

## A Kinetics Review of Atmospheric Reactions Involving H<sub>x</sub>O<sub>y</sub> Compounds

D. D. DAVIS

*Chemistry Department, University of Maryland, College Park, Maryland*

Received November 6, 1973

Some 49 reactions involving compounds of the type H<sub>x</sub>O<sub>y</sub> have been examined in terms of their possible significance to stratospheric and mesospheric chemistry. Of this set of 49, some 20 processes were evaluated to be of potential importance. Within this subset of 20, the rate constants for 8 of these reactions were indicated as either having undergone a significant reevaluation within the last 2 years or were due to be reevaluated based on new data. A discussion of new experimental data resulting in these reevaluations is presented. Finally, recommendations are made as to the need for new experimental work.

Quelques 49 réactions impliquant des composés de type H<sub>x</sub>O<sub>y</sub> ont été examinées en fonction de leur importance possible dans la chimie stratosphérique et mésosphérique. De ce nombre, 20 réactions se sont révélées d'un intérêt potentiel.

Dans ce sous-ensemble de 20, les constantes de vitesse de 8 de ces réactions sont reliées soit à une réévaluation significative pendant les 2 dernières années, soit étaient dues pour être réévaluées en se basant sur de nouvelles données. On discute des nouvelles données expérimentales résultant de ces réévaluations. Finalement des recommandations sont faites quant au besoin de nouveaux travaux expérimentaux. [Traduit par le journal]

Can. J. Chem., 52, 1405 (1974)

### Introduction

In an effort to systematically examine the stratospheric and mesospheric reaction kinetics of H<sub>x</sub>O<sub>y</sub> compounds, this author has elected to classify these reactions into five major groups:

- [A] H<sub>x</sub>O<sub>y</sub> + H<sub>x</sub>O<sub>y</sub> → products  $x, y = 0,1,2$
- [B] H<sub>x</sub>O<sub>y</sub> + H<sub>u</sub>O<sub>v</sub> → products  $x, y = 0,1,2;$   
 $u, v = 0,1,2$
- [C] H<sub>x</sub>O<sub>y</sub> + SO<sub>2</sub> → products  $x, y = 0,1,2$
- [D] H<sub>x</sub>O<sub>y</sub> + CO → products  $x, y = 0,1,2$
- [E] H<sub>x</sub>O<sub>y</sub> + CH<sub>4</sub> → products  $x, y = 0,1,2$

The possible encounters of type A, B, C, D, and E have been summarized in the form of two reaction grids (see Table 1).

From grid I, it can be seen that some 28 independent reactions of type A and B must be considered. Grid II shows another 21 reactions of types C, D, and E. An immediate question, therefore, is whether or not all 49 processes are of atmospheric significance, and hence must be used in chemical modelling studies. Fortunately, the answer to this question is no. Many of those reactions listed can be ruled out on thermodynamic or kinetic grounds. For example, in the case of reaction 26, O<sub>2</sub> + O<sub>2</sub> → O<sub>3</sub> + O, the endothermicity of this process is ~93 kcal/mol. Thus, an activation energy of at least 93 kcal/mol

is to be expected. At the temperatures of the stratosphere and mesosphere, 210–273 °K, reaction 26 would clearly be unimportant. In the preceding example, a quick inspection of the thermodynamics of the reaction was sufficient to reject the process as not being of atmospheric importance. For a large number of reactions, however, careful kinetic comparisons need to be made with other possible competing reactions. In other cases, a modelling sensitivity test can be performed in which the rate constant for the reaction of interest is allowed to take on a range of values. The atmospheric importance of a particular reaction is then ascertained by a careful examination of the effect that this variation has on the output data of the model.

In the case of the 49 reactions listed in grids I and II, this author has used simple thermodynamic and kinetic arguments in conjunction with the modelling results of Crutzen (1), Hesstvedt (2), Johnston (3), and Nicolet (4), to reduce this set to 20 key processes. These 20 reactions have been labelled in Table 1 by placing the reaction number in parentheses. The list includes processes 3, 6, 7, 9, 10, 11, 13, 14, 16, 18, 20, 23, 24, 25, 30, 31, 33, 37, 38, and 44.

