

## Zirconium Cocatalysis of the Cobalt-Catalyzed Autoxidation of Alkylaromatic Hydrocarbons

ARTHUR W. CHESTER,<sup>1</sup> ERIC J. Y. SCOTT, AND PHILLIP S. LANDIS<sup>1</sup>

*Central Research Division Laboratory, Mobil Research and Development Corp., Princeton, New Jersey 08540*

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Zirconium (and hafnium) compounds are remarkably effective cocatalysts for the cobalt-catalyzed autoxidation of alkyl aromatics in acetic acid. The autoxidation of *p*-xylene to terephthalic acid in the presence of zirconium and other metal salts has been studied at 100°C, 1 atm O<sub>2</sub>. Only Zr and Hf salts are very effective, increasing yields from 40 to 90% and decreasing induction times from 325 to 135 min. Th shows moderate activity. Zr and Hf salts are unique in (a) their ability to attain greater than sixfold coordination in solution and (b) their high stability toward reduction to lower oxidation states. A kinetic investigation of the zirconium acetate-cocatalyzed autoxidation of toluene at 87°C suggests that Zr favors Co(III) acetate monomer formation by formation of a weak Zr-Co complex.

### INTRODUCTION

The important role of cobalt in metal-catalyzed autoxidation of alkylaromatic hydrocarbons has been detailed (1). Ichikawa (2) has reported that salts of zirconium and other similar metals are effective cocatalysts in such systems when present in relatively small amounts. We have investigated both the scope and kinetics of this effect to obtain further insight into the mechanisms of transition metal catalyzed autoxidations.

### METHODS

For the scoping studies, the oxidation reactor was a jacketed 125-ml round bottomed flask, fitted with condenser, stirrer and thermometer. Water was refluxed in the outer jacket to maintain a reaction temperature of 100°C (other liquids could be used to maintain different temperatures).

<sup>1</sup> Current address: Mobil Research and Development Corp., Paulsboro, N.J. 08066.

Oxygen was admitted into the reactor through a sensitive pressure regulator set at 1.01 atm, a Wet Test meter and a drying tower. In each experiment, 0.1 mole of the aromatic substrate (*p*-xylene or *p*-toluic acid) and 1.4 moles acetic acid (85 g) were used. Cobalt was added as either cobalt(II) acetate tetrahydrate or cobalt(III) acetate. Each reaction was run for 22-24 hr. The solid terephthalic acid (TPA) was then filtered and washed with excess acetic acid (TPA is insoluble in acetic acid, while *p*-toluic acid is soluble). The solid TPA was dried and weighed. Yields quoted in this study are based on the weight of the dried TPA obtained in this manner. Esterification of some of the dried solid products always showed the presence of small amounts of *p*-carboxybenzaldehyde (2%) and *p*-toluic acid (1-5%). This oxidation technique is simple and reproducible. The data provide yields of TPA both from direct measurement (weight of washed and dried product) and from oxygen stoichiometry.

For the kinetic investigation, the general procedure, methods of analysis and most of the chemicals were the same as previously described (1).

Competitive autoxidations were studied using the standard apparatus. Toluene and toluene derivatives were run in pairs to establish their relative autoxidation rates in the presence and in the absence of zirconyl acetate. Concentrations were 0.5 *M* toluene or toluene derivative, 0.5 *M* chlorobenzene (internal standard), 0.25 *M* cobaltic acetate and 0.025 *M* zirconyl acetate. It is difficult to obtain good relative rate data for autoxidation reactions as is evident from a typical run (Fig. 5). After an apparent induction period the rates of autoxidation of both compounds are increased when zirconyl acetate is present. Rates were therefore compared by averaging the ratios of conversions over a number of equal time increments. Ratios involving conversions of less than 10% were ignored in view of limited accuracy at small conversions, the induction period and the fact that Co(III) acetate had not attained a relatively steady value.

Cobalt(III) acetate was prepared by passing ozone through an acetic acid solution of cobalt(II) acetate tetrahydrate (1). The product was analyzed for both Co(II) and Co(III) iodometrically. Other metal acetates were obtained commercially, except for scandium and hafnium acetates, which prepared by refluxing the chlorides with a 2:1 acetic-acetic anhydride mixture.

## RESULTS

The autoxidation of *p*-xylene to TPA proceeds via intermediate formation of *p*-toluic acid. The second step, oxidation of *p*-toluic acid, is generally much slower than the initial oxidation of *p*-xylene. In the experiments that follow, oxygen absorption curves give a qualitative indication of the rate of the first step, while TPA yields are a qualitative indication of the rate of

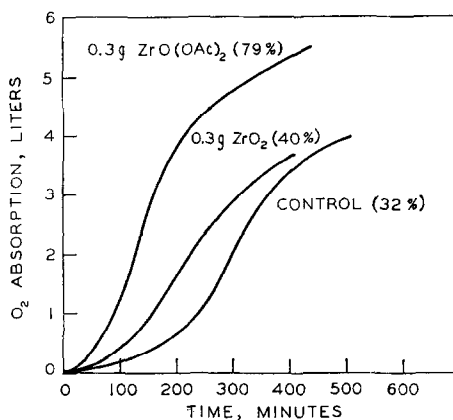


FIG. 1. Effect of Zr compounds on *p*-xylene autoxidation. TPA yields in parenthesis. Conditions: 100°C, 1.01 atm O<sub>2</sub>, 0.1 mole *p*-xylene, 1.4 moles acetic acid, 2.4 g Co(III) acetate.

the second step (except where *p*-toluic acid is the substrate).

