Oxidation of Alkyl Aromatic Hydrocarbons by Potassium 12-Tungstocobaltate(III)[1]

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The oxidation of alkyl aromatic hydrocarbons by the heteropoly compound $K_5[Co^{III}O_4W_{12}O_{36}] \cdot H_2O$ was examined in order to determine whether inner- or outer-sphere electron transfer occurs when aromatic radical cations are formed during oxidations by metal ions. The oxidations were conducted at 96° in a heterogeneous system composed of solid $K_5[Co^{III}O_4W_{12}O_{36}] \cdot H_2O$ and the pure hydrocarbon (toluene and *o*-, *m*-, and *p*-xylene). The oxidation products were diphenylmethane derivatives, demonstrating the intermediate formation of benzyl carbonium ions. The oxidation of toluene in the presence of excess benzene produced diphenylmethane. The proposed mechanism consists of radical cation formation *via* outer-sphere oxidation in which the electron is removed from the aromatic π system and conducted through the tungstate framework to the Co^{III} ion. The radical cation expels a proton and the resulting benzyl radical is similarly oxidized to the carbonium ion. In aqueous acetic acid a similar mechanism appears to hold.

Recent reports[2,3] have shown that the oxidation of alkyl aromatic hydrocarbons by cobalt(III) acetate and a species identified[4] as the hexachlorocobaltate(III) anion proceed *via* intermediate formation of aromatic radical cations. The electron transfer has been characterized as occurring *via* an electrophilic interaction,[2] but the details of this interaction, *i.e.*, whether the electron transfer is the result of an inner- or outer-sphere process, could not be determined. It was desirable, therefore, to seek metal oxidants, capable of aromatic radical cation production, with which the electron-transfer mechanism could be more clearly defined.

Gillard[5] has recently shown that the excited triplet states of octahedral Co^{III} are better oxidants than the singlet ground states, but prior excitation to the excited states is necessary before reduction could occur. Tetrahedral Co^{III}, with a ground-state configuration $e^3t_2^3$ (^5E), is easily reduced without excitation by electron transfer to the low-energy e orbital, resulting in the configuration $e^4t_2^3$ ($^4A_2$), the ground state of tetrahedral Co^{III}. Tetrahedral Co^{III} has been observed in yttrium garnets,[6] but is of little interest for chemical reactions in this form. The only other known occurrence is in yellow potassium 12-tungstocobaltate(III),[7-10] $K_5[Co^{III}O_4W_{12}O_{36}]$, which is of more interest as an oxidant for aromatic hydrocarbons.

Heteropoly ion chemistry has been reviewed.[11,12] Crystalline $K_5[Co^{III}O_4W_{12}O_{36}] \cdot 20H_2O$ has the "Keggin" structure with tetrahedral Co^{III};[13-15] the Co^{II} form is isomorphous.[14] Electron exchange between the Co^{II} and Co^{III} compounds in solution is relatively rapid and proceeds *via* an outer-sphere electron transfer[16] unaccompanied by atom transfer.[17] Such electron transfer may occur *via* the tungstate framework of the heteropoly ion (a process responsible for "heteropoly blue" formation[18]). Thus a known outer-sphere electron transfer agent is being used as an oxidant for alkyl aromatics to determine whether such a process is feasible.

Experimental Section

The tungstocobaltates were prepared by literature methods.[7-9] The preparations are briefly described below.

Potassium hydrogen 12-tungstocobaltate(II) (1) was prepared by treating potassium 11-tungstodicobaltate(II)[7] with dilute hydrochloric acid. Partial evaporation of the resulting blue solution produced blue-green needles.

Potassium 12-tungstocobaltate(III) (2) was prepared by addition of solid potassium persulfate to a solution of the potassium 11-tungstodicobaltate(II) in 2 *M* H_2SO_4. The yellow solid was recrystallized three times from boiling water, resulting in yellow crystals.