In the following text, Table 2 is presented which gives the experimental status of each of the above reactions. In each case, there is first a qualitative statement given as to why the

TABLE 1. Reaction grid showing possible encounters of the type\* A, B, C, D, E

	H	OH	HO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	O( <sup>3</sup> P)	O <sub>2</sub>	O <sub>3</sub>
Grid I							
H	1	2	(3)	4	5	(6)	(7)
OH		8	(9)	(10)	(11)	12	(13)
HO <sub>2</sub>			(14)	15	(16)	17	(18)
H <sub>2</sub> O <sub>2</sub>				19	(20)	21	22
O( <sup>3</sup> P)					(23)	(24)	(25)
O <sub>2</sub>						26	27
O <sub>3</sub>							28
Grid II							
SO <sub>2</sub>	29	(30)	(31)	32	(33)	34	35
CO	36	(37)	(38)	39	40	41	42
CH <sub>4</sub>	43	(44)	45	46	47	48	49

\*Parentheses indicate key reactions.

reaction is considered to be important. Next, a list of all recent rate constant evaluations is presented. And finally, if any new kinetic data has been reported since the most recent evaluation, this work is cited and its possible influence on previous evaluations discussed. In those cases where the recommended value for a rate constant has changed significantly from one evaluation to another, further discussion is given explaining the basis for this change.

### Discussion

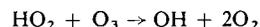
Of the 20 reactions listed in the previous text, the rate constants for 8 of these have either recently undergone a significant reevaluation or would now appear to be due for one based on new rate data. The reactions of interest are 6, 13, 18, 24, 33, 37, 38, and 44.

Reaction 6 was recently reevaluated by the CIAP Kinetics review group (5), and was assigned a somewhat lower temperature dependence and a higher pre-exponential factor than given in the review by Baulch *et al.* (6) (CIAP,  $E = -680$  cal/mol,  $A = 6.7 \times 10^{-33}$ ; Baulch *et al.*,  $E = -1000$  cal/mol,  $A = 4.1 \times 10^{-33}$ , for M = Ar or He). The new evaluation is based on the 300 °K data reviewed by Baulch *et al.* and the more recent low temperature work by Davis and Wong (7) and Kurylo (8), using flash photolysis-resonance fluorescence techniques. A quick calculation shows that at stratospheric temperatures of 220 °K, the new rate constant would be nearly 1.5 times smaller than that given by the evaluation of Baulch *et al.* This is not the case, however, since the third body efficiency for N<sub>2</sub> reported by Davis and Wong

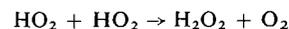
(7) and Kurylo (8) is nearly 3 times larger than the old value quoted. The net effect, therefore, is a rate constant at stratospheric temperatures (for M = N<sub>2</sub>) which is ~1.5 times larger than that calculated from the previous evaluation by Baulch *et al.*

Although the value of the rate constant for reaction 13 (OH + O<sub>3</sub> → HO<sub>2</sub> + O<sub>2</sub>) changed by nearly a factor of 20 from 1971 to 1973, its value is now considered to be reasonably well established. The new evaluation quoted is based on the work of DeMore (9) and Anderson and Kaufman (10). These results were recently corroborated at 300 °K from investigations by Kurylo (8) and Davis and Schiff (11). In all, three different experimental techniques have now been used to examine this system: low intensity steady-state photolysis; discharge-flow with resonance fluorescence detection; and flash photolysis-resonance fluorescence.

Reaction 18 (HO<sub>2</sub> + O<sub>3</sub> → OH + 2O<sub>2</sub>) was believed for many years to be far too slow to be of any significance in atmospheric chemistry. The value of the rate constant now recommended, however, would indicate that this reaction may be of some importance. The latest results of Simonaitis and Heicklen (12), involving a relative rate study of the competing system



and



give a rate constant of  $\sim 3.5 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 220 °K. This can be compared with the calculated value from the CIAP evaluation of  $\sim 2.0 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

