interaction of H<sub>2</sub>O with a crown ether, where it was noted that the water molecule is too small to fill the whole macrocyclic cavity and is therefore not coordinated by all the oxygen atoms. It is, nonetheless, difficult to rationalize the present results with the measured proton affinities of Kebarle and co-workers. The best explanation, perhaps, revolves around the calculations of Singh and Kollman<sup>12</sup> which suggest that dipole alignment of the oxygens in the ring to the proton accounts for the increased proton affinity. In the current case, with a polar but neutral hydrogen halide guest, this dipole alignment should be less, given that the operative forces are dipole-dipole, rather than ion-dipole. The best comparison to make, if the data were available, would be binding energies of the hydrogen halides to dimethyl ether compared to the crown ethers.

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One major difference between the spectra of the complexes of HF and HCl with  $(CH_3)_2O$  and the current complexes is the bandwidth of the hydrogen stretching motion. For example, the bandwidth of the HF stretching mode in its complex with 12crown-4 was approximately 80 cm<sup>-1</sup>, while for the HF-O(CH<sub>3</sub>)<sub>2</sub> complex<sup>25</sup> it was 13 cm<sup>-1</sup>. For the HCl complexes reported here, bandwidths were on the order of several hundred wavenumbers, again considerably greater than for HCl with simple ethers. This additional broadening either may reflect a range of conformations of the hydrogen-bonded complex, which would then average out to yield a very broad absorption, or may reflect some mobility of the hydrogen halide in the complex.

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Registry No. HF, 7664-39-3; HCl, 7647-01-0; D<sub>2</sub>, 7782-39-0; Ar, 7440-37-1; 1,4-dioxane, 123-91-1; 1,3,5-trioxane, 110-88-3; 12-crown-4, 294-93-9; 18-crown-6, 17455-13-9; dimethyl ether, 115-10-6.

# A Flash Photolysis-Shock Tube Kinetic Study of the H Atom Reaction with O<sub>2</sub>: $H + O_2 \rightleftharpoons OH + O$ (962 K $\leq T \leq$ 1705 K) and $H + O_2 + Ar \rightarrow HO_2 + Ar$ $(746 \text{ K} \le T \le 987 \text{ K})$

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Rate constants for the reactions  $H + O_2 \rightarrow OH + O(1)$  and  $H + O_2 + M \rightarrow HO_2 + M(2)$  were measured under pseudo-first-order conditions by the flash photolysis-shock tube technique that employs the atomic resonance absorption detection method to monitor [H]. Rate data for reaction 1 were obtained over the temperature range from 962 to 1705 K, and the results are well represented by the Arrhenius expression  $k_1(T) = (2.79 \pm 0.32) \times 10^{-10} \exp(-16132 \pm 276 \text{ cal} \text{mol}^{-1}/RT) \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>. The mean deviation of the experimentally measured rate constants from those calculated by using this expression is  $\pm 16\%$  over the stated temperature range. The recent shock tube data of Frank and Just (1693-2577 K) were combined with the present results for  $k_1(T)$  to obtain the following Arrhenius expression for the overall temperature span (962–2577 K):  $k_1(T) = (3.18 \pm 0.24) \times 10^{-10} \exp(-16439 \pm 186 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The mean deviation of the experimentally measured rate constants from this expression is  $\pm 15\%$  over the entire temperature range. Values for the rate constant for the reverse of reaction 1 were calculated from each of the experimentally measured  $k_1(T)$  values with expressions for the equilibrium constant derived by using the latest JANAF thermochemical data. These  $k_{-1}(T)$  values were also combined with similarly derived values from the Frank and Just data. This combined data base showed that  $k_{-1}(T)$ was essentially constant between 962 and 2577 K with an average value of  $2.05 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and a one standard deviation uncertainty of  $0.42 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Kinetic results were also derived for reaction 2 from the difference between the experimental first-order [H], decays and the corresponding calculated  $k_1(T)$  values. The temperature span over which  $k_2$  data could be determined was limited to 746 K  $\leq T \leq$  987 K. Although these rate data exhibit a slight negative temperature dependence, the magnitude of the uncertainties in the  $k_2$  results and the limited temperature span that could be covered preclude the calculation of reliable Arrhenius parameters. Instead, a simple average value may be used to represent this rate constant,  $k_2 = (7.1 \pm 1.9) \times 10^{-33}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, where the error limit is given at the one standard deviation level. All the results obtained are compared with those of previous investigations.

#### Introduction

The reactions between atomic hydrogen and molecular oxygen

$$H + O_2 \rightarrow OH + O \tag{1}$$

$$H + O_2 + M \rightarrow HO_2 + M$$
 (2)

are among the most important elementary reactions in gas-phase combustion. Reaction 1 is the major branching step in the  $H_2/O_2$ mechanism,<sup>1</sup> and this mechanism is an essential subset of the hydrocarbon oxidation mechanism as well.<sup>2-6</sup> Reaction 2 is a chain terminating step in the  $H_2/O_2$  mechanism in the lower range of combustion temperatures and it is in direct competition with reaction 1.1,6

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Although the rate constant for reaction 1 has been extensively studied,<sup>7-12</sup> significant discrepancies in experimentally measured rate constants persist in the literature. The evaluation of Baulch et al.<sup>7</sup> recommends the following expression for the rate constant between 700 and 2500 K:

$$k_1(T) =$$
  
3.7 × 10<sup>-10</sup> exp(-16790 cal mol<sup>-1</sup>/RT) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>

The suggested error limits for eq I are  $\pm 30\%$  in the temperature range quoted. This expression was chosen because it was consistent with the trend of the majority of evaluated experimental data. The results of Gutman, Schott, and co-workers<sup>13-15</sup> were specifically excluded in this evaluation7 because of the "low" activation energy values derived for reaction 1. In addition, eq I was constrained to be consistent with a zero activation energy for reaction -1. On the basis of the extant data, Baulch et al.<sup>7</sup> considered it to be unlikely that reaction -1 could have a negative activation energy; and thus the activation energy for reaction 1 should not be less than the endothermicity. More recent experimental<sup>16,17</sup> and theoretical<sup>18-20</sup> studies, which have clearly shown  $k_{-1}(T)$  to have a slightly negative temperature dependence, do not contradict the rationale used by Baulch et al.<sup>7</sup> because, presumably, there is no energy barrier for reaction -1.16-20

In a study published shortly after the review of Baulch et al.,<sup>7</sup> Schott<sup>10</sup> combined new measurements with some earlier results to derive the following expression for  $k_1(T)$  between 1250 and 2500 K:

2.02 ×  
$$^{-7}T^{-0.907} \exp(-16629 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The review of Cohen and Westberg<sup>9</sup> does not cite Schott<sup>10</sup> but it does include the earlier work.<sup>13-15</sup> Values for  $k_1$  reported by Cohen and Westberg<sup>9</sup> are higher than those from eq II by 6% at 1250 K and 24% at 2500 K. The expression recommended by Warnatz<sup>8</sup> relies heavily on the later Schott study,<sup>10</sup> and agrees with eq II to within about 3% over the entire temperature range, 1250-2500 K. Additionally, the trajectory calculations of Miller<sup>19</sup> agree remarkably well with Schott's expression, eq II. However, eq II is in clear disagreement with eq I. Whereas the two expressions agree to within about 10% at 1250 K, at 2500 K the  $k_1$  value calculated from eq II is more than a factor of 2 less than that calculated with eq I.

In their shock tube study, Pamidimukkala and Skinner<sup>11</sup> derived the following expression:

$$k_1(T) =$$

 $k_1(T) =$ 

10

 $2.0 \times 10^{-10} \exp(-16098 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (III)

The temperature range of eq III is 1000-2500 K, and the quoted

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uncertainty in this expression is about  $\pm 30\%$ . Equation III yields  $k_1(T)$  values that are consistently smaller (by about 30%) than those calculated by using eq I. By contrast, eq III and eq II cross. At 1250 K, the  $k_1$  value calculated from eq III is 21% smaller than that from eq II, but at 2500 K it is 33% larger.

Recently, Frank and Just<sup>12</sup> reported results from a shock tube study of reaction 1, in which [O] and [H] profiles were monitored, over the temperature range 1693-2577 K:

$$k_1(T) = (4.05 \pm 0.55) \times 10^{-10} \exp(-17269 \pm 525 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(IV)

Values for  $k_1(T)$  from this experimental study, eq IV, are nearly identical with those calculated by using eq I;  $k_1$  values from eq I are about 5% and 1% larger than those from eq IV at 1700 and 2500 K, respectively. As expected, eq IV does not agree with eq II, the expression of Schott.<sup>10</sup> At 1700 K, the value of  $k_1$  calculated from eq IV is 41% larger than that from eq II. At 2500 K, the  $k_1$  value from eq IV is more than 2 times that from eq II.

