844. *Competitive Oxidations. Part III.*[1] *Oxidations at Low Temperatures Induced by Light.*

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The relative rates of consumption of alkanes by the attack of radicals generated by photolysis of ketones in the presence of an excess of oxygen have been determined. The relative reactivities of different C–H bonds towards these radicals, which are presumed to be alkylperoxy, have been estimated. The reactivities are the same as those found for the chain-carrying radicals in hydrocarbon oxidations at low temperatures and are intermediate between those found for chlorine atoms and methoxyl radicals.

Although the oxidation of hydrocarbons has been extensively studied above 290°, little work has been done on photo-initiated oxidations at lower temperatures. This is understandable, because much of the high-temperature work has consisted of the measurement of induction periods and maximum rates of pressure change. Neither sort of observation is appropriate to photolytic systems. This series of papers [1,2] describes studies of competitive oxidations in which the relative rates of consumption of two hydrocarbons mixed with oxygen are measured. These measurements were first made with and without initiators present above 290° and are here extended to lower temperatures with the oxidation initiated by the photolysis of ketones.

The photolysis of a symmetrical ketone effectively yields two alkyl radicals at 145° or above. These radicals react rapidly with oxygen to form alkylperoxy-radicals. Our experiments show that a radical, which may be alkylperoxy, its isomer, or its decomposition product, exists which will attack alkanes. If this radical is called Y•, then we can write

$$Y\cdot + R_aH \xrightarrow{k_a} R_a\cdot + YH$$

$$Y\cdot + R_bH \xrightarrow{k_b} R_b\cdot + YH$$

The relative rate constants, k_a and k_b, are given by

$$\frac{k_a}{k_b} = \frac{\log [R_aH]_{\text{initial}} - \log [R_aH]_{\text{final}}}{\log [R_bH]_{\text{initial}} - \log [R_bH]_{\text{final}}}. \tag{1}$$

This relation is accurate only if Y• truly represents a single species (or, if a mixture, then species of identical reactivity), if alkanes are consumed by no other reactions, and if the alkyl radicals $R_a\cdot$ and $R_b\cdot$ are efficiently prevented (by reaction with oxygen or by other means) from re-forming alkanes. Consideration of the validity of these assumptions is best deferred until after the results have been presented.

Table 1 shows that k(neopentane)/k(propane) obtained from the above equation is independent of total pressure (100—500 mm.), oxygen : hydrocarbon ratio (2 : 1 to 10 : 1), hydrocarbon : ketone ratio (1·5 : 1 to 15 : 1), and relative hydrocarbon concentration (3 : 1 to 1 : 3), and of whether the initial source of radicals is acetone or diethyl ketone. Table 2 shows k(ethane)/k(neopentane) to be independent of the period of illumination (30—170 min.) at 230°. The conditions were varied at random for all hydrocarbon pairs studied over as wide a range as would permit adequate consumption of reactants in a reasonable time; k_a/k_b was never found to depend on them. It was necessary to use an oxygen : ketone ratio of at least 3 : 1 to suppress completely the formation of alkanes and the dimer corresponding to the alkyl radical formed in the ketone photolysis; usually the excess of oxygen was much greater. Table 3 lists the results for all hydrocarbon pairs

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[1] Part II, Falconer, Knox, and Trotman-Dickenson, *J.*, 1961, 782.

[2] Knox, Smith, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1958, **54**, 1509; Seventh Symposium on Combustion, Butterworths, London, 1959, p. 126.

when the ketones photolysed were acetone, diethyl, di-isopropyl, and di-t-butyl ketone. From these figures the relative reactivities at 230° listed in Table 4 were calculated.

The assumptions made in the deduction of equation (1) can now be considered. The photolyses of the ketones are known to yield alkyl radicals and carbon monoxide. There are three reasons for thinking that the alkyl radicals do not attack the hydrocarbons directly. Methyl radicals yield no methane when acetone is photolysed in the presence of even a few mm. of oxygen under comparable conditions;[3] alkanes that might come from such alkyl attack are not formed; and the relative reactivities are different from those found for methyl radicals.

TABLE 1.

Reaction of neopentane–propane mixtures is oxygen sensitized by alkyl radicals.

