Mechanisms of Aromatic Substitution. Role of Cation-Radicals in the Oxidative Substitution of Arenes by Cobalt(III)

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Abstract: Benzene and other electron-poor aromatic compounds are readily oxidized by the powerful one-electron oxidant, cobalt(III) trifluoroacetate, to ring-substituted aryl esters in solutions of trifluoroacetic acid. The formation of phenyl trifluoroacetate in high yields requires two Co(III) for each benzene oxidized, and the kinetics of oxidation are first order in each component. A mechanism is presented for oxidative substitution involving cation-radicals as intermediates generated from arenes by electron transfer to Co(III), followed by subsequent reaction with nucleophiles. Esr studies of aromatic cation-radicals formed by oxidation of arenes with cobalt(III) trifluoroacetate are presented. Co(III) oxidation of arenes is compared to anodic oxidation, and factors relating to the formation and reactions of aromatic cation-radicals are delineated. Since oxidative substitution of arenes can be promoted by both one-equivalent and two-equivalent metal oxidants, a mechanistic distinction is made between those, such as Co(III), which proceed by cation-radicals formed by electron transfer and others, such as Pb(IV), which involve prior electrophilic substitution followed by reductive elimination of an aryl–lead(IV) intermediate.

Aromatic substitution is most commonly carried out with electrophilic species. Reaction of arenes with nucleophiles (:N) potentially constitutes an alternative pathway to aromatic substitution, provided it can be coupled to an oxidizing agent, *e.g.*

$$\text{Ar–H} + :\text{N}^- \xrightarrow{-2e} \text{Ar–N} + \text{H}^+ \qquad (1)$$

Indeed, we have now found that oxidative substitution of benzene and other electron-poor arenes may be achieved with the powerful one-electron oxidant, cobalt(III) trifluoroacetate.[1]

Heretofore, oxidation with other less potent cobalt(III) oxidants, including the binuclear acetates[2] and heteropoly derivatives,[3] has been limited to electron-rich arenes such as the alkylbenzenes. However, toluene undergoes preferential oxidation at the methyl group, and benzene as well as the halobenzenes are generally inert to these cobalt(III) oxidants. The role of aromatic cation-radicals as intermediates in the side-chain oxidation of alkylbenzenes with cobalt(III) has been presented.[2]

The use of cobalt(III) trifluoroacetate overcomes the previous inaccessibility of cation-radicals derived from relatively electron-poor arenes. In this report we wish to relate the oxidative substitution of these arenes by cobalt(III) trifluoroacetate in eq 1 ($N = CF_3CO_2$), to the formation of aromatic cation-radical intermediates. Oxidative substitution proceeding *via* cation-radicals is distinguished in this study from a different route involving prior electrophilic substitution which is taken by lead(IV).[4] General mechanisms for aromatic substitution by way of direct electrophilic attack or charge-transfer processes will be discussed in the light of these conclusions.

Results

Oxidation of Benzene with Cobalt(III) Trifluoroacetate. Stoichiometry. Benzene is readily oxidized by cobalt(III) in high yields to phenyl trifluoroacetate in trifluoroacetic acid (TFA) solutions at room temperature according to eq 2.

$$C_6H_6 + 2Co^{III}(O_2CCF_3)_3 \xrightarrow{\text{TFA}} C_6H_5O_2CCF_3 + 2Co^{II}(O_2CCF_3)_2 \qquad (2)$$

The reaction is exothermic and could be followed visually, since the color of the solution changed from dark green to light brown upon completion (~30 min). Phenyl trifluoroacetate and unreacted benzene were analyzed by gas chromatography of the reaction mixture directly or after quantitative separation of the volatile fraction from the Co(II) residue on a vacuum line. The visible absorption spectrum of the reaction mixture finally was that of cobalt(II) trifluoroacetate.

The yield of phenyl trifluoroacetate approached quantitative when the molar ratio of Co(III) to benzene was approximately 2. With an excess of Co(III), phenyl trifluoroacetate was further oxidized to a mixture of diesters (*vide infra*). Furthermore, the yield of phenyl trifluoroacetate was lower when more than stoichiometric amounts of benzene were present due to oxidative condensations of benzene. Significantly, biphenyl is selectively oxidized by Co(III) even in the presence of a tenfold excess of benzene. Thus, the rapid oxidation of biphenyl under these conditions precluded its detection, but we infer that it was a product in reactions carried out in the presence of excess benzene (*vide infra*).

The yields of phenyl trifluoroacetate were generally higher when the reactions were carried out in the presence of 10% (v) trifluoroacetic anhydride (TFA-A), but were unaffected by changes in the absolute concentrations of the reactants. The yields of ester were the same when the reaction was carried out under nitrogen or in an atmosphere of up to 50 psig oxygen.

Kinetics of the Oxidation of Benzene by Cobalt(III) Trifluoroacetate. The spectral changes occurring

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[1] (a) S. S. Lande, C. D. Falk, and J. K. Kochi, *J. Inorg. Nucl. Chem.*, 33, 4101 (1971); (b) R. Tang and J. K. Kochi, *ibid.*, in press; (c) S. S. Lande and J. K. Kochi, *J. Amer. Chem. Soc.*, 90, 5196 (1968).

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

[3] A. W. Chester, *J. Org. Chem.*, 35, 1797 (1970).

[4] J. R. Campbell, J. R. Kallman, J. T. Pinhey, and S. Sternhell, *Tetrahedron Lett.*, 1763 (1972); 5369 (1973).

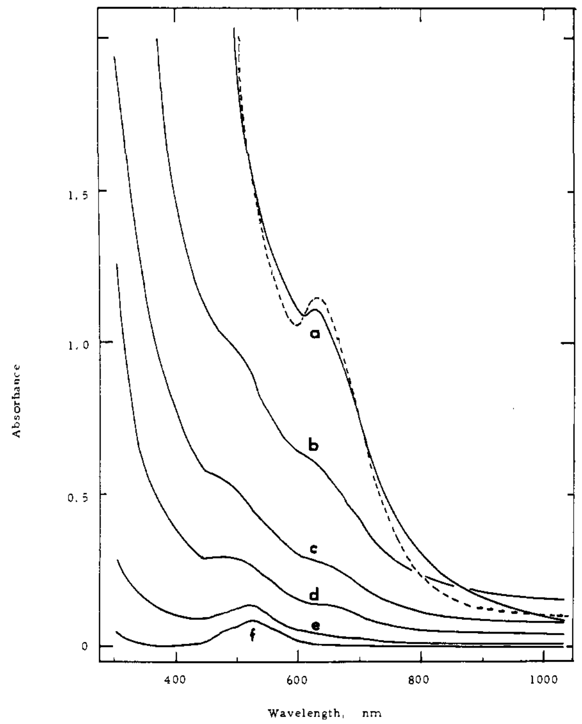

Figure 1. Spectral changes due to addition of 2.7×10^{-2} *M* benzene to 6.1×10^{-3} *M* cobalt(III) trifluoroacetate in TFA-A at at 25°; (- - - -) Co(III) only. Start of scan: (a) 0.1 min, (b) 3 min, (c) 6 min, (d) 9 min, (e) 13 min, (f) 20 min. The spectrum of the final solution (f) is that of cobalt(II) trifluoroacetate.

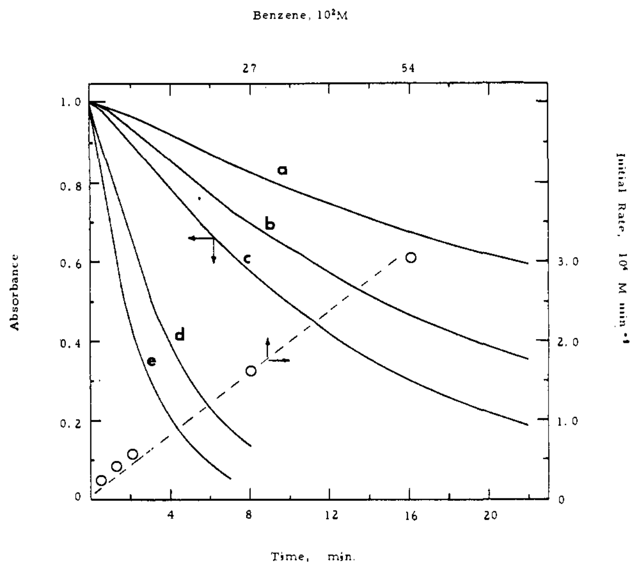

Figure 2. Rates of reaction of 5.8×10^{-3} *M* cobalt (III) with various concentrations of benzene followed at 660 nm and 21°: (a) 1.7×10^{-3}, (b) 4.1×10^{-3}, (c) 6.8×10^{-3}, (d) 2.7×10^{-2}, (e) 5.4×10^{-2} *M* benzene in TFA-A solutions; (○) scale on top and right margins.

