test, and it was spinnable. The reprecipitation of its benzene solution from methanol was repeated to give the yellow powder VII: mp 110–120°; mol wt 2170; ir (KBr) 3030, 3000, 2925–2840 (CH_2), 1600 (benzene ring), 1500, and 615 cm^{-1} (CS).

Anal. Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00. Found: C, 83.06; H, 5.90.

Reaction with Benzaldehyde.—To a solution of benzaldehyde (1.33 g, 0.0125 mol) in 30 ml of THF was added 53 ml of THF solution of monosodium thiobenzophenone (0.5 mol/l.), and the mixture was refluxed under nitrogen. The deep red of the thioketyl was not changed and the viscosity of the mixture was increased. After 3 hr the mixture was cooled and 100 ml of water was added. After removal of the solvent, the residue was extracted with ether. The ether layer was washed with water. The water layer was acidified with hydrochloric acid to give a yellow-green precipitate. The precipitate was recrystallized from petroleum ether (bp 40–60°) to give 0.3 g of benzoic acid: mp 122–124° (sublimed at 100°); ir (KBr) 3100–3000, 2950–2500 (COOH), 1700 (C═O), 1600 cm^{-1} (benzene ring).

Removal of solvent from the ethereal layer gave a yellow oil. On distillation of this oil under nitrogen, 3 g of a blue-violet oil distilled, bp 150–165°. This oil changed from blue-violet to brown after 2 or 3 days in air. This brown oil (3 g) was stirred with a solution of 5 ml of acetic acid and 3.1 ml of 30% hydrogen peroxide at room temperature for 2 days. The white crystals were precipitated from the mixture. Recrystallization of the white precipitate from ether yielded 0.1 g of white needle crystals: mp 130–140°; mol wt 315; ir (KBr) 3100–3000, 1600 (benzene ring), 1500, 1350 ($-SO_2$), 1130 cm^{-1} (S═O).

To a solution of benzaldehyde (1.5 g, 0.014 mol) in 10 ml of THF was added 30 ml of THF solution of disodium thiobenzophenone (0.46 mol/l.). The mixture was refluxed under nitrogen for 3 hr. The dark red of the dianion complex gradually turned to yellow and sodium chloride was precipitated. After 3 hr the mixture was cooled, poured into crushed Dry Ice to remove any unreacted dianion complex, and diluted with 100 ml of water. After removal of the solvent, the residue was extracted with ether and the extracts were washed with water and dried (Na_2SO_4). Removal of the solvent left a white powder which on recrystallization from ether gave 1.3 g (33.4%) of white needle crystals of ω,ω'-diphenylacetophenone (IX): mp 136–137° (lit.[6] mp 137°); ir (KBr) 3070, 3050, 3010, 1680 (C═O), 1600 cm^{-1} (benzene ring).

Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92; mol wt, 272. Found: C, 88.21; H, 6.05; mol wt, 276.

Reaction with Benzonitrile.—To a solution of benzonitrile (2.58 g, 0.025 mol) in 30 ml of THF was added 50 ml of a THF solution of monosodium thiobenzophenone (0.5 mol/l.). The mixture was refluxed under nitrogen. After 3 hr the mixture was cooled and poured into acidic ethanol (10 ml of concentrated hydrochloric acid and 100 ml of ethanol), and it turned blue-violet in color. After removal of the solvent the residue was distilled under nitrogen to give 1.0 g (39% recovered yield) of benzontrile, bp 75–76° (9 mm), and 1.4 g (28% recovered yield) of thiobenzophenone, bp 138–140° (3 mm).

Next the reaction of a THF solution of disodium thiobenzophenone (26 ml, 0.5 mol/l.) with benzonitrile (2.58 g, 0.025 mol) was made by the same method as described above. When the dianion complex was added to benzonitrile, immediately the color of the mixture turned from deep red to red-violet. After 3 hr the mixture was poured into aqueous methanol. After removal of the solvent, the residue was extracted with ether. A pink powder (0.2 g), which was insoluble in ether, was recrystallized from chloroform to give 0.12 g of white needle crystals, 2,4,6-triphenyl-1,3,5-triazine (X), mp 234–236°. The ethereal extract was partially evaporated to induce crystallization and 0.45 g (22.1%) of 2,4,6-triphenyl-1,3,5-triazine (X) was obtained: mp 234–236° (lit.[11] mp 233–233.5°); ir (KBr) 3000–3050, 1590 (benzene ring), 1520, 1460 cm^{-1}.

Anal. Calcd for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.41; H, 5.00; N, 13.62.

The ether was evaporated from the filtrate to give 1.3 g of polymeric precipitate which was spinnable. It was dissolved in benzene and precipitated from petroleum ether (bp 42–55°) to give 0.4 g of a yellow powder: mp 105–120°; ir (KBr) 3080, 3040, 1660, 1640, 1600, 1495 cm^{-1}; mol wt 892. *Anal.* Found: C, 84.25; H, 6.49.

Registry No.—I, 19495-83-1; II, 21129-36-2; VI, 34519-98-7; VII (copolymer), 9036-08-2; VII (repeating unit), 34521-12-5; benzyl chloride, 100-44-7; *p*-dichloroxylene, 623-25-6; benzaldehyde, 100-52-7; benzonitrile, 100-47-0; thiobenzophenone, 1450-31-3.

[11] P. Eitner and F. Krafft, *Chem. Ber.*, **25**, 2267 (1892).

