Reactions of Oxygenated Radicals in the Gas Phase. Part 12.[1] The Reactions of Isopropylperoxyl Radicals and Alkenes

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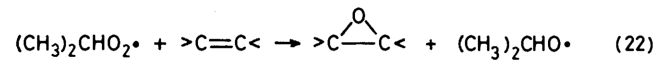
The co-oxidation of *trans*-2,2'-azopropane and some aliphatic alkenes has been studied between 303 and 408 K. From the yields of molecular products, rate data have been obtained for the reaction of isopropylperoxyl radicals and the following alkenes, 2-methylbut-2-ene, 2-methylbut-1-ene, 2-methylpropene, propene, and 3-fluoropropene [reaction (22)]. It is shown that the isopropylperoxyl radical is less reactive than methylperoxyl but still shows distinct electrophilic character in these reactions.



$$(CH_3)_2CHO_2\cdot + {>}C{=}C{<} \longrightarrow {>}C\overset{O}{—}C{<} + (CH_3)_2CHO\cdot \quad (22)$$

In this series, rate data have been reported for the reactions of alkoxyl and alkylperoxyl radicals in the gas phase between 300 and 450 K. Several papers have been concerned with self-reactions of the radicals and others with addition and abstraction processes with hydrocarbons, aldehydes, and ketones. All these data are helpful towards our understanding of the problems associated with the mechanism of gas-phase oxidation processes, including those in the atmosphere.

In Part 11,[1] it was shown that it is possible to determine the rates of addition reactions between isopropylperoxyl radicals and alkenes, using a system in which a mixture of *trans*-2,2'-azopropane and an alkene is photo-oxidised. In this study, several alkenes were chosen in order to investigate in detail the way in which changes in the structure of the alkene affect its reactivity towards the isopropylperoxyl radical. It then becomes possible to compare the reactivity of this radical with that of other oxygenated radicals which react, by addition, with alkenes, *e.g.* methylperoxyl,[2] hydroperoxyl,[3,4] and peracetyl.[5-7] For, in a complex oxidation system such as that in the atmosphere, there are many different radicals competing for the reactive fuel molecules.

Experimental

The apparatus and methods of analysis of reactants and products were described in an earlier paper.[8] *trans*-2,2'-Azopropane was prepared from isopropylamine [9] and purified to 99% by preparative g.c. No *cis*-2,2'-azopropane was detectable.

Results

The products of the photo-oxidation of *trans*-2,2'-azopropane between 303 and 408 K are acetone, propan-2-ol, isopropyl hydroperoxide, and *cis*-2,2'-azopropane.[1,8,10] In all experiments, the yields of acetone equalled those of the hydroperoxide and alcohol. At 343 K and above, acetaldehyde becomes detectable.

In order to study the effect of varying the structure of the alkenes on their reactivity towards isopropylperoxyl radicals, 2-methylbut-2-ene, 2-methylbut-1-ene, 2-methylpropene, propene, and 3-fluoropropene were chosen. On their addition, the only product observed to be formed from the hydrocarbons was the corresponding epoxide (Table 1).

On varying the concentration of the alkene, the yields of acetone, propan-2-ol, isopropyl hydroperoxide, and acetaldehyde were unaffected. However there is a linear dependence between the yield of epoxide and the alkene. Figures 1 and 2 give examples of the results obtained.

