(with formation of ketone as in eq 6)]. Because of the apparent intrusion of a reaction such as eq 6, we do not yet know whether to attribute any of the increased chain length at 100° to escape of free RO· radicals from eq 12b. Clarifying experiments are in progress.

Registry No.—*n*-BuO_2H, 4813-50-7; *sec*-BuO_2H, 13020-06-9; α-tetralyl hydroperoxide, 771-29-9.

Homolytic Decompositions of Hydroperoxides. IV.[1a-c] Metal-Catalyzed Decompositions

R. HIATT,[1d] K. C. IRWIN, AND C. W. GOULD

Stanford Research Institute, Menlo Park, California

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t-Butyl hydroperoxide has been decomposed by a variety of cobalt salts and compounds of other metals (Fe, V, Mn, Ce, and Pb). In chlorobenzene or alkanes at 25–45° half-lives for decomposition of 0.1 *M* *t*-BuO_2H by 10^{-4} *M* catalyst ranged from 1 to 10 min. Products included approximately 88% *t*-BuOH, 11% *t*-Bu_2O_2, 1% acetone, and 93% O_2. Decompositions in alcohol–chlorobenzene mixtures yielded more acetone but were only *ca.* one-hundredth as fast as in pure chlorobenzene. Reactions in all solvents were subject to autoretardation owing partly to formation of aldehydes and carboxylic acids and partly to changes in the catalyst which caused its eventual precipitation. Decompositions of α-cumyl, *n*-butyl, and *sec*-butyl hydroperoxides were normally one-fourth to one-tenth as fast as those of *t*-BuO_2H. *n*-BuO_2H and *sec*-BuO_2H yielded 70% O_2 and the corresponding alcohol and aldehyde or ketone in a ratio of about 2. The results suggest that these reactions are essentially the same as free-radical-induced decompositions but are initiated by metal ion–hydroperoxide interactions. Generally speaking the choice of metal ion, as long as it can undergo a facile one-electron redox reaction, has little influence on either products or rates of decomposition except in the presence of olefins.

Metal ion catalyzed decompositions of hydroperoxides are important in metal ion catalyzed autoxidations of hydrocarbons. While it is generally agreed that these autoxidations are initiated by radicals generated from ion hydroperoxide interactions,[2,3] the interactions themselves and the mechanisms by which useful products arise from the hydroperoxides are poorly understood despite numerous investigations.[4] This report shows how metal-catalyzed decompositions are related to free-radical-induced decompositions (parts II[1b] and III[1c]). Only about a third of our experiments are reported.

Experimental Section

Materials.—Hydroperoxides and chlorobenzene were obtained and purified by the methods described in parts II[1b] and III.[1c] *n*-Pentane, cyclohexane, *n*-heptane, and 2,2,4-trimethylpentane were Matheson Coleman and Bell "Chromatograde" reagents, refluxed for 6 hr over CaH_2 and distilled.

Cobaltous stearate ($CoSt_2$) and cobaltous 2-ethylhexanoate ($CoOct_2$) were prepared by the methods of Dyer[5] and of Vold.[6] An aqueous solution of the sulfate was added to a neutralized ethanol solution of the carboxylic acid and the precipitate was collected and dried at 90° in vacuum. Infrared absorptions of the compounds at 1708 cm^{-1} revealed that they contained 15–20% of the free carboxylic acid, as did the cobaltous stearate obtained from K & K Laboratories. Two reprecipitations of the salts with acetone from a hexane solution gave acid-free catalysts (less than 0.5%) of decreased solubility in chlorobenzene and a higher then theoretical amount of cobalt (Table I). Cobaltic stearate ($CoSt_3$), prepared by treatment of a solution of $CoSt_2$ in acetic and stearic acids with an excess of H_2O_2, also contained free acid which was removed as above.

TABLE I

ANALYSES OF REPRECIPITATED COBALT SALTS

Salt	% cobalt Experimental[a]	% cobalt Theory
Cobaltous laurate	15.05	12.88
Cobaltous stearate	10.59	9.42
Cobaltous 2-ethylhexanoate	20.50	17.06
Cobaltic stearate	14.04	6.89
$CoCO_3$[b]	49.08	49.55

[a] Analyses were by West Coast Analytical Laboratory by both polarography and reduction to metal. [b] Baker reagent grade.

The high percentage of cobalt in these compounds indicated their formula to be $[Co(RCO_2)_2]_x[Co(RCO_2)(OH)]_y$.[6] The analysis of the cobaltic stearate showed it to be nearer CoOSt than $CoSt_3$.

Cobaltous acetylacetonate (CoA_2) was obtained from K & K Laboratories and dried at 60° under vacuum. Cobaltic acetylacetonate (CoA_3) was prepared by oxidation of the cobaltous salt with H_2O_2 in the presence of excess acetylacetone and recrystallized. V^{III}, Fe^{III}, Ni^{II}, Mn^{II}, and Ce^{II} acetylacetonates, vanadous octoate, and cobalt salicylalethylenediimine were obtained from K & K Laboratories and used without further purification.