Selectivity Differences of Some Cobalt Catalyst Systems in the Liquid Phase Oxidation of Alkyl Aromatics[1]

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A study of the products obtained in the oxidation of *p-tert*-butyltoluene and 2,2-bis(*p*-tolyl)propane at 182° and 200 psig O_2 in a mixed solvent consisting of chlorobenzene and acetic acid, and in the presence of cobaltous acetate–hydrochloric acid catalyst, has revealed some significant differences in oxidation products as compared with similar experiments using the cobalt–bromide and cobalt acetate–2-butanone catalyst systems at 182 and 138°, respectively. The use of the chloride catalyst results in carbon–carbon bond cleavage during the oxidation process and leads to significant amounts of products such as *p*-toluic acid, *p*-methylacetophenone, terephthalic acid, and *p*-acetylbenzoic acid in addition to the expected *p-tert*-butylbenzoic acid and 2,2-bis(*p*-carboxyphenyl)-propane. These results are most easily explained by a radical mechanism involving a chloride ion to chlorine atom chain.

Several important industrial processes for the liquid phase oxidation of toluene or xylenes to benzoic or phthalic acids are based on cobalt catalyst systems.[2]

The use of cobalt acetate and a ketone or aldehyde activator for the oxidation of xylenes or toluenes in acetic acid to carboxylic acids at 100° has been described by Brill.[3] Cobalt or manganese salts and various bromide promoters have been used in acetic acid solvent for the oxidation of alkyl aromatics over a range of temperatures up to 200°.[4–9] The mechanism of such

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[1] A limited preliminary account appeared in *Chem. Commun.*, 1166 (1971).

[2] The patent literature on these oxidations runs into hundreds of patents; literature references will be restricted mainly to publications dealing with mechanisms.

[3] W. F. Brill, *Ind. Eng. Chem.*, **52**, 837 (1960).

[4] D. A. S. Ravens, *Trans. Faraday Soc.*, **55**, 1768 (1959).

[5] A. S. Hay and H. S. Blanchard, *Can. J. Chem.*, **43**, 1306 (1965).

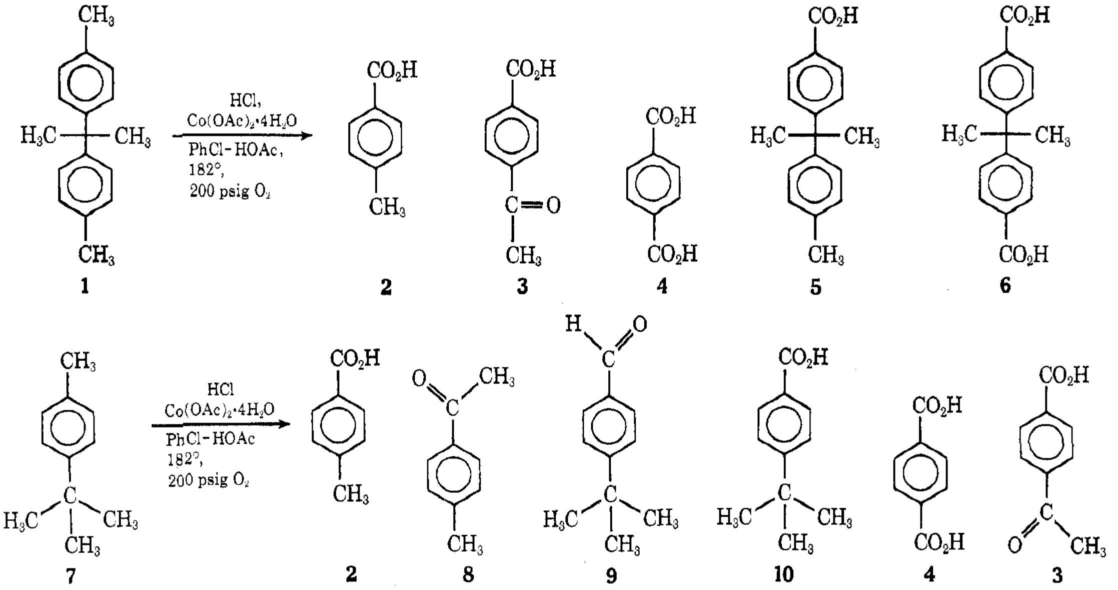
[6] T. Takaya, T. Koga, and T. Hara, *Bull. Chem. Soc. Jap.*, **39**, 654 (1966).

[7] Y. Kamiya, T. Nakajima, and K. Sakoda, *ibid.*, **39**, 2211 (1966).

[8] C. E. H. Bawn and T. K. Wright, *Discuss. Faraday Soc.*, **46**, 164 (1968).

[9] E. K. Fields and S. Meyerson, *Advan. Chem. Ser.*, **76**, 395 (1968).

SCHEME I



high-temperature (100–200°) metal-catalyzed oxidations is not yet well understood, as pointed out by Walling.[10] A system using chloride instead of bromide as promoter with cobalt for oxidation of *p*-xylene or *p*-toluic acid to terephthalic acid in high yields in the mixed solvent system acetic acid–chlorobenzene has recently been described.[1] Direct electron-transfer mechanisms have been suggested or implied for the oxidation of aromatic substrates by Co(III)[3,11–16] or Mn(III)[11,17,18] at low temperatures (<100°). Radical mechanisms have been suggested for the bromide-promoted cobalt[4,5,8] or manganese[19] catalyzed oxidations, and for cobalt or manganese acetate catalyzed oxidations of isopropyl benzenes at 130–150°.[20,21]

Heiba and coworkers[15] have suggested that the high-temperature (>100°) catalytic oxidation of alkylbenzenes at high concentration of catalyst proceeds predominantly *via* an electron-transfer process. It does not seem likely that mechanistic data obtained at low temperatures can be extrapolated to the high-temperature region, nor is it likely that kinetic data based on O$_2$ absorption rates obtained in the high-temperature region can serve to distinguish between radical and electron transfer mechanisms. In this study we demonstrate differences in selectivity toward attack at methyl *vs. tert*-butyl groups as a function of the catalyst system which may be useful in distinguishing between the two types of mechanism.

