Gas- and liquid-phase oxidations of butane

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These are the fragment ions formed from the unrearranged cyclohexene-3,3,6,6-d_4 ion, assuming that the mechanisms in Schemes I and II are valid for the reactions induced by EI. The increased ion currents may, therefore, indicate that, as might be expected,[38,39] on raising the electron energy the rates of the fragmentation reactions are enhanced to a greater degree than the rates of the allylic rearrangements effecting H–D randomization.

Conclusion

The same reactions of cylohexene appear to be induced by FI at 10^{-11}–10^{-5} sec and by nominally 12-eV EI, although the amount of internal excitation energy is somewhat greater in the case of EI. The same H–D rearrangements appear to be induced in cyclohexene-3,3,6,6-d_4 by both EI and FI. The reactions induced by FI should not be significantly influenced by external electric fields at times $>2 \times 10^{-11}$ sec. We, therefore, conclude that with cyclohexene and cyclohexene-3,3,6,6-d_4 the reactions induced by low-energy (nominally 12 eV) EI are probably essentially similar in nature to the reactions occurring at 10^{-11}–10^{-5} sec following FI. Major differences are likely to be limited to reaction rates being somewhat more rapid following EI due to greater internal excitation energies.

Gas- and Liquid-Phase Oxidations of n-Butane

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Abstract: The rates and products of t-Bu_2O_2-initiated oxidations of n-butane have been studied in the gas and liquid phase at 100 and 125°. After allowance for concentration changes, effects of phase change at 125° are surprisingly small. In neat liquid butane at 125°, yields of hydroperoxide are as high as 77% at low rates of initiation. As the rate of initiation increases and as the concentration of butane decreases, yields of sec-butyl alcohol and methyl ethyl ketone (chain termination products) and of ethanol and acetaldehyde (cleavage products of sec-BuO· radicals) increase, and kinetic chain lengths decrease. With 0.044 M butane in the gas phase, less than 0.5 molecule of butane is consumed per initiating t-BuO· radical, and oxidation of methyl radicals (from t-BuO· radicals) accounts for much of the oxygen consumed. The methyl and ethyl (peroxy) radicals from cleavage of t-BuO· and sec-BuO· radicals complicate determinations of some important ratios of rate constant, but we estimate that 50–70% of the interactions of sec-BuO_2· radicals are nonterminating (in either phase). The ratio of cleavage to propagation for sec-BuO· radicals measured in separate experiments is about eight times as large as for t-BuO· radicals in the liquid phase and significantly larger than estimated from oxidation experiments. From the ratio of sec-BuOH to n-BuOH formed, we calculate that the relative reactivities of the secondary and primary C–H bonds for attack by peroxy radicals at 100° is about 45:1.

Earlier fundamental studies of autoxidations of hydrocarbons have been concerned with liquid-phase oxidations below 100°, gas-phase oxidations about 250°, and reactions of alkyl radicals with oxygen in the gas phase at 25°. In a previous investigation of the transitions between these three regions, we studied the rates and products of oxidation of isobutane[2] between 50 and 155°. We now have extended that investigation to n-butane in order to determine the effects of temperature, concentration, and phase change on the rates and products of oxidation of n-butane, to establish the most important elementary steps, and to compare the oxidations of n-butane and isobutane.

Experimental Section

Materials. Oxygen (Matheson) and n-butane (Phillips) were research grade gases. Di-*tert*-butyl peroxide (Lucidol) was distilled under vacuum; no *tert*-butyl alcohol or acetone was detected by glpc. We prepared sec-Bu_2O_2 in 98% purity by the procedure of Mosher, *et al.*[3]

Procedures. The equipment, techniques, and procedures used for this work were similar to those used previously for isobutane[2] except for the analyses of neat n-butane.

When benzene was used as a solvent, it was first weighed into the reaction flask. n-Butane, measured in a larger calibrated vessel and introduced into this flask through a capillary side arm and stopcock, was frozen, and a known amount of oxygen was forced into the flask with a Toepler pump. Initiator from a tared microliter syringe was then injected through another capillary side arm fitted with a serum cap. After the flask was charged, both capillary arms were sealed off, and the flask was immersed in a constant temperature bath. During liquid-phase runs, the vessel was shaken with a Burrell wrist-action shaker. Oxidation was stopped by quickly cooling the flask to room temperature.

Analyses. Analyses on noncondensable gases were carried out by the same procedures used in isobutane experiments,[2] using a Cu–CuO combustion furnace coupled to a gas buret. Mixtures of CO and H_2 from sec-Bu_2O_2 experiments were analyzed by mass

(1) (a) Stanford Research Institute; (b) Bell Laboratories.
(2) D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, *Advan. Chem. Ser.*, No. 76, 40 (1968).
(3) F. Welch, H. R. Williams, and H. S. Mosher, *J. Amer. Chem. Soc.*, 77, 551 (1955).

Table I. Rates of Oxidation (R_O) of n-Butane in the Liquid Phase at 100 and 125°

| Run no. | Temp, °C | Reaction time, min | Liquid vol, ml | Initial concentrations, M | | | Reactants consumed, mM | | Rates —M/min × 10^6— | |
				t-Bu$_2$O$_2$ × 10^3	Benzene	n-BuH	t-Bu$_2$O$_2^a$	O$_2$	R_O	R_i^a
23	100	1544	15	1.87	0	8.12	0.118	4.38	2.83	0.158
102	100	1508	20.12	2.44	0	8.12	0.150	4.72	3.13	0.199
6	100	1439	17	41.8	0	8.12	2.5	20.9	14.5	3.41
15	100	1462	8.9	63.2	0	8.12	3.8	26.0	17.8	5.16
25	100	4339	4.3	65.9	0	8.12	11.7	84.6	19.5	5.38
110	100	284	7.78	38.4	0	8.12	0.768	6.56	23.4	3.12
111	100	1124	7.94	2.25	0	8.12	0.167	4.34	3.84	0.18
93	125	1452	12.1	0.914	9.34	0.19	0.647	3.73	2.57	0.891
89	125	1230	11.5	0.899	9.27	0.386	0.582	2.86	2.32	0.948
75	125	960	10.70	0.897	8.85	0.717	0.499	4.10	4.27	1.04
91	125	960	8.02	0.915	7.59	1.69	0.509	8.78	8.48	1.06
52	125	935	9.00	0.927	4.76	3.89	0.507	15.2	16.26	1.08
57	125	907	9.55	0.933	1.27	6.23	0.500	20.6	22.71	1.10
82	125	489	18.3	0.902	0.015	7.04	0.306	11.4	23.37	1.12
104	125	201	19.35	1.94	b	7.04	0.330	7.70	38.3	2.99
106	125	201	18.95	1.93	b	7.04	0.329	8.02	39.8	2.99
31	125	178	8.9	2.91	0	7.04	0.429	6.4	36	4.6
100	125	178	7.4	33.2	0	7.04	5.01	37.2	204	50.6

[a] R_i = rate of initiation = 2Δ[t-Bu$_2$O$_2$]/time, calculated from k_d = 8.47 × 10^{-4} min at 125° [extrapolated from data of L. Batt and S. W. Benson, *J. Chem. Phys.*, **30**, 895 (1962)]; k_d = 4.08 × 10^{-5} min at 100° (in toluene solution, ref 10). [b] Solutions containing approximately 0.1% benzene because initiator was added as a benzene solution.