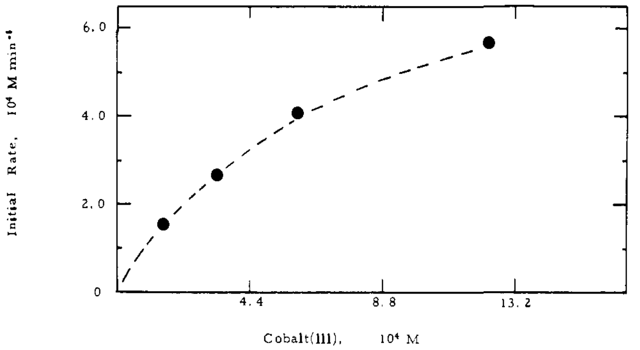

Figure 3. Effect of cobalt(III) concentration on the rate of the oxidation of 4.1×10^{-3} *M* benzene followed at 660 nm and 25°.

Table I. Effect of Co^{II} and Salts on the Oxidation of Benzene by Co(III)[a]

Additive	Concn, *M*	Add./Co(III), *M*/*M*	Initial rate, 10^4 *M* sec^{-1} [b]
None	0		2.4
$Co^{II}(O_2CCH_3)_2$	6.26×10^{-3}	1.1	1.3
$Co^{II}(O_2CCH_3)_2$	1.14×10^{-2}	2.0	1.3
$Co^{II}(O_2CCH_3)_2$	3.68×10^{-2}	6.4	1.2
$Co^{II}(O_2CCH_3)_2$	1.19×10^{-1}	20.6	0.81
LiO_2CCF_3	1.3×10^{-2}	2.3	3.0
LiO_2CCF_3	4.5×10^{-2}	7.8	3.3
LiO_2CCH_3	5.1×10^{-2}	8.8	3.5

[a] Oxidation of 4.1×10^{-3} *M* C_6H_6 by 5.8×10^{-3} *M* Co(III) in TFA at 25°. [b] Disappearance of Co(III) measured at 660 nm; extrapolated to zero time.

during the oxidation of benzene by Co(III) in TFA are illustrated in Figure 1. It is noteworthy that upon the addition of benzene to a solution of Co(III), there is an immediate change in the absorption spectrum as shown in Figure 1 (curves a and b).[5] The change in absorbance followed at 660 nm showed an apparent first-order decay in the presence of excess benzene. The initial rates of disappearance of Co(III) obtained by a variation in the benzene and Co(III) concentrations were first order in benzene (Figure 2) and roughly first order in Co(III) as illustrated in Figure 3.

$$-d[Co(III)]/dt = k[C_6H_6][Co(III)] \qquad (3)$$

The rate of oxidation of benzene was apparently retarded by the addition of cobalt(II).[5] The kinetic dependence on Co(II), however, leveled off rapidly beyond one equivalence. The addition of lithium acetate and lithium trifluoroacetate similarly retarded oxidation, but the effect was significantly less than that observed with Co(II) as shown in Table I.

The absorption spectrum of cobalt(III) trifluoroacetate in trifluoroacetic acid was also studied in the presence of various amounts of Co(II) to probe for possible binuclear mixed valence Co(II)–Co(III) complexes. In the concentration ranges of Co(III) and Co(II) used in this study, the absorption spectra of the mixtures simply consisted of the superposition of the individual spectra. No enhancement of the absorbances or new absorption bands could be discerned.

The deuterium isotope effect on the rate of oxidation of benzene was determined by a competition method using a 30-fold excess of a 1:1 mixture of C_6D_6 and C_6H_6. The phenyl trifluoroacetate was quantitatively separated from the reaction mixture *in vacuo*, and analyzed by a gas chromatograph–mass spectrometer combination. The relative abundances of the two parent molecule ions indicated an isotopic ratio for $C_6H_5O_2CCF_3^+/C_6D_5O_2CCF_3^+$ of 1.05 ± 0.1. No scrambling occurred under these conditions since oxi-

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(5) This behavior (which is discussed later) somewhat complicates the determination of accurate kinetic data, and the results presented in Figures 2 and 3 were determined by extrapolation.

dation of C_6D_6 in TFA afforded only $C_6D_5O_2CCF_3$, and conversely C_6H_6 in TFA-d_1 produced only $C_6H_5O_2CCF_3$.

The kinetic isotope effect was also examined by determining the rates of disappearance of 3.2×10^{-3} *M* Co(III) in trifluoroacetic acid solutions separately containing 4.1×10^{-3} *M* C_6H_6 or C_6D_6. The decay of the absorption band of Co(III) at 650 nm was the same (1.5×10^{-4} *M* min^{-1}) for both solutions within experimental error.

Oxidation of Phenyl Trifluoroacetate by Cobalt(III) Trifluoroacetate. Phenyl trifluoroacetate (0.27 *M*) was oxidized in a solution of 0.31 *M* Co(III) in TFA solution at 25°. The reaction required approximately 30 hr for completion and the three isomeric diesters were formed in 67% yield based on Co(III) as shown in Table II.

Table II. Oxidation of Phenyl Trifluoroacetate by Cobalt(III) Trifluoroacetate[a]

Product	Yield (%) Co(III)[b]	Yield (%) $C_6H_5O_2CCF_3$[c]	$t_{1/2}$, 10^{-3} min[d]
$C_6H_5O_2CCF_3$			0.35
o-$C_6H_4(O_2CCF_3)_2$	17	15	2.3
m-$C_6H_4(O_2CCF_3)_2$	6	5	1.2
p-$C_6H_4(O_2CCF_3)_2$	44	39	2.3

[a] In 8 ml of 10% TFA-A–TFA containing 2.5 mmol of Co(III) and 2.2 mmol of phenyl trifluoroacetate. [b] Based on Co(III) charged. [c] Based on phenyl trifluoroacetate recovered (0.8 mmol). [d] Time required for one-half disappearance of Co(III) spectrophotometrically.

The trifluoroacetate diesters of catechol, resorcinol, and hydroquinone were also prepared and their rates of oxidation by Co(III) were separately examined under a standard set of conditions. The results in Table II indicate that the isomeric mixture of diesters obtained from the oxidation of phenyl trifluoroacetate represents the kinetically controlled distribution since none of the isomers can be selectively oxidized in the presence of excess phenyl trifluoroacetate. Furthermore, the mass spectrum of phenyl trifluoroacetate, recovered after a slight excess was treated with Co(III) in trifluoroacetic acid-d_1, showed no evidence of deuterium incorporation.

The high relative yields of ortho and para diesters in Table II is reminiscent of a general pattern for electrophilic aromatic substitution. Similarly, the oxidation of 0.83 *M* chlorobenzene by 0.33 *M* Co(III) afforded only *o*- and *p*-chlorophenyl trifluoroacetates in 18 and 35%, respectively, after 4 hr at 28°. Interestingly, a small but significant amount (6%) of phenyl trifluoroacetate was also formed. The latter was a reaction product since it was not generated in the absence of Co(III), and the chlorobenzene used in this study was not contaminated with benzene.

$$\mathrm{ClC_6H_5 + Co(III)}\!\left\langle\begin{array}{ll} \xrightarrow{\mathrm{TFA}} \textit{o,p}\text{-}\mathrm{ClC_6H_4O_2CCF_3} & \quad (4) \\ \xrightarrow{\phantom{\mathrm{TFA}}} \mathrm{C_6H_5O_2CCF_3} & \quad (5) \end{array}\right.$$

Oxidation of Toluene by Cobalt(III) Trifluoroacetate. Toluene was oxidized by Co(III) under conditions analogous to those used for benzene. In a typical experiment, a solution of cobalt(III) trifluoroacetate in TFA was chilled to 0°, and the desired amount of toluene was added. An exothermic reaction ensued and the solution immediately changed color to red. Benzyl trifluoroacetate and tolyl dimers were the principal products formed in approximately 10 and 5% yields, respectively. Dilution studies indicate a slight but general improvement in yields at lower concentrations of Co(III). Other variations in procedure such as the simultaneous mixing of dilute solutions of Co(III) and toluene or mixing the components at −78° and then slowly raising the temperature had no dramatic effect on these yields.

