

## Reinvestigation of the Rate Coefficients for O+H<sub>2</sub> and O+CH<sub>4</sub>

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hand, repulsion potentials have very steep dependence on distance. In any case, it is impossible to give acceptable quantitative arguments. We must therefore conclude that our results cannot exclude the  $\nu_2$  assignments of Sponer and Teller<sup>14</sup> (see Table I) but the evidence from the present work favors higher values. There is no precedent for matrix solvent shifts of 100% to higher frequencies. Such shifts would have to be assumed to reconcile the assignment by Sponer and Teller with our measurements.

### The Dimer

The assignment of band "b" to a dimeric molecule is based upon the results of double-oven experiments, its position, and on the analogy with the zinc halides<sup>1</sup>

where the isotopic structure of this band could be correlated with a proposed structure of the dimer. This structure consists of a planar rhombus with two additional halogens attached to the metal atom. One of the infrared-active vibrations of this  $D_{2h}$  molecule is of species  $b_{3u}$ . In this mode the central ring moves against the external halides in analogy with the motion of the central metal atom in the linear triatomic monomer molecule. A pseudo "isotope effect" may be calculated by substituting the combined mass of the rhombus of the dimer for the metal-atom mass, assuming the same stretching force constant in both molecules. The calculated positions of the dimer absorption differ by 1%-20% from the observed frequencies. This is considered to support our tentatively proposed structure for this molecule.

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## Reinvestigation of the Rate Coefficients for $O+H_2$ and $O+CH_4$

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(Received 7 November 1968)

The improved version of the wide-temperature-range, fast-flow reactor with ESR detection employed at this laboratory for a series of atom-molecule rate measurements has been used to reinvestigate the reactions  $O+H_2 \rightarrow OH+H$  [1] and  $O+CH_4 \rightarrow OH+CH_3$  [3] which had been previously measured with the original apparatus. The new data are uniformly lower than before, implying a systematic error in the old results. The revised Arrhenius expressions are  $k_1 = 3.2 \times 10^{13} \exp(-10200/RT)$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> valid in the range 500°-900°K, and  $k_3 = 2.0 \times 10^{13} \exp(-9200/RT)$  over 400°-900°K. The new results are in better agreement with other data in the literature. Our previous measurements on  $O+C_2H_6 \rightarrow OH+C_2H_5$  and  $O+D_2 \rightarrow OD+D$  have also been checked and do not require revision.

### INTRODUCTION

Confession being good for the soul, and accuracy being good for science, we wish to report that we have repeated our earlier measurements<sup>1</sup> of the rate coefficients for the reactions



and



with results which we believe to be more reliable. The reinvestigation was occasioned largely by the fact that our original data on  $k_1$  were uniformly higher than those of Clyne and Thrush<sup>2</sup> obtained by essentially the same method (except for the atom detection technique). Despite considerable checking, no satisfactory explanation for this disturbing discrepancy was apparent. Subsequent to our work, Brown and Thrush<sup>3</sup>

reported data on  $k_3$  (now using the same ESR atom-detection method) which were also lower than ours by about the same amount as  $k_1$ . In view of this, and because we had greatly improved our apparatus and technique since the first experiments, it seemed worthwhile to repeat the measurements of these very important reactions. The new results remove most of the discrepancies mentioned above, and considerably improve a comparison<sup>4</sup> between theory and experiment for the isotope effect in Reaction [1].

### EXPERIMENTAL

The basic apparatus originally described<sup>1</sup> was modified and improved as noted in two of the succeeding papers in that series,<sup>5,6</sup> so that the latest version described in Ref. 6 was used for the present work. As compared with the original, the most im-

<sup>1</sup> A. A. Westenberg and N. deHaas, J. Chem. Phys. **46**, 490 (1967).

<sup>2</sup> M. A. A. Clyne and B. A. Thrush, Proc. Roy. Soc. (London) **A275**, 544 (1963).