Table II. Products of Oxidations of Neat n-Butane in the Liquid Phase at 100 or 125°a

| | Run | | | | | | |
	6	15	25	110	111	31	100
Temp, °C	100	100	100	100	100	125	125
ΔO$_2$	20.9	26.0	84.6	6.56	4.34	6.4	34.2
Δt-Bu$_2$O$_2^b$	2.5	3.8	11.7	0.77	0.17	0.4^b	4.5^b
CO				0.72	<0.1		
CO$_2$				<0.01	0		
RO$_2$H^c:BuO$_2$H	12.1	14.4	32.6	4.06	3.73	4.6	16.7
EtO$_2$H^d	0.6	1.1	2.4	0.26	0.10	0.3	5.2
RO$_2$H/ΔO$_2$, %	61	60	41	62	86	77	59
t-BuOH + MeOH^e	5.2	6.6	17.5	0.72	0.31	0.51	7.6
Me$_2$CO			5.2	0.29	0.0091		Present
sec-BuOH^f	15	19	56	3.1	5.9	4.6	23
sec-BuOH^g	3.9	5.4	27	-0.6	2.44	0.5	7.8
n-BuOH^f				0.1	0.27		
MeCOEt	1.9	3.2	13.9	0.07	0.33	0.2	3.3
EtOH^f	0.7	1.4	4.2	0.22	0.21	0.3	6.9
EtOH^g	0.2	0.4	2.0	-0.04	0.11	0	2.2
AcH	0.7	1.2	1.7	0.65	0.12	0.5	4.1
Butenes				<0.1	<0.1		
% ΔO$_2$ in products	75	77	67	84	93,^h 136^i	86	82
Δn-BuH^j	18.7	23.4	77.7	4.2	4.1	5.6	35.2
Conversion % on n-BuH	0.13	0.32	0.95	0.066	0.065	0.09	0.66

[a] See Table I for some details; all concentrations mM; all products determined by glpc unless otherwise noted. [b] Values at 125° are experimental; others are as in Table I. [c] By iodometric titration.[2,3] [d] Calculated on the basis that BuO$_2$/Et$_2$OH = (sec-BuOH)$_{glpc}$ + (n-BuOH)$_{glpc}$/(EtOH)$_{glpc}$ and that a 90% yield of each alcohol results from Ph$_3$P reduction of each hydroperoxide. [e] MeOH is not resolved from t-BuOH by glpc. [f] Experimental values including alcohols formed from Ph$_3$P reduction of the hydroperoxides. [g] Corrected for alcohol formed from hydroperoxide.[c,d] [h] Excludes excess sec-BuOH but includes termination products. [i] Includes excess sec-BuOH. [j] ΣRO$_2$H + corrected sec-BuOH + corrected EtOH + AcEt; see text.

spectrometry. In some of the oxidation runs, n-butane was distilled from the reaction vessel at −80°, and the residual products were dissolved in benzene. In other runs, all the reaction mixture was distilled into a trap, benzene or xylene was added, and analyses were performed directly on the chilled solutions. One portion of the product solution was analyzed for hydroperoxide by the Wibaut[4a] or the Hiatt[4b] iodine titration method; another was treated with 10% excess triphenylphosphine to reduce the hydroperoxide to alcohol, then analyzed by glpc on a 10-ft Carbowax-20M on Chromosorb P column. Control experiments showed

that such reduction of sec-BuO$_2$H (but not other secondary hydroperoxides) gave only a 90% yield of the expected sec-BuOH and that no by-products appeared during glpc. Alcohol yields have been corrected accordingly.

In two very low conversion runs (<0.1%) at 100°, these procedures were modified in the following way.

(1) All reactants were checked by glpc for trace amounts of products expected from oxidation of n-BuH and, where found, were corrected; a trace of toluene in xylene solvent was similarly corrected when using toluene as internal standard.

(2) After removal of permanent gases (O$_2$, CO) about 2% of the reaction mixture (800 μmol) was distilled out at −80°, trapped, and analyzed for CO$_2$ by mass spectrometry.

(3) After addition of about 1 ml of xylene solvent to the reaction mixture, most (∼90%) of the n-BuH was removed by distil-

(4) (a) J. P. Wibaut, H. B. van Leeuwen, and B. van der Wal, *Recl. Trav. Chim. Pays-Bas*, **73**, 1033 (1954); (b) R. R. Hiatt, C. W. Gould, and F. R. Mayo, *J. Org. Chem.*, **29**, 3461 (1964).

lation at −96 or at −80° to facilitate handling the samples at room temperature.

(4) Hydroperoxide titers were measured as before on the xylene solution.

(5) Toluene was added to the xylene solution as internal standard and the mixture, sealed in a bulb with a Swagelok fitting plus a Teflon-clad serum cap, was analyzed by flame ionization glpc using a 20 ft × $^1/_8$ in. column of Carbowax-20M on Chromosorb P. Temperature programming between 70 and 175° facilitated rapid removal of less volatile xylene. This column resolves all known products except for butenes from n-butane and MeOH from t-BuOH. The n-BuH distillate also contained small amounts of most products and was analyzed after expansion to the gas phase by glpc in much the same way as the xylene solution, particularly for AcH, the major codistillate.
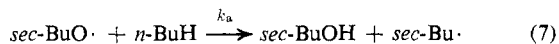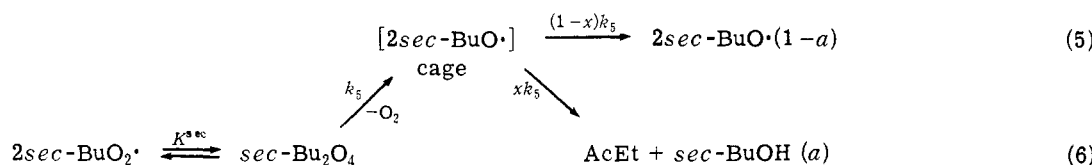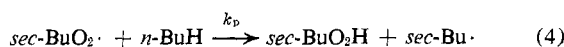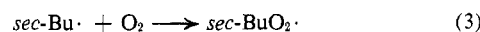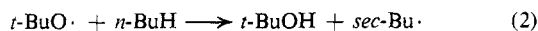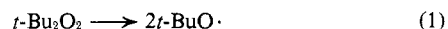
Products in the gas-phase samples of n-BuH distillate significantly decreased in concentration with time, suggesting that polar products such as AcH were being absorbed by the vessel walls. Procedures such as heating the vessel or adding H_2O to desorb the products gave erratic results. Alternative procedures to 3, to avoid distilling n-BuH and a double analysis, also gave unreliable results when tried on prepared mixtures of products in n-BuH.

A glpc procedure for analyses of sec-Bu_2O_2 solutions utilized a $^1/_8$ in. × 10 ft didecyl phthalate (5% on Chromosorb G) column at 85°. From the absence of sec-BuOH or AcEt, no decomposition of sec-Bu_2O_2 occurred during glpc.

In our tabulated data, liquid-phase concentrations of n-BuH and benzene (where used) are corrected for partitioning between the gas and liquid phases by use of Raoult's law, liquid and vapor density,[5] and vapor pressure data.[6]

Liquid-Phase Oxidations

General Mechanism. n-Butane has been oxidized previously[7] in the liquid phase at 145°. Conversions were high and the products, acetic acid and methyl ethyl ketone,· were mostly secondary products. Although these data may be useful for high conversion processes, they tell us little about the initial propagation and termination steps.

Our oxidations were carried out at both 100 and 125°. Conversions of n-butane were always kept below 1%, usually below 0.5%, and in two cases below 0.1%, to avoid secondary oxidation. Excess oxygen was present in all runs. Rates are summarized in Table I and products in Table II.

Measured yields of hydroperoxides, based on consumed oxygen, for oxidation of the neat hydrocarbon ranged from 41 to 86% at 100° and from 59 to 77% at 125°. The other products were smaller amounts of sec-butyl alcohol, n-butyl alcohol, ethanol, acetaldehyde, methyl ethyl ketone, acetone, and $tert$-butyl alcohol from the initiator. Trace amounts of butenes were found in low conversion runs, but their origin is uncertain. A small amount of CO was formed in all the runs but was

(5) R. H. Perry, et al., "Chemical Engineers Handbook," 4th ed, Section 3, 1963, p 156.

(6) T. Earl Jordan, "Vapor Pressure of Organic Compounds," Interscience, New York, N. Y., 1954, Chapter 1.

(7) E. A. Blyumberg, G. E. Zaikov, and N. M. Emanuel, Neftekhimiya, 1, 235 (1961).

measured in only two. No significant amounts of CO_2 were found. About 70–90% of the oxygen consumed is accounted for. Because of the low conversions of n-butane, the absolute amounts of products are small, and some loss of product, particularly AcH, during analyses could not be avoided (see Experimental Section). Control experiments with about 7 mM sec-BuO_2H in pentane (to facilitate product analyses) gave only 4% decomposition in 1500 min at 100°. Addition of pentanone did not increase the rate of decomposition of sec-BuO_2H.