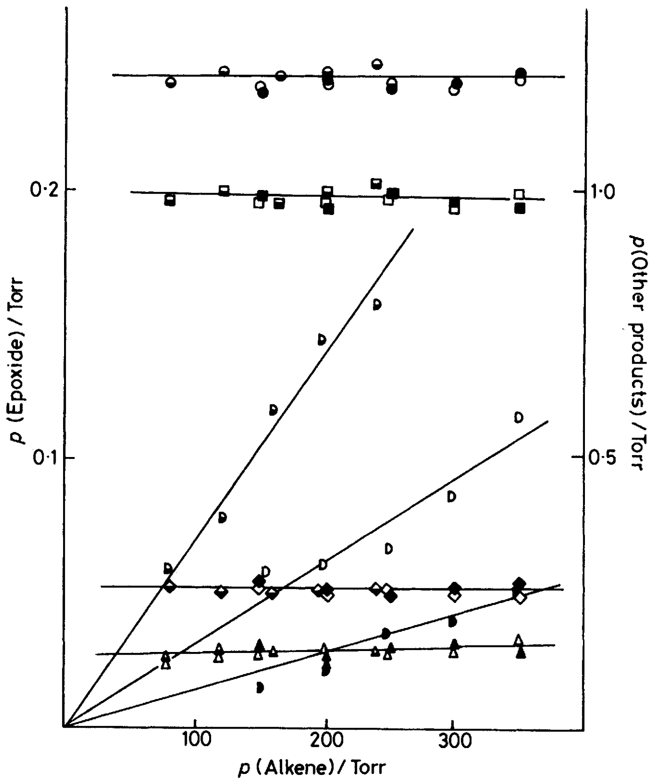


Figure 1. Photo-oxidation of *trans*-2,2'-azopropane and some alkenes. With propene: ○, acetone; □, isopropyl hydroperoxide; ◇, propan-2-ol; △, acetaldehyde; D, 1,2-epoxypropane. With 3-fluoropropene: ●, acetone; ■, isopropyl hydroperoxide; ♦, propan-2-ol; ▲, acetaldehyde; ▶, 3-fluoro-1,2-epoxypropane. With 2-methylpropene: ◒, acetone; ⬓, isopropyl hydroperoxide; ⬙, propan-2-ol; , ◭ acetaldehyde; ◗, 2-methyl-1,2-epoxypropane

The initial pressure of oxygen has a significant effect on the concentration of all oxygen products. As the oxygen pressure is increased, the yields of propan-2-ol, acetaldehyde, and epoxide decrease; those of acetone and isopropyl hydroperoxide increase. An example of the results is given in Figure 3. The yields of all the products become sensibly independent of oxygen pressure when oxygen is in considerable excess.

Table 1. Photo-oxidation of *trans*-2,2′-azopropane and some alkenes

trans-2,2′-Azopropane (5 Torr)

