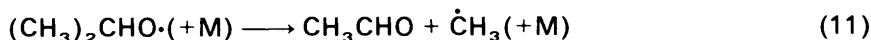


## Reactions of Oxygenated Radicals in the Gas Phase. Part 16.<sup>1</sup> Decomposition of Isopropoxyl Radicals

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The photo-oxidation of *trans*-2,2'-azopropane has been studied between 333 and 434 K. The main products are propan-2-ol, isopropyl hydroperoxide, and acetone. Acetaldehyde becomes an increasingly important product as the temperature and pressure are increased. By altering the total pressure of the system, using nitrogen as diluent, quantitative data for the rate of decomposition of isopropoxyl radicals may be obtained.  $k_1$ , varies markedly with pressure between 20 and 760 Torr in this temperature regime.



Although the reactions of alkoxy radicals are of importance in the combustion and photo-oxidation of hydrocarbons and related compounds, there are comparatively few rate data available. Some blame can be attached to the methods usually adopted, namely by competitive systems in which the data for the reference reaction, the free radical 'clock',<sup>2</sup> are suspect.

The decomposition of alkoxy radicals is one example. It has been suggested many times<sup>3-8</sup> that the unimolecular decomposition of these radicals is pressure dependent but it is only relatively recently that Batt and his co-workers<sup>8-12</sup> have systematically examined the effect of pressure, over a wide range, on *t*-butoxy radicals using tetrafluoromethane,<sup>11</sup> nitrogen,<sup>11</sup> argon,<sup>12</sup> and sulphur hexafluoride<sup>11</sup> as inert gases.

The effect of pressure on the rate of decomposition of isopropoxyl radicals has been studied several times.<sup>4-6</sup> It is shown that as the pressure is increased, the pre-exponential factor appears to decrease and the activation energy increase, in conflict with the evidence obtained for *t*-butoxy radicals.<sup>9</sup> In this study we eschewed the two methods generally used to prepare isopropoxyl radicals, the decomposition of isopropyl nitrite<sup>13-15</sup> and di-isopropyl peroxide.<sup>4</sup> Instead, they were generated by the photo-oxidation of 2,2'-azopropane. The mechanism of the reaction is well understood<sup>16-18</sup> and allows for reactions such as the decomposition of the isopropoxyl radical to be studied over a wide range of conditions.

### Experimental

The apparatus and methods of analysis of reactants and products have been described.<sup>17</sup> As before, *trans*-2,2'-azopropane was prepared from isopropylamine by a modified method based on that due to Stowell.<sup>19</sup> Its purity was >99% by gas chromatography, the main contaminant being pentane (the solvent). There were minute traces of propene, propane, and 2,3-dimethylbutane but no oxygenated compounds, nor *cis*-2,2'-azopropane,<sup>20</sup> were detectable.

### Results

As previously reported,<sup>17,18</sup> the principal products formed in the photo-oxidation of 2,2'-azopropane are acetone, propan-2-ol, isopropyl hydroperoxide, and *cis*-2,2'-azopropane below 333 K. Above this temperature, significant amounts of formaldehyde, acetaldehyde, and methanol are also formed. The photolysis products of the azo compound, propane, and 2,3-dimethylbutane, were not observed but traces of propene could sometimes be detected.

In this paper, we concentrate on results obtained between 333–434 K, in which region acetaldehyde is a product. In a

