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OXIDATIVE ADDITION OF BENZYL CHLORIDES TO TETRACARBONYLCOBALTATE

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Summary

A kinetic study of oxidative addition of benzyl chloride to $Na[Co(CO)_4]$ is described. The rate was determined in several aprotic and protic solvents and various counter ions were used. The results indicate the importance of leaving group (Cl^-) assistance by cations and protic solvents. The influence of substituents in the benzene ring of benzyl chloride and the entropy factor are consistent with such assistance.

The reaction between anionic transition metal carbonyls and organic halides (eq. 1) is commonly used to form metal—carbon bond-containing species which are often catalytically active.

$$RX + M(CO)_n{}^{m-} \rightarrow RM(CO)_n{}^{(m-1)^-} + X^- \quad (1)$$

Recent studies have revealed some features of this fundamental organometallic reaction, such as the importance of ion pairing for $Na_2Fe(CO)_4$ [1] and $NaMn(CO)_5$ [2] and of alkyl radical formation in reactions of $NaFeC_5H_5(CO)_2$ [3].

In the first two cases, kinetic determinations have shown opposite effects on the reaction rate of cation complexing agents. Thus with $Na_2Fe(CO)_4$ the reaction is 2×10^4 times faster in *N*-methylpyrrolidone than in tetrahydrofuran (THF), while with $NaMn(CO)_5$ the presence of cation complexing agents such as hexamethylphosphoramide significantly lowers the rate. This difference in behaviour can be explained in terms of differing contributions relative to R—X bond breaking from cation assistance.

We describe below a study of the reaction of benzyl chlorides with $NaCo(CO)_4$, a well known catalyst for the carbonylation of organic halides [4].

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Results

The reaction between benzyl chloride and $NaCo(CO)_4$ gives benzylcobalt tetracarbonyl complexes according to eq. 2

$$C_6H_5CH_2Cl + NaCo(CO)_4 \rightarrow [C_6H_5CH_2Co(CO)_4] + NaCl \qquad (2)$$

Some aspects of this reaction have already been described [5].

The low stability and high reactivity of alkylcobalt carbonyl complexes, necessary features for their participation in the catalytic cycle, do not allow the reaction to be monitored via their formation but only from the disappearance of the infrared band of $Co(CO)_4^-$ at about 1890—1930 cm^{-1} (depending on the solvent). No significant decomposition of $NaCo(CO)_4$ was observed in the absence of the benzyl chloride and in the kinetic time scale. The reaction was shown to be of first order in each of the two reactants (see eq. 3). Values of the second-order rate constants, k_2, are given in Table 1.

$$\text{rate} = k_2[C_6H_5CH_2Cl][NaCo(CO)_4] \qquad (3)$$

stants, k_2, are given in Table 1.

Activation parameters were determined in several solvents and are listed in Table 2. The effects on the rate in THF at 50°C of substituents in the aromatic ring and of the cation are shown in Tables 3 and 4. The kinetic data indicate that:

(a) alcohols are among the best solvents

(b) in aprotic solvents the rate decreases in the sequence anisole > isopropyl ether > n-propyl ether > THF > acetonitrile > dimethylformamide

TABLE 1 [a]

KINETIC DATA FOR REACTION OF BENZYL CHLORIDE WITH $Na[Co(CO)_4]$

Solvent	$k_2 \times 10^3$ M^{-1} sec^{-1}
Methanol	3.6 ± 0.4
Ethanol	4.9 ± 0.5
1-Propanol	7.3 ± 0.7
2-Propanol	8.1 ± 0.8
1-Pentanol	8.05 ± 0.8
2-Pentanol	12.8 ± 0.8
2-Methyl-2-butanol	22.4 ± 0.6
Cyclohexanol	11.4 ± 0.8
Methanol/18-crown-6 [b]	2.8 ± 0.3
2-Methyl-2-butanol/15-crown-5 [b]	3.5 ± 0.3
Ethylene glycol	11.0 ± 0.5
Tetrahydrofuran	0.42 ± 0.04
n-Propyl ether	1.11 ± 0.01
Isopropyl ether	11.1 ± 0.5
Anisole	12.7 ± 0.8
Tetrahydrofuran/18-crown-6 [b]	0.001 ± 0.0005
Anisole/18-crown-6 [b]	0.44 ± 0.04
Acetonitrile	0.02 ± 0.01
N,N-Dimethylformamide	0.01 ± 0.005

[a] All the experiments were run under N_2, at 50°C using $[NaCo(CO)_4]$ 0.025 *M* and $[PhCH_2Cl]$ 0.05—0.604 *M*;
[b] $[NaCo(CO)_4]/[Crown] = 1$.

