Oxygenation of Toluene with Diisopropyl Peroxydicarbonate–Metal Salt. Variation in the Salt Component[1]
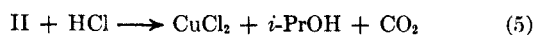
Michael E. Kurz[2] and Peter Kovacic
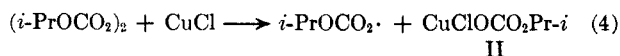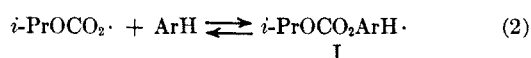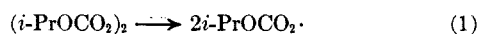
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio   44106

Aromatic oxygenation of toluene to tolyl isopropyl carbonates by diisopropyl peroxydicarbonate–metal salt in acetonitrile was studied with a variety of inorganic components in relation to yield and orientation. Of the cupric salts investigated, the halides proved to be superior, while those of perchloric and tetrafluoroboric acids gave low yields of ester and the ones from weak acids were ineffective. Evidence is presented to substantiate the mode of regeneration (metathesis of $CuXOCO_2Pr$-i with HX) of the apparent effective oxidant, cupric halide, needed to perpetuate the chain reaction with the copper halides. Oxygenation with ferric chloride as catalyst in both neat and solvent systems produced a change in isomer distribution which is ascribed to the involvement of isopropoxycarboxy radicals complexed with the metal halide. The impact of our results on earlier theoretical interpretations[3] for this system is discussed. In a sampling of other metal salts, only osmium tetrachloride, ruthenium trichloride, and sodium hexachloroiridate gave appreciable yields of oxygenated product. Certain nonmetallic promoters were also scrutinized. Values were obtained for relative rates with toluene–benzene and *m*-xylene–benzene in the presence of several of the metal halides. The active catalysts are apparently characterized by the ability to participate readily in one-electron transfer. Our proposals concerning the mechanistic pathway for this oxygenation category are discussed in detail elsewhere.[4,5]

Aromatic oxygenation with peroxydicarbonates has been accomplished under the agency of two classes of metal halides. With potent Friedel–Crafts catalysts, reaction proceeded with introduction of an electrophilic oxygen species resulting from heterolytic fission of the peroxide.[6–9] Phenolic derivatives,[7,8a] e.g., carbonate esters, were the initial products in this low temperature (0°) reaction which required a 2:1 ratio of catalyst/peroxide for optimum results.[6]

Oxygenation with diisopropyl peroxydicarbonate has also been carried out in the presence of cupric chloride, with toluene being converted in excellent yield to a mixture of tolyl isopropyl carbonates.[4,10] Evidence was presented for the incursion of a radical chain mechanism (eq 1–5) involving isopropoxycarboxy radicals

$$(i\text{-PrOCO}_2)_2 \longrightarrow 2i\text{-PrOCO}_2\cdot \tag{1}$$

$$i\text{-PrOCO}_2\cdot + \text{ArH} \rightleftharpoons i\text{-PrOCO}_2\text{ArH}\cdot \tag{2}$$
$$\text{I}$$

$$\text{I} + \text{CuCl}_2 \longrightarrow i\text{-PrOCO}_2\text{Ar} + \text{CuCl} + \text{HCl} \tag{3}$$

$$(i\text{-PrOCO}_2)_2 + \text{CuCl} \longrightarrow i\text{-PrOCO}_2\cdot + \text{CuClOCO}_2\text{Pr-}i \tag{4}$$
$$\text{II}$$

$$\text{II} + \text{HCl} \longrightarrow \text{CuCl}_2 + i\text{-PrOH} + \text{CO}_2 \tag{5}$$

and copper salt in the role of redox agent. The concept of attack by the oxy radical onto the aromatic nucleus (eq 2), followed by oxidative conversion to the substituted product (eq 3), is consistent with available evidence and prior analogy.[4,5,10] Induced decomposition by cuprous salt ensued (eq 4). This oxygenation

category displays substantial improvement over previous, related types.[11]

With toluene, a small fraction of the alkoxycarboxy radicals underwent decarboxylation (eq 6) leading to by-products attributable to isopropoxy radicals. When insufficient or ineffective catalyst was utilized, this side reaction became more important.

$$i\text{-PrOCO}_2\cdot \longrightarrow i\text{-PrO}\cdot + \text{CO}_2 \tag{6}$$
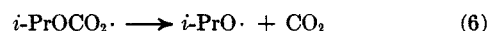
A logical extension was to scrutinize the ability of other salts to act as oxidants in this novel system, based on yield of aryl alkyl carbonate as a gauge. This report is concerned with salts of copper and iron, as well as other metals, in addition to a few nonmetallic candidates. Studies aimed at resolving an apparent conflict in the literature concerning the theoretical aspects of oxygenation with dialkyl peroxydicarbonates–ferric chloride are also presented.[12]

Results and Discussion

A. Copper Salts.—Diisopropyl peroxydicarbonate was allowed to decompose in the presence of toluene and a variety of copper salts in acetonitrile solvent at 60° for 2–4 hr according to the standard procedure (toluene/peroxide/metal salt in 17.3:1:0.3 molar ratio) (Table I). The cupric salts comprised those derived from both strong and weak acids. In addition data from two cuprous halides are included.

With cupric chloride, as described earlier,[4] an 85% yield of tolyl isopropyl carbonates was obtained. Use of cupric bromide resulted in a diminution of the oxygenation process and somewhat different orientation for the aromatic product, whereas the pseudo halide, cupric thiocyanate, produced only 4% of the carbonate esters. The cupric salts of the strong acids, perchloric and tetrafluoroboric, were mildly effective (26 and 14% yield, respectively). It is significant that the isomer distributions were drastically altered relative to the

(1) Paper VIII, Aromatic Oxygenation.
(2) From the Ph.D. Thesis of M. E. K., Case Western Reserve University, Cleveland, Ohio, 1967.
(3) G. A. Razuvaev, N. A. Kartashova, and L. S. Boguslavskaya, *J. Org. Chem. USSR*, **1**, 1965 (1965).
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(5) M. E. Kurz and P. Kovacic, paper VI, unpublished data.
(6) P. Kovacic and S. T. Morneweck, *J. Am. Chem. Soc.*, **87**, 1566 (1965); S. T. Morneweck, Ph.D. Thesis, Case Institute of Technology, 1965.
(7) P. Kovacic and M. E. Kurz, *J. Am. Chem. Soc.*, **87**, 4811 (1965).
(8) (a) P. Kovacic and M. E. Kurz, *J. Org. Chem.*, **31**, 2459 (1966); (b) P. Kovacic and M. E. Kurz, *ibid.*, **31**, 2011 (1966).
(9) For recent reveiws of electrophilic oxygenation process, see R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishing Co., New York, N. Y., 1965, and L. S. Boguslavskaya, *Russ. Chem. Rev.*, **34**, 503 (1965).
(10) P. Kovacic and M. E. Kurz, *J. Am. Chem. Soc.*, **88**, 2068 (1966).

(11) For reviews of aromatic substitution by oxy radicals, see G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press Inc., New York, N. Y., 1960, Chapter 7; R. O. C. Norman and J. R. L. Smith, "Oxidases and Related Redox Systems," Vol. I, T. E. King, H. S. Mason, and M. Morrison, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965.
(12) For a preliminary account of part of this work, see P. Kovacic and M. E. Kurz, *Chem. Commun.*, 321 (1966).

