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# TETRACARBONYL COBALTATE ION SUPPORTED ON ANION EXCHANGERS AS A NEW HETEROGENIZED HOMOGENEOUS CATALYST: SYNTHESIS OF ACIDS AND ESTERS FROM ORGANIC HALIDES

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## Summary

Catalysts consisting of tetracarbonyl cobaltate anion supported on commercially available anion exchange resins are readily prepared. Carbonylation of organic halides using this heterogenized catalyst leads either to acids or esters depending on the conditions. Some features of this catalytic system and the possible reaction mechanism are discussed.

## Introduction

Heterogenization of homogeneous catalysts has received much attention in the last years [1]. These "hybrid phase catalysts" [1b] were developed with the aim of combining the best features of homogeneous and heterogeneous catalysis. In the transition metal catalyzed carbonylation of organic halides, catalysts were conveniently heterogenized by means of the liquid–liquid phase transfer technique [2]; continuous extraction of acids by the alkaline aqueous phase enabled separation of the products from the catalyst-containing phase. During our studies in this area we have developed a new method of heterogenizing tetracarbonyl cobaltate using anion exchange resins as supports [3]. Inorganic anions anchored to these resins have recently been successfully used as reagents in some organic reactions [4], and examples of reactions catalyzed by transition metal carbonyls bound to these supports have been reported [5].

## Results and discussion

We have found that tetracarbonyl cobaltate anion rapidly and quantitatively exchanges with a commercially available anion resin (eq. 1). $Co_2(CO)_8$ was also used

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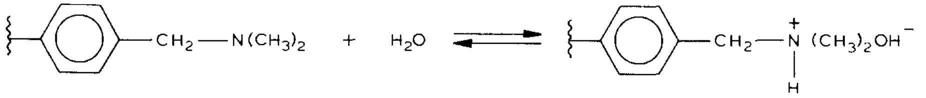
(1)

( R = CH$_3$ or CH$_2$CH$_2$OH , H ; X$^-$ = Cl$^-$ , OH$^-$ )

as a tetracarbonyl cobaltate precursor. Weak base anion exchange resins such as Kastel A 101 (Montedison) and Amberlite IRA A 93 (Rohm and Haas) which do not contain quaternary ammonium groups can also be employed; this is probably due to the interaction of tetracarbonyl cobaltate with ionic species formed on the polymer as shown in eq. 2.


(2)

The anchoring reaction was carried out in an alcoholic medium and monitored by the disappaerance of the characteristic infrared frequency of cobaltate anion. When the amount of $Co(CO)_4^-$ used was three or four times less than the exchange capacity of the resin, the reaction was over within a few minutes at 25°C (Fig. 1), and was practically instantaneous at 55°C.

The infrared spectrum of the polymers at the end of the reaction showed the band of tetracarbonyl cobaltate. Other metal carbonyl bands were absent in the infrared region, whatever anion exchanger was used.

The resin-bound tetracarbonyl cobaltate species proved to be an effective catalyst for carbonylation of organic halides. Some results are shown in Table 1. Taking the carbonylation of benzyl chloride as model system some features of this catalytic system can be discerned: (i) The yields varied very little with the nature of the support (entries 1, 2, 4, 5); (ii) efficiency of the homogeneous system (entry 6) was reached only by lowering the $RX/Co(CO)_4^-$ ratio (entry 3). For higher ratios the

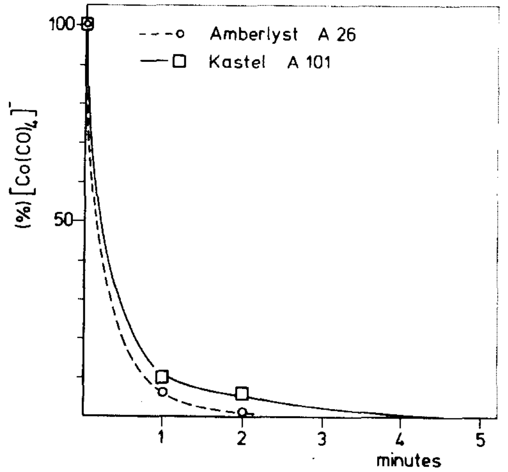


Fig. 1. Anchoring rate at 25°C (4 equivalents of resin per mole of cobaltate).

