Transition Metal Chelates as Catalysts in the Oxidation of Nitrosobenzene. Oxygen Transfer from Alkyl Peroxy Radicals[1a,b]

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Abstract: The reaction of nitrosobenzene with *tert*-butyl hydroperoxide in benzene or cyclohexane, as initiated by di-*tert*-butyl peroxyoxalate or by hydrocarbon-soluble β-diketonates of a number of transition metals, yields nitrobenzene rapidly and quantitatively. The rate law observed for the peroxalate-initiated reaction is consistent with a radical chain mechanism involving both $t\text{-BuO}\cdot$ and $t\text{-BuO}_2\cdot$, in which $t\text{-BuO}\cdot$ is diverted, in part, to the spin adduct $\text{Ph(BuO)NO}\cdot$, conversion to nitrobenzene occurs by oxygen-atom transfer from $t\text{-BuO}_2\cdot$, and the principal mode of termination is the reaction of $t\text{-BuO}_2\cdot$ with $\text{Ph(BuO)NO}\cdot$. Changes in the kinetic picture when metal chelates are substituted for peroxalate reflect variation in the modes of initiation. Catalytic action by the dipivaloylmethane chelate of Co(II), Co(dpm)_2 (which is rapidly converted to a mixture of Co^{II} and Co^{III} under the reaction conditions), and by Mn(acac)_3, appears to occur *via* a straightforward two-step initiation sequence in which the 2+ state of the metal reacts with hydroperoxide, yielding $\text{BuO}\cdot$, after which the 3+ state reacts with a second hydroperoxide, yielding $\text{BuO}_2\cdot$. Overall specific rates for initiation in these cases are determined principally by the rate constant for the second step. The fully chelated and substitution-inert Co(dpm)_3 exhibits practically no catalytic activity under our conditions. Catalysis by VO(dpm)_2 is complicated by the formation of a complex, $\text{VO(dpm)}_2\text{–BuO}_2\text{H}$ ($K_{\text{assn}} = 1.9 \times 10^3\ M^{-1}$ at 25°), which may undergo unimolecular homolysis, forming $\text{BuO}\cdot$, or, alternatively, may react with a second hydroperoxide, again forming $\text{BuO}\cdot$. Cyclization of vanadium between the 4+ and 5+ oxidation states occurs. Catalysis by Pb(dpm)_2 involves two lead centers in the initiation sequence and is subject to competitive inhibition by high concentrations of hydroperoxide. A bimolecular reaction between two units of $\text{Pb(dpm)}_2\text{–BuO}_2\text{H}$, yielding two butoxide radicals and Pb^{IV}, is proposed as the rate-determining step in a path which retains the free-radical character of the catalyzed oxidation but bypasses Pb^{III}.

Although a vast body of information concerning oxidations by hydroperoxides, as catalyzed by transition metal compounds, is now available, both in the patent and in the journal literature,[2] kinetic studies of these processes have not as yet been commensurately rewarding. Such oxidations commonly yield several products and are often subject to autoinhibition. Moreover, interpretation of the kinetic picture is frequently complicated by uncertainty as to the nature of the metal catalyst in the system at hand, by changes in this catalyst as the reaction proceeds, and, in some cases, by partial precipitation of catalytic material.

The present report describes the oxidation of nitrosobenzene with *tert*-butyl hydroperoxide in the presence of a variety of transition metal ions. The latter are employed as chelated diketonates, which are well characterized and are soluble in hydrocarbons. A number of the catalyzed oxidations, which are free radical in character, proceed with ease, forming nitrobenzene quantitatively

$$t\text{-BuO}_2\text{H} + \text{C}_6\text{H}_5\text{NO} \xrightarrow{\text{cat.}} \text{C}_6\text{H}_5\text{NO}_2 + t\text{-BuOH}$$

Our experiments indicate that this conversion occurs by oxygen-atom transfer from $t\text{-BuO}_2\cdot$, and nitrosobenzene is thus implicated as an extremely efficient scavenger of alkyl peroxy radicals. The high specificity of this oxidation, the apparent simplicity of the propagation sequence, and the ease in following the progress of the reaction have allowed us to focus our attention on the initiation step(s) under unusually mild conditions, and we have obtained evidence pointing to several peculiarities of initiation behavior associated with the various individual metals.

Experimental Section

Materials. *tert*-Butyl, cumyl, and *tert*-amyl hydroperoxides (Lucidol products) were purified by vacuum distillation and analyzed iodometrically as described.[3] Nitrosobenzene (Aldrich) was purified by recrystallization from ethanol. Acetylacetone and dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione) (Aldrich) were used as received. Cyclohexane and benzene (both Matheson Spectroquality) were dried over 4A molecular sieves before use.

The following acetylacetonates (acac derivatives) and dipivaloylmethanates (dpm derivatives) were prepared by literature procedures: Co(dpm)_2,[4] Na(dpm),[4] Co(acac)_2,[5] Mn(acac)_3,[6] Co(dpm)_3,[4] Ni(dpm)_2,[4] Fe(acac)_3,[7] Cu(dpm)_2,[4] V(acac)_3 (recrystallized from acetylacetone),[8] and $\text{UO}_2\text{(acac)}_2$.[9] The chelates Th(acac)_4, Zr(acac)_4, In(acac)_3, Zn(acac)_2, and Cd(acac)_2, as well as various acetylacetonates of platinum group and rare earth metals (each obtained from Research Inorganic Chemical Corp.), were used as received.

VO(dpm)_2, as prepared by the method of Selbin,[10] was obtained as a green powder and was purified by vacuum sublimation; mp 195–197°.[11]

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[1] (a) Paper III in the series, "Metal Ion Catalysis of Oxygen Transfer Reactions." (b) This work was sponsored by the National Science Foundation (Grant GP-23136). Support is gratefully acknowledged. (c) Postdoctoral Research Associate.

[2] For recent reviews, see (a) G. Sosnovsky and D. J. Rawlinson in "Organic Peroxides," Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1971, pp 153–268; (b) A. R. Doumaux, Jr., in "Oxidation," Vol. II, R. L. Augustine and D. J. Trecker, Ed., Marcel Dekker, New York, N. Y., 1971, pp 141–186.

[3] E. S. Gould, R. R. Hiatt, and K. C. Irwin, *J. Amer. Chem. Soc.*, **90**, 4573 (1968).

[4] G. S. Hammond, D. C. Nonhebel, and C-H. S. Wu, *Inorg. Chem.*, **2**, 73 (1963).

[5] J. B. Ellern and R. O. Ragsdale, *Inorg. Syn.*, **11**, 82 (1968).

[6] R. G. Charles, *ibid.*, **7**, 183 (1963).

[7] W. C. Fernelius and J. E. Blanch, *ibid.*, **5**, 130 (1957).

[8] D. Grdenic and B. Korpar-Colig, *Inorg. Chem.*, **3**, 1328 (1964).

[9] A. E. Comyns, B. M. Gatehouse, and E. Wait, *J. Chem. Soc.*, 4655 (1958).

[10] J. Selbin, G. Maus, and D. L. Johnson, *J. Inorg. Nucl. Chem.*, **29**, 1735 (1967).

[11] Melting points, determined on a Thomas-Hoover apparatus in open capillaries, are uncorrected. Microanalyses were carried out by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

Anal. Calcd for VO($C_{11}H_{19}O_2$)$_2$: C, 60.98; H, 8.78. Found:[11] C, 60.88; H, 8.83.