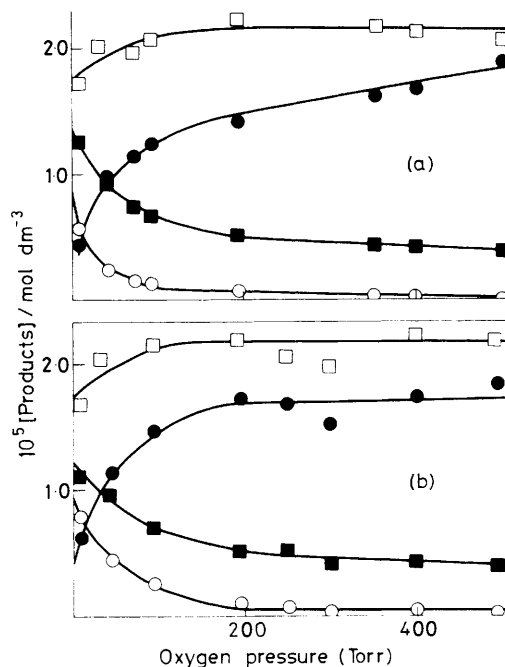
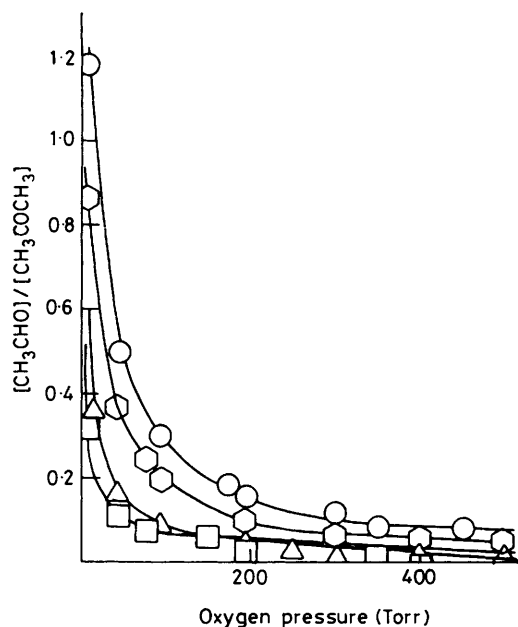


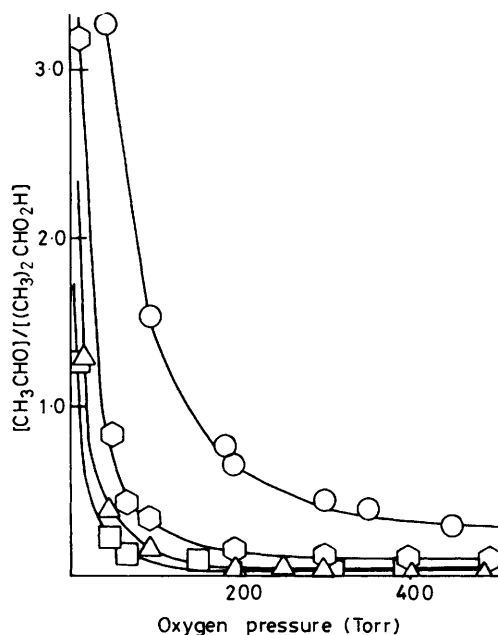
Figure 1. Photo-oxidation of *trans*-2,2'-azopropane. *trans*-2,2'-Azopropane, 5 Torr; total pressure (with nitrogen), 500 Torr. ○, Acetaldehyde; □, acetone; ■, propan-2-ol, ●, isopropyl hydroperoxide. Reaction time, 3 600 s. The lines show simulated yields of products. (a) 333 K; (b) 434 K

series of experiments, the pressure of oxygen was varied, keeping the total pressure constant by adding nitrogen. Increasing the pressure of oxygen, the yields of acetone and isopropyl hydroperoxide increase while those of acetaldehyde and propan-2-ol decrease. Figure 1 shows an example of this. The ratios of yields of acetaldehyde with acetone (Figure 2), propan-2-ol (Figure 3), and isopropyl hydroperoxide (Figure 4) decrease as the pressure of oxygen increases.

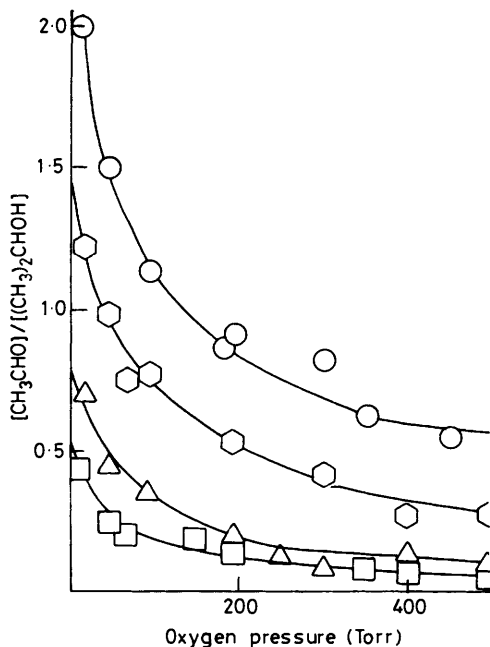
A series of experiments was then performed at different temperatures, with constant mixtures of 2,2'-azopropane and oxygen but in which the overall pressure was varied by altering the initial pressure of nitrogen. On increasing the nitrogen pressure, the rates of formation of acetone, propan-2-ol, and isopropyl hydroperoxide decrease. However, results for acetaldehyde are more complex. On increasing the initial pressure, the rate of formation of acetaldehyde increases, passes