Iron phthalocyanine (FePCN) was obtained from the Pigment Colors Division of Du Pont.

Lead naphthenate ($PbNap_2$) manganous octoate, and cupric octoate were Nuodex solutions, 24, 8, and 8%, respectively, by weight in metal.

Procedures.—Reactions in mixtures of chlorobenzene with protic solvents were started by syringing 0.2–3 ml of neat hydroperoxide into 20 ml of the catalyst-containing solution immersed in a constant-temperature bath. Reactions in alkanes were refluxed to exclude oxygen from the air and expel that produced by the peroxide decomposition. Flasks were immersed in a bath 10–15° warmer than the reflux temperature of the solvent. Boiling chips were used to minimize superheating.

Rates of decomposition were measured by pipetting aliquots into a stop bath of 1:10 AcOH–*i*-PrOH and determining residual hydroperoxide by reflux iodometric titration (part II[1b]).

For most analyses of products a gas chromatograph with thermal conductivity sensing was used. Columns were packed with a 20% loading of Carbowax 20M or didecyl phthalate on Chromosorb P. Residual hydroperoxides were reduced to al-

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[1] Part I: R. Hiatt, T. Mill, and F. R. Mayo, *J. Org. Chem.*, **33**, 1416 (1968). Equations 1–16 appear in part I. (b) Part II: R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *ibid.*, **33**, 1421 (1968). Equations 17–24 appear in part II. (c) Part III: R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *ibid.*, **33**, 1428 (1968). Equations 12a and b appear in part III. (d) To whom all correspondence should be addressed at Brock University, St. Catherines, Ontario, Canada.

[2] N. Uri, *Nature* **177**, 1177 (1956).

[3] E. T. Denisov and N. M. Emanuel, *Usp. Khim.*, **29**, 1409 (1960).

[4] Reference 3 contains a useful summary of work to 1960. This report considers some more recent investigations.

[5] E. Dyer, K. R. Carle, and D. E. Weiman, *J. Org. Chem.*, **23**, 1464 (1958).

[6] R. D. Vold and G. S. Hattiangdi, *Ind. Eng. Chem.*, **41**, 2311 (1949).

cohols with triphenylphosphine (Ph_3P) before analysis; unreduced dialkyl peroxides, except t-Bu_2O_2, were decomposed to mixtures of alcohols and ketones in the column. Dialkyl peroxides were preserved on columns with only 2% loading of didecyl phthalate, and were analyzed using a chromatograph with flame ionization detection. Evolved gases were trapped and analyzed by a mass spectrometer.

Decompositions in Chlorobenzene

***t*-Butyl Hydroperoxide Rates and Products.**—t-BuO_2H (0.1–0.2*M*) in chlorobenzene at 25° was entirely decomposed by millimolar amounts of a variety of catalysts including cobaltous stearate, 2-ethylhexanoate, acetylacetonate, and salicylalethylenediimine, cobaltic stearate, iron phthalocyanine, acetylacetonates of V^{III}, Mn^{II}, Ce^{IV}, and Nuodex preparations (octoates or naphthenates) of Co^{II}, Mn^{II}, Pb^{II}, and V^{III}. Times for decomposition in Table II varied from a few minutes for cobalt carboxylates or FePCN to several days for cobaltous salicylalethylenediimine or Pb napthenate (at 50°). Each mole of the more active catalysts decomposed more than 1000 mol of hydroperoxide before becoming deactivated.

TABLE II

RATES AND PRODUCTS OF METAL ION CATALYZED DECOMPOSITIONS OF 0.1 *M* t-BuO_2H IN CHLOROBENZENE

Temp, °C	Catalyst	Concn, m*M*	$t_{1/2}$, min	Products, %[a] t-BuOH	t-Bu_2O_2	AcMe
22.7	$CoSt_3$	26	27	86.6	12.7	0.5
25	$CoOct_2$	10	5	87.8	11.8	0.5
25	FePCN	4.7	7	84.7	14.6	1
25	CoA_2	500	14	87.8	11.5	0.5
25	CoSal	71	366	85.1	13.7	1
25	$CoOct_2$ HOAc	10 3.5	10	86.5	13.1	0.5
45	$CoSt_3$	6.5	7.5	89.3	9.2	1.5
45	$CoSt_3$	26	2.1	89.4	9.1	1.5
45	$CoSt_3$	190	<0.3	88.6	9.8	1.5
45	$CoOct_2$	10	1.3	89.0	8.8	2
50	$PbNap_2$	265	250	88.7	9.2	2

[a] Mole % based on t-BuO groups found. Total t-BuO products found ranged from 96 to 102% of t-BuO_2H decomposed.

At room temperature cupric octoate (Nuodex solution) and the acetylacetonates of Ni^{II}, Co^{III}, and Fe^{III} were inert[7] toward t-BuO_2H. FeA_2 decomposed only half a mole of hydroperoxide per mole of catalyst.

