Table I. Kinetics for the Reduction of *t*-Butyl Halide by Organotin Hydride in Cyclohexane at 25°

RX	R'$_3$SnH	Reaction order [ACHN]	Reaction order I[a]	Reaction order [RX]	Reaction order [R'$_3$SnH]	Concentration range, *M* [ACHN] × 10^3	Concentration range, *M* [RX]	Concentration range, *M* [R'$_3$SnH]	Concentration range, *M* [RX]/-[R'$_3$SnH]
t-BuBr	Ph$_3$SnH	0.54 ± 0.1	0.58 ± 0.05	0 ± 0.1	0.95 ± 0.1	0.7–3.4	2.41–8.7	0.03–0.25	10–70
t-BuCl	Ph$_3$SnH	0.40 ± 0.05	0.52 ± 0.05	0.90 ± 0.05	0 ± 0.1	0.7–11.0	0.35–7.5	0.08–0.60	2.5–25
t-BuBr	*n*-Bu$_3$SnH			0 ± 0.1	0.87 ± 0.1		0.42–2.8	0.03–0.25	2.2–90
t-BuCl	*n*-Bu$_3$SnH		0.60 ± 0.10	See text	See text		0.41–9.0	0.07–0.44	1.7–130

[a] Light intensity.

ΔH was found to be $-(40 \pm 4)$ kcal/mole for each of the four reactions studied.

The kinetics are summarized in Table I. Chain termination is bimolecular since the over-all rates are proportional to (light intensity)$^{1/2}$ at constant ACHN concentration and to [ACHN]$^{1/2}$ at constant light intensity. The kinetics show an interesting dependence on the nature of both the halide and the hydride. In the case of *t*-butyl bromide, reaction 2 is rate determining with both hydrides, and termination occurs by reaction 4. For the reaction of *t*-butyl chloride with triphenyltin hydride, reaction 3 is rate determining and termination occurs by reaction 6. However, with *t*-butyl chloride and tri-*n*-butyltin hydride, reactions 2 and 3 are of comparable rate. The kinetics are estimated to deviate from approximately first order in [chloride] and zero order in [hydride] at [chloride]/[hydride] ratios above about 5 to zero order in [chloride] and first order in [hydride] at ratios below about 80. Termination can therefore occur by reactions 4, 5, or 6. The predominant mode of termination depends on the relative concentration of the two reactants.

The absolute rate constants of these reactions are given in Table II. They have been determined by the rotating sector method.[3] Rates of chain initiation were determined both by the inhibitor method and by comparison of the rates of photoinitiated and thermal-initiated reactions.[3] At an ACHN concentration of 3.4×10^{-2} *M* and with full light intensity the rate of initiation was about 3.5×10^{-8} *M* sec^{-1}. Under these typical conditions chain lengths were in the range (3×10^2)–(5×10^3).

Table II. Absolute Rate Constants for the *t*-Butyl Halide–Tin Hydride Reaction in Cyclohexane at 25°

Reaction	Rate constant, *M*$^{-1}$ sec^{-1}
t-Bu· + Ph$_3$SnH	5×10^6
t-Bu· + *n*-Bu$_3$SnH	3×10^6
Ph$_3$Sn· + *t*-BuCl	3×10^4
n-Bu$_3$Sn· + *t*-BuCl	1.5×10^4
t-Bu· + *t*-Bu·	2×10^9
Ph$_3$Sn· + Ph$_3$Sn·	3×10^9
n-Bu$_3$Sn· + *n*-Bu$_3$Sn·	1.5×10^9
t-Bu· + *n*-Bu$_3$Sn·	2×10^9

The rate constants for chain termination are consistent with essentially diffusion-controlled processes. The over-all reaction is rapid because the propagation steps are extremely fast. This work will be described in more detail at a later date.

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[4] National Research Council Postdoctorate Fellow, 1965–1967.