The low yields of benzyl trifluoroacetate were not due to further oxidation since it is much less reactive than toluene, but can be partly attributed to the rapid oxidative polymerization of toluene to tolyl dimers and trimers. Bibenzyl was not separated from the other tolyl dimers by gas chromatography, but the mass spectrum of the mixture indicated the principal components to be isomeric methyldiphenylmethanes and/or bitolyls.

$$\mathrm{CH_3C_6H_5 + Co(III)}\!\left\langle\begin{array}{ll} \xrightarrow[\mathrm{CH_3C_6H_5}]{} \mathrm{C_6H_5CH_2O_2CCF_3} & \quad (6) \\ \xrightarrow{\phantom{\mathrm{CH_3C_6H_5}}} \mathrm{(C_7H_7)_2 + (C_7H_7)_3,\ etc.} & \quad (7) \end{array}\right.$$

The two tolyl trimer fractions also showed similar mass spectral cracking patterns, and probably represented mixtures of isomers of the benzyl derivatives of bitolyls and methyldiphenylmethanes. Higher oligomers were also present but not examined.

The absence of cresyl esters among the products of toluene oxidation was striking, since acyloxylation was the predominant path in the oxidation of benzene, phenyl trifluoroacetate, fluorobenzene, chlorobenzene, and benzotrifluoride. The three isomeric trifluoroacetates of *o*-, *m*-, and *p*-cresol were, therefore, prepared separately and subjected to oxidation conditions. Typically, a solution of the ester and toluene in TFA-A was cooled to 0° and a solution of 0.22 *M* Co(III) added slowly. Visually, the reaction was complete on mixing. Since the cresyl ester content was the same before and after addition of Co(III) in all three cases, they could not have been formed during the oxidation of toluene.

The effect of added neutral salt on the oxidation of toluene was also examined. Anhydrous lithium trifluoroacetate (10 mmol) was added to a 0.2 *M* (1 mmol) solution of Co(III); only benzyl trifluoroacetate and tolyl dimers but no cresyl esters were detected by gas chromatographic analysis after toluene (1.9 mmol) was added.

The oxidation of toluene by Co(III) in TFA was much too rapid to follow by conventional techniques. The kinetic isotope effect was examined, therefore, in solutions of TFA containing 25% (v) acetic acid (*vide supra*). Under these conditions, the initial rate of disappearance of Co(III) [followed at 650 nm] was 1.4×10^{-3} *M* min^{-1} in a solution containing 4.95×10^{-3}*M* Co(III) and 3.38×10^{-3} *M* toluene. The same rate using toluene-d_8 was 1.3×10^{-3} *M* min^{-1}, from which we deduce that $k_H/k_D = 1.08 \pm 0.1$.

Substituent Effects on the Oxidation of Arenes by Cobalt(III) Trifluoroacetate. A variety of other substituted arenes were also treated with cobalt(III) trifluoroacetate under a standard set of conditions. The rate of oxidation was followed spectrally by the disappearance of the absorption band of Co(III) at 660 nm. The relative reactivities of substituted benzenes obtained in this manner are listed in Table III according to decreasing rates.

An accurate comparison of the reactivities of arenes

Table III. Reactivity of Substituted Benzenes with Cobalt(III) Trifluoroacetate.[a] Comparison with the Frequencies for the Charge-Transfer Absorption in Complexes of Tetracyanoethylene with Substituted Benzenes[b]

Arene	Concn, 10^3 *M*	Time,[c] min	$\lambda_{\max}$, nm	ν, 10^3 cm^{-1}
Anisole	3.7	<0.2	505	198
p-Cymene	2.6	<0.2		
Toluene	3.8	<0.2	411	243
Iodobenzene	3.6	<0.2		
tert-Butylbenzene	2.6	<0.2	415	241
Phenyl acetate	3.2	0.5	368	272
Phenyl pivalate	3.2	0.5	370	270
Benzyl bromide	3.4	3.0	382	262
p-Tolyl trifluoroacetate	2.4	3.0		
Benzyl acetate	2.8	6.5	384	260
Benzene	4.1	16.5	385	259
Bromobenzene	3.8	18.0	394	254
Chlorobenzene	3.9	19.0	370	270
Fluorobenzene	4.3	52	355	282
Benzyl trifluoroacetate	2.4	>120	362	276
Phenyl trifluoroacetate	2.5	350	342	292
Benzotrifluoride	3.3	>1300	325	308

[a] In solutions of 1 *M* cobalt(III) trifluoroacetate in 10% (v) trifluoroacetic anhydride–trifluoroacetic acid at 25°. [b] In methylene chloride solutions at 25°. Only the low energy band is listed. [c] Time corresponds to half-disappearance of Co(III) monitored by absorbance change at 660 nm.

toward Co(III) is complicated by several factors. The stoichiometry of the oxidation is not known in all cases, since the products may also be readily oxidized further. The determination of the Co(III) concentration spectrally is obscured by the formation of a preequilibrium complex (*vide infra*). Nonetheless, the ordering of the reactivities of arenes in Table III is generally correct, *i.e.*, electron-rich arenes generally being the most reactive. The difference in reactivity of phenyl acetate and phenyl trifluoroacetate is striking, and accounts for the high yields of phenyl trifluoroacetate obtainable during the oxidation of benzene in TFA. The strongly deactivating effect of the trifluoromethyl group is also shown by the slow oxidation of benzotrifluoride, which afforded a mixture of isomeric trifluoromethylphenyl trifluoroacetates in 75% yield after prolonged reaction at 28°. The presence of α hydrogens is not responsible for the high reactivity of phenyl acetate since phenyl pivalate is oxidized essentially at the same rate.

Spectral Studies of Aromatic Cation-Radicals from the Oxidation of Arenes by Cobalt(III) Trifluoroacetate. The spectral changes occurring during the oxidation of reactive arenes were too fast to observe with our conventional instrumentation. However, if the spectral change during oxidation of chlorobenzene, one of the least reactive arenes, is observed at one wavelength (630 nm), there is an initial rapid increase in absorbance, followed by a decay as shown in Figure 4. The enhanced absorbance varies with the arene oxidized, but we are unable as yet to obtain the absorption spectra of the intermediate(s) responsible for the initial hyperchromic shift.

With most arenes, the electronic absorption spectrum of the reaction examined on completion of the reaction corresponded to that of cobalt(II) trifluoroacetate (pink). Anisole, however, reacted with Co(III) on mixing to produce an intense blue-green solution, which on dilution with TFA showed absorption bands at 390 (0.58), 426 (0.35), 700 (0.32), and 790 (0.2) nm (absorbance). The esr spectrum of the solution is in accord with the stable paramagnetic species formed from the dimerization of the anisole radical-cation generated by oxidation of anisole with Pb(IV).[6] Phenyl acetate was also rapidly oxidized by Co(III) to produce an orange-yellow solution which persisted for approximately 30 min.

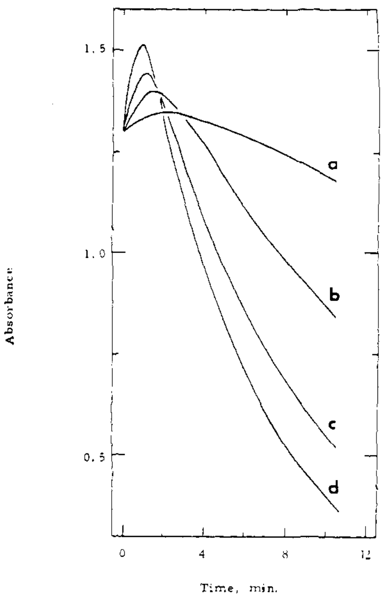
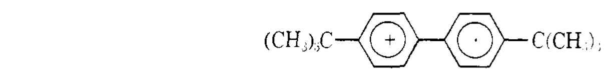


Figure 4. Time-dependent spectral changes during the oxidation of chlorobenzene by 6.9 × 10^{-3} *M* cobalt(III) in TFA-A at 25° followed at 630 nm: (a) 2.04, (b) 6.12, (c) 12.2, and (d) 18.3 × 10^{-3} *M* chlorobenzene solutions.

The oxidation of *tert*-butylbenzene and biphenyl afforded transient blue solutions containing arene radical-cations. The aromatic coupling process described earlier in eq 7 is shown by the esr spectrum of the *p*,*p*′-di-*tert*-butylbenzene cation-radical in Figure 5, obtained during the oxidation of *tert*-butylbenzene with cobalt(III) trifluoroacetate. The esr spectrum of the analogous *p*,*p*′-bitolyl cation-radical was also readily obtained from the cobalt(III) oxidation of *p*,*p*′-bitolyl under similar conditions.



