

Oxidation by Metal Salts. V.¹ Cobaltic Acetate Oxidation of Alkylbenzenes

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Abstract: The cobaltic acetate oxidation of alkyl aromatic hydrocarbons was studied and an electron-transfer mechanism involving the intermediacy of aromatic radical cations was proposed. This mechanism was indicated by the high ρ value of -2.4 (correlated with σ^+ at 65°) obtained from the relative reactivity of substituted toluenes, and the unusually low reactivity of cumene relative to toluene. The radical cation intermediates were detected by epr flow techniques in a few cases. The addition of lithium chloride lead to a dramatic enhancement of the reactivity of cobaltic acetate. In the presence of chloride ions the relative reactivity of substituted toluenes yielded a ρ value of -1.35 (correlated with σ^+ at 24°). The effect of chloride ions on the ρ value was attributed to the formation of a cobaltic complex of relatively high oxidation potential and lower selectivity. The effect of chloride ion concentrations on the nuclear *vs.* side-chain products was also studied.

Although the cobalt acetate catalyzed air oxidation of alkylbenzenes to the corresponding mono- and dicarboxylic acids forms the basis of several commercial processes,² the mechanistic role of cobalt is not very clear. The requirement of relatively high cobalt concentration in such systems is surprising. It indicates that oxidation under such conditions may not proceed *via* a classic free-radical chain reaction in which cobalt merely decomposes hydroperoxide intermediates to alkoxyl and peroxy radicals.^{3,4}

The gradual transformation of cobalt catalyst to the higher valency state in the period preceding the maximum oxidation rate, as well as the observation that the induction period decreased with increasing cobaltic ion concentration, suggested interaction between the cobaltic salt and the aromatic hydrocarbon.^{2,5} The exact nature of this interaction was not clearly demonstrated, although a mechanism consisting of direct benzylic hydrogen atom abstraction by the cobaltic salt was proposed.⁵

As an extension of our studies on the oxidation of aromatic hydrocarbons by metal salts,^{6,7} we investigated the direct reaction of cobaltic acetate with aromatic hydrocarbons in the absence of oxygen, with the intention of clarifying the exact nature of this interaction. In this article, we present a reaction mechanism indicated by our results as well as a comparison of cobaltic acetate with other metal acetate oxidants. The effect of added anions such as chloride ions on the selectivity and reactivity of cobaltic acetate is also discussed.

Results

Oxidation of Toluene. The oxidation of toluene by cobaltic acetate in acetic acid at temperatures ranging

(1) Part IV: E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **90**, 5905 (1968).

(2) W. F. Brill, *Ind. Eng. Chem.*, **52**, 837 (1960).

(3) C. Walling, "Free Radical in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 427.

(4) A. S. Hay, J. W. Eustance, and H. S. Blanchard, *J. Org. Chem.*, **25**, 616 (1960).

(5) (a) T. Morimoto and Y. Ogata, *J. Chem. Soc., B*, 62 (1967); (b) *ibid.*, 1353 (1967).

(6) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **90**, 1082 (1968).

(7) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, **91**, 138 (1969).

from 37° to reflux yielded two major products, benzyl acetate and benzaldehyde, in 50–90% yield based on the cobaltic ion consumed. Minor amounts of benzaldehyde diacetate, xylene, methylbenzyl acetate, and benzyl dimers (mainly methyldiphenylmethane) were also detected by vapor phase chromatography. Typical product yields under various conditions are shown in Table I. Added acetate ions in the form of potassium acetate led to an enhancement of the reaction rate, but had little effect on the products obtained. The reaction temperature, however, did have an influence on the products, with higher over-all yields obtained at lower temperatures.

The Oxidation of 2-Methylnaphthalene. The cobaltic acetate oxidation of 2-methylnaphthalene at 70° in acetic acid gave three major products: 2-naphthaldehyde, 1-acetoxy-2-methylnaphthalene, and 2-acetoxymethylnaphthalene. The addition of potassium acetate accelerated the rate of disappearance of cobaltic acetate, but had little effect on the product distribution (Table II). The oxidation of 2-methylnaphthalene by cobaltic acetate differed from its oxidation with either manganic acetate or lead tetraacetate in that there was no measurable $-\text{CH}_2\text{OAc}$ adduct detected.

Thermolysis of Cobaltic Acetate. The main gaseous products produced in the thermolysis of cobaltic acetate in acetic acid containing potassium acetate were CO_2 and methane. The yield of CO_2 always exceeded that of methane. The addition of 2-methylnaphthalene decreased the yields of both CO_2 and methane as shown in Table III. In the presence of 2-methylnaphthalene, less than 0.02 mole of methane was produced per mole of cobaltic acetate reduced.

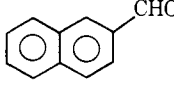
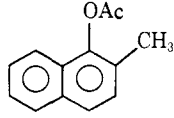
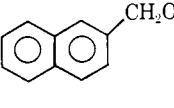
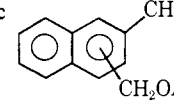
Relative Reactivity. Attempts were made initially to study the relative rates of cobaltic acetate oxidation of various hydrocarbons by following the disappearance in cobaltic ion spectrophotometrically in the 610–650- μ range. Solutions containing approximately 10^{-2} *M* hydrocarbon, 10^{-3} *M* potassium acetate, and 10^{-4} *M* cobaltic ion were used at 45 – 50° . Linear first-order plots for the disappearance of Co^{III} were obtained for the first 20% reaction, after which point the reactions slowed down substantially. This retardation may be

Table I. Products from the Oxidation of Toluene by Cobaltic Acetate

Reaction conditions				Millimoles of product/100 mmoles of Co ^{III}						
[Toluene]	[Co ^{III}]	[KOAc]	T, °C	C ₆ H ₅ -CH ₂ OAc	C ₆ H ₅ -CHO	C ₆ H ₅ -CH(OAc) ₂	CH ₃ -C ₆ H ₄ -CH ₂ OAc	Xylenes	Benzyl dimers	Yield ^a
1	0.2		110	22	3.9	0.1	0.5	0.2	0.8	63
0.2	0.04		110	15	4.2	0.6	1.4	0.2	0.9	69
1	0.2	1	110	18	3.8	0.1	0.7	0.2	0.6	55
1	0.2	1	70	22	3.5	0.3	0.4	0.1	1.9	64
1.2	0.3	1	37 ^b	31	7.3				2	94

^a This calculation is based on the stoichiometry of 2 moles of cobaltic acetate per mole of benzyl acetate and 4 moles of cobaltic acetate per mole of benzaldehyde produced. ^b 48% reaction in 43 hr.

