

cedure used to obtain electronic spectra, 5 mL of a 1.0–1.5 mM solution of the ATCr complex was stirred with 1.46 g of silica gel to form a slurry; the solvent was then evaporated under a stream of N₂. This sample was transferred to the test tube portion of the cell, and 7 mL of cyclohexane was added to it. The slurry was then placed in the path of the laser beam for short intervals of time with a maximum conversion of 15%. A fresh slurry was used for each photolysis period. The optically dense slurries were stirred by a cyclohexane-saturated N₂ purge as described above. After each photolysis period, the purge was disconnected and a portion of the slurry was poured into the cuvette portion of the cell. The cell was gently shaken for several minutes to ensure dense, reproducible packing of the silica gel in the optical path. Disappearance of the complex was monitored at 350 nm.

For both solutions and slurries, disappearance quantum yields, ϕ_d , were calculated by using a computer program.² Good linearity

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in the data were found including extrapolation to zero conversion at zero time. Values of ϕ_d are based on at least three complete sets of data with five data points per set. The quantum yields are uncorrected for reflective and scattering losses; reproducibility was $\pm 15\%$.

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Registry No. Cr(CO)₆, 13007-92-6; Mn₂(CO)₁₀, 10170-69-1; (benzene)tricarbonylchromium(0), 12082-08-5; (acetophenone)tricarbonylchromium(0), 12153-11-6; (acenaphthene)tricarbonylchromium(0), 81434-75-5.

Cleavage of Acylcobalt Carbonyl with Hydridocobalt Tetracarbonyl

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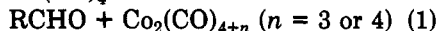
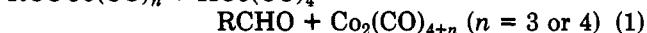
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The reaction $\text{CH}_3(\text{CH}_2)_4\text{COC}(\text{CO})_4 + \text{HCo}(\text{CO})_4 \rightarrow \text{CH}_3(\text{CH}_2)_4\text{CHO} + \text{Co}_2(\text{CO})_8$ proceeds with second-order kinetics (first order in each reactant), $k_2 = 1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 23 °C. Contrary to earlier reports we find that the rate is independent of the partial pressure of CO. Less viscous solvents give somewhat faster rates. The kinetic isotope effect, $k[\text{HCo}(\text{CO})_4]/k[\text{DCo}(\text{CO})_4]$, is equal to 3.6. Although no direct evidence has been secured, our results suggest that the mechanism of the reaction involves fast reversible homolysis of the acyl compound followed by hydrogen abstraction from $\text{HCo}(\text{CO})_4$ in the rate-controlling step. The reaction of $\text{HCo}(\text{CO})_4$ with $\text{RCOC}(\text{CO})_4$ is slower than its reaction with $\text{Ph}_2\text{C}=\text{CH}_2$ but faster than its reaction with 1-pentene. The kinetic data strongly suggest that the slow step in stoichiometric hydroformylation is very likely the initial π complexation of olefin with $\text{HCo}(\text{CO})_3$ rather than the final cleavage step of the acyl complex to aldehyde.

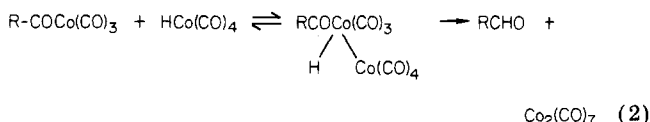
Introduction

The mechanism of the cleavage of acylcobalt carbonyls with $\text{HCo}(\text{CO})_4$ (eq 1) remains unresolved despite more

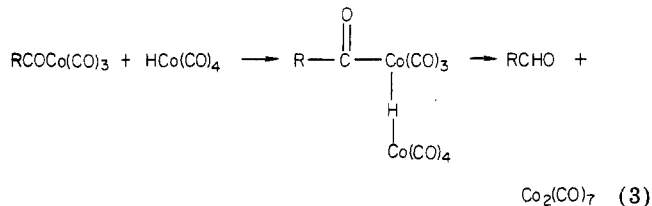


than 40 years of investigations of the oxo process in which this reaction is assumed to play a major role. Equation 1 is crucially important in the stoichiometric reaction¹ and is thought to also play a role in the catalytic process.²

The usual proposal for the mechanism of reaction 1 involves oxidative addition followed by reductive elimination. Because acylcobalt tetracarbonyl and hydridocobalt tetracarbonyl are both coordinatively saturated, it is assumed that in the cleavage reaction one of them is a tricarbonyl species and that the most likely candidate is the acyl compound. The reaction has thus been written as in eq 2³ or a somewhat similar formulation in which the



hydrogen is not completely transferred to the acyl complex in the transition state.^{4a,b} More recently the generalized process of which eq 2 is an example has been called a binuclear reductive elimination.⁵ The process has also been visualized as occurring by hydrogen transfer from the metal hydride to the coordinatively unsaturated second metal center, without metal–metal bond assistance, followed by reductive elimination.⁵ In the example under discussion this would be represented by eq 3 without specifying



whether the binuclear species is an intermediate or a transition state.