Alkene	Reactant (Torr)		Total pressure (Torr)	T/K	t/min	Products (Torr)				
	Alkene	Oxygen				Acetone	Isopropyl hydroperoxide	Propan-2-ol	Acetaldehyde	Epoxide
3-Fluoropropane	300	400	750	393	120	0.64	0.55	0.13	0.08	0.018
					150	0.81	0.65	0.15	0.09	0.025
					180	0.91	0.79	0.20	0.10	0.020
					210	1.10	0.87	0.22	0.13	0.029
					240	1.28	0.94	0.28	0.14	0.031
Propene	400	300	750	373	120	0.66	0.53	0.16	0.03	0.025
					180	0.95	0.76	0.22	0.06	0.036
					210	1.13	0.83	0.29	0.07	0.046
					240	1.24	0.91	0.34	0.09	0.061
	250	400	750	393	120	0.68	0.57	0.13	0.09	0.039
					150	0.85	0.71	0.18	0.09	0.054
					180	0.91	0.81	0.21	0.12	0.066
					210	1.17	0.96	0.23	0.14	0.074
					240	1.26	1.01	0.29	0.17	0.094
	200	500	750	408	120	0.62	0.57	0.08	0.09	0.062
					150	0.79	0.70	0.10	0.11	0.080
					180	0.92	0.85	0.12	0.13	0.084
					210	1.09	0.93	0.14	0.15	0.087
					240	1.17	1.07	0.16	0.13	0.120
2-Methylpropene	200	450	700	373	120	0.67	0.55	0.13	0.03	0.030
					180	0.98	0.80	0.21	0.04	0.051
					210	1.15	0.87	0.24	0.04	0.053
					240	1.29	0.95	0.31	0.04	0.055
	200	450	750	393	60	0.35	0.29	0.05	0.03	0.030
					90	0.48	0.45	0.09	0.05	0.062
					120	0.66	0.55	0.11	0.07	0.072
					180	0.87	0.83	0.20	0.10	0.12
					240	1.18	0.96	0.24	0.15	0.13
	50	450	750	408	120	0.61	0.57	0.11	0.08	0.027
					150	0.76	0.69	0.12	0.11	0.040
					180	0.89	0.82	0.16	0.14	0.050
					210	1.08	0.89	0.18	0.16	0.062
					240	1.17	0.98	0.23	0.18	0.064
2-Methylbut-1-ene	80	300	500	363	60	0.33	0.28	0.09	0.02	0.031
					90	0.52	0.40	0.11	0.03	0.042
					120	0.61	0.55	0.14	0.03	0.058
					180	0.96	0.70	0.26	0.04	0.080
					240	1.24	0.89	0.38	0.08	0.12
	80	400	500	393	90	0.47	0.45	0.08	0.08	0.10
					120	0.65	0.55	0.11	0.09	0.15
					150	0.78	0.69	0.15	0.11	0.17
					180	0.93	0.78	0.17	0.12	0.21
					210	1.09	· · ·	0.22	0.13	0.26
					240	1.18	0.98	0.26	0.12	0.28
	80	400	500	408	120	0.64	0.54	0.10	0.12	0.22
					150	0.73	0.70	0.12	0.14	0.26
					180	0.89	0.80	0.17	0.18	0.32
					210	1.05	0.93	0.20	0.20	0.38
					240	1.14	0.96	0.22	0.24	0.41
2-Methylbut-2-ene	40	400	500	303	60	0.39	0.27	0.12	—	0.010
					120	0.76	0.49	0.26	—	0.012
					180	1.09	0.67	0.43	—	0.021
					240	1.43	0.82	0.60	—	0.024
	40	400	500	323	60	0.36	0.30	0.09	—	0.014
					90	0.56	0.41	0.16	—	0.025
					120	0.73	0.52	0.20	—	0.028
					180	1.03	0.70	0.34	—	0.047
					240	1.37	0.84	0.50	—	0.062
	40	400	500	363	60	0.34	0.32	0.08	0.01	0.062
					120	0.68	0.54	0.13	0.03	0.11
					150	0.84	0.63	0.17	0.04	0.15
					180	1.00	0.81	0.23	0.05	0.17
					240	1.27	0.94	0.33	0.08	0.25

— None detected. · · · Result not recorded.

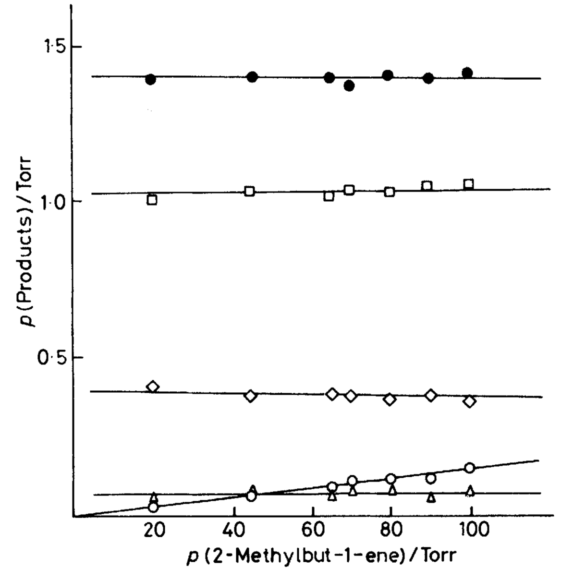


Figure 2. Photo-oxidation of *trans*-2,2′-azopropane and 2-methylbut-1-ene at 363 K. Analyses at 240 min. *trans*-2,2′-Azopropane, 5 Torr; oxygen, 300 Torr; total pressure (with nitrogen), 500 Torr. ●, Acetone; □, isopropyl hydroperoxide; ◇, propan-2-ol; ○, 2-methyl-1,2-epoxybutane; △, acetaldehyde