Results

The Cobalt Chloride System.—The oxidation of 2,2-bis(*p*-tolyl)propane (**1**) and *p*-*tert*-butyltoluene (**7**) resulted in extensive carbon–carbon bond cleavage (see Scheme I).

Results for the oxidation of **1** and **7** are presented in Tables I and II.

TABLE I[a]
OXIDATION PRODUCTS OF 2,2-BIS(*p*-TOLYL)PROPANE (**1**)

	Run no	
Products, %^{b}	1	2
p-Toluic acid	5.3	4.8
Terephthalic acid *p*-Acetylbenzoic acid	28.7	27.2
Monoacid **5**	10.8 (8.6)^c	12.3
Diacid **6**	47.6 (35.6)^c	48.5
Unidentified	7.6	7.1
Carbon dioxide, l. (STP)	1.0	

[a] **1** (6.0 g, 26.7 mmol), Co(OAc)$_2$·4H$_2$O (0.25 g, 1 mmol), HCl (2 mmol), PhCl (45 ml), HOAc (30 ml), O$_2$ (200 psig, 5.1 l.), 2 hr at 182°. [b] Per cent of total peak area of methyl esters. [c] Actual yield of carboxylic acids using internal standard and predetermined response factors.

TABLE II[a]
OXIDATION PRODUCTS OF *p*-*tert*-BUTYLTOLUENE (**7**)

	Run no.				
Products, %^{b}	1	2^c	3^c	4^d	5^d
p-Toluic acid	6.5	6.2	8.6	5.6	6.2
p-Methylacetophenone	10.1	9.8	10.1	11.9	12.8
p-*tert*-Butylbenzoic acid	29.7	30.6	30.3	31.2	31.8
Terephthalic acid	8.3	6.5	7.7	6.5	7.7
p-Acetylbenzoic acid	17.2	16.9	20.2	14.5	14.2
Carbon dioxide, l. (STP)	0.7	0.7	0.7	0.6	0.6

[a] *p*-*tert*-Butyltoluene (5.0 g, 33.7 mmol), Co(OAc)·4H$_2$O$_2$ (0.25 g, 1 mmol), HCl (2 mmol), PhCl (45 ml), HOAc (30 ml), O$_2$ (200 psig, 5.1 l.), 2 hr at 182°. [b] Yields of the compounds calculated as acids (except for *p*-methylacetophenone) using internal standard. [c] Run in a glass liner in the titanium reactor, O$_2$ (200 psig, 4 l.). [d] Run for 5 min at 182°.

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(10) C. Walling, *J. Amer. Chem. Soc.*, **91**, 7590 (1969).

(11) P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *ibid.*, **88**, 5473 (1966).

(12) T. Morimoto and Y. Ogata, *J. Chem. Soc. B*, 62 (1967).

(13) T. Morimoto and Y. Ogata, *ibid.*, 1353 (1967).

(14) K. Sakota, Y. Kamiya, and N. Ohta, *Can. J. Chem.*, **47**, 387 (1969).

(15) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **91**, 6830 (1969).

(16) A. Onopchenko, J. G. D. Schulz, and R. Seekircher, *Chem. Commun.*, 939 (1971).

(17) P. J. Andrulis, Jr., and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **88**, 5483 (1966).

(18) T. Aratani and M. J. S. Dewar, *ibid.*, **88**, 5479 (1966).

(19) J. R. Gilmore and J. M. Mellor, *Chem. Commun.*, 507 (1970).

(20) R. Van Helden, A. F. Bickel, and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **80**, 1237 (1961).

(21) R. Van Helden, A. F. Bickel, and E. C. Kooyman, *ibid.*, **80**, 1257 (1961).

To demonstrate that *p*-methylacetophenone is one of the major intermediates in the oxidation of **7**, several attempts were made to oxidize this ketone using the chloride system; no reaction occurred. However, in the presence of toluene, *p*-methylacetophenone is readily oxidized to *p*-toluic acid, terephthalic acid, and *p*-acetylbenzoic acid, the toluene being oxidized to benzoic acid (Table III)

TABLE III[a]

OXIDATION PRODUCTS OF TOLUENE AND *p*-METHYLACETOPHENONE

	Run no. 1	2	3
Feed			
Toluene, g	3	3	5
p-Methylacetophenone, g	3	3	
Products, %[b]			
p-Toluic acid	9.4	9.4	
Recovered *p*-methylacetophenone	7.1	8.0	
Terephthalic acid	37.5	35.3	
p-Acetylbenzoic acid	24.6	26.3	
Benzoic acid	87.4	85.6	93.7
Carbon dioxide, l.	0.5	0.4	0.3

[a] $Co(OAc)_2 \cdot 4H_2O$ (0.25 g, 1 mmol), HCl (2 mmol), HOAc (30 ml), PhCl (45 ml), O_2 (200 psig, 5.1 l.), 2 hr at 182° [b] Yields calculated as acids (where applicable) using internal standard.

p-tert-Butylbenzoic acid can be oxidized alone or cooxidized with toluene using the chloride system to give terephthalic acid, *p*-acetylbenzoic acid, and benzoic acid from toluene (Table IV).

TABLE IV[a]

OXIDATION PRODUCTS OF TOLUENE AND *p-tert*-BUTYLBENZOIC ACID

	Run no. 1	2	3	4
Feed				
Toluene, g			3	3
p-Butylbenzoic acid, g	5	5	3	3
Products, %[b]				
Recovered *p-tert*-butylbenzoic acid	52.1	52.5	28.0	31.0
Terephthalic acid	8.6	8.6	17.8	19.6
p-Acetylbenzoic acid	23.2	22.1	32.1	26.8
Benzoic acid			76.7	66.9
Carbon dioxide (l.)	0.3	0.4	0.8	0.9

[a] $Co(OAc)_2 \cdot 4H_2O$ (0.25 g, 1 mmol), HCl (2 mmol), HOAc (30 ml), PhCl (45 ml), O_2 (200 psig, 5.1 l.), 2 hr at 182°. [b] Yields calculated as acids using internal standard.