**Figure 2.** Photo-oxidation of *trans*-2,2'-azopropane. Variation of product ratios with oxygen pressure. *trans*-2,2'-Azopropane, 5 Torr; total pressure (with nitrogen), 500 Torr.  $\square$ , 333 K;  $\triangle$ , 343 K;  $\circ$ , 353 K;  $\circ$ , 373 K. Reaction time, 3 600 s. The lines show simulated ratios of product yields



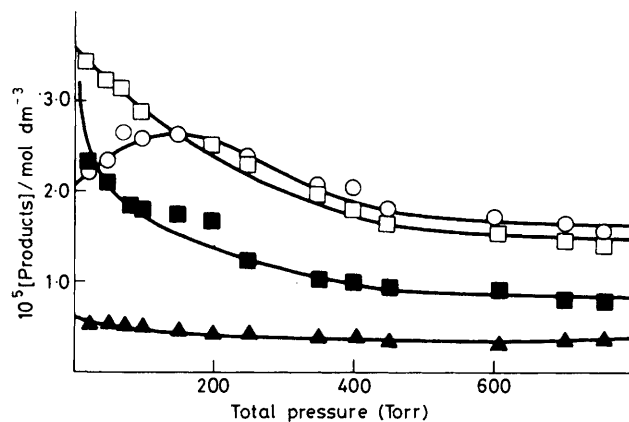
**Figure 4.** Photo-oxidation of *trans*-2,2'-azopropane. Variation of product ratios with oxygen pressure. *trans*-2,2'-Azopropane, 5 Torr; total pressure (with nitrogen), 500 Torr.  $\square$ , 333 K;  $\triangle$ , 343 K;  $\circ$ , 353 K;  $\circ$ , 373 K. Reaction time, 3 600 s. The lines show simulated ratios of product yields



**Figure 3.** Photo-oxidation of *trans*-2,2'-azopropane. Variation of product ratios with oxygen pressure. *trans*-2,2'-Azopropane, 5 Torr; total pressure (with nitrogen), 500 Torr.  $\square$ , 333 K;  $\triangle$ , 343 K;  $\circ$ , 353 K;  $\circ$ , 373 K. Reaction time, 3 600 s. The lines show simulated ratios of product yields

through a maximum and then, like the other products, decreases. An example of this behaviour is shown in Figure 5.

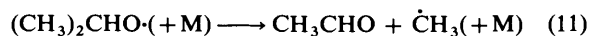
In all experiments the amount of *cis*-2,2'-azopropane quickly reaches a stationary value<sup>17</sup> which also varies with total pressure and apparently with temperature (Table 1).



**Figure 5.** Photo-oxidation of *trans*-2,2'-azopropane. *trans*-2,2'-Azopropane, 5 Torr; oxygen, 10 Torr. Total pressure varied by addition of nitrogen. Temperature 373 K. Reaction time, 3 600 s.  $\circ$ , Acetaldehyde;  $\square$ , acetone;  $\blacksquare$ , propan-2-ol;  $\bullet$ , isopropyl hydroperoxide. The lines show simulated yields of products

## Discussion

The mechanism for the photo-oxidation of *trans*-2,2'-azopropane has been discussed in detail.<sup>16-18</sup> Below 333 K, reactions (1)–(10) account for the rates of formation of products over a wide range of conditions (Table 2). At 333 K and above, isopropoxyl radicals, besides undergoing reactions (4), (5), (7), and (9), also decompose relatively quickly by reaction (11). This reaction becomes increasingly important as the temperature is raised and acetaldehyde becomes a major product. Methyl radicals react rapidly with oxygen to yield



**Table 1.** Photo-oxidation of *trans*-2,2'-azopropane: formation of *cis*-2,2'-azopropane. From a mixture of *trans*-isomer, 5, Torr; oxygen 10, Torr; nitrogen as diluent

