Reactions of Oxygenated Radicals in the Gas Phase. Part 11.[1] Reaction of Isopropylperoxyl Radicals with 2,3-Dimethylbut-2-ene

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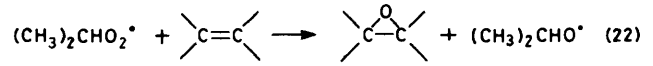
The reaction of isopropylperoxyl radicals with 2,3-dimethylbut-2-ene has been studied between 303 and 363 K, using the photo-oxidation of *trans*-2,2′-azopropane as a source of the radicals. The only product formed from the alkene is 2,3-dimethyl-2,3-epoxybutane. From a detailed study of the products, Arrhenius parameters for reaction (22) of log (A/dm^3 mol^{-1} s^{-1}) = 7.96 ± 0.50 and E/kJ mol^{-1} = 40.87 ± 1.78 have been obtained.



ONE of the most profitable methods of obtaining rate data for addition and abstraction reactions of radicals in the gas phase is by comparing the rate of formation of a molecular product with the rate of formation of another product from a reference reaction. For example, competition reactions have been exploited in considerable depth for the reactions of methyl [2] and hydroperoxyl [3] radicals.

In this paper, we introduce a method by which reactions of alkylperoxyl radicals may be studied, radicals which play a key role in atmospheric chemistry. The example given is the reaction between isopropylperoxyl radicals and an alkene, 2,3-dimethylbut-2-ene, which may be represented by the overall equation (22) (see later).

The photo-oxidation of *trans*-2,2′-azopropane has been studied in detail,[4-6] and rate data for the overall self-reactions [4] $2(CH_3)_2CHO_2^{\bullet} \longrightarrow$ products, and the individual non-terminating and terminating steps (3a and b) [5] have been determined. In the following experiments, the alkene was added to the system. By determining the rate of formation of the epoxide, it is possible to obtain rate data for the addition reaction between an alkylperoxyl radical and the unsaturated hydrocarbon.

EXPERIMENTAL

The apparatus and methods of analysis of reactants and products were described in an earlier paper.[4] As before, *trans*-2,2′-azopropane was prepared from isopropylamine and purified to >99% (by g.l.c.); no *cis*-2,2′-azopropane was detectable.[7]

RESULTS

(a) *Variation of Photolysis Time.*—Mixtures of *trans*-2,2′-azopropane, oxygen, and nitrogen (added as a diluent to complete a constant total pressure) were photolysed, the time varying between 30 and 240 min. The products are acetone, propan-2-ol, isopropyl hydroperoxide, and *cis*-2,2′-azopropane.

A second series of experiments was carried out under the same conditions, with the addition of 2,3-dimethylbut-2-ene. The concentrations of products were similar to those formed during the photo-oxidation of *trans*-2,2′-azopropane itself; the only other product was 2,3-dimethyl-2,3-epoxybutane, its rate of formation being linear (Figure 1). The sum of yields of propan-2-ol and isopropyl hydroperoxide equals that of acetone.

(b) *Variation of Initial Pressure of 2,3-Dimethylbut-2-ene.*—The initial concentration of 2,3-dimethylbut-2-ene was varied, while the concentrations of reactants were kept constant. The yield of the epoxide increases linearly with initial concentration of alkene while the yields of acetone, propan-2-ol, and isopropyl hydroperoxide are independent (Figure 2). Again the sum of yields of propan-2-ol and isopropyl hydroperoxide equals that of acetone.