The experiments described in Table V were carried out to illustrate the importance of both hydrochloric acid and the mixed solvent.

A benzylic methyl group need not be present for oxidation to occur, as illustrated by the oxidation of *tert*-butylbenzene to benzophenone and benzoic acid using the chloride system.[1]

TABLE V[a]

CONTROL EXPERIMENTS

	Run no. 1[a]	2[a]	3[c]	4[c]	5[d]
Products, %[b]					
p-Toluic acid	2.1	2.6	3.0	2.6	<0.1
p-Methylacetophenone	6.5	7.4	5.8	5.3	<0.1
p-tert-Butylbenzoic acid	31.4	35.6	42.1	40.9	27.0
Terephthalic acid	0.3	0.9	0.7	1.1	<0.1
p-Acetylbenzoic acid	1.1	2.7	2.7	3.4	<0.1
Carbon dioxide, l. (STP)	0.9	1.2	0.9	0.9	0.6

[a] *p-tert*-Butyltoluene (5.0 g, 33.7 mmol), $Co(OAc)_2 \cdot 4H_2O$ (0.25 g, 1 mmol), HOAc (30 ml), PhCl (45 ml), O_2 (200 psig, 5.1 l.), 2 hr at 182°. PhCl may provide some chloride under these conditions. [b] Yields calculated as acids (where applicable) using internal standard. [c] Same as *b* except solvent was HOAc only (75 ml) and HCl (2 mmol) also present. [d] Same as *b* except solvent was HOAc only (75 ml), no HCl.

The Cobalt Bromide System.—The oxidation of **1** was carried out as described for the chloride system except that NaBr (0.1 g, 1 mmol) was substituted for HCl. Products found by glc analysis of the methyl esters were 2,2-bis(*p*-carbomethoxyphenyl)propane (**11**, 98%), 2-(*p*-carbomethoxyphenyl)-2-(*p*-tolyl)propane (**13**, 0.7%) and dimethylterephthalate (1% of the total peak area). Using an internal standard and response factors, the calculated yield of **6** was 86 mol %. *p-tert*-Butyltoluene was oxidized as above to give **10** in 94% yield. The yield of **4** was <1 mol %. *tert*-Butylbenzene was not oxidized under these conditions.[1]

The Cobalt Chloride–Bromide System.—Because of the very different results obtained in the oxidation of *p-tert*-butyltoluene using the CoCl and CoBr systems, some experiments were carried out in which both chloride and bromide were present. *p-tert*-Butyltoluene (5 g, 33.7 mmol), cobaltous acetate tetrahydrate (0.25 g, 1 mmol), hydrochloric acid (2 mmol), sodium bromide (1 mmol), chlorobenzene (45 ml), acetic acid (30 ml), and oxygen (200 psig, 5.1 l.) were allowed to react for 2 hr at 182°. The yields of products were as follows: *p-tert*-butylbenzoic acid, 72.7%; terephthalic acid, 13.4%; *p*-acetylbenzoic acid, 5.3%.

The experiment was repeated with *tert*-butylbenzene (5 g, 37.2 mmol) for 7 hr; 4.8 g of *tert*-butylbenzene was recovered; and no acetophenone was observed.

The Cobalt–2-Butanone System.[3,22]—Hydrocarbon **1** (4 g, 17.8 mmol) was oxidized with $Co(OAc)_2 \cdot 4H_2O$ (0.5 g, 2 mmol), 2-butanone (3 ml), water (3 ml), acetic acid (75 ml), and oxygen (200 psig, 5.1 l.) for 1 hr at 138°. Product analysis (glc) of the methyl esters gave diester **11** (95%) and monoester **13** (5% of the total peak area). The yield of **6** was 88.4% and of **5** was 5% as calculated using an internal standard and responses factors.

The oxidation was repeated using **7** (5 g, 33.7 mmol) instead of **1**. The yield of **10** was 96%; no terephthalic acid was observed in the oxidation of **1** or **7**.

Discussion

The oxidation behavior of most hydrocarbons in the liquid phase at low temperatures (<100°) is now well understood. A good recent review was published by Mayo.[23]

The autoxidation of alkyl aromatics has been studied[24,25] and the individual termination and propagation rate constants have been measured for the xylenes, toluene, ethylbenzene, cumene, and others. It is

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[22] Oxidations using this system were found to have erratic induction periods.

[23] F. R. Mayo, *Accounts Chem. Res.*, **1**, 193 (1968).

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

[25] L. Sajus, *Advan. Chem. Ser.*, **75**, 59 (1968).

apparent that the relatively large termination rate constant for the termination reaction (eq 1) is responsible

$$2ROO\cdot \xrightarrow{k_t} \text{nonradical products} + O_2 \tag{1}$$

for the low (2–3)[25] chain length in the autoxidation of the primary benzylic hydrogens in alkyl benzenes. As a consequence, hydroperoxides are not accumulated in the reaction products of toluene or xylene autoxidations. The rate-accelerating effect in hydrocarbon autoxidations of transition metal ions is thought to be due to the ability of the ions to produce radicals from hydroperoxides by the following sequence of reactions[5,26]

$$ROOH + M^{2+} \longrightarrow RO\cdot + OH^- + M^{3+} \tag{2}$$

$$ROOH + M^{3+} \longrightarrow ROO\cdot + H^+ + M^{2+} \tag{3}$$

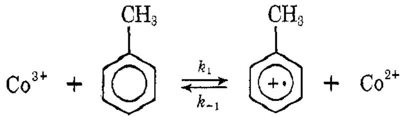
(eq 2, 3). The radicals produced can then initiate further chains. Walling[10] has recently pointed out that the rates of some commercial oxidations of alkyl aromatics are in excess of limiting rates predicted by a kinetic analysis. Under these conditions, the usual propagation step (eq 4) must be unimportant in the

$$ROO\cdot + RH \xrightarrow{k_p} ROOH + R\cdot \tag{4}$$

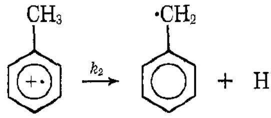
consumption of RH and other reaction sequences must be invoked. Scott[27] has suggested eq 5, rather than eq 2, as a major path for the oxidation of Co(II) to Co(III).

