J. Chem. Soc., Faraday Trans. 1, 1982, **78**, 2535-2546

Reactions of Oxygenated Radicals in the Gas Phase

Part 9.—Self-reactions of Isopropylperoxy Radicals

BY LESLIE T. COWLEY

Shell Research Limited, Thornton Research Centre, P.O. Box 1,
Chester CH1 3SH

AND DAVID J. WADDINGTON* AND ALLAN WOOLLEY†

Department of Chemistry, University of York, Heslington, York YO1 5DD

Received 23*rd November*, 1981

The principal products of the photo-oxidation of *trans*-2,2′-azopropane between 333 and 373 K are acetone, isopropyl alcohol, isopropyl hydroperoxide, acetaldehyde, formaldehyde, methyl alcohol and *cis*-2,2′-azopropane. The reaction mechanism has been simulated in detail, and, in conjunction with results obtained earlier for the overall self-reaction of isopropylperoxy radicals, the following rate data have been obtained for the reactions

$$2(CH_3)_2CHO_2\cdot \rightarrow (CH_3)_2CHOH + (CH_3)_2CO + O_2 \qquad (3a)$$

$$2(CH_3)_2CHO_2\cdot \rightarrow 2(CH_3)_2CHO\cdot + O_2 \qquad (3b)$$

k_{3b}/k_{3a} increases with temperature, from 1.39 ± 0.04 at 302 K to 1.83 ± 0.04 at 333 K and 2.80 ± 0.08 at 373 K. Values of A_{3a} and A_{3b} of $2.44 \pm 0.31 \times 10^7$ and $1.38 \pm 0.26 \times 10^9$ dm^3 mol^{-1} s^{-1} and E_{3a} and E_{3b} of 12.0 ± 1.0 and 21.3 ± 1.5 kJ mol^{-1} were determined.

In this series of papers[1, 2] the importance of obtaining reliable rate data for the reactions of oxygenated radicals in the gas phase, so that reaction mechanisms for combustion and atmospheric processes may be rigorously tested, has been emphasised.

In two of these papers rate data have been obtained for the overall effective bimolecular self-reactions of isopropylperoxy radicals, using u.v. spectroscopic techniques,[1] over a temperature range 302-373 K,

$$2(CH_3)_2CHO_2\cdot \rightarrow \text{products} \qquad (\text{obs})$$

and for the individual processes[2]

$$2(CH_3)_2CHO_2\cdot \rightarrow (CH_3)_2CHOH + (CH_3)_2CO + O_2 \qquad (3a)$$

$$2(CH_3)_2CHO_2\cdot \rightarrow 2(CH_3)_2CHO\cdot + O_2 \qquad (3b)$$

at 302 K. This provided, for the first time, values of elementary rate constants, directly determined, for these two reactions.

The shortage of elementary data is seen to be particularly unfortunate when it is remembered that measurements of overall self-reaction rate constants have raised as many fascinating problems as they have solved. For example, the value of the overall rate constant depends on the nature of the alkyl group of the alkylperoxy radical involved, for which present theory is unable to account successfully. The problem may be more tractable if the individual, rather than the overall, rate parameters are considered.

---

† Present address: University College School, Frognal, London NW3 6XH.

Further, once the Arrhenius parameters of these individual reactions are known, it should be possible to obtain rate data for other reactions of alkylperoxy radicals, *e.g.* abstraction and addition reactions, using the self-reactions as the control in competition with the reaction being studied. In this way, important data may be obtained to help us understand the complex behaviour of alkylperoxy radicals in gas-phase reactions.

In this paper results for the self-reactions of isopropylperoxy radicals over the temperature range 302-373 K are presented.

EXPERIMENTAL

The apparatus and methods of analysis of products and reactants were described in an earlier paper.[2] As before, *trans*-2,2′-azopropane was prepared from isopropylamine and purified to > 99% (by gas chromatography); no *cis*-2,2′-azopropane was detectable.[3]

RESULTS

The products of photolysis of *trans*-2,2′-azopropane, both in the presence and absence of oxygen, were confirmed by gas chromatography and mass-spectral analyses.

In the absence of oxygen, the products at 333 and 373 K are similar to those found at 302 K,[2] *cis*-2,2′-azopropane, propane, propene and 2,3-dimethylbutane (fig. 1). The rates of formation of propane and propene are indistinguishable and the ratio of the rates of formation of these products to that of 2,3-dimethylbutane is constant as reaction proceeds, but varies slightly with temperature (fig. 1). The rate of formation of *cis*-2,2′azopropane decreases with time until a stationary concentration of the isomer is achieved.

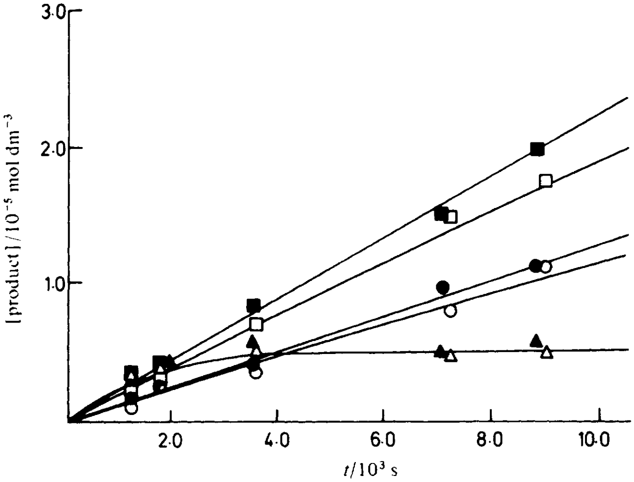

FIG. 1.—Photolysis of *trans*-2,2′-azopropane. 2,2′-*trans*-azopropane, 5 Torr; nitrogen, 495 Torr. □, ■, 2,3-Dimethylbutane at 333 and 373 K; ○, ●, propene and propane at 333 and 373 K; △, ▲, *cis*-2,2′-azopropane at 333 and 373 K. (1 Torr = 101 325/760 Pa.)