TABLE 2

ACTIVATION PARAMETERS IN SEVERAL SOLVENTS

Solvent	$k_2 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ at 20°C	at 35°C	at 50°C	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
Isopropyl ether	0.55 ± 0.05	2.4 ± 0.2	11.1 ± 0.5	19.2 ± 0.4	−8.0 ± 1
Et. glycol	0.67 ± 0.06	2.4 ± 0.2	11.1 ± 0.5	18.0 ± 0.3	−12.0 ± 0.8
Methanol	0.36 ± 0.04	1.2 ± 0.1	3.6 ± 0.4	14.7 ± 0.1	−24.2 ± 0.2
THF	0.07 ± 0.01	0.12 ± 0.01	0.42 ± 0.04	11.5 ± 0.5	−38.8 ± 0.8

TABLE 3

SUBSTITUENTS EFFECT ON k_2 VALUES IN THF AT 50°C

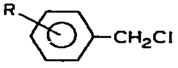
	$k_2 \times 10^3\ M^{-1}\ \text{sec}^{-1}$
R = H	0.42 ± 0.04
R = *p*-CN	0.51 ± 0.05
R = *p*-Cl	0.61 ± 0.06
R = *p*-CH_3	0.87 ± 0.08
R = *p*-OCH_3	4.4 ± 0.4
R = *m*-OCH_3	0.32 ± 0.03

TABLE 4

COUNTER ION EFFECT ON k_2 VALUES IN THF AT 50°C

Cation	$k_2 \times 10^3\ M^{-1}\ \text{sec}^{-1}$
Na^+	0.42 ± 0.04
Li^+	0.042 ± 0.005
K^+	0.26 ± 0.03
Cs^+	0.16 ± 0.02
$C_6H_5CH_2\overset{+}{N}(C_2H_5)_3$	0.02 ± 0.003

(c) crown ethers decrease the reaction rate by a factor of 420 in DIF, 30 in anisole, 6 in 2-methyl-2-butanol, and 1.3 in methanol

(d) the rate varies with the cation in THF in the sequence $Na^+ > K^+ > Cs^+ > Li^+ > Et_3N^+ - CH_2C_6H_5$

(e) substituents in the benzene ring of benzyl chloride have little effect on the rate but electron releasing groups do raise the rate.

(f) the reaction is strongly influenced by a large entropy term.

Discussion

The results reported show that the reaction of $NaCo(CO)_4$ with benzyl chloride is clearly effected by ion-pairing phenomena, as is the case with $NaMn(CO)_5$ and $Na_2Fe(CO)_4$. However the behaviour of $NaCo(CO)_4$ is closest to that of $NaMn(CO)_5$, probably because both are monocharged species and have similar nucleophilic reactivities towards organic halides; the order of reactivity $Na_2Fe(CO)_4$ [1] > $NaMn(CO)_5$ [2] > $NaCo(CO)_4$ can be deduced even though data for homogeneous reactions are not available for all these species.

The most interesting feature of the anionic cobalt carbonyl system is the

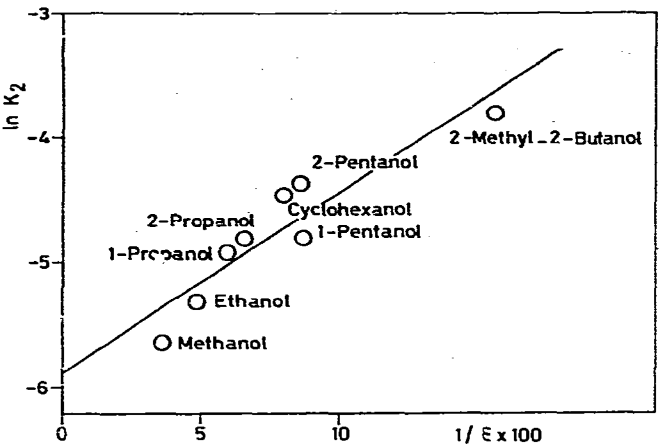


Fig. 1. ln K_2 (see Table 1) versus $1/\epsilon$ in alcoholic solvents.