TABLE I
COPPER SALTS AS OXYGENATION CATALYSTS[a]

| | Products, %[b] | | | | | | | | |
| Copper salt | Tolyl isopropyl carbonates | | | Isopropyl alcohol | Acetone | Benzaldehyde | Benzyl X[c] | $\Sigma_{i\text{-Pr}}$, %[d] |
	Yield	o	m	p					
CuCl$_2$[e]	85	57	15	28	114	16	1	6[f]	107
CuBr$_2$[g]	39	55	21	24	125	43	2	16[h]	103
Cu(SCN)$_2$[i]	4	65	13	22	160	35	1	5[j]	100
Cu(ClO$_4$)$_2$·6H$_2$O	26	73	8	19	158	22	3	3[k]	103
Cu(BF$_4$)$_2$[g,l]	14	79	7	14	162	24	1	2[k]	100
Cu(benzoate)$_2$[g]	2				103	67	8	8[m]	86
Cu(acac)$_2$[n]	2				160	20	2	11[o]	91
Cu(OAc)$_2$·H$_2$O	1				122	56	3	13[p]	90
Cu(OAc)$_2$·H$_2$O[q]	0						1	11[r]	
CuCl[e,g]	5	58	15	27	132	55	2	18[s]	96
CuBr[g]	16	54	22	24	147	41	1	16[t]	102
None[e]	1	51	13	36	120	68	2	15[u]	95

[a] Reaction conditions were toluene/diisopropyl peroxydicarbonate/catalyst (17.3:1:0.3) at 60°, 2 hr, acetonitrile solvent; see general procedure. [b] See Experimental Section for yield basis. [c] X = chloride, bromide, benzyl or isopropoxycarboxy. [d] Material balance, isopropyl groups; based on isopropyl groups/peroxide = 2:1. [e] See ref 4. [f] Chloride (5%), bibenzyl (1%). [g] Initially homogeneous, subsequently heterogeneous. [h] Bromide (15%), bibenzyl (1%). [i] Heterogeneous throughout. [j] Unidentified. [k] Bibenzyl. [l] As a 44% aqueous solution. [m] Bibenzyl (6%), benzyl isopropyl carbonate (1%), unidentified (1%). [n] Acetylacetonate. [o] Bibenzyl (1%), unidentified (10%). [p] Bibenzyl (12%), unidentified (1%). [q] Sodium acetate added in 80-fold excess to cupric acetate; acetic acid solvent. [r] Benzyl acetate. [s] Chloride (12%), bibenzyl (6%). [t] Bromide (14%), bibenzyl (2%). [u] Bibenzyl (13%), benzyl isopropyl carbonate (1%), unidentified (1%).

cupric chloride case. The weak acid salts (acetate, benzoate, and acetylacetonate) were virtually impotent as catalysts for oxygenation. The similarity of the products (acetone, isopropyl alcohol, and materials arising from the benzyl radical) and the lack of any rate enhancement compared to the thermal decomposition indicated very little involvement of the metal salt.

Oxidation of the aromatic complex (eq 3), like that of other carbon radicals,[13,14] appears to possess the components of both ligand[15,16] and electron[17,18] transfer.[5] Those cupric salts which behave well as ligand transfer agents, e.g., the halides,[13] served best as oxygenation catalysts, with the typical electron-transfer types, e.g., perchlorate,[13] functioning to a lesser extent. Copper derivatives of the weaker acids are intermediate in ligand-transfer–electron-transfer activity.[13] A possible explanation for their ineffectiveness may be self-association. For example, cupric acetate exists in a dimer–monomer equilibrium in acetonitrile solution.[19,20] In the dimeric form cupric acetate was found to possess negligible activity as an oxidant for alkyl radicals.[17] However, monomer-producing conditions[17,21] (cupric acetate in the presence of a large excess of acetate ion in acetic acid) did not suffice to bring about nuclear attack. A more detailed discussion of the implications for our system of catalysis by these various agents is presented elsewhere.[4,5]

Replacement of the cupric species by cuprous chloride[4] or bromide led to drastic reductions in yield although the isomer distributions remained essentially unchanged (Table I). The bromide also behaved analogously to the chloride[4] in that it eliminated the usual short induction period and accelerated the rate of peroxide

decomposition at least in the earlier stages of reaction. The drastic reduction in yield and eccentric rate behavior in reactions carried out with the monovalent entities reflect the seeming inability of the mixed cupric salt (II) formed in the induced decomposition of the peroxide (eq 4) to function as an oxidant.[4] Thus, unless a source of halide is available for metathesis (eq 5), the chain is apparently broken.[4,5] With cupric chloride, generation of hydrochloric acid in the oxidation step (eq 3) provided the requisite ligand, whereas with cuprous chloride, the necessary supply of halide was not at hand. Another factor contributing to low yield may be the extremely rapid breakdown of the peroxide by the cuprous species.

This marked dependence on the nature of the ligand prompted further tests. The copper salts present at the end of typical reactions with cupric and cuprous chloride were isolated and analyzed. In the former case, evidence indicated the presence of cupric chloride. However, the salt from cuprous chloride contained a substantial amount of organic residues.[22] These findings are in accord with the apparent necessity of eq 5 in the oxygenation chain.

According to the scheme, hydrochloric acid is generated during the reaction (eq 3), but does not enter into the over-all stoichiometry (eq 7). An attempt was

$$(i\text{-PrOCO}_2)_2 + \text{ArH} \xrightarrow{\text{CuCl}_2} \text{ArOCO}_2\text{Pr-}i + i\text{-PrOH} + \text{CO}_2 \quad (7)$$

made to purge the acid gas during the course of cupric chloride-catalyzed reaction, but none could be detected in the effluent vapor. Furthermore, the pH in several of the systems investigated generally remained near 6. The exchange reaction presumably consumes the hydrogen halide with reasonable facility. Addition of hydrogen chloride to a reaction mixture promoted by cuprous chloride constituted a more direct test for participation of eq 5 (Table II). Indeed a substantial increase in the aromatic substitution process (60% yield) was observed when equimolar amounts of the

(13) J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).
(14) J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **84**, 3946 (1962).
(15) J. K. Kochi and R. V. Subramanian, *ibid.*, **87**, 1508 (1965).
(16) J. Kumamoto, H. E. De La Mare, and F. F. Rust, *ibid.*, **82**, 1935 (1960).
(17) J. K. Kochi and R. V. Subramanian, *ibid.*, **87**, 4855 (1965).
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(19) J. K. Kochi and H. E. Mains, *J. Org. Chem.*, **30**, 1862 (1965).
(20) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1965).
(21) J. K. Kochi and R. V. Subramanian, *Inorg. Chem.*, **4**, 1527 (1965).

(22) It is doubtful that the isolated salt is II since there is nearly quantitative evolution of carbon dioxide from the cuprous chloride reactions.

TABLE II

EFFECT OF ADDED HALIDE ON OXYGENATION OF TOLUENE WITH DIISOPROPYL PEROXYDICARBONATE–COPPER HALIDE[a]

Catalyst	Catalyst/ peroxide, M	Additive	LiX/ peroxide, M	Tolyl isopropyl carbonates				Isopropyl alcohol	Acetone	Benzalde- hyde	Benzyl X[c]	$\Sigma_{i\text{-}Pr}$, %[d]
				Yield	o	m	p					
CuCl•	0.3[f]	None		5	58	15	27	132	55	2	18[g]	96
CuCl	0.3[f]	LiCl	0.3	64	56	15	29	114	15	1	4[h]	97
CuCl	0.3	HCl[i]		60	58	15	27	136	17	<1	3[h]	106
CuCl[j]	0.3	HCl[k]		19	65	15	20			5	25[l]	
CuCl	0.3[f]	LiBr	0.3	27	55	20	25	135	27	1	17[m]	95
None	n	LiCl	0.3	0				154	60	4	14[h]	107
CuBr	0.3[n]	None		16	54	22	24	147	41	1	16[o]	102
CuBr	0.3[n]	LiBr	0.3	13	51	23	26	146	53	<1	12[p]	106
CuBr	0.3[n]	LiCl	0.3	35	56	18	26	129	31	<1	6[q]	98
CuCl₂•	0.1[n]	None		27	57	15	28	120	46	<1	17[r]	97
CuCl₂	0.1[n]	LiCl	0.2	55	59	15	26	130	33	<1	11[h]	109
CuCl₂•	0.1	HCl[k]		12	72	11	17			4	32[t]	
CuCl₂•	0.2[n]	None		59	57	15	28			<1	14[h]	
CuCl₂	0.2	LiCl	0.2	77	57	15	28	120	20	<1	5[h]	108
CuCl₂	0.2[n]	CuCl	0.1	32	58	15	27	134	43	1	17[h]	104
CuCl₂•	0.3	None		85	57	15	28	114	16	1	5[h]	107
CuCl₂	0.3	LiCl	0.3	72	58	15	27	124	13	<1	5[h]	104
CuBr₂	0.3[n]	None		39	55	21	24	125	43	2	16[o]	103
CuBr₂	0.3	LiBr	0.3	15	52	21	27	130	64	<1	7[p]	104