The products and kinetics in the early stages of both the liquid- and gas-phase oxidations of n-butanes are largely explained by the following steps, most of which also apply to the oxidation of isobutane. Such small amounts of n-BuOH were found that we can neglect the participation of n-BuO_2· in the overall scheme.

$$t\text{-}Bu_2O_2 \longrightarrow 2t\text{-}BuO \cdot \tag{1}$$

$$t\text{-}BuO \cdot + n\text{-}BuH \longrightarrow t\text{-}BuOH + sec\text{-}Bu \cdot \tag{2}$$

$$sec\text{-}Bu \cdot + O_2 \longrightarrow sec\text{-}BuO_2 \cdot \tag{3}$$

$$sec\text{-}BuO_2 \cdot + n\text{-}BuH \xrightarrow{k_p} sec\text{-}BuO_2H + sec\text{-}Bu \cdot \tag{4}$$

$$[2sec\text{-}BuO \cdot] \xrightarrow{(1-x)k_5} 2sec\text{-}BuO \cdot (1-a) \tag{5}$$

$$2sec\text{-}BuO_2 \cdot \underset{K^{sec}}{\rightleftharpoons} sec\text{-}Bu_2O_4 \qquad AcEt + sec\text{-}BuOH \ (a) \tag{6}$$

$$sec\text{-}BuO \cdot + n\text{-}BuH \xrightarrow{k_a} sec\text{-}BuOH + sec\text{-}Bu \cdot \tag{7}$$

$$sec\text{-}BuO \cdot \xrightarrow{k_d} Et \cdot + AcH \tag{8}$$

Et· radicals then react like sec-Bu· radicals. In reactions 5 and 6, a represents the fraction of all sec-BuO_2· and x the fraction of all caged sec-BuO· radical interactions that are terminating. If the Et· radicals give rise to EtO_2· and EtO· radicals by reactions like 3–7 and with the same rate constants, then the following steady-state equation, like one developed for isobutane,[2] applies

$$-d[O_2]/dt = R_O = R_i/2a + (R_i/2k_t)^{1/2}k_p[\text{BuH}] \tag{9}$$

where R_i is the rate of production of initiating radicals. Because of our assumption above, a refers here to interactions of both EtO_2· and sec-BuO_2· radicals, and the last term in eq 9 is the oxygen uptake associated with formation of ethyl and butyl hydroperoxides. The $R_i/2a$ term is then the sum of two other terms, $R_i/2$ and $R_i(1 - a)/2a$, which correspond, respectively, to oxygen appearing in termination products and to oxygenated products that are neither hydroperoxide nor termination products (e.g., sec-BuOH and cleavage products of sec-BuO· radicals, except EtO_2H).

According to eq 9, a plot of R_O against [n-BuH] at constant R_i should be a straight line with intercept $R_i/2a$ as [n-BuH] approaches zero. In Figure 1, the rates of oxidation of butane with 0.9 mM t-Bu_2O_2 in benzene solution at 125° show the oxidation to be less than first order in hydrocarbon at high butane concentrations and

higher than first order at low concentrations. Such behavior is often found on dilution of aliphatic hydrocarbon by an aromatic solvent.[8,9] From the value of the intercept 0 to 2×10^{-6} M/min, and an average value for R_i of $(1.04 \pm 0.06) \times 10^{-6}$ M/min, a may be as small as 0.2 and as large as 1. From the slope of most of the curve in Figure 1, 3.70×10^{-6}, $k_p/(2k_t)^{1/2} = 0.0036$ (min $M)^{-1/2}$.

Calculation of a, x, and k_5/k_6. The calculations in this section show that although the overall rate of termination by sec-$RO_2\cdot$ radicals at 100° may still be almost 100 times as fast as for t-$RO_2\cdot$ radicals,[10,11] the rates of interactions are nearly comparable. Thus, a significant fraction of sec-$RO_2\cdot$ radicals also must interact to form caged pairs of sec-$RO\cdot$ radicals, many or all of which may diffuse from the cage to form excess alcohol and cleavage products. The somewhat faster and concurrent concerted termination path provides the bulk or possibly all of the termination for sec-$RO_2\cdot$ radicals at 100° but contributes less than half the total rate of interaction above 150° where a significant and probably major fraction of interactions gives free sec-$RO\cdot$ radicals.

The products of oxidation in Table II can also be used to calculate a. From eq 9, a is defined as the fraction of crossed- and self-interactions of sec-$BuO_2\cdot$ and $EtO_2\cdot$ radicals that terminate, and a is measured by the sum of the terminating products of reactions 5 and 6 and divided by the sum of all products of these reactions. At high hydrocarbon and low initiator concentrations, formation of cleavage products is minor. The value of a then depends primarily on interaction of sec-$BuO_2\cdot$ radicals, and the products of interactions of $EtO_2\cdot$ radicals can be neglected. Since both reactions 5 and 6 of sec-$BuO_2\cdot$ radicals give sec-BuOH (not sec-BuO_2H), terminating products of eq 5 and 6 are measured by twice the MeCOEt formed; the other products of eq 5 are measured by the sec-BuOH (not counting that from sec-BuO_2H) in excess of the MeCOEt, i.e., sec-BuOH — MeCOEt (reaction 7) plus one-half the total cleavage products, (EtOH + AcH)/2 (reaction 8). On this basis, six of the seven experiments in Table II give, respectively, $a = 0.58, 0.47, 0.64$, and 0.3 at 100°, and 0.36 and 0.39 at 125°. (No value was calculated for run 111 because of the suspiciously high value for sec-BuOH corrected.) The highest value of a in each group is from a run carried out at a higher concentration of initiator, giving more cleavage products, and should therefore give a poorer approximation for a. To the extent that the cleavage products listed (particularly AcH) were oxidized further or lost, or both, the estimated contribution of cleavage is too low and a is too large. To the extent that sec-BuOH and sec-BuO_2H were oxidized or decomposed to AcEt, a is also too large. If corrected for the small amount of decomposition of sec-BuO_2H, a becomes slightly larger. Thus, these product studies suggest that a, the fraction of sec-$BuO_2\cdot$ interactions that terminates in neat liquid butane, is 0.3–0.6 at 100° and 0.18–0.35 at 125°.

(8) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044, 1250 (1964).

(9) D. G. Hendry and G. A. Russell, *J. Amer. Chem. Soc.*, **86**, 2368 (1964).

(10) J. E. Bennett, D. M. Brown, and B. Mile, *Trans. Faraday Soc.*, **66**, 386 (1970).

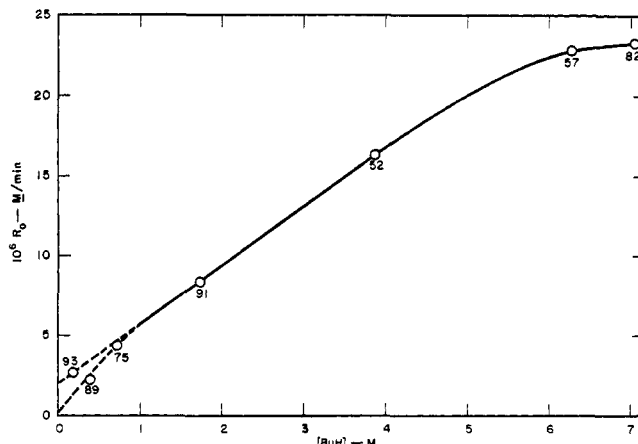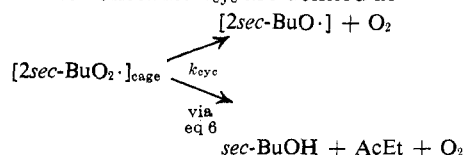(11) J. A. Howard, K. Adamic, and K. U. Ingold, *Can. J. Chem.*, **47**, 3803 (1969).

Figure 1. Rate of oxidation (R_O) with 0.9 mM t-Bu_2O_2 at 125° of n-butane as a function of its concentration in benzene.

From the data of Hiatt and Szilagyi on decompositions of sec-Bu_2O_2 in toluene,[12] x, the fraction of interactions of $2sec$-BuO$\cdot$ radicals that terminate, appears to range from 0.52 at 35° to 0.35 at 110° and 0.28 at 140°. These numbers are based mainly on yields of bibenzyl obtained from sec-BuO$\cdot$ radicals that escaped from the solvent cage and are corrected for the 30% of peroxide that decomposed to hydrogen and methyl ethyl ketone by a nonradical mechanism. However, the authors[12] suggest that if only part of the escaping sec-BuO$\cdot$ produces bibenzyl, x may be as small as zero.

