ORGANIC AND BIOLOGICAL CHEMISTRY

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Oxygen-18 Tracer Studies of Alkylperoxy Radicals. I. The Cumylperoxy Radical and Chain Termination in the Autoxidation of Cumene[1]

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Under conditions causing no spontaneous interconversion of isotopic species of molecular oxygen, cumene has been autoxidized with mixtures of $O^{18}O^{18}$ (1–6%) and $O^{16}O^{16}$, with azobis-isobutyronitrile as initiator. The reaction was followed kinetically by mass spectrometric analysis of the gas. As the oxygen is consumed, $O^{16}O^{18}$ appears at such a rate as to indicate that the well known interaction between cumylperoxy radicals occurs head to head, producing oxygen and cumyloxy radicals, 1.7–2.6 times for each chain-terminating step in the reaction. This number is a linear function of the kinetic chain length. Kinetic equations are derived and the mechanism is discussed. Kinetic isotope effects are shown to be small in the reaction of oxygen with free radicals and with photo-excited rubrene.

Introduction

The reaction sequence represented in eq. 1–3 fits the kinetics and products of many autoxidations of hydrocarbons, ethers, aldehydes and unsaturated esters

$$\text{Initiator} \longrightarrow \text{R}\cdot \qquad (1)$$

$$\text{R}\cdot + \text{O}_2 \longrightarrow \text{ROO}\cdot \qquad (2)$$

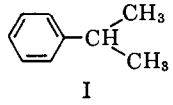
$$\text{ROO}\cdot + \text{RH} \longrightarrow \text{ROOH} + \text{R}\cdot \qquad (3)$$

Chain termination, in the absence of an inhibitor or retarder, can occur by interaction of any pair of radicals normally present.

$$\left.\begin{array}{ll} \text{R}\cdot & + \text{R}\cdot \\ \text{ROO}\cdot & + \text{ROO}\cdot \\ \text{ROO}\cdot & + \text{R}\cdot \end{array}\right\} \longrightarrow \text{end of chain} \qquad \begin{array}{l}(4)\\(5)\\(6)\end{array}$$

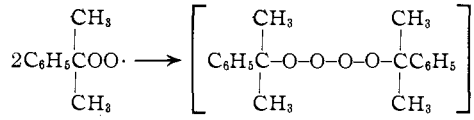
In many familiar autoxidations, including that of cumene, the form of the kinetics varies as oxygen pressure is increased, but reaches a limit at a fraction of an atmosphere pressure, above which there is no further change. This is generally recognized as evidence that reaction 5, the interaction of two alkylperoxy radicals, is the only important chain-terminating step in the region of 1 atm. pressure.[2–5]

Speculation concerning the nature of reaction 5 has taken various forms. In the present paper we are concerned with the relatively simple case in which RH is cumene (I), and where accordingly there is no α-hydrogen atom in the radical ROO·. Despite a small negative isotope effect from deuterium substitution in the β-position of cumene,[6] products of hydrogen



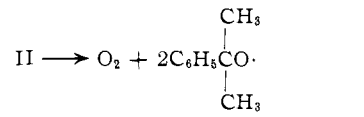
I

abstraction, such as α-methylstyrene or its reaction products, have not been found even under conditions of short kinetic chain length in the autoxidation of cumene. Blanchard's finding of acetophenone[7] and a slowly titrating peroxide supported the over-all process 5a–c, leaving open the question of whether the tetroxide II occurs as a discrete intermediate or only as a transition state, but making it clear that the occurrence of reaction 5 is necessary but not sufficient for chain termination. Recently Milas and Djokic[8] have isolated a pentane-soluble solid from the reaction of ozone with potassium *t*-butyl peroxide at −78° which, as might be expected of di-*t*-butyl tetroxide, decomposed between −30 and 0° to yield equivalent amounts of di-*t*-butyl peroxide and gaseous oxygen. This finding strongly supports the view that II has the properties of a molecular species and has at least a transitory existence in the scheme leading to chain termination in the autoxidation of cumene.