Total initial pressure (Torr)	Stationary yield of <i>cis</i> -isomer (Torr)			
	333K	353K	373K	393K
20	0.03	0.02	0.02	0.03
50	0.06		0.03	0.03
70		0.04	0.04	
100	0.08	0.06	0.04	0.05
150	0.10		0.05	
200	0.13	0.10	0.06	0.08
250			0.08	
300	0.16	0.12		0.09
350			0.09	0.10
400		0.12	0.11	0.11
450			0.12	0.11
500	0.18	0.13		0.12
600	0.17	0.17	0.14	0.13
700	0.20	0.18	0.14	
760			0.15	0.14

**Table 2.** Rate constants used in the simulation of the photo-oxidation of *trans*-2,2'-azopropane

	333 K	343 K	353 K	373 K
(1) $RN_2R \rightarrow 2R\cdot + N_2$				
(2) $R\cdot + O_2(+M) \rightarrow RO_2\cdot(+M)$	$3.1 \times 10^8$	$3.1 \times 10^8$	$3.1 \times 10^8$	$3.1 \times 10^8$
(3a) $2RO_2\cdot \rightarrow (CH_3)_2CO + (CH_3)_2CHOH + O_2$	$3.0 \times 10^5$	$3.7 \times 10^5$	$4.2 \times 10^5$	$5.4 \times 10^5$
(3b) $2RO_2\cdot \rightarrow 2RO\cdot + O_2$	$6.0 \times 10^5$	$7.9 \times 10^5$	$1.0 \times 10^6$	$1.5 \times 10^6$
(4) $2RO\cdot \rightarrow (CH_3)_2CO + (CH_3)_2CHOH$	$1.0 \times 10^{10}$	$1.0 \times 10^{10}$	$1.0 \times 10^{10}$	$1.0 \times 10^{10}$
(5) $RO\cdot + O_2 \rightarrow (CH_3)_2CO + HO_2\cdot$	$5.5 \times 10^5$	$7.4 \times 10^5$	$8.1 \times 10^5$	$1.2 \times 10^6$
(6) $RO_2\cdot + HO_2\cdot \rightarrow RO_2H + O_2$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$
(7) $RO_2\cdot + RO\cdot \rightarrow (CH_3)_2CO + RO_2H$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$
(8) $RO\cdot + RO_2H \rightarrow (CH_3)_2CHOH + RO_2\cdot$	$6.2 \times 10^7$	$6.6 \times 10^7$	$7.0 \times 10^7$	$7.8 \times 10^7$
(9) $RO\cdot + HO_2\cdot \rightarrow (CH_3)_2CHOH + O_2$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$
(10) $HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$	$2.2 \times 10^9$	$2.2 \times 10^9$	$2.2 \times 10^9$	$2.2 \times 10^9$
(11) $RO\cdot(+M) \rightarrow CH_3CHO + Me\cdot(+M)$	$5.0 \times 10^1$	$1.5 \times 10^2$	$3.5 \times 10^2$	$1.2 \times 10^3$
(12) $Me\cdot + O_2(+M) \rightarrow MeO_2\cdot(+M)$	$3.1 \times 10^8$	$3.1 \times 10^8$	$3.1 \times 10^8$	$3.1 \times 10^8$
(13a) $2MeO_2\cdot \rightarrow 2MeO\cdot + O_2$	$9.6 \times 10^7$	$9.6 \times 10^7$	$9.6 \times 10^7$	$9.6 \times 10^7$
(13b) $2MeO_2\cdot \rightarrow HCHO + MeOH + O_2$	$1.8 \times 10^8$	$1.8 \times 10^8$	$1.8 \times 10^8$	$1.8 \times 10^8$
(14a) $MeO_2\cdot + RO_2\cdot \rightarrow MeO\cdot + RO\cdot + O_2$	$1.6 \times 10^7$	$1.7 \times 10^7$	$1.8 \times 10^7$	$2.0 \times 10^7$
(14b) $MeO_2\cdot + RO_2\cdot \rightarrow HCHO + ROH + O_2$	$1.6 \times 10^7$	$1.7 \times 10^7$	$1.8 \times 10^7$	$2.0 \times 10^7$
(14c) $MeO_2\cdot + RO_2\cdot \rightarrow (CH_3)_2CO + MeOH + O_2$	$1.6 \times 10^7$	$1.7 \times 10^7$	$1.8 \times 10^7$	$2.0 \times 10^7$
(15) $RO_2\cdot + MeO\cdot \rightarrow HCHO + RO_2H$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$
(16) $MeO\cdot + O_2 \rightarrow HCHO + HO_2\cdot$	$5.5 \times 10^5$	$7.4 \times 10^5$	$8.1 \times 10^5$	$1.2 \times 10^6$
(17) $MeO_2\cdot + RO\cdot \rightarrow (CH_3)_2CO + MeO_2H$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$
(18) $MeO\cdot + RO_2H \rightarrow MeOH + RO_2\cdot$	$6.2 \times 10^7$	$6.6 \times 10^7$	$7.0 \times 10^7$	$7.8 \times 10^7$
(19) $RO\cdot + MeO_2H \rightarrow ROH + MeO_2\cdot$	$6.2 \times 10^7$	$6.6 \times 10^7$	$7.0 \times 10^7$	$7.8 \times 10^7$
(20) $MeO\cdot + MeO_2H \rightarrow MeOH + MeO_2\cdot$	$6.2 \times 10^7$	$6.6 \times 10^7$	$7.0 \times 10^7$	$7.8 \times 10^7$
(21) $MeO_2\cdot + HO_2\cdot \rightarrow MeO_2H + O_2$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$	$9.2 \times 10^8$