[Ketone] init. (mm.)	$[O_2]$ init. (mm.)	[Neopentane] init. (mm.)	[Neopentane] final (mm.)	[Propane] init. (mm.)	[Propane] final (mm.)	$\frac{k(\text{neopentane})}{k(\text{propane})}$	
Methyl radicals, (i) *at* 145.							
14a	320	3·85	2·90	11·65	7·90	0·72	Mean 0·67
12b	160	6·08	4·94	18·32	13·57	0·69	
14a	240	11·34	9·64	3·76	2·96	0·67	
17a	70	15·47	12·86	5·13	3·81	0·63	
15c	245	10·74	8·60	3·56	2·52	0·65	
	(ii) *At* 230°.						
17	65	9·28	7·76	26·70	21·05	0·76	Mean 0·74
15	330	9·44	7·95	27·15	21·55	0·74	
5	70	13·27	12·30	38·13	34·08	0·68	
20	440	29·52	24·10	9·78	7·62	0·80	
18	75	40·57	36·40	13·43	11·50	0·72	
19	460	28·47	22·05	9·43	6·75	0·76	
4	205	30·20	27·45	10·00	10·00	0·73	
16	90	16·53	13·44	5·48	5·48	0·70	
Ethyl radicals, (i) *at* 145°.							
14c	180	4·04	3·14	12·16	8·36	0·67	Mean 0·67
15d	265	11·64	10·06	3·86	3·08	0·66	
17c	365	14·34	11·23	4·76	3·32	0·67	
	(ii) *At* 230°.						
19	280	10·11	7·88	29·09	20·90	0·76	Mean 0·76
19	95	10·16	7·71	29·24	20·15	0·75	
18	435	32·70	23·45	10·83	7·10	0·78	
11	70	27·35	21·90	9·04	6·86	0·78	
8	85	27·41	22·70	9·09	7·02	0·73	
12	155	17·05	12·59	5·65	3·80	0·76	

All runs were of 30 min., except *a* 160, *b* 260, *c* 180, and *d* 145 min.

TABLE 2.

Reactions of ethane–neopentane mixtures at 230°.

Exp. (min.)	[Ketone] init. (mm.)	$[O_2]$ init. (mm.)	[Ethane] init. (mm.)	[Ethane] final (mm.)	[Neopentane] init. (mm.)	[Neopentane] final (mm.)	$\frac{k(\text{ethane})}{k(\text{neopentane})}$	
Methyl radicals.								
30	12	115	13·77	12·62	7·03	6·08	0·59	Mean 0·57
60	16	130	20·05	16·48	10·25	7·28	0·57	
90	16	115	23·90	18·42	12·20	7·54	0·54	
170	15	80	24·23	17·28	12·37	6·78	0·57	
Ethyl radicals.								
30	14	320	17·34	14·22	8·86	6·14	0·54	Mean 0·56
60	16	415	34·96	25·06	17·84	10·10	0·58	

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[3] Hoare and Walsh, *Trans. Faraday Soc.*, 1957, **53**, 1102; Christie, *Proc. Roy. Soc.*, 1958, *A*, **244**, 411; Wenger and Kutschke, *Canad. J. Chem.*, 1955, **33**, 496; Hanst and Calvert, *J. Phys. Chem.*, 1959, **63**, 71.

The reaction of methyl radicals with oxygen is of the third order:[3] first order with respect to methyl radicals, oxygen molecules, and third bodies. The reaction, $\mathrm{Me\cdot + O_2 + M \longrightarrow MeO_2\cdot + M}$, is the only one that is likely to show this behaviour. It is possible that the high pressure of oxygen may have been needed partly to serve as a third body in the suppression of the formation of ethane from acetone. There is good evidence, therefore, that methyl radicals yield methylperoxy-radicals and that the other radicals react similarly. The alkyl radicals formed by hydrogen abstraction must also react with oxygen and cannot re-form their parent alkane. Hence an alkylperoxy-chain could be established. The relative rates of attack observed might therefore be attributable to the radicals released by the alkane mixture, not to those that come from the ketone. The similar behaviour of systems with initial radicals as different as methyl and t-butyl suggests that a chain might not affect the results. This conclusion is supported by the observation that alteration in the proportions of the hydrocarbons does not alter the ratio of the rate constants.

TABLE 3.

Reaction of hydrocarbon mixtures.