Pb(dpm)$_2$ was prepared by addition of 4.0 g of dipivaloylmethane to a mixture of 1.6 g of lead nitrate, 30 ml of water, and 2 ml of concentrated aqueous ammonia. The mixture was stirred at room temperature for 1 hr, and the white precipitate which formed was filtered off, washed with EtOH, and then redissolved in a minimum volume of acetone. The resulting preparation was filtered, and the chelate reprecipitated by addition of water. The product was washed with ethanol, air-dried, and sublimed at 100° (0.1 mm). The complex was a white powder: mp 129–130°; $\lambda_{\max}^{\text{cyclohexane}}$ 273 nm (ϵ 30,800).

Anal. Calcd for Pb($C_{11}H_{19}O_2$)$_2$: C, 46.06; H, 6.63. Found: C, 46.18; H, 6.73.

MoO$_2$(dpm)$_2$ was prepared by a modification of the procedure of Pinnavaia and Clements.[12] To a solution of 4.0 g of sodium molybdate dihydrate in 25 ml of water was added 5.0 ml of concentrated HNO_3, then 5.0 g of dipivaloylmethane. The mixture was stirred vigorously at room temperature for 3 hr. The yellow organic layer was separated and 5 ml of EtOH added to induce crystallization. The pale yellow crystals were filtered off, dried in air, and sublimed at 100° (0.1 mm), mp 132–134°.

Ce(dpm)$_4$ was prepared by addition of a solution of 4.0 g of dipivaloylmethane in 10 ml of ethanol to a solution of 2.0 g of cerium(IV) ammonium nitrate in 5 ml of water. The resulting dark red solution was stirred for 12 hr. Aqueous ammonia (20 ml, 10%) was added dropwise, and the crystals which formed were filtered off. Several recrystallizations from hot ethanol yielded dark red crystals: mp 278–281°; $\lambda_{\max}^{\text{benzene}}$ 370 nm (ϵ 13,800).

Anal. Calcd for Ce($C_{11}H_{19}O_2$)$_4$: C, 60.54; H, 8.71. Found: C, 61.09; H, 8.70.

Di-*tert*-butyl peroxyoxalate[13a] and triphenylmethyl hydroperoxide[13b] were prepared by literature methods and were stored at −15°.

Preliminary Observations. The 1:1 stoichiometry of the reaction between nitrosobenzene and *t*-BuO$_2$H at 25°, as initiated by peroxalate, Co(dpm)$_2$, Mn(acac)$_3$, VO(dpm)$_2$, and by Pb(dpm)$_2$, was established by spectrophotometric titration at 760 nm, the absorption maximum for nitrosobenzene (ϵ 53). To a benzene solution containing 0.06 mmol of nitrosobenzene and 0.002 mmol of initiator was added *t*-BuO$_2$H in small portions. Absorbances were recorded after allowing sufficient time for reaction (generally several hours) after each addition. No absorbance changes occurred after more than an equimolar quantity of hydroperoxide had been added, and plots of nitrosobenzene consumed *vs.* mol of hydroperoxide added were linear with unit slope. Similar additions were carried out in cyclohexane, but after each addition an aliquot was diluted 25-fold and the absorbance at 245 nm ($\lambda_{\max}$ for nitrobenzene) measured; conversion to nitrobenzene, as based on comparison with standard solutions of the latter, exceeded 96%.

Attempts to oxidize azobenzene to azoxybenzene under similar conditions, monitoring the solution at 440 nm, were unsuccessful. No reaction was observed, either at 25 or at 65°, after 2 hr in the presence of dpm derivatives of VO^{2+}, Co^{2+}, Pb^{2+}, or Cu^{2+}.

Rate Measurements. Reactions were carried out in benzene or cyclohexane at 25.0 ± 0.1° and were followed at 760 nm using a Cary 14 recording spectrophotometer. Metal catalyst concentrations were generally in the range 10^{-6}–10^{-4} *M*, peroxalate concentrations in the range 10^{-2}–10^{-1} *M*, hydroperoxide in the range 0.02–0.4 *M*, and $(C_6H_5NO)_{\text{init}}$ near 10^{-2} *M*.[14] Reactions were generally initiated by adding hydroperoxide to a mixture of the catalyst and nitrosobenzene. Short induction periods were observed, after which the disappearance of nitrosobenzene was linear with time. Typical times for total reaction were 30–300 sec with induction periods approximately one-fifth these values. Rates from replicate runs generally agreed to within better than 5%, and, in keeping with the zero-order character of the reaction, did not depend on the initial concentration of nitrosobenzene. Catalyst solutions were used within 1 hr after preparation, for the activities of a number of catalysts in solution were found to decrease gradually on standing. More pronounced catalyst deterioration was observed when catalyst and hydroperoxide were mixed and allowed to stand for extended intervals before addition of nitrosobenzene.[15] *n*-Butyl vanadate, (*n*-BuO)$_3$VO, was an effective catalyst, but rates varied erratically for reactions catalyzed by this very easily hydrolyzed vanadium(V) ester.

A number of oxidations, as initiated by metal chelates and by di-*tert*-butyl peroxyoxalate, were carried out under air-free conditions, using a 1.0-cm anaerobic spectrophotometric cell with an external reservoir compartment. Solutions of nitrosobenzene and catalyst were added to the cell, and a known solution of hydroperoxide was added to the reservoir. After four freeze-pump-thaw degassing cycles, cooling with Dry Ice–acetone, the solutions were warmed to 25°, the contents of the two compartments were mixed, and the reaction was monitored spectrophotometrically in the usual fashion. For the peroxalate-catalyzed reaction, and for those catalyzed by Co(dpm)$_2$, Co(acac)$_2$, Mn(acac)$_3$, Ru(acac)$_3$, and VO(dpm)$_2$, estimated reaction rates were not affected by this degassing procedure. Oxidations catalyzed by Pb(dpm)$_2$ were slightly faster when carried out under atmospheric oxygen than under degassed conditions, whereas the reverse appeared to hold true for Ru(acac)$_3$-catalyzed oxidations; kinetic measurements with these catalysts were carried out with degassed solutions. The catalytic activity of Ce(dpm)$_4$ was comparable to that of VO(dpm)$_2$, but the Ce(IV)-catalyzed oxidations were markedly accelerated by O_2. Even under oxygen-free conditions, although rates were reproducible, no chemically meaningful kinetic pattern was discernible with this chelate.[16]

A few experiments with other peroxides were carried out. Oxidations with cumyl and *tert*-amyl hydroperoxide appeared to exhibit much the same kinetic pattern as *t*-BuO$_2$H, with reaction rates approximately 20% less under comparable conditions. Triphenylmethyl hydroperoxide was considerably less active than the others and presented a less easily tractable kinetic picture. No oxidation occurred when di-*tert*-butyl peroxide was substituted for hydroperoxide. Oxidations with each of the catalysts were severely retarded by 2,6-di-*tert*-butyl-4-methylphenol ("Ionol") at the 10^{-4} *M* level. Oxidations were negligibly slow when ethanol, rather than benzene or cyclohexane, was used as a solvent.

Metal–Hydroperoxide Interactions. The spectra of four of the chelates, Co(acac)$_2$, Co(dpm)$_2$, VO(dpm)$_2$, and Ce(dpm)$_4$, were rapidly altered on addition of *t*-BuO$_2$H. The stoichiometry of the reactions of the Co(II) complexes could be shown, by spectrophotometric titration at 600 nm, in the absence of oxygen, to correspond to 2Co(II)/hydroperoxide; moreover, the specific rate of oxidation of Co(dpm)$_2$ in cyclohexane could be measured under pseudo-first-order conditions by adding small volumes of hydroperoxide solution to a known excess of Co(dpm)$_2$ and following the change in absorbance with time.