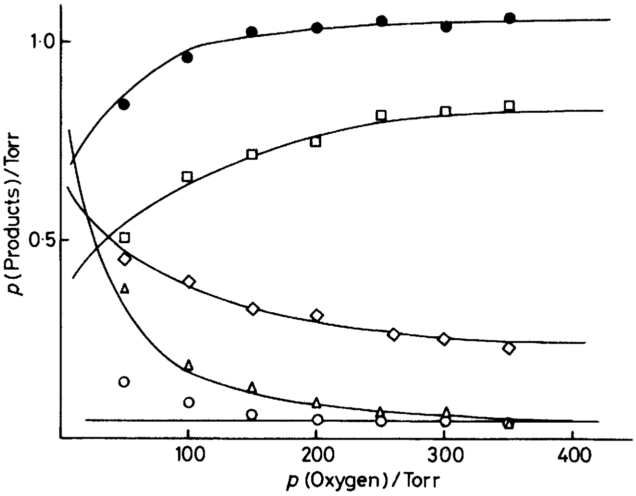


Figure 3. Photo-oxidation of *trans*-2,2′-azopropane and propene at 373 K. Analyses at 180 min. *trans*-2,2′-Azopropane, 5 Torr; propene, 400 Torr; total pressure (with nitrogen), 760 Torr. ●, Acetone; □, isopropyl hydroperoxide; ◇, propan-2-ol; ○, 1,2-epoxypropane; △, acetaldehyde

Discussion

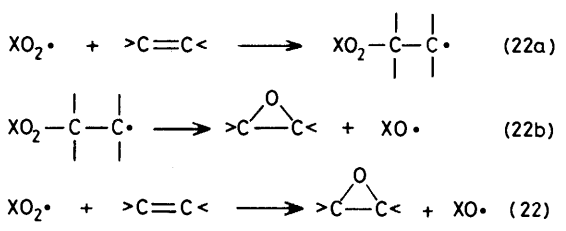
The reaction mechanism for the photo-oxidation of *trans*-2,2′-azopropane has been discussed in considerable detail.[1,8,10] Below 343 K, the reaction products can be explained in terms of reactions (1)—(10).

Above *ca.* 340 K, the decomposition of isopropoxyl radicals must be considered,[11] and the resulting methyl radicals yield methylperoxyl and methoxyl radicals. Additional reactions (11)—(21) must therefore be included in the mechanism.[1,10]

$$RN_2R \longrightarrow 2R\cdot + N_2 \tag{1}$$
$$R\cdot + O_2(+M) \longrightarrow RO_2\cdot(+M) \tag{2}$$
$$2RO_2\cdot \longrightarrow (CH_3)_2CO + (CH_3)_2CHOH + O_2 \tag{3a}$$
$$2RO_2\cdot \longrightarrow 2RO\cdot + O_2 \tag{3b}$$
$$2RO\cdot \longrightarrow (CH_3)_2CO + (CH_3)_2CHOH \tag{4}$$
$$RO\cdot + O_2 \longrightarrow (CH_3)_2CO + HO_2\cdot \tag{5}$$
$$RO_2\cdot + HO_2\cdot \longrightarrow RO_2H + O_2 \tag{6}$$
$$RO_2\cdot + RO\cdot \longrightarrow (CH_3)_2CO + RO_2H \tag{7}$$
$$RO\cdot + RO_2H \longrightarrow (CH_3)_2CHOH + RO_2\cdot \tag{8}$$
$$RO\cdot + HO_2\cdot \longrightarrow (CH_3)_2CHOH + O_2 \tag{9}$$
$$HO_2\cdot + HO_2\cdot \longrightarrow H_2O_2 + O_2 \tag{10}$$