Hydrocarbon pair	Temp.	Alkyl radical	No. of runs	k_a/k_b
Methane–cyclopropane	230°	Me	4	0·13 ± 0·03
	230	Et	5	0·12 ± 0·02
Cyclopropane–ethane ……	145	Me	4	0·45 ± 0·02
	145	Et	3	0·45 ± 0·02
	145	$\mathrm{Pr^i}$	1	0·48
	145	$\mathrm{Bu^t}$	2	0·54 ± 0·02
	230	Me	5	0·49 ± 0·02
	230	Et	6	0·52 ± 0·01
	230	$\mathrm{Pr^i}$	3	0·52 ± 0·00
	230	$\mathrm{Bu^t}$	3	0·55 ± 0·03
Ethane–propane	145	Me	7	0·39 ± 0·04
	145	Et	4	0·39 ± 0·02
	230	Me	13	0·04 ± 0·02
	230	Et	5	0·42 ± 0·01
	230	$\mathrm{Pr^i}$	2	0·43 ± 0·01
	230	$\mathrm{Bu^t}$	2	0·45 ± 0·01
Ethane–neopentane	230	Me	4	0·57 ± 0·01
	230	Et	2	0·56 ± 0·02
Neopentane–propane	145	Me	5	0·67 ± 0·03
	145	Et	3	0·67 ± 0·00
	230	Me	8	0·74 ± 0·03
	230	Et	6	0·76 ± 0·01
Propane–isobutane	145°	Me	3	0·70 ± 0·02
	145	Et	3	0·70 ± 0·01
	145	$\mathrm{Pr^i}$	1	0·67
	145	$\mathrm{Bu^t}$	1	0·68
	230	Me	4	0·69 ± 0·02
	230	Et	4	0·70 ± 0·00
	230	$\mathrm{Pr^i}$	3	0·73 ± 0·02
	230	$\mathrm{Bu^t}$	3	0·70 ± 0·01
Propane–butane	145	Me	1	0·59
	145	Et	2	0·61 ± 0·04
	230	Me	5	0·61 ± 0·02
	230	Et	4	0·60 ± 0·01
Butane–propene	145	Me	3	0·20 ± 0·02
	145	Et	4	0·22 ± 0·02
	230	Me	3	0·38 ± 0·01
	230	Et	3	0·38 ± 0·01

TABLE 4.

Initial radical	Methane	Ethane	Propane	Cyclo-propane	n-Butane	Iso-butane	Neo-pentane
Me …………………	0·06	1	2·5	0·49	4·1	3·6	1·8
Et …………………	0·06	1	2·4	0·52	4·1	3·5	1·8
$\mathrm{Pr^i}$ …………………	—	1	2·3	0·52	—	3·2	—
$\mathrm{Bu^t}$ …………………	—	1	2·2	0·54	—	3·2	—

An attempt was made to measure the chain length in one system. Acetone was photolysed in the presence and absence of an isobutane–oxygen mixture. 0·6 molecule of isobutane was removed for each methyl radical released (as determined from the yield of carbon monoxide in the absence of the mixture). This indicates that two-thirds of the attack can be attributed to radicals from (methyl + oxygen) and one-third from (isobutane + oxygen). This argument is over simplified, since the oxygen may quench excited acetone molecules and lower the primary quantum yield. Hence the chains could be longer.

Even if alkylperoxy-radicals are initially formed by the alkyl radicals it is not certain that they attack the hydrocarbons. They might decompose to yield other radicals.

Methylperoxy- might form methoxyl radicals,[4] but it is unlikely that methoxyl radicals play a great part in the system as the observed consumption of hydrocarbons is very different from that predicted by the methoxyl results shown in Table 5. Other alkoxyl radicals probably react like methoxyl. Alternatively, methylperoxy-radicals could decompose to formaldehyde and hydroxyl, and the hydroxyl radicals could attack the alkanes. The other alkyl radicals might decompose to hydroxyl radicals and acetaldehyde or ethylene oxide, acetone or propylene oxide, and isobutene oxide respectively. Table 5 shows that hydroxyl radicals in aqueous solution at 17·5° are clearly less selective than the radicals studied here, and at higher temperatures the hydroxyl radicals are probably still less selective. Thus chlorine atoms react like hydroxyl radicals near room temperature and are much less selective at 250°. Further, hydroxyl is probably more solvated by water than the activated complex that it forms. As with chlorine atoms,[5] this circumstance will increase its observed selectivity above the level for the gas phase. Accordingly it is unlikely that much alkane is removed by hydroxyl attack.