R = Pr<sup>i</sup>

Rate constants in  $dm^3 mol^{-1} s^{-1}$ , except for (11) which are given as  $s^{-1}$ .

methylperoxy radicals, thus complicating the system, for methylperoxy radicals can undergo the reactions suggested for isopropylperoxy and further they undergo cross-reactions (Table 2).

A computer model of the system<sup>17,18,21</sup> designed to simulate its time-composition behaviour was used, in which a numerical integration procedure was employed for the solution of 'stiff' differential equations. The values of the rate constants chosen for the reactions are discussed in detail in several papers<sup>17,18,22,23</sup> and show that the reaction scheme is quantitatively consistent with experimental data (Figures 1—5). The value for  $k_{11}$  was varied until the simulations fitted over the temperature range and the range of oxygen pressures at constant overall pressure. Figure 1 gives an example of the results obtained at five different temperatures, between 333 and 434 K. The way of presenting results in Figures 2—4 is particularly sensitive,

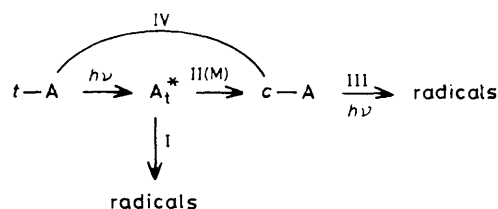
demonstrating that the proposed scheme provides a reasonable way of describing the reaction. Acetone was chosen as a reference for two reasons. It is formed principally as a product of bimolecular reactions (4), (5), (7), (14c), and (17); secondly it is least affected by changes in oxygen concentration (Figure 1), since reactions of isopropoxy and isopropylperoxy radicals, either with radicals or with oxygen, leads to its formation.<sup>17,18</sup>

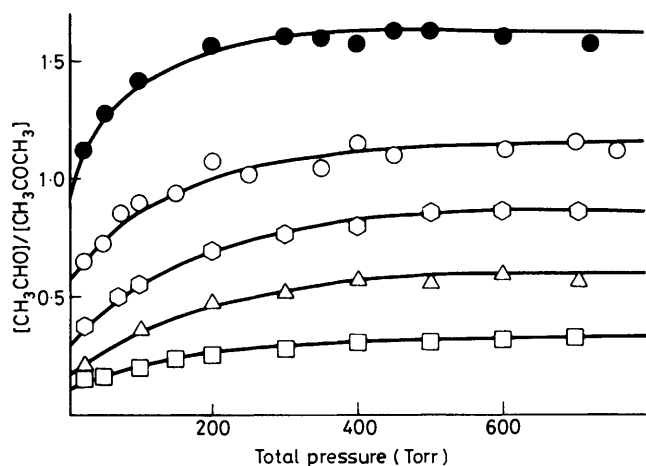
Acetaldehyde is formed solely by reaction (11) and thus determination of its rate of formation provides a route for determining the rate parameters for the reaction, not only when the temperature is changed, as described above, but also when the total pressure is varied. A series of experiments was performed between 333 and 373 K in which the only variable was the pressure of inert gas, nitrogen (Figure 5).

