Inhibition of Oxidative Induced Decomposition of (αα′-Diphenyl)azoethane by Transition Metal Ions. Interactions of Metal Ions with α-Phenylethylperoxyl Radical

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(αα′-Diphenyl)azoethane (APE) decomposes faster in the presence of oxygen than in its absence by a factor $>10^2$. This oxidative-induced decomposition is suppressed by radical scavengers and transition metal ions both in their lower and higher valence states. The inhibiting effects of metal ions have been ascribed to their fast interactions with and stabilization of peroxyl radicals. When the metal concentration is low, the induced decomposition is observed after a specific suppression time which is determined by the concentration ratio of APE to metal ions. The effects of ligand and additives such as pyridine and carboxylic acid on the rate and products of decomposition of APE are also discussed.

TRANSITION metal ions play a significant role in the autoxidation of organic compounds and numerous studies have been carried out on the rate and mechanism of metal-catalysed oxidations from both fundamental and practical points of view.[1] Although their primary effects are to produce radicals and accelerate oxidation by the reactions with hydroperoxide, substrate, and oxygen, inhibition by metal complexes, especially by metal ions in lower valence states, has also been observed in some cases.[1-4] This phenomenon has been described as catalyst–inhibitor conversion by Betts and Uri [3] or dual function catalysis by Knorre *et al.*[4] However, the interpretations of these inhibition effects vary. It may be assumed that the interactions of metal ions with peroxyl radicals are important, and knowledge of these interactions provides a clue to the understanding of the inhibiting functions of metal ions. It is also observed that the interaction of metal ions with peroxyl radicals affects the product distribution as well.

The objective of this paper is to obtain information on the interactions of transition metal ions with peroxyl radicals. (αα′-Diphenyl)azoethane (APE) was chosen as the peroxyl radical source since upon thermal decomposition under oxygen it gives α-phenylethylperoxyl radical, the chain-carrying radical in the autoxidation of ethylbenzene whose rate and mechanism are now well understood. This interaction can also conveniently be compared to that of peroxyl radical with metal ions in the oxidation of ethylbenzene.

EXPERIMENTAL

Materials.—(αα′-Diphenyl)azoethane was synthesized either by the method of Cohen *et al.*[5] or by the modified method of Shelton and Liang,[6] and purified by repeated recrystallization from ethanol, m.p. 70.2—70.5 °C, $\lambda_{max.}$ (EtOH) 356 nm (ε 48.6), in agreement with the literature value [5-8] (Found: C, 80.63; H, 7.61; N, 11.75. Calc. for $C_{16}H_{18}N_2$: C, 80.24; H, 7.65; N, 11.47%). Quantitative (100.3%) nitrogen evolution was observed upon complete decomposition of APE at 115 °C in 250 min.

Chlorobenzene, 1-phenylethanol, and acetophenone were purified by conventional methods. Acetic acid, decanoic acid, and pyridine were used without further purification. Manganese(II) and cobalt(II) decanoates were prepared from the corresponding chlorides. Various metal acetylacetonates were used as received. Metal phthalocyanine complexes were kindly supplied by Dr. Bansho, National Chemical Laboratory for Industry. 4-Methyl-2,6-di-t-butylphenol (MBP) used as a radical scavenger was recrystallized from methanol several times.

Procedures.—The decomposition of APE was carried out in an ampoule immersed in a thermostatted silicone oil-bath. The rate of gas absorption or evolution was measured by following the pressure change using a pressure transducer. Initial and final gases in the reaction vessel were determined by a Toepler pump and subsequent gas analyses by g.l.c. using active charcoal and molecular sieve 13X columns. Condensable products were analysed by g.l.c. after treatment of the products with triphenylphosphine to reduce the hydroperoxide to alcohol. Acids were analysed as methyl esters obtained by the treatment with diazomethane. The peroxide content was determined by iodimetric titration and hydrogen peroxide was measured separately by the use of catalase. It was ascertained that catalase decomposed hydrogen peroxide quantitatively over the pH range 3—8.