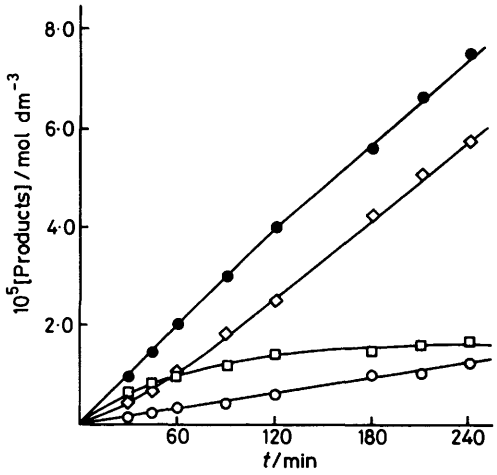


FIGURE 1 Photo-oxidation of *trans*-2,2′-azopropane and 2,3-dimethylbut-2-ene at 303 K. *trans*-2,2′-Azopropane, 5 Torr; oxygen, 50 Torr; 2,3-dimethylbut-2-ene, 20 Torr; nitrogen, 425 Torr. ●, Acetone; □, isopropyl hydroperoxide; ◇, propan-2-ol; ○, 2,3-dimethyl-2,3-epoxybutane. Experimental points are shown; the lines are from calculations following simulations

(c) *Variation of Initial Pressure of Oxygen in the Presence of 2,3-Dimethylbut-2-ene.*—The yield of acetone is unaltered on varying the initial concentration of oxygen, while the yield of isopropyl hydroperoxide increases and that of propan-2-ol decreases (Figure 3). However, the sum of yields of propan-2-ol and isopropyl hydroperoxide continues to equal that of acetone. The yield of the epoxide shows a little fall as the concentration of oxygen increases.

(d) *Variation of Total Pressure in the Presence of 2,3-Dimethylbut-2-ene.*—On decreasing the total pressure of the system (by reducing the initial concentration of the diluent, nitrogen), the yields of formation of acetone, propan-2-ol,

and isopropyl hydroperoxide increase, while that of the epoxide is constant (Figure 4).

(e) *Variation of Temperature.*—In these experiments, a high concentration of oxygen was used in order to suppress

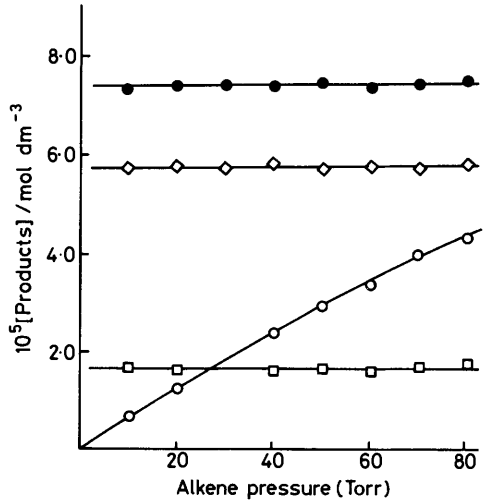


FIGURE 2 Photo-oxidation of *trans*-2,2′-azopropane and 2,3-dimethylbut-2-ene at 303 K: the effect of alkene pressure on the rate of reaction. *trans*-2,2′-Azopropane, 5 Torr; oxygen, 50 Torr; nitrogen added to give total pressure of 500 Torr. Time, 240 min. For key, see Figure 1. Experimental points are shown; the lines are from calculations following simulations

the formation of other products, such as acetaldehyde and formaldehyde, which may play an important role in the epoxidation of alkenes.

Acetaldehyde was detected at 343 K and above; its

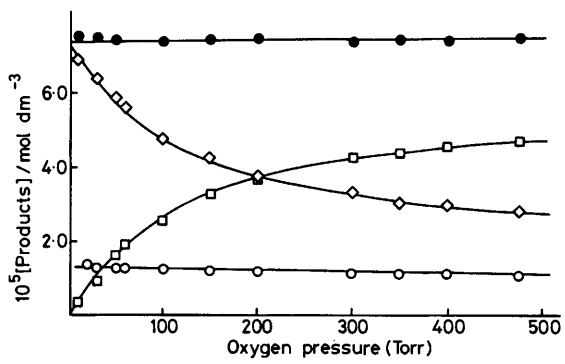


FIGURE 3 Photo-oxidation of *trans*-2,2′-azopropane and 2,3-dimethylbut-2-ene at 303 K: the effect of oxygen pressure on the rate of reaction. *trans*-2,2′-Azopropane, 5 Torr; 2,3-dimethylbut-2-ene, 20 Torr; nitrogen added to give total pressure of 500 Torr. .Time, 240 min. For key, see Figure 1. Experimental points are shown; the lines are from calculations following simulations

concentration increased with temperature. An example of the reaction profile is given in Figure 5. The yield of 2,3-dimethyl-2,3-epoxybutane also increased as the temperature was raised.