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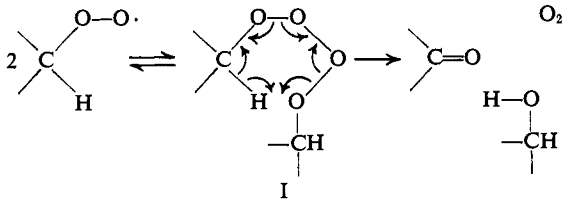
Received November 27, 1967

The Self-Reaction of *sec*-Butylperoxy Radicals. Confirmation of the Russell Mechanism[1,2]

Sir:

Rate constants for chain termination in the oxidation of hydrocarbons giving primary or secondary peroxy radicals are generally considerably faster than for hydrocarbons giving tertiary peroxy radicals.[3] About 10 years ago Russell proposed[4] that the self-reaction of secondary peroxy radicals involved a cyclic transition state. The recent discovery that di-*t*-butyl tetroxide is a stable species below −85°[5] supports Russell's suggestion[4] that "I may actually be an intermediate that is formed rapidly and reversibly and which decomposes slowly in an irreversible manner." The decomposition of I will not violate the Wigner spin-conservation rule if the oxygen is eliminated in the singlet state,[6] either $^1\Sigma_g{}^+$ or $^1\Delta_g$.[7] Alternatively, the oxygen could be eliminated in its triplet ground state, $^3\Sigma_g{}^-$, if the ketone is also formed in its excited triplet state.[8] We have now identified singlet oxygen in the



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(1) Absolute Rate Constants for Hydrocarbon Oxidation. IX. For part VIII see J. A. Howard, K. U. Ingold, and M. Symonds, *Can. J. Chem.*, in press.

(2) Issued as N.R.C. No. 9992.

(3) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **45**, 793 (1967).

(4) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

(5) P. D. Bartlett and G. Guaraldi, *ibid.*, **89**, 4799 (1967).

(6) The present experiments were started after this point was brought to the authors' attention by Professor Russell.

(7) The over-all reaction is exothermic by over 100 kcal/mole (Russell[4] estimates 157 kcal/mole) and there is therefore plenty of energy available to form either electronically excited singlet state of oxygen. The $^1\Sigma_g{}^+$ state is 37.5 kcal and the $^1\Delta_g$ state is 22.5 kcal above the triplet ground state.

(8) Organic materials undergoing autoxidation luminesce very weakly with a maximum emission generally in the range 420–450 mμ.[9] The emitter of this bluish luminescence appears to be an electronically excited carbonyl compound (n,π*).[9] Transitions from both the triplet and singlet states are observed in the oxidation of methyl ethyl ketone

self-reaction of *sec*-butylperoxy radicals and have thus obtained strong experimental support for the Russell mechanism of termination. The following gives some additional experimental support for this mechanism.

Our general technique was similar to that employed by McKeown and Waters.[13] The formation of singlet oxygen was inferred by the isolation of 9,10-diphenylanthracene 9,10-*endo*-peroxide from a reaction carried out in the presence of 9,10-diphenylanthracene (DPA), a compound known to be a fairly efficient trap for singlet oxygen.[13–15] The peroxy radicals were produced from *sec*-butyl hydroperoxide[16] by oxidation with ceric ion.

$$C_2H_5(CH_3)C(H)OOH + Ce^{4+} \longrightarrow C_2H_5(CH_3)C(H)OO\cdot + H^+ + Ce^{3+}$$

DPA (1 g) in 50 ml of benzene containing 20 g of *sec*-butyl hydroperoxide (0.22 mole) was floated on 100 ml of water. The mixture was stirred gently so that the boundary between the two layers was not too badly broken and, in the dark, excess ceric ammonium nitrate (183 g (0.33 mole) in 200 ml of water) was added to the aqueous layer through a capillary tube over ~2 hr. The organic layer was separated, washed with water, evaporated under reduced pressure, and chromatographed through alumina (150 g), initially with benzene–*n*-hexane (1:6) and finally with benzene. All the DPA had been consumed in the reaction. The *endo*-peroxide (0.040 g)[17] was the second crystalline compound eluted.[18] This compound was identical (melting point[19] and infrared and X-ray spectra) with authentic *endo*-peroxide prepared both by oxidizing DPA in sunlight[20] and by the procedure of McKeown and Waters of oxidizing alkaline hydrogen peroxide with bromine in a similar two-phase system.[13] In this last reaction, McKeown and Waters obtained 0.5 g of *endo*-peroxide from 1 g of DPA in 50 ml of chlorobenzene and 0.32 mole of oxygen,[21] but in repeating this experiment we obtained only 0.35 g. The ceric oxidation of 0.22 mole of *sec*-butyl hydroperoxide produces 0.11 mole of oxygen. The singlet oxygen from the *sec*-butylperoxy radicals was therefore trapped at about one-third to one-fourth of the efficiency with which it was trapped from the Br_2–H_2O_2 reaction, assuming, of course, that only singlet oxygen is produced in both reactions. The *endo*-peroxide is decomposed rather slowly by ceric ion under the experimental conditions. Its lower yield from the peroxy radical reaction may possibly be due to a solvent effect[14b] or to the quenching of singlet oxygen to its triplet ground state by the cerium ions. However, the low yield is more probably due to the destruction of DPA in other reactions which presumably involve free radicals[22] since free radicals are not involved in the H_2O_2–Br_2 reaction. In the H_2O_2–Br_2 reaction the DPA is accounted for almost quantitatively as *endo*-peroxide and unreacted DPA.[13]