Some of the photolysis products in the presence of oxygen are similar to those at 302 K, *cis*-2,2′-azopropane, acetone, isopropyl alcohol and isopropyl hydroperoxide.

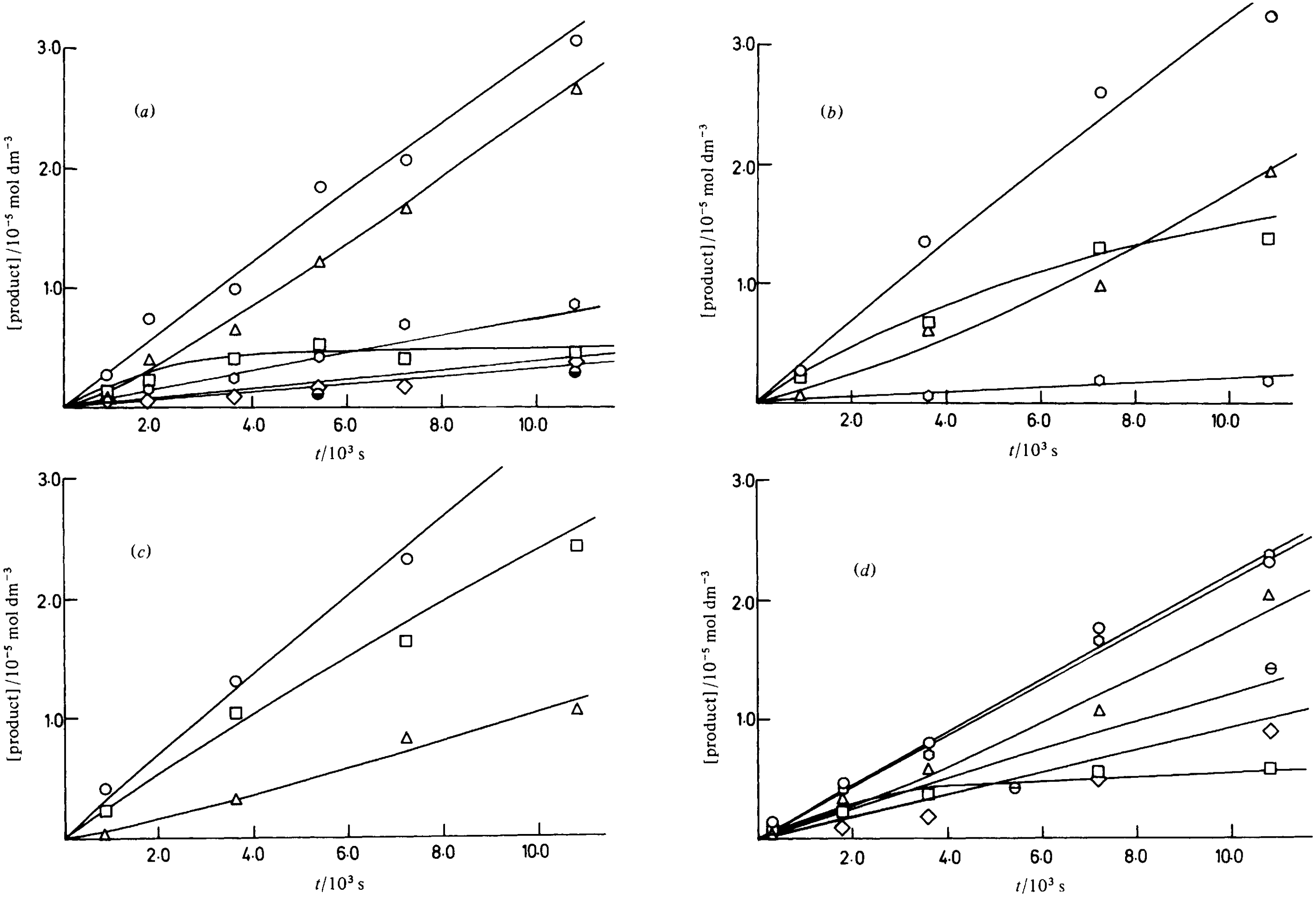

FIG. 2.—Photo-oxidation of 2,2′-azopropane at 333 K. ○, Acetone; □, isopropyl hydroperoxide; △, isopropyl alcohol; ⬡, acetaldehyde; ◒, formaldehyde; ◇, methyl alcohol. Experimental points are shown; the lines are from calculations following simulations (*a*) 2,2′-Azopropane, 5 Torr; oxygen, 10 Torr; nitrogen, 485 Torr. (*b*) 2,2′-Azopropane, 5 Torr; oxygen, 50 Torr; nitrogen, 445 Torr. (*c*) 2,2′-Azopropane, 5 Torr; oxygen, 495 Torr. (*d*) 2,2′-Azopropane, 5 Torr; oxygen, 10 Torr; nitrogen, 485 Torr.