Table II. Products from Oxidation of 2-Methylnaphthalene (0.28 M) by Cobaltic Acetate, Manganic Acetate, and Lead Tetraacetate

Oxidant	KOAc, M	Product yields, % ^a				
						
Co(OAc) ₃ , 0.088 M, 70°			19	18	32	
Co(OAc) ₃ , 0.088 M, 70°	1.2		11	13	32	
Mn(OAc) ₃ , 2H ₂ O, 0.18 M, 90°	1.2			3	3	
Pb(OAc) ₄ , 0.082 M, 90°	1.2		3	33	11	
						56
						16

^a Based on the oxidant consumed, assuming 2 equiv per side chain and nuclear acetate and 4 equiv per -CH₂OAc adduct and aldehyde.

Table III. Gaseous Products Obtained from the Thermolysis of Cobaltic Acetate in the Presence and Absence of 2-Methylnaphthalene (2-MeN)

[Co ^{III}]	[KOAc]	[2MeN]	Temp, °C	Product ratio (M)		
				CO ₂ /Co ^{III}	CH ₄ /Co ^{III}	CO ₂ /CH ₄
0.09	1.5		105	0.21	0.05	4.1
0.09	1.5	0.28	105	0.075	0.019	4.0
0.09	1.5		50	0.26	Trace	
0.09	1.5	0.28	50	0.06	Trace	

due to the buildup of Co^{II} during the course of the reaction. The addition of cobaltous acetate was shown to decrease the rate of reaction dramatically.

The rate constants obtained in this manner ($\sim 10^{-3} M^{-1} \text{sec}^{-1}$) indicated a relative reactivity order as follows: *p*-xylene > toluene \cong ethylbenzene > cumene \cong *p*-chlorotoluene. This method of determining relative reactivities, however, was of limited accuracy because the rate of disappearance of Co^{III} in the presence of hydrocarbons at such low concentrations was not much greater than its background disappearance in the absence of hydrocarbons (using 25-fold excess *p*-xylene (0.008 M), the rate was only 2.5 times that of the thermal self-decomposition of cobaltic acetate).⁸ The observed rate, however, increased as the hydrocarbon concentration was increased, although not as rapidly. Furthermore, some of the initial products of the cobaltic acetate oxidation of alkylaromatic hydrocarbons are the corresponding alcohols and aldehydes which are oxidized faster than the starting material, thus leading to variations in stoichiometry. These limitations of the spectrophotometric method prompted us to consider a relatively more accurate technique for determining relative reactivities, the competitive technique.

Competitive Rates of Oxidation of Substituted Toluenes by Cobaltic Acetate. Competitive rates of oxida-

(8) The same problem was observed in the oxidation of toluene by cobaltic perchlorate in aqueous acetonitrile: T. A. Cooper, A. A. Clifford, D. J. Mills, and W. A. Waters, *J. Chem. Soc., B*, 793 (1966); T. A. Cooper and W. A. Waters, *ibid.*, 687 (1967).

tion of various hydrocarbons were studied using cobaltic acetate in the presence of potassium acetate at 65°. The following reactant concentrations were used: $2.5 \times 10^{-2} M$ for each of the hydrocarbons, 0.25 M potassium acetate, $2.5 \times 10^{-2} M$ chlorobenzene or *o*-dichlorobenzene as an internal standard, and 0.16 M cobaltic acetate in glacial acetic acid. The reactions usually required between 5 and 10 days at 65° until all the cobaltic acetate had disappeared. All the reactions were run in triplicate and analyzed twice by vapor phase chromatography (Table IV).

Oxidation of Toluene with Cobaltic Acetate in the Presence of Lithium Chloride. The addition of lithium chloride to a solution of cobaltic acetate in acetic acid greatly accelerated the reduction of cobaltic ion. Cobaltic acetate, which normally required over 1 week to be reduced at 65°, reacted in less than 2 hr at room temperature in the presence of a tenfold excess of lithium chloride.

The addition of chloride ion dramatically changed the absorption spectrum of the cobaltic acetate solution as shown in Figure 1. Almost immediately after mixing, a strong peak appeared at 460 m μ having an extinction coefficient of about 2000, together with a somewhat weaker peak around 600 m μ . When the reaction was complete, both of these peaks had disappeared and only the expected spectrum of tetrahedral cobaltous chloride remained. The rate of decay of the intermediate as measured by the disappearance of the 460-m μ peak was

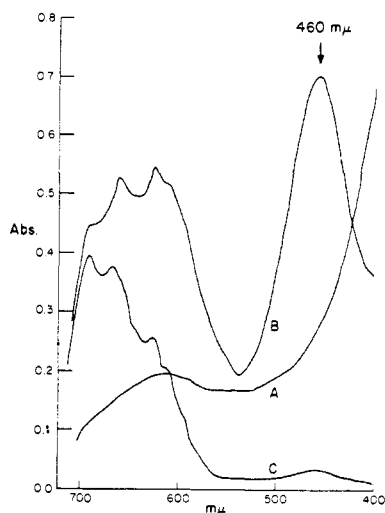


Figure 1. Spectral changes in the presence of chloride ion: A = 10^{-3} M Co^{3+} acetate in HOAc; B = 1 ml of 10^{-3} M Co^{3+} solution, 2 ml of 0.5 M LiCl immediately after mixing; C = after ~ 0.5 hr reaction.

shown to be first order and dependent on chloride ion concentration. The exact nature of this intermediate, presumably a cobalt(III) chloride complex, is currently under investigation.⁹

Table IV. Comparison of the Relative Rates of Oxidation by Cobaltic Acetate and the Ionization Potentials and π -Complex Stabilities of Various Alkylbenzenes

Alkylbenzene	$\text{Co}(\text{OAc})_3$, 65°	$\text{Co}^{3+} + \text{Cl}^-$, 24°	IP_1^a , eV	K^b	K^c
Durene		275	8.03	1.01	54.2
2-Methyl- naphthalene		33			
1,2,4-Trimethyl- benzene		20	8.27		
Mesitylene		5.7	8.39	0.68	17.3
<i>p</i> -Xylene	10.3	5.2	8.45	0.61	7.6
<i>m</i> -Xylene	3.1	3.7	8.56	0.60	6.0
Toluene	1	1	8.82	0.51	3.7
Toluene- <i>d</i> ₃		0.27			
Ethylbenzene	1.3	2.1	8.76	0.45	
Cumene	0.3	0.3		0.36	
<i>t</i> -Butylbenzene		≤ 0.07	9.35		
<i>n</i> -Nonane	0.1 (90°)		10.21		

^a R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965.
^b Stability constant for picric acid π complex: H. D. Anderson and D. L. Hammick, *J. Chem. Soc.*, 1089 (1950). ^c Stability constant for tetracyanoethylene π complex: R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, 86, 2778 (1958).