$$RO_2\cdot + \text{Co(II)} \longrightarrow R'CHO + \text{Co(III)} + OH^- \tag{5}$$

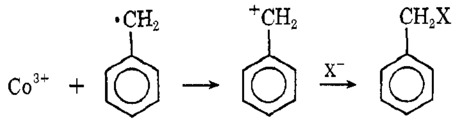
It is now well established[14,15,28] that Co(III) complexes in a variety of solvents (usually acetic acid) can oxidize alkyl aromatics such as toluene by direct electron transfer (from the aromatic to cobalt) in the absence of oxygen at temperatures below 100°.



(6)



(7)



(8)

In the presence of oxygen, such a mechanism must include a sequence of reactions involving reaction of benzyl radicals with oxygen instead of eq 8. Such an electron-transfer mechanism in the presence of oxygen has indeed been suggested by Brill[3] for the oxidation of *p*-xylene to terephthalic acid using cobaltous acetate and 2-butanone in acetic acid at 100°. Dewar and coworkers[11] have suggested a similar mechanism involving the propagating steps after eq 7. In the Brill system, Co^{3+} presumably arises from the reaction of Co^{2+} with peroxides derived from 2-butanone. Morimoto and Ogata[12,13] also suggest that cobalt acetate catalyzed toluene autoxidation at 90° proceeds, at least in part, *via* the direct electron transfer scheme. Finally, Heiba, *et al.*,[15] have suggested that all commercial oxidations of alkylbenzenes proceed predominantly *via* such a mechanism, and Onopchenko, *et al.*,[16] have shown recently that, in the Co(III)-catalyzed cooxidation of *p*-cymene and *n*-butane, *p*-isopropylbenzoic acid is the major product obtained, presumably by an electron transfer mechanism.

$$PhCH_2\cdot + O_2 \longrightarrow PhCH_2O_2\cdot \tag{9}$$

$$Co^{2+} + PhCH_2O_2\cdot \longrightarrow PhCH_2O_2^- + Co^{3+} \tag{10}$$

$$PhCH_2O_2^- + H^+ \longrightarrow PhCH_2O_2H \tag{11}$$

Free radical mechanisms have also been suggested. Such a mechanism would involve an initial abstraction of H from the alkyl aromatic by some species such as Br·, Cl·, RO·, ROO·, etc. (or their complexes with metal ions) and does not imply that no electron transfer takes place at all, since it must occur at some stage of the reaction if a Co(II)–Co(III) redox cycle is to be established. Such a mechanism, most likely in the bromide system and the chloride system, might be formulated as follows, to illustrate only how X· could

$$\text{Initiating radical} + HX \longrightarrow X\cdot\ (X = Br\cdot) \tag{12}$$

$$X\cdot + RH \longrightarrow R\cdot + HX \tag{13}$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \tag{14}$$

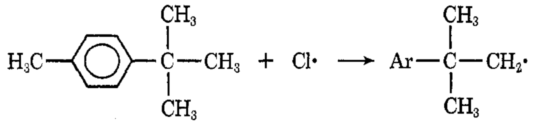
$$RO_2\cdot + HX \longrightarrow RO_2H + X\cdot \tag{15}$$

$$Co^{3+} + X^- \longrightarrow Co^{2+} + X\cdot \tag{16}$$

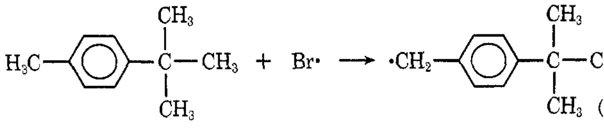
$$HX + O_2 \longrightarrow X\cdot + HO_2\cdot \tag{17}$$

be involved in the chain reaction; other sequences such as eq 1–5, are probably involved too. Bromine atoms have been suggested as being involved in these oxidations[4,6,8,25] and reactions 16 and 17 have been proposed[4,6,8] for X = Br. Reaction 16 is known to occur in acetic acid solution for X = Cl.[15] Cooper and Waters[29] have observed that the oxidation of di-2-chloroethyl ether by Co^{3+} is autocatalytic and have proposed a chain reaction involving chlorine atoms and the oxidation of chloride to chlorine atoms by Co^{3+}.

Detailed mechanisms of metal-catalyzed autoxidations of alkylbenzenes under conditions of commercial processes (100–200°) are ill-defined and probably complex.[10] The results of this study, based on the unique differences in oxidation products of **1** and **7** as a function of catalyst, suggest a free-radical mechanism for the bromide and chloride systems. The observed products for the chloride and bromide systems are compatible in every respect with a mechanism involving initial abstraction of hydrogen by Cl·, Br·, or a cobalt complex involving Cl· or Br· (eq 18, 19).



(18)



(19)

Using the data in Walling's book[30] for liquid phase chlorination at 80°, the relative reactivity per hydrogen

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[26] A. E. Woodward and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **75**, 6189 (1953).

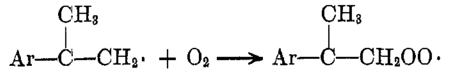
[27] E. J. Y. Scott, *J. Phys. Chem.*, **74**, 1174 (1970).

[28] T. A. Cooper, A. A. Clifford, D. J. Mills, and W. A. Waters, *J. Chem. Soc. B*, 793 (1966).