[a] Reaction conditions were toluene/peroxide (17.3:1), acetonitrile solvent, 60°, 2 hr; see general procedure. [b] See Experimental Section for yield basis. [c] X = chloride, bromide, or benzyl. [d] Material balance, isopropyl groups; based on isopropyl groups/peroxide = 2:1. [e] See ref 4. [f] Heterogeneous throughout. [g] Chloride, 12%, bibenzyl, 6%. [h] Mainly chloride with <1% bibenzyl. [i] HCl/peroxide = 0.3. [j] Unchanged peroxide = 40%. [k] Saturated by continuous flow of HCl. [l] Chloride (15%), bibenzyl (10%). [m] Chloride (10%), bromide (7%). [n] Initially homogeneous, subsequently heterogeneous. [o] Bromide (15%), bibenzyl (1%). [p] Bromide. [q] Chloride (4%), bromide (2%). [r] Chloride (12%), bibenzyl (5%). [s] Unchanged peroxide (58%). [t] Chloride (28%), bibenzyl (4%).

acid and cuprous chloride were employed in concert. The instantaneous development of an orange-brown color provided further evidence for cupric chloride formation. However, use of a HCl/CuCl molar ratio greater than one (Table II, entry 4) only slightly enhanced the oxygenation yield, with marked retardation of peroxide decomposition (*vide infra*).

Introduction of equivalent amounts of chloride in the form of the lithium salt (cuprous chloride catalyst) resulted in nearly identical enhancement in the amount of aromatic ester (64% yield). In a control experiment it was ascertained that lithium chloride itself does not promote oxygenation. Added bromide also was able to contribute to the formation of an effective oxidant, though less efficiently than chloride. A similar trend (increased yield of aryl isopropyl carbonate) was noted with chloride in conjunction with cuprous bromide. However, bromide gave essentially no change (Table II, entry 8). The reaction mixtures containing copper and one type of halide ligand gave isomer distributions for the ester product dependent on the nature of the halogen ($o/m/p$ = 57:15:28 for copper chloride and 53:22:25 for copper bromide.) In those cases involving equimolar amounts of chloride and bromide, very similar orientations ($o/m/p$ = 55:19:26) were observed, between the extremes noted for the individual ligands.

The initial solution of the copper and lithium halides in acetonitrile resembled that of the copper halide alone (orange-brown with cupric chloride, pale yellow-green with cuprous chloride, dark green with cupric bromide, and nearly colorless with cuprous bromide). When the peroxide was added to the cuprous halide–lithium halide mixture, an immediate change to the color of the corresponding cupric salt was brought about. Many of the mixtures became heterogeneous as time progressed.

Earlier, we reported that the ester yield decreased when less than a certain minimum amount of cupric chloride (0.3 molar ratio of catalyst/peroxide) was used.[4] Addition of small quantities of lithium chloride to the systems deficient in cupric chloride resulted in marked increases in oxygenation (Table II, entries 11 and 14.) In contrast, introduction of cuprous chloride (Table II, entry 15) gave a decreased yield, perhaps a reflection of too rapid generation of alkoxycarboxy radicals. When the optimum level of cupric chloride was augmented with chloride, the yield of aryl isopropyl carbonate actually declined to a noticeable extent. An even more significant adverse effect on oxygenation was observed when the cupric chloride reaction was carried out in the presence of excess hydrogen chloride (Table II, entry 12). Similarly, bromide added at the optimum cupric bromide:peroxide ratio caused a marked decrease in aromatic substitution (Table II, entry 19). No alteration in isomeric constitution arose from these variations.

The considerable enhancement afforded from inclusion of chloride ion in the cuprous chloride system supports the proposed metathesis reaction (eq 5) as a continuous process for regeneration of cupric halide. This is analogous to the interpretation invoked in ligand transfer oxidation of butyl radicals by copper salts in the presence of chloride ion.[15] The fact that the chain process in oxygenation is comparatively sluggish and demands a fairly large minimum of cupric salt initially can perhaps be attributed in part to the necessity of this exchange step. The improvement in yield when chloride is added to mixtures low in cupric chloride is in accord with this reasoning. Another factor which likely contributes to a minor extent is the wasting of chloride ion in benzyl chloride formation. Whereas the mixed copper salt (II) is apparently not able to per-

TABLE III

OXYGENATION WITH DIISOPROPYL PEROXYDICARBONATE IN NEAT SYSTEMS[a]

| | | Tolyl isopropyl carbonates | Diisopropyl carbonate | Benzalde- hyde | Benzyl chloride | | | | Gas evolution |
Catalyst	Temp, °C					Bibenzyl	CO$_2$[c]	Σ$_{CO_2}$, %[d]	cc/min[e]
None[f]	60	2[g]	0	1	0	39	187	96	7
	50[h]	3[g]	0	1	0	38			1
FeCl$_3$	60	31[i]	18	5	31	3[j]	152	100	18
	50[h]	38	27	5	25	2[j]	135	100	3
FeCl$_2$	60	8[g,k]	2	2	14	14	187	99	l
CuCl$_2$	60	7[g]	9	1	23	27	175	97	9
SbCl$_5$	60	6[m]	0	4	34	11[j]	180	94	7

[a] Reaction conditions were toluene/peroxide/catalyst (16.25:1:0.11–0.15), 3–6 hr, heterogeneous; see general procedure.   [b] See Experimental Section for yield basis.   [c] Determined by method B; see ref 4.   [d] Material balance, carbon dioxide groups; based on CO$_2$ groups/peroxide = 2:1.   [e] Apparent rate.   [f] Homogeneous reaction.   [g] Benzyl isopropyl carbonate (2–3%) also present.   [h] 24 hr. [i] o/m/p = 64:3:33.   [j] Mixture of bibenzyl and methyldiphenylmethanes.   [k] o/m/p = 65:4:31.   [l] Erratic behavior, but qualitatively faster than all other runs in the early stages of reaction, with subsequent decline.   [m] Benzyl isopropyl carbonate (1%) also present.

form as an oxidant for ester formation, it is capable of converting benzyl radical to benzyl halide as evidenced by the extensive amount of this product in the cuprous halide case. Such pronounced specificity in the nature of the copper salt is not characteristic of the per ester–olefin reactions.[13,19,23]

The harmful effect on oxygenation promoted by cupric chloride (0.3 molar ratio to the peroxide) from the introduction of excess chloride suggests formation of chloro–cupric complexes (eq 8) which apparently are ineffective or less efficient as oxygenation catalysts. The illustrated equilibria are well documented for acetonitrile systems.[24,25]

$$CuX_2 + X^- \underset{-X^-}{\overset{+X^-}{\rightleftharpoons}} CuX_3^- \underset{-X^-}{\overset{+X^-}{\rightleftharpoons}} CuX_4^{2-} \qquad (8)$$
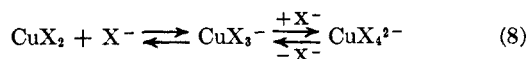
The lesser efficiency of the bromide may be due to the rather complex equilibria entailing this species which reportedly exist in acetonitrile solvent (eq 9 and 10)[24] with the end result that the active catalyst is present in only low concentration. CuBr$_3^-$ in acetonitrile is believed to be green,[25] the hue of our systems containing cupric bromide. Addition of bromide to cupric bromide facilitates formation of the CuBr$_4^{2-}$ complex[25] which is purple (eq 8), again the color we observed. The equilibrium analogous to eq 9 does not lie as far to the right for cupric chloride which would partially rationalize the differences in the effectiveness of the two salts.

$$2CuBr_2 \rightleftharpoons Cu(I) + CuBr_3^- + {}^1/_2Br_2 \qquad (9)$$

$$2Cu(II) + 2Br^- \rightleftharpoons 2Cu(I) + Br_2 \qquad (10)$$
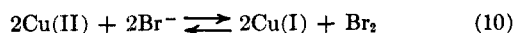
This study points up the sensitivity of oxygenation to both the nature and quantity of the ligand available to the cupric ion. On the basis of orientation data, the active salts can be divided into two categories,[5] the halides and the highly ionic types derived from strong acids. However, note that even within these groupings, the oxidants differ to some extent according to the o/m/p ratios. With the mixed halide ligands, the participating species may be the unsymmetrical cupric halide or else a mixture of cupric chloride and cupric bromide. Since acetonitrile is known to form complexes with copper salts,[19] the role of solvent should also be considered.