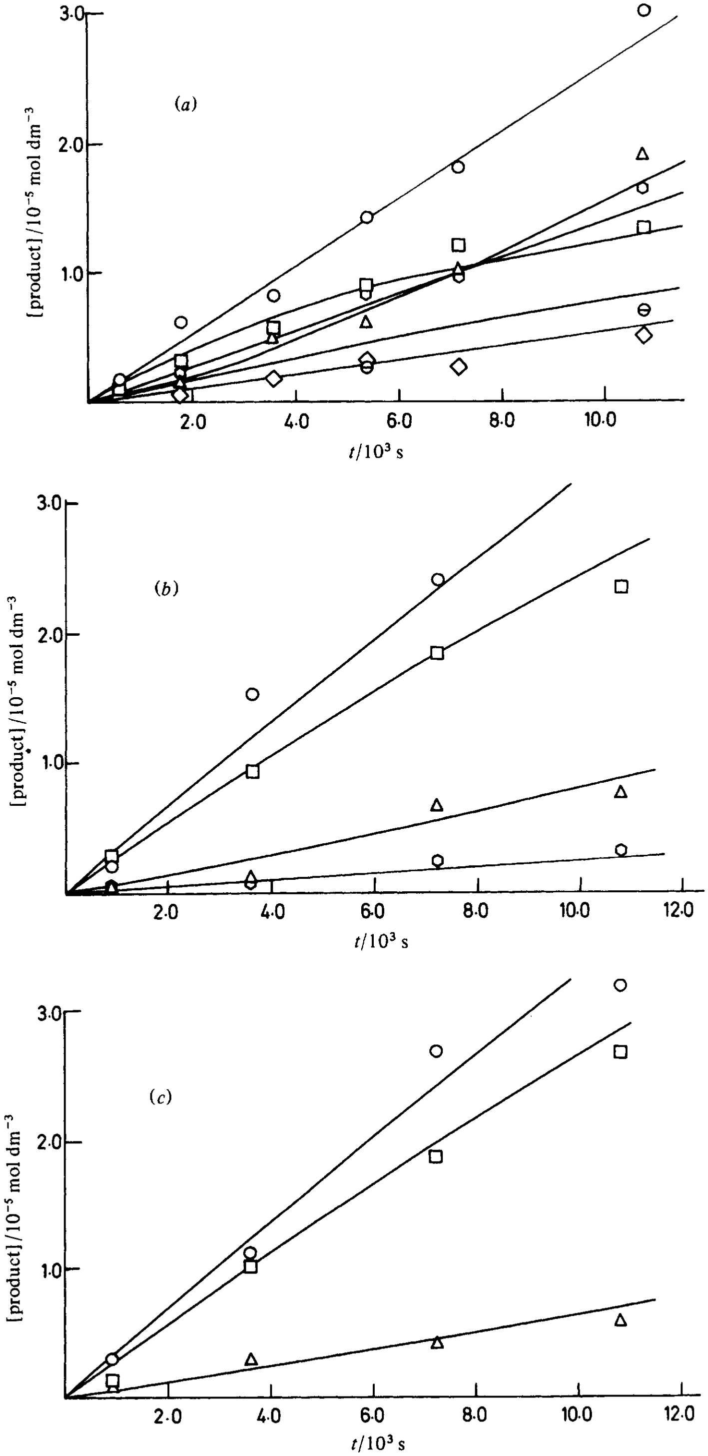

FIG. 3.—Photo-oxidation of 2,2′-azopropane at 373 K. (*a*) 2,2′-Azopropane, 5 Torr; oxygen, 25 Torr; nitrogen, 470 Torr. (*b*) 2,2′-Azopropane, 5 Torr; oxygen, 200 Torr; nitrogen, 295 Torr. (*c*) 2,2′-Azopropane, 5 Torr; oxygen, 495 Torr. For key, see fig. 2.

However, at 333 and 373 K significant amounts of formaldehyde, acetaldehyde and methyl alcohol are also formed. Propane and 2,3-dimethylbutane were not observed; however, traces of propene were detected. The rates of formation of all the oxygenated products vary with photolysis time and with temperature (fig. 2 and 3).

The initial oxygen pressure was varied, keeping the total pressure (with nitrogen) constant. As the oxygen pressure is increased, the yield of isopropyl alcohol decreases while that of isopropyl hydroperoxide increases. The sums of their concentrations equals that of acetone at high oxygen pressures, the formation of formaldehyde, acetaldehyde and methyl alcohol being suppressed on increasing the oxygen pressures.

As at 302 K,[2] the rate of decomposition of 2,2′-azopropane was determined by measuring the rates of formation of hydrocarbons, at constant total pressure. This gave a rate constant for the reaction

$$(CH_3)_2CHN_2CH(CH_3)_2 \rightarrow 2(CH_3)_2\dot{C}H + N_2 \qquad (1)$$

of $1.5 \times 10^{-5}\ s^{-1}$, which was independent of temperature.