Experimental rate data on reaction 2 also exhibit marked scatter. Baulch et al.<sup>7</sup> based their recommendation on selected low-temperature studies and high-temperature shock tube work. Their expression for either He or Ar as the third-body collider is

## $k_2(T) =$

**(I)** 

(II)

 $4.1 \times 10^{-33} \exp(+994 \text{ cal mol}^{-1}/RT) \text{ cm}^{6} \text{ molecule}^{-2} \text{ s}^{-1} (\text{V})$ 

The uncertainty in eq V is  $\pm 50\%$  in the temperature range, 300-2500 K. The results of Gutman et al.<sup>14</sup> and Slack<sup>21</sup> agree reasonably well with eq V. However, the  $k_2(T)$  results of the shock tube study of Pamidimukkala and Skinner<sup>11</sup> are about a factor of 3 smaller than those of eq V.

The present investigation was undertaken with the purpose of resolving the discrepancies in the rate constant measurements, as noted above. Rate constants for reactions 1 and 2 were measured with the flash photolysis-shock tube (FP-ST) technique<sup>22,23</sup> employing atomic resonance absorption spectropho-tometry (ARAS)<sup>24-26</sup> to monitor [H]<sub>1</sub>. The rate constant,  $k_1(T)$ , was measured in the temperature range 962–1705 K, and  $k_2(T)$ values were derived between 746 and 987 K. The results of the present study are compared to those of previous experimental and theoretical investigations.

Additionally, equilibrium constant values for reaction 1 were calculated by using JANAF thermodynamic data<sup>27</sup> and used in conjunction with the present experimentally measured  $k_1(T)$  values to determine the rate constant for reaction -1. These results are also compared to those of previous experimental and theoretical work in the literature.

#### **Experimental Section**

The FP-ST technique<sup>22,23</sup> and the ARAS detection method<sup>24-26</sup> have been used extensively in this laboratory.<sup>28-30</sup> Appropriate

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corrections for nonideal shock behavior due to hydrodynamic boundary layer buildup have also been described previously.<sup>23,28</sup> Initial test gas pressures  $(P_1)$  were varied from about 10 to about 30 Torr and initial test gas temperatures  $(T_1)$  ranged from 296 to 301 K.

Hydrogen atoms were produced by the photodissociation of either  $NH_3^{23a,31}$  or  $H_2O^{32,33}$  in the reflected shock regime. Radiation from the flash lamp passed through a 10 cm focal length Suprasil lens that effectively cuts off at a wavelength of about 165 nm. Flash energies were varied from 150 to 1050 J so that the initial H atom concentration, [H]<sub>0</sub>, was always less than about  $2 \times 10^{12}$  atoms cm<sup>-3</sup> in the various mixtures. At this concentration level, secondary reactions of H atoms with other species are negligible during the time frame of the experimental observations. Thus, H atoms are depleted only by reactions 1 and 2, and by reaction with either  $NH_3$  or  $H_2O$ .

Precautions were taken to avoid potential complications that might arise from the formation of O atoms by photodecomposition of  $O_2$ . This was accomplished by two methods. In the " $O_2$  flash" method, pure  $O_2$  was flowed through the flash lamp at a pressure of about 1/2 atm, effectively creating a built-in filter which blocked transmission in the 170-nm region<sup>31</sup> and thus prevented the photolysis of  $O_2$ . The second method involved flowing pure  $O_2$ in the volume that connected the flash lamp to the endplate of the shock tube, while pure  $N_2$  was flowed through the body of the flash lamp. This O<sub>2</sub> filter method provided a greater H atom yield at a given source molecule concentration and flash energy compared to the  $O_2$  flash method. Both methods were equally effective at preventing the photodissociation of  $O_2$ . This was verified experimentally by monitoring the O atom concentration in  $O_2/Ar$  mixtures that were flashed under reaction conditions.

When NH<sub>3</sub> was used as the photolytic source molecule, it was possible to use either method to prevent the photodissociation of  $O_2$ . However, this was not the case when  $H_2O$  was used since the O<sub>2</sub> flash method did not yield a sufficiently high initial H atom concentration for an accurate measurement of the decay constant to be made. As a result, only the  $O_2$  filter method could be used to avoid O<sub>2</sub> photolysis. Additional experiments, with water as the source molecule, that used  $N_2$  in the flash lamp (without any type of oxygen filtering system) were also performed; and the rate constants from these experiments were consistent with the rest of the data set.

After their formation by flash photolysis, H atoms are depleted by the following reactions:

$$H + O_2 \rightarrow OH + O \tag{1}$$

$$H + O_2 + M \rightarrow HO_2 + M$$
 (2)

and

$$H + NH_3 \rightarrow NH_2 + H_2 \tag{3}$$

or

$$H + H_2O \rightarrow OH + H_2 \tag{4}$$

In this study, [M] is taken to be the overall concentration (density), which includes Ar, O<sub>2</sub>, and NH<sub>3</sub> or H<sub>2</sub>O. In these experiments, however, argon was the effective third-body collider because O<sub>2</sub>



Figure 1. First-order plot from the raw data in the inset.  $k_{obsd} = 1741$  $\pm$  48 s<sup>-1</sup>, and  $k_{bi}^{app} = 3.29 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Inset: typical photomultiplier signal observed after flash photolysis in the reflected shock regime.  $P_1 = 10.87$  Torr,  $[O_2] = 5.218 \times 10^{16}$  molecules cm<sup>-3</sup>,  $[NH_3] = 1.022 \times 10^{15}$  molecules cm<sup>-3</sup>, and T = 853 K.

and  $NH_3$  (or  $H_2O$ ) were held to very low concentrations. Even considering the greater third-body efficiency of NH<sub>3</sub> (or H<sub>2</sub>O), the maximum possible contribution by this species to the termolecular reaction rate never exceeded about 1% of that due to Ar.

The concentrations of  $O_2$ , Ar, and  $NH_3$  (or  $H_2O$ ) are always maintained in large excess over [H], and therefore, each of these reactions follows pseudo-first-order kinetics. Consequently,

$$d[H]/dt = -k_{obsd}[H]$$
(VI)

where

or

$$k_{\text{obsd}} = k_1[O_2] + k_2[O_2][M] + k_3[NH_3]$$
 (VIIa)

$$k_{\text{obsd}} = k_1[O_2] + k_2[O_2][M] + k_4[H_2O]$$
 (VIIb)

depending on whether  $NH_3$  or  $H_2O$  is used as the photolyte. In the range of H atom concentrations used in these experi-

ments, Beer's law is always valid, 23a, 26d and therefore, absorbance  $(ABS = Kl[H]_{t})^{23}$  is directly proportional to  $[H]_{t}$ . Thus

$$\ln (ABS)_t = -k_{obsd}t + C \qquad (VIII)$$

and a plot of ln (ABS), versus time has a slope equal to  $-k_{obsd}$ . Figure 1 shows a typical photomultiplier trace and the corresponding first-order plot of ln (ABS) versus time according to eq VIII

All H atom decays obeyed first-order kinetics, usually over more than two half-lives, with no evidence of complex kinetic behavior. This observation was further supported by results from computer simulations which took secondary reactions into account. These results clearly demonstrated that secondary reactions were unimportant under the conditions of the present experiments.

The rate constants for reactions 3 and 4 have been directly measured in the appropriate temperature range in separate experiments.<sup>28,34</sup> Therefore the contribution of reaction 3 or 4 to the experimentally observed H-atom depletion rate was readily determined. The net first-order rate constant,  $k'_{obsd}$ , due to reactions 1 and 2 was derived by rearrangement of (VIIa) or (VIIb) to give

$$k'_{\text{obsd}} = k_{\text{obsd}} - k_3[\text{NH}_3]$$
(IXa)

or

$$k'_{\text{obsd}} = k_{\text{obsd}} - k_4[\text{H}_2\text{O}] \qquad (\text{IXb})$$

<sup>(28)</sup> Michael, J. V.; Sutherland, J. W.; Klemm, R. B. J. Phys. Chem. 1986, 90, 497.  $k_{H+NH3}(T) = 1.06 \times 10^{-18} T^{2.39} \exp(-5119 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , 750 K  $\leq T \leq 1777$  K.

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<sup>(33)</sup> Stief, L. J.; Payne, W. A.; Klemm, R. B. J. Chem. Phys. 1975, 62, 4000.

<sup>(34)</sup> Michael, J. V.; Sutherland, J. W. J. Phys. Chem. 1988, 92, 3853.  $k_{\rm H+H_{2O}}(T) = 4.58 \times 10^{-10} \exp(-11573 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, 1246 \text{ K} \le T \le 2297 \text{ K}.$ 

and thus

$$k'_{obsd} = k_1[O_2] + k_2[O_2][M]$$
 (IX)

Reaction mixtures were chosen so that the contribution from reaction 3 or 4 was always less than about 25%, and usually less than about 10%. At temperatures above about 1450 and 1700 K, the respective rates of reactions 3 and 4 became large compared with that of reaction 1. Mixtures in which the ammonia or water concentration was low enough to keep the contribution of reaction 3 or 4 sufficiently small failed to yield initial H atom concentrations high enough to make accurate measurements of the first-order rate. This criterion therefore largely determined the high-temperature limits of the various data sets.

The  $H_2O/O_2/Ar$  mixtures used in this study exhibited no problems with respect to maintaining their stability during preparation, storage, and use in the shock tube. This was thoroughly investigated in a separate kinetic study of reaction 4.<sup>34</sup> In the present study, the repeatability of the measured decay constants was not affected by the age of the mixtures, and, in the temperature range in which reaction 1 is the only important reaction, rate constants obtained at the same temperature from different mixtures agreed within experimental error.