(5a)

II



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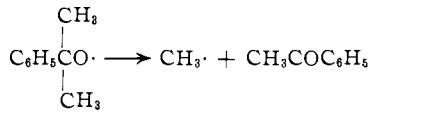


(5c)

It will be noted that the sequence 5a–c still does not include any chain termination and therefore can represent only a portion of the over-all process 5. In our preliminary communication[1] we suggested that chain termination corresponded to that portion of reaction 5b in which the cumyloxy radical pair undergoes recombination within the solvent cage to give dicumyl peroxide. This would indeed have been consistent with the amount of slowly titrating peroxide found by Blanchard. However, other work in this Laboratory[9–11] has shown that the coupling of *t*-butoxy radicals is not fast enough to occur to any detectable extent within the solvent cage, and the same is likely to be true of the cumyloxy radical. Evidence presented later in this paper also indicates that chain termination is by free radicals and not by caged pairs. The numerous possibilities for chain termination by the methyl radical produced in 5c, and by its oxidation products, will be considered in part III of this series. Even if every cumyloxy radical cleaves according to 5c, and every methyl radical adds oxygen, the methylperoxy radical, because of its three α-hydrogen atoms, will have very different properties from the cumylperoxy radical with respect to chain termination.[12]

With his product studies, Blanchard introduced the concept of a non-chain-terminating process associated

(1) A preliminary communication on these results appeared in *Tetrahedron Letters*, **No. 24**, 30 (1960).

(2) E. J. Bowen and E. L. Tietz, *J. Chem. Soc.*, 234 (1930).

(3) H. J. L. Bäckström, *Z. physik. Chem.*, **B25**, 99 (1934).

(4) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (London), **A198**, 252 (1949).

(5) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 418–427, 442–447.

(6) C. E. Boozer, B. W. Ponder, J. C. Trisler and C. E. Wightman, *J. Am. Chem. Soc.*, **78**, 1506 (1956).

(7) H. S. Blanchard, *ibid.*, **81**, 4548 (1959).

(8) N. A. Milas and S. M. Djokic, *Chem. Ind.* (London), 405 (1962).

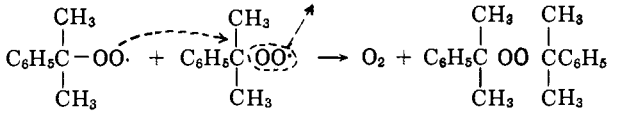
(9) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).

(10) P. D. Bartlett, B. A. Gontarev and H. Sakurai, *ibid.*, **84**, 3101 (1962).

(11) P. D. Bartlett and H. Sakurai, *ibid.*, **84**, 3408 (1962).

(12) G. A. Russell, *ibid.*, **79**, 3871 (1957).

with reaction 5 which could be recognized by the formation of acetophenone. In the present work we approach the same process through the study of the oxygen which is re-emitted in the sequence 5a–5b. This oxygen is recognizable in the special case when the oxygen fed to the oxidation is a non-equilibrium mixture richer in the isotopic species $O^{18}O^{18}$ than in the species $O^{16}O^{18}$, with normal oxygen, $O^{16}O^{16}$, predominating. Every cumylperoxy radical will have the O-isotopic composition of one of the oxygen molecules which reacted with the cumene, while every oxygen molecule re-emitted in reaction 5b will be made up of one atom from each of two such molecules, thus increasing the amount of $O^{16}O^{18}$, or O_2^{34}, as the reaction proceeds. Any reaction, such as the displacement step 5d



(5d)

or the termination mechanism of Boozer and co-workers,[6] which would produce oxygen with unchanged isotopic composition, would pass undetected by the present method. We can, then, measure quantitatively the total rate of all reactions emitting oxygen-34. If we know the relative probabilities of formation of the different isotopic species, we can derive from this measurement the rate of reaction 5a–b. By knowing the rate of chain initiation, and hence of chain termination, we can arrive at a value of the quantity β, representing the number of times per chain termination that reaction 5a–b occurs. If this number is less than one, we shall know that there is also some chain termination in which 5a–b does not occur (oxygen either not being emitted at all or being formed by the isotopic pattern of reaction 5d). If β is greater than one, then 5a–b may be involved in all the chain termination, or there may be some undetectable reaction of the 5d type, with much reinitiation by the cumyloxy radicals from 5b or the methyl radicals from 5c.