TABLE 2. Table of kinetic rate data\*

[3] $\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$ (a)			
OH + OH (b)			
H <sub>2</sub> O + O (c)			
Atmospheric significance			
i. Important source of H <sub>2</sub> in the middle and upper mesosphere			
ii. Of some importance in the mesosphere and upper stratosphere as a loss reaction for odd hydrogen			
Evaluations			
Baulch <i>et al.</i> (6)	(a) $4.2 \times 10^{-11} \exp(-350/T)$	290–800 °K	
	(b) $4.2 \times 10^{-11} \exp(-950/T)$	290–800 °K	
	(c) No recommendation		
CIAP (5)	Same as above		
New rate data			
Westenberg and deHaas (17)	(a):(b):(c)	e.s.r.-discharge-flow technique	300 °K
	0.62:0.27:0.11		
Will not significantly influence CIAP value			
[6] $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$			
Atmospheric significance			
i. Major source of HO <sub>2</sub> in the mesosphere and stratosphere			
ii. Major loss reaction for H atoms in the mesosphere and stratosphere			
Evaluations			
Baulch <i>et al.</i> (6)	$4.1 \times 10^{-33} \exp(500/T)$	300–2000 °K	
	M = Ar; Ar(1.0), He(1.8), N <sub>2</sub> (2.1), O <sub>2</sub> (1.7), H <sub>2</sub> O(70)		
CIAP (5)	$6.7 \times 10^{-33} \exp(290/T)$	203–404 °K	
	M = Ar; Ar(1.0), He(1.0), N <sub>2</sub> (3.1), O <sub>2</sub> (3.1), H <sub>2</sub> O(25)		
New rate data: none			
[7] $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$			
Atmospheric significance			
i. Important OH source in the mesosphere and the middle and upper stratosphere			
ii. Moderately important loss reaction for H atoms in the mesosphere and upper stratosphere			
Evaluations			
NBS	$2.6 \times 10^{-11}$	300 °K	
CIAP (5)	Same as above		
New rate data: None			
[9] $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$			
Atmospheric significance			
i. Important source of H <sub>2</sub> O in both the stratosphere and mesosphere			
ii. Major loss reaction for odd hydrogen (OH, HO <sub>2</sub> , H)			
Evaluations			
Kaufman (23) (estimate)	$k = 1 \times 10^{-11}$	300 °K	
Lloyd (19) (estimate)	$1.7 \times 10^{-11} \exp(-500/T)$	300 °K	
Hochanadel <i>et al.</i> (24)	$2 \times 10^{-10}$	300 °K	
CIAP (5)	$2 \times 10^{-11} < k < 2 \times 10^{-10}$ 300 °K		
New rate data: None			
[10] $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$			
Atmospheric significance			
i. Important loss reaction for OH throughout the stratosphere			
ii. Important loss reaction for H <sub>2</sub> O <sub>2</sub> in the stratosphere			
Evaluations			
Baulch <i>et al.</i> (6)	$1.7 \times 10^{-11} \exp(-910/T)$	300–800 °K	
NBS	Same as above		
CIAP (5)	Same as above		
New rate data: None			

TABLE 2. (Continued)

[11] $\text{OH} + \text{O}(^3\text{P}) \rightarrow \text{O}_2 + \text{H}$	
Atmospheric significance	
i. Major source of H atoms in both the stratosphere and mesosphere	
ii. Major loss reaction for OH in both the stratosphere and mesosphere	
iii. Major loss reaction for $\text{O}(^3\text{P})$ in the mesosphere	
Evaluations	
Baulch <i>et al.</i> (6)	$3.8 \times 10^{-11}$ 300 °K
Wilson (21)	$4.2 \times 10^{-11}$ 300–1000 °K
CIAP (5)	$4.2 \times 10^{-11}$ 300–1000 °K
New rate data: None	
[13] $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	
Atmospheric significance	
i. Possible important loss reaction for $\text{O}_3$ in the middle and upper stratosphere	
Evaluations	
NBS	$1.6 \times 10^{-12} \exp(-1000/T)$ 220–450 °K
CIAP (5)	Same as above
New rate data	
Kurylo (8)	$5.0 \times 10^{-14}$ 300 °K
Davis and Schiff (11)	$7.5 \times 10^{-14}$ 300 °K
[14] $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{OH}$	
Atmospheric significance	
i. Major source of $\text{H}_2\text{O}_2$ in both the stratosphere and mesosphere	
ii. Moderately important loss reaction for odd hydrogen (H, $\text{HO}_2$ , OH) in the lower and middle stratosphere	
Evaluations	
Baulch <i>et al.</i> (6)	$3.3 \times 10^{-12}$ 300 °K
NBS	$3 \times 10^{-11} \exp(-500/T)$ 300–1000 °K
CIAP (5)	$3 \times 10^{-11} \exp(-500/T)$ 300–1000 °K
New rate data: None	
[16] $\text{HO}_2 + \text{O}(^3\text{P}) \rightarrow \text{OH} + \text{O}_2$	
Atmospheric significance	
i. One of the major loss reactions for $\text{HO}_2$ in the mesosphere and the upper and middle stratosphere	
ii. One of the major OH sources in the mesosphere and the upper and middle stratosphere	
iii. One of the major loss reactions for odd oxygen [ $\text{O}(^3\text{P})$ ; $\text{O}_3$ ] in the mesosphere and upper stratosphere	
Evaluations	
Lloyd (19)	$8 \times 10^{-11} \exp(-500/T)$ (estimated)
CIAP (5)	Same as above
New rate data: None	
[18] $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	
Atmospheric significance	
i. A possible significant source of OH at mid-stratospheric altitudes (see discussion section)	
Evaluations	
CIAP (5)	$k = 1 \times 10^{-12} \exp(-1875/T)$ 220–450 °K
New rate data	
Simonaitis and Hecklen (12)	$3.3 \times 10^{-14} \exp(-1000/T)$ 225–298 °K
Relative rate measurement, $k/k_a$ , where $k_a$ is $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	
Assumed $k_a$ had zero temperature dependence	
[20] $\text{H}_2\text{O}_2 + \text{O}(^3\text{P}) \rightarrow \text{OH} + \text{HO}_2$ (a) $\rightarrow \text{H}_2\text{O} + \text{O}_2$ (b)	
Atmospheric significance	
i. Moderately important loss reaction for $\text{H}_2\text{O}_2$ in the mesosphere and upper stratosphere	
Evaluations	
CIAP (5)	$k(a + b) = 3.6 \times 10^{-11} \exp(-2950/T)$ 283–373 °K
New rate data: None	