The cobaltic acetate oxidation of toluene under nitrogen in the presence of lithium chloride yielded four products in over 80% yield based on the Co^{III} consumed: benzyl chloride, benzyl acetate, benzaldehyde, and chlorotoluene (Table V). The major product was always benzyl chloride, with the nuclear chlorinated product being significant only at high lithium chloride concentrations (≥ 1.2 M).

Oxidation of 2-Methylnaphthalene with Cobaltic Acetate in the Presence of Lithium Chloride. The

(9) A. W. Chester, E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *Inorg. Nucl. Chem. Lett.*, in press.

Table V. Reaction of Toluene (1.13 M) with Cobaltic Acetate (0.091 M). Effect of Lithium Chloride

LiCl, M	Yield of products, % ^a			
	$\text{ClC}_6\text{H}_4\text{CH}_3$	$\text{C}_6\text{H}_5\text{CHO}$	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	$\text{C}_6\text{H}_5\text{-CH}_2\text{OAc}$
2.1	32	5	46	1
1.2	6	4	76	4
0.73	0.7	11	78	5
0.24		24	70	6

^a Yields were calculated on the assumption that benzyl chloride, benzyl acetate, and chlorotoluene require 2 equiv of $\text{Co}(\text{OAc})_3$ /equivalent of product, and that benzaldehyde requires 4 equiv of $\text{Co}(\text{OAc})_3$ /equivalent of product.

cobaltic acetate oxidation of 2-methylnaphthalene in the presence of lithium chloride yielded the four major products shown in Table VI. The ratio of the two nuclear substituted products to the two side-chain products was found to depend on the chloride concentration used.

Table VI. Reaction of 2-Methylnaphthalene (0.28 M) with Cobaltic Acetate (0.09 M) in the Presence of LiCl at 40°

Conditions	A	B
LiCl, M	1.2	0.12
Reaction time, hr	<1	48
Co^{3+} reacted, %	100	63

Products	Yield, ^a %	
	60	12
	1	3
	6	5
	6	25
Ratio of nuclear/side chain	5	0.5

^a Based on Co^{3+} reacted, assuming the requirement of 4 equiv/mol of aldehyde formed and 2 equiv for each of the other products formed.

Competitive Rate Studies in the Presence of LiCl. Competitive rates of oxidation of numerous hydrocarbons were studied using cobaltic acetate in the presence of LiCl. The following reactant concentrations were used: 3.33×10^{-2} M in each of two hydrocarbons, 3.33×10^{-2} M chlorobenzene or *o*-dichlorobenzene as reference, 6.67×10^{-1} M LiCl ($9 \times \text{Co}^{\text{III}}$ concentration), and 7.67×10^{-2} M cobaltic acetate in glacial acetic acid. Unreacted starting material was analyzed by vapor phase chromatography of the reaction mixture. All reactions were run at room temperature in triplicate and each was analyzed twice by vpc. In all cases, the stoichiometry of Co^{III} used per hydrocarbon reacted was greater than 2, indicating further oxidation of the initially formed products. For all reactants faster than *p*-chlorotoluene, this value averaged 3.0 molecules of cobalt ion disappeared per molecule of hydrocarbon reacted. When less reactive hydrocarbons were used, the stoichiometry increased drastically,

indicating that the cobaltic complex decomposed partially without oxidizing the hydrocarbon. The relative reactivities per molecule obtained from these competitive experiments are shown in Table IV.

Discussion

Our studies on the oxidation of aromatic hydrocarbons revealed several distinct differences between the oxidation by cobaltic acetate and those by manganic acetate and lead tetraacetate. Unlike the manganic and lead tetraacetate^{6,7} oxidations of toluene, which led predominantly to $-\text{CH}_2\text{OAc}$ adducts (methylbenzyl acetate), only trace amounts of these adducts were formed with cobaltic acetate. The major products were benzyl acetate and benzaldehyde (see Table I). The oxidation of 2-methylnaphthalene with cobaltic acetate also differed from the oxidation with lead tetraacetate or manganic acetate in that there was no measurable $-\text{CH}_2\text{OAc}$ adduct produced (see Table II). The formation of the $-\text{CH}_2\text{OAc}$ adducts was previously explained in terms of a free-radical mechanism involving addition of the $\cdot\text{CH}_2\text{COOH}$ radical, formed either directly as in the thermolysis of manganic acetate or by methyl radical attack on acetic acid as in the case of lead tetraacetate.

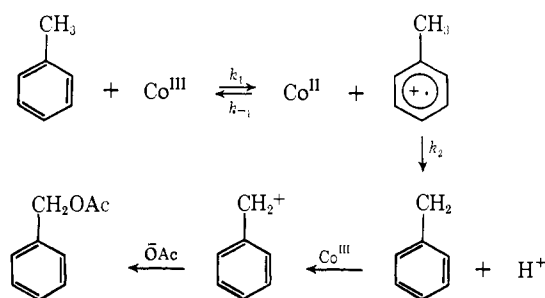
The effect of added cupric acetate on the oxidation of toluene by cobaltic acetate also differed from that observed in the oxidation with manganic or lead tetraacetate. While the addition of cupric acetate greatly decreased the extent of oxidation of toluene by both manganic or lead tetraacetate, very little effect was observed in the oxidation by cobaltic acetate. The effect of cupric acetate in the oxidation by lead tetraacetate or manganic acetate was consistent with the proposed free-radical mechanism, since Cu^{II} is a known effective radical interceptor.¹⁰

These results suggested that the oxidation of aromatic hydrocarbons by cobaltic acetate is *not* a free-radical mechanism comparable to that observed in the case of lead tetraacetate or manganic acetate.

Finally, in accord with this interpretation, the competitive oxidation of cumene by cobaltic acetate was found to be slower than toluene¹¹ (see Table IV), while in the oxidation by manganic acetate or lead tetraacetate, cumene reacted twice as fast as toluene as would be expected on the basis of a free-radical mechanism.

Mechanism

We, therefore, propose the following mechanism to account for the oxidation of aromatic hydrocarbons by cobaltic acetate.



(10) J. K. Kochi and R. V. Subramanian, *J. Am. Chem. Soc.*, **87**, 4855 (1965).