Argon (scientific grade, 99.9999%) and ammonia (electronic grade, 99.999%) were obtained from MG Industries. Water was purified by distillation and passage through an ultrapurification system (Millipore Corp.). Both  $NH_3$  and  $H_2O$  were bulb-to-bulb distilled in a greaseless, all-glass, high-vacuum gas handling system; the middle one-third fractions were retained. The helium used as the shock tube driver gas and in the resonance lamp was "Ultra-high Purity" grade (99.999%) and was obtained from Linde Division, Union Carbide.

#### Results

As a first step in the analysis of the data, it was necessary to determine the temperature range over which reaction 1 is the only important channel. The low-temperature limit of this range may be defined as the lowest temperature at which the contribution of reaction 2 to the overall H atom depletion rate is negligible, within experimental error. Analysis of data below this temperature must take both reactions 1 and 2 into account, while analysis of data above this temperature involves only reaction 1. For experiments in which the initial test gas pressure  $(P_1)$  was either 10 or 15 Torr, the low-temperature limit occurred at 962 K. For the 30 Torr runs, the limit was 1011 K. A further explanation of the procedure is given below.

Also, blank runs were performed routinely to assure that H atoms were only produced photolytically from the source compounds,  $NH_3$  or  $H_2O$ . In blank runs that omitted  $NH_3$  or  $H_2O$ , shock heating and photolysis were performed to verify that H atoms were not generated to any measurable extent from impurities. In other blank runs, reaction mixtures that included  $NH_3$  or  $H_2O$  were shock heated, but not photolyzed, to assure that H atoms were only produced photolytically (and not pyrolytically) from these source compounds.

 $H + O_2 \rightarrow OH + O$ . The rate constant data for reaction 1 are listed in Table I and shown in the Arrhenius plot of Figure 2. In Table I, the data are grouped into sets according to initial pressure, reactant composition, and the photolytic source molecule and filtering combination used.

As discussed in the Experimental Section, all of the observed decays were first order. The bimolecular rate constant,  $k_1$ , was calculated from the experimentally determined first-order rate constant,  $k'_{obsd}$ , by neglecting the  $k_2[O_2][M]$  term (expression IX) at temperatures above about 950 K. This low-temperature limit on the measurement of  $k_1$  was established by selecting (iteratively) data only from those runs to which reaction 2 contributed less than 10–15% to the total H atom decay rate,  $k'_{obsd}$ . Thus,  $k_1$  was calculated from

$$k_1 = k'_{\text{obsd}} / [O_2] \tag{X}$$

In eq X, species concentrations are determined from the initial temperature, pressure, and composition of the reactant mixture,



Figure 2. Two-parameter Arrhenius plot of the  $k_1(T)$  data of Table I. The solid line is the expression  $k_1 = (2.79 \pm 0.32) \times 10^{-10} \exp(-16132 \pm 276 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

and the thermodynamic conditions in the reflected shock regime. These conditions are calculated by using corrections to ideal shock theory that have been discussed thoroughly.<sup>23</sup>

The rate constant results generally show good agreement between the data sets. However, rate constants from the  $H_2O$ photolyte-O2 filter data set are systematically larger than the other three sets by about 60%. The main problem with these H<sub>2</sub>O photolyte– $O_2$  filter data was the unusually low initial H atom concentrations that were obtained. Even with the rather large flash energies ( $\sim 1000 \text{ J}$ ) that had to be employed, the [H]<sub>0</sub> was  $\leq 8 \times 10^{11}$  atoms cm<sup>-3</sup> for most of these experiments because the  $O_2$  filter blocked photolysis of  $H_2O$  as well as that of  $O_2$ . As a result, the first-order decays obtained in these experiments had a poorer signal-to-noise ratio than the decays of the other data sets; and thus the rate constant measurements of this set exhibit much greater error and scatter than those of the other sets. Although several possibilities were explored for this discrepancy between the H<sub>2</sub>O photolyte-O<sub>2</sub> filter data and the rest of the rate data for  $k_1$ , no satisfactory explanation was apparent. For example, the H<sub>2</sub>O third-body efficiency is well-known to be substantially larger than that for argon.<sup>6,7,18</sup> Therefore, two series of experiments were performed in which (1) the [H<sub>2</sub>O] was reduced by a factor of 2; and (2) the initial reaction mixture pressure was reduced from 15 to 10 Torr. These changes reduced the H<sub>2</sub>O density to about one-third of its original value, but they did not lead to improved rate constant results. In view of the consistently large rate constant values and large error of the H<sub>2</sub>O photolyte-O<sub>2</sub> filter data, it was appropriate to exclude this data set from the final analysis of  $k_1(T)$ . Even so, these data are included in Table I. Also, it is important to note that for the three remaining data sets, that include 159 individual data points, no systematic difference in rate constant results was observed for wide variations in both the initial pressure and the reaction mixture composition. The value for  $k_1(T)$  derived from the three self-consistent data sets is well represented by the two-parameter least-squares fit (962  $K \leq T \leq 1705 \text{ K}$ :

$$k_1(T) = (2.79 \pm 0.32) \times 10^{-10} \exp(-16132 \pm 276 \text{ cal mol})$$

$$0^{-10} \exp(-16132 \pm 276 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(XI)

The mean deviation of the experimentally measured rate constant values from those calculated by using eq XI is  $\pm 16\%$  over the

TADIEL D.A.	Conceant Date	for the Decetion	$\mathbf{U} \perp \mathbf{O} \rightarrow \mathbf{O}\mathbf{U} \perp \mathbf{O}$
IADLE I: KAR	e Constant Data	IOF LINE REACTION	$\mathbf{n} + \mathbf{v}_1 \rightarrow \mathbf{v}_{\mathbf{n}} + \mathbf{v}_1$

