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Online ATR-IR investigations and mechanistic understanding of the carbonylation of epoxides – the selective synthesis of lactones or polyesters from epoxides and CO

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Abstract

In situ ATR-IR spectroscopy is applied as a powerful tool to study the factors that control the reaction of epoxides with carbon monoxide in the presence of [Lewis acid]$^+$[Co(CO)$_4$]$^-$ salts. Based on these investigations, a consistent mechanistic scheme is presented, comprising the main lactone and polyester products and minor components, e.g., acetone and crotonic acid derivatives. β-Alkoxy-acyl-cobalttetracarbonyl species are shown to be key intermediates from which two reaction routes start in dependence of the applied Lewis acid (LA). Labile LA–alkoxy combinations favor a backbiting process of the oxygen function on the Co–acyl bond, primarily producing lactone products. More stable LA–alkoxy entities are unreactive toward PO conversion and afford a polymerization reaction after the addition of a nucleophile. In that case, the Lewis acid remains bonded to the chain end.

Keywords: Online ATR-IR spectroscopy; Catalytic carbonylation; Epoxides; Lactones; Aliphatic polyesters

1. Introduction

The insertion of CO into organic substrates through transition metal catalyzed reactions is of importance for numerous transformations in heterogeneous and homogeneous catalysis [1–5]. In addition, hydroformylation – the addition of carbon monoxide and hydrogen to olefins – is a widely industrially applied homogeneous catalytic carbonylation process [3,6]. The catalytic reaction itself was already discovered in 1938 by Roelen, using the system $Co_2(CO)_8/CO/H_2$ [7]. Since then, hydroformylation research has led to a profound understanding of the elementary steps of the catalytic cycle and from this perception, significant improvements were achieved by the application of cobalt, rhodium or ruthenium-based (phosphane) catalysts [8]. Carbonylation reactions in the absence of hydrogen also found ways into technical application and are nowadays connected to important industrial synthesis like the "Monsanto process" for the production of acetic acid from methanol [9] and the "Reppe carbonylation" to yield carboxylic acids from olefins and alkynes [10]. Other substrate molecules like epoxides or aziridines were also subjected to carbonylation and hydroformylation conditions during the time of pioneering studies on carbonylative transformations in the 1950s and 1960s [11–13]. Little attention was given to these starting materials thereinafter. Nevertheless, putative derived product structures such as lactones, polyesters or polyamides are of substantial technical importance. Aliphatic polyesters for example result from epoxides and CO either directly or via a lactone intermediate. The latter in turn is produced by a ring expanding carbonylation of epoxides [14]. In the last two years, important progress was achieved in the carbonylation of epoxides to lactones [15] and directly to polyesters [16]. We present here a

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comprehensive mechanistic outline of the carbonylation reaction of epoxides yielding lactones, polyesters, acetone and crotonic acid derivatives in various amounts in dependence of catalysts, cocatalysts and reaction conditions.

2. Results and discussion

An ATR-IR spectrometer attached to a high-pressure autoclave unit was used for in situ online investigation in order to gain insight into rates and product distributions of epoxide carbonylation reactions. This analytical tool gives a variety of information under reaction conditions (high pressure and temperature) relevant to catalysis: identity and quantity of key structures, kinetics with no sample handling, and online recording of possibly short-lived (organometallic) intermediates (see Fig. 1).

3. ATR-IR investigation of the carbonylation process

Basic information of epoxide carbonylation reactions was taken from well-studied hydroformylations. $HCo(CO)_4$ is presumed to be a potential catalyst that activates epoxides through protonation and subsequent ring opening by the $Co(CO)_4^-$ nucleophile (Scheme 1).

Mixtures of $HCo(CO)_4$ and epoxides were studied with the objective of gaining insight into individual mechanistic steps in the absence of hydrogen. It is known, that $HCo(CO)_4$ decomposes easily to H_2, $Co_2(CO)_8$, higher carbonyl clusters and other products. For this reason, it was decided to prepare $HCo(CO)_4$ in situ from $Et_4NCo(CO)_4$ and HBF_4. Quantitative formation of $HCo(CO)_4$ [17] was detected after the addition of $HBF_4^*OEt_2$ to a solution of $Et_4NCo(CO)_4$ in diglyme under 20 bar carbon monoxide pressure (Fig. 2). Significant changes were instantaneously observed in the IR spectrum after addition of propylene oxide to this reaction mixture (Fig. 3). New absorptions appeared at 2107, 2041, 2022, 2003 and 1710 cm^{-1}; simultaneously, the bands associated with $HCo(CO)_4$ disappeared, indicating the quantitative formation of an acyl-cobaltcarbonyl species (Fig. 4).