Toluene and *p*-cymene reacted with cobalt(III) trifluoroacetate on mixing, but the pink color of Co(II) indicated no stable cation-radicals. However, if the oxidation of toluene was carried out carefully at low temperatures (−47°), an esr spectrum with $\langle g \rangle = 2.0027$ was obtained. The hyperfine splittings in the spectrum were consistent with a doublet (7.71 G) of quartets (14.10 G) similar to the principal features of the spectrum of the toluene cation-radical adsorbed on a silica gel surface.[7] Esr spectra of more stable mononuclear cation-radicals have been generated from polyalkylbenzenes and cobalt(III) acetate in trifluoroacetic acid

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(6) D. L. Allara, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 319 (1965); V. D. Parker, *et al.*, *Tetrahedron Lett.*, 2271 (1972).

(7) T. Komatsu, A. Lund, and P. O. Kinell, *J. Phys. Chem.*, 76, 1721, 1727 (1972).

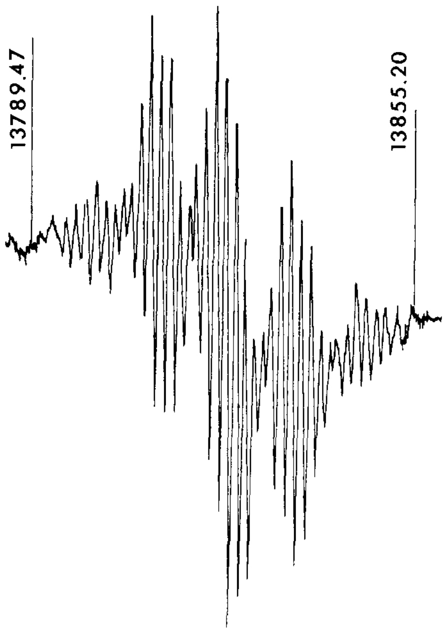

Figure 5. Esr spectrum of p,p'-di-*tert*-butyldiphenyl cation-radical with $\langle g \rangle = 2.0027$ from the oxidation of *tert*-butylbenzene with cobalt(III) trifluoroacetate in solutions of CH_2Cl_2–TFA at −30°. Proton nmr field markers are in kHz.

by a rapid flow method.[8] We have observed esr spectra of similar arenes in a static system using cobalt(III) trifluoroacetate, *e.g.*

Benzene, fluorobenzene, and chlorobenzene also produced transient paramagnetic species on treatment with cobalt(III) trifluoroacetate. Relatively high yields of radicals were indicated, judging from the intensity of the esr spectra. However, the cation-radicals formed directly by removal of an electron from these arenes are extremely short-lived, and the observed esr spectra (of which Figure 6 is representative) are probably due to a mixture of oligomeric species derived by further additions of the parent cation-radical to another arene [compare eq 7].[9]

Discussion

Mechanism for Oxidative Substitution *via* Aromatic Cation-Radicals. The oxidation of benzene to phenyl trifluoroacetate is formally a two-equivalent change according to eq 1 (N = trifluoroacetate). The overall second-order kinetics suggests the involvement of only one Co(III) and one benzene in, or prior to, the rate-determining step. Such an oxidation may proceed *via* two successive one-electron transfer steps, such as that presented in Scheme I.[10] The retardation of the rate by Co(II) supports the reversible formation of the radical-cation in the first step of Scheme I. The limited magnitude of the effect can be attributed to the high solvolytic reactivity of the benzene cation-radical in eq 9. The absence of a primary hydrogen kinetic isotope effect is also accommodated by Scheme I, although a small inverse secondary isotope effect is to be expected.

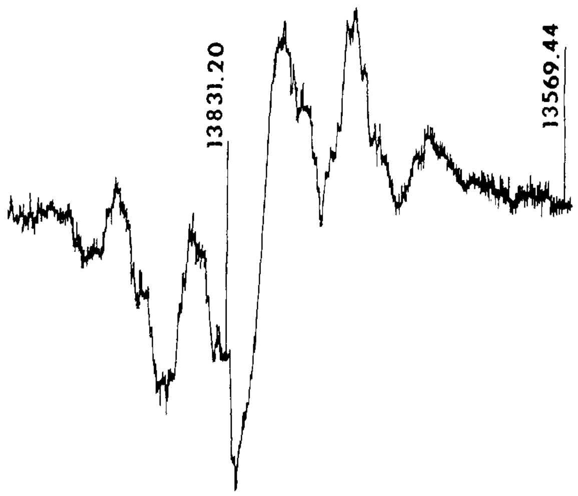

Figure 6. Esr spectrum ($\langle g \rangle = 2.0032$) obtained from the oxidation of benzene with cobalt(III) trifluoroacetate in CH_2Cl_2–TFA at −48°. The partial resolution of the hyperfine features of the spectrum are due to slight overmodulation.

The electron transfer mechanism in Scheme I is in accord with evidence accumulated for the oxidation of electron-rich arenes by various metal oxidants, especially those involving cobalt(III) acetate and manganese(II) acetate.[2,11] Although cobalt(III) trifluoroacetate is distinguished from other cobalt(III) oxidants by its ability to effect oxidation of benzene and other electron-poor arenes, we propose that the same basic mechanism pertains. Central to this mechanism is the formation[12] and the subsequent destruction of the arene cation-radical.

The transient hyperchromic shift observed during the

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[8] R. M. Dessau, S. Shih, and E. I. Heiba, *J. Amer. Chem. Soc.*, **92**, 412 (1970).

[9] M. J. Shaw, J. A. Weil, H. H. Hyman, and R. Filler, *ibid.*, **92**, 5096 (1970).

[10] (a) The ligands on cobalt will be included hereafter only if required for the discussion. (b) Other reactive intermediates such as trifluoroacetoxy radicals or cations are quite unlikely, because they are either too unstable or energetically and chemically inaccessible from cobalt(III).

[11] (a) P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, **88**, 5473 (1966); (b) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, **91**, 138 (1969).

[12] Cobalt(III) complexes have been studied in a variety of other electron transfer processes proceeding by both inner-sphere and outer-sphere mechanisms.[13] The oxidation of alkyl-aromatic hydrocarbons can be effected by the heteropoly 12-tungstocobaltate(III), which is known to participate in outer-sphere electron transfer processes.[3] The latter is in accord with the general inertness of the inner sphere of cobalt(III) and the lability of the outer-sphere complexes.[14] Coordinatively saturated cobalt(III) cations are capable of stepwise coordination of electron-donor molecules in the outer coordination sphere, which can result in an increase of the intensity of the charge-transfer band in the electronic spectra.[15] The presence of charge-transfer bands in the absorption spectra of outer-sphere complexes of cobalt(III) is analogous to the donor–acceptor electronic interactions in molecular complexes of arenes with iodine and related compounds.[16] Photoinduced charge-transfer reactions have been observed with outer-sphere cobalt(III) complexes.[17]

[13] R. L. Linck, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, **5**, 303 (1972); G. Geier and C. H. Brubaker, Jr., *Inorg. Chem.*, **5**, 321 (1966).

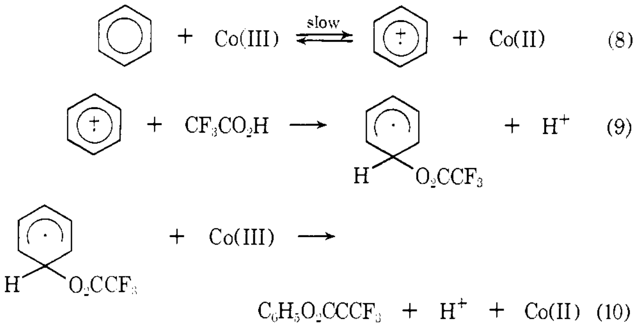
[14] V. E. Mironov, *Russ. Chem., Rev.*, **39**, 319 (1970).

[15] R. Larsson, *Acta Chem. Scand.*, **11**, 1405 (1957); **12**, 708 (1958); M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944); H. Yoneda, *Bull. Chem. Soc. Jap.*, **28**, 125 (1955).

[16] L. J. Andrews and R. N. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964; G. Briegleib, "Elektronen-Donator Acceptor Komplexe," Springer-Verlag, West Berlin, 1961.

[17] A. W. Adamson and H. H. Sporer, *J. Amer. Chem. Soc.*, **80**, 3865 (1958); V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970, p 193 ff.