The yields of acetone, propan-2-ol, and isopropyl hydroperoxide decrease as the temperature is increased. However, the sum of yields of propan-2-ol and isopropyl hydroperoxide equals that of acetone and acetaldehyde.

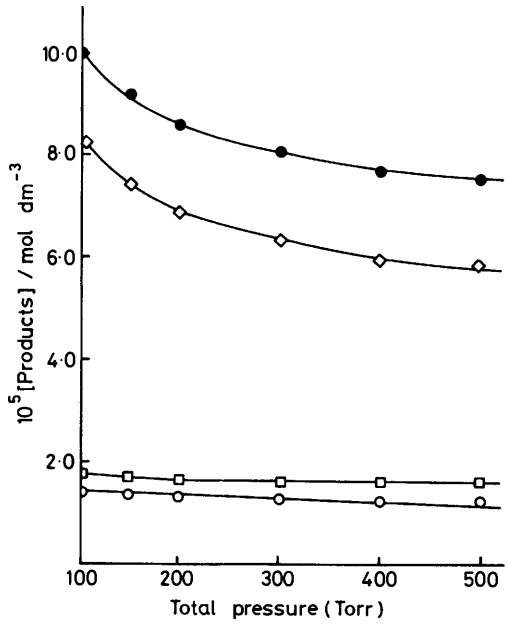


FIGURE 4 Photo-oxidation of *trans*-2,2′-azopropane and 2,3-dimethylbut-2-ene at 303 K: the effect of nitrogen on the rate of reaction. *trans*-2,2′-Azopropane, 5 Torr; oxygen, 50 Torr; 2,3-dimethylbut-2-ene, 20 Torr; nitrogen pressure varied. Time, 240 min. For key, see Figure 1. Experimental points are shown; the lines are from calculations following simulations

DISCUSSION

Origin of Products formed from the Photo-oxidation of 2,2′-Azopropane.—The products formed during the photo-oxidation of *trans*-2,2′-azopropane can be discussed in terms of an initiation reaction (1) which is

$$(CH_3)_2CHN_2CH(CH_3)_2 \xrightarrow{h\nu} 2(CH_3)_2\dot{C}H + N_2 \quad (1)$$

responsible for the formation of isopropyl radicals. This is not a simple process as can be seen by the curvature of

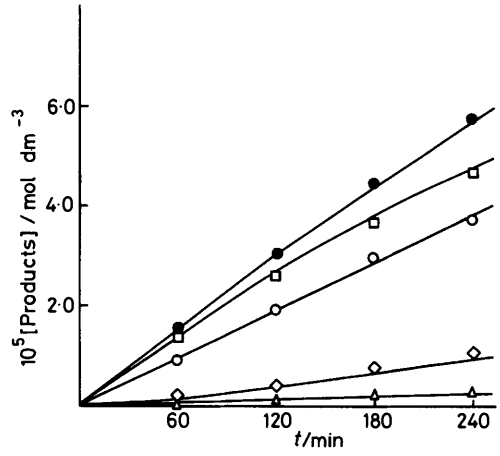


FIGURE 5 Photo-oxidation of *trans*-2,2′-azopropane and 2,3-dimethylbut-2-ene at 363 K. *trans*-2,2′-Azopropane, 5 Torr; oxygen, 450 Torr; 2,3-dimethylbut-2-ene, 20 Torr; nitrogen, 25 Torr. ●, Acetone; □, isopropyl hydroperoxide; ◇, propan-2-ol; ○, 2,3-dimethyl-2,3-epoxybutane; △, acetaldehyde. Experimental points are shown; the lines are from calculations following simulations

the Stern–Volmer plots [8,9] and the formation of the *cis*-isomer.

Nevertheless, the observed product yields, in the presence or absence of oxygen (except for *cis*-2,2′-azopropane), are consistent with the hypothesis that products are formed from isopropyl radicals and that neither the reactions of the excited intermediates nor the *cis*-azo-compound play a role in determining relative product yields.[4,6]

Thus we need only be concerned with the oxidation of the isopropyl radicals and the subsequent reactions of the alkoxyl and peroxyl radicals. The rate of formation of isopropyl radicals can be represented by the overall rate of reaction (1).