Fig. 5 is a time-dependent ATR-IR stack-plot of the above reaction sequence. The cobalttetracarbonylate anion of $Et_4NCo(CO)_4$ was observed (1889 cm^{-1}) in a first stage. The addition of one equivalent HBF_4 at 0 °C initiated the immediate formation of a mixture of free $Co(CO)_4^-$-anions and $HCo(CO)_4$ (1889 cm^{-1}, resp. 2117,

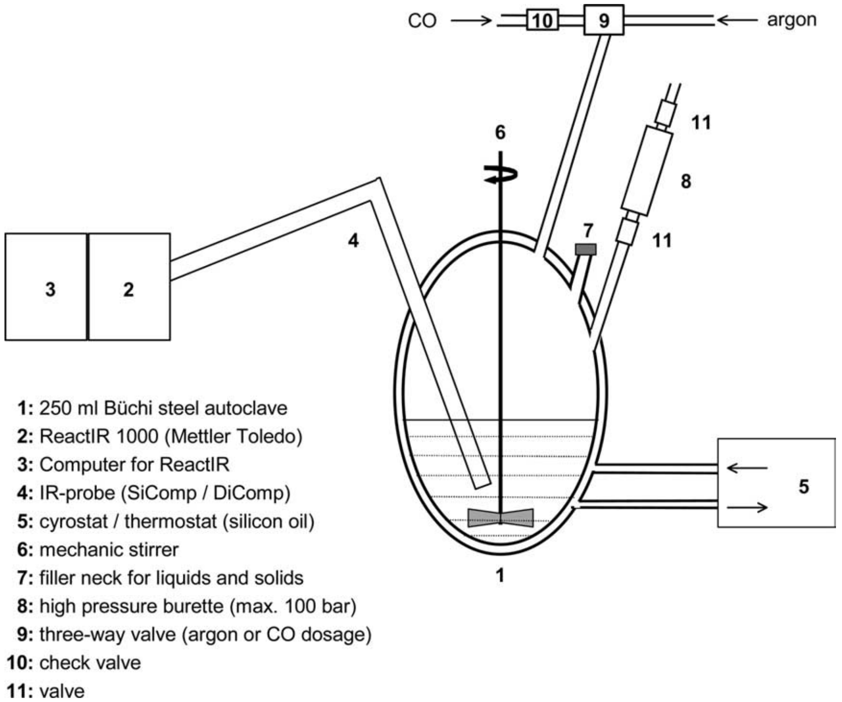
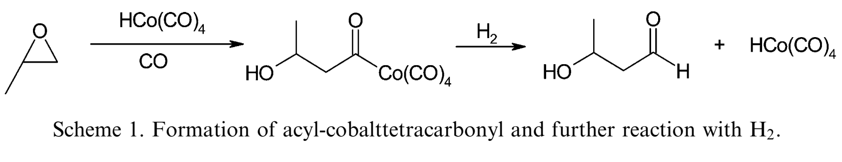


Fig. 1. ATR-IR/autoclave setup for online measurements.



Scheme 1. Formation of acyl-cobalttetracarbonyl and further reaction with H_2.