RESULTS

Decomposition of APE in the Absence of Oxygen.—APE was decomposed first in the absence of oxygen to study the rate and mechanism of decomposition. The rate of decomposition measured by the rate of nitrogen evolution was found to be independent of both initial APE concentration and the presence or absence of radical inhibitor (MBP) which suggests that the induced decomposition of APE by α-phenylethyl radical is negligible. The rate constant of unimolecular decomposition k_d was 1.19×10^{-5} s^{-1} at 90 °C in chlorobenzene. The activation energy for decomposition was 35.0 kcal mol^{-1}, which is in fair agreement with 32.6 kcal mol^{-1} determined by Cohen and his co-workers.[5]

The complete decomposition of APE at 115 °C in α-chloronaphthalene under vacuum gave *ca.* 90% *meso-* and racemic-2,3-diphenylbutane and 9.2% ethylbenzene. Little styrene was observed, much less than ethylbenzene. This

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[1] N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, ' Liquid Phase Oxidation of Hydrocarbons,' Plenum Press, New York, 1967.

[2] N. M. Emanuel and A. B. Gagarina, *Russ. Chem. Rev.*, 1966, **35**, 260.

[3] A. T. Betts and N. Uri, *Adv. Chem. Ser.*, 1968, **76**, 160.

[4] D. G. Knorre, L. G. Chuchukina, and N. M. Emanuel, ' The Oxidation of Hydrocarbons in the Liquid Phase,' ed. N. M. Emanuel, Pergamon, London, 1965, p. 164.

[5] S. G. Cohen, S. J. Groszos, and D. B. Sparrow, *J. Amer. Chem. Soc.*, 1950, **72**, 3947.

[6] J. R. Shelton and C. K. Liang, *Synthetic Org. Chem.*, 1971, 204.

[7] S. Seltzer and E. J. Hamilton, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 3775.

[8] F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, 1970, **92**, 867.

must be ascribed to the polymerization of styrene formed. The above results show that APE gives primarily α-phenylethyl radicals which mostly recombine in the absence of oxygen to give 2,3-diphenylbutanes; there is only minor disproportionation as observed by Greene.[8]

Induced Decomposition of APE under Oxygen.—It was found that APE decomposed extremely fast in the presence of oxygen. This is quite interesting since azo-compounds have been accepted as stable toward free radicals and little induced decomposition has been observed except in special cases.[9,10] Typical examples are shown in Table 1. Decomposition under nitrogen is also included for comparison. With sufficient oxygen (runs 2 and 3), APE decomposed completely in 20 min and gave nitrogen quantitatively. With insufficient oxygen (runs 4 and 5), APE decomposed rapidly until the oxygen was exhausted, then it decomposed slowly with the same rate as that under nitrogen. It was found that introduction of more oxygen after initial oxygen was exhausted brought about resumption of the rapid induced decomposition. The ratio of oxygen absorbed to nitrogen evolved in the induced decomposition was *ca.* 2.2.

TABLE 1

Oxidative induced decomposition of APE at 90 °C in 10 ml chlorobenzene

Run no.	[APE]/ mmol	t/min	$[O_2]^0$/ mmol	-10^7d[Gas]/dt/ mol l s^{-1}	$\Delta[O_2]$/ mmol	$\Delta[N_2]$/ mmol	$\frac{\Delta[O_2]}{\Delta[N_2]}$	$\frac{[R(-H)O]^a}{[ROH]}$
1	0.500	120	0	−5.93		0.046 1		
2	0.129	62	0.660	143	0.300	0.134	2.24	2.95
3	0.259	120	1.013	514	0.602	0.252	2.39	
4	0.502	60	0.733	668	0.717	0.331	2.16	2.29
5	0.500	120	0.749	702	0.738	0.354	2.09	

[a] R(−H)O, acetophenone; ROH, 1-phenylethanol.