DISCUSSION

The initiation reaction for the photo-oxidation of *trans*-2,2′-azopropane is complex.[4-7] However, we are only concerned with the subsequent reactions of isopropyl radicals, and the complexity of the initiation processes do not affect directly the kinetics of these reactions.[2]

On photolysis of 2,2′-azopropane, as at 302 K, equimolar proportions of propene and propane are formed, the yields of the C_3 hydrocarbons being smaller than that of 2,3-dimethylbutane. The three products are formed from self-reactions of isopropyl radicals formed from reaction (1):

$$(CH_3)_2CHN_2CH(CH_3)_2 \rightarrow 2(CH_3)_2\dot{C}H + N_2. \qquad (1)$$

The ratio of rate constants for the disproportionation and combination reactions, k_d/k_c, alters slightly on increasing the temperature. Our value of $0.45 \pm 0.20 \exp(-676 \pm 120/\boldsymbol{R}T)$ compares with values obtained earlier of $0.4 \pm 0.1 \exp(-1090 \pm 105/\boldsymbol{R}T)$[8] and $0.36 \exp(+1130/\boldsymbol{R}T)$,[9] where T is in K. Our figures are found for less extensive data than those used by earlier workers; they serve as a check on our analytical procedures and as a means of obtaining a value of k_1.

The results for the photo-oxidation of *trans*-2,2′-azopropane correspond to the following mechanism:[2]

$$RN_2R \rightarrow 2R\cdot + N_2 \qquad (1)$$

$$R\cdot + O_2(+M) \rightarrow RO_2\cdot(+M) \qquad (2)$$

$$2RO_2\cdot \rightarrow (CH_3)_2CO + (CH_3)_2CHOH + O_2 \qquad (3a)$$

$$2RO_2\cdot \rightarrow 2RO\cdot + O_2 \qquad (3b)$$

$$2RO\cdot \rightarrow (CH_3)_2CO + (CH_3)_2CHOH \qquad (4)$$

$$RO\cdot + O_2 \rightarrow (CH_3)_2CO + HO_2\cdot \qquad (5)$$

$$RO_2\cdot + HO_2\cdot \rightarrow RO_2H + O_2 \qquad (6)$$

$$RO_2\cdot + RO\cdot \rightarrow (CH_3)_2CO + RO_2H \qquad (7)$$

$$RO\cdot + RO_2H \rightarrow (CH_3)_2CHOH + RO_2\cdot \qquad (8)$$

$$RO\cdot + HO_2\cdot \rightarrow (CH_3)_2CHOH + O_2 \qquad (9)$$

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2\cdot \qquad (10)$$

(where R = isopropyl).

A computer model of the system,[2, 10] designed to simulate the time-composition behaviour of a homogeneous gas-phase reaction, was used in which a numerical integration procedure was employed for the solution of 'still' differential equations. An optimisation procedure was used to find the ratio k_8/k_5.

This model allowed for the effect of initial oxygen pressure on the relative yields of products, and from it a value of k_{3b}/k_{3a} was obtained of 1.39 at 302 K.[2] As k_{obs} had been determined directly spectroscopically it was possible to obtain values of k_{3b} and k_{3a} independently.[2]

The most striking difference in product distribution between the results obtained at 302 K and in the temperature range reported in this paper, 333-373 K, is the formation of significant amounts of formaldehyde, acetaldehyde and methyl alcohol. The formation of C_1 and C_2 compounds requires that a carbon-carbon bond is broken, and the logical precursor is the isopropoxy radical.[11-15] On decomposition, acetaldehyde and a methyl radical are formed:

$$(CH_3)_2CHO\cdot\ (+M) \rightarrow CH_3CHO + \dot{C}H_3\ (+M). \qquad (11)$$

Methyl radicals react rapidly with oxygen to yield methylperoxy radicals:

$$\dot{C}H_3 + O_2\,(+M) \rightarrow CH_3O_2\cdot\ (+M). \qquad (12)$$

The introduction of methylperoxy radicals into the system complicates the reaction mechanism, for they may undergo all the reactions suggested for isopropylperoxy radicals and, further, the two forms of alkylperoxy radicals will undergo cross-reactions.

Thus one has to add reactions (13*a*) and (13*b*)-(21) to the scheme:

$$2MeO_2\cdot \rightarrow 2MeO\cdot + O_2 \qquad (13a)$$

$$2MeO_2\cdot \rightarrow HCHO + MeOH + O_2 \qquad (13b)$$

$$MeO_2\cdot + RO_2\cdot \rightarrow MeO\cdot + RO\cdot + O_2 \qquad (14a)$$

$$MeO_2\cdot + RO_2\cdot \rightarrow HCHO + ROH + O_2 \qquad (14b)$$

$$MeO_2\cdot + RO_2\cdot \rightarrow (CH_3)_2CO + MeOH + O_2 \qquad (14c)$$

$$RO_2\cdot + MeO\cdot \rightarrow HCHO + RO_2H \qquad (15)$$

$$MeO\cdot + O_2 \rightarrow HCHO + HO_2\cdot \qquad (16)$$

$$MeO_2\cdot + RO\cdot \rightarrow (CH_3)_2CO + MeO_2H \qquad (17)$$

$$MeO\cdot + RO_2H \rightarrow MeOH + RO_2\cdot \qquad (18)$$

$$RO\cdot + MeO_2H \rightarrow ROH + MeO_2\cdot \qquad (19)$$

$$MeO\cdot + MeO_2H \rightarrow MeOH + MeO_2\cdot \qquad (20)$$

$$MeO_2\cdot + HO_2\cdot \rightarrow MeO_2H + O_2. \qquad (21)$$

There is no shortage of rate constants quoted for some of these reactions, and one has to exercise considerable care in choice when using them in simulation procedures. It is important not only to be able to justify choice but also to test them in the mechanism. In this work we tested the mechanism by varying reaction pressures, total pressure and temperature; in addition there were, as will be described later, some further experiments.