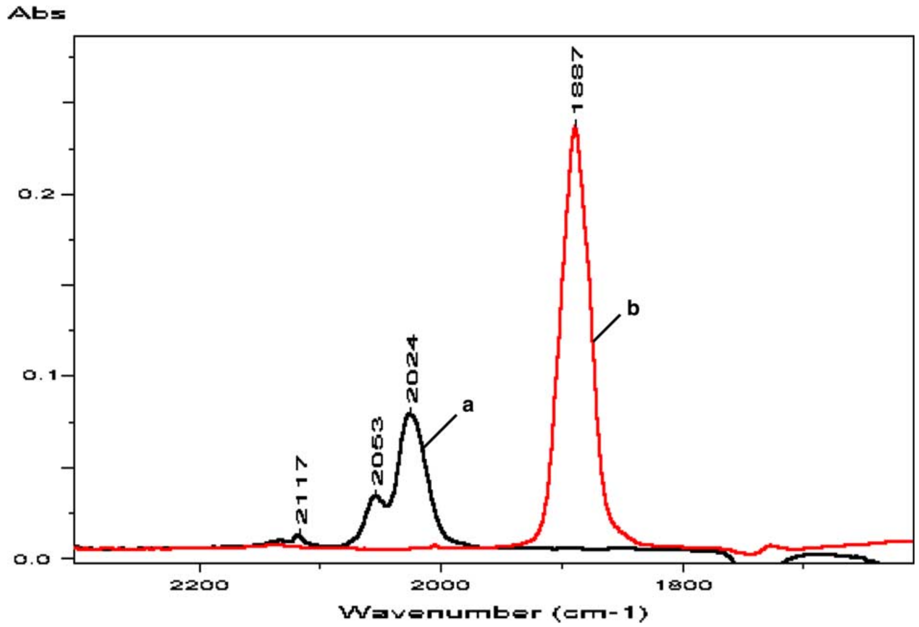


Fig. 2. ATR-IR spectroscopic monitoring of the in situ synthesis of $HCo(CO)_4$ (a: 2117, 2053 and 2024 cm^{-1}) from $Et_4NCo(CO)_4$ (b: 1887 cm^{-1}) and HBF_4.

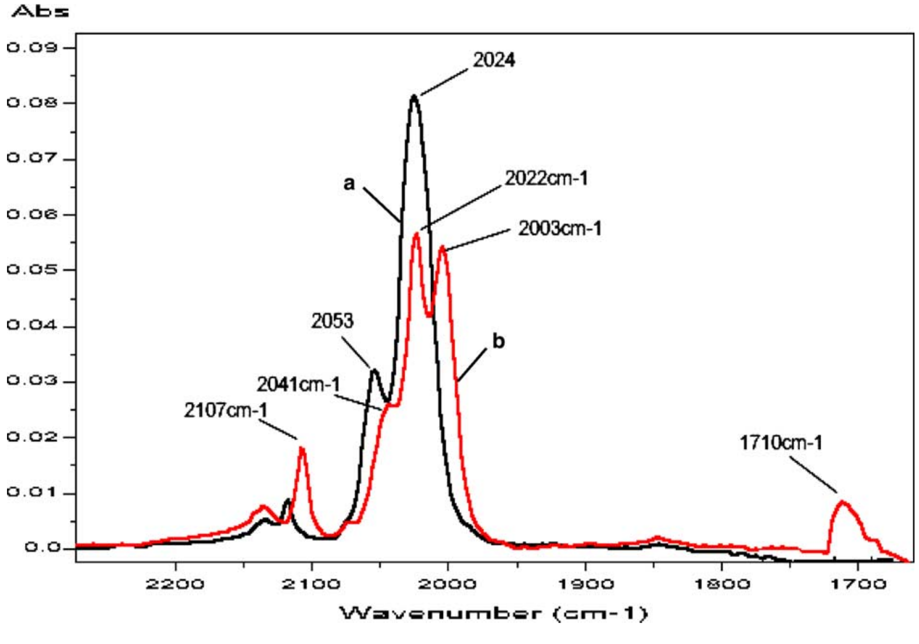


Fig. 3. ATR-IR spectroscopic detection of the formation of the acyl complex $HO–CH(CH_3)CH_2CO–Co(CO)_4$ (a: 2107, 2041, 2022, 2003 and 1710 cm^{-1}) from $HCo(CO)_4$ (b: 2117, 2053 and 2024 cm^{-1}) by PO addition under CO.

2053, 2024 cm^{-1}). This mixture remained unchanged for 20–30 min. $HCo(CO)_4$, apparently stable at 0 °C, was present in the IR-spectrum after the addition of another 0.5 equivalents of HBF_4 as the only species. Finally, β-alkoxyacyl-cobalttetracarbonyl was formed within 2 min after the subsequent addition of propylene oxide (50 equivalents relative to $Et_4NCo(CO)_4$ at 0 °C).

The reaction mixture comprising acyl-cobalttetracarbonyl, HBF_4 and propylene oxide was heated to 75 °C to induce the formation of carbonylation products (Table 1, entry 6). However, only decomposition of acyl-cobalttetracarbonyl and the simultaneous formation of $Co_2(CO)_8$ (2072, 1847 cm^{-1}, Fig. 6) was observed under these conditions. It is presumed, that the strong acidic condition were responsible for the decomposition reactions.