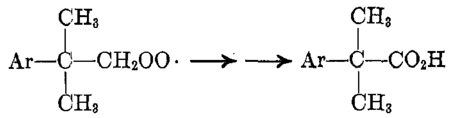
[29] T. A. Cooper and W. A. Waters, *ibid.*, 464 (1967).

[30] C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 360, 371.

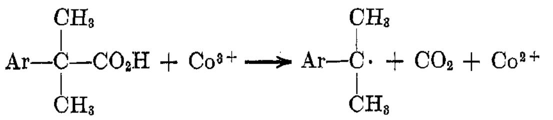
in toluene is 1.0 *vs.* 0.22 for *tert*-butylbenzene. Accounting for all hydrogens, the reactivity is 3:2 for benzylic methyl *vs.* tertiary butyl. The additional 100° increase in temperature at which the oxidation is carried out would be expected to further decrease the selectivity in the abstraction reaction. In contrast to chlorination, *tert*-butylbenzene fails to undergo side-chain bromination under any conditions (see ref 30, p 371), whereas toluene is readily brominated to give benzyl bromide at 20°. Equations 20 and 21 illustrate



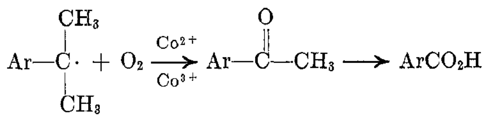
$$\mathrm{Ar{-}}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2\cdot} + \mathrm{O_2} \longrightarrow \mathrm{Ar{-}}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2OO\cdot} \qquad (20)$$



$$\mathrm{Ar{-}}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2OO\cdot} \longrightarrow \longrightarrow \mathrm{Ar{-}}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CO_2H} \qquad (21)$$



$$\mathrm{Ar{-}}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CO_2H} + \mathrm{Co^{3+}} \longrightarrow \mathrm{Ar{-}}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}\cdot + \mathrm{CO_2} + \mathrm{Co^{2+}} \qquad (22)$$



$$\mathrm{Ar{-}}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}\cdot + \mathrm{O_2} \xrightarrow[\mathrm{Co^{3+}}]{\mathrm{Co^{2+}}} \mathrm{Ar{-}}\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}CH_3} \longrightarrow \mathrm{ArCO_2H} \qquad (23)$$

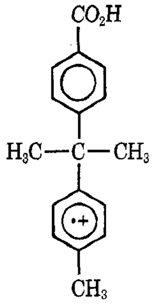
a reasonable and probable reaction sequence for converting the primary alkyl radical to carboxylic acid; others involving cobalt catalysis and free-radical rearrangements could be invoked. The reaction in eq 22 is well known[31] even at low temperature for carboxylic acids which can give relatively stable radicals. The reaction sequence shown in eq 23 has been demonstrated[20,21] for the cobalt-catalyzed autoxidation of isopropyl benzenes.

Additional evidence for an initial nonselective radical attack in the chloride system is the finding that appreciable amounts of *p*-toluic acid and *p*-methylacetophenone are obtained in the oxidation of *p-tert*-butyltoluene. These products are not observed in the oxidation of toluene; therefore, they cannot have arisen from addition of methyl or acetyl radicals to the aromatic ring followed by loss of the *tert*-butyl group.

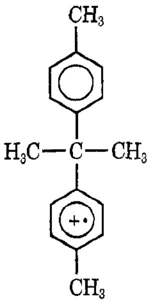
Reported[32] oxidation potentials for Co^{2+}–Co^{3+} (−1.84 V), Mn^{2+}–Mn^{3+} (−1.5 V), Cl^-–Cl_2 (−1.36 V), and Br^-–Br_2 (−1.07 V) (in aqueous acidic solution) give support to the radical hypothesis, since we have found that Mn^{2+} is not effective as a catalyst for the chloride system, whereas it is known to be an effective catalyst in the bromide system.

The results obtained for the mixed bromide–chloride catalyst in the oxidation of *p-tert*-butyltoluene and *tert*-butylbenzene also suggest initial radical attack. In the reaction with *tert*-butylbenzene, bromide ion can act as an effective inhibitor until all the bromide is completely converted to bromine atoms.

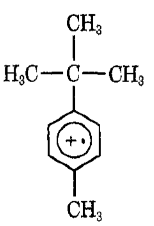
In comparing the ratio of cleavage products to products with an intact carbon skeleton in the oxidation of 2,2-bis(*p*-tolyl)propane and *p-tert*-butyltoluene using the chloride system (Tables I and II), it is obvious that this ratio is >1 for **7** and <1 for **1**. This observation is consistent with the statistical distribution of aliphatic and benzylic hydrogens in the two compounds (3:1 for **7** and 1:1 for **1**) and their abstraction by Cl·. It is inconsistent with an electron transfer mechanism such as that proposed by Heiba[8,15] for toluene oxidation in acetic acid by cobaltic acetate–lithium chloride. If cleavage products are to be explained by loss of either $\cdot CH_3$ or $^+CH_3$ from cation radicals A, A′, or B, B′, one should reasonably expect



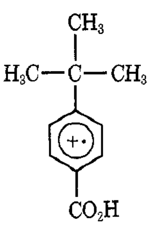
A′



A



B



B′

such a process to be favored in A or A′ relative to B or B′ if there is considerable bond breaking in the transition state leading to cleavage. The opposite result is observed, however, in agreement with the "Hammond postulate" as applied to the reaction of Cl· with RH. Appreciable C–C bond cleavage has not been observed by us in the Co–2-butanone system or by Onopchenko, *et al.*,[16] in the oxidation of *p*-cymene and *p-tert*-butyltoluene; however, Heiba, *et al.*,[15] have reported C–S bond cleavage in the oxidation of *p*-methoxybenzylphenyl sulfide by Co^{3+} in the presence of LiCl at room temperature; they have also reported a correlation between ionization potential and rates of oxidation of alkyl aromatics by cobaltic acetate–lithium chloride in acetic acid in support of the electron transfer mechanism. A plot of the data of Fields[33] for the autoxidation of the same alkyl aromatics in acetic acid using a cobalt acetate–bromide catalyst gives no such correlation, indicating that the mechanisms are probably not related.