*Autoxidations with Co(III).* When Co(III) acetate was used instead of Co(II) with the aromatic substrate, the induction period normally observed (*vide infra*) was eliminated. Oxygen absorption curves for the oxidation of *p*-xylene in the presence of Co(III) in the presence and absence of Zr are shown in Fig. 1. Note that solid ZrO<sub>2</sub> had virtually no effect while the soluble acetate, ZrO(OAc)<sub>2</sub>, radically increased both the rate of reaction and final yield.

In the oxidation of *p*-toluic acid, two effects were studied: the effect of zirconium acetate and the effect of increasing the cobalt(III) levels. The results are shown in Fig. 2. The addition of up to 10× the "standard" quantity of cobalt(III) increased the reaction rate and yields in a nonlinear manner. However, the addition of only  $1.5 \times 10^{-3}$  moles ZrO(OAc)<sub>2</sub> to the "standard" Co(III) charge (Co/Zr = 6.7) gave a TPA yield equivalent to that obtained at 10× the initial Co(III) level. Moreover, the rate of reaction was significantly faster in the presence of ZrO(OAc)<sub>2</sub>. The use of ZrO(OAc)<sub>2</sub> in the absence of cobalt gave no reaction at all (also true for *p*-xylene).

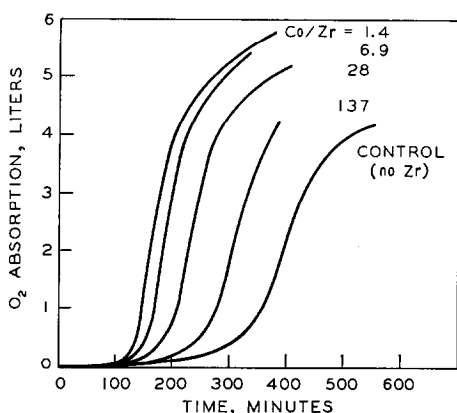


Fig. 3. Effect of Zr concentration on *p*-xylene autoxidation. See Table 1 for conditions.

*Oxidations with cobalt(II).* The remaining oxidations were all run with added cobalt(II), rather than Co(III), in order to examine the effect of Zr on the induction time as well as yields. Induction times were determined at the intersection of the initial and maximum oxidation slopes and visually correspond to the appearance of green Co(III) acetate in the reaction mixture.

The effect of zirconium concentration on the cobalt-catalyzed oxidation of *p*-xylene was studied. The oxygen absorption curves are shown in Fig. 3 and the data in

Table 1. The lowest level of Zr (with Co/Zr = 137) produced a dramatic increase in yield and decrease in induction time. At Co/Zr below about 7 there was little further improvement in either yield or induction time. Oxidation rates appeared about equal for the Zr-cocatalyzed experiments, except for the lowest Zr level.

*Cocatalytic effect of other metal acetates.* A series of other metal acetates were investigated for possible cocatalytic effect. Figure 4 shows oxygen absorption curves for some of these other compounds. Induction times and yields are listed in Table 2 for the entire series. Hafnium showed an almost identical effect as zirconium, as expected from its very similar chemistry. Of the remainder, only thorium showed any effect on yield (and therefore on *p*-toluic acid oxidation rate). The group IIIA acetates (Sc, Y, La) had a notable effect on induction time, but none on yield (rate). Of the remainder, only gallium showed a positive effect, very similar to the effect of thorium, while others had a distinct inhibitory effect (Tl, U, Be, Ce).

*Kinetics of autoxidation of toluene and substituted toluenes.* A typical cobalt-cata-

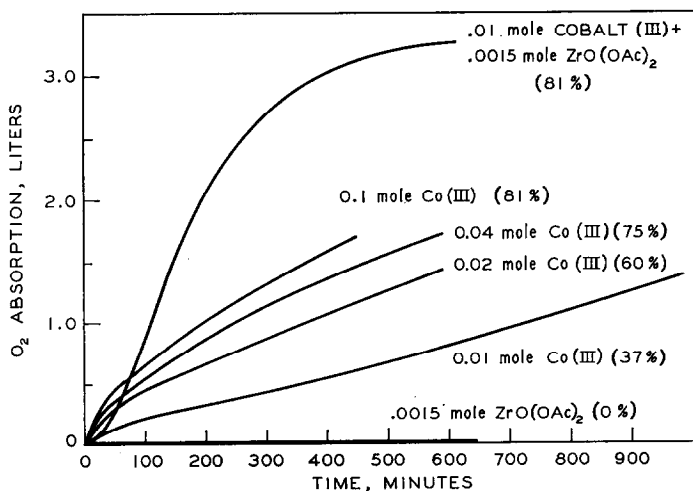


Fig. 2. Effect of Cobalt (III) and Zirconium on the autoxidation of *p*-toluic acid. TPA yields in parentheses. Conditions: 100°C, 1.01 atm O<sub>2</sub>, 0.1 mole *p*-toluic acid, 1.4 moles acetic acid, Co and Zr as given.

lyzed autoxidation of toluene to benzoic acid in the presence of zirconyl acetate is shown in Fig. 5. The cocatalyzed reaction is complicated by exhibiting autocatalytic features. Initially the reaction follows the zirconium-free autoxidation (the "induction period"). The rate then increases to a maximum, and subsequently decreases. This rate dependence is similar to that found in autocatalytic systems.