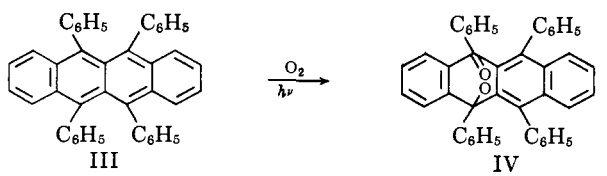
Experimental Method

The details of the experiments, and a representative kinetic experiment, are described in detail in part II of this series, the paper immediately following this one. The same type of apparatus and procedure was used in all the kinetic experiments referred to below.

Stability of Isotopic Oxygen to Exchange.—A number of tests were made to determine the extent to which the molecular species of elementary oxygen maintain their integrity under various physical and chemical conditions.

Effect of Ultraviolet Light.—A sample of gaseous oxygen containing molecules of masses 36, 34 and 32 in the proportions 3.88, 0.43 and 95.69%, respectively, was sealed in a Pyrex tube with a little argon as a standard of reference and irradiated for 1 hr. at a distance of 8 in. from a G.E. sun-lamp. The mass composition had changed in this time to 3.49, 1.42 and 95.09%. The over-all per cent O^{18}, which should remain the same, was thus 4.10 before and 4.20 after the irradiation. The more than threefold increase in O_2^{34} concentration shows that ultraviolet light transmitted by Pyrex is capable of producing a slow equilibration among the molecular species of oxygen.

Formation of a Transannular Peroxide.—Under conditions identical with those of the previous experiment, 0.986 g. of rubrene



III IV

(III) dissolved in 2 ml. of chloroform and sealed in Pyrex under an atmosphere of the same labeled oxygen mixture was exposed to the same light for 1 hr. The red color of the rubrene disappeared. The residual oxygen was sampled and analyzed in the mass spectrometer. The transannular rubrene peroxide (*IV*) was isolated and decomposed after evacuation; the evolved oxygen was also examined in the mass spectrometer. Table I summarizes the results.

TABLE I

ISOTOPIC COMPOSITION OF OXYGEN IN RUBRENE OXIDATION

	Peak heights					Composition, %		
Sample	28	32	34	36	40	O_2^{36}	O_2^{34}	O^{18}
Initial	62.3	3300	15.0	138.8	504	3.88	0.43	4.10
Residue	123.9	2259	14.6	98.7	1134	4.16	.62	4.47
Regenerated	91.2	2280	16.7	104.7	0.6	4.36	.70	4.71
Control	49.5	2712	40.6	99.6	431	3.49	1.42	4.20

In view of the fact that the statistical equilibrium would have masses 34 and 36 in the amounts of 7.86 and 0.17%, it is clear that the conversion of oxygen into the transannular rubrene peroxide and back again does not effect equilibration of the isotopic molecular species. Indeed, the presence of the colored hydrocarbon may have screened the oxygen from undergoing the amount of light absorption and isotopic redistribution which occurred in the control tube, although a small amount of such redistribution is evident.

Several experiments were run in order to determine whether the presence of reactive free radicals (whether through rapidly reversible reactions or by a general paramagnetic effect) might cause equilibration of the isotopic species. A sample of 12 ml. of oxygen (at about $^2/_3$ atm.) was heated for 11 hr. at 76.5° with a solution of 90 mg. of benzoyl peroxide in 1.5 ml. of chlorobenzene, during which time about 25% of the peroxide decomposed. The 36/34 peak ratio was 7.53 before and 7.99 after this treatment, showing no equilibration, although some oxygen was consumed.

In one arm of a tube with a break seal was placed a 0.033 *M* solution of cobaltous acetate in acetic acid, in the other enough *t*-butyl hydroperoxide to make the solution 0.55 *M* in this component. The tube was evacuated and filled with 8–10 ml. of the O_2^{36}–O_2^{32}–Ar mixture. The tube was then shaken at room temperature for 10 hr. and the gas analyzed. The ratio of the peaks at masses 36 and 40 was 0.207 before and 0.211 after the experiment, during which the total oxygen increased by 140%. Therefore equilibration of isotopic species of oxygen was not promoted by the presence of the *t*-butoxy radical, the *t*-butylperoxy radical, cobaltous or cobaltic ions.