In the radical-induced decompositions of sec-BuO_2H in benzene solution at 45° by Hiatt, *et al.*,[13] 1.0 hydroperoxide was decomposed per initiating radical, corresponding to $a = 1$. Similar experiments at 100° were less successful,[13] because secondary reactions involving oxygen and the peroxide decomposition products prevented the use of kinetic chain length as a measure of a.

Values of k_5/k_6 were calculated from the relationship $(1 - a)/a = (1 - x)k_5/(xk_5 + k_6)$, which corresponds to $k_5/k_6 = (1 - a)/(a - x)$. From this relation the lower limits of k_5/k_6 are 2.3–0.67 for $x = 0$ and $a = 0.3$–0.6 at 100°; k_5/k_6 becomes infinite as x becomes very close to a and negative for $x > a$. For $x = 0.1$ and $a = 0.3$–0.6, $k_5/k_6 = 3.5$–0.80. The best values appear to be 0 $< x < 0.1$, and 1 $< k_5/k_6 < 2$ at both 100 and 125°, 0.3 $< a < 0.5$ at 100° and 0.3 $< a < 0.4$ at 125°.

These values of k_5/k_6 are in fair agreement with our extrapolation of data on the interactions of tertiary and secondary alkylperoxy obtained at lower temperatures. Recent experiments by two groups of workers[10,11] have shown that for the equilibrium between two tertiary alkylperoxy radicals and a tetraoxide molecule (corresponding to K^{sec} in eq 5 and 6), $\Delta H°$ and $\Delta S°$ are nearly the same for a wide variety of alkyl groups. It seems reasonable then that, for simple alkylperoxy radicals, $K^{sec} \sim K^{tert}$. From a simple steady-state treatment of reactions 5 and 6, $k_{cyc} = k_6 K^{sec}$ and $k_{cage} = k_5 K^{sec}$ where the rate constants k_{cyc} are defined as

$$[2sec\text{-}BuO_2\cdot]_{cage} \xrightarrow[\substack{\text{via} \\ \text{eq } 6}]{k_{cyc}} \begin{array}{l} [2sec\text{-}BuO\cdot] + O_2 \\ \\ sec\text{-}BuOH + AcEt + O_2 \end{array}$$

(12) R. Hiatt and S. Szilagyi, *ibid.*, **48**, 615 (1970).

(13) R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *J. Org. Chem.*, **33**, 1428 (1968).
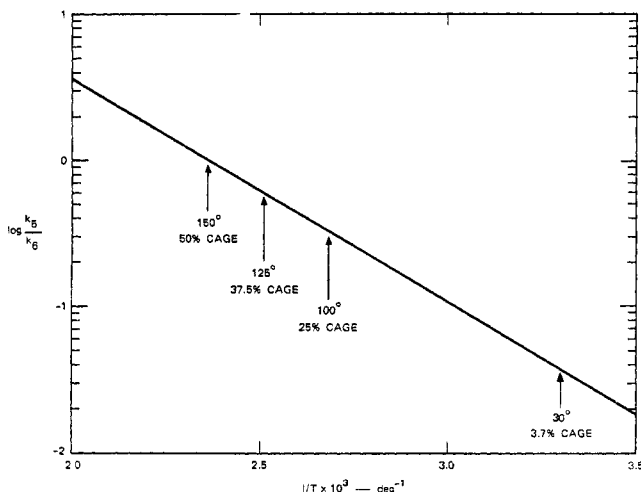
Figure 2. Ratio of the contributions of cage and concerted paths (k_5/k_6) for the interaction of $2sec$-$BuO_2\cdot$ radicals as a function of temperature for $\Delta E = 7.1$ kcal/mol.
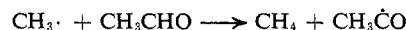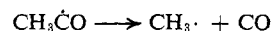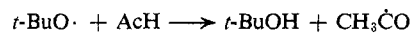
At 30° and below, rate and isotope effect studies[10,14] indicate that sec-$RO_2\cdot$ radicals terminate mostly or entirely by a fast, cyclic process corresponding to k_{cyc} above with an average value at 30° of $k_{cyc} = 10^6$ l./(mol sec) and with an activation energy of 1.9 kcal/mol (estimated for the self-termination of secondary heptyl-peroxy radical).[10] Rate parameters for k_{cage} may be estimated on the basis that they must be similar to those for $2t$-$RO_2\cdot$ radicals for which cage recombination is the only path leading to termination. At 30° rate constants for termination for t-$RO_2\cdot$ radicals range from 1.4×10^3 to 7.3×10^3 $(M$ sec$)^{-1}$ for tertiary butyl-peroxy and 2-methyl-2-pentylperoxy radicals, respectively,[11] with corresponding energies of activation of 8.7 and 9.3 kcal/mol. Taking an average value of 4.5×10^3 $(M$ sec$)^{-1}$ and $a = 0.13$ gives 3.6×10^4 $(M$ sec$)^{-1}$ for the total rate of interactions of t-$RO_2\cdot$ radicals equal to k_{cage} for sec-$RO_2\cdot$ radicals at 30°.

Combining the values above, $k_{cage}^{(30°)}/k_{cyc}^{(30°)} = (3.6 \times 10^4)/(1.0 \times 10^6) = 0.036$ and from the definition of the constants, $k_5^{(30°)}/k_6^{(30°)} = 0.036$ and $E_5 - E_6 = 9.0 - 1.9 = 7.1$ kcal/mol. Extrapolating k_5/k_6 using an Arrhenius plot (Figure 2), $k_5^{(100°)}/k_6^{(100°)} = 0.33$ and $k_5^{(125°)}/k_6^{(125°)} = 0.60$. These values are in good agreement with the lower value of $k_5/k_6 = 0.7$, calculated from our data.

Abstraction–Cleavage Ratio for sec-$BuO\cdot$ Radicals in n-Butane. To avoid the problems associated with analysis for AcH in n-butane, we have carried out several experiments with sec-Bu_2O_2 to measure the ratio of abstraction (reaction 7) to cleavage (reaction 8) of sec-$BuO\cdot$ radicals at 100° in isobutane. The value of k_a/k_d in n-BuH was then estimated from the value in i-BuH using data for t-$BuO\cdot$ radicals in these two solvents:[15] $(k_a/k_d)^{t\text{-}BuO\cdot} = 1.5(t$-BuH$)$; $(k_a/k_d)^{t\text{-}BuO\cdot} = 0.72(n$-BuH$)$.

From reactions 7 and 8 $k_a/k_d = [sec$-$BuOH]/[AcH]\cdot[RH]$. However, we must modify this equation to take into account several complications in the decomposition of sec-Bu_2O_2. One is the formation of AcEt and H_2

(14) J. A. Howard and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 1056 (1968).
(15) D. Allara, T. Mill, K. C. Irwin, and H. Richardson, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, PHYS 37, 38.

from a concurrent homolytic scission of peroxide;[12] a second is possible formation of some sec-BuOH and AcEt by cage combination of sec-$BuO\cdot$ radicals, the amount of which can be estimated from the excess of AcEt over H_2; the third complication is conversion of some AcH to CO, presumably *via* the sequence

$$t\text{-BuO}\cdot \ + \ AcH \longrightarrow t\text{-BuOH} \ + \ CH_3\dot{C}O$$

$$CH_3\dot{C}O \longrightarrow CH_3\cdot \ + \ CO$$

$$CH_3\cdot \ + \ i\text{-BuH} \longrightarrow CH_4 \ + \ t\text{-Bu}\cdot$$

$$CH_3\cdot \ + \ CH_3CHO \longrightarrow CH_4 \ + \ CH_3\dot{C}O$$

Thus, the modified form of the equation used to calculate k_a/k_d is

$$\frac{k_a}{k_d} = \frac{[sec\text{-BuOH}] - ([AcEt] - 2[H_2]) - [CO]}{([AcH] + [CO])[RH]} \quad (10)$$

Three experiments with degassed solutions of 0.094–0.099 M sec-Bu_2O_2 in i-BuH were run at 100° for 30–68 hr. Product analyses indicated the presence of both CO and H_2 in noncondensable gases. Neither ethane nor methane, the presumed products from reaction of Me· or Et· radicals with i-BuH, were found by our procedures. More AcEt was found in runs 115 and 117 than expected from H_2 analyses. Results are summarized in Table III.