Spectral changes occurring with the chelates of VO^{2+} and Ce(IV) indicated the rapid establishment of equilibria in which these metals could be predominantly converted to hydroperoxo complexes[17] with excess *t*-BuO$_2$H. Association constants for the complexes were estimated from measurements of spectra at known hydroperoxide concentrations.

Results and Discussion

Peroxalate-Initiated Reaction. Intervention of *t*-

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[12] T. J. Pinnavaia and W. R. Clements, private communication.

[13] (a) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960); (b) D. E. Bissing, C. A. Matuszak, and W. E. McEwen, *ibid.*, **86**, 3824 (1964).

[14] At or below this concentration, no complications arising from the monomer–dimer equilibrium involving nitrosobenzene were noted.

[15] Addition of *t*-BuO$_2$H to Pb(dpm)$_2$ in benzene or cyclohexane yields a yellow species, the formation of which (second-order rate constant 14 M^{-1} sec^{-1} in benzene at 25°) is much slower than the Pb(dpm)$_2$ catalyzed oxidation of nitrosobenzene under corresponding conditions and is not inhibited by Ionol. The yellow substance, in the quantities formed, does not appear to affect the rate of the catalyzed oxidation. On prolonged standing, such solutions yield PbO$_2$.

[16] In the absence of added catalysts, very slow oxidation of nitrosobenzene, at a rate proportional to *t*-BuO$_2$H, was observed, but this could be eliminated by degassing. Observed oxidation rates in the presence of a number of marginal metal catalysts were significantly reduced by degassing; catalysts in this category included Co(dpm)$_3$, Rh(acac)$_3$, Ni(dpm)$_2$, Fe(acac)$_3$, MoO$_2$(dpm)$_2$, Cr(acac)$_3$, Pr(acac)$_3$, Cu(dpm)$_2$, and V(acac)$_3$. The oxygen-catalyzed reaction, for which we can offer no reasonable mechanism, appears to be inhibited by the following metal chelates: Pt(acac)$_2$, Pd(acac)$_2$, Th(acac)$_4$, Zr(acac)$_4$, In(acac)$_3$, Zn(acac)$_2$, and Cd(acac)$_2$. Acetylacetone itself and UO$_2$(acac)$_2$ were without effect under our reaction conditions, as was Na(dpm). The sodium derivative has been found to catalyze the decomposition of *t*-BuO$_2$H under conditions more severe than ours; see V. K. Tsyskovskii, S. S. Botkina, E. K. Prokof'ev, and Yu. L. Moskovich, *Zh. Prikl. Khim.* (*Leningrad*), **45**, 1299 (1972).

[17] The more striking of these changes, the formation of a deep red hydroperoxo–vanadium(IV) complex ($\lambda_{\max}$ 508 nm), is similar to that already described in greater detail for VO(acac)$_2$ in the presence of *t*-BuO$_2$H. See C. C. Su, J. W. Reed, and E. S. Gould, *Inorg. Chem.*, **12**, 337 (1973).

BuO_2 Radicals. The oxidations of nitrosobenzene, as initiated both by *tert*-butyl peroxalate and by the chelates of Co^{2+}, Mn^{3+}, VO^{2+}, and Pb^{2+}, give nearly quantitative yields of nitrobenzene. The induction periods observed in each case, the inhibition by traces of 2,6-di-*tert*-butyl-4-methyl phenol,[18] and the fractional reaction orders appearing in the rate laws leave little doubt that we are dealing with a series of radical chain processes. Moreover, catalytic action by $V(acac)_3$, $MoO_2(dpm)_2$, and $Mo(CO)_6$, which are effective catalysts for nonchain electrophilic oxygen transfer reactions of hydroperoxides,[19] is marginal under our conditions.

The most straightforward kinetic picture appears to be associated with the reaction initiated by peroxalate. At hydroperoxide levels 0.005–0.4 *M*, nitrosobenzene levels 0.0075–0.02 *M*, and peroxalate 0.003–0.12 *M*, disappearance of nitrosobenzene, after short induction periods, follows the rate law

$$\text{rate} = -d(\text{PhNO})/dt = k_{\text{obsd}}(\text{In})^{1/2}(\text{BuO}_2\text{H})^{1/2}(\text{PhNO})^0$$

with $k_{\text{obsd}} = 7.0 \pm 0.5 \times 10^{-4}$ sec^{-1} in benzene, and $2.9 \pm 0.2 \times 10^{-4}$ sec^{-1} in cyclohexane at 25°. Typical kinetic data for peroxalate-initiated oxidations appear in Table I.

Table I. Typical Kinetic Data for the Oxidation of Nitrosobenzene with *tert*-Butyl Hydroperoxide, as Initiated by Di-*tert*-butyl Peroxyoxalate[a]

[Peroxalate], $M \times 10^2$	[t-BuO_2H], M	Rate (obsd) $\times 10^5$ [b]	Rate (calcd) $\times 10^5$ [c]
1.01	0.100	2.30	2.23
		2.18[d]	2.23
		2.10[e]	2.23
		2.30[f]	2.23
	0.150	2.70	2.73
1.84	0.100	2.94	3.00
1.01	0.200	3.00[d]	3.16
		3.2	3.16
1.01	0.300	3.9	3.87
3.46	0.100	4.2	4.15
1.01	0.400	4.4	4.43
		4.3[d]	4.43
7.05	0.100	6.0	5.85
12.1		8.1	7.75
1.01	0.020	0.42[e,g]	
	0.040	0.62[e,g]	
	0.080	0.81[e,g]	

[a] Reactions under pseudo-zero-order conditions at 25°. Solvent, benzene. $[\text{PhNO}]_{\text{init}} = 0.0120$ *M* unless otherwise indicated. [b] Rates in *M* sec^{-1}. [c] Rate (calcd) $= 7.03 \times 10^{-4}(\text{In})^{1/2}(\text{BuO}_2\text{H})^{1/2}$ (see text). [d] Reactions run in the absence of air (see Experimental Section). [e] $[\text{PhNO}]_{\text{init}} = 0.0015$ *M*. [f] $[\text{PhNO}]_{\text{init}} = 0.0060$ *M*. [g] Reactions in cyclohexane at 25°.