TABLE 2. (Continued)

[23] $O(^3P) + O(^3P) + M \rightarrow O_2 + M$		
Atmospheric significance		
i. Moderately important loss reaction for $O(^3P)$ in the mesosphere and upper stratosphere		
Evaluations		
Johnston (3)	$3.80 \times 10^{-30} T^{-1} \exp(-170/T)$	1000 < T < 8000; M = O <sub>2</sub>
CIAP (5)	Same as above	
New rate data		
Campbell and Gray (25)	$4.8 \times 10^{-33}$	298 °K; M = N <sub>2</sub>
	$10.1 \times 10^{-33}$	196 °K; M = N <sub>2</sub>
Should not alter evaluation by Johnston significantly		
[24] $O(^3P) + O_2 + M \rightarrow O_3 + M$		
Atmospheric significance		
i. Major reaction of $O(^3P)$ in the stratosphere and mesosphere		
ii. Only known source of O <sub>3</sub> in the stratosphere and mesosphere		
Evaluations		
Johnston (3)	$4.6 \times 10^{-35} \exp(1050/T)$	200–1000 °K; M = O <sub>3</sub>
	$1.2 \times 10^{-35} \exp(1050/T)$	M = Ar
CIAP (5)	$6.6 \times 10^{-35} \exp(510/T)$	M = Ar; 200–346 °K
	Relative M efficiencies: Ar (1.0) N <sub>2</sub> (1.6) O <sub>2</sub> (1.7) H <sub>2</sub> O (15)	
New rate data: None		
[25] $O(^3P) + O_3 \rightarrow 2O_2$		
Atmospheric significance		
i. An important loss reaction for O <sub>3</sub> in the upper and middle stratosphere		
Evaluations		
Johnston (3)	$2.0 \times 10^{-11} \exp(-2410/T)$	200–1000 °K
NBS	$2.0 \times 10^{-11} \exp(-2410/T)$	188–1000 °K
CIAP (5)	$1.9 \times 10^{-11} \exp(-2300/T)$	220–1000 °K
New rate data: None		
[30] $OH + SO_2 + M \rightarrow HSO_3 + M$		
Atmospheric significance		
i. A possible important reaction in the conversion of SO <sub>2</sub> to sulfuric acid aerosol		
Evaluations: None		
New rate data		
Davis <i>et al.</i> (20)	$\sim 3 \times 10^{-31}$ ; M = H <sub>2</sub> O;	Relative rate measurement 300 °K (The reference reaction in this system was OH + CO → CO <sub>2</sub> + H)
Davis and Schiff (11)	Reaction is in the high pressure fall region above ~10 Torr of He. At 500 Torr He, the effective bimolecular rate constant is $2.5 \times 10^{-3}$	Flash photolysis – resonance fluorescence 300 °K
[31] $HO_2 + SO_2 \rightarrow OH + SO_3$		
Atmospheric significance		
i. A possible important reaction in the conversion of SO <sub>2</sub> to sulfuric acid aerosol		
Evaluations		
CIAP (5)	$8.7 \times 10^{-16}$	300 °K
New rate data: None		

TABLE 2. (Concluded)