Table III. Abstraction–Cleavage Ratio for sec-$BuO\cdot$ at 100° in 7.46 M Isobutane

Expt	115	116	117
Time, hr	29.7	68	65.4
$[sec\text{-}Bu_2O_2]_0$, mM	98.5	94.2	98.0
$\Delta[sec\text{-}Bu_2O_2]$, m$M$	14.7	29.2	32.7
CO	0.8		3.1
		20^a	
H_2	1.1		
AcH	8.5	17.5	10.5
sec-BuOH	15.2	19.5	32.1
AcEt	4.1	9.4	14.2
Mass balance, %^{b}	97	62^a	91
k_a/k_d, l./mol (eq 10)	0.18	0.11^c	0.23

^{a} Approximate value, sample lost. ^{b} (AcEt + sec-BuOH + AcH + CO)/(2Δsec-Bu_2O_2). ^{c} Not corrected for CO formation.

Values of k_a/k_d calculated from eq 10 are shown in Table III. Run 115 gave too little CO and H_2 to make reliable corrections on sec-BuOH and AcH but did give an excellent material balance. Since the mass spectrometry sample for run 116 was lost, excess AcEt was assumed to be zero. Run 117 gave a useful total product analysis, although the 91 % material balance was poorer than for run 115. If we neglect run 116, and average the other two, $(k_a/k_d)^{i\text{-}BuH} = 0.20 \pm 0.03$ M^{-1}.

To be useful in interpreting the butane oxidation experiments, we converted the value of $(k_a/k_d)^{i\text{-}BuH}$ to the corresponding value in n-butane by using the average relative reactivity of n-butane and isobutane toward t-BuO· and t-AmO· radicals at 100°:[15] $k_a^{n\text{-}BuH}/k_a^{i\text{-}BuH} = 0.48$ for t-BuO·; $k_a^{n\text{-}BuH} = k_a^{i\text{-}BuH} = 0.66$ for t-AmO·. If the same relative reactivities apply for sec-BuO· radicals, $(k_a/k_d)^{n\text{-}BuH}$ for sec-BuO· radicals is $0.20 \times 0.57 = 0.11$ M^{-1}. Comparison of sec-BuO· and t-AmO· radicals[15] shows that the sec-BuO· radical cleaves about eight times as fast as t-BuO· but only about one-fourth as fast as the t-AmO· radical at 100°.

Presumably the difference between sec-BuO· and t-AmO· radicals, where both lose an Et· radical, is due to added relief of steric compression in t-AmO· radicals.

This value of $(k_a/k_d)^{n\text{-BuH}}$ can now be compared with those values estimated from oxidations of n-butane in Table II. We assume (1) that total EtOH is the best measure of cleavage since it is present in all but one experiment in an amount equal to or greater than AcH and (2) that AcEt is formed only in terminations of sec-BuO· or sec-BuO$_2$· radicals that also give sec-BuOH. After correcting the [sec-BuOH] for [AcEt], eq 10 (with EtOH instead of AcH) gives the following values of k_a/k_d: experiment 6, 0.13 M^{-1}; experiment 15, 0.32 M^{-1}; and experiment 25, 0.21 M^{-1}. Butane conversions in these experiments were 0.13, 0.32, and 0.95%, respectively. Very low conversion experiments (110 and 111) gave unreliable values owing to very low or very high values of sec-BuOH. Some secondary oxidation of sec-BuOH to AcEt occurs with increasing conversion; in experiment 25 there is more AcEt than can be formed in termination. Nonetheless, all but the first k_a/k_d values are two–three times as high as our independently measured value, 0.11, indicating that abstraction of hydrogen from products by sec-BuO· radicals may be important even at 0.13% conversion.

Temperature Effects. The section on calculation of a, x, and k_5/k_6 suggests that a is only about 0.6 as large at 125° as at 100°; the formation and separation of sec-BuO· radicals are faster at higher temperatures in agreement with the data in Figure 2 and with the findings of Hiatt and Szilagyi[12] on sec-BuO· radical interactions. Assuming that $x = 0$ (the value that gives the best fit of our experimental to calculated values for k_5/k_6), and taking an average value of 0.39 for a at 125°, we calculate that $(k_5/k_6)^{125°} = 1.6$ compared with a value of 0.7 at 100°. Thus, k_5/k_6 changes by a factor of 2.3 over the range of 100–125° in good agreement with the factor of 1.8 taken from Figure 2. Chart I brings out other effects of temperature.

Chart I. Products of Liquid-Phase Oxidations of 100 mol of n-Butane at 100 and 125°

100BuH + 30t-BuO· → 22.5t-BuOH + 6.7AcMe +

Run 25 at 100°   42   34.5   18   3   2.6   2.2

sec-BuO$_2$H + sec-BuOH + AcEt + EtO$_2$H + EtOH + AcH

Run 31 at 125°   82   9   3.6   5.4   0   9

100BuH + 16t-BuO· → 9.3t-BuOH

Increasing the reaction temperature from 100 (run 25) to 125° (run 31) with about the same rate of initiation increases the kinetic chain length and the yield of sec-BuO$_2$H by factors of about 2, decreases markedly the yields of chain termination products (sec-BuOH and AcEt), but increases the amount of chain cleavage (compare yields of C$_2$ products in these experiments) in spite of a decrease in interactions of RO$_2$· radicals. Considering the competitions involved, higher temperature thus favors reaction 4 over 6, 5 over 6, and 8 over 7. If we calculate $(k_a/k_d)^{125°}$ for sec-BuO· and t-BuO· radicals as we did in the previous section on the abstraction-cleavage ratio, we find that there is more cleavage of both radicals at 125°. A similar increase in the ratio of cleavage (reaction 8) to abstraction (reaction 7) with increasing temperature has been observed by Hiatt and Szilagyi for sec-butoxy[12] and by others for tert-butoxy, isopropoxy, and ethoxy radicals,[16] consistent with the

idea that the activation energies for these cleavage reactions are always larger than those for abstraction by 2–8 kcal/mol.

Values of $k_p/(2k_t)^{1/2}$ have been calculated from the neat liquid-phase data in Table I and eq 9 (the $R_i/2a$ term was neglected because of the long chains considered). At 100°, values of 0.87, 0.63, 0.89, and 0.66 × 10^{-3} (M min)$^{-1/2}$ were obtained for runs 102, 23, and two additional runs not listed in Table I, respectively, with an average value of (0.76 ± 0.12) × 10^{-3}. At 125° values of 3.1, 2.3, and 3.0 × 10^{-3} (M min)$^{-1/2}$ were obtained for runs 106, 31, and 104, respectively, with an average value of (2.8 ± 0.3) × 10^{-3}. These ratios give $E_p - E_t/2 = 15.3 ± 3$ kcal/mol. If we make the simplifying assumption that all termination is via concerted reaction 6 and take E_t for sec-heptylperoxy radicals as 1.9 kcal/mol,[10] $E_p = 16.3 ± 3$ kcal/mol. Inclusion of reaction 5 in the calculation of E_t will raise the value of E_t (since $E_t^5 > E_t^6$, see below) thus lowering the value of E_p; our calculated value is thus an upper limit. From consideration of activation energies for a variety of radical abstractions, Knox[17] has estimated E_p for a thermoneutral propagation reaction should be about 10 kcal/mol, about the same as the value found by Benson,[18] 8–10 kcal/mol, for exothermic abstractions by polyatomic radicals from polyatomic molecules. Since the n-butane propagation step (reaction 4) is about 3.5 kcal/mol endothermic,[19] the E_p expected from Knox's thermoneutral value is about 15.5 kcal/mol, in good agreement with our experimental value of $E_p \leq 16.5 ± 3$ kcal/mol.

Cooxidations of Butane and Isobutane. This section shows that cooxidation of isobutane and n-butane gives a relative reactivity of 4:1 per molecule for attack by RO$_2$· radicals. This result combined with other data indicates that the rates of abstraction by the RO$_2$· radicals on their parent alkanes (k_p^i/k_p^n) are in the ratio of 1.3:2.0, which leads to a difference of activation energies for propagation of 1.2–1.5 kcal/mol, close to the experimental values. Estimates of the relative rates of self-reaction of sec- and t-BuO$_2$· radicals, based on these data, range from 360 to 860 compared with an estimate of 104 from independent data.