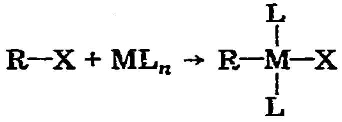
great importance of leaving group assistance (Cl^-) by protic solvents or cations. Both of these effects are present in alcoholic solvents, the assistance by the cation being less important in alcoholic solvents of high polarity. The sequence of rates in these solvents parallels the dielectric constant of the solvent as expected for an attractive dipole-ion reaction (Fig. 1). The observed increase in the rate with decreasing dielectric constant of the protic solvent can be interpreted in terms of increased leaving group (Cl^-) assistance by the cation (Na^+). Further support for this hypothesis is that crown ethers, complexing agents for the cation, lower the rate in these solvents. The observed decrease is higher in less polar alcohols.

Table 1 shows also that the rates in aprotic solvents are strongly and inversely dependent on the cation-coordinating abilities of the solvents. Thus in dimethylformamide, the best coordinating solvent used, the rate is 360 times less than in methanol. Furthermore a strong decrease in the rate is observed on adding crown ethers to aprotic solvents (THF, anisole). These facts can be explained by regarding a tight ion pair as the kinetically dominant species.

Previous spectroscopic studies of $NaCo(CO)_4$ have shown that $Co(CO)_4^-$ forms ion pairs with alkali metals in solvents of low dielectric constant [6]. The importance of ion pairing is evident from the influence of the cation ($Na^+ > K^+ > Cs^+ > Li^+ > NR_4^+$) on the rate in THF. The surprisingly slight increase of the rate caused by electron releasing substituents is consistent with the great importance of leaving group assistance, and supports the view that such assistance is more important than the nucleophilic attack by $Co(CO)_4^-$.

Finally, the large negative values of $\Delta S^{\ddagger}$ indicate that the transition state is very rigid, as in the case of a four center reaction. Probably leaving group assistance also plays a very important role in the reaction of $NaMn(CO)_5$ [2] but is not significant in the case of $Na_2Fe(CO)_4$ [1]. The assistance is likely to be less important with a higher nucleophilicity of the anionic carbonyl and a higher stability of the C—M σ-bond.

The conclusion reached above can be used to explain the high reactivity of neutral metal complexes in oxidative addition of organic halides [7]. In this case both the halogen and the organic group become bound to the metal (eq. 4), and the high reactivity can be attributed to the very effective leaving group assistance achieved via formation of the M—X bond.



$$R{-}X + ML_n \rightarrow R{-}\overset{\overset{L}{|}}{\underset{\underset{L}{|}}{M}}{-}X \qquad (4)$$

(M = Ni, Pd, Rh; X = Cl, Br, I)

Experimental

The benzyl halides were commercially available or were prepared by standard procedures. Sodium tetracarbonylcobaltate was prepared by reduction of $Co_2(CO)_8$ with sodium amalgam in THF [8]. K, Li, Cs and $C_6H_5CH_2N(Et)_3$ salts were prepared by metathetis from $NaCo(CO)_4$ or $Co[Co(Co)_4]_2$. Solvents were distilled under N_2. All the kinetic runs were made under nitrogen. Samples were analysed by UNICAM SP1100 infrared spectrophotometer using 0.1 mm CaF_2 cells.

General procedure for the kinetic determinations

$NaCo(CO)_4$ (~190 mg) and the solvent (40 ml) were placed under N_2 in a flask (50 ml) equipped with a condenser, a magnetic stirring bar and a serum cup. The temperature was controlled to ±0.1°C by means of a constant-temperature bath. When the solution had reached the bath temperature a sample was removed and analysed to give the initial concentration, and the benzyl halide was then added. At appropriate times samples were withdrawn and analysed by IR.

Good linear first order plots were obtained under pseudo first order conditions (e.g. with 0.604 *M* $PhCH_2Cl$ and 0.024 *M* $NaCo(CO)_4$ in THF) and good second order plots when the reactants were present in comparable concentrations (e.g. 0.043 *M* $PhCH_2Cl$ and 0.023 *M* $NaCo(CO)_4$.

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