Experience of simulations of the system at 302 K indicated that mutual and cross-reactions involving only alkoxy and hydroperoxy radicals are of no importance to the overall kinetics of the system. Initial simulations suggested that this is also so at 333 and 373 K. Indeed, the predicted concentrations of methoxy radicals are even lower than those of either isopropoxy or hydroperoxy radicals. Bimolecular reactions involving only isopropoxy, methoxy and hydroperoxy radicals were, therefore, omitted from the present mechanism and subsequent computer simulations. The predicted concentrations of methylperoxy radicals are also very low, typically 3×10^{-3} that of isopropylperoxy. The reaction between these radicals and others in very low concentration (alkoxy and hydroperoxy) are therefore also of no significance during simulations, and were also omitted from the mechanism. Nevertheless, in order to test these assumptions in simulations, rate constants for the reactions had to be chosen.

Values chosen for the rate constants for reactions (2), (4), (6), (7), (9) and (10) are discussed in an earlier paper.[2] Reactions (15), (17) and (21) are exothermic radical–radical reactions, and values of between 10^8 and 10^9 dm^3 mol^{-1} s^{-1} are reasonable. It was found that by setting k_7 to be 9.2×10^8 dm^3 mol^{-1} s^{-1} the absolute magnitudes of k_5 and k_8 are determined; these in turn give good agreement between the simulation and experimental results over all oxygen pressures studied. The precise values of k_{15}, k_{17} and k_{21} do not affect the overall simulation results and were set equal to k_7.

For results at temperatures above 302 K, the key reaction to add to the mechanism is reaction (11):

$$(CH_3)_2CHO\cdot(+M) \rightarrow CH_3CHO + \dot{C}H_3(+M). \tag{11}$$

There is a wide range of quoted values for the Arrhenius parameters for this reaction.[13, 15] There is even confusion on whether the A factor increases or decreases on increasing the pressure of the system. The most satisfactory values for k_{11}, from our simulations, were 1.39×10^2 s^{-1} at 333 K and 1.20×10^3 s^{-1} at 373 K, at the pressures used. These values are in broad agreement with those found later in separate experiments in which the effect of changing pressure on reaction (11) was studied in detail.[16]

Values used for k_{13a} and k_{13b} are those determined by Parkes.[17] These values were obtained at room temperature, but Parkes[18] suggests that the activation energy for these reactions is close to zero. Although Parkes suggests that there is a further terminating reaction in which methyl peroxide is formed, the compound was not detected under any of the conditions studied. As the experimental results also tallied with product studies of photo-oxidation of azoethane,[19] it seems that the contribution from this reaction is small, and it has been left out of the present simulations.

Parkes[17] suggests that the rate constant for the cross-reaction between methylperoxy and t-butylperoxy radicals is closer to the value of that for the self-reactions of methylperoxy radicals than of that for the self-reaction of t-butylperoxy radicals. Thus values used for k_{14a}, k_{14b} and k_{14c} have been arbitrarily weighted by a factor of 2 towards the corresponding self-reaction of methylperoxy radicals. In the absence of further evidence this procedure seems as satisfactory as any other. An error of much less than an order of magnitude in the values used for these rate constants is suggested. Such an error will not have a profound effect upon the simulations as the alternative self-reactions lead to the same products.

Absolute rate constants for reactions (5) and (8) at 302 K, and at higher temperature reactions (18), (19) and (20), are difficult to assign. However, as a first step, an optimisation procedure was used[2] to obtain relatively precise values of the ratio k_8/k_5 of 166 ± 5, 103 ± 5 and 62 ± 3 at 302, 333 and 373 K, respectively.

Reaction (5) is one of the most important in the reaction scheme, the value assigned to k_5 having a profound effect on the simulated product distributions. Its importance is particularly apparent when the effect of varying oxygen pressure is considered. We have used the Arrhenius parameters from the corresponding reaction between methoxy radical and oxygen [reaction (16)] which were obtained by Batt and Robinson;[20] these explain successfully the results not only on varying pressures of oxygen isothermally, but also on altering the temperature.

The only reported value for the corresponding reaction to (8) comes from a liquid-phase study[21] of the radical-induced decomposition of several tertiary hydroperoxides; a value for the rate constant for abstraction from hydroperoxides of the hydroperoxidic hydrogen by alkoxy radicals of *ca.* 4×10^6 dm^3 mol^{-1} s^{-1} at 303 K was suggested.

From the present results it can readily be seen that attack on isopropyl hydroperoxide must be taking place and, moreover, that this attack is reduced by increasing the oxygen pressure, strongly suggesting that the attacking species is the isopropoxy radical. The absolute value of k_8 must be high enough to compete favourably with termination reactions (3*a*) and (7). Reaction (7) is the major alternative fate for isopropoxy radicals to reactions (5) and (8), and it is therefore the value assigned to reaction (7) that decides what absolute values of k_5 and k_8 will produce a good fit of simulated to experimental results. This, coupled with the ratio k_8/k_5 obtained, leads to values of k_8 (and by analogy k_{18}, k_{19} and k_{20}) of 5.0×10^7, 6.2×10^7 and 7.7×10^7 dm^3 mol^{-1} s^{-1} at 302, 333 and 373 K. Following our estimates, Kirsch and Parkes have suggested that the rate constant for the reaction between alkoxy radicals and t-butyl hydroperoxide is *ca.* 6×10^7 dm^3 mol^{-1} s^{-1} between 298 and 373 K.[2] This indicates that the reaction is faster than the reaction in which an alkoxy radical abstracts a tertiary hydrogen from 2-methylpropane.[23] This would agree with the proposition that the activation energy for the following general reaction

$$XH + \cdot Y \rightarrow X\text{---}H\text{---}Y \rightarrow X\cdot + YH$$

can be represented by the difference between the energies of the X—H bond and the summation of the energies of the X---H and Y---H bonds.[24] The total bond energy of the three-body transition state is thus dependent upon the X---H and Y---H distances and the values for the bond dissociation energies of X—H and Y—H.