[33] SO <sub>2</sub> + O( <sup>3</sup> P) + M → SO <sub>3</sub> + M	
Atmospheric significance	
i. Considered to be of possible importance in the conversion of SO <sub>2</sub> to sulfuric acid aerosol	
Evaluations	
Schofield (15)	1 × 10 <sup>-33</sup> exp (500/T) for M = Ar, O <sub>2</sub> , N <sub>2</sub> , He; 250–1000 °K
CIAP (5)	Same as above
New rate data	
Davis <i>et al.</i> (16)	3.4 × 10 <sup>-32</sup> exp (-1120/T) for M = N <sub>2</sub> 353–220 °K
	Flash photolysis – resonance fluorescence
	Relative efficiencies N <sub>2</sub> :He:Ar:SO <sub>2</sub> 1.0:0.45:0.87:60
New data will have a significant effect on previous evaluations	
[37] OH + CO → CO <sub>2</sub> + H	
Atmospheric significance	
i. Only important atmospheric process known to convert CO to CO <sub>2</sub> in the stratosphere and mesosphere	
ii. Important loss reaction for OH in the lower stratosphere	
Evaluations	
Schofield (15)	1.1 × 10 <sup>-12</sup> exp (-515/T)
Baulch, Drysdale, and Lloyd	9.3 × 10 <sup>-13</sup> exp (-540/T)
Wilson (21)	5.1 × 10 <sup>-13</sup> exp (-300/T) 200–2000 °K
CIAP (5)	5.1 × 10 <sup>-13</sup> exp (-300/T) 200–2000 °K
New rate data	
Westernberg and deHaas (17)	1.33 × 10 <sup>-13</sup> exp (-0.0/T) 450–300 °K
Zellner and Smith (18)	2.1 × 10 <sup>-13</sup> exp (-50/T) 470–215 °K
Davis <i>et al.</i> (16)	2.05 × 10 <sup>-13</sup> exp (-70/T) 373–220 °K
New rate data will have a moderate effect on previous evaluations	
[38] HO <sub>2</sub> + CO → CO <sub>2</sub> + OH	
Atmospheric significance	
i. Considered at one time to be of possible importance in the conversion of CO to CO <sub>2</sub> in the stratosphere	
Evaluations	
Lloyd (19)	~1 × 10 <sup>-24</sup>
CIAP (5)	≤1 × 10 <sup>-19</sup>
New rate data: None	
[44] OH + CH <sub>4</sub> → CH <sub>3</sub> + H <sub>2</sub> O	
Atmospheric significance	
i. Major initial step in the oxidation of CH <sub>4</sub> in the stratosphere	
Evaluations	
Wilson (21)	4.77 × 10 <sup>-11</sup> exp (-2500/T) 300–2000 °K
CIAP (5)	Same as above
New rate data	
Davis <i>et al.</i> (26)	2.5 × 10 <sup>-12</sup> exp (-1700/T) 240–373 °K Flash photolysis – resonance fluorescence
New data will have a significant effect on previous evaluation	

\*The units for all rate constants reported in this table are in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-2</sup>.

Although the disagreement is only a factor of 2 it must be pointed out that all reported studies on this system have involved indirect measurements, with complex chemistry. It is not unreasonable, therefore, that the value of this rate constant could change in future evaluations by as much as a factor of 3. A final point that should be made in regards to reaction 18 is the role it might play in defining the ozone profile in the stratosphere. Whereas, it might first appear that an increase in the value of  $k_{18}$  would necessarily cause a reduc-

tion in the predicted ozone profile, Crutzen (1) has recently carried out calculations which indicate something quite different. Crutzen's argument is that an increase in  $k_{18}$  would cause an increase in the stratospheric OH concentration and this in turn would reduce the level of NO<sub>2</sub> via the reaction



The subsequent reduction in NO<sub>2</sub> could then cause a lowering of the efficiency of the NO-

$\text{NO}_2$  catalytic cycle and thereby preserve  $\text{O}_3$ . His calculations show, in fact, that the faster value of  $k_{18}$  now being used could cause a very slight increase in the predicted profile of  $\text{O}_3$ .

Reaction 24 is one of the key reactions in the stratosphere. It is believed to be the single important source of ozone, and hence, any variation in the value of  $k_{24}$  has nearly a linear effect on an atmospheric model of the stratosphere. From Table 2, it can be seen that a significant change in the rate expression for this process took place from the 1968 Johnston review to the 1973 CIAP evaluation. This re-evaluation was based on the recent work of Huie, Herron, and Davis (14), who made direct measurements of the rate constant for this system using the technique of flash photolysis-resonance fluorescence. The temperature range covered was 200–346 °K. From Fig. 1, it can be seen that the agreement between Johnston's evaluation (derived from the equilibrium constant and the  $k$  value for the reverse reaction) and the results of Huie *et al.* is within 10% at 298 °K. At stratospheric temperatures of 220 °K, the difference in  $k$  values is a factor of 2, the newer value (5) being a factor of 2 lower.

Reaction 33 has received considerable atten-

tion the last few years due to its possible importance in the conversion of  $\text{SO}_2$  to sulfuric acid aerosol in the now well-known Junge aerosol belt (16–22 km). Nearly all of the work reviewed by Schofield (15) was carried out at 300 °K and the experimental techniques employed were mainly either discharge flow systems with e.s.r. detection or indirect photochemical methods. Because the reaction was known to be third order, Schofield assigned a negative temperature dependence to the reaction of  $-1000$  cal/mol. More recently, Davis, Schiff, and Fischer (16) using the flash photolysis-resonance fluorescence technique examined this reaction over a temperature range of 353–220 °K for  $\text{M} = \text{N}_2$ , He, Ar, and  $\text{SO}_2$ . In this study a static reaction cell configuration was employed in which pressures as high as 1500 Torr could be used. Their results indicated lower values for the third order rate constants at 300 °K for all M gases employed; most importantly, the results showed the reaction to have a positive temperature dependence of 2000 cal/mol. The explanation given for the observed positive temperature dependence was that the third order reaction proceeded via a two step mechanism. The first step would involve the formation of the spin allowed triplet  $\text{SO}_3$  molecule. The second step, the intersystem crossing of the  $\text{SO}_3$  triplet to the single ground state  $\text{SO}_3$ , could then give rise to the observed positive temperature dependence. A comparison of the rate constants at 220 °K shows the results of Davis *et al.* (16) nearly 2 orders of magnitude lower than that predicted from Schofield's equation (15). If the results from this new study are correct, the importance of reaction 33 to the  $\text{SO}_2$  aerosol conversion mechanism would appear to be negligible. A possible exception to this conclusion, however, would be if the reaction of triplet  $\text{SO}_3$  with  $\text{H}_2\text{O}$  was found to be much faster than for the same reaction involving ground state singlet  $\text{SO}_3$ . The latter species would be formed from reaction 31 ( $\text{HO}_2 + \text{SO}_2 \rightarrow \text{OH} + \text{SO}_3$ ).