The effects of reactant concentrations on the induction period and the maximum autoxidation rate are shown in Table 3. The degree of reproducibility is illustrated by Runs 3 and 8. Apparent orders were found by keeping initial concentrations of all but one reactant constant, and plotting  $\log$  (reciprocal induction period) and  $\log$  (maximum rate) against  $\log$  (concentration) (Table 4).

The marked increase in induction period with increasing hydrocarbon concentration (as exemplified by a negative reaction order of  $-0.35$  for toluene) is also observed in the autoxidation of *p*-chlorotoluene (Fig. 6). The negative orders with respect to Co(II) acetate are illustrated by marked inhibitions in both the induction period and the region of maximum rate (Figs. 7 and 8).

TABLE 1

Effect of Zirconium Concentration on the Cobalt(III)-Catalyzed Autoxidation of *p*-xylene at 100°C and 1.00 atm O<sub>2</sub><sup>a</sup>

Moles ZrO(OAc) <sub>2</sub> × 10 <sup>5</sup>	Induction time (min)	TPA yield (%)
0	325	40
7.3	260	72
36	190	87.5
145	150	90
730	135	88

<sup>a</sup> Cobalt(II) = 0.01 mole, *p*-xylene = 0.1 mole, acetic acid = 1.4 moles.

Inasmuch as the orders with respect to Co(II) are negative, the apparent orders with respect to Co(III) must therefore be  $>1.4$  for the induction period and  $>0.1$  for the maximum rate. The fractional order for Zr suggests that the active Zr species in monomeric, but is derived from a multimer, although other interpretations of the fractional order are possible.

In catalyst pretreatment experiments (Table 5), it was found that the induction time was reduced only when zirconyl acetate, cobalt(III) acetate and oxygen were present together. Increasing the pre-

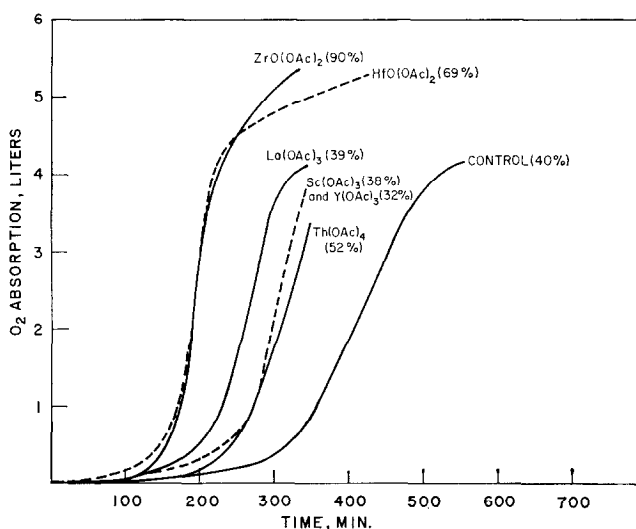


FIG. 4. Effect of various metal acetates on *p*-xylene autoxidations. See Table 2 for conditions.

TABLE 2

Effect of Metal Acetates on the Cobalt(II)-Catalyzed Autoxidation of *p*-xylene at 100°C and 1.01 atm O<sub>2</sub><sup>a</sup>

Metal acetate	Moles × 10 <sup>3</sup>	Induction time (min)	TPA yields (%)
—	—	325	40
ZrO(OAc) <sub>2</sub>	1.45	150	90
HfO(OAc) <sub>2</sub>	1.3	165	69
Sc(OAc) <sub>3</sub>	1	260	38
Y(OAc) <sub>3</sub>	1	245	32
La(OAc) <sub>3</sub>	1	215	39
Th(OAc) <sub>4</sub>	1	265	52
UO <sub>2</sub> (OAc) <sub>4</sub>	1	>400	33
GaO(OH)	1	270	51
In(OAc) <sub>3</sub>	1	270	31
Tl(OAc) <sub>3</sub>	1	>400	14
Zn(OAc) <sub>2</sub>	1	170	34
Be <sub>2</sub> O(OAc) <sub>6</sub>	1	>400	18
Ce(OAc) <sub>3</sub>	1	>400	—

<sup>a</sup> Cobalt(II) = 0.01 mole, *p*-xylene = 0.1 mole, acetic acid = 1.4 moles.

treatment period further reduced the induction time. No oxygen absorption was observed during the pretreatment.

The relative cobalt-catalyzed autoxidation rates of toluene and toluene derivatives were compared in the presence and absence of zirconyl acetate. The results, shown in Table 6, indicate that zirconyl acetate has no effect on the relative autoxidation rates of toluene derivatives despite the fact that the overall autoxidation rates have been greatly enhanced, i.e., the rate-determining step in the autoxidation appears to be unchanged.

