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CONTRIBUTION OF PHASE TRANSFER TECHNIQUE TO RESOLVE THE PROBLEM OF SEPARATION BETWEEN THE CATALYST AND THE PRODUCT IN THE CATALYTIC CARBONYLATION OF HALIDES.

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SUMMARY

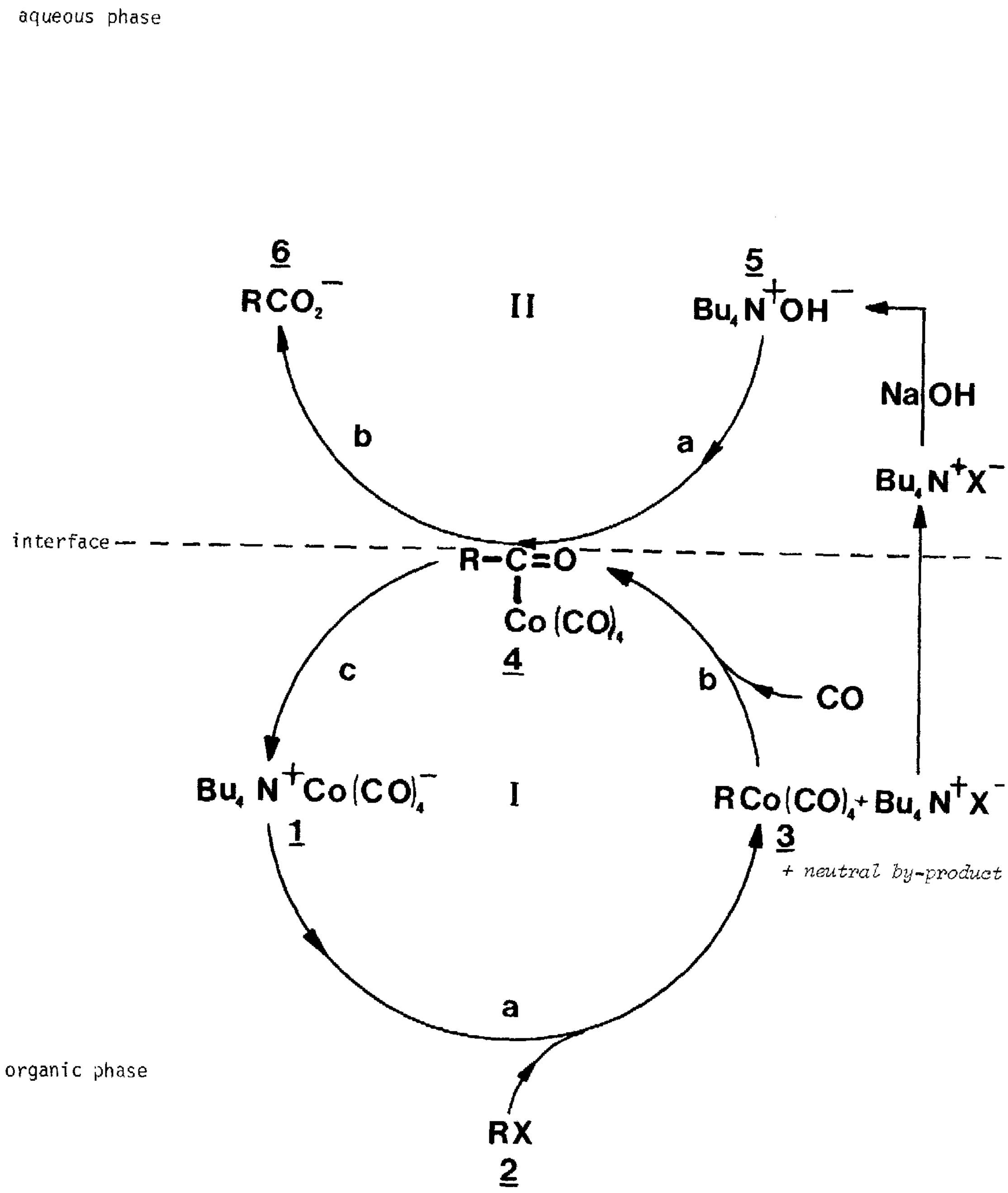
Study of carbonylation of benzyl bromide in a biphasic liquid-liquid system shows that the catalytic ion pair $Bu_4N^+Co(CO)_4^-$ stays in the organic layer and that the carbonylated product $C_6H_5CH_2CO_2^-$ stays in the aqueous one.