If we now consider the following reactions

$$RH + RO\cdot \rightarrow R\cdot + ROH$$
$$RO_2H + RO\cdot \rightarrow RO_2\cdot + ROH$$

it can be seen that given similar transition states the magnitude of the activation energies will be determined essentially by the bond dissociation energies ($D^\ominus$) of ROO—H and R—H. The bond dissociation energy of ROO—H of *ca.* 366 ± 8 kJ mol^{-1} can be calculated based on the assumption that the bond dissociation energy of ROO—H is the same as the bond dissociation energy of HOO—H.[25] A value for the latter is obtained from a value for the standard heats of formation of the hydroperoxyl radical[26] and the standard heats of formation of hydrogen peroxide and hydrogen atoms. $D^\ominus$ (ROO—H) thus is much lower than the O—H bond dissociation energy in other molecules. For example, in the case of t-butyl alcohol[27] the value is 440 kJ mol^{-1}. It is also lower than that accepted for the C—H bond dissociation energy in 2-methylpropane,[24] 380.4 kJ mol^{-1}, which explains the results from independent experiments we carried out. 2-Methylpropane and t-butyl hydroperoxide were added to 2,2′-azopropane + oxygen mixtures and photolysed. The experiments show conclusively that the hydroperoxide is consumed much more rapidly than the hydrocarbon,[27] confirming that the activation energy for hydrogen abstraction by isopropoxy radicals from 2-methylpropane is significantly larger than that for abstraction of hydrogen, RO_2—H, by isopropoxy radicals from alkyl hydroperoxides. The correlation between the activation energy for hydrogen abstraction and the strength of the original H—X bond, when the attacking species are the same, seems very reasonable. The success of the calculations of Zavitsas[24, 28] adds considerable weight to such assumptions. To confirm that the alternative abstraction from a C—H bond in the hydroperoxide was unlikely, as suggested by considering the bond dissociation energies, the reaction was added to the simulations. The reaction yields hydroxy radicals, and these in turn react with reactant and products. Indeed it was not possible to simulate the reaction successfully.

The mechanism predicts the formation of small amounts of methyl hydroperoxide. However, even under the most favourable conditions for its formation, it would account for less than 1% of total products. The failure to detect this ubiquitous compound is not a serious indictment of the proposed mechanism.

At high oxygen concentrations, even at 373 K, the reaction is much simplified, as the formation of acetaldehyde, formaldehyde and methyl alcohol are supressed. Thus the rate of reaction (5) is much faster than that of reactions (4), (8), (9) and (11), and in the early stages of reaction[2]

$$\frac{d[(CH_3)_2CO]/dt}{d[(CH_3)_2CHOH]/dt} = (k_{3a}+2k_{3b})/k_{3a}.$$

Values for this ratio were found by determining the rates of formation of acetone and isopropyl alcohol at low extents of photolysis in the presence of excess oxygen (table 1). Using these results, the rate constants and Arrhenius parameters for reactions (3*a*) and (3*b*) are obtained (tables 1 and 2).

TABLE 1.—VALUES OF RATE CONSTANTS FOR THE REACTIONS

$2(CH_3)_2CHO_2\cdot \rightarrow$ products (obs)

$2(CH_3)_2CHO_2\cdot \rightarrow (CH_3)_2CO+(CH_3)_2CHOH+O_2$ (3*a*)

$2(CH_3)_2CHO_2\cdot \rightarrow 2(CH_3)_2CHO\cdot +O_2$ (3*b*)

T/K	$\frac{(k_{3a}+2k_{3b})}{k_{3a}}$	$\frac{k_{3b}}{k_{3a}}$	k_{obs}/ 10^5 dm^3 mol^{-1} s^{-1}	k_{3a}/ 10^5 dm^3 mol^{-1} s^{-1}	k_{3b}/ 10^5 dm^3 mol^{-1} s^{-1}
302[a]	3.78±0.10	1.39±0.04	8.1±0.5	2.15±0.10	2.99±0.20
333	4.65±0.10	1.83±0.04	16.2±1.2	3.5±0.7	6.4±1.3
373	6.60±0.20	2.80±0.08	35.6±2.0	5.4±1.1	15.0±3.0

[a] Obtained earlier.[1, 2]

The assumptions made in finding k_{3a} and k_{3b} appear to be justified. k_{obs} does not vary with oxygen pressure,[1] as predicted by the model, confirming that $(k_{3a}+2k_{3b}) = k_{obs}$ under the conditions of the experiments. At low pressures of oxygen, the rates of reactions (7) and (8) are significant. However, the rates of reactions (5) and (6) are reduced, the overall effect being that the observed rate constant of self-reactions, k_{obs}, remains constant as the oxygen pressure is varied although the rates of formation of individual products change.