The decomposition of t-BuO_2H, as initiated by peroxalate in benzene at 25°, has been shown to form t-BuO· and t-BuO_2· as the only intermediates,[20] whereas decomposition of the peroxalate in the absence of hydroperoxide produces just t-BuO·.[13a] Since the oxidation of nitrosobenzene does not proceed at a measurable rate in the absence of hydroperoxide, t-BuO_2· is implicated as the active oxidizing species in the present reaction. Moreover, in view of the ease with which C-nitroso compounds react with organic radicals in general[21] and alkoxy radicals in particular[22] to form stable nitroxides, at least partial diversion of t-BuO· to Ph(t-BuO)NO· is to be expected. Our observations are consistent with the following chain mechanism (eq 1–4) in which conversion to nitrobenzene

$$\text{In} \xrightarrow{k_1} 2\text{BuO}\cdot + 2\text{CO}_2 \tag{1}$$

$$\text{BuO}\cdot + \text{PhNO} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Ph(BuO)NO}\cdot \tag{2}$$

$$\text{BuO}\cdot + \text{BuO}_2\text{H} \xrightarrow{k_3} \text{BuOH} + \text{BuO}_2\cdot \tag{3}$$

$$\text{BuO}_2\cdot + \text{PhNO} \xrightarrow{k_4} \text{PhNO}_2 + \text{BuO}\cdot \tag{4}$$

occurs by oxygen-atom transfer from t-BuO_2·.[23] No bimolecular termination step, or combination of steps, involving BuO· or BuO_2·, but no other species, fits our rate law. However, steady-state treatment[24] of the sequence above, with termination by reaction 5,

$$\text{BuO}_2\cdot + \text{Ph(BuO)NO}\cdot \xrightarrow{k_5} \text{inactive products}^{25} \tag{5}$$

leads to the expression

$$\text{rate} = \left[\frac{2k_1k_3k_4k_{-2}}{k_2k_5}\right]^{1/2}(\text{In})^{1/2}(\text{BuO}_2\text{H})^{1/2}(\text{PhNO})^0$$

in accordance with the observed kinetic picture. No kinetic indication appears for termination by dimeriza-

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(18) See, for example, K. U. Ingold, *Advan. Chem. Ser.*, No. **75**, 302 (1968).

(19) (a) N. Indictor and W. F. Brill, *J. Org. Chem.*, 30, 2074 (1965); (b) M. N. Sheng and J. G. Zajacek, *Advan. Chem. Ser.*, No. **76**, 418 (1968); (c) R. Hiatt and C. McColeman, *Can. J. Chem.*, **49**, 1712 (1971).

(20) (a) A. Factor, C. A. Russell, and T. G. Traylor, *J. Amer. Chem. Soc.*, 87, 3692 (1965); (b) R. Hiatt, J. Clipsham, and T. Visser, *Can. J. Chem.*, 42, 2754 (1964).

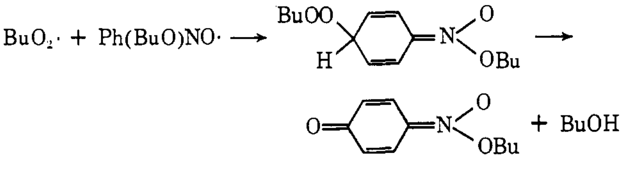
(21) (a) A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer, *Tetrahedron Lett.*, 2115 (1966); (b) C. Lagercrantz and S. Forshult, *Nature (London)*, **218**, 1247 (1968); (c) G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Amer. Chem. Soc.*, **90**, 7141 (1968); (d) I. H. Leaver and G. C. Ramsay, *Tetrahedron*, **25**, 5669 (1969); (e) K. Torssell, *ibid.*, **26**, 2759 (1970); (f) S. Terabe and R. Konaka, *J. Amer. Chem. Soc.*, **93**, 4306 (1971).

(22) An esr study of t-BuO(Ph)NO· radicals formed by the decomposition of di-*tert*-butyl peroxalate in solutions containing nitrosobenzene has been reported by A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer, and J. D. W. van Voorst [*Tetrahedron Lett.*, 385 (1967)]. These authors point out the structural similarity between this radical and the $PhNO_2H$· radical described by R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963).

(23) (a) Related reactions, in which oxygen atoms are transferred from RO_2· to nitrogen in arylamines, have been described by K. Adamic, D. F. Bowman, and K. U. Ingold [*J. Amer. Oil Chem. Soc.*, **47**, 109 (1970)]. For evidence of oxygen transfer from RO_2· to phosphorus, see C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **81**, 1243 (1959); and S. A. Buckler, *ibid.*, **84**, 3093 (1962). (b) Oxidations of nitroso compounds by peroxo derivatives under nonradical conditions have been described by K. M. Ibne-Rasa, C. G. Lauro, and J. O. Edwards [*J. Amer. Chem. Soc.*, **85**, 1165 (1963)], and by O. Ogata and T. Akada [*Tetrahedron*, **28**, 15 (1972)]. Oxidation of 2-methyl-2-nitrosopropane *via* oxygen atom transfer from NO_2 has been described by P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 1379 (1972).

(24) See, for example, the treatment described by L. Bateman [*Quart. Rev., Chem. Soc.*, **8**, 147 (1954)], which assumes long kinetic chains. We calculate a chain length of 115 for the peroxalate-initiated reaction when (In) = 0.01 *M* and (t-BuO_2H) = 0.3 *M*.

(25) We thank "Referee I" for suggesting the termination sequence



in analogy to the mode of decay of *tert*-butyl phenylnitroxide [A. R. Forrester and R. H. Thomson, *Nature (London)*, 203, 74 (1964)]. For reactions of peroxy radicals with diaryl nitroxides, see I. T. Brownlie and K. U. Ingold, *Can. J. Chem.*, **45**, 2427 (1967).

tion of nitroxide radicals and subsequent disproportionation, a process for which there is evidence in the absence of alkyl peroxy radicals.[26]

Since the initiator participates neither in the butoxide–nitroxide equilibrium (step 2), the propagation (steps 3 and 4), nor the termination reaction (step 5) in the sequence above, any variation in rate or in reaction order resulting from substitution of one initiator for another may be taken to reflect changes only in initiation. In particular, the rates of initiation, R_i values, associated with various catalysts in this study are related to observed oxidation rates

$$(\mathrm{rate})_A/(\mathrm{rate})_B = [(R_i)_A(\mathrm{BuO_2H})_A/(R_i)_B(\mathrm{BuO_2H})_B]^{1/2}$$

where A and B refer to parallel experiments carried out with different catalyst preparations. The experiments with di-*tert*-butyl peroxalate, for which the specific rate of initiation is estimated as 1.7×10^{-5} sec^{-1},[27] allow us to place the various initiation rates on an absolute kinetic scale.

Catalysis by $Co(dpm)_2$ and by $Mn(acac)_3$. The most powerful oxidation catalyst in the present series is $Co(dpm)_2$;[28] at the 10^{-6} *M* level, reaction rates with this catalyst are comparable to those with 10^{-2} *M tert*-butyl peroxalate.

With (BuO_2H) in the range 0.01–0.1 *M*, catalytic quantities of the pink $Co(dpm)_2$ are converted largely to a green Co(III) species in less than 1 sec; this oxidation, in the absence of nitrosobenzene, may be followed under pseudo-first-order conditions (Table II) and has been found to be first order in each reaction component.

Table II. Kinetic Data for Oxidation of $Co(dpm)_2$ with $t\text{-}BuO_2H^a$

$[Co^{II}]_{init}$, $M \times 10^4$	$[BuO_2H]_{init}$, $M \times 10^5$	k, M^{-1} sec$^{-1\,b}$
5.00	1.60	200
	3.20	222
	6.40	210
2.08	1.60	193

[a] Reactions at 25.0° in cyclohexane. Oxygen excluded. Increases in absorbance at 600 nm (λ_{max} for Co^{III}) followed as a function of time. Path length, 10.0 cm. [b] $k = (Co^{II})^{-1}(BuO_2H)^{-1} \cdot [d(Co^{III})/dt]$.

$$\frac{d(Co^{III})}{dt} = -\frac{2d(BuO_2H)}{dt} = 2.0 \times 10^2(Co^{II})(BuO_2H)$$

(cyclohexane, 25°)

This kinetic picture, in conjunction with the observed 2:1 stoichiometry, suggests the sequence

$$Co^{II} + BuO_2H \xrightarrow{k\,=\,100\ M^{-1}\ \mathrm{sec}^{-1}} \begin{cases} Co^{III}OH \\ BuO\cdot \end{cases} \xrightarrow[\text{rapid}]{Co^{II}} Co^{III}\text{–}OBu$$

for the preliminary conversion, after which the added cobalt may be considered to exist as an equilibrium mixture of Co(II) and Co(III) species with the latter greatly predominating.