The principal support for the oxidative addition–reductive elimination proposal in the cobalt case is the

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Table I. Rate of $\text{CH}_3(\text{CH}_2)_4\text{COCO}(\text{CO})_4 + \text{HCo}(\text{CO})_4$ Reaction^a

$10^2[\text{HCo}(\text{CO})_4]$	$10^2[\text{RCOCO}(\text{CO})_4]$	hexanal, %	10^2k^b	CO, atm
6.72	6.72	78	1.00	1
7.42	7.42	78	1.05	O (N ₂)
7.16	7.16	54 ^c	1.28	4
15.45	7.72	96	1.10	1
6.58	12.68	96	1.05	1

^a At 23 °C in ether solution. ^b $\text{M}^{-1} \text{s}^{-1}$; ± 0.2 . ^c Conducted in a Paar shaking apparatus for approximately 15 min.

Table II. Effect of Solvent on $\text{CH}_3(\text{CH}_2)_4\text{COCO}(\text{CO})_4 + \text{HCo}(\text{CO})_4$ ^a

$10^2[\text{HCo}(\text{CO})_4]$	$10^2[\text{RCOCO}(\text{CO})_4]$	solvent	$10^2k, \text{M}^{-1} \text{s}^{-1}$	viscosity ^b (20 °C), cP
7.80	7.80	<i>n</i> -C ₁₆ H ₃₄	0.40	3.34
7.68	7.68	CCl ₄	0.41	0.969
7.40	7.40	CHCl ₃	0.77	0.58
6.72	6.72	Et ₂ O	1.00	0.233
7.66	7.66	<i>n</i> -C ₅ H ₁₂	1.22	0.240

^a At 23 °C under 1 atm CO. The value of the rate constant in CHCl₃ is ± 0.3 and in the other solvents ± 0.1 . ^b "Handbook of Chemistry and Physics", 46th ed.; CRC Press: Cleveland, OH, 1965.

claim^{3,6} that the presence of CO inhibits the reduction of the acylcobalt carbonyl by hydridocobalt tetracarbonyl. We now find that this is in fact not the case and consequently neither eq 2 nor 3 eq are likely pathways to the aldehyde. We are inclined to believe that the cleavage by $\text{HCo}(\text{CO})_4$ involves the acylcobalt tetracarbonyl and that the reaction may be radical in character. Such a suggestion was made earlier⁷ but without experimental support, as the last step in the catalytic hydroformylation.

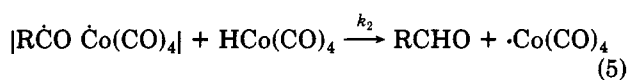
Results and Discussion

Most of the present work deals with the reaction of hexanoylcobalt tetracarbonyl with $\text{HCo}(\text{CO})_4$. The acyl compound is prepared in excellent yield by reacting $\text{NaCo}(\text{CO})_4$ in appropriate solvents, usually ether, with hexanoyl chloride.

Our kinetic data, Table I, show that the rate of reaction 1 is independent of CO partial pressure and that the reaction is second order (first order in each reactant). In some experiments that yield of aldehyde was essentially quantitative, and in most of the reactions, good second-order plots were obtained over about 2 half-lives.

Table II gives data on solvent effects. Our $\text{NaCo}(\text{CO})_4$ was prepared in ether and the ether evaporated and then replaced by the solvent of choice. Considering the manipulations involved and the instability of the reactants,⁸ one must exercise caution in drawing conclusions from the data in Table II. However, it does appear that the least viscous solvents give the fastest rates as might be expected for a radical cage mechanism. However, the mechanism of binuclear reductive elimination reaction is highly dependent on solvent,^{4c} and further investigations of the present reaction are clearly needed to bolster mechanistic suggestions.