<sup>3</sup> J. M. Brown and B. A. Thrush, Trans. Faraday Soc. **63**, 630 (1967).

<sup>4</sup> A. A. Westenberg and N. deHaas, J. Chem. Phys. **47**, 4241 (1967).

<sup>5</sup> A. A. Westenberg and N. deHaas, J. Chem. Phys. **47**, 1393 (1967).

<sup>6</sup> A. A. Westenberg and N. deHaas, J. Chem. Phys. **50**, 707 (1969).

portant changes in the fast-flow system were the use of a larger-diameter reaction tube and a general cleaning up of various sources of pressure drop, so that faster reactions could be measured more easily and reliably. A new large access hole ESR detection cavity<sup>6</sup> was a great advantage in this connection.

The only significant change in technique from the original work<sup>1</sup> on Reactions [1] and [3] was that it was no longer necessary to take relative O-atom signal readings at each injector position with the stable reactant on and off. This "on-off" procedure is only necessary when movement of the injector itself (with no stable reactant flowing) affects the atom signal at the ESR cavity. Since resorting to a  $H_3BO_3$  coating<sup>5</sup> on the reactor and injector probe the loss of O atoms on the injector itself has been negligible, so that the simpler procedure of having the stable reactant "on" at all times for the atom decay measurement was feasible. We do not believe the on-off procedure was responsible for the different results obtained previously on  $k_1$  and  $k_3$  since, as will be noted later, we have checked much of our data on other reactions using both methods. But the simplified method does lead to somewhat smoother O-decay plots and less data scatter.

All of these new runs were performed with O atoms furnished by discharging a trace (<0.5%) of  $O_2$  in argon or helium. Under these conditions the amount of residual  $O_2$  in the system was negligible, so the situation was equivalent to that in the earlier work where O was furnished by titrating N with NO. The tendency for the measured values of  $k_3$  in the previous experiments to be somewhat higher when discharged  $O_2$  rather than N+NO was used as the O source must have been due to the larger concentrations of  $O_2$  (1%–3%) employed. No such tendency was observed in the present work, and it has been shown several times<sup>4,6,7</sup> that results in this type of measurement are independent of whether N+NO or discharging a very small  $O_2$  concentration is used as the O source. The latter may be preferable in that it avoids any possible complications by excited  $N_2$  from the discharge.

## RESULTS AND DISCUSSION

The new data on  $k_1$  are summarized in Table I and plotted in Fig. 1 (open circles). The results at the first two temperatures in Table I were also obtained with our modified apparatus although they had been reported previously.<sup>4</sup> The O-atom source was the N+NO titration for these two temperatures and they are the only data for which the on-off technique was used. The present results are uniformly about 40%