A solution of **potassium persulfate**, 0.0975 *M* in an aqueous phosphate buffer solution of pH 8,[13–15] was decomposed at 59.8° over a period of 23.5 hr. in the presence of labeled oxygen. Oxygen was evolved, the total amount of O_2^{32} increasing by 70%. At the same time the O^{18} in the oxygen became diluted not by the corresponding factor, but by 142%, evidence that in this case molecular oxygen was undergoing exchange with the aqueous system. The 36/34 peak ratio changed during this experiment from 3.81 to 0.56.

All the other free radical sources investigated were capable of generating carbon free radicals and therefore of fixing oxygen as in any autoxidation. All such systems consume oxygen and produce O_2^{34} in relative amounts consistent with the view that the isotopic interconversion is coupled with interaction of $RO_2\cdot$ radicals.

Isotope Effects.—Most of the reactions studied in this series of papers are processes involving several elementary reactions which could be subject to oxygen kinetic isotope effects. In a few cases the reaction was simple enough to permit an estimate of the magnitude of this effect for a single elementary step. In the autoxidation of azobis-α-phenylethane (part V) the chains are long and very little oxygen is given back on termination. In this reaction $k(O_2^{36})/k(O_2^{32})$ for oxygen uptake appeared to be 0.98 at 39.76° and 0.99 at 90.85°. In the styrene–oxygen–iodine system, likewise, where oxygen is not given off on termination, $k(O_2^{36})/k(O_2^{32})$ was estimated as 0.97 and $k(O_2^{34})/k(O_2^{32})$ as 0.98. These values are all supported by consistent kinetics throughout the runs and a linear plot of log *y* against log *w* (see derivations, below). A single determination of the residual gas after photoaddition of oxygen to rubrene suggested an over-all $k(O^{18})/k(O^{16})$ of 0.96.

No kinetic measurements were made of an oxygen evolution uncomplicated by oxygen addition.

From the cases just cited, it is evident that kinetic isotope effects in autoxidation by mixtures of O_2^{32} and O_2^{36} are not greater than 2 or 3% and may be neglected in comparison with the substantial changes in isotopic composition which are the subject of this series of papers.

(13) P. D. Bartlett and J. D. Cotman, Jr., *J. Am. Chem. Soc.*, **71**, 1419 (1949).

(14) I. M. Kolthoff and I. K. Miller, *ibid.*, **73**, 3055 (1951).

(15) W. K. Wilmarth and A. Haim in J. O. Edwards, "Peroxide Reaction Mechanisms," Interscience Publishers, Inc., New York, N. Y., 1962, p. 175.

Derivation of Kinetic Equations

To extract a maximum of information from the mass spectrometric results we need equations relating the amounts of the isotopic species of oxygen to the total amount of oxygen entering the reaction in step 2 and re-emitted in step 5. The following derivation provides such equations. In view of the very small isotope effect described in the previous section, all isotope effects are neglected. Because of the nature of the experimental method (see part II), the kinetic derivations are made in terms of total moles of gas in the reaction vessel, rather than the conventional moles per liter in solution. It is an implicit assumption in this treatment that the efficient stirring keeps equilibrium concentrations of all gaseous species in all parts of the solution and gas phase throughout a kinetic experiment. It is further assumed that every interaction of two $RO_2\cdot$ radicals produces one oxygen molecule of some sort. Let

r = fraction of chain terminations which are not consequent upon collisions of $RO_2\cdot$ radical pairs (negligible for cumene autoxidation)
$1 - r$ = fraction of chain terminations which are consequent upon collisions of $RO_2\cdot$ radical pairs
p = fraction of such collisions which produce oxygen molecules with statistical distribution of the O^{18} (*i.e.*, which occur head to head, as in 5a–5b)
$1 - p$ = fraction of collisions of $RO_2\cdot$ pairs which leave the O–O bonds of the original oxygen molecules unbroken (as in 5d)
β = molecules of oxygen evolved per chain-terminating encounter of radicals
$1/q$ = fraction of reactions between $RO_2\cdot$ radicals which lead to chain termination, so that $\beta = (1 - r)q$
x = moles O_2^{32}; $M_x = x/w$
y = moles O_2^{34}; $M_y = y/w$
z = moles O_2^{36}; $M_z = z/w$
$w = x + y + z$
a = atom fraction of $O^{18} = M_x + {}^1/_2M_y$
f_y = statistical fraction of O_2 generated which is O_2^{34}
$f_y = 2a(1 - a)$; $f_z = a^2$
C_x, C_y, C_z, C_w = rate of consumption of species x, y, z, w in the reaction $R\cdot + O_2 \longrightarrow RO_2\cdot$
G_x, G_y, G_z, G_w = rate of generation of species x, y, z, w in encounters between $RO_2\cdot$ radicals
$b = C_w - G_w$ = measured decrease of oxygen in moles/sec. $= -\mathrm{d}w/\mathrm{d}t$