From the above considerations, $E_p = 15.8 ± 1.5$ kcal/mol for isobutane[1] seems high because this propagation step should be thermoneutral.[19] To obtain a direct estimate of the difference in E_p for n-butane and isobutane, we oxidized two neat liquid mixtures of isobutane and n-butane at 100° to less than 1% conversion. The mole ratios of isobutane/n-butane were 0.233 and 1.0, and the respective concentrations of t-Bu$_2$O$_2$ were 61 and 90.4 mM. The product ratios (t-BuOH + t-BuO$_2$H)/(sec-BuOH + sec-BuO$_2$H) were 0.938 and 4.0, respectively, after correction for t-BuOH from the initiator. The product ratios are assumed to measure the relative rates of attack on the butanes by RO$_2$· radicals. From these data and the copolymerization products equation,[20] isobutane is 4.0 times as reactive as

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(19) S. W. Benson, J. Chem. Educ., **42**, 502 (1965).
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Table IV. Rates of Reaction of n-Butane with Excess Oxygen in the Gas Phase at 125°

Run no.	Time, min	Initial concn, mM		Reactants consumed, mM		Rates, M/min $\times$ 10^8	
		n-BuH	t-Bu$_2$O$_2$	O$_2{}^a$	t-Bu$_2$O$_2$	$R_0{}^b$	$R_i{}^b$
40	988	43.8^c	0.84	1.24	0.48	125	97
88	956	47.7	0.84	1.13	0.47	119	99
120	972	93.4	0.797	1.41	0.448	145	92
26	960	150.5	0.972	2.19	0.534	228	111
39^d	976	256.0	0.815	2.32	0.460	238^d	94
37^e	1081	291.0	1.070	4.52	0.643	418^e	119
4	1314	298.6	0.910	4.00	0.610	304	92
31	947	342.0	0.91	2.72	0.50	288	106
146	901	384.0	0.208	0.928	0.111	103	24
122	883	362.0	0.886	2.63	0.467	298	106
148	927	378.0	2.67	9.32	1.451	1004	313
6	204	364.0	9.34	2.10	1.486	3610	1460
129	996	690.0	0.839	4.40	0.479	442	96
38	936	700.0	0.83	3.33	0.46	356	98
95	971	1000.0	0.889	5.61	0.498	578	103

^{a} Calculated as in footnote a of Table I. ^{b} ΔO$_2$/time or $2\Delta t$-Bu$_2$O$_2$/time. ^{c} Corresponds to a pressure of 1.1 atm. ^{d} Vessel approximately 90% coated by Teflon. ^{e} Pyrex surface area increased about 51 times by packing.

n-butane toward either t-BuO$_2\cdot$ or sec-BuO$_2\cdot$ radicals. However, Howard and Ingold[21] have found secondary peroxy radicals to be ten times as reactive as tertiary peroxy radicals in hydrogen abstraction from the same hydrocarbon at 30°. This corresponds to about six times at 100°. Hence the ratio of the rate constants for the reaction of t-BuO$_2\cdot$ radicals with isobutane ($k_p{}^i$) to the rate constant for sec-BuO$_2\cdot$ radicals with n-butane ($k_p{}^n$) is only one-sixth of 4 and $k_p{}^i/k_p{}^n = 0.67$.

If we now assume that the A factor of $k_p{}^n$ is four times as large as for $k_p{}^i$ (because of the larger number of reactive hydrogen atoms) and assign the 2.7-fold difference in reactivity per hydrogen atom to the difference in activation energies, we obtain $\Delta E_p = 0.5$ kcal/mol in excellent agreement with the individual experimental values, 16.3 and 15.8 kcal/mol.

The relative rate constants for termination between two sec-BuO$_2\cdot$ radicals, $k_t{}^{sec}$, and two t-BuO$_2\cdot$ radicals, $k_t{}^{tert}$, can also be calculated from the cooxidation data. From the average value of $k_p{}^{tert}/(2k_t{}^{tert})^{1/2} = 0.029$ (M min)$^{-1/2}$ for isobutane at 100°, the corresponding ratio 7.6 $\times$ 10^{-4} (M min)$^{-1/2}$ for n-butane, and the ratio of the k_p values above we obtain ($k_t{}^{sec}/k_t{}^{tert})^{1/2} = 25$ and $k_t{}^{sec}/k_t{}^{tert} = 625$. We can calculate this same ratio by extrapolation of other data. From an average of rate constants for self-termination of t-BuO$_2\cdot$ radicals measured by several workers[22] at 30° and from an activation energy of 9.0 kcal/mol,[11] a value of 2.6 $\times$ 10^4 l./(mol sec) at 100° is obtained. From the rate constant for self-termination of sec-BuO$_2\cdot$ radicals measured by Howard and Ingold[23] at 30° and an activation energy (for sec-heptylperoxy radicals) of 1.9 kcal/mol,[10] a value of 2.7 $\times$ 10^6 l./(mol sec) at 100° is obtained, giving $k_t{}^{sec}/k_t{}^{tert} = 104$, about one-third as large as our measured value. We believe this discrepancy is due largely to the composite experimental errors in both sets of data.

Selectivities of Alkoxy and Alkylperoxy Radicals. We have found no previous report of n-BuOH as a product in the oxidation of n-BuH. Although the amount is too small to affect material balances, its

presence in experiment 110 (Table II) affords an opportunity to calculate approximately the relative reactivity of primary and secondary C–H bonds toward RO$_2\cdot$ radicals. Of 0.33 mM initiating t-BuO$\cdot$ radicals, 0.28 mM will abstract ($k_a/k_d = 0.73$),[15] and an additional 0.18 mM sec-BuO$\cdot$ will also abstract (see above). We can estimate that the ratio of attack by t-BuO$\cdot$ radicals on the primary and secondary C–H bonds in n-BuH, $k_a{}^{pri}/k_a{}^{sec}$, is 1:6 per bond or 1:4 per molecule.[15] Thus, of 0.46 mM RO$\cdot$ radicals (both t-BuO$\cdot$ and sec-BuO$\cdot$), about 0.09 mM will attack primary C–H bonds giving just about one-third of the n-BuOH found, and the remainder will attack secondary C–H bonds. If the remaining 0.18 mM sec-BuO$\cdot$ and 5.35 mM sec-BuOH (corrected for 0.16 mM termination products as well) results from attack by sec-BuO$_2\cdot$ radicals, we can calculate the relative reactivities of single, secondary, and primary C–H bonds toward sec-BuO$_2\cdot$ radicals, $k_p{}^{sec}/k_p{}^{pri}$, as $(5.35/0.18)(3/2) = 45$. Thus, the selectivity of sec-BuO$_2\cdot$ radicals is about five times that of sec-BuO$\cdot$ or t-BuO$\cdot$ radicals toward the C–H bonds of n-BuH.[15] A recent measurement on n-pentane with added t-BuO$_2$H at 100° gives a value for selectivity of t-BuO$_2\cdot$ radical of $k_p{}^{sec}/k_p{}^{pri} = 38$.[24]

Gas-Phase Oxidations

Products. Gas-phase oxidations of n-butane at 125° were carried out with excess oxygen to conversions below 0.5%. The rates of oxidation are given in Table IV and the products in Table V.

There is little effect of reactor walls on rates or initial products, but there is some decomposition of sec-BuO$_2$H. One oxidation was carried out at 125° in a Pyrex vessel in which about 90% of the inner surface was covered with a layer of Teflon (experiment 39 in Table IV) and another in a vessel packed with Pyrex tubing, which increased the Pyrex surface area by a factor of 51 (experiment 37). The latter vessel had about 500 times as much exposed glass as the former. The rate in the Teflon coated vessel is about 0.78 times as fast as the rough control (run 4, Table IV), whereas the rate in the packed vessel is about 1.38 times as fast. Further, the average yield of hydroperoxide for 240–300 mM butane is 22 $\pm$ 4% based on ΔO$_2$ for seven

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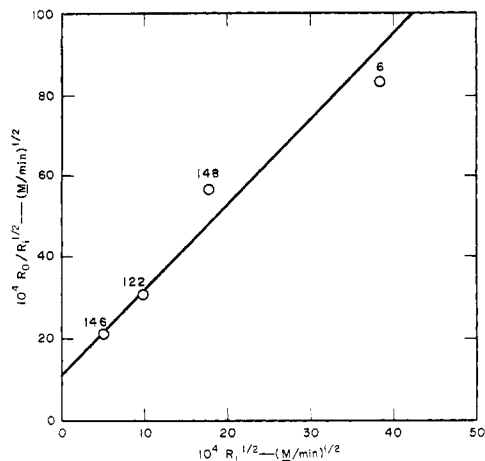
Chart II. Products of Gas-Phase Oxidations of n-Butane at 125° (Assumed Intermediate Radicals Are in Parentheses)