*Effect of polar products on zirconium co-catalysis.* Experiments dealing with the effects of Zr on autoxidation of intermediates show no effect. The nature of the evidence is as follows: If polar intermediates such as benzyl intermediates have an effect on the Zr/Co(III) autoxidation, one would expect a reciprocal effect of

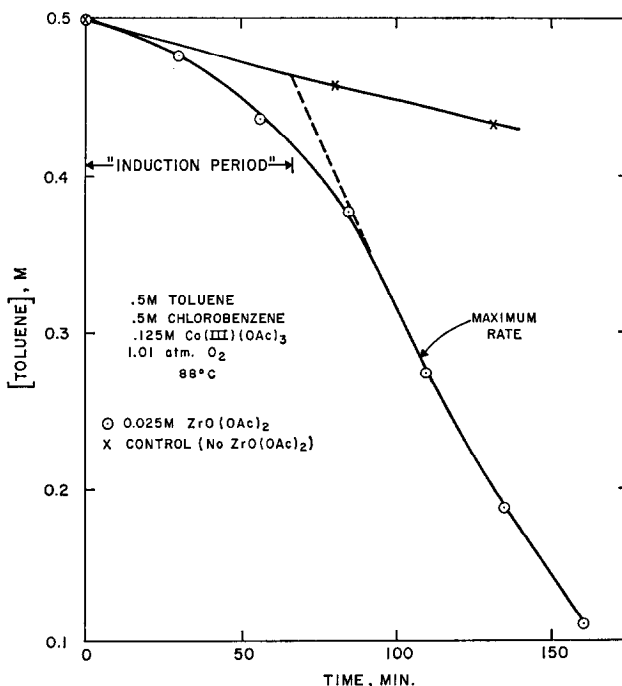


FIG. 5. Co(III) acetate-catalyzed autoxidation of toluene in acetic acid at 88°C in the presence and absence of zirconyl acetate.

TABLE 3

Kinetic Data for the Co(III) Acetate Autoxidation of Toluene in Acetic Acid at 87°C  
in the Presence of Zirconyl Acetate

	Initial concn ( <i>M</i> )			[Co(III)] <sub>ss</sub> <sup>b</sup>	Induction period (min)	Maximum rate (10 <sup>5</sup> <i>M</i> sec <sup>-1</sup> )
	Toluene <sup>a</sup>	Co(III)	ZrO(OAc) <sub>2</sub>			
1	0.5	0.25	0.025	0.135	20	7.2
2	0.5	0.188	0.025	0.108	46	7.0
3	0.5	0.125	0.025	0.073	67	6.7
4	0.5	0.063	0.025	—	>135	—
5	0.5	0.125	0.0063	0.070	120	4.4
6	0.5	0.125	0.100	0.076	23	12.7
7	1.0	0.125	0.025	0.068	85	10.9
8	0.5	0.125	0.025	0.073	68	6.4

<sup>a</sup> This is also the concentration of the internal standard, chlorobenzene.

<sup>b</sup> Steady-state concentration of Co(III) acetate.

zirconium on oxidation reactions involving Co(II), Co(III), oxygen and the intermediate. At the low concentrations of zirconium used and at Zr/Co(III) ≤ 0.2 no effect of Zr was observed on the rates of the following reactions in acetic acid solution: (a) The oxidation of Co(II) to Co(III) by benzylhydroperoxide, (b) The oxidation of Co(II) to Co(III) in the presence of oxygen and benzaldehyde, (c) The oxidation of benzyl alcohol by Co(III) in the absence of oxygen.

#### DISCUSSION

Zirconium (and hafnium) clearly acts as a true homogeneous cocatalyst in the cobalt-catalyzed autoxidation of alkylaromatic hydrocarbons as evidenced by the lack of a significant effect of solid ZrO<sub>2</sub>

(with Co) and of ZrO(OAc)<sub>2</sub> in the absence of cobalt.

Comparison of the various metal salts (Table 2) leads to the conclusion that the cocatalytic activity is derived from (a) an ability to attain greater than sixfold coordination in solution, and (b) high stability toward reduction to lower oxidation states.

The availability of more than six coordination sites is a common property of Zr and Hf (the acetylacetonates have coordination numbers of 8), but one not generally observed for other similar metal salts. An octahedral, monomeric Zr(IV) complex in solution may more easily distort in order to coordinate to incoming groups, whether organic or cobalt species, than other metal ions. The potentially larger coordination number is one factor that differentiates Zr and Hf from the metals surrounding them in the periodic table.