The rate expression for the reaction of OH with CO (process 37) has undergone several changes in the last 10 years. In 1963, for example, the activation energy was listed as 10 kcal/mol; in 1965, 7.7 kcal/mol; in 1967, 2.5 kcal/mol; again in 1967, 1.0 kcal/mol; in 1972, 0.6 kcal/mol; and finally in 1973,  $E_{\text{act}} \approx 0.06$  kcal/mol. The near zero activation energy now being suggested is the result of new studies in 1973 by

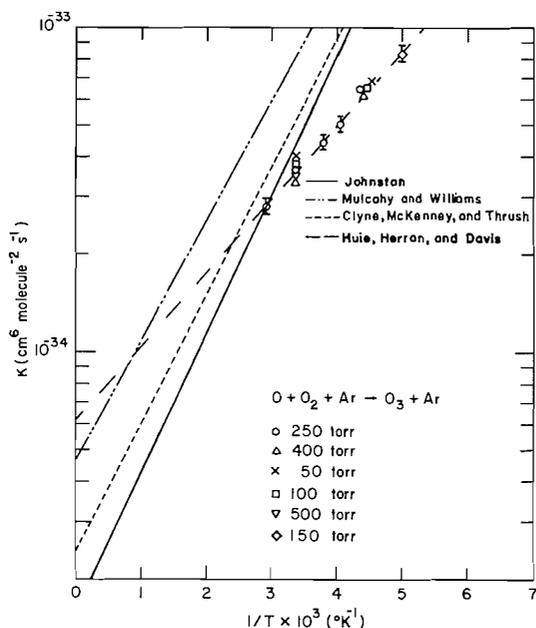


FIG. 1. Arrhenius plot for the reaction  $\text{O}(^3\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ ; — Johnston (3), (····) Mulcahy and Williams (27), (----) Clyne *et al.* (28), (-·-·-) Huie *et al.* (14).

Westenberg and deHaas (17), Zellner and Smith (18), and Davis, Schiff, and Fischer (16). The techniques employed in these three independent studies include discharge flow - e.s.r. detection, flash photolysis - absorption spectroscopy, and flash photolysis - resonance fluorescence. All three involved direct measurements of the OH radical concentration *vs.* reaction time. Below 373 °K, the data all lie within ~10% of each other. Since the temperature dependence for this reaction now appears to be very small it is quite possible that it does not, in fact, reflect a small threshold energy for the reaction but rather a small temperature dependence in the pre-exponential factor. The fact that the low temperature data do not extrapolate linearly into the high temperature results on this reaction could be due to two reasons: (1) the high temperature data are systematically in error because of the much more complex nature of the chemistry at these temperatures; or (2) the simple Arrhenius expression is inadequate for treating this system over an extended temperature range. The latter possibility has been considered by both Westenberg and deHaas and Zellner and Smith who applied transition state theory to this system. Both sets of calculations predicted strong curvature in the  $\ln k$  *vs.*  $1/T$  plot at temperatures above ~500 °K.

The rate constant for the reaction of HO<sub>2</sub> with CO (process 38) has also undergone some enormous fluctuations in the last 2 years. This reaction was listed in the set of 20 important atmospheric reactions because of the recently reported *k* value for this process of 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This result, reported by Westenberg and deHaas, would have made this reaction the single most important atmospheric oxidation path for conversion of CO to CO<sub>2</sub>. Previous to the Westenberg and deHaas measurement, Lloyd's 1971 evaluation (19) (based primarily on high temperature data) listed the value of the rate constant as 10<sup>-24</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The 1973 CIAP evaluation is based on the newer results of Davis, Payne, and Stief (20) and Simonaitis and Heicklen (12). Both studies gave values in the range of 10<sup>-19</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, making reaction 38 of negligible importance to atmospheric modelling efforts. Two of the major differences between the experiments carried out by the latter two groups and those by Westenberg and deHaas

were the total pressure and gas compositions. In Westenberg's experiments a low pressure discharge flow system with e.s.r. detection of H, O, and OH was employed, whereas Davis *et al.* (20) and Simonaitis and Heicklen (12) used high pressure photochemical methods containing large amounts of water vapor. It has been suggested by Davis *et al.* that a possible explanation for the 8 orders of magnitude difference might have been the presence of vibrationally and rotationally excited OH or HO<sub>2</sub> in Westenberg's experiments (17).