The rates of formation of propan-2-ol, isopropyl hydroperoxide, and acetone decrease, in proportion, as the pressure of nitrogen increases. This must be due to the decrease in the rate of formation of isopropylperoxy radicals as the total pressure is raised, which, in turn, is dependent on reaction (1). Reaction (1) is a complex process which accounts for both elimination of nitrogen and *cis-trans*-isomerisation. Various studies have

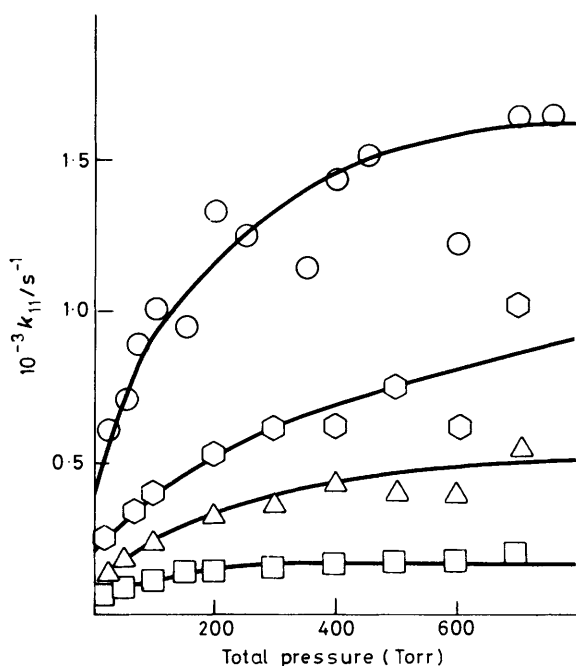
explained the curvature obtained in Stern-Volmer plots<sup>24,30</sup> (and which we ourselves observed) and the reaction can be described in terms of the processes in the Scheme.

Thus, on adding nitrogen, the overall rate of forming isopropyl and hence isopropylperoxy radicals will fall, accounting

**Scheme.**



**Figure 6.** Photo-oxidation of *trans*-2,2'-azopropane. *trans*-2,2'-Azopropane, 5 Torr; oxygen, 10 Torr. Total pressure varied by addition of nitrogen. Reaction time, 3 600 s.  $\square$ , 333 K;  $\triangle$ , 343 K;  $\diamond$ , 353 K;  $\circ$ , 373 K;  $\bullet$ , 393 K. The lines show simulated ratios of product yields



**Figure 7.** Effect of total pressure on  $k_{11}$  at different temperatures.  $\square$ , 333 K;  $\triangle$ , 343 K;  $\diamond$ , 353 K;  $\circ$ , 373 K

for the effect of added nitrogen on the rate of formation of acetone, propan-2-ol, and isopropyl hydroperoxide (Figure 5) and the increase in the proportion of *cis*-2,2'-azopropane amongst the products.

However, the results for acetaldehyde are more complex. On increasing the total pressure, the rate of formation of acetaldehyde passes through a maximum, even though the rate of formation of isopropylperoxy radicals falls. However, if the rate of formation of acetaldehyde is compared with the rate of formation of acetone (the latter is a measure of *extent* of reaction), the result becomes clearer, for this ratio increases on increasing pressure (Figure 6) as would be expected if reaction (11) is indeed pressure dependent under these conditions.

**Table 3.** Decomposition of the isopropoxyl radical: values of  $S$ ,  $B$ , and  $D$  used for the Kassel integrals

(a) Values of  $S$  and  $B$

$T/K$	333	343	353	373
$S$	4.95	5.00	5.20	5.70
$B$	26.0	25.2	24.5	24.0

(b) Values of  $D$

Total pressure (Torr)	$T/K$			
	333	343	353	373
20	6.19	6.29	6.28	6.31
50	5.89	5.90		5.91
70			5.76	5.77
100	5.59	5.60	5.60	5.61
150	5.41			5.44
200	5.29	5.29	5.30	5.31
250				5.22
300	5.11	5.12	5.12	
350				5.07
400	4.99	4.99	5.00	5.01
450				4.96
500	4.89	4.90	4.90	
600	4.81	4.82	4.82	4.83
700	4.74	4.74	4.75	4.77
760				4.73

The results obtained on altering pressure were then simulated. It was possible to simulate the reactions successfully if the rate constants for reactions (1) and (11) were altered.  $k_1$  was obtained, for each pressure, from the rate of formation of acetone and  $k_{11}$  from that of acetaldehyde. Results for the effect of pressure on  $k_{11}$  at different temperatures are summarised in Figure 7. The rate constant increases rapidly as the pressure is increased to *ca.* 200 Torr, the effect being most pronounced as the temperature is increased. We did not observe a limiting value for the rate constant below 760 Torr.