It is most straightforward to suppose that the alkylperoxy-radicals attack the alkanes directly to form hydroperoxides. The nature of the alkyl groups would not be expected to have much effect on the reactivities of the radicals, when the free electron is so far removed from the point at which the structures vary. The hydroperoxy-radical, which we have previously suggested is the chain carrier in the higher-temperature oxidations, might by the same reasoning be expected to have the same reactivity as methylperoxy. It is unlikely that the hydroperoxy-radical is important at low temperatures because it can only readily be released by a reaction such as $\mathrm{Me_3C{\cdot}O{\cdot}O} \longrightarrow \mathrm{Me_2C{:}CH_2} + \mathrm{HO_2{\cdot}}$ which results in the formation of an equivalent amount of olefin. Olefins are indeed the major initial products of alkane oxidations at about 300° but were not detected in the

TABLE 5.

Relative reactivities of hydrogen atoms in hydrocarbons, $\mathrm{X{\cdot}} + \mathrm{RH} = \mathrm{XH} + \mathrm{R{\cdot}}$.

		Environment of hydrogen atom					E †	
Radical	Temp.	Methyl	Cyclopropyl	Prim.	Sec.	Tert.	(ethane)	Ref.
F	25°	0·8	0·9	1	1·2	1·4	0·3	*a*
OH	17·5	0·6	0·18	1	4·7	9·8	—	*b*
Cl	25	0·004	0·003	1	4·6	8·9	1·0	*c*
	250	0·03	0·03	1	3	3	1·0	*c*
Oxid.*	230	0·09	0·52	1	4·5	13·2	—	1
MeO·O	230	0·10	0·52	1	4·8	13·4	—	*h*
EtO·O	230	0·10	0·55	1	4·6	12·4	—	*h*
Pr^{i}O·O	230	—	0·52	1	4·0	13·2	—	*h*
Bu^{t}O·O	230	—	0·54	1	3·0	13·1	—	*h*
MeO	230	—	0·35	1	8	27	7·1	*d*
CF$_3$	182	0·08	—	1	6	36	7·5	*e*
Me	182	0·04	0·55	1	7	50	11	*f*
Br	98	0·002	—	1	250	6300	13·4	*g*

* This refers to the chain-carrying radical in oxidations; the figures quoted were obtained by a small extrapolation of the results to the condition where $O_2/RH = 0$.

† E(ethane) is the activation energy in kcal. mole^{-1} for the abstraction of H from ethane by a radical.

References: *a*, Fettis, Knox, and Trotman-Dickenson, *J.*, 1960, 1064. *b*, Bérces and Trotman-Dickenson, preceding paper. *c*, Knox and Nelson, *Trans. Faraday Soc.*, 1959, **55**, 937; Pritchard, Pyke, and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1955, **77**, 2629. *d*, Shaw and Trotman-Dickenson, *J.*, 1960, 3210; Bérces and Trotman-Dickenson, *J.*, 1961, 348. *e*, Ayscough, Polanyi, and Steacie, *Canad. J. Chem.*, 1955, **33**, 743; Ayscough and Steacie, *ibid.*, 1956, **34**, 103; Ayscough, *J. Chem. Phys.*, 1956, **24**, 944; Pritchard, Pritchard, Schiff, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849. *f*, Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955. *g*, Kistiakowsky and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 469; Anson, Fredricks, and Tedder, *J.*, 1959, 918; Fettis, Knox, and Trotman-Dickenson, *J.*, 1960, 4177. *h*, This work.

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[4] Bell, Raley, Rust, and Vaughan, *Discuss. Faraday Soc.*, 1951, **10**, 242.

[5] Russell, *J. Amer. Chem. Soc.*, 1957, **79**, 2977.

present work at low temperatures. The decomposition of alkylperoxy- to hydroperoxy-radicals and olefin must therefore have a high temperature coefficient.

The only considerable difficulty in accepting the hypothesis that attack is by hydroperoxy-radicals is that the selectivities correspond to those for radicals which would attack ethane with activation energies of 5—6 kcal. mole^{-1}. This is low by comparison with the activation energies of the chain-carrying steps in the autoxidation of olefins in solution; [6] It is also low compared with the value reported by Burgess and Robb [7] for the attack of t-butylhydroperoxy-radicals on isobutane in the mercury-photosensitised oxidation above 300°, but this value is reliable only if their mechanism is strictly correct, the mechanism does not allow for the formation of isobutene which is obtained in large quantities in oxidations at these temperatures. The present work on butane–propene gives

$$\begin{aligned} k(\text{butane})/k(\text{propene}) &= 8{\cdot}2 \exp(-3070/\boldsymbol{R}T) \text{ with acetone} \\ &= 5{\cdot}7 \exp(-2710/\boldsymbol{R}T) \text{ with diethyl ketone} \end{aligned}$$

This difference in activation energy suggests a value of 8—10 kcal. mole^{-1} for butane. On the other hand, the mode of attack on olefins is not known. The removal may occur in two steps, one of which may involve an equilibrium and could result in a negative overall activation energy. The negligible differences in activation energy for attack on primary and tertiary hydrogen atoms are evidence in favour of low activation energies for the primary removal of hydrogen atoms from alkanes.