Scheme I



mixing of cobalt(III) trifluoroacetate and arenes can be attributed to the formation of molecular complexes.[18] Electron transfer in such complexes would involve a vertical, *i.e.* Franck–Condon process, the energetics of

$$\mathrm{Co(III)} + \mathrm{ArH} \rightleftharpoons [\mathrm{Co(III)ArH} \longleftrightarrow \mathrm{Co(II)ArH}\cdot^{+}] \quad (11)$$

which should correlate with the frequencies of the charge-transfer absorption.[19] The relative values for the tetracyanoethylene–arene complexes indeed correspond rather well with the relative rates of oxidation of the substituted arenes by cobalt(III) trifluoroacetate as shown in Table III.[20]

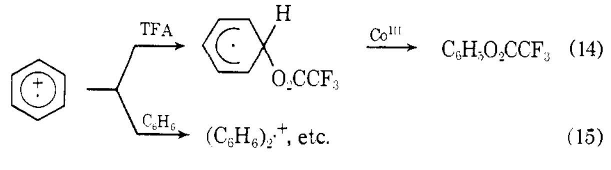
The presence of trifluoroacetic acid is an important factor in the oxidation of benzene with cobalt(III). Similarly, the activation of the metal oxidant in trifluoroacetic or stronger acids has been observed with Pb(IV), Mn(III), Ce(IV), Co(III), and Cu(II).[21] Moreover, the electrophilic properties of Cu(I), Hg(II), Tl(III), and Pb(IV) acetates are also enhanced by replacement of the ligand with trifluoroacetate.[22] We associate the increased reactivity of cobalt(III) trifluoroacetate to the presence of cationic species,[1] which readily undergo electron transfer with arenes, *e.g.*

$$\mathrm{Co^{III}(O_2CCF_3)_3} \rightleftharpoons [\mathrm{Co^{III}(O_2CCF_3)_2}^{+}\ \mathrm{CF_3CO_2}^{-}] \quad (12)$$

$$\mathrm{Co^{III}(O_2CCF_3)_2}^{+} + \mathrm{ArH} \rightleftharpoons \mathrm{Co^{II}(O_2CCF_3)_2} + \mathrm{ArH}\cdot^{+} \quad (13)$$

Highly acidic media also serve an additional function during electron-transfer oxidations. Thus, arene cation-radicals with electron-donor substituents are particularly stable in solvents of such weak nucleophilic properties as trifluoroacetic acid. Indeed, this medium has been recently found to be ideally suited for the chemical as well as the electrochemical generation of a variety of cation-radicals derived from electron-rich arenes.[8,23] We attribute the poor yields of aryl trifluoroacetates obtained with such arenes to the relatively high stability of the cation-radicals in trifluoroacetic acid. Under these conditions the esr spectrum of the arene cation-radical itself or that of the adduct to another arene may be observed as presented earlier.

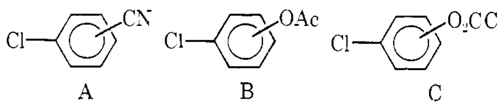
Reactions of Aromatic Cation-Radicals. The principal fate of the cation-radical generated by Co(III) oxidation of benzene is solvation (eq 14), despite the poor nucleophilic properties of trifluoroacetic acid. Competitive attack on another benzene (eq 15) is important only if it is present in excess.



The oxidative acyloxylation of other electron-poor arenes in good yields relative to biaryl formation is consistent with this competition, since electron-withdrawing substituents increase the electrophilic properties of the cation-radical and decrease the susceptibility of the parent arene to electrophilic attack by the cation-radical. We deduce from the substitution pattern observed with the halobenzenes and phenyl trifluoroacetate that solvation of the arene cation-radical follows the charge distribution.[24] Interestingly, the ortho/para ratio of the isomeric chlorophenyl trifluoroacetates obtained during the oxidation of chlorobenzene (ortho/para = 0.52) is more akin to that of electrophilic substitution (*e.g.*, nitration, ortho/para = 0.43) than it is to that of homolytic substitution (*e.g.*, benzoyloxylation, ortho/para = 1.6).[25]

Selectivity in the reaction of the chlorobenzene cation-radical varies with the nucleophile, and Table IV

Table IV. Reaction of Chlorobenzene Cation-Radical with Nucleophiles[a]



	Substitution, %		
Arene isomer	A	B	C
Ortho	50	37	18
Meta	<0.5	6	<0.1
Para	50	58	35
Ortho/para	1	0.64	0.52

[a] Cyanation and acetoxylation studies carried out electrochemically (see ref 26).

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(18) There are a number of examples of arene–metal complexes extant: A. Z. Rubezhov and S. P. Gubin, *Advan. Organometal. Chem.*, 10, 347 (1972); T. A. Stephenson, *MTP* (*Med. Tech. Publ. Co.*) *Int. Rev. Sci.: Inorg. Chem., Ser. One*, 6, 401 (1972); J. F. Helling, S. L. Rice, D. M. Braitsch, and T. Mayer, *Chem. Commun.*, 930 (1971).

(19) (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970); T. G. Traylor, *et al.*, *Pure Appl. Chem.*, 30, 599 (1972); (b) R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, 80, 2778 (1958).

(20) Both phenyl acetate and pivalate are oxidized by Co(III) at much faster rates than would be expected from the correlation based on the frequencies of the charge-transfer complexes (compare Table III). Electrophilic cleavage of the cation-radical by loss of an acylium ion may provide the driving force, which is hampered by fluorine substitution in accord with the much slower rate of oxidation of phenyl tri-

$$\mathrm{C_6H_5O_2CCH_3}\cdot^{+} \longrightarrow \mathrm{C_6H_5O}\cdot + \mathrm{CH_3CO^{+}},\ \text{etc.}$$

fluoroacetate. The half-wave potential for the oxidation of phenyl acetate is quite low compared to other monosubstituted benzenes. [L. Eberson and K. Nyberg, *J. Amer. Chem. Soc.*, 88, 1686 (1966)] and similar processes may be operable in electrooxidations.

(21) (a) R. O. C. Norman, C. B. Thomas, and J. S. Willson, *J. Chem. Soc. B*, 518 (1971); (b) R. E. Partch, *J. Amer. Chem. Soc.*, 89, 3662 (1967); J. B. Aylward, *J. Chem. Soc. B*, 1268 (1967); (c) J. K. Kochi, *et al.*, *J. Amer. Chem. Soc.*, 90, 6686 (1968); 92, 2540 (1970); 94, 843 (1972).

(22) H. C. Brown and R. A. Wirkkala, *J. Amer. Chem. Soc.*, 88, 1447, 1453 (1966); A. McKillop, *et al.*, *Tetrahedron Lett.*, 2423, 2327 (1969); R. G. Salomon and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 559 (1972).

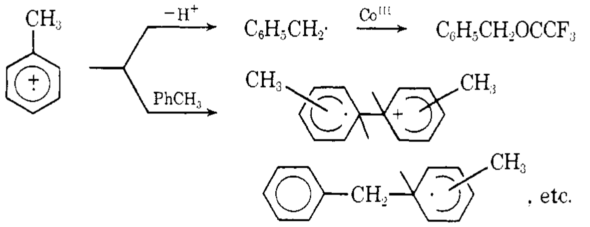
(23) V. D. Parker, *et al.*, *Tetrahedron Lett.*, 156, 471 (1972); C. C. Yang, A. E. Phland, and W. W. Mansfield, *J. Phys. Chem.*, 76, 1504 (1972).

(24) There are also other paths for the reaction of arene cation-radicals, since the formation of phenyl trifluoroacetate from the oxidation of chlorobenzene suggests that solvation may occur at the 1 position followed by loss of chlorine.

(25) P. B. D. LaMare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation," Butterworths, London, 1959, p 79 ff; H. Hart, *Accounts Chem. Res.*, 4, 337 (1971); M. E. Kurz and M. Pellegrini, *J. Org. Chem.*, **35**, 990 (1970).

shows a comparison of the cyanation,[26a] acetoxylation,[26b] and trifluoroacetoxylation of the chlorobenzene cation-radical. The trend toward increased selectivity in the pattern for aromatic substitution (given by the ortho/para ratio) in this cation-radical with decreased nucleophilic strength shows an interesting parallel with Brown's correlation of the variation of selectivity with the strength of the electrophile in electrophilic aromatic substitution.[27] That is, the selectivity shown by the arene cation-radical to attack by nucleophiles has similar characteristics to that exhibited by arenes during electrophilic attack.