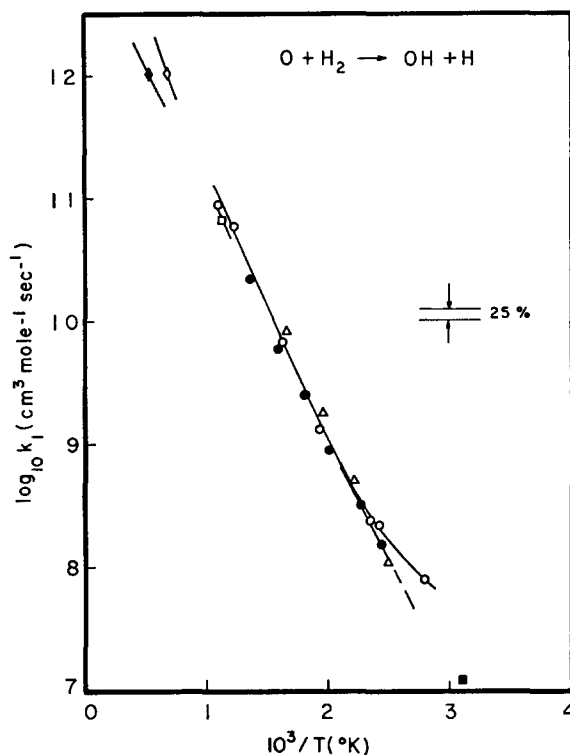


Fig. 1. Arrhenius plot of  $k_1$  for  $O + H_2 \rightarrow OH + H$ :  $\circ$ , this work;  $\bullet$ , Clyne and Thrush<sup>2</sup>;  $\triangle$ , Wong and Potter<sup>8</sup>; ---, Hoyermann, Wagner, and Wolfrum<sup>9</sup>;  $\square$ , Azatyan, Voevodsky, and Nalbandyan<sup>10</sup>;  $\diamond$ , Gutman and Schott<sup>11</sup>;  $\blacklozenge$ , Ripley and Gardiner<sup>12</sup>;  $\blacksquare$ , Campbell and Thrush.<sup>13</sup>

lower than our original data, and are generally in excellent agreement with Clyne and Thrush<sup>2</sup> as Fig. 1 shows. The stirred reactor data of Wong and Potter<sup>8</sup> which agreed very well with our earlier values are now, of course, somewhat higher on the whole, but in view of their larger scatter this is probably not serious. Since our early work, Hoyermann *et al.*<sup>9</sup> have reported some results on  $k_1$  in the range 373°–478°K by a fast-flow technique with ESR detection very similar to our own. As shown on Fig. 1, their data tend to be somewhat lower than ours below about 420°K, and are in better agreement with both Clyne and Thrush and Wong and Potter here. The  $CO-O_2-H_2$  mixture ignition-limit results of Azatyan *et al.*<sup>10</sup> in the 840°–930°K range are in excellent agreement with ours at the same temperatures.

In view of our improved technique and the better agreement with other well-defined work on this reaction, we believe the new data to be more reliable than those in Ref. 1. Despite much detective work, it is not certain where the systematic error entered into our earlier data. However, it seems most likely that one of the flow calibrations ( $H_2$  or carrier) must

<sup>7</sup> A. A. Westenberg and N. deHaas, *Twelfth Symposium on Combustion* (The Combustion Institute, Pittsburgh, Pa., 1969) (to be published).

<sup>8</sup> E. L. Wong and A. E. Potter, *J. Chem. Phys.* **43**, 3371 (1965).

<sup>9</sup> K. Hoyermann, H. G. Wagner, and J. Wolfrum, *Ber. Bunsenges. Physik. Chem.* **71**, 599 (1967).

TABLE I. Summary of measurements of the rate coefficient  $k_1$  for  $O+H_2 \rightarrow OH+H$ . Helium or argon carrier.

Temperature (°K)	Pressure (mm)	Velocity (cm/sec)	$[H_2]$ (moles/cm <sup>3</sup> )	$k_1$ (cm <sup>3</sup> mole <sup>-1</sup> sec <sup>-1</sup> )
357 <sup>a</sup>	2.64	310	$2.37 \times 10^{-8}$	$8.6 \times 10^7$
	2.68	290	1.97	8.6
	3.07	230	2.38	8.1
	2.85	230	1.34	8.4
	2.28	300	1.06	6.6
	4.08	280	2.32	7.6
	4.05	280	2.29	6.9
	2.42	470	1.37	9.2
	2.75	410	1.61	8.1
				$8.0 \pm 0.7$
412 <sup>a</sup>	2.73	470	$1.39 \times 10^{-8}$	$2.1 \times 10^8$
	1.91	550	1.18	2.4
	2.97	360	1.83	2.1
	3.11	360	2.49	2.0
				$2.2 \pm 0.1$
423	2.41	370	$0.82 \times 10^{-8}$	$2.2 \times 10^8$
	2.46	370	1.23	2.2
	3.42	320	1.44	2.7
	3.35	310	0.80	2.7
	2.30	490	1.23	2.2
				$2.4 \pm 0.2$
514	1.86	950	$3.53 \times 10^{-8}$	$1.25 \times 10^9$
	1.87	980	5.41	1.33
	2.52	730	7.29	1.31
	2.68	690	7.68	1.38
				$1.32 \pm 0.04$
613	2.53	1340	$3.76 \times 10^{-9}$	$6.8 \times 10^9$
	2.16	1230	4.06	6.6
	2.14	1250	3.54	7.4
	2.12	1240	2.53	6.6
	2.07	1240	1.58	6.4
				$6.8 \pm 0.3$
812	1.55	2330	$12.84 \times 10^{-10}$	$6.0 \times 10^{10}$
	1.60	1980	7.10	7.0
	1.00	5650	3.62	6.1
	1.90	2950	6.85	5.6
	1.70	2170	9.31	5.5
	1.70	2130	3.56	5.2
				$5.9 \pm 0.5$
910	1.31	3010	$8.59 \times 10^{-10}$	$10.0 \times 10^{10}$
	1.30	3100	13.73	9.0
	1.77	4160	10.24	8.5
	1.76	4110	5.92	9.1
	0.80	5050	5.44	8.0
	0.82	5110	8.92	8.0
	0.75	5330	3.27	9.2
	1.20	3320	5.30	9.5
				$8.9 \pm 0.6$

