Journal of Organometallic Chemistry, 198 (1980) C36—C38

Preliminary communication

THE MECHANISM OF THE STOICHIOMETRIC PHASE TRANSFER CARBONYLATION OF BENZYL BROMIDE BY THE COBALT CARBONYL ANION

HERVE DES ABBAYES and ANNE BULOUP

Laboratoire de Chimie des Organométalliques, ERA CNRS No. 477, Université de Rennes, 35042 Rennes Cedex (France)

(Received July 3rd, 1980)

Summary

The kinetics of the stoichiometric phase-transfer carbonylation of benzyl bromide by the cobalt carbonyl anion have been investigated. Pseudo first order constants vary linearly with the amount of tetrabutylammonium chloride present. The effect of the solvent is partly due to its ability to extract the ion pair $Bu_4N^+Co(CO)_4^-$ into the organic phase. This ion pair is barely soluble in water and the amount of $Co(CO)_4^-$ anion in the organic phase is kept constant by a simple anion exchange mechanism without migration of the tetrabutylammonium cation.

There has been considerable interest in the application of phase transfer catalysis to organic reactions [1], and several studies have been directed towards the understanding of the mechanism [2]. Recently, carbonylation of organic halides, which plays a key role in many catalytic processes [3], was accomplished by phase transfer catalysis in several synthetic procedures for which reasonable but speculative mechanisms were proposed [4]. We report below some details of the kinetics of the stoichiometric carbonylation of benzyl bromide by the cobalt carbonyl anion (eq. 1), with emphasis on the phase transfer mechanism.

$$C_6H_5CH_2Br \xrightarrow[H_2O,\ \text{organic solvent},\ CO]{Na^+Co(CO)_4^-,\ Bu_4N^+Cl^-} C_6H_5CH_2COCo(CO)_4 \quad (1)$$

Despite the complexity of the system and of the reaction*, good pseudo

---

*Complex $C_6H_5CH_2COCo(CO)_4$ cannot be isolated and has to be transformed into the triphenylphosphine derivative $C_6H_5CH_2COCo(CO)_3P(C_6H_5)_3$ for separation [5]. By-products such as $C_6H_5CH_3$, $(C_6H_5CH_2)_2$, $(C_6H_5CH_2)_2CO$ accompany the organometallic. The amount of these does not seem to be strongly dependent on the solvent. These aspects and the detailed mechanism of the action of $Co(CO)_4^-$ on $C_6H_5CH_2Br$ will be discussed in a separate paper.

TABLE 1

KINETIC DATA OF THE REACTION I[a]

Solvent	10^5 k_{obs} (s^{-1})	10^3 $c_{org.max}$ Bu_4N^+ (mol l^{-1})	10^3 $c_{org.found}$ $Co(CO)_4^-$ (mol l^{-1})	10^2 k_2 (mol^{-1} s^{-1})
C_6H_6	6.9	5	5.1	1.38
CH_2Cl_2	20	5	4.9	4
$i\text{-}Pr_2O$	11	5	1.6	6.9

[a] Kinetic measurements were made in a thermostated cell at 20°C ± 0.1° under one atmosphere of CO, containing a two phase system: water:10 ml, organic phase 10 ml, $Na^+Co(CO)_4^-$ 2 mmol, $C_6H_5CH_2Br$ 0.5 mmol, $Bu_4N^+Cl^-$ as the phase transfer catalyst, and naphtalene as an internal standard for GC analysis. A stable stirring speed of 1100 rpm was provided by an electronically monitored magnetic stirrer. Rate constants were independent of the stirring speed above 900 rpm.

first order plots were obtained by following the disappearance of benzyl bromide. The observed rate constants (rate = $k_{obs}(C_6H_5CH_2Br)$) were found to vary linearly with the amount of the quaternary ammonium salt present in the range 0.001—0.01 mol l^{-1}; in the absence of the ammonium cation the reaction was extremely slow. For a given quantity of $Bu_4N^+Cl^-$ present (0.005 mol l^{-1}), the value of k_{obs} depends on the solvent, as shown in Table 1.