The oxidation of nitrosobenzene, as catalyzed by cobalt added originally as $Co(dpm)_2$, closely follows the rate expression

$$\mathrm{rate_{obsd}} = k(Co)_T^{1/2}(BuO_2H)(PhNO)^0$$

when $(Co)_T$, the total concentration of added cobalt, is in the range $1.0\text{–}15.0 \times 10^{-6}$ *M*, and (BuO_2H) lies between 0.025 and 0.2 *M*. Typical data are given in Table III.[29]

Table III. Kinetic Data for the Oxidation of Nitrosobenzene with *tert*-Butyl Hydroperoxide, as Catalyzed by $Co(dpm)_2$ and by $Mn(acac)_3{}^a$

Catalyst	(Cat), $M \times 10^5$	$(t\text{-}BuO_2H)$, M	Rate (obsd) $\times 10^{5\,b}$	Rate (calcd) $\times 10^{5\,c}$
$Co(dpm)_2$	0.650	0.0250	1.06	1.15
	0.060	0.100	1.37	1.39
	0.120		1.95	1.96
	0.150		2.19	2.20
	0.650	0.050	2.36	2.30
	0.300	0.100	3.1	3.11
	0.650	0.0750	3.5	3.44
	0.600	0.100	4.5	4.41
	0.650	0.100	4.6	4.59
	0.650	0.150	6.8	6.88
	1.50	0.100	7.0	6.98
	0.650	0.200	9.0	9.18
$Mn(acac)_3$	3.96	0.0250	1.37	1.39
	0.710	0.100	2.46	2.34
	3.96	0.0500	2.74	2.77
	1.42	0.100	3.4	3.31
	3.96	0.0750	4.2	4.16
	2.85	0.100	4.8	4.70
	3.96	0.100	5.6	5.54
	5.70	0.100	6.7	6.64
	3.96	0.150	8.4	8.32
	11.4	0.100	9.3	9.41
	3.96	0.200	11.2	11.1

[a] Reactions under pseudo-zero-order conditions at 25°. Solvent, benzene. $(PhNO)_{init} = 0.0120$ *M*. [b] Rates in *M* sec^{-1}. [c] Rate (calcd) $= k_{cat}(cat)^{1/2}(BuO_2H)$, where $k_{cat} = 1.80 \times 10^{-1}$ $M^{-1/2}$ sec^{-1} for $Co(dpm)_2$, and 8.82×10^{-2} $M^{-1/2}$ sec^{-1} for $Mn(acac)_3$.

With two oxidation states of cobalt present, two modes of initiation, reactions 6 and 7, should be considered.[28a] The rate of initiation, R_i, as resulting from a combination of the two processes, may be shown to be[28a]

$$Co^{III} + BuO_2H \xrightarrow{k_6} Co^{II} + BuO_2\cdot + H^+ \qquad (6)$$

$$Co^{II} + BuO_2H \xrightarrow{k_7} {}^{III}Co\text{-}OH + BuO\cdot \qquad (7)$$

$$R_i = [2k_6k_7/(k_6 + k_7)](Co)_T(BuO_2H)$$

Since the overall rate is proportional to $R_i^{1/2}$ and in-

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(26) (a) K. Adamic, D. F. Bowman, and K. U. Ingold, *J. Amer. Chem. Soc.*, **92**, 1094 (1970). (b) The effect of solvent on the rate of the peroxalate-initiated reaction is in accord with evidence that nitroxide radicals are more strongly solvated in benzene than in cyclohexane. See, for example, W. G. Bentrude and A. K. MacKnight, *J. Amer. Chem. Soc.*, **92**, 5260 (1970).

(27) This value is obtained by extrapolation of the data of Bartlett, Benzing, and Pincock,[13a] who also present evidence that there is virtually no recombination of BuO· radicals within the solvent cage.

(28) (a) For a recent study, and review of earlier work, concerning the effects of Co(II) derivatives on the decomposition of $t\text{-}BuO_2H$, see R. Hiatt, K. C. Irwin, and C. W. Gould, *J. Org. Chem.*, **33**, 1430 (1968). (b) The oxidation of Co(II) to Co(III) with $t\text{-}BuO_2H$ in acetic acid has been studied by W. H. Richardson, *J. Amer. Chem. Soc.*, **87**, 247 (1965).

(29) The original choice of $Co(dpm)_2$, rather than $Co(acac)_2$, as a Co^{II} catalyst was dictated by the desire to avoid complications due to polymerization of the latter chelate in solution [see, for example, F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, 3, 1 (1964)]. However, preliminary experiments with $Co(acac)_2$ indicate that this catalyst obeys the same type of rate law as does $Co(dpm)_2$ (with $k_{cat} = 0.105$ $M^{-1/2}$ sec^{-1}), suggesting that under conditions of catalysis the small equilibrium concentration of Co^{II} is present principally in the monomeric form.

cludes an additional factor of $(BuO_2H)^{1/2}$ arising from the propagation sequence, the combined initiation mechanism is in accord with the observed rate law. If our interpretation of the preliminary conversion is correct, the specific rate of oxidation of $Co(dpm)_2$ in the absence of nitrosobenzene corresponds to $2k_7$ and greatly exceeds k_6. The specific rate for initiation then further simplifies to $2k_6$. Comparison with the peroxalate-initiated reaction leads to the figure 1.09 M^{-1} sec^{-1} for k_6, as contrasted to a value near 10^2 M^{-1} sec^{-1} for k_7.

A very similar picture, featuring cyclization between Mn^{II} and Mn^{III} species, both active in bimolecular initiation with hydroperoxide, appears to apply to the reaction as catalyzed by $Mn(acac)_3$, which obeys the same type of rate law as the $Co(dpm)_2$ reaction (Table III). The rate constant for the composite initiation process is 0.54 M^{-1} sec^{-1}. Although we have not been able directly to evaluate specific rates for either of the individual steps, the extreme ease with which manganese(II) diketonates are converted to Mn^{III} under mild oxidizing conditions[4,6] leads us to suspect that, as with cobalt, the specific rate of initiation by Mn^{II} is substantially greater than that by Mn^{III}, and lends support to a specific rate near the indicated lower limit for reaction 8, the analog of (6).

$$Mn^{III} + BuO_2H \xrightarrow{k_8} Mn^{II} + BuO_2\cdot + H^+ \qquad (8)$$
$$k_8 \geqslant 0.26\ M^{-1}\ \text{sec}^{-1}\ (25°, \text{benzene})$$

Note that, under our conditions, the tris-chelate $Co(dpm)_3$, in solution, is nearly catalytically inactive in the oxidation of nitrosobenzene. The contrast with the behavior of $Co(dpm)_2$ which, at the hydroperoxide levels employed here, is converted almost quantitatively to a Co(III) species, doubtless reflects the need for ease of substitution at the Co(III) center,[30] and suggests that initiation step (6) involves coordination of hydroperoxide at that site. The observed catalytic capabilities of $Mn(acac)_3$ and the more erratically behaving $Ce(dpm)_4$ (see Experimental Section) are in accord with the greater degree of substitution lability at these metal centers.[31]

Catalysis by $VO(dpm)_2$. Addition of hydroperoxides to chelates of VO^{2+} (but not to $V(acac)_3$ or to vanadium(V) esters)[17] in nonpolar solvents results in the rapid formation of intensely absorbing red materials. Spectral data pertaining to the reaction of $VO(dpm)_2$ with t-BuO_2H, indicating the resulting species to be a 1:1 complex having an association constant 1.9 × 10^3 M^{-1} at 25°, are given in Table IV.[32] At higher concentrations of hydroperoxide, this complex fades, but the fading appears to result from the superposition of two effects, the reversible formation of still another species, presumably a diperoxo complex, and an irreversible oxidation of the 1:1 complex.