$$RO\cdot(+M) \longrightarrow CH_3CHO + Me\cdot(+M) \tag{11}$$
$$Me\cdot + O_2(+M) \longrightarrow MeO_2\cdot(+M) \tag{12}$$
$$2MeO_2\cdot \longrightarrow 2MeO\cdot + O_2 \tag{13a}$$
$$2MeO_2\cdot \longrightarrow HCHO + MeOH + O_2 \tag{13b}$$
$$MeO_2\cdot + RO_2\cdot \longrightarrow MeO\cdot + RO\cdot + O_2 \tag{14a}$$
$$MeO_2\cdot + RO_2\cdot \longrightarrow HCHO + ROH + O_2 \tag{14b}$$
$$MeO_2\cdot + RO_2\cdot \longrightarrow (CH_3)_2CO + MeOH + O_2 \tag{14c}$$
$$RO_2\cdot + MeO\cdot \longrightarrow HCHO + RO_2H \tag{15}$$
$$MeO\cdot + O_2 \longrightarrow HCHO + HO_2\cdot \tag{16}$$
$$MeO_2\cdot + RO\cdot \longrightarrow (CH_3)_2CO + MeO_2H \tag{17}$$
$$MeO\cdot + RO_2H \longrightarrow MeOH + RO_2\cdot \tag{18}$$
$$RO\cdot + MeO_2H \longrightarrow ROH + MeO_2\cdot \tag{19}$$
$$MeO\cdot + MeO_2H \longrightarrow MeOH + MeO_2\cdot \tag{20}$$
$$MeO_2\cdot + HO_2\cdot \longrightarrow MeO_2H + O_2 \tag{21}$$

$R = Pr^i$



A computer model designed to simulate the time-composition behaviour of this complex system was used, in which a numerical integration procedure was employed for the solution of the resulting ‘ stiff ’ differential equations.[1,8,10,12] The values for the rate constants used in the simulation were obtained from the present series of experiments and others were estimated using known reliable data from analogous reactions (Table 2). These values have been discussed in detail.[8,10,13]

The only extra product formed on addition of the hydrocarbon is the epoxide, suggesting that, as in the autoxidation of alkenes in the gas phase,[14,15] it is the $XO_2\cdot$ (where X is an alkyl, alkenyl, or acyl group) radical which is the principal reactant.[5,16,17] It has been shown, for peracetyl radicals, that the radicals form an adduct with the alkene which subsequently undergoes ring closure[5] [reactions (22a and b)] Hence the reactions leading to epoxidation can be described in terms of a simple equation (22).[1,2,5]

The absence of unsaturated carbonyl compounds or alcohols indicates that abstraction reactions from the alkenes are of minor importance under these conditions. Indeed some are found as very minor products in the autoxidation of but-2-ene[17] and 2-methylbut-2-ene[18] at 550 K and above, and

Table 2. Rate constants used in the simulation of the photo-oxidation of *trans*-2,2′-azopropane. Rate constants in $dm^3\ mol^{-1}\ s^{-1}$ *

Reaction	303 K	323 K	363 K	373 K	393 K	408 K
(2)	3.1×10^8	3.1×10^8	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	4.6×10^5	5.4×10^5	6.3×10^5	7.1×10^5
(3b)	3.0×10^5	5.6×10^5	1.2×10^6	1.5×10^6	2.1×10^6	2.6×10^6
(4)	1.0×10^{10}	1.0×10^{10}	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	1.1×10^6	1.2×10^6	1.7×10^6	2.1×10^6
(6)	9.2×10^8	9.2×10^8	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	9.2×10^8	9.2×10^8
(8)	5.0×10^7	5.8×10^7	7.4×10^7	7.8×10^7	8.6×10^7	9.1×10^7
(9)	9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8
(10)	2.2×10^9	2.2×10^9	2.2×10^9	2.2×10^9	2.2×10^9	2.2×10^9
(11)			8.5×10^2	1.2×10^3	4.0×10^3	7.5×10^3
(12)			3.1×10^8	3.1×10^8	3.1×10^8	3.1×10^8
(13a)			9.6×10^7	9.6×10^7	9.6×10^7	9.6×10^7
(13b)			1.8×10^8	1.8×10^8	1.8×10^8	1.8×10^8
(14a)			2.2×10^7	2.4×10^7	2.9×10^7	3.4×10^7
(14b)			1.9×10^7	2.0×10^7	2.2×10^7	2.4×10^7
(14c)			1.9×10^7	2.0×10^7	2.2×10^7	2.4×10^7
(15)			9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8
(16)			1.1×10^6	1.2×10^6	1.7×10^6	2.1×10^6
(17)			9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8
(18)			7.4×10^7	7.8×10^7	8.6×10^7	9.1×10^7
(19)			7.4×10^7	7.8×10^7	8.6×10^7	9.1×10^7
(20)			7.4×10^7	7.8×10^7	8.6×10^7	9.1×10^7
(21)			9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8

* Units for reaction (11) are s^{-1}.

