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Phase-Transfer Catalysis

Carbonylation of Chloromethylated Polystyrene Resins with NaCo(CO)$_4$ in Phase-Transfer Catalysis

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Dedicated to Prof. C. I. Simionescu on his 65th birthday

SUMMARY

The carbonylation of chloromethylated and partial quaternizated chloromethylated polystyrene resins with cobalt tetracarbonyl anion in phase-transfer conditions is described.

INTRODUCTION

On the basis of studies carried out in a single phase, the phase-transfer carbonylation of organic halides has been carried out using cobalt tetracarbonyl anion as catalyst (1-3).

It seemed conceivable to us that this catalyst should also be useful in polymer chemistry, particularly for carbonylation of chloromethylated polystyrene resins in phase-transfer conditions.

EXPERIMENTAL

The syntheses were carried out in argon atmosphere, using carefully purified solvents and reagents. Chloromethylated styrene-2%-divynylbenzene (SDVB-2), and styrene-8%-divynylbenzene (SDVB-8) copolymers were prepared according to published methods (4-5). Partial quaternizated resins were obtained by the reaction of the chloromethylated copolymers SDVB-2 (18.4% Cl, 20 g) with a solution of 80 g Et$_3$N in 400 ml benzene at 70°C for 12 h (SDVB-Q-1), 24 h (SDVB-Q-2), and 72 h (SDVB-Q-3), respectively. The sample SDVB-Q-4 was prepared by treating of 20 g resin SDVB-8 (16.2% Cl) with a solution of 20 g Et$_3$N in 400 ml benzene at 70°C for 40 h. The sodium tetracarbonyl cobaltate was prepared by the method of Edgell and Lyfard (6).

The reactions were carried out in a glas autoclave of 250 ml internal capacity equipped with magnetical stirrer, gas inlet and pressure-regulating device. This autoclave was charged in argon stream with diphenylether and resin beads, and heated at 50°C for 24 hours. After cooling to room temperature 50% aqueous solution of NaOH, tetrabutylammonium chloride, and sodium tetracarbonyl cobaltate were added. The autoclave was then closed and connected to a source of carbon monoxide under pressure. First, the autoclave was flushed once with carbon monoxide (5 atm.). After relasing this carbon

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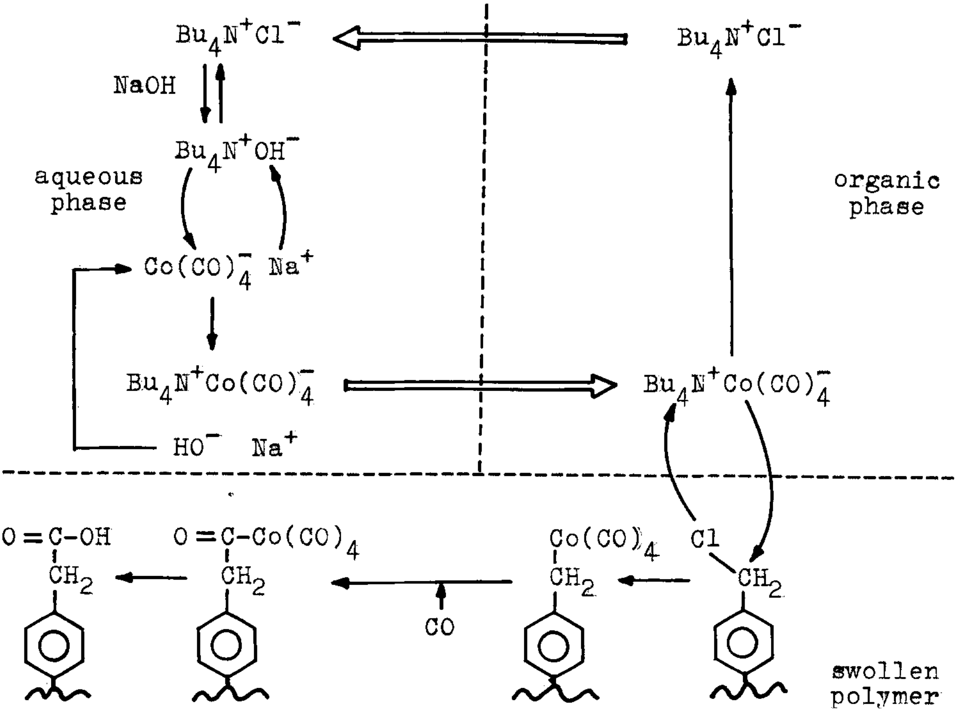
monoxide, the autoclave was then pressurized to dessired CO pressure, and then heated by stirring (1000 r.p.m) at 50°C for 72 hours. After filtration and extraction with dichloromethane, the polymer was washed repeatedly with THF, acetone, THF-H_2O 3:1, methanol, and finally 4% HCl solution. After drying overnight at 60°C under vacuum the polymer was weigthed. A sample of 2 g of polymer was treated with 20 ml of a 10% (w/w) solution of H_2O_2 in 100 ml three-necked flask equipped with magnetical stirrer and connected to a constant pressure gas burrette. After treating with H_2O_2 the polymer was dryed at 60° in vacuum and used as analytical sample for elementary analysis and ionic exchange capacity measurements.