Therefore, a second set of reaction conditions was used to study a mixture of acyl-cobalttetracarbonyl,

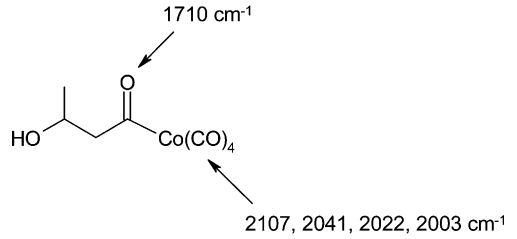


Fig. 4. Characteristic IR absorptions of the acyl-cobalttetracarbonyl complex resulting from treatment of $HCo(CO)_4$ with PO and carbon monoxide. Synthesis, characterization and reactions of acyl-cobalt-carbonyl complexes are already reviewed in literature [18].

excess $Et_4NCo(CO)_4$ and PO for its carbonylation activity. In contrast to the previous experiments, less than one equivalent HBF_4 was added to $Et_4NCo(CO)_4$ and PO in diglyme at 0 °C. After heating to 75 °C, now a slow formation of β-butyrolactone (1829 cm^{-1}) is observed and no decomposition of the acyl-complex occurred within 1 h (Fig. 7) (Table 1, entry 7). The rate of lactone formation was relatively low, but the reaction is remarkably selective.

We further tested a variety of tetracarbonyl cobaltate salts for the carbonylation of propylene oxide to learn more about the dependence of activity on the nature of the LA-fragment (Table 1) [15].

All experiments that were conducted to induce carbonylation reactions of epoxides by using $Co(CO)_4^-$-salts with cations of low Lewis acidity (e.g., $PPNCo(CO)_4$ or $Et_4NCo(CO)_4$, PPN: bis(triphenylphosphoranylidene)ammonium) failed [15b] (Table 1, entries 1 and 2). The characteristic absorption of the $Co(CO)_4^-$-anion (1889 cm^{-1}) was invariable over several hours; no carbonylation product was detected. ^1H NMR spectroscopy of the reaction mixture confirmed this observation (PO and solvent signals only). These results are consistent with theoretical considerations [15a] and suggest that the $Co(CO)_4^-$-anion by itself is not nucleophilic enough to induce ring opening of the epoxide substrate [19].

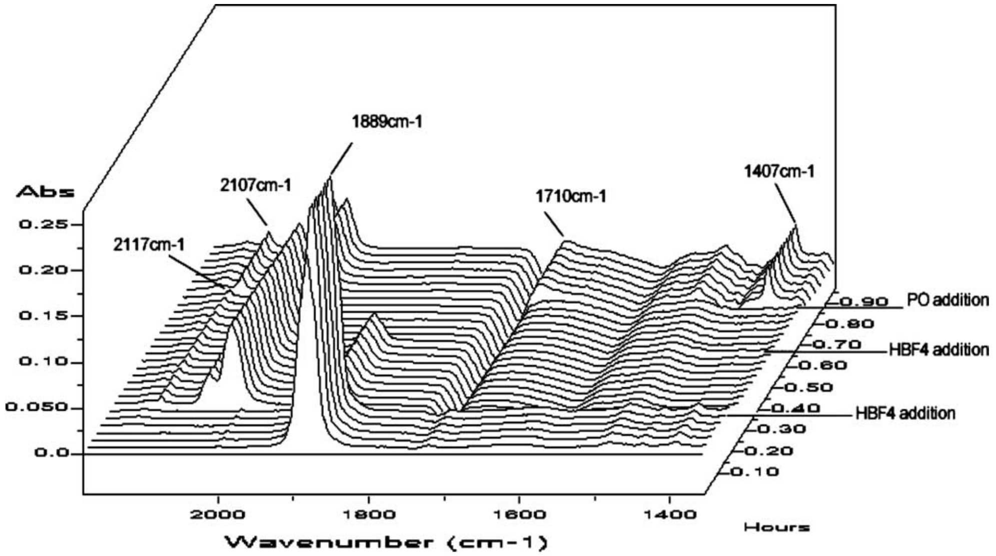


Fig. 5. ATR-IR stack plot for the conversion of $Et_4NCo(CO)_4$ (1889 cm^{-1}) to $HCo(CO)_4$ (2117, 2053 and 2024 cm^{-1}) and further to the acyl complex $HO–CH(CH_3)CH_2CO–Co(CO)_4$ (1407 cm^{-1}: characteristic PO absorption).