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(24) W. Schneider and A. V. Zelewsky, *Helv. Chim. Acta*, **46**, 1848 (1963).
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B. Iron Salts.—Oxygenation was also carried out with ferric chloride as the promoter. The majority of the work with this agent was performed in a neat system (toluene/peroxide/catalyst = 16.3:1:0.1–0.5) at 60°, as a tie in with a recent literature report (*vide infra*). The results for ferric chloride at both 50 and 60° are presented in Table III along with the corresponding data for the conrol runs. In addition, experiments carried out with ferrous chloride, cupric chloride, and antimony pentachloride are included.

Tolyl isopropyl carbonates (31%) are produced with ferric chloride at 60° along with substantial amounts of products derived from the benzyl radical. Diisopropyl carbonate was also detected. Slightly better results were forthcoming at the lower temperature in accord with previous findings in related systems.[4] Less than 2% of the aromatic derivative was formed in the decomposition without metal halide, with bibenzyl (39%) being the major product. Ferrous chloride also acted as a catalyst for oxygenation (8%), but in an inept fashion. The isomeric compositions from these two salts were similar. The side products were found in quantities intermediate between the ferric chloride-catalyzed and noncatalyzed situations. At either temperature reactions run in the presence of the iron salts were faster than the thermal decompositions, and whereas ferric chloride greatly reduced the induction period, ferrous chloride essentially eliminated it. Qualitatively, the reaction with the latter salt appeared to be faster during the initial stages, but subsequently decreased in rate. Since the results parallel those obtained with the copper halides in acetonitrile solvent,[4] the analogous chain process (eq 2–5) involving iron is proposed.

Cupric chloride gave rise to only a small amount of oxygenation, presumably because of its very poor solubility in toluene. Antimony pentachloride, although soluble, was not very effective. The apparent rates in these two explorations were quite similar to the noncatalyzed case, further illustrating failure to establish the desired chain sequence.

Table IV shows the effect of varying the ferric chloride/peroxide ratio. Similar yields from aromatic substitution were obtained throughout the range studied, as well as for the dialkyl carbonate by-product. Benzyl chloride was the major aromatic by-product at lower catalyst/peroxide ratios, while methyldiphenylmethanes predominated at higher ratios, presumably

TABLE IV

VARIATION IN CATALYST/PEROXIDE RATIO WITH DIISOPROPYL PEROXYDICARBONATE–TOLUENE–FERRIC CHLORIDE[a]

Catalyst/peroxide, M	Tolyl isopropyl carbonates	Diisopropyl carbonate	Benzaldehyde	Benzyl chloride	C₁₄H₁₄[c]	CO₂[d]	ΣCO₂, %[e]
0.12	31[f]	18	5	31	3	152	100
0.20	35[g]	19	5	20	5	168	111
0.51	29	h	7	1	16	175	

[a] Reaction conditions were toluene/peroxide (16.25:1), 60°, 3–4 hr, heterogeneous mixture; see general procedure. [b] See Experimental Section for yield basis. [c] Methyldiphenylmethanes contaminated with small amounts of bibenzyl. [d] Determined by method B, see ref 4. [e] Material balance, carbon dioxide groups; based on CO_2 groups/peroxide = 2:1. [f] $o/m/p$ = 63:3:34. [g] $o/m/p$ = 65:4:31. [h] Not determined.

the peroxide–ferric chloride adduct. Since the metal is readily reduced and presumably in intimate contact with the radical, might there be some contribution from the illustrated structure IV? Admittedly, this approach is quite speculative since there is no indication from a large volume of previous work for conversion of oxy radicals to oxonium ions.[19] In any event, complexing by the Lewis acid halide should accentuate the electrophilic character of the oxy radical, which would be reflected in the isomer distribution.

$$i\text{-PrO}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{O}\overset{\delta^+}{--}\text{FeCl}_2\text{--Cl}^{\delta-}$$
IV

TABLE V

EFFECT OF FRIEDEL–CRAFTS CATALYSTS ON OXYGENATION WITH DIISOPROPYL PEROXYDICARBONATE–METAL HALIDE[a]

Metal halide	Salt/peroxide, M	Tolyl isopropyl carbonates Yield	o	m	p	Isopropyl alcohol	Acetone	Benzaldehyde	Benzyl chloride	Σi-Pr, %[c]	Unchanged peroxide, %[d]
FeCl₃	0.3	5	60	5	35	158	38	1	26	100	e
FeCl₃	1.0	40	61	5	34	116	31	11[f]	43	94	6
FeIC₃	2.1	39	64	5	31	132	27	6[f]	12	99	20
CuCl₂[g]	0.3	85	57	15	28	114	16	1	5	107	0
CuCl₂[h]	0.3	19	70	9	21	126[i]	12	1	28	92	24
SbCl₅	1.0	2	57	15	28	177	10	1	31	95	22
CuCl₂[j]	0.3	51	61	16	23	129	28	1	13	104	0
ZnCl₂[k]	0.3	1				134	75	1	1[l]	105	0

[a] Reaction conditions were toluene/peroxide (17.3:1), acetonitrile solvent, 60°, 3 hr; see general procedure. [b] See Experimental Section for yield basis. [c] Material balance, isopropyl groups; based on isopropyl groups/peroxide = 2:1. [d] Determined by iodometry; see Experimental Section. [e] Not determined. [f] May contain chlorotoluenes which have the same retention time in glpc. [g] See ref 4. [h] Plus SbCl₅ (1:1 molar ratio to the peroxide). [i] Isopropyl chloride (26%) also present. [j] Plus ZnCl₂ (1:1 molar ratio to the peroxide). [k] Initially homogeneous, subsequently heterogeneous. [l] Bibenzyl (18%) also present.

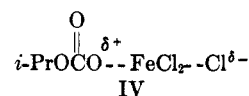*via* ferric chloride catalyzed alkylation of toluene by benzyl chloride.

A speculative route to diisopropyl carbonate would involve complexing[3,26] of ferric chloride with $-CO_2Pr$-i moieties, or isopropyl alcohol, yielding positively charged isopropyl groups capable of attacking isopropoxycarboxy anions present in II. Material balance based on carbon dioxide residues was excellent in all of the experiments.

Upon modifying to a homogeneous mixture by use of acetonitrile, the quantity of ferric chloride needed for optimum results became more critical. For example, with a catalyst/peroxide proportion of 0.3, only 5% oxygenation occurred, while 40% was noted at a 1:1 ratio (Table V). Additional amounts of ferric chloride caused no appreciable change. The large catalyst requirement suggests a medium effect. Orientation of the ester product was quite constant in all of the ferric chloride runs, whether neat ($o/m/p$ = 64:3:33) or in solvent ($o/m/p$ = 61:5:34). The low amount of *meta* isomer contrasts quite sharply with that from copper chloride ($o/m/p$ = 57:15:28). We feel that the attacking entity in the iron systems is a complex (III) of the isopropoxycarboxy radical with ferric

$$i\text{-PrO}\overset{\overset{\displaystyle O---\text{FeCl}_3}{\|}}{\text{C}}\text{O}\cdot$$
III

chloride. This coordinated species could be generated directly from the components, or through homolysis of

We were able to obtain experimental support for the general hypothesis. Antimony pentachloride, a fairly good agent for complexing with carbonyl groups, is ineffective in bringing about substitution by peroxide[3] (Table V). A system containing a 1:1 ratio of antimony pentachloride–peroxydicarbonate with the optimum amount of cupric chloride did give oxygenation, but in substantially lower yield than with the copper entity alone. Significantly, in the isomer distribution ($o/m/p$ = 70:9:21) the low *meta* value obtained with ferric chloride was approached. Therefore, we submit that antimony pentachloride is interacting at the carbonyl function as proposed for ferric chloride. Of pertinence are the reports that ferric chloride[3,27] and antimony pentachloride[3] form complexes with dialkyl peroxydicarbonates. A similar reaction mixture composed of peroxide/zinc chloride/cupric chloride (1:1:0.3) in solvent failed to produce a prominent change in the isomeric composition of the tolyl isopropyl carbonates. This was expected since zinc chloride generally displays quite low catalytic activity.

