±310	1540±270		
ΔH (kcal mol ⁻¹)					$-(20.0\pm0.4)$				$-(20.6\pm0.4)$	-(20.6±0.3)
ΔS (cal K ⁻¹ mol ⁻¹)					-(33.6±0.9)				-(35.6±0.9)	-(35.5±0.9)

The uncertainties represent one standard deviation.

^bIn units of cm^3 molecule⁻¹ s⁻¹.

rived from Eq. (16) are smaller because part of the decay was attributed to the abstraction reaction, reaction (3); they were fit to yield

$$k_a = (6.1 \pm 0.5) \times 10^3 \exp[-(1540 \pm 270)/T] \text{ s}^{-1}.$$
(25)

The data derived from this model is probably less accurate because values of k_a at greater temperature are less consistent, as indicated in Fig. 4 by the much greater error limits. The values derived by assuming $k_3=0$ were fitted to yield

$$k_a = (1.7 \pm 0.3) \times 10^6 \exp[-(3500 \pm 360)/T] \text{ s}^{-1}.$$
(26)

The values k_a at lower temperatures are similar to values of k_d determined experimentally in the absence of OH, indicating that diffusion of HOC₆H₆ away from the probed volume dominates. The reaction that is responsible for the additional decay of HOC₆H₆ is uncertain. One possibility is decomposition of HOC₆H₆ to H₂O and C₆H₅,

$$HOC_6H_6 \rightarrow H_2O + C_6H_5 \tag{27}$$

in which $\Delta H^0 \approx 11.9$ kcal mol⁻¹. The observed activation energy for k_a is consistent with this value.

IV. CONCLUSION

By analysis of the temporal profile of [OH] in the reaction of OH with C_6H_6 , we determined the detailed rate coefficients k_f , k_r , and k_a , and consequently the equilibrium constant of the title reaction. The temperature dependence of the equilibrium constant yields $\Delta H^0 = -(19.9 \pm 1.2)$ kcal mol⁻¹ and $\Delta S^0 = -(33.4 \pm 2.5)$ cal K⁻¹ mol⁻¹, more negative than previous values. The H-abstraction channel is negligible in the temperature range of our work. The rate coefficient of the forward reaction, k_f , was determined to have a small negative temperature dependence, contrary to previous reports but consistent with similar reactions.

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