The products of the chain decompositions (Table II) at 25° were approximately 86% t-BuOH, 12% t-Bu_2O_2, 0.5% acetone, and 93% O_2 (based on $^1/_2$ O_2 from each t-BuO_2H), independent of the catalyst or the rate of decomposition. No methanol was found. Glpc analysis indicated some formaldehyde (not estimated quantitatively); Dean and Skirrow[8] found 3.8% under similar conditions. Decompositions at 45° gave only 9% t-Bu_2O_2, although this peroxide was stable under the conditions of the reaction.

Kinetics of Decomposition.—Some autoretardation occurred in all decompositions, but the least occurred in reactions catalyzed by cobalt carboxylates or iron phthalocyanine. For the latter, plots of log [t-BuO_2H] *vs.* time were linear to at least 70% decomposition, with slopes proportional to catalyst concentration. With $[t\text{-}BuO_2H]_0$ varied from 0.05 to 0.5 *M* and with 0.01 to 0.45 m*M* catalyst, the rate expression was first order in each reactant within experimental error (eq 25 where

$$-d[t\text{-}BuO_2H]/dt = k_2[t\text{-}BuO_2H][M] \qquad (25)$$

M = $CoSt_2$, $CoSt_3$, $CoOct_2$ or FePCN). Table III shows the second-order rate constants[9] and over-all activation energies for these catalysts. The rate constants for $CoSt_2$ and $CoSt_3$ were very similar; the rate at which a solution initially containing $CoSt_2$ or $CoSt_3$ became a steady-state equilibrium mixture of cobaltous and cobaltic (indicated by the color change on addition of t-BuO_2H) was too fast to measure using a Cary spectrophotometer. For $CoOct_2$ in chlorobenzene, Richardson[10] has shown the equilibrium to be about 55% cobaltous and 45% cobaltic. FePCN also underwent a rapid color change from deep green to light yellow.

TABLE III

RATE CONSTANTS AND ACTIVATION ENERGIES FOR DECOMPOSITIONS OF HYDROPEROXIDES IN CHLOROBENZENE

Temp, °C	R in RO_2H[a]	Catalyst[b]	k_2[c]	E_a
25.0	t-Bu	$CoOct_2$	23.2 ± 1.5	12
45.0			81.6 ± 5.5	
22.7		$CoSt_3$	1.66[d]	22
45.0			21.9 ± 1.1	
45.0		$CoSt_2$	17.1 ± 1.2	
0.0		FePCN	11.0 ± 0.8	9
22.5			37.7 ± 0.1	
23.5	n-Bu	$CoOct_2$	5.2[d]	
45.0		$CoSt_3$	3.1 ± 0.2	
45.0	α-Cumyl	$CoOct_2$	21[d]	

[a] Initial [RO_2H] varied from 0.05 to 0.5 *M*. [b] [Catalyst] varied from 0.013 to 0.45 m*M*. [c] Second-order rate constants (eq 25) in units of liter/mole/second. [d] Only one run.

Decompositions catalyzed by CoA_2 gave curved plots of log [t-BuO_2H] *vs.* time. The sharp decrease in initial rate had no orderly relationship to decreasing [t-BuO_2H] but was related to the oxidation of the initial cobaltous complex to the apparently much less active CoA_2^+. Determining Co^{II} concentrations spectrophotometrically, and rates and hydroperoxide concentration titrimetrically from parallel runs, gave a rate expression

$$-d[t\text{-}BuO_2H]/dt = k[t\text{-}BuO_2H][Co^{II}]^{1/2}$$

Retarders and Autoretardation.—Decompositions were retarded by addition of millimolar amounts of materials which strongly complex metal ions. These included carboxylic acids, aldehydes, EDTA, triethylenetetramine, 1,10-phenanthroline, and acetylacetone. Some typical effects are shown in Table IV. O_2, H_2O, and 0.1 *M* t-BuOH were not retarders (although the fading of the deep blue color of $CoOct_2$ solutions on addition of H_2O indicated aquation of the complex). Ionol (2,6-di-t-butyl-p-cresol) retarded FePCN-cata-

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[7] Cuprous salts, of course, do reduce hydroperoxides [J. K. Kochi, *J. Amer. Chem. Soc.*, **85**, 1958 (1963)] and can give long-chain decompositions if alkyl radicals are present in the system to reduce Cu^{II} back to Cu^{I}. Richardson [*ibid.*, **88**, 975 (1966)], while confirming our results at 25°, has shown that cupric octoate will oxidize hydroperoxides at 50°.

[8] M. H. Dean and G. Skirrow, *Trans. Faraday Soc.*, **54**, 849 (1958).

[9] The approximately 10% uncertainty in these constants was entirely random and apparently resulted from adventitious impurities. In one instance careless handling of the PhCl solvent caused reactions in it to proceed about half as fast as usual. Ordinarily rates were fairly reproducible and are in good agreement with those of Richardson.[10]

[10] W. H. Richardson, *J. Amer. Chem. Soc.*, **87**, 1096 (1965).