No other data for the separate self-reactions of alkylperoxy radicals have been

TABLE 2.—VALUES OF ARRHENIUS PARAMETERS FOR THE REACTIONS

$2(CH_3)_2CHO_2\cdot \rightarrow \text{products}$ (obs)

$2(CH_3)_2CHO_2\cdot \rightarrow (CH_3)_2CO + (CH_3)_2CHOH + O_2$ (3*a*)

$2(CH_3)_2CHO_2\cdot \rightarrow 2(CH_3)_2CHO\cdot + O_2$ (3*b*)

reaction	A/dm^3 mol^{-1} s^{-1}	E/kJ mol^{-1}
obs[a]	$1.43 \pm 0.10 \times 10^9$	18.7 ± 0.5
3*a*	$2.44 \pm 0.31 \times 10^7$	12.0 ± 1.0
3*b*	$1.38 \pm 0.26 \times 10^9$	21.3 ± 1.5

[a] Obtained earlier.[1]

reported. The Arrhenius parameters for the overall self-reaction in the liquid phase of but-2-yl-, cyclopentyl-, cyclohexyl-, phenylethyl- and hexadecyl-peroxy radicals have been determined,[29] A_{obs} being in the range $(1\text{-}10) \times 10^9$ dm^3 mol^{-1} s^{-1} and E_{obs} in the range 7-13 kJ mol^{-1}. However, in a recent study of the self-reactions of isopropylperoxy radicals in the liquid phase, Furminsky *et al.* report values for rate constants between 175 and 229 K which are very close to the values predicted by the Arrhenius parameters given in this work.[30] Before the Arrhenius parameters of the separate reactions are discussed in detail, the values for other systems are needed. In a subsequent paper, the reactions of ethylperoxy radicals are described.

The lines drawn in fig. 2 and 3 are the results produced by computer simulation using the chemical model just described. The success of the simulation technique is illustrated in particular when the temperature is varied and when the initial oxygen pressure is altered.[2] To show how quantitative conclusions concerning rate constants can be made using the simulation technique it is useful to consider the effect of changing the values of k_5 and k_8. As discussed earlier, it is the ratio of these two rate constants which govern the change in the relative rates of formation of isopropyl alcohol and isopropyl hydroperoxide as the oxygen pressure is changed. If the rate constants are changed to say $k_5 = 6 \times 10^2$ dm^3 mol^{-1} s^{-1} and $k_8 = 1 \times 10^5$ dm^3 mol^{-1} s^{-1} at 302 K, values which give the required ratio of rate constants, the simulated results bear no resemblance to the experimental ones. However, if the value of k_7 is set at 1.84×10^6 dm^3 mol^{-1} s^{-1}, thus returning to the original value of the constant $(k_5 + k_7)/k_8$ and, in addition, if k_4, k_9 and k_{10} are each given a value of 1×10^6 dm^3 mol^{-1} s^{-1}, then the simulation once more fits the experimental results well. The implication of this result is clear; if the ratio of k_8/k_5 is kept at 166 and the experimentally determined rate constants, k_7, k_{3a} and k_{3b} are untouched, then it is always possible to produce simulated results which match the experimental results well. However, this is only true if we abandon the chemical intuition which makes certain values for unmeasured rate constants acceptable. The arguments put forward when discussing the individual rate constants show that the fit between simulated and experimental results is obtained in this case only by ignoring large sections of chemical knowledge. This is clearly unacceptable when perfectly good simulations can be obtained if this knowledge and its subsequent implications are taken into account. It is with some justification, therefore, that quantitative limits are put on the absolute values of k_5 and k_8 using the evidence of the present work.

If the chemical model is a valid one, the computer simulation should be capable of predicting the behaviour of radicals in the system. Fig. 4 illustrates that, indeed,

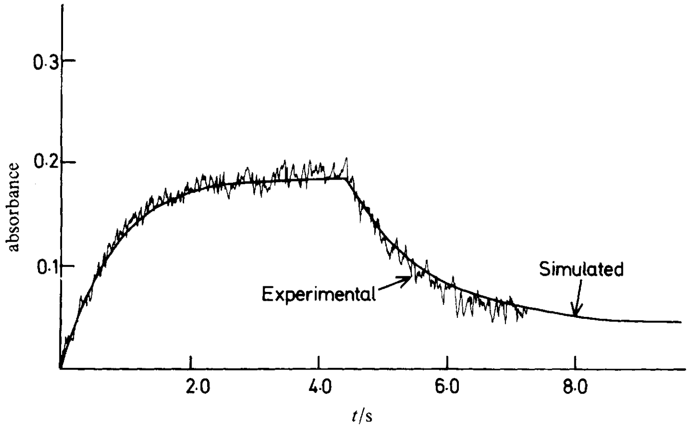

FIG. 4.—Photo-oxidation of 2,2′-azopropane at 302 K. Changes in absorption due to isopropylperoxy radicals.