<sup>a</sup> New data reported in Ref. 4. O from  $N+NO \rightarrow N_2+O$ .

have been at fault, even though these were checked when the original discrepancy showed up. Since the critical-flow jewelled orifices used for metering had to be calibrated outside of their location in the main apparatus, it is possible that a source of error was introduced (a small obstruction in the orifice, or a leak) in changing the jewel from the calibration system to the reactor.

In the 500°–900°K range the present data have the same Arrhenius slope as before, i.e.  $E_1 = 10.2$  kcal/mole, but a lower pre-exponential factor, so that the revised Arrhenius expression fitting our data over the linear portion of the solid line drawn through the open circles in Fig. 1 is (cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup>)

$$k_1 = 3.2 \times 10^{13} \exp(-10\,200/RT).$$

The high-temperature extrapolation of this line passes between the two sets of data reported by Gutman and Schott<sup>11</sup> (1300°–1670°K) and Ripley and Gardiner<sup>12</sup> (1400°–2500°K) shown in Fig. 1. Both of these were obtained from measurements in shocked H<sub>2</sub>–O<sub>2</sub> mixtures, the former by monitoring the O-atom increase “end on” during the induction period behind reflected shocks, and the latter by measuring the length of the induction period behind incident shocks as defined by the first detectable OH concentration. The shock-wave data are not particularly sensitive for determining  $k_1$ , but the agreement with our extrapolated results is reasonable. In view of this we prefer our value of  $E_1 = 10.2$  kcal/mole to the lower value of 8.8 advocated recently by Campbell and Thrush,<sup>13</sup> as the latter would extrapolate much below the data of Ref. 11.

The low-temperature end of the  $k_1$  data is less well defined at present. As noted above, our lowest-temperature point (357°K) is considerably higher than that of Ref. 9 near this temperature, and recently Campbell and Thrush<sup>13</sup> have given the value at 320°K shown in Fig. 1 which is much below that implied by our curve. This low-temperature value<sup>13</sup> was obtained in a rather complex reacting environment and required correction for three other reactions as well as wall losses, so its reliability is questionable and further study of  $k_1$  at low temperature would be useful.

To make sure that the systematic error discovered in our previous work was confined only to some of the data reported in our first paper<sup>1</sup> and did not persist after the apparatus had been modified, we have checked our results<sup>4</sup> on the isotopic reaction

<sup>10</sup> V. V. Azatyan, V. V. Voevodsky, and A. B. Nalbandyan, Kinet. Catalysis **2**, 340 (1961). A numerical error in these results was corrected by V. V. Azatyan in Armenian Chem. J. **20**, 577 (1967).<sup>11</sup> D. Gutman and G. L. Schott, J. Chem. Phys. **46**, 4576 (1967).  
<sup>12</sup> D. L. Ripley and W. C. Gardiner, Jr., J. Chem. Phys. **44**, 2285 (1966).<sup>13</sup> I. M. Campbell and B. A. Thrush, Trans. Faraday Soc. **64**, 1265 (1968).