RESULTS AND DISCUTION

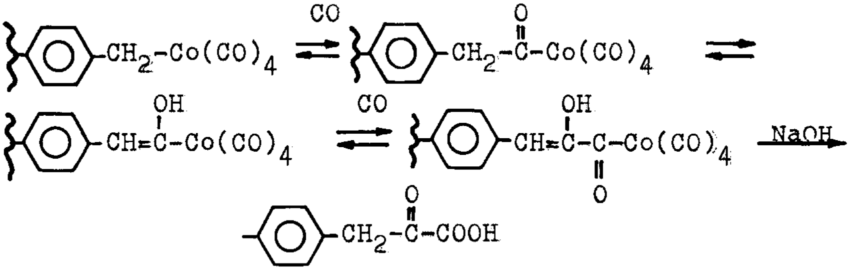
Our three phase system consists of a polymer phase swollen in diphenylether with an aqueous solution of NaOH to which $NaCo(CO)_4$ and Bu_4NCl are added. Since the $Bu_4N^+Co(CO)_4^-$ ion pair thus produced is rather insoluble in water (7) the probable reactions involved in this carbonylation process follows the general scheme:



Scheme 1

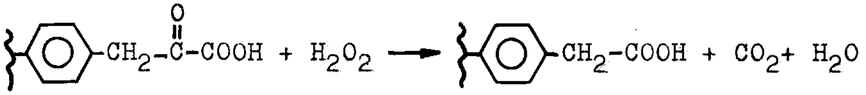
The negative charged $Co(CO)_4^-$ nucleophil is extracted by the positive Bu_4N^+ ion as $Bu_4N^+Co(CO)_4^-$ ion pair into the organic phase and then transfered to the swollen polymer, where the oxidative addition occurs.

An interesting aspect of this system is the possibility to obtain phenyl pyruvic acid groups besides the phenylacetic groups, due to carbonylation process :



(1)

As indication of the presence of the pyruvic sites attached to the polymer, the formation of carbon dioxide was determined in the reaction between carbonylated resin and H_2O_2:



(2)

Table 1 Carbonylation of chloromethylated polystyrene resin in phase-transfer conditions[a]

Sample[b]	CO pressure atm	Residual chlorine content %	CO_2 evolved ml/g	Functionalization[c] yield%	
				Elemental analysis	Ionic capacity data
SDVB-2(18.4)	1.5	0.88	5.4	95	92
	3.0	0.53	11.2	97	94
S.D.VB-2(5.7)	1.5	0.33	1.4	94	90
	3.0	0.28	3.2	95	90
SDVB-8(16.5)	1.5	2.07	5.8	87	83
	3.0	1.96	9.6	88	82
SDVB-8(6.2)	1.5	1.22	2.1	80	75
	3.0	1.02	4.5	83	75

(a) Experimental conditions: resin 20 g, diphenylether 70ml, 50% NaOH aqueous solution 50 ml, Bu_4NCl 1.5 g, $NaCo(CO)_4$ 1 g; 50°C ; 72 hours.