A final reaction whose rate expression would appear to be due for a reevaluation is process 44. The 1972 evaluation by Wilson (21) gives the activation energy as ~5 kcal/mol. This evaluation excluded (or minimized) the low temperature data of Greiner (22) and instead relied more upon the numerous high temperature results. However, the newer low temperature data (373-240 °K) of Davis, Schiff, and Fischer (16) corroborate the earlier results of Greiner, giving an activation energy of ~3.4 kcal/mol. In the latter study by Davis *et al.*, low flash energies which produced no more than 10<sup>10</sup>-10<sup>11</sup> OH radicals/cc were used in combination with resonance fluorescence detection. The probability of secondary reactions being important, therefore, appears to be quite small. As in the OH + CO system, the low temperature data for process 44 do not extrapolate linearly into the high temperature results. The explanation for this behavior is probably similar to that for the OH-CO reaction.

### Recommendations for New Experimental Work

Thus far very little has been said about the reliability of the rate constants quoted in the text. However, since the recommending of new experimental work necessarily reflects the uncertainty in available rate data, an acceptable magnitude for this uncertainty must now be indicated. In this case, those reactions which this author feels are in need of additional work would typically have uncertainties of no smaller than ±50%, and in some cases the uncertainties might be as high as plus or minus a factor of 5.

It is this author's opinion that there are three general areas where additional experimental work would be desirable. These include: (1) ozone reactions, 7, 13, and 18; (2) SO<sub>2</sub> reactions, 30, and 31; and (3) radical-radical reactions, 3,

9, 11, 14, and 16. In the case of the first group mentioned, there have been no direct measurements of the temperature dependence of process 7 (presumably small) and only two measurements at 300 °K. The value of the rate constant for reaction 13 appears to be well established at 300 °K, but additional direct measurements of the temperature dependence of this process seem to be justified at this time. As pointed out earlier in the text, there have been no direct measurements of the reaction of HO<sub>2</sub> with O<sub>3</sub>.

The two homogeneous gas phase reactions which now appear to provide a possible explanation for the presence and location of the Junge aerosol belt are processes 30 and 31. Only preliminary data at 300 °K are now available for reaction 30 and only relative rate measurements at 300 °K have been completed for reaction 31. Both must be studied as a function of temperature, and reaction 30 must be investigated also as a function of total pressure.

One of the most neglected areas of experimental kinetics has been that of radical-radical reactions. These measurements are necessarily difficult since absolute concentrations of transient species must be determined. In most cases, the rate constants quoted for these fast reactions have been estimated only. With the possible exception of reaction 14, very few direct measurements exist at 300 °K, and almost no temperature dependence studies have been carried out. Processes 3, 9, 11, 14, and 16 are of critical importance to present modelling efforts since in many regions of the atmosphere they control the important ratios HO<sub>2</sub>:OH; O:OH; and H:OH.

The author would like to thank Professor Harold Schiff for extending to him an invitation to present this review paper on atmospheric kinetics. He would also like to express his appreciation to the CIAP office of the U.S. Department of Transportation and the IAGA Committee for providing financial support to allow this author to attend the IAGA meeting in Koyoto, Japan.