Run 40 (43.8 mM BuH)

100BuH
+
295O₂
+
114t-Bu₂O₂

(100sec-BuO₂·) → 19sec-BuO₂H + 5sec-BuOH + 26AcEt + (50sec-BuO·)

14AcH + 7EtOH + 28EtO₂H ← (50Et·) + 50AcH

(228t-BuO·) → 38t-BuOH + 159Me₂CO + (159Me·)

36MeOH + 19CO

370 O + 228 C + 560 H unaccounted for

Run 31 (342 mM BuH)

100BuH
+
174O₂
+
32t-Bu₂O₂

(100sec-BuO₂·) → 17sec-BuO₂H + 20sec-BuOH + 19AcEt + (44sec-BuO·)

21EtOH + 23EtO₂H ← (44Et·) + 44AcH

(64t-BuO·) → 23t-BuOH + 38AcMe + (38Me·)

CO

176 O + 49 C + 156 H unaccounted for

Run 38 (700 mM)

100BuH
+
180O₂
+
25t-Bu₂O₂

(100sec-BuO₂·) → 24sec-BuO₂H + 10sec-BuOH + 22AcEt + (44sec-BuO·)

13EtOH + 31EtO₂H ← (44Et·) + 44AcH

(50t-BuO·) → 21t-BuOH + 22AcMe + (22Me·)

3CO

165 O + 47 C + 152 H unaccounted for

Table V. Products of Oxidations of n-Butane in the Gas Phase at 125° a

	Run 40	88	31	38
Initial n-BuH	43.8	47.7	342.0	700.0
ΔO₂	1.24	1.13	2.72	3.33
Δt-Bu₂O₂ b	0.48	0.47	0.50	0.46
CO c	0.08		0.02	0.06
CO₂ d		0.12		
RO₂H e sec-BuO₂H	0.080	0.14	0.26	0.45
EtO₂H	0.116		0.36	0.57
RO₂H/ΔO₂, %	16	12	23	31
t-BuOH	0.16		0.36 f	0.38 f
AcMe	0.67		0.59	0.41
MeOH	0.15			
sec-BuOH g	0.09		0.55	0.58
sec-BuOH h	0.02		0.31	0.18
AcEt	0.11		0.30	0.40
EtOH g	0.13		0.76	0.74
EtOH h	0.03		0.33	0.24
AcH i	0.27		0.67	0.83
ΔBuH j	0.42		1.6	1.9
ΔO₂ in products, %	71		69	73

a Additional data in Table IV; all concentrations mM; all products determined by glpc unless otherwise noted. b Calculated as in footnote a of Table I. c Estimated by combustion analysis; value uncertain within a factor of two. d Isolated by fractional distillation at −116°; determined by mass spectrometry. See footnote d, Table II. f Measured as the sum of t-BuOH + MeOH peaks but taken as pure t-BuOH from the t-BuOH–AcMe–t-Bu₂O₂ balance. g See footnote f, Table II. h See footnote g, Table II. i Corrected for only 70-75% recovery of AcH in control runs. j sec-BuO₂H + corrected sec-BuOH + AcEt + (corrected EtOH + EtO₂H + AcH)/2; see text.

runs, some of which are given in Table IV. The 22% yield in the Teflon vessels indicates no wall effects, whereas the 14% yield in the glass-packed vessel indicates only a 22% reduction of yield by the large amount

of packing. These effects are so small for the large change in surface that we have neglected wall effects.

The following experiment shows that there is some heterogeneous decomposition of sec-butyl hydroperoxide: 5.94 mM peroxide was heated at 125° for 15.75 hr in the presence of 361 mM neopentane (∼12 atm at 125°) to minimize diffusion. By iodometric titration, 15% of the hydroperoxide was decomposed, corresponding to a half-life of 58 hr. Since the half-life of this peroxide is about 5 hr in dilute solution at 180°,[25] most of the decomposition at 125° must occur on the walls; it could account for a small amount of the oxidation products in Table V.

Studies of products made at three different butane pressures (Table V) revealed only primary products and carbon oxides. Searches for acetic, propionic, and butyric acids on a FFAP (fatty acid) glpc column and for bifunctional alcohols and ketones, cyclic ethers, and epoxides on a Carbowax-20M column disclosed none of these compounds.

Chart II presents some material balances normalized and extrapolated to 100 butane molecules consumed. The amount of cleavage of the sec-BuO· radicals is taken as half of the sum of the C₂ products; AcH alone is not a measure of cleavage at short-chain lengths, since it may also be formed in terminations by EtO₂· radicals.[26] CO₂ found accounted for 11% of the consumed O₂ in run 88 (Table V), and the CO₂ yields in runs 40, 31, and 38 were probably similar. This low yield of CO₂ (and CO), our failure to find carboxylic acids and bifunctional compounds containing alcohol and ketone groups, and also the high ratios of AcH to EtO₂H +

(25) R. Hiatt and K. C. Irwin, J. Org. Chem., 33, 1436 (1968).
(26) In Table V, as much or more AcH than EtO₂H + EtOH (corrected) is reported. That the reverse relation applies in Table II is probably due to poorer recoveries of AcH from the much larger quantities of BuH used in liquid-phase runs.

Figure 3. Rates of gas-phase oxidations (R_O) of 370 mM n-butane at 125° as a function of rate of initiation (R_i).

Figure 4. Rates of gas-phase oxidation (R_O) of n-butane at 125° as a function of butane concentration.

EtOH found, indicate that little secondary oxidation is occurring. Since some of the t-BuO· groups consumed are missing from the products (t-BuOH + AcMe < $2\Delta t$-Bu$_2$O$_2$), one or both of these products is incompletely recovered (or oxidized further). The material balances are greatly improved if one corrects for unrecovered acetone and t-BuOH and then assumes that the remaining missing C, H, and O atoms are in undetermined formaldehyde, CO$_2$, and H$_2$O.

The ratio t-BuOH/acetone is not proportional to the n-butane concentration; the apparent values of k_7/k_8 for t-BuO· radicals are 5.5, 1.8, and 1.3 in experiments 40, 31, and 38. The data in Chart II indicate smaller ratios (more cleavage) for sec-BuO· radicals or loss of sec-BuOH in secondary oxidations.

The major features of the oxidation of 700 mM n-butane (23 atm) are shown by run 38. (1) The chain length (ΔBuH/$2\Delta t$-Bu$_2$O$_2$ = 2.0) indicates that one-half of the products are formed by chain propagation, in agreement with the appearance of 31% of the consumed oxygen as hydroperoxides. (2) The 44% conversion of the consumed butane to C$_2$ products indicates that EtO$_2$· (and EtO·) and sec-BuO$_2$· (and sec-BuO·) radicals are of roughly equal importance in product formation, and the amount of acetone formed (22 mol/100 mol of n-butane consumed) indicates that there are about half as many MeO$_2$· radicals involved in the reaction as EtO$_2$· radicals. (3) Of 100 sec-BuO$_2$· radicals formed, about 24 propagate giving sec-BuO$_2$H, and 76 give termination products or alkoxy radicals in radical–radical interactions. Since on a statistical basis most of the radical interactions involve one sec-BuO$_2$· and one EtO$_2$· (or MeO$_2$·) radical, a in eq 9 may be estimated directly as 25/76 = 0.33. Here the number of terminations is measured by the 25 pairs of initiating t-BuO· radicals, and the number of interactions is approximated by the number of sec-BuO$_2$· radicals that did not propagate. (For the unlikely limiting case where all the RO$_2$· interactions involve $2sec$-BuO$_2$·, a = 25/38 = 0.66.) (4) If cleavage (reaction 8) and abstraction (reaction 9) are the only reactions of sec-BuO· radicals, the fraction of sec-BuO· radicals that cleave is between 100 and 81%, depending on whether all the sec-BuOH is counted as a termination product of sec-BuO$_2$· radicals or all is counted as an abstraction product of sec-BuO· radicals.
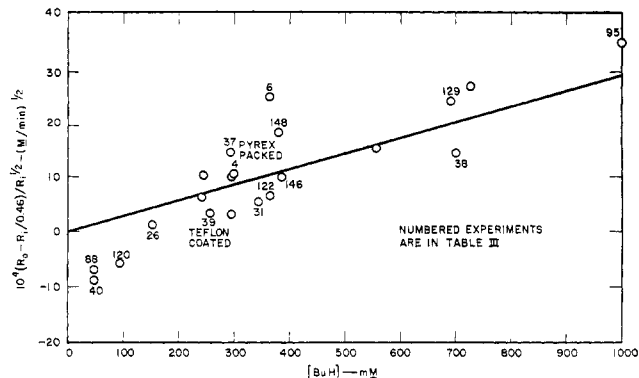
The major effects of decreasing butane concentration are best seen by comparing runs 38 and 40, with the highest (700 mM) and lowest (44 mM) concentrations (Table V and Chart II). (1) The chain length decreases from 2.0 to 0.44, the contribution of radical–radical reactions to product formation increases, and the yield of hydroperoxide decreases from 31 to 16% on the O$_2$ consumed. (2) The percentage conversion of n-butane into C$_2$ products increases from 44 to 50%, probably accompanied by a change in cleavage of sec-BuO· radicals from a minimum of 81 to a minimum of 91% (for run 38 above). (3) The ratio ΔO$_2$/ΔBuH increases from 1.80 to 2.95, mostly because of increased consumption of oxygen by Me· and Et· radicals. (4) In the 44 mM run, the value for a cannot be satisfactorily estimated by the method used for run 38 because the 114 terminating interactions considerably exceed the 81 sec-BuO$_2$· radicals available. In run 31, a similar calculation of a gives 32/83 = 0.39, slightly larger than the value of 0.33 in the 700 mM run, but more EtO$_2$· and MeO$_2$· radicals are involved in the radical–radical interactions. This point is discussed further in the next section.