A scheme that is consistent with the above experimental facts is given in eq 4–6. In this scheme the homolysis step



is rapid and reversible. The subsequent reaction in which the acyl radical abstracts the hydrogen atom from $\text{HCo}(\text{CO})_4$ is rate controlling. A somewhat similar scheme was proposed earlier involving a coordinatively unsaturated acylmolybdenum carbonyl⁹ but was rejected on the ground that exchange between groups was not observed when two different R groups were involved in the reversible reaction analogous to eq 4. We have no direct evidence for radical formation but if the radicals formed by k_1 were locked in a solvent cage or constituted a geminate radical pair in very small concentration, exchange may not be possible to observe. We do not observe an ESR signal with ether solutions of our hexanoylcobalt tetracarbonyl. We have also attempted to observe a CIDNP effect in the ¹H NMR spectrum of the reaction, focusing on the aldehyde proton, but the results are ambiguous and we will attempt to resolve this in a separate investigation. The scheme shown above is intrinsically more complicated than the $\text{Ph}_2\text{C}=\text{CH}_2 + \text{HCo}(\text{CO})_4$ reaction in which we did observe a CIDNP effect⁹ in the ¹H NMR spectrum of Ph_2CHCH_3 formed in the reaction. We prefer the radical mechanism rather than the direct intermolecular hydrogen transfer between the two coordinatively saturated species, although this can not be ruled out.

We have previously shown¹⁰ that nitriles promote the dissociation of cobalt tetracarbonyls to tricarbonyls. Were the acylcobalt tricarbonyl the species that reacts with $\text{HCo}(\text{CO})_4$, one might expect an enhancement of the rate of reaction 1 in the presence of nitriles. We find that in the presence of benzonitrile our reaction rate is unaffected. The retarding effect of an atmosphere of CO on the rate of the stoichiometric hydroformylation¹¹ must be due to inhibition of formation of the olefin hydrocarbonyl π complex and not because of subsequent steps in the reaction.

The reaction of acylcobalt tetracarbonyl with alcohols is known¹² to proceed as in eq 7. The $\text{HCo}(\text{CO})_4$ produced

$$\text{R-COCO}(\text{CO})_4 + \text{R}'\text{OH} \rightarrow \text{RCO}_2\text{R}' + \text{HCo}(\text{CO})_4 \quad (7)$$

may then react with acyl to give aldehyde, and the mixture of products obtained will depend on the relative rates of the two reactions with the acyl. When equimolar quantities of acyl and EtOH were mixed, the reaction gave, after 90 min at 23 °C, a 55% yield of ester and a 14% yield of

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aldehyde. In a reaction conducted to test the competitive rates of the acyl compound with EtOH and with $\text{HCo}(\text{CO})_4$, an ether solution of the acyl was treated with a solution containing equimolar quantities of $\text{HCo}(\text{CO})_4$ and EtOH. After 45 min at 23 °C, a 69% yield of hexanal and a 10% yield of ester were obtained (GLC). Obviously the acyl reacts faster with $\text{HCo}(\text{CO})_4$ than with EtOH. Usually, when the ester is the desired product, the reaction is run in the presence of a base such as an amine.¹² Because of our knowledge of the second-order rate constants for reactions of $\text{HCo}(\text{CO})_4$ with the acylcobalt tetracarbonyl and with 1,1-diphenylethylene,¹³ it was of interest to conduct reaction 7 in the presence of $\text{Ph}_2\text{C}=\text{CH}_2$. When 1 mmol of diphenylethylene was added to 2 mmol of the acyl and 2 mmol of EtOH, 0.39 mmol of Ph_2CHCH_3 (78% yield) was obtained. The yield of ester was 1.32 mmol (66%), and less than 5% aldehyde was formed. When reaction 7 was carried out in the presence of 1-pentene, relatively little hydroformylation of the pentene was observed. The relative rate of reaction with $\text{HCo}(\text{CO})_4$ is therefore $\text{Ar}_2\text{C}=\text{CH}_2 > \text{RCOC}(\text{CO})_4 \gg \text{RCH}=\text{CH}_2$.

Reactions of aryl-substituted ethylenes with $\text{HCo}(\text{CO})_4$ are known to proceed by a free radical mechanism, and in most of these reactions an inverse isotope effect is observed.¹⁴ These reactions involve a radical pair intermediate formed in an endothermic reaction. The rate-determining step in the acylcobalt reaction is eq 5 which is clearly an exothermic reaction. Accordingly we anticipated a normal isotope effect in the reaction and indeed found $k[\text{HCo}(\text{CO})_4]/k[\text{DCo}(\text{CO})_4] = 3.6$.

Experimental Section

Preparation of $\text{NaCo}(\text{CO})_4$, $\text{CH}_3(\text{CH}_2)_4\text{COCO}(\text{CO})_4$, and $\text{HCo}(\text{CO})_4$. $\text{Co}_2(\text{CO})_8$ (1.72 g) was added to an excess 1% Na

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amalgam suspended in 60 mL of dry ether under CO. After being stirred for about 12 h, the solution was colorless and the IR spectrum¹⁵ showed that the only cobalt species present was $\text{Co}(\text{CO})_4^-$ (1886 cm^{-1}).