The products of the oxidative induced decomposition of APE are shown in Table 2. The major products were ethylbenzene hydroperoxide, acetophenone, and 1-phenylethanol, but some benzaldehyde and methyl alcohol were also formed together with smaller amounts of benzoic acid, methyl hydroperoxide, and hydrogen peroxide. In addition, trace amounts of formic acid, ethylbenzene, and styrene were observed. Gas analysis showed the formation of a quantitative amount of nitrogen and quite a small amount of carbon dioxide, carbon monoxide, and methane.

TABLE 2

Products of oxidative induced decomposition of APE [a] (concentrations in mmol)

ΔN_2	0.280 [b]	Ethylbenzene hydroperoxide	0.180
$-\Delta O_2$	0.580	Acetophenone	0.128
ΔCO_2	Trace	1-Phenylethanol	0.080
ΔCO	~0.001	Benzaldehyde	0.058
		Benzoic acid	0.019
		Methyl alcohol	0.025
		Methyl hydroperoxide	0.015
		Hydrogen peroxide	0.011

[a] At 90 °C; APE (0.281 mmol) in chlorobenzene (10 ml); reaction time 37 min. [b] In the absence of oxygen, ΔN_2 0.007 3 mmol in 37 min.

The mechanism of oxidative induced decomposition of APE is not yet fully established, but a plausible suggestion is as follows. Since the rapid induced decomposition of APE is observed only in the presence of oxygen and since, as shown later, this induced decomposition is suppressed quite efficiently by radical inhibitor, the important primary step must be abstraction of tertiary hydrogen by, probably, α-phenylethylperoxyl radical. Although the removal of another tertiary hydrogen may then become easier due to the stabilization by resonance, the fact that no acetophenone azine was observed suggests that the resulting radical reacts exclusively with oxygen to give peroxyl radical, which may decompose into nitrogen, α-phenylethyl radical and α-hydroperoxystyrene, or diradical. The α-phenylethylperoxyl radicals must give ethylbenzene hydroperoxide by abstraction of hydrogen and also acetophenone and 1-phenylethanol by their mutual interactions. The bimolecular interaction of α-phenylethylperoxyl radicals may not always be terminating at 90 °C but some non-terminating interactions to give alkoxyl radicals may compete as well.[11,12] The β-scission of α-phenylethyloxyl radical must yield benzaldehyde, benzoic acid, methanol, methyl hydroperoxide, and other minor products. Hydrogen peroxide must arise from the oxidation of 1-phenylethanol.

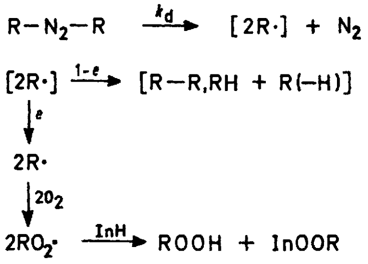
TABLE 3

Decomposition of APE under oxygen in the presence of MBP at 90 °C in chlorobenzene (10 ml)

Run no.	[APE]/ mmol	[MBP]/ mmol	t/ min	-10^7d[Gas]/dt/ l mol^{-1} s^{-1}	$t_{inhibition}$/ min
6	0.500	0.894	120	3.61	
7	0.501	0.559	123	3.60	
8	0.501	0.218	143	3.58	
9	0.500	0.197	123	3.82	
10	0.500	0.0186	120		~60 [a]

[a] Calculated inhibition time is 64.3 min, see text.

Suppression of Induced Decomposition by MBP.—Table 3 shows that the oxidative induced decomposition of APE is suppressed quite efficiently by MBP. The decomposition of



SCHEME Decomposition of APE under oxygen in the presence of MBP. The brackets indicate the solvent cage

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[9] P. Knittel and J. Warkentin, *Canad. J. Chem.*, 1975, **53**, 2275.

[10] V. Horanska, J. Barton, and Z. Manasek, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1972, **10**, 2701.