Further, the large reduction potentials necessary for reduction of the maximum oxidation states, Zr(IV) and Hf(IV), to their lower oxidation states effectively eliminates oxidation-reduction reactions of Zr and Hf from occurring and eliminates their interference in other necessary oxidation-reduction reactions during the

TABLE 4

Apparent Reaction Orders in the Zirconium-Cocatalyzed, Cobalt-Catalyzed Autoxidation of Toluene in Acetic Acid at 87°C

Reactant	Induction region	Maximum rate region	Conc range ( <i>M</i> )
Toluene	-0.35	0.7	0.5-1.0
Total Co	1.4	0.1	0.06-0.25
Zr(OAc) <sub>2</sub>	0.65	0.35	0.006-0.1
Co(II)	<0	<0	—

autoxidation. Zirconium(IV) and hafnium(IV) are virtually impossible to reduce in solution; the only known trivalent compounds are the halides, which must be prepared by reduction of the tetrahalides at high temperature with the metals themselves. This criterion does not eliminate the Group IV elements Sc, Y, and La, as their lower oxidation states are equally inaccessible; they are eliminated by virtue of their coordination numbers being no higher than 6 in solution.

In coupling these two features—large coordination number and lack of oxidation-reduction behavior—with the other necessities for cocatalysts—solubility and stability in acetic acid—it becomes clear that only Zr and Hf, of the commonly available

metals, possess these properties. It may be noted, in addition, that of the other metals investigated here, only thorium and gallium showed moderate cocatalytic activity (see Table 5). Thorium(IV) fits the criteria outlined above, i.e., the availability of more than six coordination sites and the inaccessibility of lower oxidation states.

The metals that reduce induction time, but do not increase rate of autoxidation (Sc, Y, La, Ga, In, Zn) appear to conform to the criterion for lack of oxidation-reduction behavior but do not have the ability to expand their coordination spheres. Since the induction time is related to the appearance of Co(III), these metals perhaps interfere in the thermal decomposition of Co(III). The metals that inhibit reaction

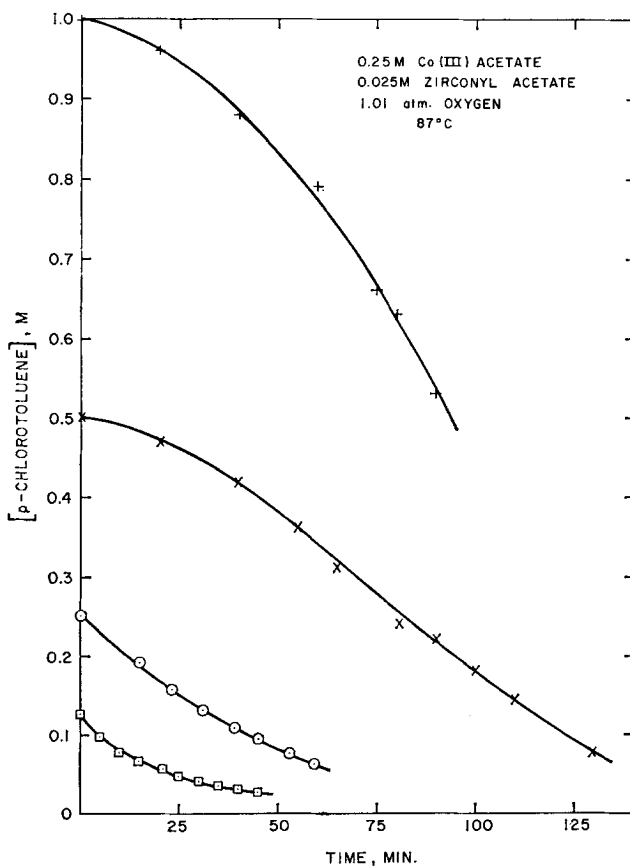


Fig. 6. Effect of initial *p*-chlorotoluene concentration on the Co(III)-catalyzed autoxidation of *p*-chlorotoluene in presence of zirconyl acetate in acetic acid.

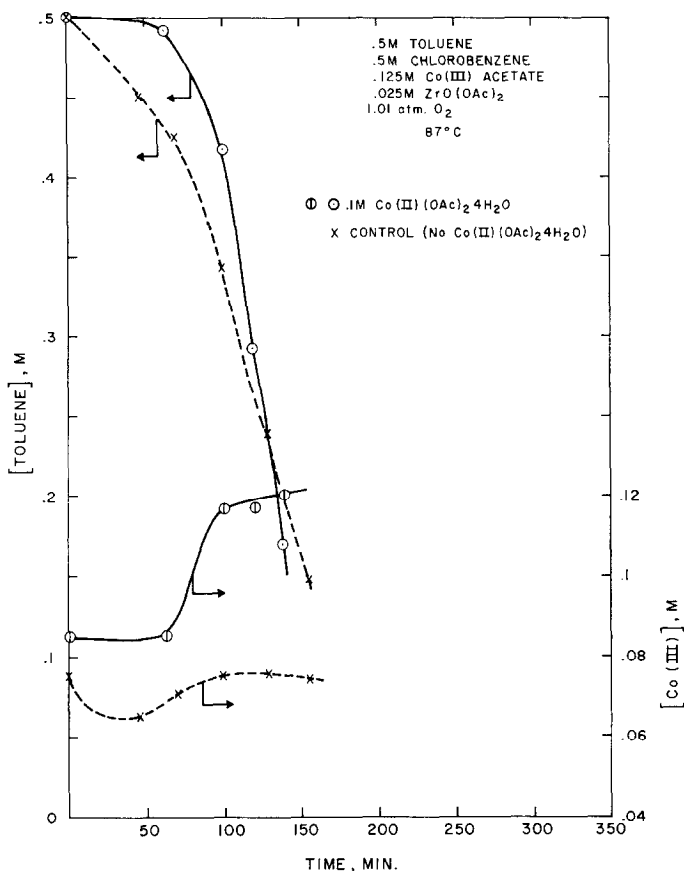


FIG. 7. Effect of Co(II) acetate tetrahydrate on the induction period of the Co(III)-catalyzed autoxidation of toluene, in the presence of zirconyl acetate.