(11) Similar experiments on the oxidation by $\text{Ce}(\text{OAc})_4$ and $\text{Pd}(\text{OAc})_2$ indicated that $\text{Ce}(\text{OAc})_4$ behaved similar to $\text{Pb}(\text{OAc})_4$ and $\text{Mn}(\text{OAc})_3$, while $\text{Pd}(\text{OAc})_2$ behaved similar to $\text{Co}(\text{OAc})_3$.

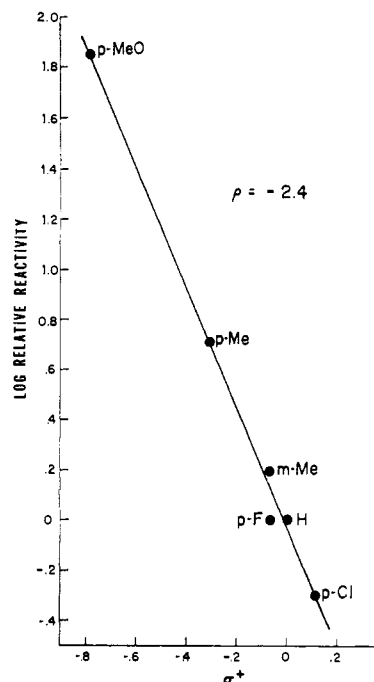


Figure 2. Relative reactivities of substituted toluenes toward cobaltic acetate in acetic acid at 65°.

The above mechanism involves the reversible interaction of Co^{III} with the aromatic hydrocarbon leading to the formation of the corresponding radical cation. The radical cation in a subsequent step loses an α proton yielding a benzyl radical. The benzyl radical is then rapidly oxidized by Co^{III} to the corresponding benzyl acetate. This mechanism is similar to that suggested for the oxidation of *p*-methoxytoluene by manganic acetate.^{7,12} An electron-transfer mechanism was also proposed for the cobaltic sulfate oxidation of olefins¹³ and the cobaltic perchlorate oxidation of polycyclic aromatic hydrocarbons in aqueous acetonitrile.¹⁴

The electron transfer mechanism can be deduced from the relative reactivity of substituted toluenes toward cobaltic acetate, which follows a linear Hammett σ - ρ relationship. A good correlation with σ^+ (Figure 2) yielded a ρ value of -2.4 . The values for *p*- and *m*-xylene used in the plot have been divided by the statistical factor 2. The high ρ value is inconsistent with any known free-radical mechanism and indicates considerable positive charge development on the aromatic hydrocarbon in the transition state. In accord with this scheme, the observed order of reactivity of substituted alkylbenzenes correlates quite well with the stability of their π complexes with tetracyanoethylene and picric acid, as well as with their reported gas phase ionization potentials (Table IV). Based on this mechanism, the cobaltic ion interaction with the aromatic π electrons is an electrophilic π interaction and hence the observed low reactivity of cumene can be well understood. Cumene has been observed to be less reactive than toluene in many systems in which a positive charge is developed either at or adjacent to an aromatic ring. Examples are electrophilic chlorination,¹⁵ the solvolysis

(12) P. J. Andrusis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966).

(13) C. E. H. Bawn and J. A. Sharp, *J. Chem. Soc.*, 1854 (1957).

(14) T. A. Cooper and W. A. Waters, *ibid.*, **B**, 687 (1967).

(15) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

of *para*-substituted benzhydryl chlorides,¹⁶ and the heats of formation of benzenonium ions.¹⁷

Supporting Evidence for the Electron-Transfer Mechanism. A. Detection of Radical Cation Intermediates.

The direct observation of radical cation intermediates in glacial acetic acid was accomplished in the case of aromatic compounds having low ionization potentials such as triphenylamine, thianthrene, 9,10-diphenylanthracene, and 9,10-dimethylantracene. Immediately upon mixing a solution of triphenylamine with cobaltic acetate in acetic acid at room temperature, one observed two peaks in the visible absorption spectrum at 480 and 660 $m\mu$. The peak at 660 $m\mu$ rapidly decreased with time while the 480 $m\mu$ peak increased. After a few minutes, the 660- $m\mu$ peak disappeared and the 480- $m\mu$ peak reached a maximum intensity before it too began to decrease. The 480- $m\mu$ peak has been assigned to the radical cation of triphenylamine ($(C_6H_5)_3N\cdot^+$) and the 660- $m\mu$ peak to the radical ion of tetraphenylbenzidine ($(C_6H_5)_2NC_6H_4C_6H_4N\cdot^+(C_6H_5)_2$).¹⁸

The formation of these radical cation intermediates was confirmed by rapid flow epr experiments. Under flow conditions the spectrum of triphenylamine radical cation was observed as 42 equally spaced lines separated by 1.1 G.¹⁹ As soon as the flow was stopped a new spectrum appeared which consisted of five broad lines separated by 4.7 ± 0.7 G. This spectrum which then gradually disappeared has been assigned to the radical cation of tetraphenylbenzidine.^{18,20}

The radical cations of thianthrene and 9,10-diphenylanthracene were also observed using a flow system, although their concentrations were considerably lower than those derived from triphenylamine. However, the addition of 12.5% (by volume) trifluoroacetic acid²¹ to the cobaltic acetate-acetic acid solution dramatically increased the observable radical cation concentration. No epr signal was observed in the absence of cobaltic ion. By this method, the known cation radicals of thianthrene,²² 9,10-diphenylanthracene,²³ and 9,10-dimethylantracene²⁴ were easily observed.

Using pure trifluoroacetic acid as the solvent for the cobaltic acetate oxidation, we were even able to observe the radical cations of *p*-methoxytoluene, hexamethylbenzene, pentamethylbenzene, and durene.²⁵ Epr signals have also been obtained for mesitylene and *p*-xylylene; however, this area is still under active investigation.

(16) E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 949 (1940).

(17) J. W. Larsen and E. M. Arnett, Abstracts of papers, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, ORGN-10.

(18) F. R. Dollish and W. K. Hall, *J. Phys. Chem.*, **69**, 2127 (1965), and references therein.

(19) D. N. Stamires and J. Turkevich, *J. Am. Chem. Soc.*, **85**, 2557 (1963); D. L. Allara, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 319 (1965).

(20) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Am. Chem. Soc.*, **88**, 3498 (1966).

(21) Previous unpublished experiments in our laboratory have indicated that the addition of a strong acid such as trifluoroacetic acid greatly increased the electron-transfer ability of the metal acetate oxidants: cf., J. M. Davidson and C. Triggs, *J. Chem. Soc., A*, 1331 (1968); S. S. Lande and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 5196 (1968); R. A. Sheldon and J. K. Kochi, *ibid.*, **90**, 6688 (1968).