Another experimental observation (retardation in over-all rate of peroxide destruction) supports the postulate that the normal oxygenation process is altered when an appropriate coordinating agent, such as ferric chloride, antimony pentachloride (Table V), hydrogen chloride (Table II), mercuric chloride, or molybdenum pentachloride (*vide infra*), is present in substantial amounts. After 3 hr (well in excess of the time needed for thermal homolysis of the peroxide), 6 to 58% of the peroxide remained unchanged. With zinc chloride,

(26) F. A. Drahowzal, "Friedel-Crafts and Related Reactions," G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 20.

(27) L. S. Boguslavskaya, N. A. Kartashova, V. E. Shurygin, and G. A. Razuvaev, *J. Gen. Chem. USSR,* **34,** 3119 (1964).

TABLE VI
DICYCLOHEXYL PEROXYDICARBONATE–TOLUENE–FERRIC CHLORIDE

Catalyst	Tolyl cyclohexyl carbonates Yield	o	m	p	Cyclohexanone	Cyclohexanol	Dicyclohexyl carbonate	Benzyl X[b]	CO2	Σcyclohexyl, %[c]	ΣCO2, %[c]
None[d]	1				41	131	0	21[e]	203	87	102
None[f]	0				41	125		24[g]	185		
FeCl3[h]	23	63	4	33	25	126	7	30[i]	165	94	98
FeCl3[j]	41	85	0	15	22	95		17[k]	153		

[a] Yields based on moles per mole of peroxide. [b] X = chloride or benzyl. [c] Material balance; based on two groups per mole of peroxide. [d] Reaction conditions were toluene/peroxide (16.4:1), 60°, 5 hr; see Experimental Section. [e] Bibenzyl. [f] Reaction conditions were toluene/peroxide (9–10:1), 50–60°; see ref 27. [g] Bibenzyl; some higher boiling material was also present. [h] Reaction conditions were toluene/peroxide/FeCl3 (16.4:1:0.13), 60°, 2 hr. [i] Benzyl chloride (28%), bibenzyl (2%), and benzaldehyde (3%). [j] Reaction conditions were toluene/peroxide/FeCl3 (11–12:1:0.13), 40–60°; see ref 3 and 30. [k] Benzyl chloride; some higher boiling material was also present.

decomposition was complete in less than 3 hr. The findings suggest that complexed peroxide decomposes less readily than the free substance. The effects of *para* substituents on the rates of thermal[28] and ferrous ion-induced[29] decompositions of diaroyl peroxides have been investigated. In both cases electron-withdrawing groups caused a rate retardation, whereas electron-donating types had the opposite effect. Hence diminution in rates of destruction of the peroxide–Lewis acid complex is not unreasonable. This effect applies only to the solvent system, since as pointed out earlier, peroxide decomposition in the neat cases was accelerated.

Quite recently, there was a report by Razuvaev and coworkers concerning the production of tolyl cyclohexyl carbonates from interaction of toluene and dicyclohexyl peroxydicarbonate in the presence of ferric chloride.[3,30] They postulated that the ester arises from ferric chloride-induced heterolytic breakdown of the peroxide affording the cyclohexyloxycarboxy cation as the electrophile. At the same time recognition was given to the presence of products characteristic of radical type reactions. Certain aspects of their work (the much lower catalyst requirement and quite different isomer distribution) were at odds with related studies[6] of Friedel–Crafts oxygenation in this laboratory (failure of ferric chloride to function as a Friedel–Crafts catalyst for oxygenation at 0°). Consequently, we felt impelled to subject the area to a more detailed scrutiny.

Dicyclohexyl peroxydicarbonate was synthesized and reinvestigated under conditions similar to those reported by the earlier workers. The results are tabulated in comparison with the prior disclosure (Table VI). Products arising from the uncatalyzed thermal decomposition of the peroxide are also included. Although our findings are for the most part in qualitative agreement with those previously reported, there exists an appreciable difference in the isomer distribution of the carbonates. In addition, products originating from the competing radical processes were present: cyclohexanol, cyclohexanone, benzyl chloride, and carbon dioxide (in agreement with Razuvaev, *et al.*)[3,30] along with small amounts of previously unreported substances (dicyclohexyl carbonate, benzaldehyde, and bibenzyl).

(28) (a) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950); (b) A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).
(29) S. Hasegawa, N. Nishimura, S. Mitsumoto, and K. Yokoyama, *Bull. Chem. Soc. Japan*, **36**, 522 (1963).
(30) G. A. Razuvaev, N. A. Kartashova, and L. S. Boguslavskaya, *J. Gen. Chem. USSR*, **34**, 2108 (1964).

In the control experiment (no catalyst) less than 1% of nuclear oxygenation accompanied the familar radical-type processes, which corresponds nicely with a prior report.[27]

Studies with the more readily available diisopropyl peroxydicarbonate under conditions simulating the Russian work gave analogous results (Table III). Striking similarities were also noted, as anticipated, in the rates of breakdown for dicyclohexyl and diisopropyl peroxydicarbonates in the neat systems (Table VII) (that of the former being slightly faster). For example, both decompositions were accelerated by roughly a factor of three in the presence of ferric chloride at 60°.

TABLE VII
RATES OF DIALKYL PEROXYDICARBONATE DECOMPOSITION, CATALYZED AND UNCATALYZED[a]

Peroxide	Catalyst[b]	Apparent rate, ml/min[c]	t1/2, min
(C6H11OCO2)2	None	5	54
(C6H11OCO2)2	FeCl3	14	17
(i-PrOCO2)2	None	3	99
(i-PrOCO2)2	FeCl3	8	37

[a] Peroxide (12.5 mmoles) in toluene solution (50 ml total); reaction conditions were toluene/peroxide (16.5–17.1:1), 60°. [b] Catalyst/peroxide = 0.13. [c] Based on carbon dioxide evolution, see method B, ref 4.

Since both of these dialkyl peroxydicarbonates undergo homolysis at an appreciable rate at the temperatures studied by the other group, we surmised that exploring somewhat lower temperatures might be instructive. Hence, it is quite significant that when the diisopropyl peroxydicarbonate–ferric chloride–toluene combination was studied at 22–24°, conditions making for very slow homolysis of the oxygen–oxygen bond, unchanged peroxide was recovered in 99% yield after 6 hr. One would not expect Friedel–Crafts catalysis, as suggested by the previous investigators,[3,30] to display such a high degree of sensitivity to relatively small variations in temperature. It should be pointed out that the present isomer distribution is markedly different from that (o/m/p = 34:11:55) reported for the product from toluene–diisopropyl peroxydicarbonate–aluminum chloride.[6] Such a drastic temperature effect is more consonant with the participation of alkoxycarboxy radicals and ferric chloride in a redox capacity as discussed in the preceding section. A more detailed investigation of the neat system with ferric chloride was carried out with diisopropyl peroxydicarbonate (*vide supra*). In earlier, related work hydroxylation of benzene by

TABLE VIII
METAL HALIDES AS CATALYSTS WITH DIISOPROPYL PEROXYDICARBONATE-TOLUENE[a]

| Metal halide | Tolyl isopropyl carbonates | | | Isopropyl alcohol | Acetone | Benzaldehyde | Benzyl chloride | Bibenzyl | $\Sigma_{i\text{-}Pr}$, %[c] |
	Yield	o	m	p						
CuCl$_2$[d]	85	57	15	28	114	16	<1	5	<1	107
CuBr$_2$[e]	39	55	21	24	125	43	2	15[f]	1	103
FeCl$_3$[g]	40	61	4	35	116	31	11[h]	43	1	94
RuCl$_3$	43	58	14	28	121	41	1	9	0	102
Na$_2$IrCl$_6$[e]	36	60	13	27	125	38	2	8	0	100
OsCl$_4$	65	59	12	29	107	22	<1	1	0	97
RhCl$_3$[e]	<1				124	79	5	0	6	102
WCl$_6$[e]	1				133	86	1[i]	5	9	110
MoCl$_5$[j,k]	2	59	7	34	135	67	1	13	1	102
MoCl$_5$[g,l]	3	55	16	29			12[h]	<1	<1	
ZrCl$_4$[e]	1				190	39	2	8	10	115
TaCl$_5$[e]	<1				126	73	1	3	11	100
NbCl$_5$[e]	1				129	76	3[m]	12	8	103
TiCl$_4$[g]	0				157	51	0	51	0	104
SbCl$_5$[g]	2	57	15	28	177	10	1	31	2	95
HgCl$_2$[j,k]	2	59	15	26	128	47	1[n]	4	13	89
CoCl$_2$·6H$_2$O	0				127	75	1	9	4	101
CoCl$_2$·6H$_2$O[o]	0				123	65	1	7	7	94
AuCl$_3$	2	62	12	26	165	33	2	20	2	100

[a] Reaction conditions were toluene/peroxide/catalyst (17.3:1:0.3), 60°, 2-3 hr, acetonitrile solvent; see general procedure. [b] See Experimental Section for yield basis. [c] Material balance, isopropyl groups; based on isopropyl groups/peroxide = 2:1. [d] See ref 4. [e] Heterogeneous. [f] Benzyl bromide. [g] Catalyst/peroxide = 1:1. [h] May contain chlorotoluenes which have the same glpc retention time. [i] Two other unknown products (1%). [j] Initially homogeneous, subsequently slightly heterogeneous. [k] Unchanged peroxide (27%). [l] Unchanged peroxide (47%). [m] Unknown product (2%). [n] Three unknown products (7, 1, and 1%). [o] LiCl added in equimolar amount with CoCl$_2$·6H$_2$O.