The reaction of alkyl radicals with molecular oxygen to produce alkylperoxyl radicals [reaction (2)] is predominant below 473 K.[10–12] The alkylperoxyl radicals undergo

$$(CH_3)_2\dot{C}H + O_2 \longrightarrow (CH_3)_2CHO_2\cdot \quad (2)$$

$$2(CH_3)_2CHO_2\cdot \longrightarrow (CH_3)_2CO + (CH_3)_2CHOH + O_2 \quad (3a)$$

$$2(CH_3)_2CHO_2\cdot \longrightarrow 2(CH_3)_2CHO\cdot + O_2 \quad (3b)$$

two self-reactions (3a and b). The alkoxyl radicals may also undergo a self-reaction (4). However, these reactions

$$2(CH_3)_2CHO\cdot \longrightarrow (CH_3)_2CO + (CH_3)_2CHOH \quad (4)$$

suggest that the rates of formation of acetone and propan-2-ol are the same and are independent of the oxygen concentration. Further reactions must be proposed which lead to the formation of isopropyl hydroperoxide at the expense of propan-2-ol but not of acetone [reaction (7)]. Reactions (5) and (6) account for the effect

$$(CH_3)_2CHO\cdot + O_2 \longrightarrow (CH_3)_2CO + HO_2\cdot \quad (5)$$

$$(CH_3)_2CHO_2\cdot + HO_2\cdot \longrightarrow (CH_3)_2CHO_2H + O_2 \quad (6)$$

$$(CH_3)_2CHO_2\cdot + (CH_3)_2CHO\cdot \longrightarrow (CH_3)_2CO + (CH_3)_2CHOOH \quad (7)$$

of oxygen on the relative rates of formation of isopropyl hydroperoxide and propan-2-ol. Reactions (8) and (9) account for the decrease in the rate of formation of isopropyl hydroperoxide and increase in that of propan-2-ol with time.

$$(CH_3)_2CHO_2H + (CH_3)_2CHO\cdot \longrightarrow (CH_3)_2CHO_2\cdot + (CH_3)_2CHOH \quad (8)$$

$$(CH_3)_2CHO\cdot + HO_2\cdot \longrightarrow (CH_3)_2CHOH + O_2 \quad (9)$$

It is unlikely that the self-reaction of the hydroperoxyl radicals [reaction (10)] will be significant under the conditions of the reaction.

$$2HO_2\cdot \longrightarrow H_2O_2 + O_2 \quad (10)$$

Above room temperature, acetaldehyde is observed, presumably formed by decomposition of isopropoxyl radicals [reaction (11)].[13] Methyl radicals react with oxygen to yield methylperoxyl radicals [reaction (12)] and

$$(CH_3)_2CHO\cdot\ (+M) \longrightarrow CH_3CHO + \dot{C}H_3\ (+M) \quad (11)$$

a series of reactions, (13)—(21), which are similar to those discussed above for isopropylperoxyl radicals, occurs.[6]

$$\dot{C}H_3 + O_2\ (+M) \longrightarrow CH_3O_2\cdot\ (+M) \quad (12)$$

$$2CH_3O_2\cdot \longrightarrow 2CH_3O\cdot + O_2 \quad (13a)$$

$$2CH_3O_2\cdot \longrightarrow CH_2O + CH_3OH + O_2 \quad (13b)$$

$$CH_3O_2\cdot + (CH_3)_2CHO_2\cdot \longrightarrow CH_3O\cdot + (CH_3)_2CHO\cdot + O_2 \quad (14a)$$

$$CH_3O_2\cdot + (CH_3)_2CHO_2\cdot \longrightarrow CH_2O + (CH_3)_2CHOH + O_2 \quad (14b)$$

$$CH_3O_2\cdot + (CH_3)_2CHO_2\cdot \longrightarrow CH_3OH + (CH_3)_2CO + O_2 \quad (14c)$$

$$CH_3O\cdot + (CH_3)_2CHO_2\cdot \longrightarrow CH_2O + (CH_3)_2CHO_2H \quad (15)$$