Table IV. Absorbance Data for Mixtures of $VO(dpm)_2$ and t-BuO_2H in Benzene[a]

$(BuO_2H)_{init}$, $M \times 10^3$	Abs (508 nm)	(Adduct), $M \times 10^4$ [b]	K_{eq}, M^{-1} $\times 10^3$ [c]
15.00	0.910	4.79	
10.00	0.910	4.79	
2.000	0.690	3.64	1.93
1.200	0.570	3.00	1.86
0.800	0.458	2.41	1.81
0.600	0.390	2.05	1.89
0.400	0.292	1.53	1.91
0.000	0.0	0	
	K_{eq} (av) = 1.88 × 10^3 M^{-1}		

[a] Measurements carried out at 25.0° in a 1.00-cm cell. $[VO(dpm)_2]_{init}$ = 4.79 × 10^{-4} M in all cases. [b] [Adduct] assumed to be proportional to absorbance. Molar absorbance for adduct calculated to be 1.90 × 10^3. [c] Calculated as $x/[(BuO_2H)_{init} - x][(VO^{2+})_{init} - x]$, where x is the concentration of the adduct.

The oxidation of nitrosobenzene, as catalyzed by $VO(dpm)_2$, exhibits the usual half-order dependence on catalyst and zero-order dependence on PhNO, but its dependence on hydroperoxide conforms to the two-term rate law

$$\frac{-d(PhNO)}{dt} = (cat)^{1/2}(BuO_2H)^{1/2}[k_V + k_V'(BuO_2H)]^{1/2}$$

in the concentration ranges (cat) = 10^{-4}–2 × 10^{-3} M, (BuO_2H) = 0.05–0.40 M, and $(PhNO)_{init}$ = 0.005–0.02 M. Typical data are given in Table V.

Table V. Kinetic Data for the Oxidation of Nitrosobenzene with *tert*-Butyl Hydroperoxide, as Catalyzed by $VO(dpm)_2$[a]

[Catalyst], $M \times 10^4$	[t-BuO_2H], M	Rate (obsd) $\times 10^5$ [b]	Rate (calcd) $\times 10^5$ [c]
1.15	0.100	1.63	1.59
2.30	0.100	2.40	2.26
6.40	0.050	2.41	2.46
4.60	0.100	3.4	3.20
6.40	0.100	3.8	3.78
9.20	0.100	4.6	4.52
6.40	0.150	5.0	4.98
6.40	0.200	6.1	6.10
18.4	0.100	6.5	6.40
6.40	0.300	8.2	8.30
6.40	0.400	10.4	10.50

[a] Reactions under pseudo-zero-order conditions at 25°. Solvent, benzene. $(PhNO)_{init}$ = 0.0120 M. [b] Rates in M sec^{-1}. [c] Rate (calcd) = $(cat.)^{1/2}(BuO_2H)^{1/2}[k_V + k_V'(BuO_2H)]^{1/2}$, where k_V = 1.53 × 10^{-5} sec^{-2} and k_V' = 7.1 × 10^{-5} M^{-1} sec^{-2}.

The two k_V terms in brackets in this rate law imply two independent initiation sequences, with the activated complex for the second of these featuring one more hydroperoxide per vanadium than that for the first. No fall-off of rate indicating conversion of the catalyst from a more to a less active form occurs during reaction; hence, cyclization of the catalyst between oxidation states may be inferred, and the catalytic activity observed for n-butyl vanadate, a vanadium(V) ester, is consistent with cyclization between V^{IV} and V^V in the diketonate system. Since conversion of $VO(dpm)_2$ to a monohydroperoxo complex is found to be very nearly complete at hydroperoxide levels near 10^{-2} M, *i.e.*, well below the concentration range used in the kinetic experiments, the

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(30) Substitution reactions at the metal center in $Co(acac)_3$ and related tris chelates of cobalt(III) may be regarded as negligibly slow at 25° in nonpolar solvents. See, for example, (a) R. W. Kluiber, *J. Amer. Chem. Soc.*, **82**, 4839 (1960); and (b) J. P. Collman and J. Y. Sun, *Inorg. Chem.*, 4, 1273 (1965).

(31) (a) For kinetic studies of substitution reactions at Mn(III) centers, see A. W. Adamson, J. P. Welker, and W. B. Wright, *J. Amer. Chem. Soc.*, 73, 4786 (1951); and R. C. Fay and T. S. Piper, *ibid.*, **85**, 500 (1963). (b) Substitution reactions at Ce(IV) centers have been studied by T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, **5**, 233 (1966).

(32) A similar spectral study of the reaction of $Ce(dpm)_4$ with t-BuO_2H at 370 nm indicates the formation of a complex of the type $Ce(dpm)_4 \cdot 2BuO_2H$ having a stability constant 13 M^{-2} in benzene at 25°.

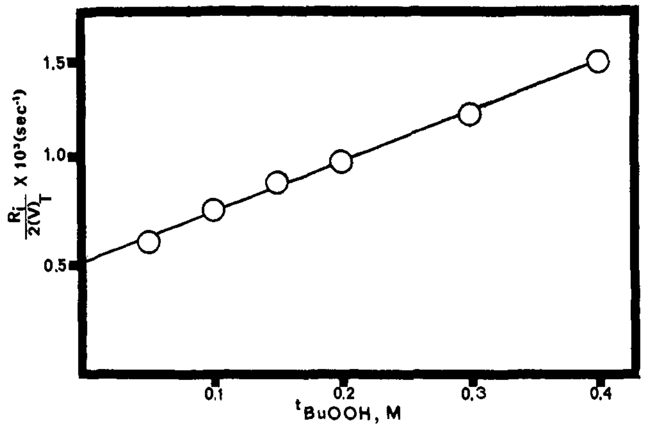


Figure 1. Catalysis, by VO(dpm)$_2$, of the oxidation of nitrosobenzene with t-BuO$_2$H; reactions in benzene at 25.0°. Variation of the ratio $R_i/2(V)_T$ with concentration of t-BuO$_2$H. R_i is the rate of initiation,[35] and $(V)_T$ the total concentration of added vanadium. Intercept of the line shown gives the value of 5.1×10^{-4} sec^{-1} for k_9, the specific rate corresponding to unimolecular homolysis of the vanadium(IV)-hydroperoxide complex. The slope of the line gives the value 2.3×10^{-3} M^{-1} sec^{-1} for k_{10}, the specific rate for reaction of this complex with a second molecule of hydroperoxide (see text).