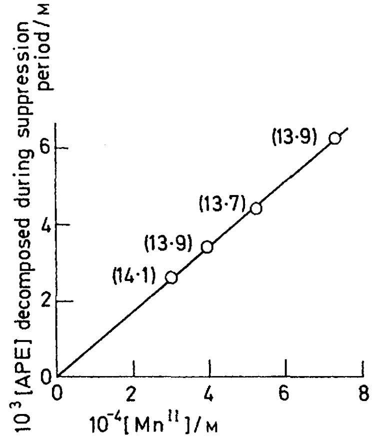
[11] D. Lindsay, J. A. Howard, E. C. Horswill, L. Iton, K. U. Ingold, T. Cobbley, and A. Ll, *Canad. J. Chem.*, 1973, **51**, 870.

[12] J. E. Bennett and R. Summers, *Canad. J. Chem.*, 1974, **52**, 1377.

APE under oxygen in the presence of MBP must proceed as shown in the Scheme. Under these circumstances, the rate of gas absorption is given by equation (1) where e and k_d

$$-d[\mathrm{Gas}]/dt = (2e - 1)k_d[\mathrm{APE}] \qquad (1)$$

represent the efficiency of radical production and unimolecular decomposition rate constant of APE respectively. Table 3 and k_d give e 0.81 at 90 °C in chlorobenzene.



Trapping of peroxyl radical by manganese(II) decanoate in the decomposition of APE in chlorobenzene under oxygen at 90 °C, $[\mathrm{APE}]_0 = 5.0 \times 10^{-2}$M. Numbers in parentheses are the calculated number of peroxyl radicals trapped by each manganese(II) ion

When the initial MBP concentration is much smaller than that of APE, rapid gas absorption was observed after a specific inhibition time which was the function of the [APE] : [MBP] ratio. The observed inhibition time agreed reasonably well with that calculated from $t_{\mathrm{inhibition}} = [\mathrm{MBP}]/ek_d\,[\mathrm{APE}]$

Effects of Addition of Transition Metal Salts.—It was found that the addition of transition metal salts was also effective in suppressing the oxidative induced decomposition of APE, implying the contribution of fast interactions between metal ions and peroxyl radicals.

(i) *Manganese*(II) *decanoate*. Table 4 shows that manganese(II) decanoate suppressed the induced decomposition and reduced the rate of gas absorption by a factor of *ca.* 10^2. Table 5 shows that a small amount of manganese(II) decanoate suppresses the induced decomposition but that rapid induced decomposition was brought about after a specific suppression time. The suppression time was dependent on the manganese(II) ion concentration at constant initial [APE] and it increased with increasing [manganese(II) decanoate]. The Figure shows a plot of APE decomposed during the suppression time as a function of initial manganese(II) decanoate concentration. A good straight line was obtained and it was calculated that *ca.* 14 radicals, probably α-phenylethylperoxyl radicals, were trapped by each manganese(II) ion before the induced decomposition took place. It was observed by u.v. analysis that manganese(II) ions were oxidized to manganese(III) ions during the suppression period.

Table 6 shows the effects of some additives on the decomposition of APE under oxygen. The addition of pyridine increased the suppression time and also the ratio of acetophenone to 1-phenylethanol. The effects of addition of acetophenone, 1-phenylethanol, and water were found to be quite small. Although small amount of acetic acid did not have any significant effect, the addition of *ca.* 2% v/v acetic acid markedly reduced the inhibiting function of manganese(II) decanoate and rapid induced decomposition was observed.