1. (a) P. J. CRUTZEN. *J. Geophys. Res.* **26**, 7311 (1971). (b) P. J. CRUTZEN. *Q. J. R. Meteorol. Soc.* **96**, 320 (1970). (c) P. J. CRUTZEN. Paper presented at the IAGA meeting, Kyoto, Japan, 1973.
2. (a) E. HESSTVEDT. Paper presented at CIAP workshop, Washington, D.C., Oct. 1972. (b) E. HESSTVEDT. *Can. J. Chem.* This issue.
3. H. S. JOHNSTON. Gas phase reaction kinetics of neutral oxygen species. *NBS-NSRDS* **20**, 1968 Supr. of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
4. (a) M. NICOLET. *Planet. Space Sci.* **20**, 1671 (1972). (b) M. NICOLET and W. PEETERMAUS. *Ann. Geophys.* **4**, 751 (1972). (c) M. NICOLET and G. BRASSEUR. *Planet. Space Sci.* **21**, 939 (1973).
5. Climatic impact assessment program, second draft of monograph I. The natural stratosphere. CIAP office, Department of Transportation, Washington, D.C.
6. D. L. BAULCH, D. D. DRYSDALE, D. G. HORNE, and A. C. LLOYD. Evaluated kinetic data for high temperature reactions. Vol 1. *In* Homogeneous gas phase reactions of the H<sub>2</sub>O<sub>2</sub> system. Butterworth, London, 1972.
7. D. D. DAVIS and W. WONG. *Int. J. Chem. Kinet.* In press.
8. (a) M. F. KURYLO. Paper presented at the AIAA meeting, Denver, Colo. June 1973. (b) M. F. KURYLO. *J. Phys. Chem.* **76**, 3518 (1972).
9. W. D. DEMORE. *Science*, **180**, 735 (1973).
10. J. G. ANDERSON and F. KAUFMAN. *Chem. Phys. Lett.* **19**, 483 (1973).
11. D. D. DAVIS and R. SCHIFF. Unpublished results.
12. (a) R. SIMONAITIS and J. HEICKLEN. *J. Phys. Chem.* **77**, 1096 (1973). (b) R. SIMONAITIS and J. HEICKLEN. *J. Phys. Chem.* **77**, 1932 (1973).
13. E. JOHNSTON. Catalytic reduction of stratospheric ozone by nitrogen oxides. AEC Report UCRL-20568.
14. R. HUIE, J. HERRON, and D. D. DAVIS. *J. Phys. Chem.* **76**, 2653 (1972).
15. K. SCHOFIELD. *Planet. Space Sci.* **15**, 643, 1336 (1967).
16. D. D. DAVIS, R. SCHIFF, and S. FISCHER. Unpublished results.
17. A. A. WESTENBERG and N. DEHAAS. *J. Phys. Chem.* **76**, 1586 (1972).
18. R. ZELLNER and I. W. M. SMITH. *J. Chem. Soc. Faraday Trans.* **11**, 1617 (1973).
19. A. C. LLOYD. Evaluation and estimated kinetic data for the gas phase reactions of the hydroperoxyl radical. NBS Report 10447. 1971.
20. D. D. DAVIS, W. PAYNE, and L. STIEF. *Science*, **179**, 280 (1973).
21. W. M. E. WILSON, JR. *J. Phys. Chem. Ref. Data*, **1**, 535 (1972).
22. N. R. GREINER. *J. Chem. Phys.* **53**, 1070 (1970).
23. F. KAUFMAN. *Ann. Geophys.* **20**, 106 (1964).
24. C. J. HOCHANADEL, J. A. GHORMLEY, and P. J. OGDEN. *J. Chem. Phys.* **56**, 4426 (1972).
25. I. M. CAMPBELL and C. N. GRAY. *Chem. Phys. Lett.* **18**, 607 (1973).
26. D. D. DAVIS, S. FISCHER, and R. SCHIFF. Unpublished results.
27. M. F. R. MULCAHY and D. J. WILLIAMS. *Trans. Faraday Soc.* **64**, 59 (1968).
28. M. A. A. CLYNE, D. J. MCKENNEY, and B. A. THRUSH. *Trans. Faraday Soc.* **61**, 2701 (1965).
29. L. I. AVRAMENKO and R. V. KOLESNIKOVA. Mechanisms and rate constants of elementary gas phase reactions involving hydroxyl. Interscience, New York, 1964. p. 25.
30. R. R. BALDWIN, A. C. NORRIS, and R. W. WALKER. 11th Symposium on Combustion. The Combustion Institute, 1965. p. 889.

31. R. V. BLUNDELL, W. G. A. COOK, D. E. HOARE, and G. S. MILNE. 10th Symposium on Combustion. The Combustion Institute, 1965. p. 445.
32. G. DIXON-LEWIS and A. WILLIAMS. 11th Symposium on Combustion. The Combustion Institute, 1967. p. 951.
33. D. D. DRYSDALE and A. LLOYD. Private communication.
34. C. P. FENIMORE and G. W. JONES. *J. Chem. Phys.* **65**, 2200 (1961).
35. R. M. FRISTROM. 9th Symposium on Combustion. Academic Press, N.Y. 1963. p. 560.
36. D. E. HOARE. *Nature*, **194**, 283 (1962); D. E. HOARE. *Proc. R. Soc. A*, **291**, 73 (1966); D. E. HOARE and G. B. PEACOCK. *Proc. R. Soc. A*, **291**, 85 (1966).
37. D. G. HORNE and R. G. W. NORRISH. *Nature*, **215**, 1373 (1967).
38. W. PAYNE, L. STIEF, and D. D. DAVIS. *J. Am. Chem. Soc.* In press.
39. WM. E. WILSON, JR., J. T. O'DONOVAN, and R. M. FRISTROM. 12th Symposium on Combustion. The Combustion Institute, 1969. p. 929.