Elemental and thermogravimetric analyses indicated that **1** was a 17-hydrate, $K_5H[Co^{II}O_4W_{12}O_{36}] \cdot 17\ H_2O$, and **2** was an 18-hydrate, $K_5[Co^{III}O_4W_{12}O_{36}] \cdot 18\ H_2O$.

Spectra.—Visible and ultraviolet spectra were determined on a Unicam SP800D spectrophotometer. The visible spectra of **1** and **2** were in agreement with those given by Simmons.[9]

The visible spectrum was used to analyze the extent of conversion of **2** to **1** in the oxidations described below. However, it was found that the intensity of the spectrum of **1** in water was significantly dependent on pH (although the position of the maximum at 16.06 kK was invariant); thus it was necessary to use a sodium acetate–acetic acid buffer (pH 4.6) for the analysis, which was performed as follows. The solid isolated from the heterogeneous oxidation (described below) was dissolved in a suitable amount of buffer solution and the visible spectrum recorded. The absorbances at 16.06 and 25.70 kK (A_1 and A_2, respectively) were read and the extent of conversion calculated from the known molar absorbances of **1** (218 and 130, respectively) and **2** (0 and 1225, respectively) by use of the equation

$$\%\ \text{conversion} = \frac{1225A_1}{218A_2 + 1095A_1} \times 100$$

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[1] A preliminary account has appeared: A. W. Chester, *Chem. Commun.*, 352 (1969).

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

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

[4] A. W. Chester, E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *Inorg. Nucl. Chem. Lett.*, **5**, 277 (1969).

[5] R. D. Gillard, *J. Chem. Soc., A*, 917 (1967).

[6] D. L. Wood and J. P. Remeika, *J. Chem. Phys.*, **46**, 3595 (1967).

[7] L. C. W. Baker and T. P. McCutcheon, *J. Amer. Chem. Soc.*, **78**, 4503 (1956).

[8] L. C. W. Baker and V. E. Simmons, *ibid.*, **81**, 4744 (1959).

[9] V. E. Simmons, Ph.D. Dissertation, Boston University, 1963.

[10] L. C. W. Baker, V. S. Baker, K. Eriks, M. T. Pope, M. Shibata, O. W. Rollins, J. H. Fang, and L. L. Koh, *J. Amer. Chem. Soc.*, **88**, 2329 (1966).

[11] L. C. W. Baker in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1962, p 604.

[12] P. G. Rasmussen, *J. Chem. Educ.*, **44**, 277 (1967).

[13] K. Eriks, N. F. Yanonni, U. C. Agarwala, V. E. Simmons, and L. C. W. Baker, *Acta Crystallogr.*, **13**, 1139 (1960); N. F. Yanonni, Ph.D. Dissertation, Boston University, 1961.

[14] N. F. Yanonni, V. E. Simmons, K. Eriks, and L. C. W. Baker, Abstracts, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1959, p 26N.

[15] J. F. Keggin, *Proc. Roy. Soc., Ser. A*, **144**, 75 (1934).

[16] P. G. Rasmussen and C. H. Brubaker, Jr., *Inorg. Chem.*, **3**, 977 (1964).

[17] G. Geier and C. H. Brubaker, Jr., *ibid.*, **5**, 321 (1966).

[18] M. T. Pope and G. M. Varga, *ibid.*, **6**, 1249 (1966), and references cited therein.

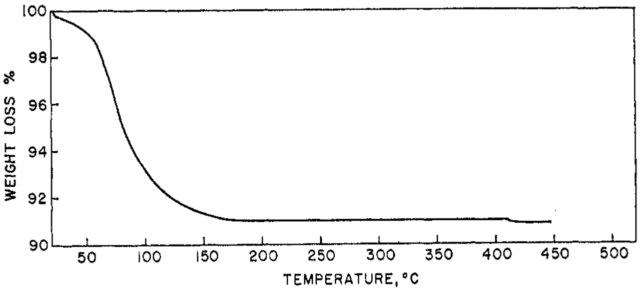


Figure 1.—Thermogravimetric analysis of $K_5[Co^{III}O_4W_{12}O_{36}]\cdot 18H_2O$ showing the loss of the last H_2O at ~420°.