	i itaite c					-1 -1									
<b>P</b> <sub>1</sub> ,		$k_{obsd}, b$		T <sub>5</sub> ,				<b>P</b> <sub>1</sub> ,		$k_{obsd},^{b}$		T <sub>5</sub> ,			
Torr	$M_{s}^{a}$	s <sup>-1</sup>	$\rho_5^c$	K	$k_1^d$	$K_1^e$	$k_{-1}$	Torr	$M_s^a$	s <sup>-1</sup>	ρs	Κ	$k_1^d$	$K_1^e$	$k_{-1}^{f}$
					Y. 8 =	1 238 ¥	10-3. Y.	= 1 263	× 10-3. N	J. Flach				·····	
10.77	2 450	3217	2 010	1515	10.66	0.0663	161, 7H <sub>2</sub> O	10.203	2 10 , 1	2012	1 0 2 7	1551	0.96	0.0751	1 21
10.77	2.400	2075	1 000	1500	10.00	0.0005	1.01	10.20	2.404	2622	1.737	1501	7.00	0.0751	1.51
10.42	2.510	5050	1.909	1000	12.32	0.0040	1.40	10.54	2.438	3023	1.972	1525	12.48	0.0682	1.83
10.34	2.612	5058	2.030	1690	15.13	0.1155	1.31	10.45	2.418	2409	1.929	1481	8.18	0.0586	1.40
10.71	2.524	4326	2.055	1588	13.79	0.0848	1.63	10.61	2.326	1599	1.892	1387	5.70	0.0404	1.41
10.32	2.566	4736	1.999	1640	15.08	0.0997	1.51								
					$X_{0_2} =$	$2.550 \times$	10 <sup>-3</sup> ; X <sub>H2O</sub>	= 2.500 2	× 10⁻³; N	$I_2$ Flash					
10.52	2.382	5616	1.921	1441	9.99	0.0503	1.98	10.82	2.190	2447	1.818	1255	4.83	0.0218	2.21
10.64	2.316	4383	1.888	1378	8.08	0.0389	2.08	10.72	2.298	3652	1.888	1361	6.66	0.0361	1.84
10.58	2.262	3238	1.836	1325	6.19	0.0307	2.01	10.72	2.127	1537	1.753	1191	3.16	0.0154	2.05
							_								
					$X_{O_2} =$	4.995 × 1	10 <sup>-3</sup> ; X <sub>NH3</sub>	= 3.000	× 10⁴; O	2 Filter					
10.31	2.142	3857	1.698	1206	4.34	0.0168	2.59	10.50	2.110	2390	1.701	1176	2.63	0.0141	1.86
10.67	2.122	3422	1.740	1187	3.75	0.0150	2.47	10.90	2.049	1638	1.709	1119	1.79	0.0099	1.80
10.47	2.301	6115	1.852	1360	6.15	0.0360	1.71	10.81	2.024	1697	1.671	1097	1.92	0.0086	2.23
10.49	2.249	4903	1.815	1308	5.05	0.0284	1.78	10.51	2 336	9184	1 885	1394	9 23	0.0416	2 22
10.54	2 1 2 1	2983	1 718	1186	3 29	0.0150	2 20	10.63	2 1 4 7	4050	1 755	1210	4 4 1	0.0172	2 57
10.54	2.121	2705	1.710	1100	5.27	0.0150	2.20	10.05	2.14/	4050	1.755	1210	7.71	0.0172	2.37
					$X_{0} =$	7.438 ×	$10^{-3}$ : X <sub>NM</sub> .	= 7.375	× 10 <sup>-4</sup> : C	) <sub>2</sub> Flash					
10.42	2.071	2764	1 647	1145	2 01	0.0117	1 71	10.47	2 094	3030	1 670	1170	216	0.0136	1 58
10.80	2.068	2624	1 704	1142	1.83	0.0115	1 59	10.48	2111	3603	1 685	1185	2.10	0.0120	1 72
10.50	2.000	2024	1 500	1092	1.53	0.0115	1.07	10.73	2.111	2205	1 400	1159	2.30	0.0177	1.72
10.52	1.003	1020	1.577	1005	0.910	0.0078	1.77	10.75	2.001	3295	1.099	1150	2.34	0.0127	1.04
10.48	1.923	1038	1.310	1013	0.819	0.0047	1.76								
					<i>Y</i> . =	1 840 X	10-2. X	= 7 375	× 10-4. O	Flach					
10.94	1 074	3700	1 622	1051	1 21	0 0042	1 01	1070	2 10 , 0	5220	1 401	1194	1 60	0.0104	1 55
10.85	1.7/4	2777	1.032	070	1.21	0.0002	1.94	10.70	2.030	10(05	1.091	1120	1.02	0.0104	1.55
10.76	1.883	2340	1.524	972	0.802	0.0033	2.42	10.80	2.128	10605	1.772	1190	3.11	0.0153	2.03
10.49	1.888	2119	1.491	976	0.737	0.0034	2.15	10.80	2.028	4198	1.677	1098	1.28	0.0087	1.48
10.31	1.981	3468	1.557	1056	1.15	0.0064	1.78	10.61	2.089	7089	1.705	1153	2.15	0.0123	1.74
					IZ a	2 (00 14	10-2 1/		· 10-4 0						
					$X_{0_2} =$	3.699 X	$10^{-2}; X_{\rm NH_3}$	= 1.375	× 10 *; C	P <sub>2</sub> Flash					
10.28	1.882	3308	1.470	962	0.594	0.0030	1.95	10.62	1.970	7384	1.611	1036	1.22	0.0056	2.18
10.43	1.956	5538	1.568	1024	0.933	0.0051	1.84	10.40	1.957	5729	1.565	1026	0.967	0.0051	1.88
10.51	1.926	3982	1.550	999	0.676	0.0042	1.63	10.71	1.976	6812	1.630	1041	1.10	0.0058	1.91
					$X_{0_2} =$	8.726 ×	$10^{-1}; X_{H_2O}$	= 4.149 2	× 10 <sup>-</sup> "; N	<sub>2</sub> Flash					
15.63	2.311	1678	2.769	1351	6.53	0.0346	1.89	15.61	2.512	4466	2.980	1552	15.90	0.0753	2.11
15.84	2.352	3097	2.842	1396	11.94	0.0420	2.84	15.37	2.348	4231	2.762	1387	17.03	0.0404	4.21
15.38	2.419	3293	2.827	1465	12.53	0.0552	1.27	15.61	2.395	3058	2.856	1436	11.58	0.0494	2.35
15.56	2.396	2404	2.837	1441	8.99	0.0503	1.79	15.76	2.511	4787	2.987	1561	17.04	0.0776	2.19
15.43	2.492	3368	2.948	1530	11.95	0.0699	1.71	15.96	2.297	3205	2,792	1346	12.75	0.0338	3.77
15.81	2 605	5555	3 093	1656	18 55	0 1046	1 77	15 41	2 643	7564	3 037	1705	26.07	0 1 2 0 5	216
15.01	2.000	6870	2 071	1572	25.00	0.1040	2 22	15.41	2.045	2605	2.057	1545	12.06	0.1205	1 79
15.40	2.555	0070	2.9/1	1575	23.77	0.0000	3.22	15.71	2.490	3093	2.704	1545	13.00	0.0730	1.70
					$X_0 =$	1.238 ×	$10^{-3}$ : X <sub>11</sub> o	= 1.263	× 10 <sup>−3</sup> : N	L. Flash					
15.40	2 4 3 6	4927	2 8 5 2	1480	12.06	0.0584	2 07	15.50	2 3 5 8	2558	2 781	1406	617	0.0665	2.01
15 20	2.430	2627	2.002	1415	0.72	0.0304	2.07	15.50	2.550	5619	2.701	1516	12 26	0.0005	1 41
15.59	2.372	5057	2.705	1415	12.43	0.0404	2.03	15.57	2.405	2010	2.903	1510	13.30	0.0437	1.41
15.52	2.411	5050	2.049	1455	12.07	0.0551	2.30	15.71	2.310	10101	2.909	15//	13.70	0.0818	1.00
15.72	2.440	3//2	2.921	1491	13.90	0.0608	2.30	15.44	2.464	4689	2.8//	1515	10.90	0.0663	1.64
15.36	2.398	4226	2.797	1446	10.63	0.0513	2.07	15.68	2.586	8428	3.025	1651	18.26	0.1031	1.77
					v -	1 650 -	10-3. V	- 1 250 3	V 10-3. N	Flach					
15 ( )	3 104	2252	3 501	1044	$A_{0_2} =$	1.030 A	10 ; A <sub>H2</sub> O	- 1.230 2	~ 10 °; N	2 FIASE	2 / 2/	1070	5 00	0.0000	0.14
13.02	2.180	2233	2.391	1240	4.94	0.0208	2.37	13.30	2.232	2385	2.030	1272	5.09	0.0238	2.14
15.56	2.140	1896	2.525	1202	4.32	0.0164	2.63	15.37	2.283	2815	2.696	1322	5.77	0.0303	1.90
15.55	2.200	2246	2.604	1254	4.88	0.0217	2.25	15.52	2.177	2187	2.589	1224	4.84	0.0185	2.61
15.51	2.291	2549	2.740	1326	5.07	0.0309	1.64	15.93	2.273	3253	2.773	1316	6.58	0.0295	2.23
					$X_{O_2} =$	1.887 × 1	10 <sup>-3</sup> ; X <sub>NH3</sub>	= 1.005	× 10⁼*; O	<sub>2</sub> Filter					
15.30	2.208	2124	2.587	1255	4.11	0.0218	1.88	15.43	2.340	3571	2.738	1393	6.44	0.0415	1.55
15.59	2.185	2534	2.608	1233	4.93	0.0195	2.53	15.58	2.265	3833	2.692	1315	7.22	0.0293	2.46
15.86	2.228	2415	2.688	1283	4.48	0.0251	1.78	15.68	2.375	4337	2.829	1424	7.58	0.0471	1.61
15.64	2.268	3786	2.696	1322	7.22	0.0303	2.38	15.55	2.355	4990	2.785	1404	9.00	0.0434	2.07
15.57	2.380	7138	2.805	1434	12.93	0.0490	2.64	15 75	2.288	4255	2.747	1337	7.84	0.0325	2.41
10.07	2.500		2.505			0.0470	a.0-1	10.70	2.200	,200	<b>_</b> ., <b>,</b> ,,	1001	7.04	0.0525	<u> </u>
					$X_{O_2} =$	2.450 × 1	10 <sup>-3</sup> ; Хнас	= 2.500 >	$\times 10^{-3}; N$	$I_2$ Flash					
15.76	2.153	2925	2.604	1200	4.28	0.0162	2.64	15.38	2.161	3377	2.543	1212	5.08	0.0174	2.93
15.38	2.237	4423	2.642	1280	6.27	0.0248	2.53		. = =						
	,			- 200		,0									
					$X_{0}$ , =	2.550 × 3	10 <sup>-3</sup> ; X <sub>H,O</sub>	= 2.500 >	× 10 <sup>−3</sup> ; N	2 Flash					
15.75	2.258	4557	2.703	1313	5.94	0.0291	2.04	15.55	2.250	4130	2.669	1301	5.45	0.0274	1.99
15.82	2.191	3688	2.635	1248	5.06	0.0211	2.40	15.88	2.244	4559	2.718	1295	5.98	0.0267	2.24
15.66	2.152	2435	2.560	1211	3.41	0.0173	1.98	15.56	2.338	5905	2.769	1388	7.28	0.0406	1.79
15.53	2.242	3797	2.647	1297	5.02	0.0269	1 86	15 70	2.310	5611	2,762	1350	7 06	0.0358	1.97
15 43	2.164	2991	2 5 5 5	1214	4 26	0.0175	2 43	15 38	2 340	5870	2 720	1304	7 27	0.0416	1 76
15 20	2 210	3574	2.555	1266	4.20	0 0 2 2 1	2.45	15.50	2.340	0261	2.727	1406	10.95	0.0410	1 75
10.47	4.4	5527	2.391	1200	7.05	0.0251	4.07	0.00	2.437	× 304	2.002	1420	10.05	0.0013	1.10