The toluene cation-radical differs strikingly from the benzene or halobenzene cation-radicals in that no nuclear acyloxylation occurs. Previous studies with cobalt(III) acetate in acetic acid also showed that loss of an α proton followed by oxidation of the benzyl radical to benzyl acetate constituted a principal reaction of the toluene cation-radical.[2]



(16)

(17)

The rapid addition of the toluene cation-radical to another electron-rich toluene to afford bitolyls cannot be circumvented with either cobalt(III) acetate or trifluoroacetate. The absence of cresyl trifluoroacetates thus suggests that the toluene cation-radical prefers these routes over reaction with TFA or even added lithium trifluoroacetate.

Comparative studies shown in Table V with electrochemically generated toluene cation-radical indicates that loss and nucleophilic attack is also dependent on the strength of the nucleophile.[26c]

Table V. Side Chain and Nuclear Substitution in Toluene Cation-Radical

Substitution reaction	Nucleophile			
	CN^- [a]	HOAc[b]	LiCl[c]	CF_3CO_2H [d]
Nuclear	>99.5	71	32	0
Side chain	<0.5	29	46	100

[a] Reference 26a. [b] Or acetate in ref 26b. [c] Data from ref 2, in which we assumed for this purpose that chlorotoluenes arose from the cation-radical by reaction with chloride, although ligand transfer of chlorine from ClCo(III) species has not been eliminated. [d] This work, corrected for oligomerization.

Electrophilic Mechanisms for Oxidative Substitution. A Caveat. The electron-transfer mechanism shown in Scheme I is not the only route available for oxidative substitution of arenes. For example, the oxidation of arenes by lead(IV) trifluoroacetate in TFA proceeds primarily, if not exclusively, *via* a nonradical process involving an electrophilic substitution.[4,20a] The detection and isolation of aryllead(IV) intermediates support a mechanism such as

$$ArH + Pb^{IV}(O_2CCF_3)_4 \longrightarrow ArPb^{IV}(O_2CCF_3)_3 + CF_3CO_2H \quad (18)$$

$$ArPb^{IV}(O_2CCF_3)_3 \longrightarrow ArO_2CCF_3 + Pb^{II}(O_2CCF_3)_2 \quad (19)$$

Oxidative substitution by this scheme requires the metal oxidant to initially effect electrophilic addition. Indeed, arenes can be metalated by a number of metal carboxylates, such as those derived from mercury(II), thallium(III), lead(IV), and palladium(II).[28] The high yields of aryl esters obtained from the oxidation of arenes including toluene with lead(IV) trifluoroacetate are traced directly to the reductive elimination from the aryllead(IV) intermediate in eq 19.[4]

Although Pb(IV) is a two-equivalent and Co(III) is a one-equivalent oxidant, an analogous electrophilic mechanism can be formulated for Co(III), *e.g.*, Scheme II.

Scheme II

$$ArH + Co^{III}(O_2CCF_3)_3 \xrightarrow{\text{slow}} ArCo^{III}(O_2CCF_3)_2 + CF_3CO_2H \quad (20)$$

$$ArCo^{III}(O_2CCF_3)_2 + Co^{III}(O_2CCF_3)_3 \longrightarrow ArO_2CCF_3 + 2Co^{II}(O_2CCF_3)_2 \quad (21)$$

The electron transfer Scheme I cannot be distinguished *a priori* from the electrophilic Scheme II based simply on the relative reactivities of various substituted benzenes toward Co(III), the kinetics or the nature and distribution of oxidation products formed. Both mechanisms depend on π-electron availability. For example, the formation of arene cation-radicals in Scheme I is determined by the ionization potentials of the respective arenes, which are directly related to the easily measurable absorption frequencies of the charge-transfer complexes.[16] In turn, the rates of electrophilic substitution of arenes in Scheme II can also be related to charge-transfer frequencies by a Hammett relationship (using σ_p^+), provided the substituent causes only a small perturbation on the benzene ring.[19] Thus, ionization potentials and Hammett parameters are indirectly related in these benzenoid systems insofar as the orbital from which the electron is removed by charge transfer has the same symmetry as the orbital which participates in para electrophilic attack. In other words, mechanistic distinctions between rate-limiting electron transfer (Scheme I) and electrophilic addition (Scheme II) cannot easily be made on the basis of substituent effects. Electron-releasing substituents facilitate and electron-attracting substituents hinder both oxidation processes. Indeed the differences between them in individual cases can be slight. It is not surprising, therefore, to find examples of oxidative substitutions of arenes which proceed competitively *via* both mechanisms.[29]

There are, however, some important differences between Pb(IV) and Co(III) which indicate contrasting mechanistic pathways. Significantly, the oxidation

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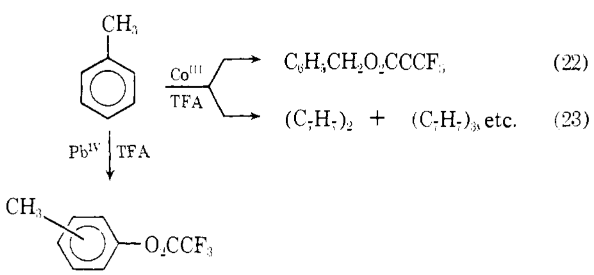
(26) (a) L. Eberson and S. Nilsson, *Discuss. Faraday Soc.*, **No. 45**, 242 (1968); (b) L. Eberson, *J. Amer. Chem. Soc.*, **89**, 4669 (1967); (c) see, however, ref 33.

(27) H. C. Brown and R. A. Wirkkala, *ibid.*, 88, 1447, 1453 (1966).

(28) A. T. Kresge, *et al.*, *J. Org. Chem.*, **32**, 745, 752, 756 (1967); E. C. Taylor and A. McKillop, *Accounts Chem. Res.*, **3**, 338 (1970); R. Criegee, *Oxid. Org. Chem.*, 1, 326 (1965); J. M. Davidson and C. Triggs, *J. Chem. Soc. A*, 1324, 1331 (1968); 1321 (1971); L. Eberson and L. Gomez-Gonzalez, *Chem. Commun.*, 263 (1971); P. M. Henry, *J. Org. Chem.*, **36**, 1886 (1971).

(29) R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. B*, 421 (1970); *J. Chem. Soc., Perkin Trans. 1*, 562 (1972).

of toluene provides a basis for making a choice, since products are quite different from Pb(IV) and Co(III) oxidations. For example, the oxidation of toluene by Pb(IV) affords high yields of products of nuclear substitution as cresyl esters and only traces of side-chain substitution as benzyl ester,[4] whereas no cresyl esters are produced during Co(III) oxidation. If we accept the earlier conclusion that Pb(IV) oxidation proceeds by plumbation, then cresyl trifluoroacetates are derived by decomposition of the cresyllead intermediate (Ar = $CH_3C_6H_4$ in eq 19). On the other hand, the absence of cresyl esters during the rapid oxidation of toluene by Co(III) suggests other distinct and facile alternatives such as those in eq 16 and 17. Furthermore, dealkylation of *tert*-butylbenzene is a significant (10%) process with Pb(IV),[4] which is consistent with an electrophilic process such as



$$t\text{-}BuC_6H_5 + Pb(O_2CCF_3)_3{}^+ \longrightarrow C_6H_5Pb(O_2CCF_3)_3 + t\text{-}Bu^+, \text{ etc.} \quad (24)$$

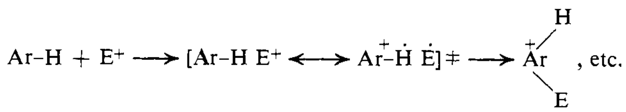
However, no dealkylation occurs during Co(III) oxidation. Moreover, significantly less *o*-chlorophenyl trifluoroacetate is formed relative to the para isomer in Pb(IV) compared to Co(III) oxidation.

According to eq 18 and 19, the relevant substitution pattern obtained in the aromatic nucleus is established during the plumbation process itself, the partial rate factors of which are characteristic of electrophilic aromatic substitution and lie between the values for nitration and bromination.[4] The similarity between such an electrophilic addition of Pb(IV) to an arene and the solvation of an aromatic cation-radical derived from cobalt(III) is striking.

Conclusion

The oxidative substitution of arenes by cobalt(III) trifluoroacetate proceeds *via* a charge-transfer mechanism shown in Scheme I, which is basically different from an electrophilic mechanism described by lead(IV) trifluoroacetate in eq 18 and 19. The unique behavior of toluene during oxidation by these reagents can be used to distinguish between these two mechanisms. Otherwise, the usual reactivity and selectivity patterns observed in arene substitution cannot readily serve to distinguish between these distinctive yet similar pathways.