Fenton's reagent was enhanced by the addition of ferric ion.[31]

C. Other Metal Salts.—A number of salts of metals other than copper and iron were also investigated. These are divided arbitrarily into halide and nonhalide types.

The complete listing of the metal halides is contained in Table VIII. With the exception of the copper halides, only those belonging to Group VIII were capable of bringing about oxygenation. Thus, in addition to the aforementioned ferric chloride catalyst, ruthenium trichloride, osmium tetrachloride, and sodium hexachloroiridate were moderately effective since aromatic substitution occurred to the extent of 43, 65, and 36%, respectively. Rhodium trichloride was the only platinum metal halide tried which was inactive, possibly the result to some degree of extremely poor solubility.

Antimony pentachloride, molybdenum pentachloride, auric chloride, titanium tetrachloride, and mercuric chloride, are examples of soluble salts which functioned poorly in the redox capacity. Since substantial amounts of antimony and titanium compounds were employed, copious quantities of benzyl chloride were generated. Tungsten hexachloride, zirconium tetrachloride, tantalum pentachloride, and niobium pentachloride were devoid of activity, due, perhaps, in part to their very poor solubility, In all these cases the acetone and isopropyl alcohol products accounted well for the material balance involving the peroxide reactant. Studies with cobaltous chloride led to no oxygenation. An attempt with this compound to generate an active species *in situ* by addition of lithium chloride was of no avail.

With the vast majority of the halides which facilitated oxygenation, the isomeric composition of the

carbonates was similar to that from cupric chloride. In relation to yield of ester, cupric chloride is the reagent of choice.

Table IX surveys the nonhalide salts of elements other than copper, most of which were soluble in the reaction mixture. Only with cobaltic ethyl xanthate was there any indication, obviously slight, of oxygenation. The ligand of the acetylacetonate-containing salts underwent hydrogen abstraction by oxy radicals resulting in higher yields of isopropyl alcohol with lesser amounts of acetone. An unidentified substance was also present which, we conjecture, may arise from radicals formed *via* toluene and the ligand as precursors.

Some general considerations of the specificity shown by the metal ion in the oxygenation reaction are in order. To enter efficiently into the chain process, the requisite properties demanded of the metallic species are the ability to reduce peroxides and to oxidize carbon radicals, apparently by one-electron transformations. Reduction of peroxides is a well-known process for a variety of metal ions,[13] e.g., copper,[13] iron,[32-34] cobalt,[32] and titanium.[35] On the other hand oxidation of carbon radicals has been extensively performed only with copper[13,19] and iron,[18] and to a lesser degree with lead[36] and cobalt.[23] Copper generally acts the most effectively in this capacity.[37]

Thus, it is not surprising that aromatic oxygenation takes place with salts of copper and iron, whereas no success is met with many of the others, e.g., mercury,

(31) J. R. L. Smith and R. O. C. Norman, *J. Chem. Soc.*, 2897 (1963).

(32) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p 95 ff.

(33) J. H. Baxendale, M. G. Evans, and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946); F. Haber and J. Weiss, *Proc. Roy. Soc.* (London), **A147**, 332 (1934).

(34) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950).

(35) W. T. Dixon and R. O. C. Norman, *Nature*, **196**, 891 (1962).

(36) J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 3609 (1965).

(37) For a recent review concerning oxidation and reduction of carbon radicals with metal ions, see J. K. Kochi, *Science*, **155**, 415 (1967).

TABLE IX

NONHALIDE METAL SALTS AS CATALYSTS WITH DIISOPROPYL PEROXYDICARBONATE–TOLUENE[a]

Metal salt	Tolyl isopropyl carbonates	Acetone	Isopropyl alcohol	Benzyl-X[c]	Benzaldehyde	$\Sigma_{i\text{-Pr}}$, %[d]
AgNO₃	0	51	151	16	2	101
Co(acac)₃[e]	0	31	175	35[f]	0	103
Fe(acac)₃	0	13	176	17[f]	1	95
Cr(acac)₃	0	25	170	0	1	98
Pd(acetate)₂[e]	0	72	115	0	10	94
Co(OCS₂Et)₃[g]	2				3	4

[a] Reaction conditions were toluene/peroxide/catalyst (17.3:1:0.3), acetonitrile solvent, 60°, 2 hr; see general procedure. [b] See Experimental Section for yield basis. [c] X = unidentified. [d] Material balance, isopropyl groups; based on isopropyl groups/peroxide = 2:1. [e] Heterogeneous. [f] X is possibly derived from the ligand. [g] Six hours; not all peroxide consumed.

TABLE X

NONMETALLIC OXIDANTS WITH DIISOPROPYL PEROXYDICARBONATE–TOLUENE[a]

Oxidant	Tolyl isopropyl carbonates Yield	o	m	p	Isopropyl alcohol	Acetone	Benzaldehyde	Benzyl halide[c]	Bibenzyl	$\Sigma_{i\text{-Pr}}$, %[d]
None[e]	0.7[f]	51	13	36	120	68	1	0	13	95
O₂[g]	6.6[h]	49	20	31	85	83	17	0	1	88
I₂[i]	6.7	48	30	22	158	28	1	8[j]	1	97
I₂[k]	5.2	55	20	25	175	21	1	3[j]	1	100
Br₂[i]	2.8	54	18	28	147	31	1	65[l]	2	90
Br₂[k]	7.0	61	12	27			1	72[l]	1	
Cl₂[m]	1.5	44	17	39			0	109[n,o]	7	
CCl₄	0				113	80	1	21[n]	1	97
NaI[i]	0				163	52	1	6[j]	1	107
LiCl[i,p]	0				154	60	4	14[n]	1	107

[a] Reaction conditions were toluene/peroxide (17.3:1), acetonitrile solvent, 60°, 2 hr; see general procedure. [b] See Experimental Section for yield basis. [c] Iodide, bromide, or chloride. [d] Material balance, isopropyl groups; based on isopropyl groups/peroxide = 2:1. [e] See ref 4. [f] Benzyl isopropyl carbonate was also present (0.5%). [g] Solution continuously saturated with oxygen. [h] Benzyl isopropyl carbonate was also present (0.1%). [i] Peroxide/oxidant = 1:0.3. [j] Benzyl iodide, tentative identification, plus other unknown products in trace amounts. [k] Peroxide/oxidant = 1:1.5. [l] Benzyl bromide. [m] Peroxide–oxidant = 1:2.25. [n] Benzyl chloride. [o] Chlorotoluenes (66%) were also present. [p] Became heterogeneous during reaction.

antimony, and titanium. The group VIII elements, iridium, ruthenium, and osmium, which can undergo redox reactions[38,39] of the requisite type, are active catalysts. On the other hand, with reference to rhodium trichloride, the +2 and +4 levels are not favored states.[39] In the case of iridium, the hexachloroiridate ion presumably acts in a redox capacity,[40] suggesting that appropriate anionic complexes can also participate as promoters. A systematic comparison of the various metallic salts is impossible owing to the nonavailability of certain ones and the lack of uniform solubility in the solvent system.