In conclusion, although an electron transfer mechanism cannot be completely ruled out for the chloride system and the bromide system, the results obtained in this study are more compatible with a free-radical mechanism involving halogen radicals as the species involved in the initial attack on alkyl aromatic substrates.

Experimental Section

General Procedure.—All oxidations were carried out in a closed system consisting of a 500-ml Parr titanium rocking autoclave equipped with a silver gasket and dual silver rupture disks in a titanium rupture disk assembly.[34] All fittings in contact with reagents were titanium. Temperature was controlled remotely *via* a Hi-Lo control circuit using an Esterline Angus thermocouple controller. Agitation was by the rocking motion of the autoclave only. The autoclave was typically charged with the reactants, slowly raised to the operating temperature, kept there for a predetermined time, and then allowed to cool to room temperature. The gas was vented through a CO_2 trap and a wet test meter. The products were analyzed by esterification and glc analysis. All operations involving reactions under oxygen pressure were carried out in a barricade by remote control.

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(31) A. A. Clifford and W. A. Waters, *J. Chem. Soc.*, 2796 (1965).

(32) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952.

(33) E. K. Fields and S. Meyerson, *Advan. Chem. Ser.*, **76**, 395 (1968).

(34) A glass liner was used in control runs to establish that no significant results were due to the metal surfaces of the bomb.

Analyses.—In the oxidation of 2,2-bis(*p*-tolyl)propane (1) the dry product mixture including catalyst was obtained by removal of solvent and vacuum drying of the residue. The solid was homogenized and a 1-g sample was refluxed for 8 hr with CH_3OH (100 ml) and concentrated H_2SO_4 (2 ml). Methanol was removed and the residue was dissolved in ether (500 ml). The ether solution was washed with water (100 ml) and aqueous $NaHCO_3$ (100 ml), dried ($CaSO_4$), and filtered. Ether was evaporated from the filtrate and the residue was dissolved in a minimum of dry acetone; a known weight of internal standard (methyl tridecanoate) was added before glc analysis. The product mixture was analyzed on a 1 ft × 0.25 in. 16% CW 20 M on 60/80 mesh AW Chromosorb P column programmed at 130–260° in a Varian Aerograph A90P3 glc instrument with linear temperature programmer.

In the oxidation of *p-tert*-butyltoluene the products were expected to be more volatile than in the previously described system; it was decided not to attempt to dry them to constant weight. The total sample (after flashing the solvent) was esterified with 400 ml of absolute methanol and 3 ml of concentrated H_2SO_4 for 14 hr. On cooling, methanol was removed, the residue was taken into ether (500 ml), and the ether solution was washed with water (100 ml) and aqueous $NaHCO_3$ (100 ml). The solution was dried over $CaSO_4$ and filtered, and the ether was removed. The residue was dissolved in a minimum of acetone, and a known weight of methyl pentadecanoate was added as internal standard. The product mixture was analyzed on a 5 ft. × 0.25 in. Carbowax 20M column. Using the conditions described above, only methyl *p*-toluate and *p*-methylacetophenone were not completely separated. Known mixtures of the components were esterified in an identical manner (including the addition of cobaltous acetate, hydrochloric acid, acetic acid, and chlorobenzene, and flashing of the solvents to leave a residue) to determine correction factors for the acids relative to methyl pentadecanoate. Errors range from 5% of the reported values for large peaks to 10% for small peaks. All glc traces were obtained in duplicate. This procedure does not account for most of the unreacted *p-tert*-butyltoluene. The latter was not routinely determined; however, in some cases, the chlorobenzene–acetic acid mixture was analyzed for *p-tert*-butyltoluene after removal from the nonvolatile products. An aliquot was treated with excess cold aqueous potassium hydroxide and the neutral layer was extracted into ether and analyzed by glc using an internal standard.

The products were identified by comparing glc retention times, melting points, and ir and nmr spectra of the components as trapped from the glc effluent with authentic samples.

Instruments.—All ir spectra were obtained on a Perkin-Elmer Model 137 sodium chloride spectrophotometer. The nmr spectra were obtained on a Varian Model A-60 spectrometer.

Materials.—Starting materials were reagent grade materials and were routinely purified. $Co(OAc)_2 \cdot 4H_2O$ was Mallinckrodt reagent grade material. NaBr was reagent grade from B and A. In the chloride system, HCl was used as a solution of a weighed sample of concentrated aqueous HCl dissolved in 99% glacial acetic acid (Du Pont).

Syntheses. 2,2-Bis(*p*-tolyl)propane (1).—Hydrocarbon 1 was prepared from α,p-dimethylstyrene by reaction with hydrogen chloride and alkylation of toluene with the tertiary chloride and aluminum chloride–nitromethane complex in 64% yield by the method of Coscia, *et al.*,[35] mp 77–78° from methanol (lit.[35,36] mp 80, 78–79°). All melting points are uncorrected.

2,2-Bis(*p*-carboxyphenyl)propane (6).—Acid 6 was prepared by the method of Coscia, *et al.*,[35] by chromic acid oxidation of 1, mp 315–317° (lit.[35] mp 313–315°).