Table 3. Rate constants for the addition of isopropylperoxyl radicals to alkenes [reaction (22)]

Alkene	T/K	(k_{22}/$dm^3\ mol^{-1}\ s^{-1}$)
3-Fluoropropene	393	0.24 ± 0.03
Propene	373	0.28 ± 0.04
	393	0.85 ± 0.10
	408	1.82 ± 0.15
2-Methylpropene	373	0.64 ± 0.03
	393	1.90 ± 0.12
	408	3.63 ± 0.11
2-Methylbut-1-ene	363	2.45 ± 0.16
	393	10.00 ± 0.30
	408	18.20 ± 0.92
2-Methylbut-2-ene	303	0.50 ± 0.03
	323	1.82 ± 0.07
	363	12.10 ± 0.60

larger amounts but still ranking as minor products, are formed during the autoxidation of 2,3-dimethylbut-2-ene.[18] However, addition reactions of oxygenated radicals still play the predominant role in the gas-phase autoxidation of alkenes. The enthalpy changes for addition of peroxyl radicals to an alkene are considerably more exothermic than abstraction reactions.[18]

The relative importance of addition between peroxyl radicals and alkenes is seen in the reaction between peracetyl [5,6,19] or methylperoxyl [2] radicals and alkenes. As in the present work, no product from the alkene, other than the epoxide, is detectable. These results contrast with those reported for the reaction of peroxyl radicals in solution where abstraction reactions are considered to be important.[20]

The presence of excess of oxygen in the system ensures that acetaldehyde formed from reaction (11) is not attacked by alkoxyl radicals and lead to the production of peracetyl radicals,[21] which in turn undergo rapid reaction with alkenes.[5—7] It can be seen that the yield of epoxide is constant as long as a large excess of oxygen is present (Figure 3).

Reaction (22) was added to the reaction mechanism and the rate constants were obtained from the simulation program (Table 1 and Figures 1—3). They are given in Table 3 and Arrhenius parameters for reaction (22), where applicable, are given in Table 4.

The A factors are similar to those obtained for the corresponding reactions of methylperoxyl radicals.[2] In both systems, the A factor decreases in magnitude on increasing the number of alkyl groups adjacent to the carbon–carbon double bond, suggesting a steric effect. However, the behaviour of alkyl radicals on addition to alkenes does not follow this simple trend.[22]

It is changes in the activation energy that determine the marked differences in rate constants as the structure of the alkene is altered, the most marked increase being as the number of alkyl groups adjacent to the double bond is increased, showing that the isopropylperoxyl radicals are electrophilic. There is a striking relationship between the ionization energy of the alkene and the rate constant, k_{22}, at a particular temperature (Figure 4), similar to that noted with peracetyl [7] and methylperoxyl [2] radicals and alkenes. Moreover, the rate of reaction between isopropylperoxyl radicals and propene is significantly higher than that with 3-fluoropropene (Table 3). This cumulative evidence suggests that one can envisage a polar contribution, $>\dot{C}-\overset{+}{C}<\ {}^{-}{\cdot}O_2R$, to the transition state. In contrast, the relative reactivity shown by methoxyl radicals on addition to chlorinated and fluorinated alkenes shows that those radicals have little electrophilic property.[23] The rates of addition are much faster; presumably the lowering of the activation energy can be attributed to the difference in the strength of the new C–O bond being formed. The bond dissociation energies, $D^{\ominus}(RO_2 - R)$ [24] and $D^{\ominus}(RO - R)$ [25] are 297 ± 8 and 340 kJ mol^{-1}, respectively.