D. Nonmetallic Oxidants.—The pertinent characteristics of selected candidates in this division are set forth in Table X. A small, but real, increase in aryl isopropyl carbonates was recorded with oxygen, iodine, and bromine. The isomer distributions varied appreciably within the individual halogen categories. We did not ascertain whether this was a concentration effect or a reflection of the nature of the oxidant. Chlorine, usually the best oxidant among the halogens studied, failed to become significantly involved in oxygenation, perhaps due to its high reactivity *vis-à-vis* toluene. Chloride and iodide did not promote the sought after pathway even though in the latter case

iodine was formed and then consumed during reaction as evidenced by color changes. Carbon tetrachloride, a fairly good organic chain transfer agent,[41] gave rise to benzyl chloride, but elicited no favorable response in relation to aromatic substitution.

The beneficial effect, albeit slight, on aromatic substitution with this type of oxidant lends added support to the notion that a radical complex undergoes oxidative rearomatization. Oxidation of the intermediate adduct (eq 3) has ample literature analogy. As examples from the phenylation reaction, yields were substantially increased in the presence of cupric salt,[42] oxygen,[43] nitro compounds,[44] and various other electron acceptors.[45] This topic is elucidated in greater detail elsewhere in this series.[5]

Competitive Oxygenations.—Relative rate data were obtained with cupric chloride,[5] cupric bromide, and ferric chloride (Table XI). Toluene–benzene and *m*-xylene–benzene were used as substrates in the presence of diisopropyl peroxydicarbonate. The $k_{\text{toluene}}/k_{\text{benzene}}$ figures are higher than the values for free-radical phenylation, in accord with the known electrophilic character of the oxy radical.[5,31] Partial rate

(38) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952, Chapters 13 and 14.

(39) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1966, p 992 ff.

(40) H. Taube, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 1, H. J. Emeleus and A. G. Sharpe, Ed., Academic Press, Inc., New York, N. Y., 1959, p 14; E. N. Sloth and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 1440 (1955); P. Hurwitz and K. Kustin, *Inorg. Chem.*, **3**, 823 (1964).

(41) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 148 ff.

(42) D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *Tetrahedron Letters*, 1477 (1967).

(43) M. Eberhardt and E. L. Eliel, *J. Org. Chem.*, **27**, 2289 (1962); R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, *J. Am. Chem. Soc.*, **84**, 4152 (1962).

(44) D. H. Hey, M. J. Perkins, and G. H. Williams, *Chem. Ind.* (London), **83** (1963); G. R. Chalfont, D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *Chem. Commun.*, 367 (1967).

(45) C. D. Hall, *Chem. Ind.* (London), 384 (1965).

factors are reported in Table XII and isomer distributions from *m*-xylene in Table XIII. The relative rate order indicates that electrophilic character of the alkoxycarboxy radical increases with alteration in the metal halide as indicated, $FeCl_3 \gg CuCl_2 > CuBr_2$. Additional treatment of the competitive oxygenation topic may be found elsewhere.[5]

Table XI

RELATIVE RATES IN AROMATIC OXYGENATION WITH
DIISOPROPYL PEROXYDICARBONATE–METAL HALIDE[a]

Catalyst	ArH'	ArH	ArH'/ArH, molar ratio	$k_{ArH'}/k_{ArH}$ Obsd	$k_{ArH'}/k_{ArH}$ Calcd
$CuCl_2$[b]	Toluene	Benzene	0.83	3.19	3.81[c]
$CuCl_2$[b]	*m*-Xylene	Benzene	0.72	11.32	15.7
$CuBr_2$	Toluene	Benzene	0.77	2.39	3.12
$CuBr_2$	*m*-Xylene	Benzene	0.72	7.12	9.87
$FeCl_3$[d]	Toluene	Benzene	0.23	1.63	7.19[e]
$FeCl_3$[d]	Toluene	Benzene	0.90	6.21	6.91[e]
$FeCl_3$[d]	*m*-Xylene	Benzene	0.20	7.80	39.4

[a] Reaction conditions were total aromatic/peroxide/catalyst (83–97:1:0.4), 60°, 1 hr, acetonitrile solvent; see Experimental Section. [b] See ref 5. [c] 3.77 average from runs at three different aromatic ratios; ref 5. [d] Catalyst/peroxide = 1:1, 2–3 hr. [e] 7.05 average.

Table XII

PARTIAL RATE FACTORS FOR TOLUENE OXYGENATION WITH
DIISOPROPYL PEROXYDICARBONATE–METAL HALIDE

Catalyst	Tolyl isopropyl carbonates o	m	p	$k_{toluene}/k_{benzene}$	Partial rate factors o_f	m_f	p_f
$CuCl_2$	56.8	15.0	28.2	3.77	6.44	1.70	6.39
$CuBr_2$	54.6	21.6	23.8	3.12	5.11	2.02	4.45
$FeCl_3$	61.5	4.8	33.7	7.05	13.0	1.02	14.3

Table XIII

ISOMER DISTRIBUTIONS FOR *m*-XYLENE–DIISOPROPYL
PEROXYDICARBONATE–METAL HALIDE

Catalyst	Xylenyl isopropyl carbonates 2,4	2,6	3,5
$CuCl_2$	65	33	2
$CuBr_2$	63	34	3
$FeCl_3$	70	29	1

Experimental Section[46]

Materials.—The indicated metal salts were used directly: ferrous chloride,[47] ferric chloride, cuprous bromide (Matheson, Coleman and Bell), cupric bromide, cobaltous chloride hexahydrate, sodium iodide (Mallinckrodt), cupric chloride, cuprous chloride (about 90% pure), cupric acetate monohydrate, silver nitrate, titanium tetrachloride, mercuric chloride (Fisher), cupric perchlorate hexahydrate, cupric thiocyanate, osmium tetrachloride, rhodium trichloride (K & K), ferric and chromium acetylacetonates (Pearsall Chemical), tungsten hexachloride, tantalum and niobium pentachlorides (Rocky Mountain Chemical), cupric tetrafluoroborate (44% aqueous solution), auric chloride (Research Inorganics), molybdenum pentachloride (Climax Molybdenum Co.), zirconium tetrachloride (Harshaw), lithium bromide (Lithium Corp. of America), antimony pentachloride (Baker and Adamson), ruthenium trichloride, and sodium hexachloroiridate (Matthey Co., Wembley, England). We wish to thank Dr. T. Stephenson for samples of these last two salts in addition to palladium acetate, and Mr. D. Coucouvanis for a sample of cobaltic ethyl xanthate. We are grateful to the Pittsburgh Plate Glass Co. for generous samples of diisopropyl peroxydicarbonate.

Aromatic Oxygenation with Diisopropyl Peroxydicarbonate.—The general procedure is described elsewhere for the reactions run in acetonitrile solvent.[4] All reaction mixtures were homogeneous unless otherwise noted.

Various modifications were applied in certain of the systems; manipulations for some of the more hygroscopic salts were carried out in a dry bag; in the case of added halide ion, the lithium halide and copper salt were dissolved in acetonitrile before addition of the peroxide. Gaseous hydrochloric acid or oxygen was introduced below the surface of the reaction mixture and a slow flow maintained throughout the duration of the decomposition, and nonmetallic oxidants were dissolved initially in solvent with subsequent peroxide addition. For the reaction involving a controlled amount of hydrochloric acid, the desired quantity of gas, generated from sulfuric acid–hydrochloric acid, was dissolved in a portion of the solvent. Aliquots were titrated with standard caustic in order to determine the exact amount of acid present. After this solution was combined with the peroxide in toluene, the mixture was then added to the copper halide in acetonitrile according to the usual manner.

In an attempt to detect hydrochloric acid, the general procedure was used except that nitrogen was continuously bubbled into the reaction mixture while the exit gas was passed into a water trap. Aliquots of the water, analyzed potentiometrically and gravimetrically ($AgNO_3$ solution), gave negative tests for hydrochloric acid. Investigation of effluent gas from a blank run (3 mmoles of hydrochloric acid in toluene–acetonitrile), treated in a similar manner, clearly showed the presence of hydrochloric acid by both methods of detection.