Table IV

Effects of Retarders on Decompositions of 0.1 *M* *t*-BuO$_2$H in Chlorobenzene

Retarder	Concn, m*M*	$k_1{}^a \times 10^3$, sec^{-1}
	0.1 m*M* CoOct$_2$ at 25°	
None		2.3
HOAc	3.2	1.1
CF$_3$CO$_2$H	3.6	0.66
EDTA[b]	*c*	<0.1
PrCHO	10	~0
	0.08 m*M* CoSt$_2$ at 45°	
None		1.4
Stearic acid	44	0.5
HOAc	5.4	1.0
1,10-Phenanthroline	13	0.5
Triethylenetetramine	6	0.18

[a] Pseudo-first-order rate constant. [b] Ethylenediamine–tetraacetic acid disodium salt. [c] PhCl solution of CoOct$_2$ shaken with the solid disodium salt and filtered before addition of *t*-BuO$_2$H.

lyzed decompositions but not those catalyzed by cobalt compounds.

The autoretardation of normal runs which occurred after 60–80% decomposition (prior to visible catalyst precipitation) was caused partly by formation of carboxylic acids (detected by ir analysis of reclaimed catalysts initially acid-free) and partly by unidentified volatile products, which, if acidic, were in too low a concentration to be detected by ir analysis or titration. Probably a third factor was decrease in catalyst solubility during the runs, although precipitation of the catalyst was usually not evident until several hours after decomposition was complete.

Other Hydroperoxides.—Reactions catalyzed by CoSt$_3$ or CoOct$_2$ showed that *n*-BuO$_2$H decomposed about one-eighth as fast and α-cumyl hydroperoxide about one-fourth as fast, respectively, as *t*-BuO$_2$H in chlorobenzene (Table III). Reactions of *n*-BuO$_2$H were strongly autoretarded by formation of *n*-PrCHO (or butyric acid if O$_2$ was not swept out).

Discussion.—A distinction must be made between catalytic decomposition, in which each metal ion decomposes many hundreds of hydroperoxide molecules, and what we shall label stoichiometric reactions, in which the ratio is nearer 1:1. Catalytic decompositions, typified here by reactions initiated by cobalt carboxylates or iron phthalocyanine, seem fairly simple. The uniformity of products and the bimolecular rate expressions suggest a radical-induced decomposition of the usual type initiated by metal ion–hydroperoxide interactions. The reactions in eq 13 and 14 are widely accepted[3] where M is a metal ion and

$$M^n + RO_2H \longrightarrow M^{n+1} + RO\cdot + OH^- \qquad (13)$$

$$M^{n+1} + RO_2H \longrightarrow M^n + RO_2\cdot + H^+ \qquad (14)$$

ligands. Catalyst dimers and hydroperoxide complexes are temporarily left in abeyance. If this is followed by an induced chain (eq 2, 3, and 4 in part I[1a]), an expression for disappearance of hydroperoxide can be developed (eq 26). Assuming a steady state for RO·

$$-d[RO_2H]/dt = k_{13}[RO_2H][M^{II}] + k_{14}[RO_2H][M^{III}] + k_2[RO\cdot][RO_2H] \qquad (26)$$

and rapid cycling of the metal ion, eq 27 and 28 apply.

$$k_{13}[RO_2H][M^{II}] = k_{14}[RO_2H][M^{III}] \qquad (27)$$

$$-d[RO_2H]/dt = (2k_3/k_4 + 3)[M^{II}][RO_2H] \qquad (28)$$

Since $M^{II} + M^{III} = M_0$, eq 29 can be written.

$$\frac{-d[RO_2H]}{dt} = (2k_3/k_4 + 3)\frac{k_{13}k_{14}}{k_{13} + k_{14}}[M]_0[RO_2H] \qquad (29)$$

For *t*-BuO$_2$H decompositions, k_3/k_4, the induced chain length *after initiation*, can be calculated from the ratio of alcohol and peroxide products, since the relationship in

$$2k_3/k_4 + 3 = \frac{[t\text{-BuOH}]_f + [\text{acetone}]_f}{[t\text{-Bu}_2O_2]_f} \qquad (30)$$

eq 30 exists where f indicates final concentration. From typical examples in Table II, $k_3/k_4 = 8.8$ at 45° (in good agreement with results from DBPO-induced decompositions) and 6.0 at 25°. This ratio can now be used to calculate the expected yield of O$_2$ (not 100%, since each initiating cycle produces a molecule of H$_2$O) (eq 31).

$$\%\ O_2 = 100(2k_3/k_4 + 2)/(2k_3/k_4 + 3) = 95\% \text{ at } 45° \qquad (31)$$

The slower rates of decomposition of *n*-BuO$_2$H and α-cumyl O$_2$H agree well with their shorter induced chain lengths.