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	(000	,													
$P_1$ ,		$k_{obsd}, b$		T <sub>5</sub> ,	_			<i>P</i> <sub>1</sub> ,		$k_{\rm obsd},^{b}$		T <sub>5</sub> ,			
Torr	$M_{\bullet}^{a}$	s <sup>-1</sup>	$\rho_5^c$	K	$k_1^d$	$K_1^e$	$k_{-1}^{f}$	Torr	$M_{s}^{a}$	s <sup>-1</sup>	$\rho_5^c$	Κ	$k_1^d$	$K_1^e$	$k_{-1}^{f}$
					X- =	4 950 × 1	0-3. Y	= 5 1 25 >	(10-4.0	. Flach					
15.63	2 043	2277	2 406	1114	$170_{2} =$	A000 0	1 77	15 50	2 045	2104	2 403	1117	1.63	0 0008	1.66
15.05	1 007	1287	2.400	1073	0.067	0.0073	1 3 3	15.39	2.043	4729	2.403	1220	2 24	0.0098	1.00
15.33	2.227	1005	2.301	1105	1 / 2	0.0075	1.59	15.70	2.157	4730	2.505	1220	J.J.	0.0101	2.25
15.42	2.032	1905	2.300	1105	1.45	0.0091	1.50	15.04	2.175	0243	2.377	1237	4.40	0.0119	2.23
15.44	2.121	3212	2.478	1180	2.29	0.0150	1.53	15.49	2.229	/342	2.010	1289	5.20	0.0259	2.03
13.66	2.136	3870	2.532	1200	2.74	0.0162	1.69	15.57	2.181	6377	2.573	1243	4.30	0.0205	2.22
					$X_{\alpha} = $	4 995 X	10 <sup>-3</sup> · X	= 3.000	K 10-4. O	). Filter					
15 38	2 1 5 8	4598	2 565	1197	3 39	0.0160	2 1 2	15 48	2 277	9084	2 704	1318	6 35	0 0297	213
15.50	2 1 2 1	3518	2 582	1163	2.56	0.0131	1 96	15.53	2 269	10760	2 703	1311	7.61	0.0288	2.64
15.87	2 1 5 8	4043	2.502	1201	2.50	0.0163	1.75	15.50	2 1 2 5	4071	2 5 2 5	1175	3.05	0.0141	2.01
15.67	2.150	2432	2.037	1103	1 80	0.0103	2 11	15.50	2.125	7038	2.323	1332	5.05	0.0141	1 72
15 34	2.050	4070	2.430	1217	3.64	0.0070	2.11	15.60	2.290	4800	2.717	1185	3.57	0.0317	2 40
15.54	2.175	4370	2.570	1217	5.04	0.0170	2.04	15.00	2.150	-000	2.550	1105	5.57	0.0149	2.40
					$X_{0} =$	1.271 × 1	$0^{-2}; X_{\rm NH},$	= 5.375 >	< 10 <sup>-4</sup> ; O	$_2$ Flash					
15.87	2.022	4782	2.426	1091	1.48	0.0083	1.79	15.57	1.940	3248	2.265	1019	1.08	0.0049	2.22
15.61	2.001	4266	2.358	1072	1.36	0.0072	1.88	15.28	2.070	5326	2.400	1134	1.65	0.0109	1.51
15.52	1.996	3449	2.337	1068	1.10	0.0070	1.56	15.53	2.109	7014	2.490	1169	2.10	0.0136	1.54
15.83	2.006	3823	2.397	1076	1.19	0.0074	1.59	15.53	2.058	4632	2.424	1123	1.41	0.0102	1.38
15.49	1.881	1914	2.167	969	0.664	0.0032	2.05								
					$X_{O_2} =$	2.484 × 1	$10^{-2}; X_{\rm NH_3}$	= 5.375 >	< 10⁴; O	2 Flash					
15.65	1.880	4072	2.196	965	0.731	0.0031	2.34	15.48	1.915	4925	2.216	998	0.875	0.0041	2.12
15.47	1.885	3216	2.177	969	0.579	0.0032	1.79	15.69	1.997	6905	2.366	1068	1.14	0.0070	1.62
15.53	1. <b>9</b> 86	6869	2.326	1058	1.16	0.0065	1.77	15.86	1.979	7654	2.374	1049	1.27	0.0061	2.07
15.24	1.971	5640	2.263	1046	0.975	0.0060	1.63	15.48	2.044	10506	2.407	1106	1.72	0.0091	1.88
					••		a_2 v								
					$X_{0_2} =$	2.500 × 1	$10^{-5}; X_{\rm NH_3}$	= 1.501 >	< 10 <sup></sup> ; O	<sup>2</sup> Filter				0.01.04	
30.51	2.269	5414	5.059	1275	3.97	0.0242	1.64	30.50	2.157	3764	4.833	1167	2.95	0.0134	2.20
30.51	2.110	3113	4.679	1137	2.52	0.0112	2.26	30.40	2.166	3905	4.822	1179	3.06	0.0144	2.13
30.67	2.181	4934	4.866	1201	3.85	0.0163	2.36	30.78	2.161	3333	4.872	1175	2.56	0.0141	1.82
30.61	2.204	6139	4.956	1209	4.74	0.0171	2.78	30.61	2.064	2237	4.600	1092	1.84	0.0083	2.21
30.60	2.318	8630	5.194	1315	6.28	0.0293	2.14	30.77	2.106	3381	4.726	1130	2.73	0.0107	2.56
30.70	2.223	5330	5.013	1227	4.02	0.0189	2.13								
					<b>V</b>	< 112 V	0-1 1/	- 1 000 1	4 10-4 0	The sh					
			4 (05		$X_{0_2} =$	0.213 X	$10^{-3}; X_{\rm NH_3}$	= 3.000 x	K 10 "; U	<sup>2</sup> Flash	4 207	1017	1 1 2	0.0040	2.26
30.39	2.109	6965	4.625	1145	2.30	0.0117	1.96	30.91	1.970	3208	4.380	1016	1.13	0.0048	2.30
30.94	2.163	10599	4.833	1193	3.37	0.0156	2.16	30.73	2.030	3480	4.514	1067	1.17	0.0070	1.67
30.36	2.049	4251	4.477	1091	1.44	0.0083	1.75	30.72	1.963	3133	4.343	1011	1.11	0.0046	2.43
30.68	2.043	4397	4.495	1090	1.49	0.0082	1.82								
					<i>Y</i> . =	1 243 X	10 <sup>-2</sup> · X	= 3.000 x	< 10 <sup>-4</sup> · O	). Flash					
30.60	1 080	5040	4 357	1020	1 07	0.0053	2 03	- 5.000 /	, 10, 0	2 1 14311					
50.00	1.700	3343	4.557	1029	1.07	0.0055	2.05								
						H <sub>2</sub> O	Photolyte/	O <sub>2</sub> Filter	Runs <sup>#</sup>						
						2		-							
					X	$c_{0}^{s} = 2.43$	$50 \times 10^{-3}$ ;	$X_{H_{2}O} = 2$	$500 \times 10^{-10}$	0-3					
10.76	2.002	775	1.649	1074	1.82	02	,	10.81	2.291	4383	1.911	1344	8.50		
10.41	2.045	1659	1.635	1112	4.00			10.51	2.227	2617	1.808	1282	5.34		
10.35	2.120	2309	1.692	1180	5.31			10.46	2.160	2998	1.738	1222	6.68		
10.87	2.092	1813	1.752	1155	4.01			10.53	2.039	1773	1.643	1110	4.26		
10.74	2.134	2460	1.768	1193	5.39			10.81	1.982	881	1.631	1059	2.12		
													-		
					2	$K_{O_2} = 2.55$	$10 \times 10^{-3};$	$X_{\rm H_{2}O} = 5.$	$000 \times 10^{-10}$	0-3					
10.33	2.177	2953	1.741	1231	5.90			10.71	2.185	3076	1.805	1242	5.86		
10.38	2.124	2251	1.704	1181	4.68			10.40	2.225	4489	1.786	1282	8.76		
10.27	2.034	1672	1.606	1099	3.84			10.66	1.993	824	1.634	1060	1.81		
10.74	2.111	2183	1.746	1173	4.43			10.64	2.057	2271	1.692	1116	4.98		
							0 14 10-3	v 0	500 N 1	n-3					
1.0.00			0.570	1100	5.25	$K_{O_2} = 2.43$	$0 \times 10^{-5};$	$X_{\rm H_{2}O} = 2.$	$500 \times 10$	1077	a 407	1120	2.07		
15.66	2.141	3550	2.572	1189	5.35			15.72	2.074	1977	2.487	1132	3.07		
15.54	2.219	4478	2.640	1267	6.41										
					,	$K_{0} = 2.52$	5 × 10-3.	$X_{\rm H} = \gamma$	500 × 10	0-3					
15 80	2 1 8 5	3330	2 648	1238	4 58	·U <sub>2</sub> - 2.52		15 51	2 105	3176	2 477	1167	4 85		
15 34	2.100	3680	2.040	1208	5 47			15 77	2.105	6131	2.667	1287	8 57		
15 22	2.100	5169	2.510	1200	7 34			15 32	2.231	6112	2.007	1207	8 70		
15.22	2.2.52	3440	2.372	1204	4 96			15.32	2.230	3150	2.007	1151	4 70		
15.59	2.130	3440	2.202	1205	7.50			15.02	1 004	1/127	2.303	1069	7.17		
10.07	2.103	2000	2.390	1213	3.73			10.40	1.793	140/	4.343	1000	2.74		
					2	$K_{02} = 2.55$	$50 \times 10^{-3}$ :	$X_{\rm H_{2}O} = 5.$	$000 \times 10$	0-3					
15.50	2.137	3435	2.522	1194	4.78			15.85	2.095	2169	2.549	1144	2.97		
15.34	2.126	2932	2.482	1184	4.11			15.34	2.055	2478	2.416	1109	3.75		
15.46	2.011	1352	2.351	1080	2.05			15.21	1.992	771	2.310	1053	1.16		
15.42	2.076	2136	2.432	1139	3.09			15.62	1.999	1693	2.374	1062	2.63		
15.57	2.081	1885	2.487	1132	2.64										