rate as well as prolong induction times (U, Tl, Ce) are all, except for Be, easily reducible in solution, in spite of being able to attain larger coordination numbers in some cases (e.g., Ce). These oxidants clearly are interfering in many steps of both the induction period and autoxidation itself by oxidizing critical intermediates.

*Kinetics.* During the autoxidations reported above, Co(III) concentrations were observed to be 10–15% higher when Zr was present. That this increase is insufficient to account for the large rate increases is demonstrated as follows: the rate law (in the absence of zirconium) for the Co(III)-catalyzed autoxidation of toluene in acetic

acid was shown (1) to be

$$-\frac{d[\text{RH}]}{dt} = k_a \frac{[\text{Co(III)}]^2[\text{RH}]}{[\text{Co(II)}]} + k_b[\text{Co(III)}]^2[\text{RH}], \quad (1)$$

where [RH] represents the toluene concentration. If the cocatalytic effect of zirconyl acetate is merely to increase the concentration of Co(III) acetate and decrease concentration of Co(II) acetate, the maximum rate of autoxidation should be predictable from Eq. (1). However, the experimental values are 4 to 10 times as great as those predicted by Eq. (1) (Table



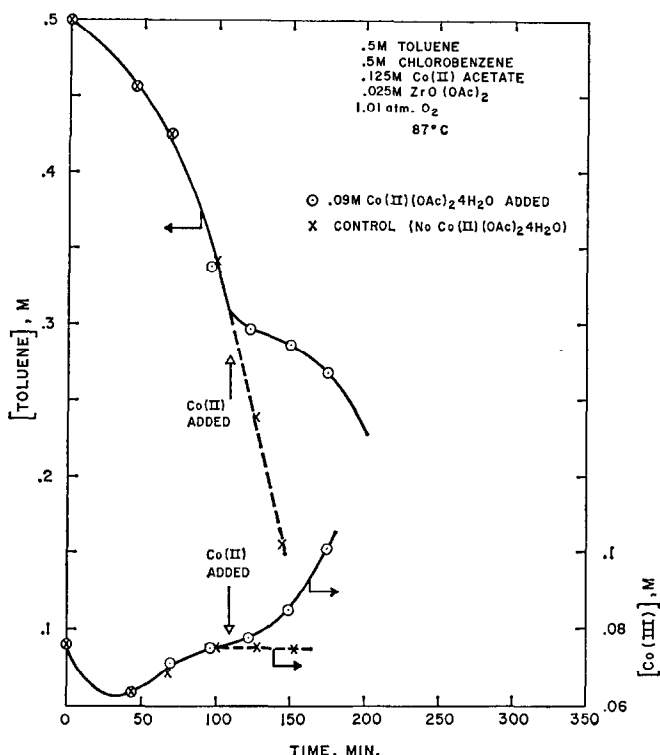


FIG. 8. Effect of the addition of Co(II) acetate tetrahydrate on the maximum rate of the Co(III)-catalyzed autooxidation of toluene, in the presence of zirconyl acetate.

7). Thus the enhancement in reaction rate in the presence of zirconyl acetate cannot be accounted for simply by the observed changes in Co(III) and Co(II) concentrations. The increased Co(III) concentrations

are the result of, rather than the reason for, zirconium cocatalysis.

The autooxidation kinetics in the presence of zirconyl acetate suggest two superimposed reactions: (a) the formation during

TABLE 5

Effect of Pretreatment on Induction Period and Maximum Rate<sup>a</sup>

	Reactants pretreated				Pretreatment period (min)	Induction period (min)	Maximum rate (10 <sup>6</sup> M sec <sup>-1</sup> )
	Zr	Co(III)	Toluene	O <sub>2</sub>			
1	No	No	No	No	0	67	6.7
2	Yes	Yes	Yes	No	80	>100	—
3	Yes	Yes	No	Yes	60	51	6.9
4	Yes	Yes	No	Yes	120	40	6.6
5	Yes	Yes	No	No	60	60	3.5
6	Yes	No	No	Yes	60	69 <sup>b</sup>	<6.9
7	No	No	No	No	0	68	6.4

<sup>a</sup> Conditions: 0.5 M toluene, 0.5 M chlorobenzene, 0.125 M Co(III) acetate, 0.025 M ZrO(OAc)<sub>2</sub>, 1.01 atm O<sub>2</sub> in acetic acid at 87°C.