An interesting corollary develops from such a conclusion; namely, electrophilic aromatic substitution can even contain a sizable electron-transfer component in the transition state



$$\text{Ar-H} + E^+ \longrightarrow [\text{Ar-H } E^+ \longleftrightarrow \overset{+\cdot}{\text{Ar-H}}\ \overset{\cdot}{E}]^{\ddagger} \longrightarrow \overset{H}{\underset{E}{\overset{+}{\text{Ar}}}}, \text{ etc.}$$

Factors involved in the actual separation of one process from the other may include a dependence on the energy of the charge-transfer transition between the electrophilic species and the arene. Moreover, the idea merits further consideration for its more general implications in view of the known similarity of the rate-limiting step involved in electrophilic substitution of arenes with that of electrophilic addition to C=C bonds. The

$$E^+ + {>}C{=}C{<} \rightleftharpoons E\cdot + {>}\overset{+\cdot}{C}{-}C{<}$$

charge-transfer concept can also be generalized to nucleophilic substitutions and additions with the roles of donors and acceptors reversed; *e.g.*

$$N{:}^- + {>}C{=}C{<} \rightleftharpoons N\cdot + {>}\overset{-\cdot}{C}{-}C{<}$$

A Comparison between Chemical and Electro-Oxidation of Arenes. The similarity between the oxidation of arenes by electron-transfer reagents and an electrochemical oxidation is noteworthy. A variety of arenes undergo anodic acetoxylation by electron-transfer mechanisms. Nuclear substitution has been observed in a number of cases, and successive one-electron transfer steps similar to those in Scheme I have been proposed.[30] The competition between loss of an α proton and solvation of the cation-radical also forms the basis of side chain and nuclear acetoxylation, respectively, in the anodic oxidation of alkylbenzenes.[31] The benzene cation-radical has been proposed as an intermediate during electrooxidation in acetonitrile solutions to form polyphenyls, but its rapid reaction even with such weak nucleophiles as benzene precludes the observation of the reverse reduction wave in the cyclic voltammogram.[32] Thus, a similar pattern of mechanisms emerges for chemical and electrochemical oxidative processes, but quantitative distinctions between them will no doubt occur as a result of kinetic differences in the various rate processes.[33] Most importantly, the structure of the electrified interface and the nature of absorbed intermediates do not allow the direct extrapolation of electrochemical observations unambiguously to chemical systems at the present time.[34]

Experimental Section

Materials. Cobalt(II) acetate tetrahydrate reagent grade was obtained from Matheson Coleman and Bell. Trifluoroacetic anhydride was prepared by slurrying trifluoroacetic acid and phosphorus pentoxide followed by distillation (bp 42°). Trifluoroacetic acid (Matheson Coleman and Bell) was dried by mixing with the anhydride followed by distillation (bp 71–72°). Trifluoroacetic

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[30] For a review, see L. Eberson and H. Schäfer, *Fortschr. Chem. Forsch.*, 21, 68 (1971).

[31] The effect of substituents is illustrated well in the electrochemical oxidation of hexamethylbenzene in TFA solutions,[23] in which cyclic voltammetry and coulometry showed that two electrons are transferred in the irreversible oxidation wave to form the pentamethylbenzyl cation followed by solvolysis. The hexamethylbenzene cation-radical is evidently a very short-lived intermediate and rapidly loses an α proton, since no reduction peak is observed. However, the presence of one trifluoroacetoxy group is sufficient to stabilize the cation-radical, and cyclic voltammetry of pentamethylbenzyl trifluoroacetate showed a one-electron wave even at relatively slow sweep rates.[23]

[32] T. Osa, A. Yildiz, and T. Kuwana, *J. Amer. Chem. Soc.*, 91, 3994 (1969).

[33] For example, the ratio of the competitive side chain to nuclear acetoxylation of toluene during chemical oxidation[2] apparently differs from that obtained in electrochemical oxidation.[26] However, the stability of cresyl acetates under reaction conditions was not reported, despite the limited material balance obtained.[2]

[34] NOTE ADDED IN PROOF. Oxidation of arenes by cobalt(III) trifluoroacetate has also been recently studied by R. A. Sheldon and J. A. Van Doorn (private communication).

Table VI. Oxidation of Benzene by Co(III)[a]

Solvent[b]	Benzene, *M*	Co(III), *M*	Co(III)/C_6H_6[c]	Yield of $C_6H_5O_2CCF_3$, % Co(III)[d]	Yield of $C_6H_5O_2CCF_3$, % C_6H_6[e]
TFA	0.11	0.20	1.8	70	92
TFA-A	0.11	0.20	1.8	94	109
TFA-A	0.055	0.10	1.9	91	102
TFA-A	0.027	0.050	1.9	93	104
TFA-A[f]	0.12	0.20	1.65	92	107
TFA-A[h]	0.12	0.20	1.70	93	103
TFA	0.22	0.20	0.91	70	80
TFA-A	0.22	0.20	0.91	92	110
TFA-A[g]	1.2	0.20	0.17	84	50
TFA-A[g]	2.2	0.20	0.090	79	29
TFA	0.055	0.20	3.6	56	102
TFA-A	0.055	0.20	3.6	28	52
TFA	0.022	0.20	9.1	10	42

[a] Reaction conducted at 26° for 30 hr with 1 mmol of Co(III) in 5 ml of solvent. [b] TFA = trifluoroacetic acid, TFA-A = trifluoroacetic acid containing 10% trifluoroacetic anhydride. [c] Molar ratio. [d] Yield based on Co(III), completely reduced to Co^{II} according to eq 1 (accuracy ± 3%). [e] Yield based on benzene used (accuracy, ± 10%). [f] Reaction conducted under a nitrogen atmosphere. [g] Conducted under 4 atm oxygen pressure. [h] Conducted under 1 atm oxygen pressure.

acid-d_1 was prepared by hydrolyzing trifluoroacetic anhydride with deuterium oxide and distillation. All arenes were commercial reagent grade materials, redistilled and analyzed by gas chromatography for impurities. Cobalt(III) acetate was prepared by ozonation of cobalt(II) acetate and converted to cobalt(III) trifluoroacetate by ligand exchange in mixtures of trifluoroacetic acid and trifluoroacetic anhydride (TFA-A).[1b]

Aryl esters were prepared from the corresponding phenols and an excess of trifluoroacetic anhydride. After the reagents were in contact overnight, the mixture was distilled at atmospheric pressure to afford esters generally in yields of 80% or more. The easily hydrolyzed aryl esters were analyzed for phenolic and other impurities by infrared and gas chromatographic analysis. Proton magnetic resonance and infrared spectra were in accord with the ester products, but the most informative data were obtained from the mass spectral cracking pattern.

Oxidation of Arenes. The oxidation of benzene was carried out with a solution of cobalt(III) trifluoroacetate,[1b] usually 1 mmol in the indicated amount of solvent (Table VI). The requisite benzene was then added and the mixture allowed to stand. Gas chromatographic analysis (10-ft Apiezon L on Chromosorb W, 130°) was carried out after the reaction was complete as indicated by the reddish brown color, unless desired otherwise. The crude mixture was first checked qualitatively for product(s), and the phenyl trifluoroacetate and benzene content was then quantitatively determined by adding a calibrated internal standard (*n*-nonane). The crude product from the TFA-A series at various Co(III) ratios (Table VI) was also subjected to gas chromatographic–mass spectral analysis, and it was shown that the gas chromatographic peak assigned to phenyl trifluoroacetate was not contaminated by other materials.

The deuterium isotope effect was measured in the presence of an approximately 30-fold molar excess of a 1:1 mixture of benzene and benzene-d_6. After the reaction was complete, most of the solvent and excess arene were removed and the phenyl trifluoroacetate was vacuum transferred and directly injected into the port of the mass spectrometer. The isotope ratio of the parent ions of the phenyl ester, *m/e* 190 and 195, were compared at 30 eV. Oxidation of benzene and benzene-d_6 separately indicated that there was no interference from the mass ions in this region. The starting benzene solution consisted of a H/D = 0.993 isotopic mixture of benzene and benzene-d_6, as measured by the *m/e* 78 and 84 peak, respectively, assuming natural ^{13}C abundance in both cases. Thus the k_H/k_D ratio obtained directly by comparing *m/e* 190–195 of the product ester is a reasonable measure of the isotope effect (with a negligible correction factor of 0.993).

The oxidation of phenyl trifluoroacetate (1 mmol) was carried out with cobalt(III), 1.9 mmol in 5 ml of 85% TFA-d_1-TFA, until all of it was reduced. The crude solution was concentrated and then subjected to gas chromatography–mass spectral analysis. The phenyl trifluoroacetate content showed no excess (P + 1) ion compared to the starting material. Analogous experiments were performed with chlorobenzene, phenyl acetate, and *tert*-butylbenzene, using 1 mmol of arene to 1 mmol of Co(III). The gc-mass spectra showed no incorporation of deuterium into the recovered arene. No phenyl trifluoroacetate was detected from the oxidation of *tert*-butylbenzene.