We have extended the range of pressures under which the decomposition of the radical has been studied. Previous experiments had been limited to 230 Torr and below.<sup>3,4</sup> Further, the earlier investigations were carried out in absence of additives,<sup>3</sup> or in presence of nitric oxide<sup>4,12</sup> or tetrafluoromethane.<sup>10</sup> The importance of using nitrogen as the inert gas has already been stressed,<sup>10</sup> particularly as rate constants are needed for combustion systems.

Although it is not possible to compare these results with those obtained in earlier studies for in the latter the pressure ranges chosen were too narrow, the present results show that the rate of decomposition of isopropoxyl radicals has a greater dependence on the presence of added diluent and over a wider range than would be expected from these earlier results. However, the present work is in line with the results obtained recently for the decomposition of *t*-butoxyl radical.<sup>10</sup> In summary, the results in Figure 7 obtained by experiment can be used to find the rate constants for reactions in which the isopropoxyl radicals are in competition with the reactions leading to decomposition.

The unimolecular decomposition of species such as the isopropoxyl radical should be amenable to theoretical treatment. RRK theory was used to see whether a relatively simple theoretical model<sup>31,32</sup> gave reasonable results for the effect of pressure on the rate constant,  $k_{11}$ , where equation (i) holds. The Kassel integral  $I(S,B,D)$  is given by equation (ii) where  $B = E/RT$ ,  $D = \log(A/Z[M])$ ,  $Z$  being the calculated

**Table 4.** Decomposition of isopropoxy radicals: values of  $k_{11(p)}/k_{11(\infty)}$ 

Total pressure (Torr)	Values of $k_{11(p)}/k_{11(\infty)}$							
	333 K		343 K		353 K		373 K	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
100	0.08	0.02	0.08	0.02	0.06	0.02	0.04	0.02
200	0.11	0.04	0.11	0.04	0.08	0.03	0.05	0.03
500	0.14	0.07	0.15	0.07	0.14	0.06	0.06	0.05
700	0.15	0.10	0.15	0.09	0.15	0.08	0.06	0.07

collision frequency and  $s$  the number of effective oscillators in the energised isopropoxyl radical.

$$k_{11(p)} = k_{11(\infty)} I(S, B, D) \quad (i)$$

$$I(S, B, D) = \frac{1}{(s-1)!} \int_0^\infty \frac{x^{(s-1)} e^{-x} dx}{1 + 10^D [x/(B+x)]^{(s-1)}} \quad (ii)$$

Golden *et al.*<sup>33</sup> have shown that  $s$ , the number of effective oscillators, may be equated to  $C_{\text{vib}}/R$  and the vibrational frequencies for the isopropoxyl radical used were based on those given by Tanaka,<sup>34</sup> for propan-2-ol, ignoring contributions from the different modes of O-H vibrational frequencies. The total number of vibrational modes in the radical is 27, of which 18 will, in this temperature region, play a significant role in the calculation.<sup>35</sup>

Parameters  $B$  and  $D$  were calculated at each temperature using Batt's values<sup>10</sup> for the Arrhenius parameters,  $E_{11(\infty)}$  72.2 kJ mol<sup>-1</sup> and  $\log(A_{11(\infty)}/s^{-1})$  14.6 (Table 3).

Values of  $Z$  were calculated by simple kinetic theory. Account was taken for collisions of isopropoxyl radicals with oxygen, nitrogen, and 2,2'-azopropane, the collision diameters being calculated by a method described by Bondi.<sup>36</sup>

Although there are considerable discrepancies between the computed and experimental values of  $k_{11(p)}/k_{11(\infty)}$ , particularly at lower temperatures and pressures, there is nevertheless qualitative agreement between the experimentally determined and calculated values for  $k_{11(p)}/k_{11(\infty)}$ . On increasing the pressure, the values increase rapidly up to 200 Torr and then tend to level off; they do not appear to reach a limiting value below 760 Torr (Table 4). Further, both sets of ratios decrease on increasing temperature.

The principal aim of the work was to obtain values for  $k_{11}$  at different pressures under conditions in which gas-phase reactions of alkoxy radicals are important. It is now possible to use these data to determine bimolecular reactions of alkoxy radicals with substrates.

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