The amount of O_2^{34} will be governed by the equation

$$\mathrm{d}y/\mathrm{d}t = G_y - C_y = G_w(pf_y + (1 - p)M_y) - C_wM_y$$

The substitutions

$$y = wM_y;\ \mathrm{d}y = w\mathrm{d}M_y + M_y\mathrm{d}w;\ -\mathrm{d}t = \mathrm{d}w/b, \text{and } G_w = C_w - b$$

lead to the equation

$$p\frac{G_w}{b}\frac{\mathrm{d}w}{w} = \frac{\mathrm{d}M_y}{M_y - f_y} = \frac{\mathrm{d}(f_y - M_y)}{f_y - M_y}$$

or

$$\log (f_y - M_y) = (pG_w/b)\log w + \text{const.} \qquad (7)$$

Equation 7 must yield a linear plot between functions of y and w throughout the entire run, while the oxygen is totally consumed and while the mole fraction (M_y) of O_2^{34} rises toward a limit and the quantity y itself passes through a maximum. Such plots are indeed found to be linear in all cases. The slope, combined with the experimental quantity b, affords a value of pG_w. The method does not give the separate values of p and G_w; however, a substantial value of the product shows that neither quantity can be equal to zero.

A parallel derivation leads to the equation

$$\log (M_z - f_z) = (pG_w/b)\log w + \text{const.} \qquad (8)$$

which, for experimental reasons, is less useful than eq. 7 for the determination of pG_w. This is because z and w change in a typical run in a parallel manner; while M_y in run 4 increases by a factor of five, M_z changes only 24% over the series of samplings. The form of eq. 8 thus gives to small variations in the quantities which make up w, and especially x, an undue effect on the slope which does not appear in eq. 7. Therefore only eq. 7 is used in the determination of pG_w. However, the consistency between the y and z data can be tested by using eq. 9, derived from eq. 8 by neglecting the very small f_z relative to M_z and replacing the latter again by z/w.

$$\log z = \left(1 + \frac{pG_w}{b}\right)\log w + \text{const.} \qquad (9)$$

In every case the plot of eq. 9 is linear and its slope can be corrected for the neglect of f_z by adding the term

$$\frac{\left(\frac{fz}{Mz}\right)_2 - \left(\frac{fz}{Mz}\right)_1}{2.3\log w_2/w_1}$$

for any two points shown in the graph to be on the line. Table II shows that the corrected slopes of eq. 9 and eq. 7, which should differ by exactly 1, differ in six runs by an average of 0.967.

TABLE II

AUTOXIDATION OF CUMENE

Run	Slope of (log z *vs.* log w)	Correction for neglected f_z	Corrected "z slope"	"y slope"	("z slope" − "y slope")	α
1	1.257	0.0098	1.267	0.275	0.992	0.0302
2	1.392	.030	1.422	.506	.916	.0599
3	1.456	.0118	1.468	.544	.924	.0173
4	1.182	.0082	1.190	.174	1.016	.0404
5	1.176	.0036	1.180	.212	0.968	.0162
6	1.390	.0222	1.412	.425	0.987	.0426
				Av.	0.967	