The mass spectra of the tolyl dimer(s) from the oxidation of toluene contained all of the fragment ions of authentic bibenzyl. The prominence of the *m/e* 167 ion (P − 15) in the dimer fraction indicated the presence of products containing large amounts of intact methyl groups. The structures of the dimers are likely to be: $CH_3C_6H_4C_6H_4CH_3$, $CH_3C_6H_4CH_2C_6H_5$, and $C_6H_5CH_2CH_2C_6H_5$. However, the presence of the large P − 15 ion suggests that bibenzyl, if present at all, was not a major component. Similarly, the principal species in the cracking pattern of each of the isomeric xylenes is the P − 15 ion.[34] The parent molecule ion is the principal species in the mass spectra of methylbiphenyls.

Analytical Methods. Nuclear magnetic resonance spectra were taken on Varian A-60 or HA-100 spectrometers. Absorption spectra were obtained in a Cary 14 spectrometer. Mass spectral analyses were performed on a Varian CH-7 spectrometer with a gas chromatographic accessory.

The stability of cobalt(III) in TFA-A was determined titrimetrically after allowing cobalt(III) trifluoroacetate in solutions of TFA-A to equilibrate at room temperature. The sample was cooled to −78° before a standard amount of ferrous solution was added. Back titration with cerium(IV) indicated the following cobalt(III) composition: 0 hr (92.5%), 1 hr (91.6%), 2 hr (91%), 5 hr (90.1%), 30 hr (87.3%), 60 hr (83.6%).

Kinetics of the Oxidation of Arenes by Co(III). The kinetics of arene oxidation were followed by the disappearance of cobalt(III) in the visible region of the optical spectrum. The reactions were carried out in 3-ml absorption cells with ground-glass fittings and contained in a thermostated compartment (25 ± 0.3°) of the spectrometer. At the appropriate time a stock solution of cobalt(III) trifluoroacetate was mixed with a solution of the arene in the same solvent in the cuvet with the aid of hypodermic syringes. The reactions were highly reproducible and could be followed consistently at several wavelengths between 580 and 800 nm.

Effect of Acetic Acid on the Oxidation of Benzene by Co(III) Species in Trifluoroacetic Acid. Benzene is inert to oxidation by cobalt(III) acetate in glacial acetic acid under conditions in which its reaction with cobalt(III) trifluoroacetate in trifluoroacetic acid is complete within 0.5 hr. On dilution of the latter to 30% (v) acetic acid, the reduction of cobalt(III) trifluoroacetate required 10 hr for completion and 4 days in 50% (v) acetic acid solutions. Furthermore, no detectable amounts of phenyl acetate could be found and the yields of phenyl trifluoroacetate decreased monotonously with the amount of acetic acid in solution. Even when the reaction was monitored as it progressed, only traces of phenyl acetate were detected. Independent studies showed that phenyl acetate is much more reactive than benzene toward further oxidation and would have been selectively destroyed. On the other hand, phenyl trifluoroacetate is oxidized at much slower rates than benzene under these conditions.

We ascribe the enhanced reactivity of Co(III) in trifluoroacetic acid to the presence of coordinatively unsaturated cationic Co(III) species. The ionization in eq 12 is consistent with the concept that trifluoroacetate is a ligand which is less apt to coordinate as strongly to the Co(III) nucleus as the acetato ligand (since it is derived from the stronger acid).[1] Dissociation of the type described in eq 12 allows for (partial) exchange of acetato ligands, which are less dissociated when the complex is diluted with glacial acetic acid, and leads to less reactive cobalt(III) species.

The effect of acetic acid was determined in TFA-A solutions containing 10, 20, and 30% (v) acetic acid. A 10-ml stock solution of cobalt(III) trifluoroacetate (0.2068 g) was prepared. A 2-ml aliquot of this solution was diluted to 10 ml with the appropriate mixed solvent and allowed to equilibrate for 4 hr. One milliliter of this solution was mixed with 2 ml of a stock solution of 8.1×10^{-2} *M* benzene in TFA-A. The times for half-disappearance of benzene were 10, 31, and 194 min in solutions consisting of 10, 20, and 30% (v) acetic acid, respectively. The kinetic isotope effect in the oxidation of benzene was carried out with stock solutions of 1.8×10^{-2} *M* cobalt(III) and separate stock solutions of 1.1×10^{-2} *M* benzene and benzene-d_6 in TFA-A.

The charge-transfer spectra of arenes were measured in methylene chloride solutions containing 5×10^{-3} *M* tetracyanoethylene(resublimed).

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Mechanism of the Chromic Acid Oxidation of Cyclobutanol[1]

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Abstract: Cyclobutanol is oxidized to a mixture of cyclobutanone, 4-hydroxybutyraldehyde, and higher oxidation products derived from further oxidation of the hydroxyaldehyde. The existence of a large deuterium isotope effect in the oxidation of 1-deuteriocyclobutanol (8.9) and the low reactivity of 1-methylcyclobutanol strongly suggest that cyclobutanone is the product of a chromium(VI) oxidation of cyclobutanol with the ketone being formed in the rate-limiting step of the reaction. Using an induced chromic acid oxidation of cyclobutanol by vanadium(IV) and an induced oxidation of 1-methylcyclobutanol by secondary alcohols, it is shown that the reaction leading to the opening of the cyclobutane ring is due to chromium(IV). This reaction leads to a free radical which is further oxidized to the corresponding hydroxycarbonylic compound. Chromium(V) seems to react with cyclobutanol to yield cyclobutanone rather than a cleavage product in a reaction which is slow enough to permit accumulation of chromium(V) to sufficient concentrations to make its bimolecular disproportionation to chromium(IV) and chromium(VI) important. Heats of combustion were used to calculate enthalpies of formation for cyclobutanol (34.6 kcal/mol) and cyclobutanone (21.9 kcal/mol). From these values it is shown that cyclobutanol and cyclobutanone have very similar strain energies (25.1 and 24.5 kcal/mol, respectively), contrary to the general expectation that a change from an sp^3- to an sp^2-hybridized carbon in a strained small ring compound should lead to a major increase in strain energy.

Small ring compounds and other strained structures often react very differently from their unstrained analogs. Their study has led not only to the discovery of new reactions and effects, but also to a deeper and more intimate understanding of many previously known reactions.

Although the chromic acid oxidation of alcohols is a reaction which has been investigated by numerous investigators over a period of many years,[2] important aspects concerning the nature of the transition state of the rate-limiting step and the role of unstable chromium compounds formed during the reaction remain poorly understood.[3] We therefore decided to investigate in detail the chromic acid oxidation of cyclobutanol in order to gain a better insight into the nature of the reaction.

Experimental Section

Materials. Cyclobutanone was synthesized from pentaerythritol, *via* pentaerythrityl tetrabromide, 1-hydroxymethyl-1-cyclobutanol, and methylenecyclobutane, by methods reported in the literature.[5] In addition, some was obtained commercially (Columbia Chemical Co.). Final purification by glpc was done on the F&M Model 500 gas chromatograph using a 0.25 in. × 144 in. Carbowax 20M column.

For the determination of heats of combustion, cyclobutanone was purified by distillation on a spinning band column (Nester-Faust), distillation through a tube filled with Linde molecular sieve (4A), purification by preparative glpc, using a polyester cross-linked diethylene glycol adipate column, and by vacuum line distillation. The final product was 99.94% pure and contained two unknown impurities (0.02 and 0.03%, respectively) and a very small amount of ether (0.006%). Physical constants: $d^{24}{}_4 = 0.924$, n^{25}D 1.4188 (lit. 1.4189), bp 99–100° (lit.[3] bp 98–100°).

Cyclobutanol was prepared by lithium aluminum hydride reduction of cyclobutanone followed by isolation through a spinning band column and final purification by glpc. 1-Deuteriocyclobutanol was prepared in the same manner, using lithium aluminum deuteride (Metal Hydrides Inc. 96.2% D). The analytically determined deuterium content of the product was 0.928 atom deuterium per molecule; the analysis was carried out by J. Nemeth, Urbana, Ill.

For the determination of heats of combustion, cyclobutanol was purified in the same manner as cyclobutanone, except that several glpc purifications were required (Carbowax 20M column). The final product was 99.92% pure. The impurities were water (0.04%), ether (0.01%), and two unknown impurities (0.01 and 0.02%,

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