The kinetic simplicity of the decompositions in PhCl (excluding those catalyzed by CoAc$_2$ which will be discussed later) makes a more complex scheme unnecessary. Catalyst dimers or higher aggregates, proposed by some workers[10–12] to explain the complex kinetics found in other solvents, probably obtain in chlorobenzene.[10] However, the degree of aggregation must remain fairly constant over the concentration range used. Complexing between catalyst and hydroperoxide[8,10,12] may occur prior to eq 13 and 14, but it appears to have no important consequences other than the retardation caused by other materials which also form strong complexes with the catalyst.[13–15]

The apparent unimportance of metal ion reactions with alkoxy or peroxy radicals in our experiments must be largely due to the low concentrations of the catalyst. Much larger concentrations are needed to reveal such reactions.[16,17] However, the stoichiometry of the FeA$_2$–*t*-BuO$_2$H reaction is probably explained by eq 32 rapidly

$$t\text{-BuO}\cdot + FeA_2 \longrightarrow FeA_2{}^+ + t\text{-BuO}^- \qquad (32)$$

following eq 13 (Fe^{III} is inert to hydroperoxides). Cobaltous ion appears to react with *t*-BuO· much less rapidly. Decompositions of *t*-BuO$_2$H under conditions where only one valence state of cobalt is active [Co(OAc)$_3$ in HOAc at 25° or K$_2$Co EDTA in HOAc–H$_2$O][8,11a] have approximately 1:1 stoichiometry. Apparently under these conditions RO$_2$H competes effectively with Co^{II} for RO·.

Decompositions in Other Solvents

Some metal-catalyzed decompositions were carried out in alkanes and in alcohol–chlorobenzene mixtures.

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(11) (a) W. H. Richardson, *J. Amer. Chem. Soc.*, **87**, 247 (1965); (b) W. H. Richardson, *J. Org. Chem.*, **30**, 2804 (1965).

(12) Y. Kamiya, S. Beaton, A. Lafortune, and K. U. Ingold, *Can. J. Chem.*, **41**, 2020 (1963).

(13) This complexing probably accounts for the effect of Ionol as well. Phenols have been shown to complex strongly with phthalocyaninelike compounds.[14] Ionol should not affect the radical chain since galvanoxyl, a radical similar to the one produced from Ionol, attacks *t*-BuO$_2$H to give the usual induced decomposition.[15]

(14) P. George, R. L. J. Lyster, and J. Bettlestone, *J. Biol. Chem.*, **236**, 3246 (1961).

(15) J. C. McGowan and T. Powell, *J. Chem. Soc.*, 238 (1960).

(16) J. K. Kochi, *J. Amer. Chem. Soc.*, **84**, 1193 (1962).

(17) W. J. deKlein and E. C. Kooyman, *J. Catal.*, **4**, 626 (1965).

TABLE V

METAL-CATALYZED DECOMPOSITIONS OF 0.1–0.3 M HYDROPEROXIDES IN REFLUXING ALKANES

R in RO_2H	Concn of catalyst, mM	$[k_1]_0$,[a] sec^{-1}	Products, %					
			ROH[a]	R=O[b]	R_2O_2[b]	S—OH[c]	S=O[c]	O_2
		With $CoOct_2$ in n-Pentane at 37.8°						
t-Bu	6.4	0.011	91		8	9	6	90
sec-Bu	6.4	0.0011						
sec-Bu	25	0.0055	61	36	3			70
n-Bu	25	0.0055	67	33				70
		With $CoOct_2$ in Cyclohexane at 81.5°						
t-Bu	5.7	0.021	88	2	11[d]	22	14	22
α-Cumyl	6.5	0.020	95	5		31	16	
sec-Bu	6.5	0.0053	50	40		12	8	
n-Bu	6.3	0.0052	65	24		16	5	
		With $CoOct_2$ except as Noted[e–f] in n-Heptane at 98.6°						
t-Bu	6.5	>0.037						
t-Bu	5.6	>0.024						
sec-Bu	6.5	0.01	49	31				
sec-Bu	81		64	27				
sec-Bu	12[f]	0.004	63	23				
sec-Bu	14[g]	0.0007	45	42				

[a] First-order rate constants calculated from time for 5% decompositions. [b] Alcohol, ketone or aldehyde, or dialkyl peroxide from hydroperoxide in mole % based on RO groups found. [c] Alcohol or ketone from solvent. [d] $C_6H_{11}O_2$-t-Bu. [e] CoA_2. [f] $MnOct_2$. [g] $VOct_3$.

We reasoned that metal ions might play a more varied and influencial role in these media, where radical-induced chains are short, than in pure chlorobenzene. Reactions in alkanes were refluxed to expel O_2 and prevent autoxidation.

Decompositions in Refluxing Alkanes. Decompositions in n-Pentane.—Decompositions of n-BuO_2H, sec-BuO_2H, and t-BuO_2H by 0.1 mM $CoOct_2$ in refluxing pentane at 38° differed little in initial rates or products (Table V) from comparable decompositions in chlorobenzene. Rate expressions were first order in hydroperoxide and apparently second order in cobalt at concentrations of $CoOct_2$ that were <0.1 mM but tended to lesser dependence at higher concentrations. Initial rates for t-BuO_2H were only one-eighth as fast when 1.6 M cumene was added.