Results and Discussion

Were there no head-to-head interaction of cumylperoxy radicals the "y slope" would be zero. The substantial value of this slope shows that reactions 5a and 5b are indeed occurring, whether as a sequence or as a single concerted process. To translate the results into terms of mechanism we first obtain pG_w by multiplying the y slope by the experimental rate of oxygen disappearance b. To find β, the number of molecules of oxygen returned by reaction 5a–b per chain termination, we have to divide G_w by the rate of chain initiation (radical pair formation); the latter quantity is obtained from the direct measurement of nitrogen evolved by the initiator, azobis-isobutyronitrile (AIBN), multiplied by its known efficiency (e) in producing free radicals $R_i = e\ \mathrm{d}(N_2)/\mathrm{d}t)$. The rate of nitrogen evolution is determined as a by-product of the mass spectrometric sampling; values of e are available from the work of Hammond, *et al.*, and of Bartlett and Funahashi.[16,17]

Table III summarizes the measurements and calculations for six runs on the autoxidation of cumene in chlorobenzene as solvent, at concentrations of cumene from 0.48 to 2.72 M, with AIBN as initiator. The values of the product $pe\beta$ vary from 1.10 to 1.73 with the concentrations of the reactants. Using the value $e = 0.66$ found by Bartlett and Funahashi[17] for galvinoxyl scavenging of the radicals from AIBN, we get values of $p\beta$ from 1.67 to 2.62. These are also the *minimal* values of β which are correct if $p = 1$; for any smaller values of p, β will of course be larger. These results agree with the conclusion of Blanchard, reached by a product study, that β is of the order of 2. There is thus no need to assume that p is anything other than 1, all the requirements of the mechanism being met by the scheme 5a–5b.

(16) G. S. Hammond, J. N. Sen and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955).
(17) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).

TABLE III

AUTOXIDATION OF CUMENE WITH LABELED OXYGEN

T = 59.85°; solvent, chlorobenzene; initiator, azobis-isobutyronitrile

	Run					
	1	2	3	4	5	6
Cumene, M	1.36	0.476	0.477	2.72	1.36	1.36
AIBN, M	0.0952	0.0949	0.0956	0.0954	0.0250	0.375
$R_i/e \times 10^8$, moles/sec.[d]	4.24	4.36	4.39	4.10	1.12	17.86
$b \times 10^8$, moles/sec.[d]	19.8	9.41	9.48	40.2	9.14	50.6
α	0.0302	0.0599	0.0173	0.0404	0.0162	0.0426
y slope	.275	.506	.544	.174	.212	0.39
$pG_w \times 10^7$, moles/sec.	.54	.48	.52	.70	.194	1.97
$C_w \times 10^7$, moles/sec.	2.52[a]	1.42[a]	1.47[a]	4.72[a]	1.10[a]	7.03[a]
$pe\beta = epG_w/R_i$[c]	1.27	1.10	1.18	1.71	1.73	1.10
$e(\nu + 1) = eC_w/2R_i$	2.97[a]	1.63[a]	1.67[a]	5.76[a]	4.91[a]	1.97[a]
$(\text{Cumene})R_i^{-1/2} \times 10^{-3}$	6.61	2.28	2.28	13.44	12.85	3.22
β	1.92[b]	1.67[b]	1.79[b]	2.59[b]	2.62[b]	1.67[b]
ν	3.50[b]	1.47[b]	1.53[b]	7.73[b]	6.44[b]	1.98[b]

[a] On the assumption that $p = 1$. [b] On the assumption that $e = 0.66$[17] and $p = 1$. [c] The calculations in this table were made by eq. 13 and 14 of part II. Use of values of R_i and b from the literature[7] gives $pe\beta = 1.43$ for run 1, 1.16 for run 3, and 1.75 for run 4. [d] To obtain R_i and b in moles/l. sec., divide by 0.050 in run 2 and by 0.040 in all other runs.

This demonstration, however, introduces a complication into the mechanism of autoxidation. If β is greater than 1, it means that the interaction of two cumylperoxy radicals is not the chain-terminating step