These check runs confirmed our published data closely (within 10%), so no revision is needed to the expression

$$k_2 = 2.0 \times 10^{13} \exp(-11\,000/RT)$$

previously given<sup>4</sup>. Since our experimental activation energy for Reaction [1] has also been confirmed by the present results, the absolute rate theory fitting procedure described in Ref. 4 is not affected. The agreement between the theoretical and experimental ratio  $k_1/k_2$  is now much better, since the new experimental data on  $k_1$  are lower than before and  $k_2$  is unchanged. Figure 2 shows the revised experimental  $k_1/k_2$  compared to the theoretical ratio determined previously.<sup>4</sup> As originally presented, the two slopes agreed reasonably well but the experimental magnitude was too high. The comparisons with the theoretical pre-exponential factors of  $A_{1t} = 5.8 \times 10^{13}$  and  $A_{2t} = 4.3 \times 10^{13}$  are now more consistent, since the experimental values  $A_1 = 3.2 \times 10^{13}$  and  $A_2 = 2.0 \times 10^{13}$  are now both low by more nearly the same factor.

Since reaction [3] had been studied in the same series of experiments as [1], a reevaluation of these data was also in order. The new data on  $k_3$  are summarized in Table II and plotted in Fig. 3. As discussed in the earlier work,<sup>1</sup> the measured stoichiometry of the reaction with its succeeding steps is  $n=4$  atoms of O consumed per CH<sub>4</sub>, so the over-all O-atom decay rates have been divided by four to get the absolute values of  $k_3$  in Table II and Fig. 3. Once again the new data are generally lower than our old data by about the same factor, so the systematic error was the same as for Reaction [1]. The new data also show less scatter because of the simpler technique employed, and the previous rather erratic behavior at the lower tem-

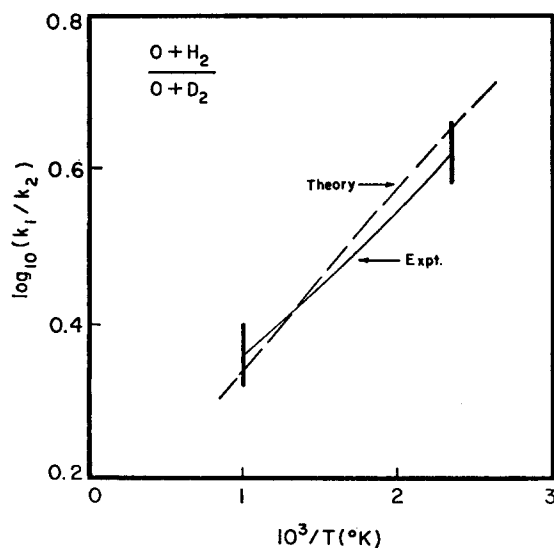


FIG. 2. Comparison of revised experimental ratio  $k_1/k_2$  with theoretical ratio derived in Ref. 4.

TABLE II. Summary of measurements of the rate coefficient  $k_3$  for O + CH<sub>4</sub> → OH + CH<sub>3</sub>.