A portion of the ether solution of $\text{NaCo}(\text{CO})_4$ was evaporated to dryness and the residue weighed (390 mg, 2 mmol) and dissolved in the appropriate solvent. The stoichiometric quantity of hexanoyl chloride in the same solvent was added at 0 °C under CO. The reaction was followed by disappearance of the 1886- cm^{-1} band. In ether, NaCl deposited and a yellow solution of $\text{CH}_3(\text{CH}_2)_4\text{COCO}(\text{CO})_4$ was formed. In other solvents the solution was red probably due to some decomposition to octacarbonyl (IR).

$\text{HCo}(\text{CO})_4$ was prepared according to the standard pyridine H_2SO_4 method.¹⁶ $\text{DCo}(\text{CO})_4$ was prepared by D_2O exchange.¹⁷

Kinetic Experiments. Rates were obtained by measuring the appearance of hexanal (GLC, 15% SE 30, 14 ft, 110 °C, He, 60 mL min^{-1}). *p*-Xylene was used as an internal standard.

In a typical experiment, a solution of $\text{HCo}(\text{CO})_4$ was syringed into an equimolar solution of the acyl compound in a closed system under CO. The total volume was 24 mL. The solution was kept at room temperature (23 °C) and sampled periodically. Kinetic analysis of the data was done by standard procedures.¹⁸

Reactions of $\text{CH}_3(\text{CH}_2)_4\text{COCO}(\text{CO})_4$ with EtOH in the Presence of $\text{Ph}_2\text{C}=\text{CH}_2$. To an ether solution of the acyl (2 mmol) was added a solution of $\text{Ph}_2\text{C}=\text{CH}_2$ (1 mmol) in EtOH (2 mmol). The reaction was stirred at 23 °C under CO, and samples were removed periodically for analysis (GLC).

Acknowledgment. We wish to thank the Standard Oil Co. of Ohio for partial financial support.

Registry No. $\text{Me}(\text{CH}_2)_4\text{COCO}(\text{CO})_4$, 16126-65-1; $\text{HCo}(\text{CO})_4$, 16842-03-8; $\text{NaCo}(\text{CO})_4$, 14878-28-5; $\text{Me}(\text{CH}_2)_4\text{COCl}$, 142-61-0; $\text{Ph}_2\text{C}=\text{CH}_2$, 530-48-3; $\text{CH}_3(\text{CH}_2)_2\text{CH}=\text{CH}_2$, 109-67-1; EtOH, 64-17-5; D_2 , 7782-39-0; $\text{Co}_2(\text{CO})_8$, 10210-68-1.

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Synthesis and Reactions of $\text{KGa}(\text{CH}_2\text{SiMe}_3)_2\text{H}_2$ and an Attempted Preparation of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{H}$. The Search for a Reductive Elimination Reaction

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The new compound $\text{KGa}(\text{CH}_2\text{SiMe}_3)_2\text{H}_2$ has been prepared from $\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ and excess KH and fully characterized by analysis and ^1H NMR and IR spectral data. The pure compound is thermally stable below 200 °C. Reaction of $\text{KGa}(\text{CH}_2\text{SiMe}_3)_2\text{H}_2$ with $\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ in benzene solution leads to the formation of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{H}$, which readily decomposes at room temperature to gallium metal, H_2 , and $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$. The experimental data suggest that $\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ decomposes by an exchange process to form $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ and unstable GaH_3 . Reductive elimination does not appear to be an observed pathway to low oxidation state gallium compounds.

Introduction

The products from the reactions of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ and $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ with KH in hydrocarbon solvents have been identified¹ as $\text{KGa}(\text{CH}_2\text{SiMe}_3)_3\text{H}$ and $\text{KIn}(\text{CH}_2\text{SiMe}_3)_3\text{H}$. These group 3 hydrido anions do not undergo simple reductive elimination reactions to form low oxidation state species and SiMe_4 , as originally proposed.^{2,3} Consequently, the synthesis of an organogallium(I) compound remains a formidable challenge. Since a reductive

$(\text{CH}_2\text{SiMe}_3)_3\text{H}$. These group 3 hydrido anions do not undergo simple reductive elimination reactions to form low oxidation state species and SiMe_4 , as originally proposed.^{2,3} Consequently, the synthesis of an organogallium(I) compound remains a formidable challenge. Since a reductive

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