An analysis on an aliquot before the introduction of $C_6H_5CH_2Br$, according to eq. 2, gave the amount of $Co(CO)_4^-$ present in the organic phase.

$$Co(CO)_4^- \xrightarrow{I_2} Co^{2+} \xrightarrow[SCN^-]{Bu_4N^+Cl^-} (Bu_4N^+)_2Co(SCN)_4^{2-} \qquad (2)$$

extracted with $CHCl_3$ (optical density at 624 nm)

As shown in Table 1, the quantity of $Co(CO)_4^-$ anion found in the organic layer and the total amount of $Bu_4N^+Cl^-$ introduced in the cell agree satisfactorily for CH_2Cl_2 and C_6H_6, but not for $i\text{-}Pr_2O$. Since the concentration of $Co(CO)_4^-$ remains constant in the organic layer, the kinetic law is

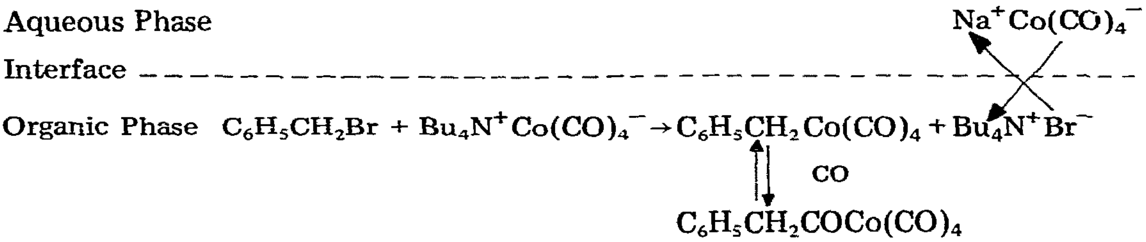
$$\text{Rate} = k_2[Bu_4N^+Co(CO)_4^-]_{org.}[C_6H_5CH_2Br]_{org.} \qquad (3)$$

and the calculated second order rate constants show that the fastest reaction occurs in $i\text{-}Pr_2O$, despite its lower ability to extract $Bu_4N^+Co(CO)_4^-$.

In a side experiment, we used the same spectrophotometric method (eq. 2) to determine the solubility of the ion pair $Bu_4N^+Co(CO)_4^-$ in water at 20°C. It was found to be very low (7×10^{-5} mol l^{-1}). Thus this two phase system probably works without back and forth transfer of the ammonium cation between the two phases: the concentration of the $Co(CO)_4^-$ anion in the organic layer is kept constant throughout the reaction by a simple anion exchange through the interface according to the following scheme*, and the reactive species is the ion pair $Bu_4N^+Co(CO)_4^-$.

---

*Such a mechanism without migration of the ammonium cation was recently demonstrated by an elegant experiment with an organic model [6].



A recent kinetic study [7] showed that in homogeneous conditions (THF), the sodium salt of the $Co(CO)_4^-$ anion is more reactive towards benzyl chloride than the triethyl benzyl ammonium salt, probably because of leaving group assistance by the sodium cation. Since such assistance is not possible under the usual phase transfer conditions, we infer that the reactivity of the cobalt tetracarbonyl anion should be lower in those systems than in $Na^+Co(CO)_4^-$ in THF. This point, which has some importance for the use of $Co(CO)_4^-$ in stoichiometric phase transfer processes, does not seem to be critical for catalytic phase transfer processes, in which this step is not necessarily rate limiting. This problem will be discussed in detail in a further paper.

References

1 W.P. Weber and G.W. Gokel, Phase Transfer Catalysis in Organic Synthesis, Springer Verlag, Berlin, 1977.
2 a) D. Landini, A. Maia and F. Montanari, J. Amer. Chem. Soc., 100 (1978) 2796; b) J.E. Gordon and R.E. Kutina, ibid., 99 (1977) 3903; c) A.W. Herriott and D. Picker, ibid., 97 (1975) 2345; d) C.M. Starks and R.M. Owens, ibid., 95 (1973) 3613.
3 T.A. Weil, L. Cassar and M. Foa, Organic Synthesis via Metal Carbonyls, vol. II, Wiley, New York, 1977, p. 517.
4 a) H. des Abbayes and A. Buloup, J. Chem. Soc. Chem. Commun., (1978) 1090; b) H. Alper, J.K. Currie and H. des Abbayes, ibid., (1978) 311; c) H. Alper and H. des Abbayes, J. Organometal. Chem., 134 (1977) C11; d) L. Cassar, M. Foa, J. Organometal. Chem., 134 (1977) C15.
5 R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc., 84 (1962) 2499.
6 D. Landini, A. Maia and F. Montanari, J. Chem. Soc. Chem. Commun., (1977) 112.
7 A. Moro, F. Foa and L. Cassar, J. Organometal. Chem., 185 (1980) 79.