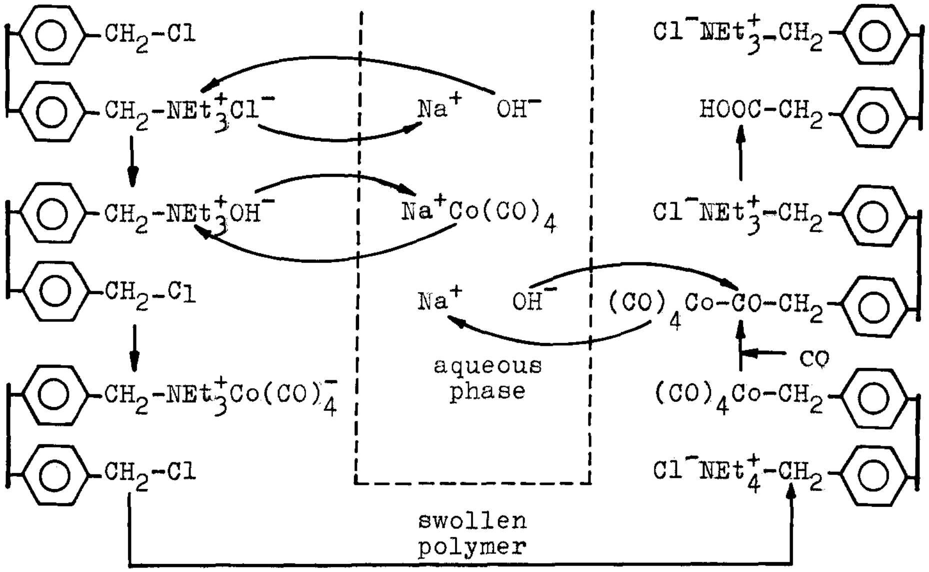
(b) Initial chlorine content in bracket.

(c) % chlorine transformed.

As it can be seen in Table 1, the carbonylation of chloromethylated polystyrene resin in phase-transfer catalysis was successful. Complete displacement of chlorine was not achieved, however, when carried out with highly cross-linked polymers even at low content of chlorine. The yields of arylpyruvic sites are affected by the carbon monoxide pressure.

Tetrabutylammonium chloride is the transfer catalyst in the three phase system. We found that the quaternary ammonium group fixed to a crosslinked chloromethylated polystyrene matrix (samples SDVB-Q) acts also as phase-transfer catalyst.

Catalysis by anionic exchange is involved in the two phase system represented in Scheme 2. The Co(CO)$_4^-$ anion is extracted by the positive Et$_3$N$^+$ ion as polymer-CH$_2$-NEt$_3^+$Co(CO)$_4^-$ ion pair into the polymer matrix where the oxidative addition occurs by site-site interaction. The results are summarised in Table 2



Scheme 2

Table 2
Carbonylation of partial quaternizated chloromethylated polystyrene resin(a)

Sample	Resin anal.%		Product anal.%		Functionalization yield% (b)
	Cl	N	Cl	N	
SDVB_Q-1	17.66	0.55	16.83	0.53	5
SDVB-Q-2	16.64	1.31	14.57	1.30	20
SDVB-Q-3	13.46	3.71	11.69	3.92	60
SDVB-Q-4	13.17	2.58	12.50	2.57	10

(a) Experimental conditions: resin 20 g, diphenylether 70 ml, aqueous solution of NaOH (40%) 50 ml, NaCo(CO)$_4$ 1 g; 72 h. 50oC;

(b) Calculated from total ionic exchange capacity data (Ref.8)

Infrared spectra taken befor and after functionalization shows that, in all cases, the C-Cl bands (670 and 1260 cm^{-1}) disappear appearing a new band for the -COOH group (1700 cm^{-1}).

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