$$CH_3O\cdot + O_2 \longrightarrow CH_2O + HO_2\cdot \quad (16)$$

$$CH_3O_2\cdot + (CH_3)_2CHO\cdot \longrightarrow CH_3O_2H + (CH_3)_2CO \quad (17)$$

$$CH_3O\cdot + (CH_3)_2CHO_2H \longrightarrow CH_3OH + (CH_3)_2CHO_2\cdot \quad (18)$$

$$CH_3O_2H + (CH_3)_2CHO\cdot \longrightarrow CH_3O_2\cdot + (CH_3)_2CHOH \quad (19)$$

$$CH_3O_2H + CH_3O\cdot \longrightarrow CH_3O_2\cdot + CH_3OH \quad (20)$$

$$HO_2\cdot + CH_3O_2\cdot \longrightarrow CH_3O_2H + O_2 \quad (21)$$

A computer model of the system,[4,6,14] 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 ' stiff ' differential equations.

The aim of the simulations is to show that the proposed reaction scheme is quantitatively consistent with the experimental behaviour and to draw conclusions concerning the magnitude of the rate constants for the elementary reactions. In order to achieve this the following technique is employed. An initial set of values for

TABLE 1

Rate constants used in the simulation of the photo-oxidation of *trans*-2,2′-azopropane

Reaction	Rate constant/dm³ mol⁻¹ s⁻¹ 303 K	323 K	343 K	363 K
(2)	3.1×10^8	3.1×10^8	3.1×10^8	3.1×10^8
(3a)	2.2×10^5	3.2×10^5	3.7×10^5	4.6×10^5
(3b)	3.0×10^5	5.6×10^5	7.9×10^5	1.2×10^6
(4)	1.0×10^{10}	1.0×10^{10}	1.0×10^{10}	1.0×10^{10}
(5)	3.0×10^5	4.9×10^5	7.4×10^5	1.1×10^6
(6)	9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8
(7)	9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8
(8)	5.0×10^7	5.8×10^7	6.6×10^7	7.4×10^7
(9)	9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8
(10)	1.0×10^{10}	1.0×10^{10}	1.0×10^{10}	1.0×10^{10}
(11)			1.6×10^2 [a]	8.5×10^2 [a]
(12)			3.1×10^8	3.1×10^8
(13a)			9.6×10^8	9.6×10^8
(13b)			1.8×10^8	1.8×10^8
(14a)			1.7×10^7	1.9×10^7
(14b)			1.7×10^7	1.9×10^7
(14c)			1.7×10^7	1.9×10^7
(15)			9.2×10^8	9.2×10^8
(16)			7.4×10^5	1.1×10^6
(17)			9.2×10^8	9.2×10^8
(18)			6.6×10^7	7.4×10^7
(19)			6.6×10^7	7.4×10^7
(20)			6.6×10^7	7.4×10^7
(21)			9.2×10^8	9.2×10^8

[a] Units are s⁻¹.

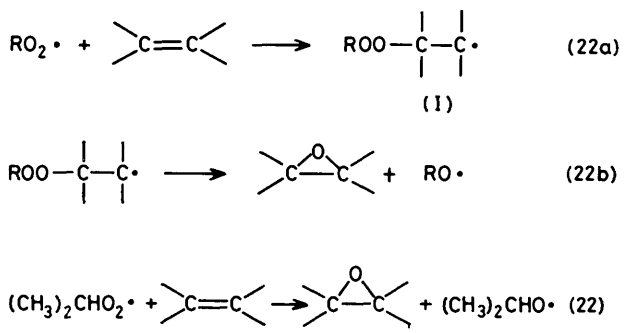
the rate constants was chosen. Some of these values were obtained from the present work, others used because of evidence from recent work carried out in this laboratory.[4,6] The rate constants were chosen from data concerned with the actual reactions, or if not available, reactions of close similarity. All the rate constants for reactions (1)—(21) used in the present work were discussed in an earlier paper [6] (Table 1).