Temperature (°K)	Pressure (mm)	Velocity (cm/sec)	[CH <sub>4</sub> ] (moles/cm <sup>3</sup> )	$k_3$ (cm <sup>3</sup> mole <sup>-1</sup> sec <sup>-1</sup> )
297	2.04	220	$2.08 \times 10^{-8}$	$1.28 \times 10^7$
	2.08	220	2.38	1.25
	2.19	230	3.23	1.24
	2.73	180	4.04	1.29
				$1.26 \pm 0.02$
363	1.75	340	$0.73 \times 10^{-8}$	$8.9 \times 10^7$
	1.96	360	1.93	8.9
	2.57	270	2.54	9.6
	2.36	260	1.27	9.4
				$9.2 \pm 0.3$
419	2.32	400	$6.89 \times 10^{-9}$	$3.3 \times 10^8$
	2.27	400	4.81	3.5
	2.24	400	3.58	3.2
	1.50	330	9.40	3.5
				$3.4 \pm 0.1$
516	1.66	1180	$1.90 \times 10^{-9}$	$2.6 \times 10^9$
	2.07	940	2.36	2.6
	1.39	1400	1.57	2.6
	1.43	1470	4.84	2.3
				$2.5 \pm 0.1$
605	1.43	1810	$0.95 \times 10^{-9}$	$1.06 \times 10^{10}$
	1.16	1700	1.01	1.08
	1.18	1690	1.53	1.14
				$1.09 \pm 0.03$
904	1.22	6720	$1.56 \times 10^{-10}$	$1.21 \times 10^{11}$
	0.70	5720	1.83	1.35
	0.52	5300	1.97	1.34
	1.12	7170	2.21	1.31
				$1.30 \pm 0.05$

peratures was not observed. The Arrhenius plot is linear above about 400°K and obeys

$$k_3 = 2.0 \times 10^{13} \exp(-9200/RT).$$

This is a somewhat larger activation energy than previously estimated,<sup>1</sup> and should be more reliable because the plot is considerably better defined than before.

The data of Brown and Thrush<sup>8</sup> shown on Fig. 3 were obtained in a fast-flow system with ESR detection by a pseudo-first-order method essentially the same as our own. The broken line shown is their total O-atom decay rate divided by  $n=4$ . They actually used  $n=3$  to derive absolute values of  $k_3$ , but do not explicitly state that this was a measured value of the

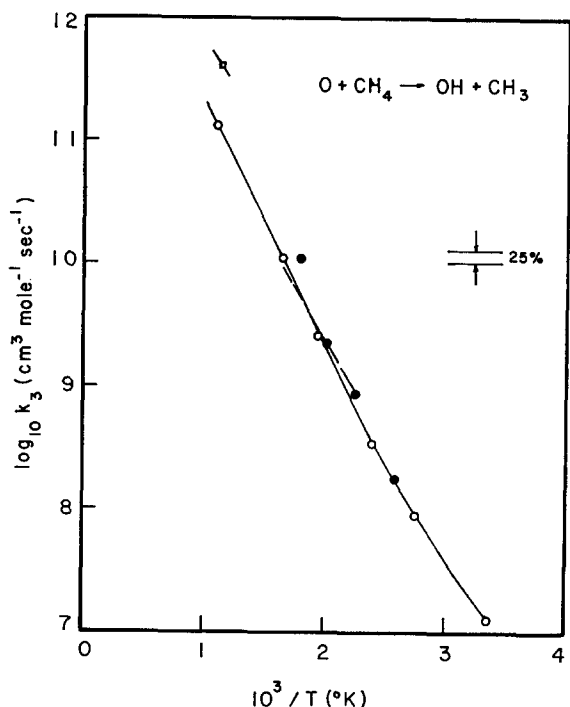


FIG. 3. Arrhenius plot of  $k_3$  for  $\text{O} + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$ :  $\circ$ , this work; ---, Brown and Thrush<sup>3</sup> using  $n=4$ ;  $\bullet$ , Wong and Potter<sup>14</sup> using  $n=4$ ;  $\square$ , Azatyan, Nalbandyan, and Meng-Yuan.<sup>15</sup>