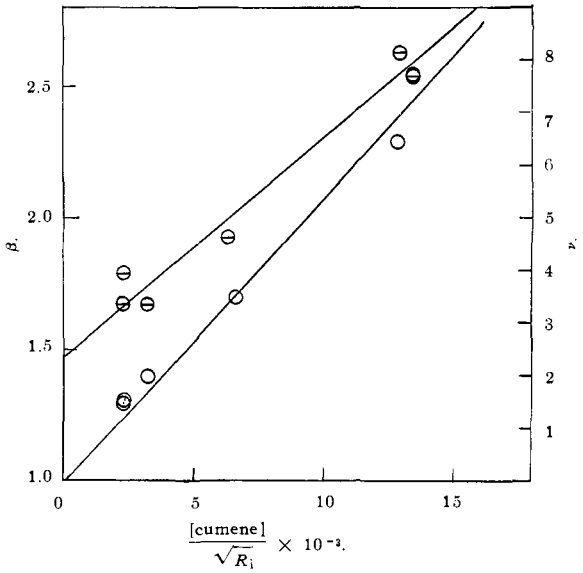


Fig. 1.—Variation of β (upper plot, barred circles) and of kinetic chain length ν (lower plot, open circles) with the ratio $[\text{cumene}]/\sqrt{R_i}$ in autoxidation.

after all, but a process which leads sometimes to chain termination and sometimes to chain continuance. The possibilities are numerous, and include at least reactions 10–17

$$2C_6H_5C(CH_3)_2O\cdot \longrightarrow (C_6H_5C(CH_3)_2O)_2 \quad (10)$$

$$CH_3\cdot + O_2 \longrightarrow CH_3OO\cdot \quad (11)$$

$$CH_3\cdot + C_6H_5C(CH_3)_2H \longrightarrow CH_4 + C_6H_5C(CH_3)_2\cdot \quad (12)$$

$$2CH_3\cdot \longrightarrow C_2H_6 \quad (13)$$

$$CH_3OO\cdot + C_6H_5C(CH_3)_2H \longrightarrow CH_3OOH + C_6H_5C(CH_3)_2\cdot \quad (14)$$

$$CH_3OO\cdot + ROO\cdot \longrightarrow O_2 + CH_2O + ROH \quad (15)$$

$$CH_3\cdot + RO\cdot \longrightarrow CH_3OR \quad (16)$$

$$CH_3\cdot + RO_2\cdot \longrightarrow CH_3OOR \quad (17)$$

five of which are chain terminating. In our preliminary communication[1] we were struck by the fact that the fraction of cases of 5a–5b which lead to termination is similar to the fraction of radical pairs from the initiator which lead to cage recombination, and we suggested that there is a second cage effect involved in the decomposition 5b, which formally resembles that of AIBN. Since that time the series of experiments now reported has shown that this cannot be the case. The fraction of cage recombination must be invariant with concentration of initiator and other molecular species, whereas the value of β changes in a characteristic manner with those concentrations which determine the kinetic chain length; the longer the kinetic chains, the more oxygen molecules are given back per chain termination. Figure 1 shows, in the lower curve, that the experimental kinetic chain length is proportional, as it should be, to the quotient $(\text{cumene})/R_i^{1/2}$, while the upper curve shows a linear relationship between β and the same quantity, the limit of β being about 1.5 for zero kinetic chain length of autoxidation. This relationship implies that the concentration of cumyloxy radical cannot be made high enough for its coupling to compete well with its cleavage and seems to rule out reaction 10 as an important mode of chain termination. This is in accord with the general failure to find dialkyl peroxides as products when cumyl hydroperoxide is decomposed under conditions producing the $RO_2\cdot$ radical.[18] It is much more likely that the sequels to reaction 11 are normally chain terminating. The high hydrogen-donating power of the methylperoxy and methoxy radicals, formaldehyde and the formyl radical can account for reaction 11 failing to be followed by chain renewal.

Finally, it should be noted that the rate constant for termination of cumene autoxidation[19] requires correction in order to be converted into a rate constant for interaction of cumylperoxy radicals. Under the conditions used by Melville and Richards the kinetic chain length was 10 at 50° and 17 at 65°. Necessary data for making the correction are lacking; however, a crude estimate can be made by assuming that the temperature coefficients of β and of kinetic chain length are similar. This affords estimated values for β of 3.0 at 50° and 4.1 at 65° under the conditions of Melville and Richards. It may be then that a somewhat closer estimate of the rate constant for reaction 5a–5b would be

$$k\,(50°) = 3.0 \times 2.8 \times 10^4 = 8 \times 10^4$$

$$k\,(65°) = 4.1 \times 3.3 \times 10^4 = 1 \times 10^5$$

obtained by multiplying the rate constant for chain termination by β.

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