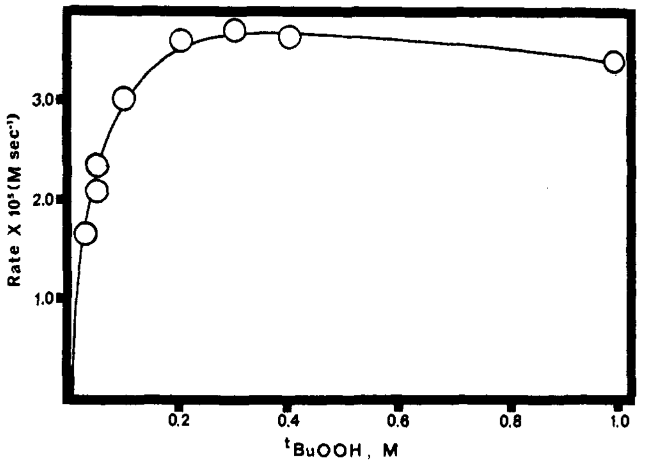
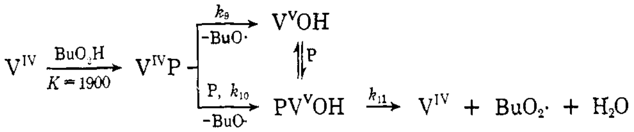


Figure 2. Catalysis, by Pb(dpm)$_2$, of the oxidation of nitrosobenzene with t-BuO$_2$H; reactions in benzene at 25.0°. Variation of pseudo-zero-order rates with concentration of t-BuO$_2$H. $[\mathrm{PhNO}]_{\mathrm{init}} = 0.010$ M; $(\mathrm{Pb^{II}}) = 2.4 \times 10^{-4}$ M. Circles indicate observed rates; the solid line represents the relation, rate $= k_{\mathrm{Pb}} \cdot (\mathrm{BuO_2H})^{1/2}(\mathrm{Pb^{II}})[1 + K_2(\mathrm{BuO_2H})]^{-1}$, where $k_{\mathrm{Pb}} = 0.047$ $M^{-1/2}$ sec^{-1}, and K_2, the competitive inhibition constant associated with formation of Pb$^{\mathrm{II}}$(BuO$_2$H)$_2$, is 2.42 M^{-1} (see text).

two initiation paths may be taken to arise from VO(dpm)$_2$-BuO$_2$H (abbreviated V$^{\mathrm{IV}}$P) and VO(dpm)$_2$-BuO$_2$H + BuO$_2$H.[33] The proposed initiation sequences are represented in Scheme I. If initial con-

Scheme I



$$\begin{tikzcd}[column sep=large] & & \mathrm{V^{V}OH} \arrow[d, shift left, "P"] & & \\ \mathrm{V^{IV}} \arrow[r, "\mathrm{BuO_2H}", "K = 1900"'] & \mathrm{V^{IV}P} \arrow[ur, "k_9", "-\mathrm{BuO}\cdot"'] \arrow[dr, "\mathrm{P},\ k_{10}", "-\mathrm{BuO}\cdot"'] & & & \\ & & \mathrm{PV^{V}OH} \arrow[u, shift left] \arrow[r, "k_{11}"] & \mathrm{V^{IV}} + \mathrm{BuO_2}\cdot + \mathrm{H_2O} & \end{tikzcd}$$

version to V$^{\mathrm{IV}}$P is virtually complete, and if k_{11} greatly exceeds both k_9 and k_{10}, the rate of initiation may be approximated as

$$R_i = 2(\mathrm{V})_{\mathrm{T}}[k_9 + k_{10}(\mathrm{BuO_2H})]$$

where $(\mathrm{V})_{\mathrm{T}}$ represents the total concentration of added vanadium, and the overall rate of oxidation thus assumes the same form as the observed rate law.[34]

A plot of $R_i/2(\mathrm{V})_{\mathrm{T}}$ *vs.* (BuO$_2$H) (Figure 1) is linear[35] with an intercept of 5.1×10^{-4} sec^{-1}, corresponding to k_9, and a slope of 2.3×10^{-3} M^{-1} sec^{-1}, corresponding to k_{10}, the rate constant for the reaction of hydroperoxide with V$^{\mathrm{IV}}$P. The latter value is only about 10^{-2} as great as the specific rates for bimolecular initiation by Mn$^{\mathrm{III}}$ and Co$^{\mathrm{III}}$ chelates, but k_9 for the vanadium system represents not only the unimolecular homolysis of V$^{\mathrm{IV}}$P, but also bimolecular initiation resulting from reaction between BuO$_2$H and peroxide-free vanadium. The relative importance of these two kinetically indistinguishable processes cannot be evaluated, but the product $k_9K_{\mathrm{V^{IV}P}}$ sets an upper limt of 0.97 M^{-1} sec^{-1} for the bimolecular contribution.

In any event, it is clear that the role of vanadium in the catalyzed oxidation of nitrosobenzene is quite unrelated to its catalytic activity in the heterolytic epoxidations of olefins.[3,19a] In the present case, vanadium catalysis closely resembles that by cobalt and manganese, with kinetic peculiarities in the vanadium system stemming principally from diversion of this metal center to a remarkably stable hydroperoxo complex.[36]

Catalysis by Pb(dpm)$_2$. The catalytic activity associated with Pb(dpm)$_2$ lies between that of Mn(acac)$_3$ and that of VO(dpm)$_2$ under similar conditions. Since the principal oxidation states of lead differ by two units rather than by one, the effectiveness of the lead chelate in this capacity is perhaps unexpected. Moreover, the oxidation, as catalyzed by Pb(dpm)$_2$, does not pre-

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(33) Evidence has been presented[17] that neither coordination of hydroperoxide nor oxidation of the vanadium(IV) center to vanadium(V) alters the diketonate groups in VO(dpm)$_2$ under the reaction conditions here employed.

(34) The alternative view that the rate of the composite initiation process is determined by the conversion of V$^{\mathrm{V}}$ to V$^{\mathrm{IV}}$ (*i.e.* that k_{11} is less than k_9 and k_{10}) appears to be much less likely. It has been shown[3,17] that vanadium(V) is substantially converted to a diperoxo complex at the present hydroperoxide levels. If reaction by V$^{\mathrm{V}}$ were rate determining, this conversion would be reflected in a leveling off of rates at high (BuO$_2$H). Note also that the rate law observed for the vanadium-catalyzed oxidation provides evidence against substantial formation of a complex V$^{\mathrm{IV}}$P$_2$. If it is assumed that conversion of more than 10% of the added VO(dpm)$_2$ to such a complex at the highest hydroperoxide levels would result in detectable deviation from the binomial form indicated, an upper limit of 0.25 M^{-1} may be calculated for the stability constant of such a complex.

(35) Values of R_i may be conveniently calculated as $(\mathrm{rate})^2k_c^{-2} \cdot (\mathrm{BuO_2H})^{-1}$, where k_c, a composite constant associated with the propagation and termination steps, and defined as $(k_3k_4k_{-2}/k_2k_5)^{1/2}$, was found to have the value 0.121 sec$^{-1/2}$ in benzene at 25° from data on the peroxalate-catalyzed oxidations.