(22) H. J. Shine, C. F. Dais, and R. J. Small, *J. Org. Chem.*, **29**, 21 (1964).

(23) R. E. Sioda and W. S. Koski, *J. Am. Chem. Soc.*, **87**, 5573 (1965).

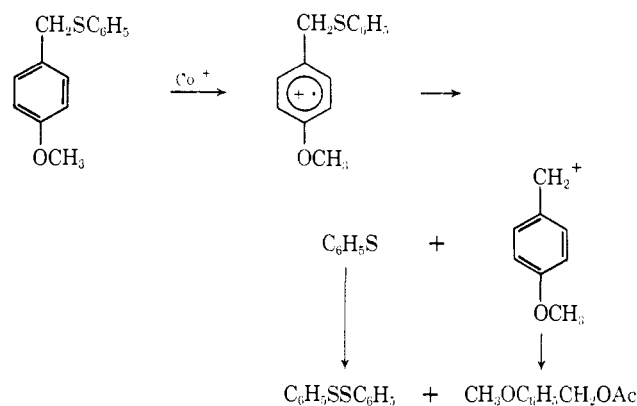
(24) J. A. Brivati, R. Hulme, and M. C. R. Symons, *Proc. Chem. Soc.*, 384 (1961).

(25) G. Vincow in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N. Y., 1968, p 151.

The detection of radical cation intermediates in the cobaltic oxidation of these aromatic hydrocarbons strongly supports the electron-transfer mechanism presented above.

B. The Oxidation of *p*-Methoxybenzyl Phenyl Sulfide.

The oxidation of *p*-methoxybenzyl phenyl sulfide by Co^{3+} in the presence of lithium chloride at room temperature gave three major products: *p*-methoxybenzyl acetate, *p*-methoxybenzaldehyde, and phenyl disulfide in approximately equimolar quantities. *p*-Methoxybenzyl phenyl sulfide was recovered unchanged when subjected to the same reaction conditions in the absence of Co^{3+} . The reaction products obtained in the presence of Co^{3+} are consistent with our proposed electron-transfer mechanism and cannot be explained on the basis of a simple free-radical mechanism. The



radical cation resulting from the interaction of *p*-methoxybenzyl phenyl sulfide with Co^{3+} can undergo cleavage to the stable phenylthiyl radical and *p*-methoxybenzyl cation in competition with the normal proton expulsion. This type of cleavage may be considered analogous to the cleavage of the radical anion from *p*-nitro-cumyl chloride into chloride ion and the corresponding benzyl radical.^{26,27}

Mechanism of Oxidation in the Presence of Lithium Chloride.

The observed relative reactivities of alkylbenzenes toward oxidation by Co^{III} in the presence of Cl^- ion also show good agreement with the relative stabilities of π complexes of alkylbenzenes with picric acid and tetracyanoethylene (TCE) (Table IV). The selectivity data argue against ionic chlorination by Cl^+ despite the fact that Cl_2 is the major product in the absence of alkylbenzenes. The relatively low reactivity of the *meta* isomers relative to the *para* compounds stands in marked contradiction to that observed in ionic chlorination.²⁸ Furthermore, very little nuclear chlorination of toluene was observed when it was oxidized under conditions comparable to those used for the relative reactivity studies. Finally, the fact that toluene reacts three times as fast as cumene and over 15 times as fast as *t*-butylbenzene argues against a free-radical mechanism, involving either $\cdot CH_3$ ²⁹ or $\cdot Cl$.³⁰

(26) N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *J. Am. Chem. Soc.*, **89**, 725 (1967); N. Kornblum, G. W. Earl, N. L. Holy, J. W. Manthey, M. T. Musser, D. H. Snow, and R. T. Swiger, *ibid.*, **90**, 7221 (1968).

(27) The reaction products can also be explained on the basis of electron transfer from the sulfur atom; this is presently under investigation.

(28) In the ionic chlorination with molecular chlorine in acetic acid at 25°, mesitylene is calculated to be 10^6 times faster than *p*-xylylene: H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 5175 (1957).

The relative reactivity of *para*-substituted toluenes toward Co^{III} in the presence of Cl^- ion follows a linear Hammett σ - ρ relationship (Figure 3). The good correlation with σ^+ yields a ρ value of -1.35 . This strongly suggests that the oxidation in the presence of Cl^- ion proceeds with the same electron-transfer mechanism proposed for the oxidation with cobaltic acetate in the absence of Cl^- ion. The major influence of added Cl^- ion is to render Co^{III} a stronger oxidant. The relatively low ρ value of -1.35 of Co^{III} in the presence of Cl^- ion is therefore understandable because the stronger and more reactive the oxidant, the lower will be its selectivity.

While the ionization potential of aromatic hydrocarbons is important in determining their relative reactivities toward oxidation by an electron-transfer mechanism, the observed isotope effect, $k_h/k_d = 3.7$, suggests that the side-chain carbon-hydrogen bond cleavage is also important in the transition state. This is consistent with the above proposed scheme in which the electron transfer from the aromatic hydrocarbon to cobalt(III) is a reversible step followed by a subsequent step involving the cleavage of the carbon-hydrogen bond. The rate of oxidation of alkylaromatic hydrocarbons will therefore depend on both the equilibrium constant K and the rate constant k_2 . As expected on the basis of this mechanism, a retardation of the oxidation rate by added Co^{II} was observed. The use of the statistical factor for the xylenes in the Hammett plot also supports this mechanism.

Nuclear Substitution in Aromatic Radical Cations.

A possible reaction of radical cations is the attack of a nucleophile on the aromatic nucleus. This type of reaction is especially important with radical cations such as 2-methylnaphthalene and *m*-methoxytoluene (Table VII). The relative extent of side chain oxidation

Table VII. Products from the Oxidation of Methyl-naphthalenes and Methoxytoluenes

Hydrocarbon	Conditions	Yield of products, % ^a		
		ArCHO	ArCH ₂ X	ArCH ₃
1-Methylnaphthalene	1.2 M KOAc, 110°	16	26	
2-Methylnaphthalene	1.2 M KOAc, 110°	17	29	12
<i>p</i> -Methoxytoluene	1.2 M LiCl, 25°	3	65	
<i>m</i> -Methoxytoluene	1.2 M LiCl, 40°	1	3	38

^a Based on Co^{3+} reacted, assuming the requirement of 4 equiv/mole of aldehyde formed and 2 equiv for each of the other products formed.

is directly related to the degree of positive charge adjacent to the methyl group relative to that in the other positions of the radical cation. The relative degree of positive charge adjacent to the methyl group in 1-methylnaphthalene radical cation is greater than the relative degree of positive charge adjacent to the methyl group in the radical cation of 2-methylnaphthalene. Similarly the relative extent of positive charge adjacent to the methyl group in the radical cation derived from *p*-methoxytoluene is greater than the relative positive

(29) J. A. Meyer, V. Stannett, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 25 (1960).