Kinetics. Equation 9 can be written as $R_O/R_i^{1/2}$ = $R_i^{1/2}/2a$ + k_p[BuH]/$(2k_t)^{1/2}$. In Figure 3, $R_O/R_i^{1/2}$ is plotted against $R_i^{1/2}$ for runs 6, 148, 122, and 146 (Table IV), where the initial hydrocarbon concentrations are between 362 and 384 mM and average 372 mM. The slope corresponds to a = 0.23 and the intercept to $k_p/(2k_t)^{1/2}$ = 0.0029 (M min)$^{-1/2}$.

Equation 9 also can be written as $(R_O - R_i/2a)/R_i^{1/2}$ = k_p[BuH]/$(2k_t)^{1/2}$. Figure 4 plots the term on the left of this equation (with a = 0.23 from Figure 3) against [BuH] for ten runs in Table IV and some additional runs not reported there. For all the runs, R_i is between 92 and 111 × 10^{-8} M/min and the average value is 99.2 × 10^{-8} M/min ($R_i^{1/2}$ = 9.96 × 10^{-4} (M min)$^{-1/2}$. The straight line is the relation expected for $k_p/(2k_t^{1/2}$ = 0.0029 (from the intercept in Figure 3).

Considering the side reactions and approximations involved (see below), Figures 3 and 4 correlate fairly well the effects of changing R_i and [BuH]. The poorest agreement in Figure 4 is for the points for [BuH] < 100 mM, where the results in the section on products suggest significant involvement of MeO$_2$· and EtO$_2$· radicals. The deviation of the experimental points from a straight line in Figure 4 is probably due to an increase in a with decreasing butane concentration. Thus, if we take a = 0.40 instead of 0.23 in calculating the ordinate for ex-

periment 120 in Figure 4, the points fall on the line shown. Similarly, at the highest butane concentration (experiment 95) the points fall on the line if $a = 0.21$. Since the value 0.23 used in Figure 4 was obtained at 0.37 M (Figure 3), this pattern suggests that a for $MeO_2\cdot$ and $EtO_2\cdot$ radicals is larger than a for sec-$BuO_2\cdot$ radicals (about 0.33 at 0.7 M butane), and that at 0.044 M butane, most of the radical interactions involved $EtO_2\cdot$ radicals. The assumptions for the product studies seem less valid than in the rate studies.

The deviations in Figure 4 could also be due to a change in $k_p/(2k_t)^{1/2}$ with concentration of butane but probably are not. We expect propagation rate constants to be roughly twofold larger[21] and self-termination rate constants[10] at least an order of magnitude larger for $EtO_2\cdot$ (and probably $MeO_2\cdot$) radicals than for sec-$BuO_2\cdot$ radicals. These changes would lead to a small decrease in $k_p/(2k_t)^{1/2}$ with decreasing concentrations of hydrocarbon, opposite to the trend needed to improve agreement in Figure 4. Possibly the effect from increasing a with decreasing hydrocarbon concentration is sufficient to overtake the opposing decrease in $k_p/(2k_t)^{1/2}$.

Discussion

Effect of Phase Change. Table VI summarizes effects

Table VI. Summary of Some Kinetic Parameters for the Gas- and Liquid-Phase Oxidations of n-Butane and Isobutane

| RH	T, °C	Phase	[RH], mM	a	$\dfrac{10^3 k_p/}{(2k_t)^{1/2}}$ $(M^{-1}$ $min)^{-1/2}$
n-Butane	125	Gas	372	0.23[a]	2.9[a]
n-Butane	125	Gas	342	0.39[b,c]	
n-Butane	125	Gas	700	0.33[b,c]	
n-Butane	125	Benzene solution	1000–7040	0.3–0.5	
n-Butane	125	Neat liquid	7040	0.4[d]	2.80[e]
n-Butane	100	Neat liquid	8120	0.47[b,f]	0.76[g]
Isobutane	100	Neat liquid	7560	0.091	29[h]

[a] Run 22, Table IV, from Figure 3. [b] Calculated from reaction products. [c] Run 31, Table V (342 mM); run 40, Table V (700 mM). [d] For run 31, Table II, $a = 0.40$; for run 100, Table II, $a = 0.36$. [e] Average of runs 106, 31, and 104, Table I. [f] Run 15, Table II. [g] Average of runs 102, 7951–23, 75 and 77, Table I. [h] Reference 1.

of phase change on the oxidation of n-butane. There is no significant difference between the gas- and liquid-
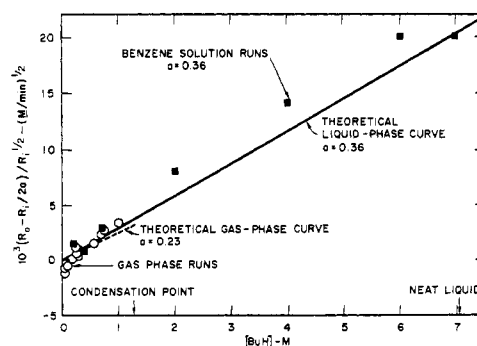
Figure 5. Rates of oxidation of n-butane in gas and liquid phase at 125°.

phase values at 125° of either a (the fraction of all peroxy radical interactions that terminate) or $k_p/(2k_t)^{1/2}$ for the same concentrations of n-butane. These relations are also shown in Figure 5, where $(R_O - R_i/2a)R_i^{1/2}$ is plotted against [BuH] for both phases, using the indicated values of a.

The insensitivity of a to phase change at 125° strongly suggests that nearly all the sec-$BuO\cdot$ radicals escape from their partners both in solution, as suggested by Hiatt and Szilagyi,[12] and in the gas phase. Then x approaches zero (like a for $2t$-$BuO\cdot$ radicals in Table VI); nearly all termination occurs by reaction 6 (with both sec-$BuO_2\cdot$ and $EtO_2\cdot$ radicals) and $a \sim k_6/(k_5 + k_6)$. At temperatures above 125°, as k_5 becomes much greater than k_6, in either nonviscous media or the gas phase (x approaches zero), some more complex termination mechanism must replace reaction 6. At high temperatures and high concentrations of n-butane, most sec-$BuO\cdot$ radicals will react by hydrogen abstraction, and long kinetic chains should be possible.

Rearrangement of Peroxy Radicals. Several workers have invoked rearrangement of peroxy radicals in order to explain the products of alkane oxidations in the gas phase.[27] We believe that the foregoing theoretical and experimental analyses show clearly that such rearrangements are not needed to explain either the kinetics or the products of oxidation, at least under these mild conditions and probably up to much higher temperatures, including the cool flame region.

(27) C. F. Cullis, F. R. F. Hardy, and D. W. Turner, *Proc. Roy. Soc.*, *Ser. A*, **251**, 265 (1959); A. Fish, *Quart. Rev., Chem. Soc.*, **18**, 243 (1964).