Thermal Studies.—Thermogravimetric and differential thermal analyses (tga and dta) were performed on the Dupont 950 thermogravimetric analyzer and the Du Pont 900 differential thermal analyzer by Mr. A. Julian.

Gas Chromatography.—Gas chromatographic analyses were performed on an F & M research chromatograph (Model 810). The helium flow rate was 32 ml/min with a 10-ft silicone Se30 on Diataport column. A temperature program (6 min at 120°, heating to 250° at 10°/min, then isothermal at 250°) was used, with a sample volume of 5 μl.

Homogeneous Oxidation of Toluene by Potassium 12-Tungstocobaltate(III).—A solution of 20 g of 2 18-hydrate in a mixture of 15 ml of water and 75 ml of acetic acid was heated at reflux with 15 ml of toluene for 55 hr. After the mixture cooled, the solid was filtered and the filtrate evaporated. The resulting solid–liquid mixture was extracted with ether; the ether extract was dried over $MgSO_4$ and evaporated to give an oil. The oil was analyzed by gas chromatography and the major product was found to be benzyl acetate (confirmed by infrared spectrum). Small amounts of other components were found but not identified.

Heterogeneous Oxidation of Alkyl Aromatic Hydrocarbons by Potassium 12-Tungstocobaltate(III). Procedure.—Oxidations were performed in a glass-stoppered reaction vessels immersed in a constant-temperature bath at 96°. About 3 g (1 mmol) of 2 monohydrate (prepared by heating the 18-hydrate at 200°; see Results and Discussion) was covered with an excess (about 10 g) of hydrocarbon in the reaction vessel and placed in the bath for 100 hr.[19] The mixture was filtered into a tared filter flask and the solid analyzed for 1 and 2 as described above. The filtrate was partially evaporated *in vacuo* and analyzed by gas chromatography.

The products of the oxidation of toluene and *p*-xylene were established by comparison of ir and uv spectra and retention times with those of known samples. The identity of 2,4′,5-trimethyldiphenylmethane (from *p*-xylene) was established by the agreement of its ir and uv spectra with those given by Dannenberg, Neumann, and Dresler.[20] The products of the *o*- and *m*-xylene oxidations were assigned by analogy and by the similarity of the retention times to those of the toluene and *p*-xylene products.

Oxidations in the presence of benzene (cross-alkylation) were performed at 80.5°. Most of the benzene was removed in the partial evaporation of the product filtrate.

Results and Discussion

Dehydration of Potassium 12-Tungstocobaltate(III).—In preliminary experiments with 2 18-hydrate, large amounts of oxygenated products (alcohols and aldehydes) were formed, presumably from the lattice water. It was, therefore, desirable to use an anhydrous form for oxidations. However, tga indicated that only 17 mol of H_2O were lost upon heating to 200°, the remaining water being lost at about 420° (Figure 1). Dta studies showed an exotherm at approximately this temperature, indicating that loss of the last water leads to decomposition. The retention of 1 mol of water was confirmed in experiments at 200° in air.

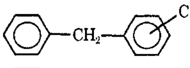
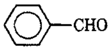
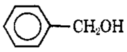
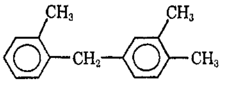
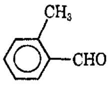
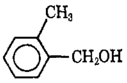
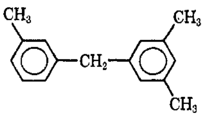
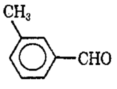
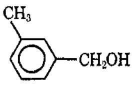
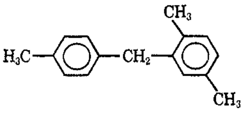
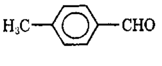
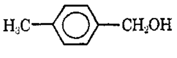
Oxidations were therefore carried out with the monohydrate. Use of the monohydrate led to increased yields of the diphenylmethane products (discussed below) and reduced quantities of the oxygenated materials.