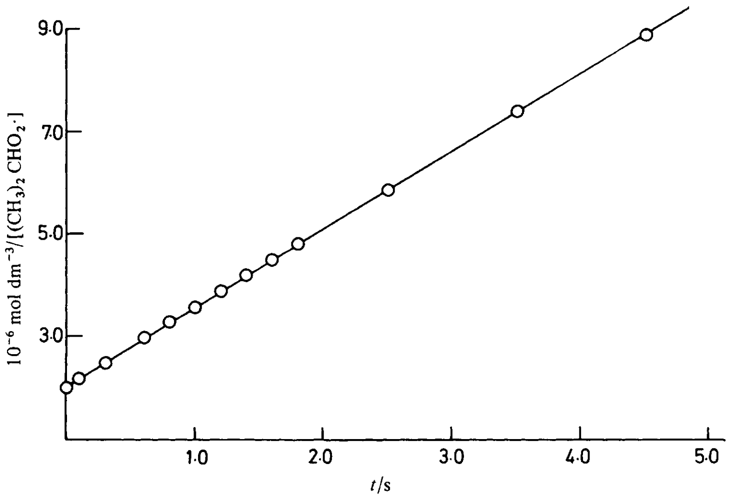

FIG. 5.—Photo-oxidation of 2,2′-azopropane at 302 K. Second-order plot for the simulated decay of isopropylperoxy radicals.

the chemical model described here is consistent with the kinetics of the reactions of isopropylperoxy radicals. The solid line in the figure is the calculated change in absorption due to isopropylperoxy radicals at 302 K. The calculation used the values of the rate constants described above. The value of k_1 in the computer simulation was changed to zero at a time corresponding to the experimental time at which the photolysis lamps were switched off. To convert the concentration profile obtained from the simulation to one of absorbance, the experimental path length and value for the absorption cross-section[27] of the isopropylperoxy radical were used (fig. 5), illustrating that if the chemical model proposed here is a true reflection of the experimental system then the isopropylperoxy radicals would display pure second-order kinetics. Simulations were also carried out which showed the effect of oxygen pressure on the rate at which isopropylperoxy radicals were formed and consumed. The computed concentration of isopropylperoxy radicals, at any photolysis time, was changed on altering the oxygen pressure from 10 to 500 Torr by $< 0.1\%$. The effect is therefore negligible and the model is consistent with the observation that k_{obs} does not vary experimentally with initial oxygen pressure.[1]

A.W. thanks the S.R.C. for a CASE studentship. We thank Dr C. Anastasi, Dr L. J. Kirsch and Dr D. A. Parkes (Shell Research Ltd) for invaluable discussions and Dr A. Prothero (also of Shell Research Ltd) for considerable assistance with the computations during the study.

[1] L. J. Kirsch, D. A. Parkes, D. J. Waddington and A. Woolley, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 2293.

[2] L. J. Kirsch, D. A. Parkes, D. J. Waddington and A. Woolley, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2678.

[3] J. C. Stowell, *J. Org. Chem.*, 1967, **32**, 2360.

[4] J. I. Abram, G. S. Milne, B. S. Soloman and C. Steel, *J. Am. Chem. Soc.*, 1969, **91**, 1220.

[5] G. O. Pritchard and F. M. Servedio, *Int. J. Chem. Kinet.*, 1975, **7**, 99.

[6] S. Chervinsky and I. Oref, *J. Phys. Chem.*, 1977, **81**, 1967.

[7] L. D. Fogel and C. Steel, *J. Am. Chem. Soc.*, 1976, **98**, 4859.

[8] R. Klein, M. D. Scheer and R. Kelley, *J. Phys. Chem.*, 1964, **68**, 598.

[9] P. Arrowsmith and L. J. Kirsch, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 3016.

[10] A. Prothero, personal communication.

[11] M. J. Yee Quee and J. C. J. Tynne, *J. Phys. Chem.*, 1968, **72**, 2824.

[12] J. H. Ferguson and L. Phillips, *J. Chem. Soc.*, 1965, 4416.

[13] A. C. Baldwin, J. R. Barker, D. M. Golden and D. G. Hendry, *J. Phys. Chem.*, 1977, **81**, 2483.

[14] D. L. Cox, R. A. Livermore and L. Phillips, *J. Chem. Soc.*, 1966, 245.

[15] L. Batt and R. T. Milne, *Int. J. Chem. Kinet.*, 1977, **9**, 141; L. Batt, *Int. J. Chem. Kinet.*, 1979, **11**, 977.

[16] N. Y. Al-Akeel and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, to be published.

[17] D. A. Parkes, *Int. J. Chem. Kinet.*, 1977, **9**, 451.

[18] D. A. Parkes, *15th Int. Symp. Combustion* (The Combustion Institute, Pittsburg, 1975), p. 795.

[19] C. Anastasi, D. J. Waddington and A. Woolley, *J. Chem. Soc., Faraday Trans. 1*, submitted for publication.

[20] L. Batt and G. N. Robinson, *Int. J. Chem. Kinet.*, 1979, **11**, 1045.

[21] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 1969, **47**, 3797.

[22] L. Kirsch and D. A. Parkes, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 293.

[23] M. A. Sway and D. J. Waddington, to be published.

[24] A. A. Zavitsas, *J. Am. Chem. Soc.*, 1972, **94**, 2779; A. A. Zavitsas and J. A. Pinto, *J. Am. Chem. Soc.*, 1972, **94**, 7390; A. A. Zavitsas and A. A. Melikian, *J. Am. Chem. Soc.*, 1975, **97**, 2757.

[25] S. W. Benson, *J. Am. Chem. Soc.*, 1965, **87**, 972.

[26] C. J. Howard, *J. Am. Chem. Soc.*, 1980, **102**, 6937.

[27] A. Woolley, *D. Phil. Thesis* (University of York, 1980).

[28] N. Y. Al-Akeel, K. Selby and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1036.

[29] J. E. Bennett, unpublished results.

[30] E. Furminsky, J. A. Howard and J. Selwyn, *Can. J. Chem.*, 1980, **58**, 677.

(PAPER 1/1831)