(36) In our hands, Ru(acac)$_3$ is a more effective catalyst for this oxidation than VO(dpm)$_2$, but less effective than Mn(acac)$_3$. Preliminary kinetic examination points to a reaction half-order in Ru(acac)$_3$ and zero order in nitrosobenzene, but other aspects remain unresolved. Moreover, we find no indication of complex formation between Ru(acac)$_3$ and t-BuO$_2$H in benzene. The pronounced catalytic action of Ru(acac)$_3$, despite its extreme reluctance to undergo ligand exchange,[37] suggests that, in this case, initiation occurs by outer-sphere reduction of hydroperoxide

$$\mathrm{Ru(acac)_3} + \mathrm{BuO_2H} \longrightarrow \mathrm{BuO}\cdot + \mathrm{Ru(acac)_3{}^{+}OH^{-}}$$

Such a mode of initiation is presumably ruled out for Co(dpm)$_3$ because of the inaccessibility of Co(IV); the outer-sphere oxidation of hydroperoxide is likewise improbable because of differences in coordination number and spin multiplicity within the Co(III)–Co(II) series.[38] Both modes are denied to Rh(acac)$_3$ because of the instability of the 2+ and 4+ states of this metal center.

(37) R. C. Fay, A. Y. Girgis, and U. Klabunde, *J. Amer. Chem. Soc.*, **92**, 7056 (1970).

(38) See, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968, p 511.

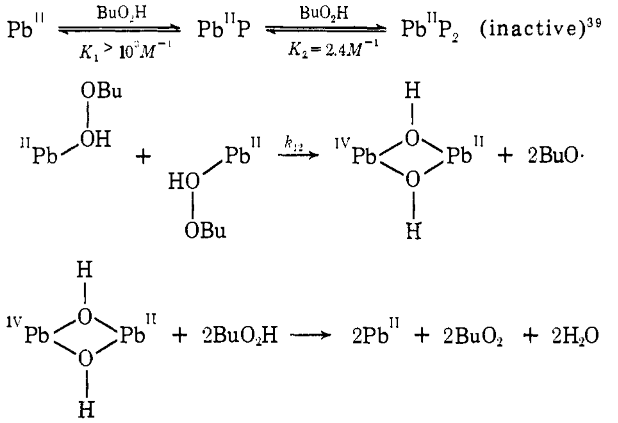
sent a simple kinetic picture. With (BuO_2H) <0.05 M, the apparent order in hydroperoxide is nearly one-half, but at higher concentrations, rates level off, and inhibition is observed (Figure 2). With (Pb) in the range 0.0002–0.002 M, oxidations are very nearly first, rather than half order, in catalyst. As with other catalysts, there are short induction periods, and rates thereafter are independent of (PhNO). Typical kinetic data appear in Table VI.

Table VI. Typical Kinetic Data for the Oxidation of Nitrosobenzene with *tert*-Butyl Hydroperoxide, as Catalyzed by $Pb(dpm)_2$[a]

[Catalyst], $M \times 10^4$	[t-BuO_2H], M	$[PhNO]_{init}$, M	Rate $\times 10^5$[b]
2.40	0.025	0.0020	1.65
2.40	0.050	0.010	2.06
2.40	0.050	0.0020	2.32
2.1	0.100	0.010	2.56
2.40	0.100	0.010	3.02
2.40	0.200	0.010	3.6
2.40	0.300	0.010	3.7
2.40	0.400	0.010	3.6
2.40	1.00	0.010	3.3
3.5	0.100	0.010	4.1
7.0	0.100	0.010	7.3
14.0	0.100	0.010	14.0

[a] Reactions under pseudo-zero-order conditions at 25°. Solvent, benzene. [b] Rates in $M\,sec^{-1}$.

Scheme II



Despite the kinetic oddities, the oxidation may once again be considered a radical-chain process with the metal undergoing cyclization between oxidation states. Observed rates are in accord with the relation

$$\text{rate} = \frac{-d(PhNO)}{dt} = \frac{k_{Pb}(BuO_2H)^{1/2}(\text{cat.})}{1 + K_2(BuO_2H)}$$

where $k_{Pb} = 4.7 \times 10^{-2}\ M^{-1/2}\ sec^{-1}$, and $K_2 = 2.42\ M^{-1}$ at 25°. The factor $(BuO_2H)^{1/2}$ may be assumed to arise, in the usual manner, from the propagation sequence, and the remainder of the expression from the initiation, the rate of which is proportional to $(\text{rate})^2_{obsd}$ and hence to $(\text{cat.})^2[1 + K_2(BuO_2H)]^{-2}$. The rate law thus implies a transition state for initiation containing two lead atoms and indicates competitive inhibition resulting from formation of an inactive complex having one more hydroperoxide per lead than the active species. Since the latter must have at least one hydroperoxide to generate the BuO· radicals involved in propagation, the inactive species must be at least a dihydroperoxo complex, $Pb^{II}P_2$. The present data fit the initiation sequence in Scheme II.

Interconversions of the various Pb^{II} species, which may be taken to be very rapid[40] in comparison to the homolytic steps in which the oxidation number of lead changes, are not accompanied by observable spectral shifts, but none would be anticipated, for it has been found[41] that substitution of one O-donor ligand for another at a Pb(II) center is without significant effect on absorbance in the accessible ultraviolet. The juxtaposition of the two oxidation states of lead in the proposed Pb(II)–Pb(IV) intermediate brings to mind the structure of crystalline Pb_3O_4, in which structurally distinct Pb^{2+} and Pb^{4+} are linked through oxygen bridges.[42] If, as seems likely, the destruction of Pb^{IV} is very rapid in the peroxidic medium employed,[43] the rate of initiation may be approximated as $4k_{12}\cdot[Pb^{II}P]^2$, and the inhibition at high hydroperoxide concentrations is quantitatively attributable to diversion of lead to PbP_2.

The chief feature of interest in the suggested mechanism is the bimolecularity of the rate-determining step. Although the details are obscure, the indicated route appears to retain the free-radical character of the catalyzed oxidation while allowing the system to bypass Pb(III). This odd-electron species has been proposed, with reservations, as an intermediate in some oxidations with Pb(IV),[44] but no convincing evidence has yet been presented that it is involved in the reactions of Pb(II).

Acknowledgment. The authors thank Drs. David Allara and William Movius for valuable discussions.

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[39] (a) The lower limit indicated for K_1 is consistent with a deviation of less than 5% from the half-order hydroperoxide dependency observed at low (BuO_2H). Chelating groups, which presumably are not altered, are omitted from this initiation scheme. (b) For recent studies of peroxo derivatives of lead in organic systems, see J. E. Bennett and J. A. Howard, *J. Amer. Chem. Soc.*, **94**, 8244 (1972).

[40] For evidence that substitution reactions at the related $d^{10}s^2$ center, Sn(II), are very rapid, see, for example, J. A. Johnson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, 32, 553 (1960).

[41] F. C. Hentz, Jr., and S. Y. Tyree, Jr., *Inorg. Chem.*, 3, 844 (1964).

[42] B. Dickens, *J. Inorg. Nucl. Chem.*, 27, 1509 (1965).

[43] For descriptions of rapid reactions of Pb^{IV} with hydroperoxides, see, for example (a) P. D. Bartlett and P. Gunther, *J. Amer. Chem. Soc.*, **88**, 3288 (1966); and (b) D. Benson and L. H. Sutcliffe, *Trans. Faraday Soc.*, **55**, 2107 (1959).

[44] See, for example (a) J. K. Kochi, J. D. Bacha, and T. W. Bethea III, *J. Amer. Chem. Soc.*, **89**, 6538 (1967); (b) W. H. Starnes, Jr., *ibid.*, **89**, 3368 (1967); (c) G. Gream and D. Wege, *Tetrahedron Lett.*, 503 (1967).