The crystallographic data for potassium 12-tungstocobaltate(III)[13] do not show a unique water molecule in the structure. The water might reside between heteropoly frameworks, bonding them together. However, the occurrence of oxygenated products indicates that it is chemically reactive. The exact location and function of the unique water molecule is unknown at this time.

Oxidation Products.—The products, yields, and product distributions for the heterogeneous oxidation of toluene and the isomeric xylenes by $K_5[Co^{III}O_4W_{12}O_{36}]\cdot H_2O$ are given in Table I. The data for the

TABLE I

THE OXIDATION OF ALKYL AROMATIC HYDROCARBONS BY POTASSIUM 12-TUNGSTOCOBALTATE(III) MONOHYDRATE AT 96° (100 HR)

Substrate	Product[a]	Distribution wt, %	Yield, %[b,c]
Toluene		77	44
		23	
		Trace	
o-Xylene		61	26
		33	
		6	
m-Xylene		67	26
		26	
		7	
p-Xylene[d]		59 (40)	40 (12)
		34 (43)	
		7 (17)	

[a] Not all possible isomers are shown for the diphenylmethane derivatives. [b] Given only for diphenylmethane derivatives. [c] Based on Co^{III} consumed and a stoichiometry of $2Co^{III}$/hydrocarbon (see text). [d] Figures in parentheses represent the result of oxidation by the 18-hydrate.

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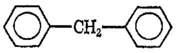
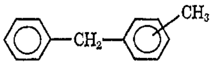
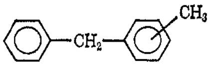
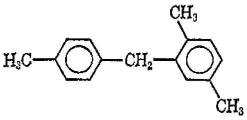
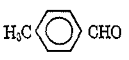
(19) Air was not rigorously excluded.

(20) H. Dannenberg, H. G. Neumann, and D. D. von Dresler, *Justus Liebigs Ann. Chem.*, **674**, 152 (1964).

oxidation in an excess of benzene are given in Table II. Production of diphenylmethane in this case constitutes, in effect, an alkylation of benzene by the benzyl group.

TABLE II
OXIDATIONS IN THE PRESENCE OF EXCESS BENZENE AT 80.5°[a]

Substrate	Mol of C_6H_6/ mol of substrate	Products[b]	Distribution, %	Yield, %
Toluene	12.0		66	Not determined
			32	
			2	
p-Xylene	15.3		45	66
			36	
			19	

[a] The monohydrate was used for these experiments; reaction time 100 hr. [b] Alcohols occurred only in trace amounts.

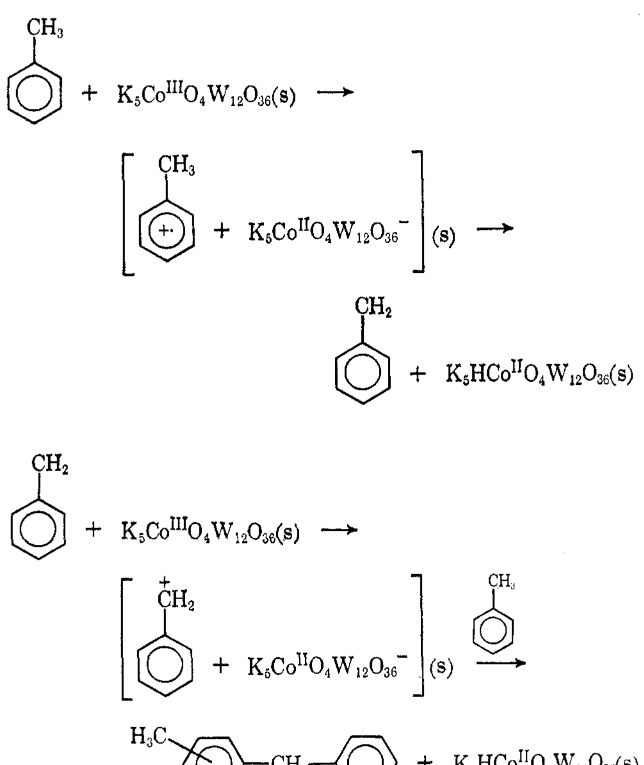
Mechanism.—It is well known that heteropoly ions oxidize many oxygen- and nitrogen-containing organic compounds with resultant formation of "heteropoly blues."[21] In all such oxidations, it is only the tungstate (or molybdate) framework that is reduced, not the central (hetero) atom. The present case thus constitutes the first example in which the central atom *alone* (tetrahedral Co^{III}) is the oxidizing agent and is reduced (to Co^{II}). The identity of the reduction product is clear from its visible spectrum, which is characteristic of tetrahedral Co^{II} and identical with that obtained with a known sample of **1**.