One of the most challenging problems met with catalytic systems is the catalyst separation. This is one of the reasons why heterogeneous systems are prefered to homogeneous ones. Considerable effort is now devoted to design systems which would combine advantages of both types, such as fluid bed catalysts and supported complex catalysts (1). Here, in a mechanistic investigation, we describe the contribution of phase transfer technique to resolve this problem on the example of catalytic carbonylation of benzyl bromide (2) :

$$RX \xrightarrow[\text{CO, base}]{Co(CO)_4^-} RCO_2H \qquad (RX = C_6H_5CH_2Br)$$

Mechanism of this biphasic liquid-liquid catalytic system, depicted on scheme 1, is supported by the following experimental findings.

First of all, the catalytic species, which is the $Co(CO)_4^-$ anion always remains in the organic layer as an ion pair with the Bu_4N^+ cation, which is the phase transfer agent : we demonstrated that this ion pair is only sparingly soluble in water (7.10^{-5} M/L at 20°C) and that there is an excellent parity between the overall Bu_4N^+ cation introduced and the amount of the $Co(CO)_4^-$ anion found in the organic layer before starting the catalytic cycle : after introducing 0,05 mM of $Bu_4N^+Cl^-$ and a moderate excess of $Na^+Co(CO)_4^-$ in a liquid-liquid system consisting of 10 ml of water and 10 ml of organic solvent (benzene or dichloromethane), we found, respectively, after a short time of stirring, 0,049 mM and 0,051 mM of $Co(CO)_4^-$ anion in the organic phase. The presence of the $Co(CO)_4^-$ anion in the organic phase was qualitatively detected by IR spectra ($\nu_{C=O}$ 1900 cm^{-1}) and quantitatively analyzed according to the following sequence :


aqueous phase
6
RCO_2^-
II
5
$Bu_4N^+OH^-$
NaOH
b
a
$Bu_4N^+X^-$
interface
$R-C=O^-$
$Co(CO)_4$
4
c
b
CO
$Bu_4N^+Co(CO)_4^-$
1
I
$RCo(CO)_4 + Bu_4N^+X^-$
3
+ neutral by-product
a
organic phase
RX
2

SCHEME 1

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

blue complex extracted
with $CHCl_3$
(O.D. at 624 nm) (3)

So, steps a (reaction of the halide on the catalyst) and b (CO insertion) of the catalytic cycle I (scheme I) entirely occur in the organic layer.

Kinetic arguments support an interfacial process for the key step of the catalytic reaction : cleavage of the acylcobalt carbonyl species 4 (Reaction II, scheme 1) by the hydroxide anion to give the carboxylate anion 6 and regenerate the catalytic ion pair 1. Disappearance of RX, which follows a good pseudo first order law up to 80 % consumption after a short induction period, strongly depends on stirring speed : for instance, in a biphasic system consisting of water (10 ml), benzene (10 ml), NaOH 2N, 0,2 mM $Na^+Co(CO)_4^-$, 0,2 mM $Bu_4N^+Cl^-$ and 2 mM $C_6H_5CH_2Br$ at 20°C and one atmosphere of CO, first order constant was $0{,}156.10^{-2}$ mn^{-1} at 700 r.p.m. and $0{,}39.10^{-2}$ mn^{-1} at 1100 r.p.m. (magnetic stirring). Same effects were found with CH_2Cl_2 as the organic phase. In another kinetic study, we found that stoechiometric carbonylation of RX in a phase-transfer system (without NaOH) does not depend on stirring speed above 900 r.p.m.

So, we infer that the step which depends on stirring speed is the cleavage of the acyl cobalt carbonyl 4. Since real phase transfer processes do not depend on the stirring speed after a minimum stirring (4), and interfacial ones strongly do (5), we conclude that this step is interfacial.

Further arguments support this conclusion : interfacial processes were proposed in phase transfer systems involving the OH^- anion (6). Moreover, when more lipophilic anions compete with OH^- for extraction as tetrabutyl ammonium ion pairs in the organic layer, there is no noticeable amount of OH^- present in it, since the onium prefers to extract first the more lipophilic anions according to the following sequence :

$$OH^- \ll Cl^- < C_6H_5CH_2CO_2^- < Br^- < I^- \quad (7a,b)$$

A competitive experiment between I^- and $Co(CO)_4^-$ showed us that $Co(CO)_4^-$ is approximately sixty times more extractible in the organic phase with Bu_4N^+ than I^- in a CH_2Cl_2-H_2O system. Consequently, the right place of each anionic species in the catalytic system is that shown on scheme 1 : particularly, all the carboxylate anion 6 produced stays in the aqueous layer and all the catalyst 1 remains in the organic one. So, provided that both catalytic species and product are anions of very different extractibilities with the phase transfer agent, the problem of separation between the catalyst and the product is simply resolved by phase transfer technique.

We are currently investigating extensions of those liquid-liquid catalytic systems

References and Notes

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