(ii) *Manganese*(II) *and manganese*(III) *acetylacetonates.* The pertinent results of the decomposition of APE under oxygen in the presence of manganese(II) acetylacetonate are summarized in Table 7. The effects of addition of pyridine, decanoic acid, and acetic acid are also included in Table 7. In general, similar results were obtained as those in the presence of manganese(II) decanoate. The rate of gas absorption decreased considerably with time, which may be ascribed to the oxidation of chelate. With increasing concentration of initial manganese(II) acetylacetonate, more carbon monoxide and dioxide were observed, which also implies the oxidation of chelate. The effect of addition of pyridine is quite remarkable. In the presence of pyridine, the rate of gas absorption increased considerably with increasing manganese(II) concentration and the

TABLE 4

Decomposition of APE in the presence of manganese(II) decanoate at 90 °C in chlorobenzene (10 ml)

Run no.	[APE]/ mmol	[Mn^{II}]/ mmol	t/min	-10^7d[Gas]/dt/ mol l^{-1} s^{-1}	$-\Delta[O_2]$/ mmol	$\Delta[N_2]$/ mmol	$-\Delta[O_2]$/ $\Delta[N_2]$	[R(−H)O]/ [ROH]
11	0.501	0.018 8	92	4.18	0.104	0.080 6	1.29	1.52
12	0.500	0.033 5	120	6.14	0.140	0.097 8	1.43	1.38
13	0.501	0.114	128	8.06	0.129	0.093 0	1.38	1.26
14	0.499	0.087 9	120	8.04	0.122	0.097 5	1.25	1.13

TABLE 5

Suppressed and induced decomposition of APE under oxygen in the presence of manganese(II) decanoate at 90 °C [APE (0.500 mmol) in chlorobenzene (10 ml)]

Run no.	[Mn^{II}]/ mmol	Reaction time (min)	Suppression time (min)	10^7R_{sup} [a]	$R_{\mathrm{max.}}$ [b]/ mol l^{-1} s^{-1}	$\Delta[O_2]$ [c]/ mmol	$\Delta[N_2]$/ mmol	$\Delta[O_2]$/ $\Delta[N_2]$	[R(−H)O]/ [ROH]	[½Mn^{3+} + HPO] [d]/ mmol
15	0.003 00	114	75		588	0.898	0.488	2.00	2.05	0.300
16	0.004 01	106	96	4.11		0.386	0.189	2.04		
17	0.005 21	156	130	4.66	352	0.778	0.374	2.07	1.79	0.260
18	0.007 26	208	186	4.86	148	0.704	0.325	2.17	1.25	0.166
19 [e]	0.003 00	542	350	3.08	11.6	0.607	0.371	1.64	4.23	0.080 2

[a] Rate of gas absorption during suppression period. [b] Maximum rate of gas absorption during oxygen-induced decomposition. [c] Oxygen was substantially exhausted. [d] Determined by iodimetric titration. [e] With added pyridine (0.2 ml).

ratio of acetophenone to 1-phenylethanol was also increased. On the other hand, the addition of decanoic acid gave higher rate of gas absorption but a lower acetophenone: 1-phenylethanol ratio. Acetic acid brought about the oxidative induced decomposition as observed previously.

Table 8 shows that manganese (III) ion was also effective in suppressing the oxidative induced decomposition. The effects of additives are similar to those in the presence of manganese(II) acetylacetonate.

(iii) *Manganese phthalocyanine.* Table 9 shows the results of decomposition of APE in the presence of manganese phthalocyanine. The characteristic feature of Table 9 is that much more acetophenone was formed than 1-phenylethanol.

Table 6

Effects of additives on decomposition of APE under oxygen in the presence of manganese(II) decanoate at 90 °C [APE (0.500 mmol) in chlorobenzene (10 ml)]

Run no.	$[Mn^{II}]$/ mmol	Additives	Concentration (mmol)	t/min	$-10^7 d[Gas]/dt$/ mol l^{-1} s^{-1}	$-\Delta[O_2]$/ mmol	$\Delta[N_2]$/ mmol	$-\Delta[O_2]/\Delta[N_2]$	[R(−H)O]/ [ROH]
20	0.017 8	Pyridine	2.585	131	3.33	0.110	0.094 2	1.17	2.41
21	0.081 9	Pyridine	0.365	120	4.13	0.130	0.090 7	1.43	1.31
22	0.079 9	Pyridine	2.585	120	2.21	0.112	0.099 0	1.13	
23	0.026 0	Acetic acid	3.162	120	533	0.708	0.358 1	1.98	2.00
24	0.049 3	Acetic acid	0.216	120	7.95	0.132	0.092 9	1.42	1.19
25	0.049 3	Decanoic acid	0.188	120	9.58	0.220	0.147 4	1.50	1.11
26	0.037 6	Water	2.376	120	4.95	0.113	0.090 1	1.26	1.11