<sup>a</sup> The errors in Mach number were typically about  $\pm 0.5\%$  or less, at the one standard deviation level. <sup>b</sup> The errors in  $k_{obed}$  ranged from about  $\pm 2\%$  to  $\pm 5\%$ , at the one standard deviation level. <sup>c</sup> Units of density are  $\times 10^{18}$  molecules cm<sup>-3</sup>. <sup>d</sup> Units of  $k_1$  are  $\times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>e</sup> Equilibrium constant for reaction 1 at temperature  $T_5$ , computed from eq XVIIa and eq XVIIb (see text). <sup>f</sup>Rate constant for reaction -1 computed via  $k_{-1} = k_1/K_1$ ; units of  $k_{-1}$  are  $\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>g</sup>X<sub>i</sub> denotes the mole fraction of species *i*. <sup>h</sup>Data from these experiments were not used in the final determinations of  $k_1(T)$  and  $k_{-1}(T)$  (see text).

TABLE I (Continued)

TABLE II: Rate Constant Data for the Reaction  $H + O_2 + M \rightarrow HO_2 + M$ 

p		1. b		<u>т</u>		D		1. b		<b>T</b>	
	Ma	Kobsd,	0. <sup>6</sup>	I 5, K	Lapp d.e	P <sub>1</sub> , Torr	MA	$\kappa_{obsd}, _{a-1}$	. (	I 5, V	1-ADD d.e
1011	111 8	3	μ5	<u> </u>	~bi	1011	IVI s	3	<i>P</i> 5	ĸ	K bi
				$X_{O_2} =$	$1.849 \times 10^{-4}$	$X_{\rm NH_3} = 7.375$	× 10 <sup>-4</sup>				
10.48	1.861	1285	1.462	954	0.449	10.93	1.861	1873	1.525	954	0.638
				<i>Y</i> . =	3 600 × 10-2	Y = 7 375	× 10-4				
10.76	1 701	2100	1 4 3 8	880	0 404*	$, \Lambda_{\rm NH_3} = 7.5757$	1 740	1461	1 247	852	0.200*
10.70	1.806	2340	1 421	003	0.404	10.40	1.747	2122	1.547	012	0.200
10.58	1.607	2349	1 217	804	0.430	10.93	1.029	2122	1.304	910	0.372
10.74	1.007	1562	1.317	004	0.100	10.05	1.050	2401	1.495	941	0.434
10.51	1.750	1502	1.552	0.00	0.312						
				$X_{0} =$	$3.703 \times 10^{-2}$	$X_{\rm NH_2} = 7.250$	× 10 <sup>-4</sup>				
10.87	1.763	1405	1.424	863	0.261	10.94	1.725	1291	1.388	833	0.247*
10.84	1.737	1475	1.390	843	0.282*	10.87	1.750	1741	1.409	853	0.329*
10.71	1.691	1108	1.319	808	0.224*	10.24	1.876	3217	1.464	954	0.581
10.82	1.709	1231	1.353	821	0.242*	10.89	1.872	3342	1.552	951	0.569
10.87	1.824	2601	1.495	911	0.461	10.76	1.780	2134	1.429	876	0.397*
										0.0	0.071
				$X_{O_2} =$	$1.271 \times 10^{-2}$	$X_{\rm NH_3} = 5.375$	× 10 <sup>-4</sup>				
15.70	1.841	1776	2.134	936	0.631	15.45	1.798	1150	2.034	901	0.427
				<i>X</i> <sub>0</sub> =	$2484 \times 10^{-2}$	Y = 5 375	× 10-4				
15.60	1 828	2364	2 108	922	0 441	15 37	1 744	1478	1 036	849	0 201 #
15.00	1 811	2058	2.100	908	0.393	15.57	1.682	17/1	1.930	800	0.301
15.45	1 634	868	1 751	773	0.323	13.71	1.062	1271	1.0/4	809	0.203
15.55	1.004	505	1.751	115	0.197						
				$X_{0} =$	$2.516 \times 10^{-2}$	$X_{\rm NH_2} = 5.375$	× 10 <sup>-4</sup>				
15.78	1.737	1585	1.989	846	0.311*	14.98	1.715	1078	1.871	821	0.225*
15.58	1.734	1340	1.960	844	0.267*	15.52	1.772	1946	2.028	869	0.375*
15.58	1.639	1044	1.798	771	0.229*	15.55	1.852	2599	2.152	935	0.468
15.44	1.633	964	1.771	767	0.214*	15.51	1.734	1450	1.956	841	0.290*
15.33	1.655	1297	1.790	786	0.285*	15.96	1.795	2280	2.116	889	0.420*
15.38	1.745	1496	1.939	858	0.301*						01.20
				$X_{0_2} =$	$6.213 \times 10^{-3}$	$X_{\rm NH_3} = 3.000$	× 10 <sup>-4</sup>				
30.83	1.935	2766	4.282	987	0.999*	30.80	1.846	1338	4.007	921	0.514
30.84	1.905	2722	4.175	969	1.01*	30.40	1.867	1614	4.011	938	0.620
30.22	1.906	2146	4.093	970	0.808						
				<i>X</i> <sub>0</sub> =	$1.210 \times 10^{-2}$	$X_{\rm M} = 3.000$	× 10 <sup>-4</sup>				
30.71	1.867	3174	4.064	935	0.632*	30.82	1 739	1545	3 716	831	0 338*
30.82	1 757	2553	3 746	851	0.557*	30.52	1.676	1333	3 486	784	0.313*
30.37	1 747	2184	3 676	841	0.485*	30.22	1.674	1475	3 203	746	0.368*
30.63	1 720	1892	3 611	877	0.428*	30.57	1 742	2012	3 605	824	0.308
30.72	1.720	1514	3 584	813	0.425	30.37	1.742	2012	3.093	054	0.443
50.72	1.707	1314	5.504	015	0.545	30.49	1.700	2402	3.737	632	0.322
				$X_{0} =$	$1.243 \times 10^{-2}$	$X_{\rm NH_3} = 3.000$	× 10 <sup>-4</sup>				
30.80	1.864	3244	4.071	933	0.628*	30.54	1.729	2023	3.642	827	0.442*
30.43	1.954	5518	4.263	1006	1.018	30.24	1.792	2340	3.791	875	0.489*
30.22	1.928	<b>529</b> 1	4.165	985	1.002*	30.65	1.712	2042	3.602	814	0.452*
30.64	1.832	2887	3.956	907	0.577*	30.82	1.655	1498	3.430	773	0.349*
30.70	1.756	2022	3.741	847	0.429*	30.55	1.721	1825	3.607	824	0.402*
30.94	1.834	2625	4.029	903	0.514*	30.54	1.675	2150	3.462	788	0.497*
30.18	1.728	2275	3.620	821	0.501*	30.67	1.620	1621	3.304	748	0.393*

<sup>a</sup> The errors in Mach number were typically about  $\pm 0.5\%$  or less, at the one standard deviation level. <sup>b</sup> The errors in  $k_{obsd}$  were  $\pm 2\%$  to  $\pm 5\%$ , at the one standard deviation level. <sup>c</sup> Units of density are  $\times 10^{18}$  molecules cm<sup>-3</sup>. <sup>d</sup> Units of  $k_{bl}^{app}$  are  $\times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>e</sup> The asterisk signifies that the experimental value for  $k_{bl}^{app}$  was used in the final determination of  $k_2$ ; see text, under Results, for details. <sup>f</sup> X<sub>i</sub> denotes the mole fraction of species *i*.

stated temperature range. Equation XI is shown as the solid line in Figure 2 along with the data used to derive this expression.

 $H + O_2 + M \rightarrow HO_2 + M$ . The data used in the determination of  $k_2$  were all obtained by using the NH<sub>3</sub> photolyte-O<sub>2</sub> flash condition. These data are given in Table II, which contains both the experimentally observed first-order decay constant,  $k_{obsd}$ , and the apparent bimolecular rate constant,  $k_{bb}^{app}$ :

$$k_{\rm bi}^{\rm app} = k_{\rm obsd} / [\rm O_2] \tag{XII}$$

In this temperature span ( $\sim$ 750 to  $\sim$ 1000 K), both reactions 1 and 2 contribute to the overall H atom depletion rate; hence,

$$k_{\rm bi}^{\rm app} = k_1 + k_2[\rm M] \tag{XIII}$$

Equation XIII provides a rationale for the evaluation of  $k_2$  from the experimentally determined  $k_{bi}^{app}$  values and the results for  $k_1(T)$ . In eq XIII,  $k_1$  may be evaluated by extrapolating the results of eq XI down to the lower temperature range. Such an extrapolation is quite reasonable since there is no indication of curvature in the Arrhenius plot of  $k_1(T)$ . Indeed, the values derived from  $k_1(T)$  over the 770–1040 K span by Eberius et al.,<sup>35</sup> and reported in ref 7, show remarkably good agreement with the value derived from eq XI.