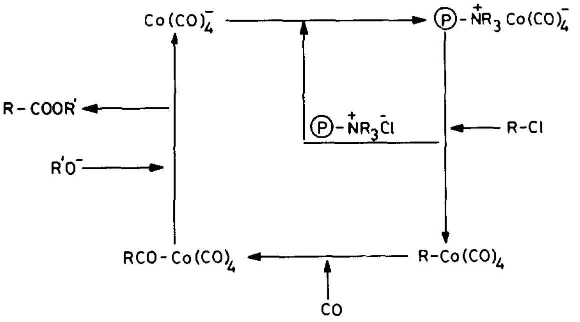
lower carbonylation rate results in increasing importance of the secondary reactions and so a decrease in yield.

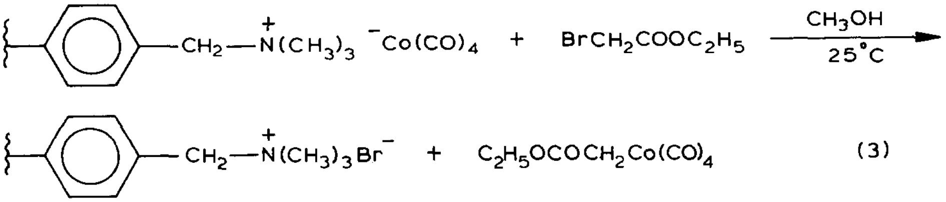
The supported catalyst, was effective for the synthesis not only of acids but also of esters (entries 9, 10). In terms of synthetic utility, the possibility of this second process is an important improvement compared with the phase transfer procedure, which is useful as heterogenizing technique only in the synthesis of acids [2].

From the practical point of view, the usefulness of the supported tetracarbonyl cobaltate depends on the ease of separating the catalyst from the reaction products and of recovering and recycling the catalyst and the support. The solution of reaction products, after separation of the solid phase, contained no catalyst, as proved by the absence of metal carbonyl bands in the infrared spectrum. No other cobalt compound was present. We have recycled the solid catalyst in seven successive carbonylations of benzyl chloride under the conditions shown in Table 1 (entry 2). Each time about 1/3 of the starting amount of $Co(CO)_4^-$ was added to replace the destroyed catalyst. About 145 moles of phenylacetic acid per mole of cobalt were obtained (total yield 93%). These experiments, although not optimized, showed not only the possibility of recovering and recycling the catalyst, but also of improving the results obtained under homogeneous conditions. At the end of the seventh cycle the solid phase was treated with aqueous HCl and the cobalt quantitatively recovered as chloride. The support was washed with water and alcohol and then recycled.

A possible reaction mechanism is shown in Scheme 1. The first step of the catalytic cycle is the interaction between the polymer-supported cobaltate and the organic halide dissolved in the liquid phase. This step gives the intermediate alkylcobalt, and this is followed, in solution, by the formation of an acyl complex by CO insertion. Nucleophilic attack on this complex leads to the carbonylation product (acid or ester) and regenerates the cobaltate: the latter immediately becomes attached to the resin, completing the catalytic cycle. In order to demonstrate such a mechanism we treated tetracarbonyl cobaltate supported on Amberlyst A26 with ethyl bromoacetate in methanol at 22°C (eq. 3).

SCHEME 1



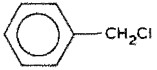
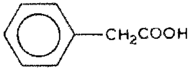
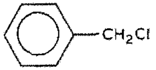
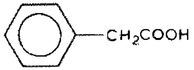
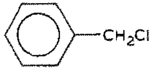
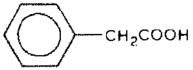
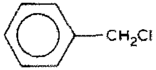
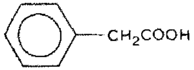
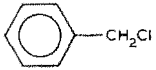
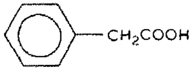


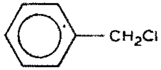
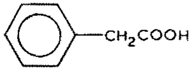
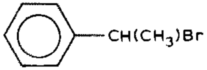
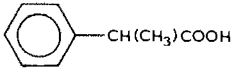
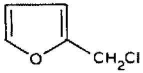
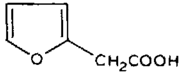
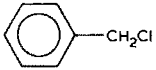
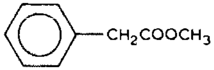
(3)