Table 7

Decomposition of APE in the presence of manganese(II) acetylacetonate at 90 °C [APE (0.500 mmol) in chlorobenzene (10 ml)]

Run no.	$[Mn^{II}]$/ mmol	Additives	Concentration (mmol)	t/min	$-10^7 d[Gas]/dt$/ mol l^{-1} s^{-1}	$-\Delta[O_2]$/ mmol	$\Delta[N_2]$/ mmol	$-\Delta[O_2]/\Delta[N_2]$	[R(−H)O]/ [ROH]
27	0.014 6			123	3.59	0.211	0.163	1.29	1.79
28	0.032 4			120	6.60	0.123	0.082 9	1.48	1.63
29	0.043 4			136	9.16	0.193	0.096 0	2.01	1.56
30	0.062 0			120	9.11	0.184	0.085 4	2.15	0.976
31	0.122			120	11.1	0.248	0.104	2.39	0.931
32	0.005 61	Pyridine	2.585	120	3.92	0.102	0.092 3	1.11	2.17
33	0.032 4	Pyridine	2.585	120	7.26	0.129	0.092 7	1.39	
34	0.064 8	Pyridine	2.585	70	27.6	0.204	0.059 5	3.42	
35	0.123	Pyridine	2.585	120	87.6	0.588	0.103	5.71	3.76
36	0.102	Decanoic acid	0.172	120	97.3	0.503	0.133	3.79	0.571
37	0.039 5	Acetic acid	3.162	24	524	0.560	0.258	2.17	1.73

Table 8

Decomposition of APE in the presence of manganese(III) acetylacetonate at 90 °C [APE (0.500 mmol) in chlorobenzene (10 ml)]

Run no.	$[Mn^{III}]$/mmol	Additives	Concentration (mmol)	t/min	$-10^7 d[Gas]/dt$/ mol l^{-1} s^{-1}	$-\Delta[O_2]/\Delta[N_2]$	[R(−H)O]/ [ROH]
38	0.032 7			120	7.55	2.78	1.14
39	0.011 8	Pyridine	2.585	120	19.2	1.84	3.73
40	0.035 8	Pyridine	2.585	120	36.5	3.00	3.47
41	0.031 8	Acetic acid	3.162	46	320	2.34	2.00

Table 9

Decomposition of APE in the presence of manganese phthalocyanine at 90 °C [APE (0.500 mmol) in chlorobenzene (10 ml)]

Run no.	$[Mn^{II}]$/mmol	Additives	Concentration (mmol)	t/min	$-10^7 d[Gas]/dt$/ mol l^{-1} s^{-1}	$-\Delta[O_2]$/ mmol	$\Delta[N_2]$/ mmol	$-\Delta[O_2]/\Delta[N_2]$	[R(−H)O]/ [ROH]
42	0.006 67			120	4.78	0.177	0.158	1.12	4.62
43	0.034 3			121	2.71	0.101	0.092 0	1.17	5.71
44	0.040 6	Pyridine	2.585	120	2.41	0.111	0.108 8	1.02	6.65
45	0.021 4	Acetic acid	3.162	60	303	0.617	0.283	2.18	2.51

Table 10

Decomposition of APE in the presence of cobalt(II) salts at 90 °C [APE (0.250 mmol) in chlorobenzene (5.0 ml)]