Studies of the behavior of the 12-tungstocobaltates in aqueous solution show that electron transfer is an outer-sphere process[16] and that the framework oxygens do not exchange with water.[17] The same is probably true in the oxidation of aromatic hydrocarbons: the oxidation occurs *via* outer-sphere electron transfer in which the heteropoly ion structure remains unchanged.

The diphenylmethane products could be formed by the attack of benzyl radicals or carbonium ions on the aromatic ring. However, benzyl radicals dimerize to form bibenzyl more rapidly than they add to aromatic rings. Since no bibenzyl products are observed, the benzyl radicals must be oxidized by the heteropoly ion to form benzyl carbonium ions. The benzyl radical can be formed by two possible paths: (a) hydrogen abstraction from a methyl group, followed by oxidation of the hydrogen atom to a proton, or (b) oxidation of the aromatic to a radical cation, followed by proton expulsion. Mechanism a seems less reasonable since there is no reason that the tungstate framework should accept a hydrogen *atom*. Also, this mechanism could not be operative in the oxidation of the radical to the carbonium ion, since no hydrogen abstraction would occur.

Mechanism b is more self-consistent. The electron transfer occurs *via* the overlap of the aromatic π system with tungstate framework "conduction" bands,[12,18] so that reduction of the framework occurs first. The framework, however, rapidly reduces the electronically less stable tetrahedral cobalt(III). The expulsion of the proton and its acceptance by the tungstate anion provides the charge balance necessary for a solid state reaction. The oxidation of the radical can occur by exactly the same process: electron transfer from the π system of the aromatic *via* the framework to the cobalt atom. The mechanism may be summarized for toluene as shown in Scheme I. The brackets indicate ion pairs formed within the solid. The steps leading to the ion pairs may in fact be equilibria. This sequence leads to a stoichiometry of $2Co^{III}$/hydrocarbon, and the yields of diphenylmethane derivatives in Tables I and II are calculated on this basis.

SCHEME I



The alcohol products result from the interaction of the carbonium ion with the remaining water in the 1-hydrate. The alcohol may be subsequently oxidized to the aldehyde in a manner similar to the above mechanism. A trace of unidentified high boiling compound is observed in the gas chromatographic analysis of the oxidation products, which may be an alcohol derived from the diphenylmethane derivative by oxidation as above.

The homogeneous oxidation of toluene in aqueous acetic acid (see Experimental Section) results in formation of benzyl acetate, indicating that a similar mech-

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(21) A. W. Seiling, Jr., Ph.D. Dissertation, Indiana University, 1962; J. H. Bellman, D. B. Borders, J. A. Buehler, and A. W. Seiling, *Anal. Chem.*, **37**, 264 (1965).

anism is operative. The carbonium ion reacts with the acetic acid solvent to form the acetate.

The electron-transfer reactions may occur at or near the solid surface, or within the crystal lattice. The crystal is composed of channels surrounded symmetrically by six heteropoly ions.[13] The channels are probably large enough to allow some penetration by the aromatic hydrocarbon, and the immediate availability of other heteropoly ions accounts for the ease of carbonium ion formation. The carbonium ion would then either diffuse out to react with other hydrocarbon molecules or react with the water in the lattice to form alcohol.

The aromatic radical cation is formed by outer-sphere electron transfer. Inner-sphere electron transfer is eliminated by the stability and nondestruction of the tungstate framework, which totally screens the cobalt(III) oxidant from direct interaction with the aromatic π system.