Isopropylperoxyl radicals react more slowly than methylperoxyl radicals, no doubt since the latter contain only one electron-releasing group while isopropylperoxyl has two. It is now possible to compare these results directly with those obtained for hydroperoxyl radicals. Their reactions have been studied by co-oxidising an alkene with 2,2,3,3-tetramethyl-

Table 4. Arrhenius parameters for addition of isopropylperoxyl, methylperoxyl, and peracetyl radicals to alkenes

	$(CH_3)_2CHO_2^{\cdot}$		$CH_3O_2^{\cdot}$ [a]		$CH_3CO_3^{\cdot}$ [b]	
Alkene	E_{22}/kJ mol^{-1}	log(A_{22} dm^3 mol^{-1} s^{-1})	E/kJ mol^{-1}	log(A_{22} dm^3 mol^{-1} s^{-1})	E/kJ mol^{-1}	log(A_{22} dm^3 mol^{-1} s^{-1})
3-Fluoropropene	71.8	8.92 *				
Propene	67.7 ± 2.5	8.92 ± 0.36			32.6	8.11 *
2-Methylpropene	62.7 ± 2.2	8.59 ± 0.19			25.0 ± 1.2	8.29 ± 0.16
2-Methylbut-1-ene	54.9 ± 0.6	8.30 ± 0.07	52.8 ± 5.4	8.60 ± 0.72	22.2	8.11 *
2-Methylbut-2-ene	48.2 ± 1.7	8.03 ± 0.35	42.4 ± 3.6	8.16 ± 0.49	16.3 ± 0.9	8.08 ± 0.12
2,3-Dimethylbut-2-ene [c]	40.9 ± 1.8	7.96 ± 0.50	36.4 ± 2.8	8.14 ± 0.32		

* Assumed A-factors. [a] Ref. 2. [b] Refs. 6 and 7. [c] Ref. 1.

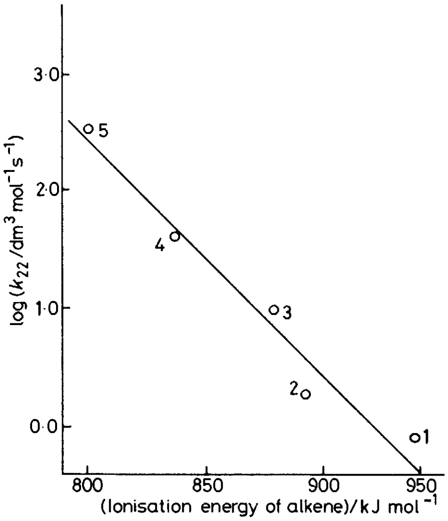


Figure 4. Variation of $\log_{10}(k_{22}/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ at 393 K) with the ionization energy of the alkene. 1, Propene; 2, 2-methylpropene; 3, 2-methylbut-1-ene; 4, 2-methylbut-2-ene; 5, 2,3-dimethylbut-2-ene[1]

butane. The rate parameters obtained for ethene are $\log_{10}$ (A/dm^3 mol^{-1} s^{-1}) 10.16 and E 80 kJ mol^{-1}.[3] As would be expected, the epoxidation of propene is appreciably faster: preliminary figures are $\log_{10}$(A/dm^3 mol^{-1} s^{-1}) 8.91 and E 58 ± 6 kJ mol^{-1}.[4] It is tempting to see a pattern emerging in which the rate of epoxidation decreases on passing from hydroperoxyl to methylperoxyl to isopropylperoxyl.

On safer ground, one can compare directly the data obtained for the addition reactions of alkylperoxyl radicals with those of peracetyl. In general, the latter are much faster[5-7] for peracetyl radicals are considerably more electropositive, due to the presence of the carbonyl group. Thus if peracyl and alkylperoxyl radicals are present in the system, in equimolar quantities, the peracyl radicals will play a considerably more important role in epoxidation reactions with alkenes and propagating the chain reaction. This comparison is also found for the relative rates of abstraction reactions between peracetyl and alkylperoxyl radicals.[21]

Acknowledgement

We are grateful to Professor R. R. Baldwin and Dr. R. W. Walker for giving us information, prior to publication. on the reaction between hydroperoxyl radicals and alkenes (refs. 3 and 4).

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Received 2nd June 1982; *Paper* 2/903