(30) G. A. Russell, A. Ito, and D. G. Hendry, *ibid.*, **85**, 2976 (1963).

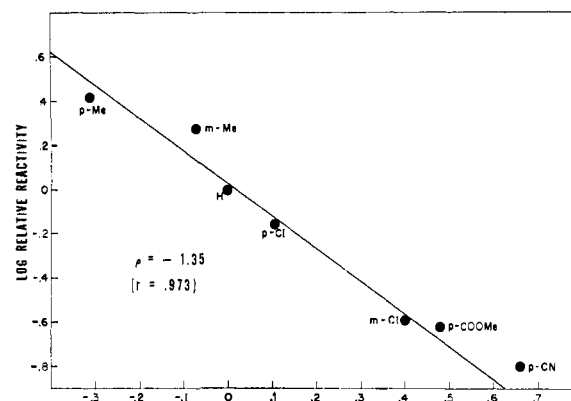
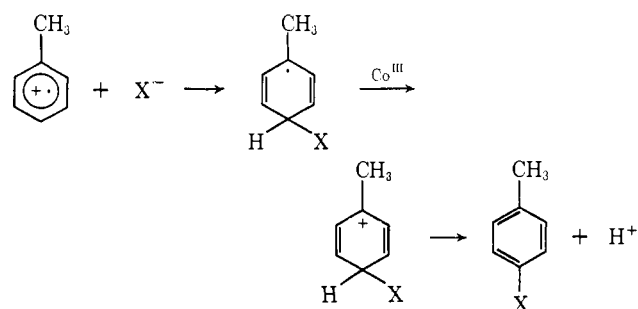


Figure 3. Relative reactivities of substituted toluenes toward cobaltic acetate in HOAc in the presence of LiCl.

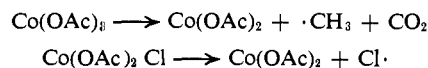
charge adjacent to the methyl group in *m*-methoxytoluene radical cation.³¹

The nucleophilic attack on the ring is also more important when relatively reactive nucleophiles such as Cl^- ions are used. Thus while the oxidation of toluene



gave no measurable nuclear acetoxylation in the presence of acetate ion, it gave considerable yields of nuclear-chlorinated products in the presence of high Cl^- ion concentrations (Table V). Similar results were also obtained with 2-methylnaphthalene (Table VI). The relative ratio of nuclear attack to side-chain attack in both cases was found to increase with an increase in the nucleophile concentration. The observed nuclear chlorinated products, at high Cl^- ion concentrations, appear not to be due to ionic chlorination since the relative reactivity of mesitylene is still comparable to *p*-xylene under our reaction conditions (Table IV). Even at Cl^- ion concentrations as high as 1.3 M mesitylene is only three times as reactive as *p*-xylene, while for ionic chlorination mesitylene should be favored by almost a factor of 10^5 .²⁸

Competitive Modes of Oxidation by Co^{III} . An interesting feature of oxidation of aromatic hydrocarbons with Co^{III} is the competitive oxidation of the ligand itself. The relative extent of these two pathways depends on the relative oxidation potential of the ligand



as compared to the aromatic hydrocarbon, as well as the relative concentrations of the two. Thus, in the absence of an added aromatic substrate, the reduction of cobaltic acetate proceeds to give methyl radical and CO_2 , similar to that observed in the decarboxylation of

(31) These conclusions are supported by molecular orbital calculations performed by Dr. S. Shih of our laboratory.

other fatty acids.³² However, very little oxidation of the acetate ligand was observed in the presence of 2-methylnaphthalene as evidenced by the decreased yield of CO₂ produced (Table III). The relative extent of the decarboxylative and the electron-transfer pathways can also be deduced from the results obtained in the oxidation of toluene with cobaltic acetate (Table I). The xylenes and the methylbenzyl acetate produced are a measure of the relative extent of the decarboxylative pathway, since they result from the methyl radical interaction such as that observed in the lead tetraacetate oxidation.⁶ The decarboxylative pathway accounts for about 3 and 8% of the products observed at toluene concentrations of 1 and 0.2 M, respectively. Beside the effect of toluene concentrations, the reaction temperature appears to influence the extent of these two pathways. Lower reaction temperature favors the oxidation of toluene *via* the electron-transfer pathway as evidenced by the high yields of the products obtained based on Co^{III} consumed. This suggests that the electron transfer from the toluene to Co^{III} is the process of lower activation energy as compared to that of the electron transfer from the acetate ion. This is in accord with the findings that alkylbenzenes undergo electrochemical oxidation at a voltage considerably lower than the discharge potential of the acetate ion.³³

In view of what we have shown about the behavior of cobaltic acetate, it is relevant to comment on the catalytic role of cobalt in the commercial oxidation of alkylbenzenes. It is well recognized that the catalytic oxidation proceeds only when cobaltic ions are present^{2,4,5} and that no oxidation takes place if cobalt is present only in the form of Co^{II}. The fact that cobaltic ions in acetic acid are responsible for oxidation suggest that the catalytic oxidation of alkylbenzenes at high concentrations proceeds predominantly *via* the electron-transfer process described above. Oxidation *via* an electron-transfer pathway could explain the observed high selectivity of substituted toluenes toward the catalytic oxidation.^{5b} Such high differences in selectivity cannot be attributed to a rate-determining step involving hydrogen abstraction by peroxy radicals which are known to display little selectivity as indicated by their low ρ value of -0.6 .³⁴ The recently determined relative reactivities of substituted toluenes toward catalytic oxidation followed the usual Hammett σ - ρ relationship with a ρ value of -2.66 at 90°. ^{5b} This value is very close to our determined ρ value of -2.4 for the interaction of cobaltic acetate with substituted toluenes in the absence of oxygen. A reaction step involving electron transfer from the substituted toluene to the cobaltic ion, must, therefore, be operating both in the presence and absence of oxygen.

Experimental Section

The organic compounds used were purchased in the purest quality available and carefully checked for impurities by vapor phase chromatography. The glacial acetic acid used was the "Analyzed Reagent" grade obtained from J. T. Baker Chemical Co.