No *endo*-peroxide was detected in the ceric oxidation of *t*-butyl hydroperoxide or hydrogen peroxide under conditions similar to those employed with *sec*-butyl hydroperoxide.[23] The limit of detection (tlc after chromatography) is estimated to be about 1 mg in both cases.[25] The self-reactions of tertiary peroxy radicals

$$2(CH_3)_3COO\cdot \rightleftarrows (CH_3)_3COOOOC(CH_3)_3 \longrightarrow (CH_3)_3CO\cdot + {}^3O_2 + \cdot OC(CH_3)_3$$

and hydroperoxy radicals

$$HOO\cdot + HOO\cdot \longrightarrow HOOH + {}^3O_2$$

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but, with hydrocarbons, emission appears to come mainly from the triplet state.[9] The excited carbonyl compound is generally believed to be formed in the chain-termination process.[9,10] However, emission from the triplet state does not necessarily imply that triplet ketone and triplet oxygen are produced together in termination since singlet ketone is very rapidly converted to the triplet. An emission in the red region of the spectrum has also been observed and has been assigned to the ${}^1\Sigma_g{}^+ \longrightarrow {}^3\Sigma_g{}^-$ transition, the excited oxygen being produced in termination[11] (*cf.*, however, ref 10). If this luminescence is indeed homogeneous rather than heterogeneous (as appears likely in hydrocarbon oxidation[10]) it is more probably derived from a dimer of the ${}^1\Delta_g$ state of oxygen.[12] In any case, the over-all chemiluminescence quantum yield (*i.e.*, the light emitted per chain terminated) is so extremely small (10^{-7}–10^{-10}) that the nature of the emitted light provides little help in determining the principle mechanism of termination.

(9) R. F. Vasil'ev, *Progr. Reaction Kinetics*, **4**, 305 (1967).

(10) For a different view see: R. A. Lloyd, *Trans. Faraday Soc.*, **61**, 2173, 2182 (1965).

(11) R. F. Vasil'ev and I. F. Rusina., *Izv. Akad. Nauk SSSR, Ser. Khim.* 1728 (1964).

(12) S. J. Arnold, E. A. Ogryzlo, and H. Witzke., *J. Chem. Phys.*, **40**, 1769 (1964); R. J. Browne and E. A. Ogryzlo., *Proc. Chem. Soc.*, 117 (1964); A. M. Viner and K. D. Bayes, *J. Phys. Chem.*, 70, 302 (1966); A. U. Khan and M. Kasha, *J. Am. Chem. Soc.*, **88**, 1574 (1966).

(13) E. McKeown and W. A. Waters, *J. Chem. Soc., Sect. B*, 1040 (1966).

(14) (a) T. Wilson, *J. Am. Chem. Soc.*, **88**, 2898 (1966); (b) E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3881 (1964).

(15) It is worth noting that the spin conservation rule also applies to the reverse of this reaction, that is, decomposition of this *endo*-peroxide gives DPA and singlet oxygen (H. H. Wasserman and J. R. Scheffer, *ibid.*, **89**, 3073 (1967)).

(16) H. R. Williams and H. S. Mosher, *ibid.*, **76**, 2987 (1954).

(17) As crystals 0.030 g was isolated and another 0.010 g was estimated to be present in mother liquors containing several minor components by thin layer chromatography. A great many minor components, which were mostly noncrystalline, were observed by tlc.

(18) The first, 0.70 g of white needles from benzene–hexane, mp 120–145° (decomposes with gas evolution); nmr and infrared spectra consistent with *cis*-9,10-di-*sec*-butylperoxy-9,10-dihydro-9,10-diphenylanthracene. *Anal.* Calcd for $C_{34}H_{36}O_4$: C, 80.28; H, 7.13; mol wt, 508.7. Found: C, 80.10; H, 7.23; mol wt, 502.