Thus, denoting the values calculated by eq XI as  $k_1^c$ , Eq XIII may be rearranged to solve for  $k_2$ ,

$$k_2 = (k_{bi}^{app} - k_1^{c}) / [M]$$
 (XIV)

This method was used to evaluate  $k_2$  for each experiment listed in Table II. However, not all of these determinations are useful in establishing the value of  $k_2$ . This is especially true for the 10 and 15 Torr experiments near the low-temperature limit (T = 962K) of the  $k_1$  analysis. Consequently, it was necessary to adopt a procedure to select those experiments that exhibited a sufficiently high contribution to the H atom depletion rate by reaction 2, and thus, to obtain reasonably accurate determinations of  $k_2$  through

<sup>(35)</sup> Eberius, K. H.; Hoyermann, K.; Wagner, H. G. Thirteenth Symposium (International) on Combustion; The Combustion Institute: Pittsburgh, 1971; p 713.

TABLE III: Rate Constant Expressions for  $H + O_2 \rightarrow OH + O$  in the Form  $k_1 = AT^n \exp(-E_a/RT)$ 

 A, cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> K <sup>-n</sup>	n	$E_{\rm a}$ , cal mol <sup>-1</sup>	T range, K	ref/error limits	
$3.7 \times 10^{-10}$	0	16790	700-2500	Baulch et al. <sup>7</sup> / $\pm$ 30%	•
$2.77 \times 10^{-7}$	-0.9	17 386	300-2500	Cohen and Westberg <sup>9</sup> /±30%	
$2.02 \times 10^{-7}$	-0.91	16 504	300-2500	$Warnatz^8/\pm 40\%$	
$2.02 \times 10^{-7}$	-0.907	16629	1250-2500	Schott <sup>10</sup>	
$8.52 \times 10^{-8}$	-0.816	16 507	250-2500	Miller <sup>19a</sup>	
$2.0 \times 10^{-10}$	0	16098	1000-2500	Pamidimukkala and Skinner <sup>11</sup> /±30%	
$(4.05 \pm 0.55) \times 10^{-10}$	0	$17269 \pm 525$	1693-2577	Frank and Just <sup>12</sup>	
$(2.79 \pm 0.32) \times 10^{-10}$	0	$16132 \pm 276$	962-1705	present study	
$(3.18 \pm 0.24) \times 10^{-10}$	0	16439 ± 186	962-2577	present study combined with ref 12	
$2.46 \times 10^{-10}$	0	15477	1000-2600	Troe <sup>18</sup>	

<sup>a</sup> Calculated using  $k_1 = K_1 k_{-1}$  (see text).



**Figure 3.** Arrhenius plot for reaction 2. The solid circles are the experimental  $k_2$  values derived from the \* data in Table II. The solid line represents the average value  $k_2 = (7.1 \pm 1.9) \times 10^{-33}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>. The dashed line was computed from eq V, the recommended value of Baulch et al.<sup>7</sup> (see text).

eq XIV. The adopted criterion was as follows: the experimentally measured bimolecular rate constant,  $k_{bl}^{app}$  (due to both reactions 1 and 2) was required to be at least 32% larger than the calculated bimolecular rate due to reaction 1, i.e.,  $k_{bl}^{app}/k_1 \ge 1.32$ . The 32% value was chosen because it represents twice the mean deviation in  $k_1(T)$ . The experimental values that fulfilled this requirement are denoted by a \* in Table II. The resulting data set of 48 individual runs shows a slight negative temperature dependence that is in accord with previous studies. However, the large scatter of the data, combined with the narrow temperature range over which the data were obtained, precludes the derivation of a precise temperature coefficient; and therefore a simple average value for  $k_2$  was computed that is valid over the limited temperature range of 746–987 K:

$$k_2 = (7.1 \pm 1.9) \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$
 (XV)

The 48 individual values for  $k_2$ , derived via eq XIV, are plotted in Figure 3. The solid line represents the average value, eq XV, and the dashed line was calculated from the recommended value of Baulch et al.<sup>7</sup>

#### Discussion

 $H + O_2 \rightarrow OH + O$ . A comparison of the present data with previous results is shown in Figure 4, and given in Table III, where the least-squares expressions from the present study are listed with those from the previous experimental studies,<sup>10-12</sup> the reviews<sup>7-9</sup> and the calculation<sup>19</sup> that were discussed in the Introduction section.

The agreement of eq XI with eq I is quite good. The two expressions agree within about  $\pm 10\%$  over the entire temperature range of the present study, 962–1705 K. This agreement, however, could be fortuitous because, in the evaluation,<sup>7</sup> the activation energy was set equal to the endothermicity. This constraint was based largely on the trend of the majority of experimental data and on the assumption that the back process, reaction -1, has no



**Figure 4.** Comparison of experimental  $k_1(T)$  data: (•) present results; (•) Frank and Just;<sup>12</sup> the solid line is eq XI,  $k_1(T) = (3.18 \pm 0.24) \times 10^{-10} \exp(-16439 \pm 186/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see text); (---) Pamidimukkala and Skinner<sup>11</sup>; (--) Schott.<sup>10</sup>

activation energy over the wide temprature range cited in the review.

Although eq XI is not inconsistent with the results of Schott<sup>10</sup> in the region of temperature overlap, the two expressions diverge. Schott's results become increasingly smaller than those from eq XI with increasing temperature. For example, at 1250 K the  $k_1$ values disagree by less than 8% while at 1700 K the disparity is nearly 30%. A similar disparate relationship is found between eq XI and the recommended expression of Warnatz<sup>8</sup> and the calaculated values of Miller.<sup>19</sup> The agreement between eq XI and the recommendation of Cohen and Westberg,9 shown in Table III, is somewhat better; however, even though the two expressions agree within their combined errors, they too diverge. As with the expressions of Schott,<sup>10</sup> Warnatz,<sup>8</sup> and Miller,<sup>19</sup> the source of this disagreement lies primarily in the temperature dependence of the preexponential factor. In the review of Baulch et al.,<sup>7</sup> it was noted that the early work of Schott, Gutman, and co-workers<sup>13,15</sup> gave  $k_1$  values of the correct magnitude. Nevertheless, these studies were rejected because the apparent activation energies were too low. The results of the present study are consistent with this conclusion. However, extending this study, to obtain direct measurements of  $k_1(T)$ , to temperatures above 1700 K would obviously be worthwhile.

The expression of Pamidimukkala and Skinner,<sup>11</sup> eq III, agress with eq XI within the combined error of the two expressions; however, the  $k_1$  values from eq III are consistently smaller (by about 25%) than those from eq XI over the whole range of temperature overlap. Since the activation energies are nearly identical, it is obvious that the source of the difference between the two expressions lies entirely in the temperature-independent preexponential factor.

The results of the present study for  $k_1(T)$  are in remarkably good agreement with those of Frank and Just<sup>12</sup> even though a region of temperature overlap just barely exists. At 1700 K, eq XI and IV agree to within about 4%, with eq IV giving the higher value for  $k_1$ . Over the temperature span of 1200 K  $\leq T \leq 2000$ K that extends above and below the point of overlap, the two expressions agree to within about  $\pm 10\%$ . Because of the very good agreement between the two studies, the experimental data of Frank and Just<sup>12</sup> were combined with the present data for  $k_1(T)$ . This combined data set is shown in Figure 4 and is well represented by the two-parameter least-squares expression (962 K  $\leq T \leq 2577$ K):

$$k_1(T) = (3.18 \pm 0.24) \times 10^{-10} \exp(-16439 \pm 186 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(XVI)

The mean deviation of the experimentally measured rate constant values from those calculated by using this expression is about  $\pm 15\%$  over the stated temperature range.

It is interesting to note that the value for  $k_1(T)$ , reported in the pioneering incident shock-ARAS work of Myerson and Watt<sup>24c</sup> (and included in the review of Baulch et al.<sup>7</sup>), agrees with eq XVI to within about  $\pm 20\%$  over the 1700–2500 K temperature span.

Lastly, a least-squares expression for  $k_1(T)$  has been derived from Troe's calculated results<sup>18</sup> for reaction -1, using  $k_1(T) = K_1(T)k_{-1}(T)$ :

$$k_1(T) = 2.46 \times 10^{-10} \exp(-15477/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(XVII)

This expression (included in Table III) yields  $k_1$  values that agree reasonably well with those derived from the combined experimental result, eq XVI. At 1000 K the calculated value is 25% larger than the experimental result and at 2600 K it is 8% smaller. This agreement appears to strengthen Troe's argument against a large extent of "recrossing" at high temperature.<sup>18</sup> This is in contrast to Miller's conclusions<sup>19</sup> that "nonstatistical recrossing" plays an important role at high temperature and that this causes  $k_1(T)$  to be "depressed" at temperatures above about 1250 K.