Decompositions of t-BuO_2H showed severe autoretardation. Plots of $1/[RO_2H]^2$ against time were linear, giving the appearance of a third-order reaction in hydroperoxide. However, inital rates (calculated from the reciprocal square plots) were proportional to $[RO_2H]_0$. We suspect that a similar autoretardation is the basis for Dyer's claim[5] that decompositions of tetralin hydroperoxide by $CoOct_2$ in cyclohexane are second order in hydroperoxide, and that these reactions are really first order.

Decompositions in Higher Boiling Alkanes.—In refluxing cyclohexane, n-heptane, or trimethylpentane, kinetic analysis of t-BuO_2H decompositions was precluded by both very rapid decomposition and rapid deactivation of the catalyst. In a typical cyclohexane run, with 0.1 M t-BuO_2H and 0.057 mM $CoOct_2$, 44% of the hydroperoxide was decomposed in the first 20 sec (the minimum time necessary to remove a sample for titration) and only 12% more decomposed during the next 30 min. More catalyst added at this point was instantly deactivated with only slight reduction of hydroperoxide concentration. Decompositions of α-cumyl O_2H were also strongly autoretarded. Estimates of initial rates (Table V) for these hydroperoxides are almost certainly low. Decompositions of n-BuO_2H and sec-BuO_3H were slower initially but showed little autoretardation.

The product distribution (where measured) was relatively insensitive to the nature of the catalyst. Table V shows that $CoOct_2$, $MnOct_2$, and $VOct_3$ all gave about the same proportions of sec-BuOH and methyl ethyl ketone from sec-BuO_2 in refluxing n-heptane.

Significant yields of oxidized solvent molecules were obtained. These were most carefully investigated for reactions of t-BuO_2H in cyclohexane, where they accounted for about half of the oxygen liberated from decomposed hydroperoxide.

Products listed in Table V are a composite from several runs analyzed by different methods and fully described in part II.[1b] In most analyses the mixed peroxide pyrolyzed and only alcohol and ketone were observed. Water was not measured quantitatively. It probably accounts for that oxygen not found elsewhere. Products of runs not carried to completion probably contained some cyclohexyl hydroperoxide. (Glpc analyses of product mixtures in which residual hydroperoxide had been reduced to alcohol by Ph_3P gave more cyclohexanol and less cyclohexanone than analyses in which residual hydroperoxide was pyrolyzed in the chromatograph.)

Discussion.—The products of decompositions in n-pentane agree nicely with the scheme proposed for reactions in chlorobenzene, modified slightly by some radical attack on solvent. For t-BuO_2H such attack produces somewhat shorter induced chains, lower yields of O_2 and t-Bu_2O_2, and some products of pentane oxidation. The relations shown in eq 13, 14′, 2, and 12 suggest that in decompositions of sec-BuO_2H and n-BuO_2H, the yields of alcohol, ketone, or aldehyde, and O_2 correspond to decomposition of three peroxide molecules per metal cycle (eq 33).

$$sec\text{-BuO}_2\text{H} + \text{M}^{\text{II}} \longrightarrow sec\text{-BuO}\cdot + \text{M}^{\text{III}} + \text{OH}^- \qquad (13)$$

$$sec\text{-BuO}_2\text{H} + \text{M}^{\text{III}} + \text{OH}^- \longrightarrow sec\text{-BuO}_2\cdot + \text{M}^{\text{II}} + \text{H}_2\text{O} \qquad (14')$$

$$sec\text{-BuO}\cdot + sec\text{-BuO}_2\text{H} \longrightarrow sec\text{-BuOH} + sec\text{-BuO}_2\cdot \qquad (2)$$

$$2\textit{sec}\text{-BuO}_2\cdot \longrightarrow \textit{sec}\text{-BuOH} + \text{AcEt} + \text{O}_2 \tag{12}$$

$$3\textit{sec}\text{-BuO}_2\text{H} \longrightarrow 2\ \textit{sec}\text{-BuOH} + \text{AcEt} + \text{O}_2 + \text{H}_2\text{O} \tag{33}$$

In refluxing cyclohexane or heptane, radical attack on solvent becomes more important and a variety of new competing reactions are introduced (part II[1b]). Although our data are inadequate for a full analysis, a simple conclusion emerges: the role of catalytic amounts of metal ions is largely limited to the primary processes of hydroperoxide destruction, that is, to eq 13 and 14. Since the products of decompositions differ little from those obtained from peroxide initiated decompositions (part II[1b]), metal ion–radical reactions must not compete effectively with the other reactions above at low concentrations of metal ions. This conclusion applies even to the production of *t*-butyl cyclohexyl peroxide which others[18] have proposed to arise *via* eq 34 and 35. Since the steady-state con-

$$\text{C}_6\text{H}_{11}\cdot + \text{M}^{\text{III}} \longrightarrow \text{M}^{\text{II}} + \text{C}_6\text{H}_{11}^{+} \tag{34}$$

$$\text{C}_6\text{H}_{11}^{+} + t\text{-BuO}_2\text{H} \longrightarrow \text{C}_6\text{H}_{11}\text{O}_2t\text{-Bu} + \text{H}^{+} \tag{35}$$

centration of *t*-butylperoxy radicals in the system is nearly equal to that of M^{III},[19] the radical–radical combination route is equally likely and less complicated.