(19) Mp 130–180° with decomposition to DPA.[20]

(20) P. F. Southern and W. A. Waters, *J. Chem. Soc.*, 4340 (1960).

(21) From 35 ml of 30% H_2O_2.

(22) 9,10-Diphenylanthracene is quite reactive toward the free radicals present in oxidizing hydrocarbons: A. M. Turner and W. A. Waters, *J. Chem. Soc.*, 879 (1956). The *meso* positions are probably most reactive: A. L. J. Beckwith, R. O. C. Norman, and W. A. Waters, *ibid.*, 171 (1958).

(23) The H_2O_2 reaction yielded essentially a single product, 0.94 g of white needles from benzene, mp 198–199° (decomposition at 250°); nmr and infrared spectra consistent with *cis*-9,10-dihydroxy-9,10-dihydro-9,10-diphenylanthracene; lit.[24] mp 195–196° for one crystal form of the *cis* isomer of this compound. *Anal.* Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53; mol wt, 364.4. Found: C, 85.47; H, 5.51; mol wt, 370.

A large number of products were formed in the *t*-butyl hydroperoxide reaction, probably because of the presence of the highly reactive *t*-butoxy radical in this system. There were two main crystalline products: first, 0.12 g of white needles from hexane, mp 191–208° (decomposition with gas evolution); nmr and infrared spectra consistent with that of *cis*-9,10-di-*t*-butylperoxy-9,10-dihydro-9,10-diphenylanthracene (*Anal.* Calcd for $C_{34}H_{36}O_4$: C, 80.28; H, 7.13; mol wt, 508.7. Found: C, 80.30; H, 7.38; mol wt, 515); second, 0.24 g of white needles from benzene, mp 181–190° (decomposition with gas evolution); nmr and infrared spectra consistent with that of 9-*t*-butylperoxy-10-hydroxy-9,10-dihydro-9,10-diphenylanthracene (*Anal.* Calcd for $C_{30}H_{26}O_3$: C, 82.54; H, 6.46; mol wt, 436.6. Found: C, 82.58; H, 6.55; mol wt, 439).

(24) C. Dufraisse and J. Le Bras, *Bull. Soc. Chim. France*, **4**,1037 (1937); C. Dufraisse and J. Houpillart. *Compt. Rend.*, **205**, 740 (1937).

(25) No *endo*-peroxide was detected from tetralin hydroperoxide either, but in this case the detection limit was not less than 100 mg because the large quantity of nonvolatile products from the hydroperoxide (ketone and alcohol) prevented purification and concentration of the *endo*-peroxide by chromatography.

therefore do not yield singlet oxygen in significant quantities.

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Rate Constants for the Self-Reactions of *n*- and *sec*-Butylperoxy Radicals and Cyclohexylperoxy Radicals. The Deuterium Isotope Effect in the Termination of Secondary Peroxy Radicals[1,2]

Sir:

It is a requirement of the Russell cyclic mechanism[3] for the self-reaction of secondary peroxy radicals that the α hydrogen on one peroxy radical is transferred to the second peroxy radical in one of the rate-controlling steps of the reaction.[4] The rate of reaction should therefore be lower the more firmly the α hydrogen is bound to the peroxy radical. Furthermore, the reaction should exhibit a deuterium isotope effect if the α hydrogen is replaced by deuterium.[3,5] We have now definitely observed both effects.

The α hydrogen will be more firmly bound in a peroxy radical derived from a saturated hydrocarbon than in one in which the peroxy group is adjacent to a π-electron system. We have measured absolute termination constants at 30° for many peroxy radicals of the latter type[6] since the parent hydrocarbons are readily oxidized. Although it is not possible to obtain a reasonable chain length by oxidizing unbranched paraffins at 30°, the termination constants for saturated peroxy radicals can be readily obtained by the following procedure. A saturated hydroperoxide, R'OOH, is added to a readily oxidizable substrate, RH, in sufficient quantity that all the peroxy radicals involved in hydrogen abstraction from RH and involved in termination are derived from the added hydroperoxide.[7] The reaction scheme can be represented as

Initiation

$$\longrightarrow \mathrm{R}\cdot \tag{1}$$

Propagation

$$\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{ROO}\cdot \tag{2}$$

(transfer)

$$\mathrm{ROO}\cdot + \mathrm{R'OOH} \longrightarrow \mathrm{ROOH} + \mathrm{R'OO}\cdot \tag{3}$$

$$\mathrm{R'OO}\cdot + \mathrm{RH} \longrightarrow \mathrm{R'OOH} + \mathrm{R}\cdot \tag{4}$$