Run no.	Metal salt [a]	Concentration (mmol)	Additives	Concentration (mmol)	$-10^7 d[Gas]/dt$/ mol^{-1} l s^{-1}	$-\Delta[O_2]/\Delta[N_2]$	[R(−H)O]/ [ROH]
46	$CoDe_2$	0.014 4			2.71	1.28	3.30
47	$CoDe_2$	0.014 1	Pyridine	2.585	0.00	1.41	3.57
48	$CoDe_2$	0.023 0	Acetic acid	3.162	18.5	1.84	10.7
49	$CoAA_2$	0.016 1			8.26	1.33	2.74
50	$CoAA_2$	0.019 7	Pyridine	2.585	31.6	2.05	4.76

[a] De = decanoate; AA = acetylacetonate.

(iv) *Cobalt and other metal salts*. Results of decomposition of APE in the presence of cobalt(II) decanoate and acetylacetonate are shown in Table 10. The cobalt(II) salts suppressed the oxidative induced decomposition of APE and, after a specific suppression time which was a function of cobalt concentration, fast oxidative induced decomposition was observed. It was found that cobalt ions gave a higher acetophenone : 1-phenylethanol ratio than manganese ions. The addition of acetic acid gave a higher rate of gas absorption, but in contrast to manganese ions the rate was much smaller than the usual oxidative induced decomposition.

Cobalt(II) acetylacetonate produced similar effects to those of manganese(II) acetylacetonate in the presence and absence of pyridine except that cobalt salts yielded a higher acetophenone : 1-phenylethanol ratio than manganese(II) salts. Although the solubility of cobalt phthalocyanine in chlorobenzene was quite low, it was effective in suppressing oxidative induced decomposition.

Other metal salts such as nickel(II) acetylacetonate, copper(II) acetylacetonate, and iron phthalocyanine suppressed the induced decomposition. *NN'*-Ethylenebis(salicylideneaminato)cobalt(II) was also found to be an efficient inhibitor and it gave a high value of 8.6 for the acetophenone : 1-phenylethanol ratio.

DISCUSSION

The results show that all the metal complexes studied in this work are effective in suppressing the rapid oxidative induced decomposition of APE. It is interesting that both manganese(II) and manganese(III) ions are capable of suppressing the induced decomposition. Since the rate of gas absorption in the presence of metal ions was approximately the same as that in the presence of MBP and since induced decomposition was not observed in the absence of oxygen, fast interactions of metal ions with peroxyl radicals are suggested. When the concentration of metal ions was low, induced decomposition was observed after a specific suppression time, which was dependent on the concentration ratio of APE to metal ion. This implies that, after the interaction with a specific amount of peroxyl radicals, the metal complexes are degraded to an unreactive form which is no longer capable of scavenging peroxyl radicals. The inhibiting ability of low valence metal complexes has been previously observed and ascribed to their reducing ability as in reaction (2),[1,13] or to an ability to complex with

$$\mathrm{RO_2\cdot + M^{n+} \longrightarrow RO_2 : M^{(n+1)+}} \qquad (2)$$

peroxyl radicals without immediate oxidation of the metal.[14]

Although colour changes in solution suggest the oxidation of metal ions to a higher valence state, the fact that each metal ion can react on average with *ca.* 14 peroxyl radicals and that higher valence metal ions can also suppress induced decomposition suggest that these inhibitions cannot solely be ascribed to reaction (2).

The interactions of metal ions at higher valence state with peroxyl radicals have been mentioned by several investigators.[15] Tochina *et al.*[16] suggested the contribution of a terminating interaction of manganese(III) ion in the oxidation of ethylbenzene. Tkac *et al.*[17] studied the reactions of cobalt(III) acetylacetonate with t-butyl hydroperoxide by e.s.r. and reported the formation of a relatively stable complex between cobalt(III) ion and peroxyl radical. However, as pointed out by Ingold,[18] the formation and stability of this kind of complex have not been verified and apparently await further work. Kharasch and his co-workers [19] proposed reaction (3) from the rate of oxygen evolution in the decomposition of hydroperoxide. Kamiya and Kashima [20] measured the