 $O + OH \rightarrow H + O_2$ . Expression XVI was used to derive rate constants for reaction -1 by employing the well-established equilibrium constant,<sup>27</sup>  $K_1(T)$ , for reaction 1:  $k_{-1}(T) = k_1(T)/K_1(T)$ . This procedure is appropriate since (1) and (-1) are elementary reactions;<sup>19,36</sup> however, its success clearly depends on the accuracy of  $K_1(T)$  and  $k_1(T)$ .  $K_1(T)$  values were calculated over the necessary temperature ranges by using data from the JANAF tables.<sup>27</sup> Two expressions are required to fit the equilibrium constant data due to curvature in  $K_1(T)$ . The expressions derived are

between 1000 and 1700 K

$$K_1(T) = (14.11 \pm 0.19) \exp(-16137 \pm 35/RT)$$
 (XVIIa)

and between 1700 and 2600 K

$$K_1(T) = (11.84 \pm 0.11) \exp(-15570 \pm 35/RT)$$
 (XVIIb)

Equations XVIIa and XVIIb are accurate to within about  $\pm 1\%$  over their respective temperature ranges.

Values for  $k_{-1}(T)$  were calculated from each  $k_1(T)$  value listed in Table I (except those from the H<sub>2</sub>O photolyte-O<sub>2</sub> filter data set). The experimental data of Frank and Just<sup>12</sup> were treated in the same way. These  $k_{-1}(T)$  values are plotted in Figure 5. The combined data base exhibits two important features. First, the  $k_{-1}(T)$  values calculated from the data of Frank and Just<sup>12</sup> are in good agreement with those from the present study. Second, the value of  $k_{-1}$  exhibits no apparent temperature dependence over



Figure 5. Plot of  $k_{-1}(T)$  data: (•) present results; (•) Frank and Just;<sup>12</sup> solid line is eq XVIII,  $k_{-1}(T) = (2.05 \pm 0.42) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see text).



**Figure 6.** Comparison of  $k_{-1}(T)$  data vs calculations:  $(\mathbf{\nabla})$  Howard and Smith;<sup>17</sup> ( $\Delta$ ) Lewis and Watson;<sup>16</sup> (---) Troe;<sup>18</sup> (---) average value of the combined data (eq XVIII, see text) shown in Figure 5 with appropriate error bars at both ends of the line.

the temperature span 962–2577 K (see Figure 5), and thus  $k_{-1}$  may be represented by a simple average of the experimental data:

$$k_{-1} = (2.05 \pm 0.42) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (XVIII)

The present combined results, eq XVIII, disagree qualitatively and quantitatively with the review of Cohen and Westberg<sup>9</sup> and the calculations of Miller.<sup>19</sup> This was expected, of course, since their  $k_1(T)$  expressions follow eq II, more or less; and eq II diverges markedly from eq XVI. For both cases,  $^{9,19} k_{-1}(T)$  values are smaller than those of eq XVIII at T > 1700 K, and at 2500 K the disparity amounts to 35%-50%. In contrast, the recent calculations of Troe<sup>18</sup> provide values for  $k_{-1}(T)$  that are in very good agreement with eq XVIII. Troe's results<sup>18</sup> decrease gradually and nearly linearly from  $2.36 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 1000 K to  $2.04 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 2600 K; but this change is too subtle to observe in the experimental data. It should be noted that Troe's results also agree well with the direct, experimental data of Lewis and Watson<sup>16</sup> (221-499 K) and Howard and Smith<sup>17</sup> (250-515 K), even though the temperature dependence in  $k_{-1}(T)$  is considerably more pronounced at low temperatures. This agreement of theory with experiment over the broad range in temperature from  $\sim 200$  to  $\sim 2600$  K is clearly shown in Figure 6.

 $H + O_2 + M \rightarrow HO_2 + M$ . The present result for  $k_2$ , eq XV, is in reasonably good agreement with the recommendation of Baulch et al.,<sup>7</sup> eq V. At 746 and 987 K, respectively, eq V yields values for  $k_2$  of 8.01 × 10<sup>-33</sup> and 6.80 × 10<sup>-33</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>. In addition, the present results are in accord with the recommendations of Slack<sup>21</sup> and Baulch et al.<sup>37</sup> In these reviews,

<sup>(36)</sup> For example, see: Castellan, G. W. Physical Chemistry; Addison-Wesley: Reading, MA, 1964.

expressions for  $k_2(T)$  are given as  $5.8 \times 10^{-33} (T/1000)^{-1.0} \text{ cm}^6$ molecule<sup>-2</sup> s<sup>-1</sup> (200 K  $\leq T \leq$  2200 K) and 1.8  $\times 10^{-32} (T/300)^{-0.8}$ cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, respectively. At 850 K, which is approximately the median temperature of the present study, Slack's expression gives a value of  $6.8 \times 10^{-33}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> and the expression of Baulch et al.<sup>37</sup> yields a value of  $7.8 \times 10^{-33}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>. In contrast, these results and that of the present study are about a factor of 3 larger than the determination of Pamidimukkala and Skinner.11

Very recenty, Hsu et al.<sup>38</sup> have undertaken a comprehensive experimental study of reaction 2. For the temperature interval 300 K  $\leq T \leq$  639 K, they report (with He as the third body):  $k_2(T) =$ 

$$(4.0 \pm 1.2) \times 10^{-33} \exp(+560 \pm 100/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$
(XIX)

It is generally accepted that the third-body efficiencies for He and Ar are about the same, and thus it is appropriate to extrapolate eq XIX to 850 K in order to make a comparison with the present value. The value computed,  $k_2(\text{He}) = 7.7 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2}$ 

Theoretical calculations on the limiting low-pressure third-order rate constant for reaction 2 have been discussed by Cobos et al.<sup>39</sup> The present result between 746 and 987 K,  $k_2 = (7.1 \pm 1.9) \times$ 10<sup>-33</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, requires the following Troe model parameters at 850 K:  $\beta_c = 0.03$  and  $\langle \Delta E \rangle = -51.4$  cal mol<sup>-1</sup>. These values for  $\beta_c$  and  $\langle \Delta E \rangle$  are in good agreement with those reported by Cobos et al.<sup>39</sup> for M = Ar at 1000 K. Indeed, this agreement was expected since Cobos et al.<sup>39</sup> based their calculations on a value for  $k_2$  of  $6.9 \times 10^{-33}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> at 1000 K.

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Registry No. <sup>-</sup>H, 12385-13-6; O<sub>2</sub>, 7782-44-7; Ar, 7440-37-1.

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## Photodissociation of Cr(CO)<sub>6</sub> in 1-Propanol and 2-Propanol: Effect of Solvent Structure on the Mechanisms of Formation of $Cr(CO)_5(OHR)$ from Photogenerated $Cr(CO)_5(ROH)$

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Picosecond absorption spectroscopy is used to examine the dynamics of formation of Cr(CO)<sub>5</sub>(OHR) from Cr(CO)<sub>5</sub>(ROH) generated by the photodissociation of CO from  $Cr(CO)_6$  in 1-propanol (1-Pro) and 2-propanol (2-Pro) solutions. The rearrangement process is considerably faster in 2-Pro than in 1-Pro despite the similar macroscopic properties of the two solvents. The dynamics in 2-Pro are similar to that observed in neat ethanol solution. These data show that the mechanism for formation of the more stable hydroxyl complex from an initially formed alkane complex depends on the structure of the coordinated solvent molecule. On the basis of bond strength data for the chromium-alkane bond, the rearrangement in 2-Pro is concluded to occur by a unimolecular displacement mechanism.

### Introduction

The chemistry of coordinatively unsaturated metal-carbonyl complexes is of current interest due to their importance as intermediates in substitution reactions.<sup>1</sup> In particular, the coordinatively unsaturated complexes  $M(CO)_5$  (M = Cr, Mo, W) exhibit a wide variety of reactivities. The structure and dynamics of these reaction intermediates have been studied by several spectroscopic techniques.<sup>2</sup> Photochemical studies in solution reveal that electronic excitation of M(CO)<sub>6</sub> results in efficient ( $\Phi \approx 0.7^3$ ) photoelimination of a single CO ligand producing a  $C_{4v}$  M(CO)<sub>5</sub> fragment.<sup>4</sup> Time-resolved studies on the photolysis of Cr(CO)<sub>6</sub> in solution show that photodissociation occurs on the subpicosecond time scale and that coordination of a single solvent molecule to the site vacated by the photoeliminated CO occurs within a few picoseconds of excitation.<sup>2a-c</sup> Recent studies on the photodissociation of  $Cr(CO)_6$  in long chain alcohols (pentanol) revealed a distribution of primary products in which either the alkane, Cr(CO)<sub>5</sub>(ROH), or hydroxyl, Cr(CO)<sub>5</sub>(HOR), part of the solvent molecule coordinates to the vacant site.<sup>2c</sup> These two types of complexes are easily distinguished by absorption spectroscopy; the hydroxyl and alkane species have absorption maxima at 460 and 505 nm, respectively. The thermodynamically most stable complex involves coordination of the hydroxyl end of the alcohol

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