The relative rates of decomposition of the different hydroperoxides in alkanes are not readily explained. In *n*-pentane (as in chlorobenzene) they are in reasonable agreement with the chain lengths for radical-induced decomposition, but this difference between tertiaries and nontertiaries persists in refluxing cyclohexane or heptane, where the radical chain contribution must be very small.

The reason for the striking difference in degree of autoretardation between tertiary and nontertiary hydroperoxides is uncertain. We tentatively suggest that formic acid, which can be produced from both t-BuO$_2$H and α-cumyl O$_2$H but not n-BuO$_2$H or *sec*-BuO$_2$H, is generated in sufficient quantity to precipitate the catalyst as insoluble cobalt formate.

Decompositions in Alcohol–Chlorobenzene Mixtures.—Decompositions of t-BuO$_2$H by CoOct$_2$ in 2:3 alcohol–PhCl mixtures were severely autoretarded by deactivation and precipitation of the catalyst. 0.001 *M* CoOct$_2$ was necessary for complete decomposition (98% in 24 hr) of 0.1 *M* hydroperoxide. Initial rates (to the accuracy measurable) were only $^1/_{100}$th as fast as in pure chlorobenzene[20] and yields of acetone were much greater (Tables VI and VII). Decompositions of *sec*-BuO$_2$H showed little autoretardation and products (Table VI) differed little from reactions in chlorobenzene.

For t-BuO$_2$H, the effects of large amounts of t-BuOH on rates and products are similar to those found in free radical-induced decompositions (part II[1b]) and must be partly due to the same factor, the enhanced rate of cleavage of *t*-butoxy radicals. However, the observed difference in initial rates is much greater than can be explained by inhibition of the radical-induced chain (which could account for a factor of 8–10 at most). It suggests that alcohol affects the rate of metal ion–hydroperoxide reactions, possibly by competing for ligand sites in the metal ion complex.

Table VI

Decompositions of 0.1 *M* BuO$_2$H by 2 m*M* CoOct$_2$ in 2:3 Alcohol–Chlorobenzene Mixtures at 25°

BuO$_2$H	Solvent	$[k_1]_0 \times 10^3$,[a] sec^{-1}	Products R$_2$O$_2$[b]	ROH[b]	R=O[b]	S=O[c]
t-BuO$_2$H	t-BuOH–PhCl	2.5	5.6		8.7	
t-BuO$_2$H	i-PrOH–PhCl	1.2	0.8	~100		101
sec-BuO$_2$H	i-PrOH–PhCl	9.2		57	37	36

[a] Average pseudo-first-order rate constant calculated at 5% decomposition. [b] Dialkyl peroxide, alcohol, or ketone from hydroperoxide in % based on RO groups. [c] Ketone from solvent in % based on hydroperoxide decomposed. Totals greater than 100% reflect lack of precision in glpc analyses.

In i-PrOH–PhCl a nearly clean reduction of t-BuO$_2$H to t-BuOH obtains. Both the cleavage of t-BuO· and the interactions of 2t-BuO$_2$· are suppressed, possibly by the reactions in eq 36 and 37. *sec*-BuO$_2$H

$$t\text{-BuO}\cdot + i\text{-PrOH} \longrightarrow t\text{-BuOH} + \text{Me}_2\dot{\text{C}}\text{OH} \tag{36}$$

$$\text{Me}_2\dot{\text{C}}\text{OH} + t\text{-BuO}_2\cdot \longrightarrow t\text{-BuO}_2\text{H} + \text{AcMe} \tag{37}$$

does not reduce cleanly under identical conditions, probably because interactions of 2*sec*-BuO$_2$·, being much faster than those of 2t-BuO$_2$· (part II[1b]), compete better with other reactions.

Complex Kinetics in Metal-Catalyzed Decompositions

Table VII summarizes typical kinetic data obtained by us and others. There is a remarkable agreement on rates of reaction and on the form of the rate expressions where these are comparable. Some investigators have held our view, that metal-catalyzed decompositions are essentially free-radical-induced decompositions initiated by metal ion–hydroperoxide interactions. Others concerned with the complexity of the kinetic expressions have proposed more complex schemes.[8,10,21] We suggest instead that the complex kinetics are simply a reflection of the metal catalyst's lack of true solubility in organic solvents. Thus, Table VII shows that most of the abnormalities are in the rate dependence on metal ion;[22] reactions are first order in hydroperoxide (or nearly so) regardless of conditions. Furthermore, the reaction order in metal ion is sensitive to solvent and temperature. The latter is most vividly demonstrated by decompositions of t-BuO$_2$H by CoOct$_2$ in chlorobenzene. Richardson's[10] results at 20° agree very well with ours at 25°; yet at 0° (where his order in [Co] varies between 0.05 and 1.5 depending on the concentration of CoOct$_2$), the rate he obtains using 0.2 m*M* CoOct$_2$ is less than one-tenth of that predicted from our results at 45 and 25°. We have found a similar nonlinear temperature dependence for reactions catalyzed by CoA$_2$ at 45, 25, and 0°. Reactions which are first order in metal ion have over-all E_a's of 9–12 kcal. Those with higher orders have E_a's of 17–22 kcal. Thus it appears that catalysts in "solution" may exist as fairly large aggregates even at concentrations of 0.1 m*M*. Increasing

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(18) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 72 (1959).