<sup>b</sup> Determined by oxygen absorption.

the induction period of an active catalytic species, and (b) the normal reaction which obeys rate law [Eq. (1)] and in which the active species plays a more dominant role than in the noncatalyzed reaction. The results are consistent with the postulate that zirconyl acetate disturbs the monomer-dimer equilibrium of Co(III) acetate. Rate law [Eq. (1)] has previously been shown to be consistent with a two-path mechanism derived from such an equilibrium (1): the term second-order in Co(III) arises from oxidation of RH to its radical cation by the predominant Co(III) dimer, while the term half-order in Co(III) arises from the oxidation of RH by the very active Co(III) monomer.

During the induction period, zirconyl acetate can form a weak complex with Co(III) acetate monomer, thus displacing the equilibrium towards the monomer. This process appears to require the presence of oxygen since the induction period is shortened only in the presence of oxygen, and no enhancement in rate is observed in the oxidation by Co(III) acetate when oxygen is absent. The Zr-Co complex may contain a peroxy or superoxy bridge—both Zr and Co are known to form such complexes. Hydrocarbons, on the other hand, inhibit formation of the complex, probably by loosely complexing with one or more of the

TABLE 6  
Relative Rates of Autoxidation of Substituted  
Toluenes with Co(III) Acetate at 87°C

Group	$\sigma^+$	Zr	
		Absent	Present
Hydrogen	0	1	1
<i>p</i> -Fluoro	0.071	1.12	—
<i>p</i> -Chloro	0.112	0.83	0.885
<i>m</i> -Chloro	0.373	0.59	0.55
<i>p</i> -Cyano	0.628	0.32	0.33

components. The fact that toluene can inhibit in this way is evidence that the complex of zirconyl acetate with the monomer is, in fact, weak.

If the effect of zirconium is only on Co(III) monomer formation and/or reactivity, then zirconium would only affect the first term of rate law [Eq. (1)]. The rate law for the oxidation in the presence of zirconium (neglecting the induction period) then becomes

$$\frac{-d[\text{RH}]}{dt} = k_a' \frac{[\text{Co(III)}]^\dagger}{[\text{Co(II)}]} [\text{RH}] + k_b [\text{Co(III)}]^2 [\text{RH}], \quad (1a)$$

where  $k_b$  has the same value as in rate law [Eq. (1)]. The observed first order rate

TABLE 7  
Calculated and Experimental Maximum Rates for the Co(III)-Catalyzed Autoxidation of  
Toluene at 87°C in the Presence of Zirconyl Acetate<sup>a</sup>

Concn (M)			Maximum rate of reaction		
[Co(III)] <sub>0</sub>	[Co(III)] <sub>ss</sub>	[Co(II)] <sub>ss</sub>	Calcd	Experimental	
			$k(10^5 \text{ sec}^{-1})$	$R_{\text{max}}(10^5 M \text{ sec}^{-1})$	$R_{\text{max}}(10^5 M \text{ sec}^{-1})$
0.25	0.135	0.115	7.38	1.85	7.2
0.1875	0.108	0.0795	4.93	1.23	7.0
0.125	0.073	0.052	2.58	0.65	6.7

<sup>a</sup> Initial conditions: 0.5 M toluene, 0.5 M chlorobenzene (internal standard), 0.025 M ZrO(OAc)<sub>2</sub>, Co(III) acetate concentrations as noted below. Toluene concentration at maximum rate ~0.25 M.

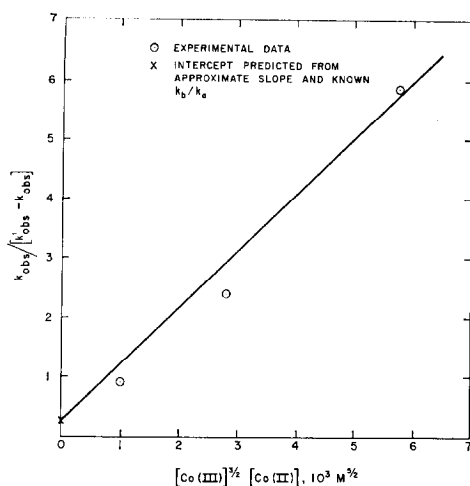


Fig. 9. Computation of  $k_a'$  from observed first order constants in the presence and absence of zirconyl acetate.

constant becomes

$$k_{\text{obs}}' = k_a' \frac{[\text{Co(III)}]^{1/2}}{[\text{Co(II)}]} + k_b [\text{Co(III)}]^2. \quad (2)$$

The ratio of the rate constant in the presence of zirconium to that in its absence is given by

$$\frac{k_{\text{obs}}}{k_{\text{obs}}' - k_{\text{obs}}} = \frac{k_a}{k_a' - k_a} + \frac{k_b}{k_a' - k_a} \times [\text{Co(III)}]^2 [\text{Co(II)}]. \quad (3)$$

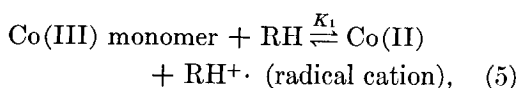
In order to evaluate the rate constants from Eq. (3) for 0.025 *M* zirconyl acetate, data from Runs 1 to 3 (Table 4) were used in conjunction with data collected previously in zirconium-free experiments (1). Tangential slopes were determined from semi-logarithmic data curves to determine apparent first-order rate constants from both data sets at identical Co(III) concentrations. A plot of these data according to Eq. (3) is shown in Fig. 9. From the known values (1) of  $k_a$  and  $k_b$ , the value of slope/intercept =  $k_b/k_a$  is 3900  $M^{-3/2}$ . The intercept could therefore be determined by estimating an approximate slope and dividing by 3900 (the estimated intercept is

shown in Fig. 9). The slope so obtained gives a value of  $5.1 \times 10^{-6} M^{1/2} \text{sec}^{-1}$  for  $k_a'$ , which is equivalent to  $5.1k_a$ .