(Continued on p. 230)

TABLE 1 [a]

SYNTHESIS OF ACIDS AND ESTERS FROM ORGANIC HALIDES CATALYZED BY POLYMER BOUND TETRACARBONYL COBALTATE

| Entry | R–X | Support [b] | Base | $T$(°C) | RX/$Co(CO)_4^-$ | Reaction time(h) | Product | Yield (%) |
|---|---|---|---|---|---|---|---|---|
| 1 |  | Amberlyst A26 | NaOH | 55 | 65 | 6 |  | 87 |
| 2 |  | Kastel A101 | NaOH | 55 | 65 | 6 |  | 91 |
| 3 |  | Kastel A101 | NaOH | 55 | 32 | 3 |  | 95 |
| 4 |  | Amberlyst A27 | NaOH | 55 | 65 | 6 |  | 83 |
| 5 |  | Amberlyst A29 | NaOH | 55 | 65 | 6 |  | 82 |

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| 6 |  | – | NaOH | 55 | 120 | 3 |  | 95 [9] |
| 7 |  | Amberlyst A26 | NaOH [c] | 15 | 15 | 16 |  | 46 [10] |
| 8 |  | Amberlyst A26 | NaOH | 25 | 20 | 4 |  | 57 |
| 9 |  | Amberlyst A26 | $K_2CO_3$ | 47 | 65 | 16 |  | 65 |
| 10 | $ClCH_2COOC_2H_5$ [d] | Kastel A101 | $K_2CO_3$ | 80 | 120 | 11 | $CH_2(COOC_2H_5)_2$ | 86 |

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[a] Unless otherwise indicated all the experiments were run in methanol under atmospheric pressure of CO. Yields and the ratios $RX/Co(CO)_4^-$ were not optimized. [b] 3 or 4 equivalents of resin per mole of $Co(CO)_4^-$ were used. [c] The base was added at one time at the beginning of the carbonylation. [d] The reaction was run in ethanol under 15 atmospheres of CO.

The presence in solution of the alkylcobalt carbonyl intermediate, $C_2H_5OCOCH_2Co(CO)_4$ was recognized by its infrared spectrum: the characteristic bands at 2111(m), 2029(s), 1711(w) $cm^{-1}$ were the same as those of solutions in methanol of this complex prepared by the literature method [7]. The presence of the alkyl cobalt complex probably means that successive steps of the catalytic cycle take place in the liquid phase. However, we have observed that the carbonylation rate in the solid–liquid system is lower than that in the one-phase process even on increasing the $Co(CO)_4^-/RX$ ratio (see Table 1). This probably means that the interaction between the solid catalyst and the organic halide is the slow step in the catalytic cycle.

Finally the absence of metal carbonyl bands in the infrared spectrum, not only at the end but also during the carbonylation, confirms that the anchoring of $Co(CO)_4^-$ to anion exchange resin is a very fast process.

## Experimental

### *Materials*

Commercially available resins were washed with acetone and dried under vacuum. α-Phenethyl bromide and 2-chloromethylfuran were prepared from the corresponding alcohols by standard procedures. $NaCo(CO)_4$ was prepared by reduction of $Co_2(CO)_8$ with sodium amalgam in THF [8].

### *General procedure for carbonylation*

*Synthesis of phenylacetic acid.* The resin (20 mmol) $NaCo(CO)_4$ (5.3 mmol), and $CH_3OH$ (100 ml) were placed under CO in a flask (500 ml) equipped with mechanical stirrer, thermometer, two dropping funnels, a glass electrode for pH measurement and a condenser connected to a burette filled with CO.

The mixture was stirred until complete disappearance of the characteristic infrared band of $Co(CO)_4^-$. The organic halide (348 mmol) and 30% NaOH aqueous solution were then gradually added during 4 h at a fixed temperature, the pH value being kept between 10.5 and 11.0. When CO absorption ceased the mixture was filtered and after the usual work-up gave the expected acid.

In the synthesis of esters, the organic halide and the base ($K_2CO_3$) were added all at one time, without any pH control.

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