$$\mathrm{RO_2\cdot + M^{3+} \longrightarrow R^+ + O_2 + M^{2+}} \qquad (3)$$

rates of decrease in cobalt(III) ions and formation of ketone in the oxidation of hydrocarbons catalysed by cobalt(III) ions and proposed reaction (4). Neither of

$$\mathrm{RO_2\cdot + M^{3+} \longrightarrow R(-H)O + \tfrac{1}{2}O_2 + H^+ + M^{2+}} \qquad (4)$$

these reactions is directly and conclusively established. However, the results of the present study demonstrate the important contribution of higher valence state metal ions with peroxyl radicals.

As shown in Tables 4 and 7, the rate of gas absorption in the suppression period increased with increasing concentration of manganese ions. This may arise from the oxidation of ligand and/or chlorobenzene. Although chlorobenzene is usually stable and inert, it is nevertheless oxidized at a slow but steady rate especially in the absence of readily oxidizable substrate. The rate of oxidation of neat chlorobenzene was 1.36×10^{-7} mol l^{-1} s^{-1} in the presence of 1.22×10^{-2}M-manganese(II) decanoate at 90 °C.

It may also be possible that peroxyl radicals complexed with manganese ions can still induce decomposition of APE. Tkac *et al.*[16] reported that peroxyl radicals which were stabilized in the ligand field of cobalt could react with an inhibitor.

Pyridine (Py) affects the rate of decomposition, but a more significant effect was observed for the products. The addition of pyridine always increased the ratio of acetophenone to 1-phenylethanol. Table 9 shows that phthalocyanine (Pc) complexes which involve a similar ligand containing nitrogen also yield much more ketone than alcohol. These results may be ascribed to reactions (5) and (6).

$$\mathrm{RO_2\cdot + Mn(Py) \longrightarrow R(-H)O + Mn(Py)(OH)} \qquad (5)$$

$$\mathrm{RO_2\cdot + Mn(Pc) \longrightarrow R(-H)O + Mn(Pc)(OH)} \qquad (6)$$

The addition of pyridine in the presence of manganese(II) and manganese(III) acetylacetonates (Tables 7 and

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8) increases the rate of decomposition of APE. This must be because chelate oxidation was accelerated and/or the acetylacetonate ligand is exchanged by pyridine to give free molecular acetylacetone which is oxidized relatively fast. Free acetylacetone may contribute as a good hydrogen donor.

Tables 6—10 show that the inhibiting effect of metal ions disappeared upon addition of sufficient acetic acid. In neutral solvents, added acetic acid must co-ordinate with the metal ions in place of other ligands and it also is associated in the outer sphere. Therefore, high concentration of acetic acid may suppress the interaction between metal ions and peroxyl radicals. When the reaction proceeds, it may give hydroperoxide, which is decomposed to give free radicals and induce the decomposition of APE.

$$RO_2\cdot + Mn^{2+} \longrightarrow (RO_2^-Mn^{3+}) \qquad (7)$$

$$(RO_2^-Mn^{3+}) + AcOH \longrightarrow ROOH + Mn^{3+} + AcO^- \qquad (8)$$

Cobalt salts give much higher acetophenone : 1-phenylethanol ratios and little hydroperoxide, especially in the presence of acetic acid. This may arise from the dehydration reaction (9) proposed by Scott [21] for the decomposition of hydroperoxide by cobalt ions.

$$ROOH + Co^{n+} \xrightarrow{AcOH} R(-H)O + H_2O + Co^{n+} \qquad (9)$$

We do not want to enter into further speculative discussion at present on the mechanism of the interactions of metal ions with peroxyl radicals. However, we believe that our results provide convincing evidence for fast interactions between the two species. It may be noteworthy that similar effects of metal ions and additives have been observed on the rate and products of metal-catalysed oxidation of ethylbenzene.[22]

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