It is also significant that the oxidation occurs by outer-sphere electron transfer in a heterogeneous system. Such reactions are usually thought to occur by direct coordination to a metal on a surface or in a crystal.

The above results indicate that it is unnecessary to seek an inner-sphere electron transfer mechanism in the oxidation of alkyl aromatics in homogeneous systems,[2-4] *e.g.*, by direct coordination, since outer-sphere electron transfer is feasible.

Registry No.—Potassium 12-tungstocobaltate(III), 12419-42-0; toluene, 108-88-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3.

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Alkylation of N-Carbethoxy Tertiary Amines with Ethyl Bromoacetate

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The alkylation of ethyl 1-piperidineacetate (I), ethyl 4-morpholineacetate (II), ethyl N,N-diethylglycinate (III), and ethyl N,N-di-*n*-butylglycinate (IV) at 25, 40, 50, and 60° with ethyl bromoacetate in absolute methanol follows second-order kinetics. The k_2, ΔE, and ΔS values at 25° are 8.86, 0.89, 5.71, and 4.22 $\times 10^{-6}$ l./(mol sec), 17.2, 18.1, 14.6, and 14.8 kcal/mol, and 26.0, 27.6, 35.6, and 35.6 eu, respectively, for the above amines.

This research study investigated the effect of the structure of tertiary amines upon the reaction rate, the energy of activation, and the entropy of activation in the alkylation of the amines with ethyl bromoacetate in absolute methanol. The four amines investigated were ethyl 1-piperidineacetate (I), ethyl 4-morpholineacetate (II), ethyl N,N-diethylglycinate (III), and ethyl N,N-di-*n*-butylglycinate (IV).

The kinetics of the reactions were determined by potentiometric titration of the bromide ion produced using a silver nitrate solution with a glass electrode and a silver–silver bromide reference electrode. The reaction rates were determined from the slopes of the second-order plots. Activation energies were determined from the slope of the Arrhenius plots, and entropies of activation were calculated from the Eyring equation.

TABLE I

Reaction Rate Constants[a]

Temp, °C (±0.1°)	$k_P \times 10^6$	$k_M \times 10^6$	$k_E \times 10^6$	$k_B \times 10^6$
5	1.47	0.106		
20	5.56	0.506		
25	8.86	0.890	5.71	4.22
40	33.9	4.00	20.8	15.2
50	80.5	10.0	49.4	32.6
60	150	23.1	86.7	60.0

Comparison of the Reaction Rates

Temp, °C, (±0.1°)	k_P/k_M	k_P/k_E	k_P/k_B	k_E/k_B
5	14.0			
20	11.0			
25	10.0	1.55	2.10	1.35
40	8.46	1.63	2.24	1.37
50	8.08	1.63	2.46	1.51
60	6.46	1.72	2.49	1.44

[a] P = ethyl 1-piperidineacetate, M = ethyl 4-morpholineacetate, E = ethyl N,N-diethylglycinate, B = ethyl N,N-di-*n*-butylglycinate.

Results and Discussion

The experimental rate constant data are summarized in Table I where a is the initial molar concentration of ethyl bromoacetate and the tertiary amine in absolute methanol. The bimolecular rate constant, k_2, is defined by the familiar equation

$$dx/dt = k_2(a - x)^2 \tag{1}$$

The values of k_2 were calculated from the titration data by plotting

$$F(x) = x/(a - x) \tag{2}$$

vs. time where the slope of the plot is equal to ak_2. All of the F(x) *vs.* t plots were linear to 200 hr and remained so for several samples for as long as 800 hr. The percent of conversion to the quaternary salt varied from 2% for II at 20° to 83% for I at 60°. Most of the experiments were carried to 800 hr and longer, and deviations from linearity were noted in several runs at the higher temperatures. The average percentage error in determining F(x) between two or more identical samples was 2.8% with a standard deviation of 6.1%. This percentage is based upon a population of 144 F(x) determinations. Since the scatter of points increases with an increase of temperature, the accuracy of the F(x) determinations was considerably improved for