Termination

$$\mathrm{R'OO}\cdot + \mathrm{R'OO}\cdot \longrightarrow \text{inactive products} \tag{5}$$

Rate constants for the self-reaction of saturated peroxy radicals derived from *n*- and *sec*-butyl hydroperoxide and cyclohexyl hydroperoxide[8] were obtained by the rotating sector method using tetralin and α-methylstyrene as the oxidation substrates. These results are compared in Table I with previously determined[6] rate constants for chain termination in oxidizing hydrocarbons which give peroxy radicals of generally similar structure except that the α hydrogen is activated by a π-electron system. In all three cases the rate constants for the self-reactions of the saturated peroxy radicals are significantly smaller than for the unsaturated radicals.

Table I. Comparison of Termination Constants ($2k_5$ in M^{-1} sec^{-1}) for Saturated and Unsaturated Peroxy Radicals at 30°

Saturated peroxy radical from	Unsaturated peroxy radical from
n-Butyl hydroperoxide (0.4×10^8)	1,4-Pentadiene (11×10^8)
sec-Butyl hydroperoxide (1.5×10^6)	3-Heptene (6.4×10^6)
Cyclohexyl hydroperoxide (2.0×10^6)	Cyclohexene (5.6×10^6)

Previous work[3,5] has suggested that replacement of the α hydrogen by deuterium reduces the rate constant for the chain termination of secondary peroxy radicals by about a factor of 2. Because of the uncertainties involved in the initial experiments, we have remeasured this isotope effect by a more sensitive procedure. Diphenylmethyl hydroperoxide and *sec*-butyl hydroperoxide (normal, or deuterated at the α position[9]) were added to an oxidizable substrate as already described. Under standard conditions, differences in the oxidation rates in the presence of normal and deuterio hydroperoxide must reflect differences in the rate constant of reaction 5 (*i.e.*, in the rate constant of termination) since all the other rate constants will be identical. The results are given in Table II. The average isotope effect, $(k_5)_\mathrm{H}/(k_5)_\mathrm{D} = 1.37 \pm 0.14$, confirms the earlier work. The α hydrogen must be transferred in the rate-determining step of chain termination.

Table II. Deuterium Isotope Effect in Chain Termination at 30°

Peroxy radical	Substrate	$(\mathrm{Rate})_\mathrm{H}/(\mathrm{rate})_\mathrm{D}$
$\mathrm{Ph_2CH(D)OO}\cdot$	Tetralin	1.21
$\mathrm{Ph_2CH(D)OO}\cdot$	Styrene	1.37
$\mathrm{Ph_2CH(D)OO}\cdot$	Diphenylmethane	1.51
$\mathrm{C_2H_5(CH_3)CH(D)OO}\cdot$	Tetralin	1.23
$\mathrm{C_2H_5(CH_3)CH(D)OO}\cdot$	Styrene	1.51

The present results taken together with the fact that singlet oxygen is evolved in the self-reaction of *sec*-butylperoxy radicals[4] provide convincing evidence that the Russell mechanism plays an important role in the termination of oxidation chains involving secondary

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[1] Absolute Rate Constants for Hydrocarbon Oxidation. X. For part IX see J. A. Howard and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 1056 (1968).

[2] Issued as N.R.C. No. 9993.

[3] G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

[4] The transition state is represented in the preceding communication.[1]

[5] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **43**, 2737 (1965), **44**, 1119 (1966).

[6] J. A. Howard and K. U. Ingold, *ibid.*, **45**, 793 (1967).

[7] J. A. Howard, W. J. Schwalm, and K. U. Ingold, Preprints of the International Oxidation Symposium, Vol. 1, Stanford Research Institute, San Francisco, Calif., 1967, p 3.

[8] A sample of which was kindly provided by R. C. Williamson, Jr., of Gulf Research and Development Co.

[9] The α-deuterio alcohols were prepared from the ketones by reduction with lithium aluminum deuteride and were then converted to the α-deuterio hydroperoxides by known methods.[10,11] The normal hydroperoxides were also prepared from the ketones by the same procedures.

[10] A. G. Davies, R. V. Foster, and A. M. White, *J. Chem. Soc.*, 1541 (1953).

[11] H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, **76**, 2987 (1954).