Preparation of Cobalt(III) Acetate. The equipment consisted of a 3-l., four-necked flask fitted with a gas bubbler, condenser, thermometer, addition funnel, and stirrer. The flask was charged with 150 g of Co(OAc)₂·4H₂O, 1 l. of glacial acetic acid, and 25 ml of

water. Oxygen was bubbled through the solution at a rate of 0.5 l./min. The solution was heated to 90° and 500 ml of 2-butanone was then added dropwise over a period of 30 min. The temperature was maintained for an additional 30 min after which the reaction mixture was cooled to room temperature. The solution was evaporated at 35–40° on a rotary evaporator at a pressure of about 4 mm. The solid obtained was dried in a vacuum desiccator over P₂O₅, yield 143 g. The conversion to cobalt(III) as determined by iodometric titration was 55%. The solutions of cobaltic acetate prepared in this manner appeared identical with those of cobaltic acetate prepared by the peracetic acid preparation of Koubek and Edwards.³⁵

The Reaction of Cobaltic Acetate with Toluene. In a typical experiment 6.0 g of cobaltic acetate containing 20 mmoles of cobalt(III) was added to 100 ml of a 1 M toluene solution in glacial acetic acid. The reaction mixture was heated at 110° under a nitrogen atmosphere until all of the cobalt(III) had reacted. As an internal standard, 3 mmoles of methyl benzoate was added to the cooled reaction mixture. The solution was diluted with 500 ml of ether and then extracted five times with ice-water (~500 ml each time). The ether layer was dried over sodium sulfate, filtered, and stripped on a rotary evaporator. The residue was then analyzed by vapor phase chromatography on an F & M Model 810 gas chromatograph with dual thermal conductivity detectors using 12 ft 0.25-in. 5% silicone OV-17 columns and temperature programming (90–300° at 6°/min, helium flow ~90 cc/min). Peak areas were measured with a Varian Aerograph Model 475 automatic integrator, and peak responses were calibrated with mixtures prepared from authentic samples.

The following products, in order of increasing retention time, were obtained: xylenes (0.04 mmole), benzaldehyde (0.78 mmole), benzyl acetate (4.36 mmoles), methylbenzyl acetate (0.10 mmol), benzylidene diacetate (0.02 mmole), an incompletely identified product having the same retention time as bibenzyl but possibly an isomer of methyl-diphenylmethane (0.05 mmole), and 4-methyldiphenylmethane (0.11 mmole). The total yield of all products was 63% based on cobalt(III) used.

The Reaction of Cobaltic Acetate with Methylnaphthalenes. A solution of 2-methylnaphthalene (0.28 M) in glacial acetic acid was heated at 70° under nitrogen for 20 hr in the presence of cobaltic acetate (0.088 M in cobalt(III) by titration). At the end of 20 hr, 74% of the cobalt(III) had reacted. The reaction mixture was poured onto ice-water, extracted with ether, washed several times with water, dried over sodium sulfate, and concentrated on a rotary evaporator. The residue was analyzed by vpc (10 ft 15% silicone SE-30 on Diatoport S) and showed three major products: (a) 2-naphthaldehyde (19% yield based on cobalt(III) reacted), which was identical with an authentic sample; (b) 1-acetoxy-2-methylnaphthalene (18%), which upon hydrolysis was identical with an authentic sample of 1-hydroxy-2-methylnaphthalene; and (c) 2-acetoxymethylnaphthalene (32%), whose nmr spectrum consisted of a singlet at τ 8.03 (3 H), a singlet at 4.92 (2 H), and a multiplet in the 2.2–2.8 region.

The corresponding reactions of lead tetraacetate and manganic acetate were performed in the same manner. Both of these reactions contained an additional product identified as acetoxymethyl-2-methylnaphthalene on the basis of its infrared and nmr spectra.⁷

The similar cobaltic acetate oxidation of 1-methylnaphthalene at 110° gave 1-naphthaldehyde (16%) and 1-acetoxymethylnaphthalene (26%).

Direct Kinetic Studies Using Visible Spectroscopy. The rates of oxidation of various hydrocarbons were measured by following the disappearance of cobalt(III) in a Cary 14 spectrophotometer at 610 m μ . Reaction solutions were placed in a stoppered 10-cm cylindrical cell thermostated at 50°. In a typical reaction, 1 ml of a 1 M toluene solution was added to 25 ml of an acetic acid solution containing 7.6×10^{-4} cobalt(III) and 3.2×10^{-3} M KOAc. Linear first-order plots were obtained for the first 20% reaction, after which point the reactions tended to slow down substantially.

Spectral changes upon the addition of chloride ion were also followed in a Cary 14 spectrophotometer by scanning in the 400–700-m μ region. In a typical experiment, 1 ml of a 10^{-3} M cobalt(III) solution in glacial acetic acid was added to 2 ml of a 0.5 M LiCl solution at room temperature in a 1-cm cell. The spectral changes were then followed for a period of 30 min, by which time the reaction was over.

(32) S. S. Lande and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 5196 (1968).

(33) L. Eberson and K. Nyberg, *ibid.*, **88**, 1686 (1966).

(34) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

(35) E. Koubek and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **25**, 1401 (1963).

Competitive Rate Studies. The cobaltic acetate oxidation of various hydrocarbons was studied by the competitive technique at 65° in sealed tube flushed with nitrogen. The reactant concentrations used were: $2.5 \times 10^{-2} M$ in each of the two hydrocarbons, 0.25 *M* in KOAc, $2.5 \times 10^{-2} M$ in chlorobenzene or *o*-dichlorobenzene used an internal standard, and 0.16 *M* in cobalt(III) acetate. Reactions required 5–10 days at 65° for all the cobaltic acetate to disappear. All reactions were run in triplicate and analyzed at least twice by vapor phase chromatography. The reaction mixtures were analyzed directly before and after reaction on 2–4-ft columns of "Polypak-1" or "Porapak-Q" using an F & M 810 chromatograph with dual flame detectors. Peak areas were determined with a plainimeter and in some cases with an Aerograph Model 475 automatic integrator. The relative reactivities were calculated from the equation

$$\frac{k_A}{k_B} = \frac{\log A_0/A_F}{\log B_0/B_F}$$

where A_0 and B_0 are the vpc areas of compounds A and B relative to the internal standard before reaction, and A_F and B_F are the corresponding area ratios after reaction.

The reactions in the presence of chloride ion were run in closed vials at room temperature. The concentrations of reactants used were $3.33 \times 10^{-2} M$ in each hydrocarbon and internal reference (chlorobenzene or *o*-dichlorobenzene), $6.67 \times 10^{-1} M$ in LiCl, and $7.67 \times 10^{-2} M$ in cobalt(III) acetate in glacial acetic acid. The reaction mixtures were analyzed in same manner as in the absence of chloride ion and the relative reactivities calculated as above.