EXPERIMENTAL

Materials.—Methane, ethane, propane, cyclopropane, butane, isobutane, and neopentane, obtained from cylinders, were degassed and stored in 2-l. bulbs. Ethylene was removed from the cylinder ethane by passing the gas through sulphuric acid and a column of charcoal saturated with bromine. Bromine vapour and bromides were removed by a 30% *NN*-dimethyl-*p*-toluidine–firebrick mixture. Propene was prepared by dehydration of isopropyl alcohol. Chromatography showed the hydrocarbons to be at least 99·5% pure. B.O.C. cylinder oxygen was used.

Acetone and diethyl ketone were of " AnalaR " grade. The di-isopropyl ketone, given by Shell Chemicals, was 99% pure. Di-t-butyl ketone was prepared by condensing t-butyl chloride and methyl pivalate over sodium sand and oxidizing the resultant mixture of ketone and alcohol with concentrated nitric acid, according to the method of Bartlett and Schneider.[8] it had b. p. 153—156°, n_D^{20} 1·4200 and chromatography indicated 95% purity; its photolysis yielded no products characteristic of alkyl radicals other than t-butyl; it was stored in a trap immersed in carbon dioxide–acetone.

Apparatus, Procedure, and Analysis.—The high-vacuum system was of conventional static design constructed of Pyrex glass except for the 300 c.c. spherical quartz reaction vessel which was enclosed in an insulated electric furnace and illuminated by a 125 w medium-pressure mercury arc focused by a quartz lens. The lamp was backed by a polished aluminium reflector, and an aluminium shutter separated the lamp from the reaction vessel.

An excess of oxygen was added to a mixture of two hydrocarbons and ketone in the reaction vessel before each run. The gases were allowed to equilibrate, and the lamp to become stable, for 15 min. before the shutter was opened to start the reaction. The temperature of the reaction vessel rose by ~5° to the stable reaction temperature when the shutter was opened. After a suitable interval the lamp was turned off and the condensable gases were frozen into a W-tube packed with crushed glass helices and immersed in liquid oxygen; the non-condensable gases were pumped through the sample tube to remove remaining condensable material. For mixtures containing methane, the W-tube was packed with activated alumina to condense the methane.

A chromatographic system of the Janak design [9] was used for analysis. Methane and

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[6] Bateman, *Quart. Rev.*, 1954, **8**, 308.

[7] Burgess and Robb, *Trans. Faraday Soc.*, 1958, **54**, 1015.

[8] Bartlett and Schneider, *J. Amer. Chem. Soc.*, 1945, **67**, 141.

[9] Janak, *Coll. Czech. Chem. Comm.*, 1954, **19**, 684, 917.

cyclopropane were separated with split columns. The first column contained 120 cm. of 40—60 mesh activated alumina poisoned with $1\frac{1}{2}\%$ of squalane; the second was 240 cm. of Sutcliffe and Speakman 32—40 mesh activated charcoal. During the analysis the two columns were first connected in series, and the methane and other permanent gases eluted on to the charcoal column and isolated. The cyclopropane was then eluted from the first column directly into the detector. Finally, the permanent gases were eluted from the charcoal. All other samples were separated on 120 cm. of 40—60 mesh activated alumina poisoned with $1\frac{1}{2}\%$ of squalane. For ethane–propane and ethane–cyclopropane mixtures the column was operated at room temperature; for propane–isobutane, propane–butane, and propene–butane at 40—45°; and for ethane–neopentane and neopentane–propane at 65—70°.

Standardization runs were carried out at each furnace temperature, by the normal procedure for a reaction but without oxygen and ketone. Systematic errors of calibration were thus eliminated. The analytical accuracy was about $\pm 1\%$.

This work has been made possible through the support and sponsorship of the U.S. Department of Army, through its European Office.

CHEMISTRY DEPARTMENT, EDINBURGH UNIVERSITY. [*Received, April* 21*st*, 1961.]