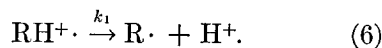
The rate constant  $k_a$  has been shown (1) to be given by

$$k_a = \left(\frac{2^3}{2}\right) k_1 K_1 K_D^{1/2}, \quad (4)$$

where  $K_D$  is the Co(III) monomer-dimer equilibrium constant,  $K_1$  is the equilibrium constant for



and  $k_1$  is the rate constant for the rate-determining step,



If the effect of zirconium were only on the monomer-dimer constant,  $K_D$ , then the monomer-dimer constant in the presence of zirconium,  $K_D'$ , would be  $(5.1)^2 = 26$  times larger than  $K_D$ . If  $K_D$  is small, e.g.,  $10^{-4} M$ , then an enhancement of  $K_D$  of that order of magnitude would still be consistent with the previously proposed mechanism (1) and rate law [Eq. (1)], since the Co(III) dimer would still be predominant, even though the monomer concentration would be an order of magnitude greater. However, if zirconium weakly complexes with the Co(III) monomer, it might also enhance the reactivity of the monomer and therefore raise the value of  $K_1$ , leading to an enhancement of  $k_a$ . The rate constant  $k_1$  would not be affected, since Co(III) is not involved.

The fivefold rate increase in the presence of zirconium can be due to an increase in any or all of  $k_1$ ,  $K_1$  and  $K_D$ . The relative reactivity data reported in Table 7 indicate that the nature of the rate-determining step is largely unchanged. However, under the conditions used (0.25 *M* cobalt), the contribution of the different terms in rate laws

[Eqs. (1) and (1a)] vary in the zirconium and nonzirconium experiments. At 0.25 *M* cobalt with 50% conversion to Co(III) {i.e., [Co(III)] = 0.125 *M*}, the contribution of the first term [Co(III) monomer] to the total rate is only approximately 5% in the absence of zirconium, but 20% in the presence of zirconium. Considering only rate and equilibrium constants which involve hydrocarbon, it follows that when zirconium is absent, we are essentially comparing values of  $k_b$ , whereas when zirconium is present, the contribution of  $(k_1K_1)$  to  $k_{obs}$  is considerably enhanced. If zirconium increases the overall rate by increasing either of the values of  $k_1$  or  $K_1$  (i.e.,  $K_1' > k_1$ ;  $K_1' > K$ ), then for any two hydrocarbons A and B we would expect that

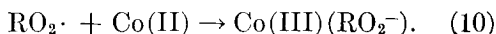
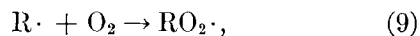
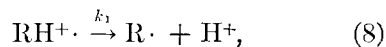
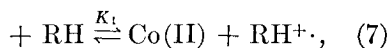
$$\frac{(k_{obs}')^A}{(k_{obs}')^B} \neq \frac{(k_{obs})^A}{(k_{obs})^B} \approx \frac{(k_b)^A}{(k_b)^B}.$$

The fact that the two ratios are approximately identical strongly suggests that the values of  $k_1$ ,  $K_1$  as well as  $k_b$  are relatively unaffected by zirconium. It is reasonable therefore to conclude that the rate enhancement by zirconium is due to the enhancement of the remaining constant,  $K_D$  (which does not involve hydrocarbon), by formation of a weak zirconyl acetate-Co(III) acetate monomer complex.

The dominance of the first term in Eq. (1a) can account for the slightly increased amounts of Co(III) observed when zirconium is present. The first term is due to oxidation of RH by the Co(III) monomer and results in production of a benzyl radical (1), which results in higher Co(III)

concentration by the following process:

Co(III) monomer



The second term in Eqs. (1) and (1a), which dominates the overall rate in the absence of zirconium, is due to oxidation of RH by the predominant Co(III) dimer. This pathway results in production of the carbonium ion,  $R^+$ , which would react further to form benzyl acetate or alcohol. No regeneration and further consumption of Co(III) occurs. Thus the increased Co(III) levels in the presence of zirconium can be accounted for by the increased reaction *via* reactions (7) to (10). In both instances Co(III) is regenerated by additional reactions involving aldehydes which are not clearly understood.

#### CONCLUSION

The cocatalytic effect of zirconium is attributable to a combination of properties not found in combination in most metal ions—large coordination number and lack of reducibility. In combination with dimeric Co(III) acetate, the additional coordination sites can bond weakly with the reactive Co(III) acetate monomer, thus increasing the monomer concentration. The poor reducibility of Zr(IV) prevents its interference in redox reactions occurring simultaneously.

#### REFERENCES

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