For reactions carried out in the absence of solvent, a modified procedure was adopted. The solution (50 ml) of peroxide (0.50 N) in toluene was placed in a three-neck flask equipped with a thermometer, a mechanical stirrer, and a gas outlet connected to an inverted graduated cylinder containing a two-thirds-saturated solution of sodium sulfate. The metal halide was weighed carefully, and then added to the solution which was quickly immersed in a constant temperature bath at 60°. Stirring was commenced, and the course of the reaction was followed by carbon dioxide evolution into the inverted cylinder. At 60°, induction periods of 1 sec, 5 sec, and 1 min marked peroxide decompositions with ferrous chloride, ferric chloride, and without catalyst, respectively. Upon cessation of gas evolution, the mixture was quenched with hydrochloric acid–ice, the salts were removed by repeated washing with cold, dilute hydrochloric acid, and then analysis was carried out as usual.

Unless otherwise noted, yields of the main and by-products are based on the stoichiometry of 1 mole per mole of peroxide (eq 7) and comprise the average of two or more runs which were in satisfactory agreement.

Product Identification. A. Organic Materials.—The usual method of isolation and identification was used for most products.[4] Diisopropyl carbonate was identified in part by its infrared spectrum (C=O, 5.75, C—O, 7.9, C—O—C, 9.1, and another band at 10.9, all of which are characteristic of carbonate esters, and *gem* dimethyl, 7.3–7.5 μ, in accord with isopropyl groups), and nmr spectrum (doublet and septet centered at δ 1.18 and 4.7, respectively, in the relative proportion of 6:1). Comparison with authentic material (infrared spectrum and glpc) provided conclusive proof of structure. A mixture of the methyldiphenylmethanes was characterized by comparison of the spectrum to those of the authentic, individual isomers.[48]

B. Copper Salts.—Metal salts resulting from reactions promoted by cupric or cuprous chloride under the standard conditions were isolated as described elsewhere.[49] Purification was not rigorous.

Analysis of the salt from the cupric chloride case showed small amounts of carbon (1.46%) and hydrogen (1.93%), with copper and chloride comprising 80.29% of the total. When adjusted to 100%, the indicated figures result.

Anal. Calcd for $CuCl_2$: Cu, 47.25; Cl, 52.75. Found: Cu, 47.90; Cl, 52.10. The corresponding material from the cuprous chloride experiment was investigated in a like fashion. Found: Cu, 39.74; C, 22.05; H, 2.90; Cl, 11.50.

The values are quite similar to those for the salt resulting from cupric chloride–*t*-butylperoxy isopropyl carbonate.[49] The

(46) Microanalyses were by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected.

(47) P. Kovacic and N. O. Brace, "Inorganic Synthesis," Vol. VI, E. G. Rochow, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 172.

(48) J. H. Lamneck, Jr., H. F. Hipsher, and V. O. Fenn, *Natl. Advisory Comm. Aeronaut.*, Tech. Note 3154, 9 (1954).

(49) M. E. Kurz and P. Kovacic, paper VII, unpublished data.

infrared spectrum and appearance of the crude salt constituted further likenesses.

Authentic Materials.—Dicyclohexyl carbonate (mp 43°, lit.[50] mp 42–42°) and diisopropyl carbonate (n^{23}D 1.3999, lit.[51] n^{15}D 1.3967) were prepared according to a literature procedure.[52] The aryl isopropyl carbonates[7] and tolyl cyclohexyl carbonates[49] are described elsewhere. The remaining products are commercially available.

Competitive Oxygenation.—The general procedure was followed with certain adaptations: duplicate experiments were performed with at least two different concentrations of the aromatic components in the cupric chloride[5] and ferric chloride cases. In all duplicate runs excellent reproducibility was observed.

Analytical Procedures. A. Gas Chromatography.—The instruments and glpc columns are described elsewhere.[4]

B. For Peroxides.—An iodometric method was taken from the literature.[53]

(50) R. L. Frank, H. R. Davis, Jr., S. S. Drake, and J. B. McPherson, Jr., *J. Am. Chem. Soc.*, **66**, 1509 (1944).

(51) P. N. Kogerman and J. Kranig, *Acta et Commentationes Univ. Tartuensis*, 3 (1927); *Chem. Abstr.*, **21**, 1729 (1927).

(52) D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959).

(53) F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens, and J. H. Langston, *J. Am. Chem. Soc.*, **72**, 1254 (1950).

C. For Product Yields.—Glpc analysis as described elsewhere[4] was used to calculate product yields. Carbon dioxide was determined by known procedures (ref 4, method B for neat systems and method A for reactions in acetonitrile).

D. Isomer Distributions.—The majority of the aryl isopropyl carbonate isomer compositions were determined directly by glpc,[4] although in some cases a combination glpc–infrared technique[4] was used.

Boron Fluoride Catalyzed Alkylation. III.[1] Ethylation with Ethyl Fluoride at Low Temperatures

RYOHEI NAKANE, TOSHIYUKI ŌYAMA, AND AKIKO NATSUBORI

The Institute of Physical and Chemical Research, Bunkyo-ku, Tokyo, Japan

Additional evidence is obtained for the formation of a termolecular oriented π complex at low temperatures by measurements of infrared spectra of the isotopic toluene–ethyl fluoride–boron fluoride complexes. Ethylation proceeds at −45 to −95° on the removal of boron fluoride from the complexes. It is suggested that for boron fluoride-catalyzed alkylation with primary alkyl halides at low temperatures a transformation from the termolecular oriented π complex into a benzenonium ion complex is involved in the rate-determining step. The intermediate benzenonium ion complex is not isolated at low temperatures.

An SN2-type displacement mechanism was proposed by Brown and coworkers[2] for Friedel–Crafts alkylation with primary alkyl halides. Olah and coworkers[3] reported the isolation of an intermediate ethyl benzenonium tetrafluoroborate complex, when ethyl fluoride dissolved in toluene was saturated with boron fluoride at −80°. The complex yielded ethyltoluene when warmed above −80°. We concluded, however, from the absorption spectrum and thermodynamic isotope effect[4] that a termolecular oriented π complex is formed when the reactants are solidified in the order of toluene, ethyl fluoride, and boron fluoride at liquid nitrogen temperature and are then allowed to warm to about −100°. If both conclusions are correct, the nature of the complexes should very much depend on the way they are prepared. To ascertain this, the low temperature infrared spectra have been taken of the isotopic toluene–ethyl fluoride–boron fluoride complexes prepared under two different conditions. The infrared spectra of the isotopic methyl fluoride–boron fluoride complexes are known,[5] but those of the isotopic ethyl fluoride–boron fluoride complexes have not yet been reported.

According to our former work a termolecular π complex is formed from toluene, *t*-butyl chloride, and boron fluoride in a mole ratio of 1 : 1 : 1 at low temperatures. When boron fluoride was withdrawn from the complex, the *t*-butylation proceeded at −95°.[1] This work has now been extended to the ethylation by decomposing the termolecular π complex at low temperatures.

Results

Infrared Spectrum of Ethyl Fluoride–Boron Fluoride Complex.—The infrared spectra of the liquid isotopic ethyl fluoride–boron fluoride complexes were observed in the region from 400 to 4000 cm⁻¹ at −105°. They are listed in Table I. The infrared spectrum of liquid C₂H₅F was also observed at −105° and is listed in Table I. It agreed well with the spectrum observed at −45°.[6] The change in the frequencies with complex formation was observed, not in the C–F stretch, but slightly in the C–H stretches. An effect of isotopic substitution of boron was observed in the regions from 1400 to 1500 cm⁻¹ and from 600 to 650 cm⁻¹, as observed on the methyl fluoride–boron fluoride complexes.[5] Thus, the 1470 and 1420-cm⁻¹ frequencies can be assigned to B–F antisymmetric stretches in the C₂H₅F–B¹⁰F₃ and C₂H₅F–B¹¹F₃ complexes. The 631 and 610-cm⁻¹ frequencies can be assigned to

(1) Part II: R. Nakane and A. Natsubori, *J. Am. Chem. Soc.*, **88**, 3011 (1966).

(2) H. C. Brown, H. W. Pearsall, L. P. Eddy, W. J. Wallace, M. Grayson, and K. L. Nelson, *Ind. Eng. Chem.*, **45**, 1462 (1953).

(3) G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **80**, 6541 (1958).

(4) R. Nakane, A. Natsubori, and O. Kurihara, *ibid.*, **87**, 3597 (1965).

(5) R. Nakane and T. Ōyama, *J. Phys. Chem.*, **70**, 1146 (1966).

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