Reaction of Toluene with Cobalt(III) Acetate in the Presence of Chloride Ion. Solutions were prepared in 25-ml volumetric flasks using 3.0 ml of toluene (the toluene contained *n*-dodecane, 0.751 g/50 ml, as an internal reference for gc analysis), 10.0 ml of a stock cobalt(III) acetate solution in acetic acid (titrated as 0.227 *N* Co(III)), and sufficient dried solid lithium chloride or lithium chloride stock solution in acetic acid (32.0 g, in 250 ml of solution) to obtain the required concentration. The solutions were diluted to 25.0 ml, purged with nitrogen, and stoppered. The stoppers were secured with spring clamps, and the flasks put in a water bath at 40° until the cobalt(III) color disappeared. The reaction required 0.5 hr for completion with $[LiCl] = 2.08 M$ but was only 60% complete in 46 hr with $[LiCl] = 0.242 M$. The reaction mixtures were worked up by diluting with water and extracting with ether. The ether extract was concentrated and analyzed quantitatively by gc. Products were identified by comparison of gc retention times with those of known compounds.

Reaction of 2-Methylnaphthalene with Cobalt(III) Acetate in the Presence of Chloride Ion. Solutions were prepared in 25-ml volumetric flasks using 1.00 g of 2-methylnaphthalene, 10.0 ml of a stock cobalt(III) solution in acetic acid (titrated as 0.227 *N* Co(III)), and 10.0 ml of lithium chloride stock solution in acetic acid (32.0 g in 250 ml of solution) to obtain $[LiCl] = 1.21 M$ or 1.0 ml to obtain 0.12 *M*. The solutions were diluted to 25.0 ml, purged with nitrogen, and stoppered. The stoppers were secured with spring clamps, and the flasks were put in a water bath at 40°. With $[LiCl] = 1.21 M$ the reaction was complete in less than 4 hr and with $[LiCl] = 0.12 M$ it was 63% complete in 48 hr. After adding 25 ml of *m*-dodecane as an internal reference for gc analysis, the reaction mixture was worked up by diluting with water and extracting with ether. The ether extract was concentrated and analyzed quantitatively by gc. Products were identified by comparison of gc retention times with those of known compounds and by infrared spectra of samples collected by gc.

Reaction of Methoxytoluenes with Cobalt(III) Acetate in the Presence of Chloride Ion. The reaction of *p*-methoxytoluene (0.33 *M*) with cobaltic acetate (0.09 *M*) in glacial acetic acid con-

taining lithium chloride (1.2 *M*) at 25° yielded two major products: *p*-methoxybenzyl acetate (65% yield based on cobaltic ion used) and *p*-methoxybenzaldehyde (3%).

The corresponding reaction of *m*-methoxytoluene at 40° after the usual workup yielded *m*-methoxybenzyl alcohol (3%), *m*-methoxybenzaldehyde (1%), and a mixture of isomers of nuclear chlorinated *m*-methoxytoluene (38%).

Reaction of 2-Methylnaphthalene with Cobalt(III) Acetate-CO₂ Measurement. The reaction was run in a 100-ml flask arranged so that nitrogen could be bubbled through the solution and so that gases would exit through a reflux condenser, pass into a gas buret and, when desired, leave the system *via* ascarite-filled adsorption tubes. With 50 ml of acetic acid, 10.0 g of potassium acetate, and 1.05 g of 2-methylnaphthalene in the flask and 0.794 g of cobalt(III) acetate (20.5% Co(III) by titration) in a side arm the system was purged with N₂, checked for leaks, and the flask was heated to 105°. Then the cobalt(III) acetate was added to the solution without opening the system by tilting the side arm. When the reaction was complete as indicated by disappearance of the cobalt(III) color, the flask was cooled and the volume of gas collected in the buret was measured. The methane content of the gas was determined by gc analysis on a silica gel column. Then the buret was emptied through the adsorption tubes and the system was flushed with nitrogen which also passed through the tubes. Carbon dioxide was determined by weighing the tubes. Acetic acid carry-over was prevented by passing the gas through sulfuric acid ahead of the ascarite tubes. The reaction mixture was worked up by diluting with water and extracting with ether. The ether extract was analyzed quantitatively by gc. Products were identified by comparison of gc retention times with known materials and by infrared spectra of samples collected by gc.

The Oxidation of *p*-Methoxybenzyl Phenyl Sulfide. *p*-Methoxybenzyl phenyl sulfide (1.11 g, 4.82 mmoles) was dissolved in glacial acetic (30 ml) containing cobaltic acetate (4.82 mmoles). The solution was purged with nitrogen and mixed with a 30-ml solution of LiCl (2 *M*) in glacial acetic acid. The reaction mixture was kept at room temperature till the cobaltic color disappeared (10 min). The reaction mixture was diluted with 300 ml of ice water and extracted with ether, dried, and evaporated. The residue was dissolved in acetic acid containing anhydrous potassium acetate for 15 min to assure the conversion of all the *p*-methoxybenzyl chloride to the corresponding acetate. The acetic acid was removed on a rotary evaporator and the residue extracted with chloroform and analyzed by vpc using phenyl benzoate as an internal standard. Typical analysis gave *p*-CH₃OC₆H₄CHO (0.864 mmol), *p*-CH₃OC₆H₄CH₂OAC (0.752 mmol), C₆H₅S-SC₆H₅ (0.715 mmole) and recovered starting material (2.85 mmoles).

Detection of Radical Cations. Visible absorption spectra were obtained on a Unicam SP-800D spectrophotometer by repeatedly scanning the 400–700-m μ range immediately after mixing 2 ml of a $10^{-2} M$ solution of triphenylamine in acetic acid with 1 ml of a $1.3 \times 10^{-3} M$ cobaltic acetate solution in a nitrogen atmosphere.

Epr data were obtained on a Varian Model V-4500, X-band spectrometer with 100-kc field modulation. A flow system similar to that prepared by Borg³⁶ was used, at flow rates of approximately 150 ml/min. The solutions used were $10^{-2} M$ hydrocarbon in acetic acid (10–20% benzene was used to dissolve the anthracene derivatives) and $5\text{--}20 \times 10^{-3} M$ cobaltic acetate in acetic acid (12.5% by volume trifluoroacetic acid was added in some cases). No signals were detected in similar experiments in the absence of cobaltic ion.

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