(19) J. R. Thomas, *J. Amer. Chem. Soc.*, **87**, 3935 (1965).

(20) At 0.1 m*M* Co; rates in alcohol–chlorobenzene mixtures were not simply related to [Co], but were nearer second order than first.

(21) H. Berger and A. F. Bickel, *Trans. Faraday Soc.*, **57**, 1325 (1961).

(22) Radical-induced decompositions may have complex kinetics, as well, under certain conditions (part II), but never in our experience has the order in initiating species been greater than unity.

TABLE VII

RATES OF DECOMPOSITION OF 0.01–0.1 *M* HYDROPEROXIDES AND REACTION ORDERS IN METAL IONS AS FUNCTIONS OF SOLVENT AND TEMPERATURE

Ref	Temp, °C	Solvent	Catalyst	[Metal ion], m*M*	k_1,[a] sec^{-1} × 10^3	n[b]	E_a[c]	t_2[c]
			t-BuO_2H					
d	20	PhCl	$CoOct_2$	8.5	2.3	~1		
g	25	PhCl	$CoOct_2$	10	2.3	1	12	45
g	25	2:3 t-BuOH–PhCl	$CoOct_2$	30	0.11	>1		
h	35	1:1 HOAc–H_2O	$K_2CoEDTA$	4440	0.038[e,f]	1 + 2	19.8	50
g	38	n-Pentane	$CoOct_2$	9.5	11	2		
d	50	HOAc	$Co(OAc)_2$	1040	0.14	1.3	19.7	70
i	55	HOAc	$Co(OAc)_2$	1000	0.20	1.4		
			α-Cumyl O_2H					
j	25	H_2O	$FeSO_4$	4[f]	1.1	1	11.1	0
g	45	PhCl	$CoOct_2$	9	1.9	1	12[k]	
k	50	1:1 HOAc–PhCl	$CoSt_2$	100	0.14	1.5–2	22.3	60
l	101	Nonane	$CoPalm_2$[m]	100	3.2	1	9.4	67
			α-Tetralyl O_2H					
n	49.7	Tetralin	$CoOleate_2$	24	0.04	1.7	17	34
o	50	PhCl	$CoDecanoate_2$	20[p]	1.0[p]	1		
q	50	1:1 HOAc–PhH	$Co(OAc)_2$	200	0.9	2		
r	50	Xylene	$CoOct_2$	10	0.77	2	17.4	25–77

[a] k_1 = rate/[RO_2H]. [b] Order in metal ion. [c] Calcd from k_1 at t and t_2. This clearly has no precise meaning when n at $t \neq n$ at t_2 but conveniently indicates the thermal coefficient of the rate. [d] See ref 10. [e] At [t-BuO_2H]$_0$ = 0.11. [f] Stoichiometric decompositions. [g] This work. [h] See ref 3. [i] See ref 8. [j] J. W. Fordham and H. L. Williams, *J. Amer. Chem. Soc.*, **72**, 4465 (1950). [k] From E. A. Kuz'mina, V. A. Shushunov, and M. K. Shchennikova [*Khim. Perekisnykh Soedin. Akad. Nauk SSSR, Inst. Obshch. i Neorgan. Khim.*, 231 (1963); *Chem. Abstr.*, **60**, 14, 360 (1964)] who agree that reactions are first order in [Co] but do not give actual rates. [l] H. Hoch and H. Kropf, *J. Prakt. Chem.*, **16**, 113 (1962). [m] Cobaltous palmitate. [n] J. Tomiska, *Collect. Czech. Chem. Commun.*, **27**, 1549 (1962). [o] A. Y. Kamiya, S. Beaton, A. Lafortune, and K. U. Ingold, *Can. J. Chem.*, **41**, 2034 (1963). [p] [M] chosen arbitrarily in order to evaluate k_1 from Ingold and coworkers'[o] bimolecular rate constant, K_2 = rate/[Co] [RO_2H]. [q] Reference 12; see also A. E. Woodword and R. B. Mesrobian, *J. Am. Chem. Soc.*, **75**, 6189 (1953). [r] See ref 5.

the temperature decreases the aggregate size (and increases the effective catalyst concentration), resulting in an extraordinarily large E_a. Considerable further work would be needed to provide more than this qualitative evaluation of the situation.

Registry No.—t-BuO_2H, 75-91-2; α-Cumyl O_2H, 80-15-9; n-BuO_2H, 4813-50-7; *sec*-BuO_2H, 13020-06-9.

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