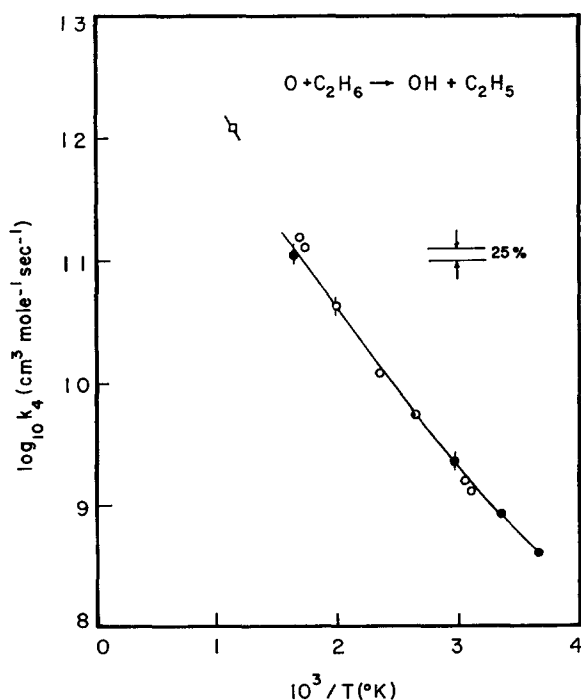


FIG. 4. Arrhenius plot of  $k_4$  for  $\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{OH} + \text{C}_2\text{H}_5$ :  $\circ$ , data of Ref. 1;  $\bullet$ , check runs of this work;  $\square$ , Azatyan.<sup>10</sup>

stoichiometry, and appear to have derived it from an assumed reaction mechanism. Their reported expression  $k_3 = 7 \times 10^{12} \exp(-7700/RT)$  based on  $n=3$  would, of course, give a line higher than that shown. Clearly, their total O-decay rate over  $450^\circ\text{--}600^\circ\text{K}$  agrees very well with our own, and we differ somewhat in the value to be taken for the stoichiometric coefficient  $n$ . Our measured value  $n=4$  was discussed earlier<sup>1</sup> and we believe it to be correct.

The stirred reactor data of Wong and Potter<sup>14</sup> derived from their total O-decay rate using  $n=4$  are also in excellent agreement with our plot, except for their highest point. The ignition limit results of Azatyan *et al.*<sup>15</sup> are considerably above our data as indicated. The data of Cadle and Allen,<sup>16</sup> which are not well defined and scatter widely, have not been included in Fig. 3.

Finally, we have checked our previous results on



since this reaction was also included in the original study.<sup>1</sup> The low-temperature range has also been extended somewhat. Apparently the systematic error entering the previous  $k_1$  and  $k_3$  had been eliminated for  $k_4$ , since the new data on  $k_4$  check the earlier results reasonably well, as Fig. 4 shows. The stoichiometric coefficient  $n=6$  was used to derive these absolute values as before.<sup>1</sup> The data on  $k_4$  at the higher temperatures are not quite as satisfactory as for the other reactions studied in that the measured O-decay rates increased somewhat with the  $\text{C}_2\text{H}_6$  flow used. This, of course, should not be the case for the pseudo-first-order model, and leads us to suspect some change in stoichiometry with increasing  $\text{C}_2\text{H}_6$ . This would not be too surprising for the complex mechanism which must follow the initial step [4] to give  $n$  as high as 6. Nevertheless, the check runs shown in Fig. 4 agreed well enough with the original data so that there is no reason to alter the original Arrhenius expression

$$k_4 = 1.8 \times 10^{13} \exp(-6100/RT)$$

valid in the  $330^\circ\text{--}600^\circ\text{K}$  range. The only other literature data known to us, the ignition limit data of Azatyan (cited in the second reference of Ref. 10), would be appreciably higher than that extrapolated from our line.

<sup>14</sup> E. L. Wong and A. E. Potter, NASA Rept. No. TN D-3371, April 1966.

<sup>15</sup> V. V. Azatyan, A. B. Nalbandyan, and T. Meng-Yuan, Kinet. Catalysis 5, 201 (1964).

<sup>16</sup> R. D. Cadle and E. R. Allen, J. Phys. Chem. 69, 1611 (1965).