TABLE 2

Computed ratios of oxygenated radicals during the photo-oxidation of *trans*-2,2′-azopropane and 2,3-dimethylbut-2-ene

T/K	$\frac{[(CH_3)_2CHO_2\cdot]}{[CH_3O_2\cdot]}$	$\frac{[(CH_3)_2CHO_2\cdot]}{[HO_2\cdot]}$	$\frac{[(CH_3)_2CHO_2\cdot]}{[(CH_3)_2CHO\cdot]}$	$\frac{[(CH_3)_2CHO_2\cdot]}{[CH_3O\cdot]}$
303		1.75×10^3	1.61×10^5	
323		1.00×10^3	1.86×10^5	
343	2.95×10^3	0.51×10^3	2.08×10^5	0.77×10^8
363	0.27×10^3	0.15×10^3	1.55×10^5	1.33×10^7
373	0.38×10^3	0.36×10^3	1.96×10^5	0.91×10^7
393	0.20×10^3	0.19×10^3	2.60×10^5	0.53×10^7
408	0.10×10^3	0.13×10^3	2.72×10^5	0.33×10^7

The only product formed in the present system from the alkene is the corresponding epoxide, 2,3-dimethyl-2,3-epoxybutane. Epoxides are formed in the autooxidation of alkenes [15-17] and it is generally assumed that these compounds are produced by attack of alkylperoxyl radicals on the double bond [reaction (22a)], similar to that observed for acylperoxyl radicals, followed by ring closure [reaction (22b)].[18] The overall reaction is given by (22).



(22a) (22b) (22)

The adduct radical (I) may, in theory, undergo either reaction (22b) or decompose to yield the alkene again. From the evidence gained in earlier work, it appears that ring closure is easily the most favourable route for the adduct. Hence reaction (22) was added to the reaction mechanism.

When the initial pressure of oxygen is increased, the rate of formation of the epoxide shows little change (Figure 3). This observation is important since hydroperoxyl radicals, and at higher temperature, methylperoxyl radicals, are also formed. However, the computer simulation predicts that the alkylperoxyl radicals are always in considerable excess (Table 2).

The conditions used in the present work ensured that acetaldehyde was a minor product. The presence of acetaldehyde in this system in a high concentration is not welcomed because it may react further to yield peracetyl radicals which undergo rapid reaction with alkenes. However, there was no evidence of any oxidation products of acetaldehyde under the conditions used and the yield of epoxide is constant as long as excess of oxygen is present.

Rate constants used for reaction (22) in the simulations were adjusted to give the best fit between experimental and simulated results. The rate constants are listed in Table 3. The Arrhenius parameters obtained for the reaction are $\log(A_{22}/\mathrm{dm^3\ mol^{-1}\ s^{-1}})$ 7.96 ± 0.50 and $E_{22}/\mathrm{kJ\ mol^{-1}}$ 40.87 ± 1.78. The A factor supports the generalised value of $\log(A/\mathrm{dm^3\ mol^{-1}\ s^{-1}})$ of 8.5 ± 0.5 suggested by Benson for the addition of alkylperoxyl radicals to alkenes.[19] Further, $\log(A/\mathrm{dm^3\ mol^{-1}\ s^{-1}})$ for the corresponding reaction with methylperoxyl radicals, using a completely different technique,[20] is 8.14 ± 0.32.

There are no data available for the addition reaction of acylperoxyl radicals and 2,3-dimethylbut-2-ene. However, the energy of activation for the reaction between acetylperoxyl radicals and 2-methylbut-2-ene is 16.34 ± 0.91 kJ mol^{-1} and it is very likely [20,21] that the reaction with the more substituted alkene will be even faster.

TABLE 3

Rate constants for the reaction between isopropylperoxyl radicals and 2,3-dimethylbut-2-ene [reaction (22)]

T/K	k_{22}/dm^3 mol^{-1} s^{-1}
303	9.0 ± 0.5
323	19.5 ± 2.6
343	54.0 ± 1.5
363	126.0 ± 5.9

This suggests that acetylperoxyl radicals react *ca.* 10^5 times faster than isopropylperoxyl radicals with an alkene. The reaction of isopropylperoxyl radicals with other alkenes is being studied to investigate further the difference in reactivities between acylperoxyl and alkylperoxyl radicals.

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