Acid 6 was also prepared by autoxidation; compound 1 (6 g, 26.7 mmol), $Co(OAc)_2 \cdot 4H_2O$ (0.25 g, 1 mmol), and NaBr (0.10 g, 1 mmol) in 75 ml of glacial acetic acid were allowed to react in a titanium Parr rocking autoclave for 90 min at 182° and 200 psig O_2 pressure (at room temperature). On cooling, the precipitate was filtered, washed with cold water (300 ml), and dried to constant weight under vacuum. A portion of the crude diacid 6 (6.71 g, 88.5%) was recrystallized twice from aqueous acetic acid, washed with water, and dried under vacuum. This sample had mp 317–319°; neut equiv 400 mg KOH/g (calcd, 395); identical ir spectrum with that of 6 as prepared by chromic acid oxidation. *Anal.* Calcd for $C_{17}H_{16}O_4$: C, 71.8; H, 5.67. Found: C, 71.7; H, 5.74.

2,2-Bis(*p*-carbomethoxyphenyl)propane (11).—Diacid 6 (1 g) was refluxed for 8 hr with methanol (100 ml) and concentrated H_2SO_4 (2 ml). On cooling, methanol was removed and water was added to the residue. The precipitate was recrystallized three times from methanol to give 11: mp 106.5–108° (lit.[35,37] mp 107–107.5°, 101–102°); nmr ($CDCl_3$) δ 1.75 [s, 6, $(CH_3)_2C(Ar)_2$], 3.9 (s, 6, CO_2CH_3), 7.2–8.1 (m, 8, aromatic A_2B_2).

2(*p*-Cyanophenyl)-2-(*p*-tolyl)propane (12).—*p*-Cyanoacetophenone (10 g, 0.069 mol) was dissolved in ether (300 ml) and the solution was cooled with Dry Ice–acetone. An ether solution of CH_3MgI (125 ml) prepared from Mg (1.7 g, 0.069 mol) and CH_3I (9.8 g, 0.069 mol) was added in portions under N_2 with stirring. The reaction mixture was allowed to come to room temperature and decomposed with 400 ml of saturated aqueous NH_4Cl solution. The ether layer was dried ($CaSO_4$) and filtered and ether was removed. The residue (9.2 g) exhibited the following functional groups (ir), 3400 (s, -OH), 2200 (-CN), and 1685 cm^{-1} (w, >C=O), indicating that it was probably a mixture of a little starting material and *p*-cyanocumyl alcohol. The alcohol was expected to be thermally unstable and was, therefore, not distilled but rather was converted directly to nitrile 12. The above residue (9.2 g), toluene (100 ml), and H_2SO_4 (250 ml, 80%) were stirred vigorously for 4 hr at room temperature. The mixture was poured on ice and extracted with ether (400 ml), the ether layer was washed with aqueous $NaHCO_3$, dried ($CaSO_4$), and filtered, and the ether was evaporated. The residue was distilled. The major fraction (5.0 g, 30.8%), bp 130–135° (0.25 mm), was recrystallized from methanol to give 12: mp 67.5–68°; nmr ($CDCl_3$) δ 1.6 [s, 6, $(CH_3)_2C(Ar)_2$], 2.25 (s, 3, CH_3Ar) and 7.05–7.6 (m, 8, aromatic); ir 2230 (s, -CN), 817 cm^{-1} (s, 1, 4-substituted aromatic). *Anal.* Calcd for $C_{17}H_{17}N$: C, 86.8; H, 7.28. Found: C, 86.9; H, 7.10.

2-(*p*-Carboxyphenyl)-2-(*p*-tolyl)propane (5).—Nitrile 12 (2 g, 0.85 × 10^{-2} mol) was refluxed for 16 hr with KOH (6 g) in 50 ml of 5:1 methanol–water. Methanol was removed under vacuum, and the residue was diluted with water (200 ml) and acidified with dilute HCl. The precipitate was filtered, recrystallized from aqueous acetic acid, and dried under vacuum to give 5 (2 g, 92.5%): mp 163–164°; nmr ($CDCl_3$) δ 1.67 [s, 6, $(CH_3)_2C(Ar)_2$], 2.3 (s, 3, CH_3Ar), 7.05–8.15 (m, 8, aromatic), 12.5 (s, 1 CO_2H). *Anal.* Calcd for $C_{17}H_{18}O_2$: C, 80.3; H, 7.13. Found: C, 80.1; H, 7.08.

2(*p*-Carbomethoxyphenyl)-2-(*p*-tolyl)propane (13).—Acid 5 (1.0 g, 3.9 × 10^{-3} mol) was refluxed for 8 hr with absolute methanol (100 ml) and concentrated H_2SO_4 (2 ml). Methanol was removed and the residue was dissolved in ether (500 ml). The ether solution was washed with water (10 ml) and aqueous $NaHCO_3$ (100 ml), dried ($CaSO_4$), and filtered, and the ether was evaporated to give residue 13 (1.0 g, 94.8%): bp 136–140° (0.3 mm); nmr ($CDCl_3$) δ 1.65 [s, 6, $(CH_3)_2C(Ar)_2$], 2.28, (s, 3, CH_3Ar), 3.8 (s, 3, CO_2CH_3), 7.05–8.1 (m, 8, aromatic). *Anal.* Calcd for $C_{18}H_{20}O_2$: C, 80.6; H, 7.51. Found: C, 80.8; H, 7.28.

Registry No.—**1**, 1823-31-0; **5**, 6278-37-1; **6**, 7425-84-5; **7**, 98-51-1; **11**, 34454-33-6; **12**, 34454-34-7; **13**, 34454-35-8; HCl, 7647-01-0; $Co(OAc)_2$, 71-48-7; PhCl, 108-90-7; HOAc, 64-19-7; NaBr, 7647-15-6; toluene, 108-88-3; *p*-methylacetophenone, 122-00-9; *p-tert*-butylbenzoic acid, 98-73-7.

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[35] A. T. Coscia, *et al.*, *J. Org. Chem.*, **26**, 1398 (1961).

[36] R. R. Hiatt, U. S. Patent 2,719,871 (1955).

[37] C. E. Schweitzer, U. S. Patent 2,794,822 (1957).