Table 1
All reactions were carried out at 75 °C and 60 bar CO pressure

No.	Catalyst	Epoxide	Reaction time [h]	Results
1	$Et_4NCo(CO)_4$	PO	20	No reaction
2	$PPNCo(CO)_4$	PO	20	No reaction
3	$Hg[Co(CO)_4]_2$	PO	20	No reaction
4	$Zn[Co(CO)_4]_2$	PO	20	5–10% PO consumption
5	$NaCo(CO)_4$	PO	20	5–10% PO consumption
6	$HCo(CO)_4$/excess HBF_4	PO	4	Acyl-$Co(CO)_4$/no carbonylation
7	$HCo(CO)_4$/excess $Et_4NCo(CO)_4$	PO	2	Acyl-$Co(CO)_4$/slow lactone formation
8	$Ph_3SiCo(CO)_4$	PO	4	Acyl-$Co(CO)_4$ (stable)

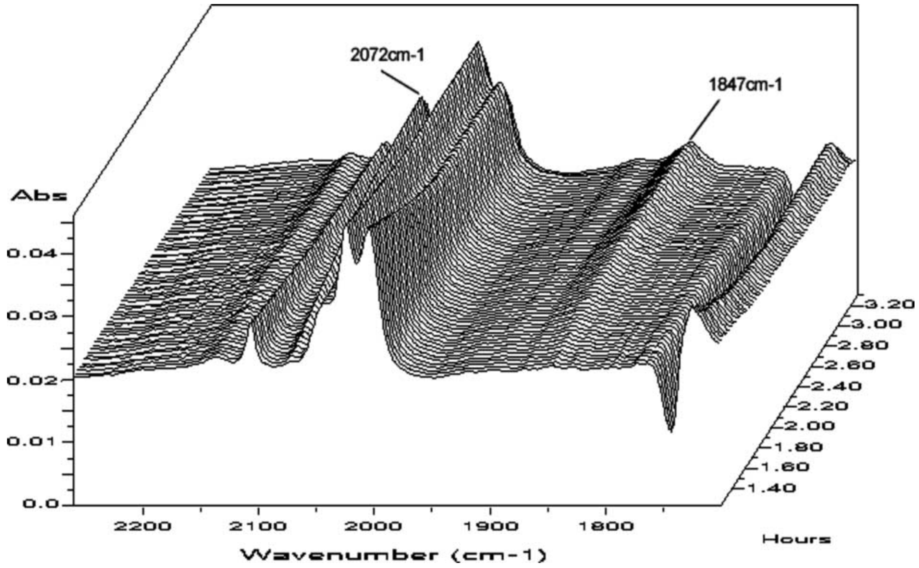


Fig. 6. Reactivity of HO–CH(CH_3)CH_2CO–Co(CO)$_4$ in the presence of excess HBF_4 and PO. $Co_2(CO)_8$ (2072 and 1847 cm^{-1}) is detected instead of PO carbonylation products. (The absorptions of $Co_2(CO)_8$ (2042 and 2001 cm^{-1}) overlap with the bands of the acyl-cobaltcarbonyl species (2041, 2022 and 2003 cm^{-1}). For this reason the free absorptions (2072 and 1847 cm^{-1}) are used for characterization.)

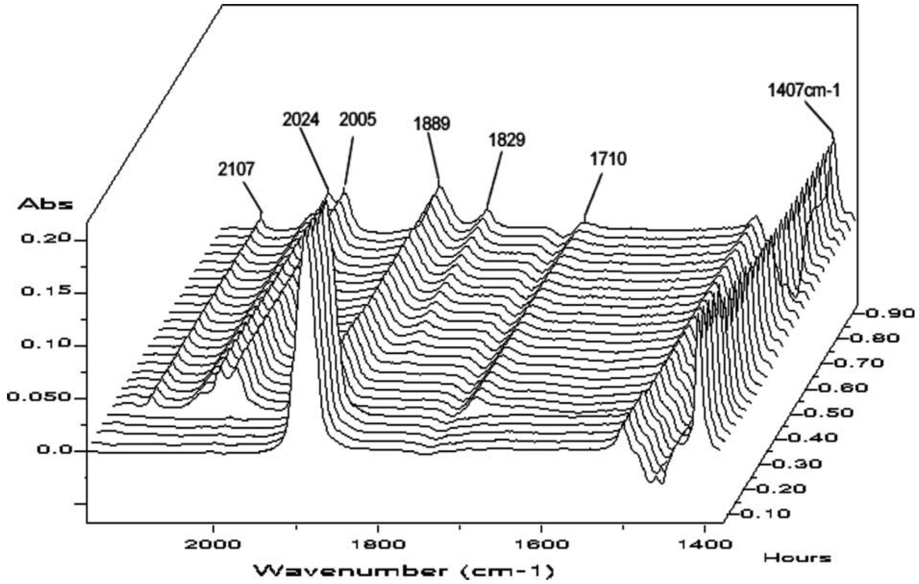
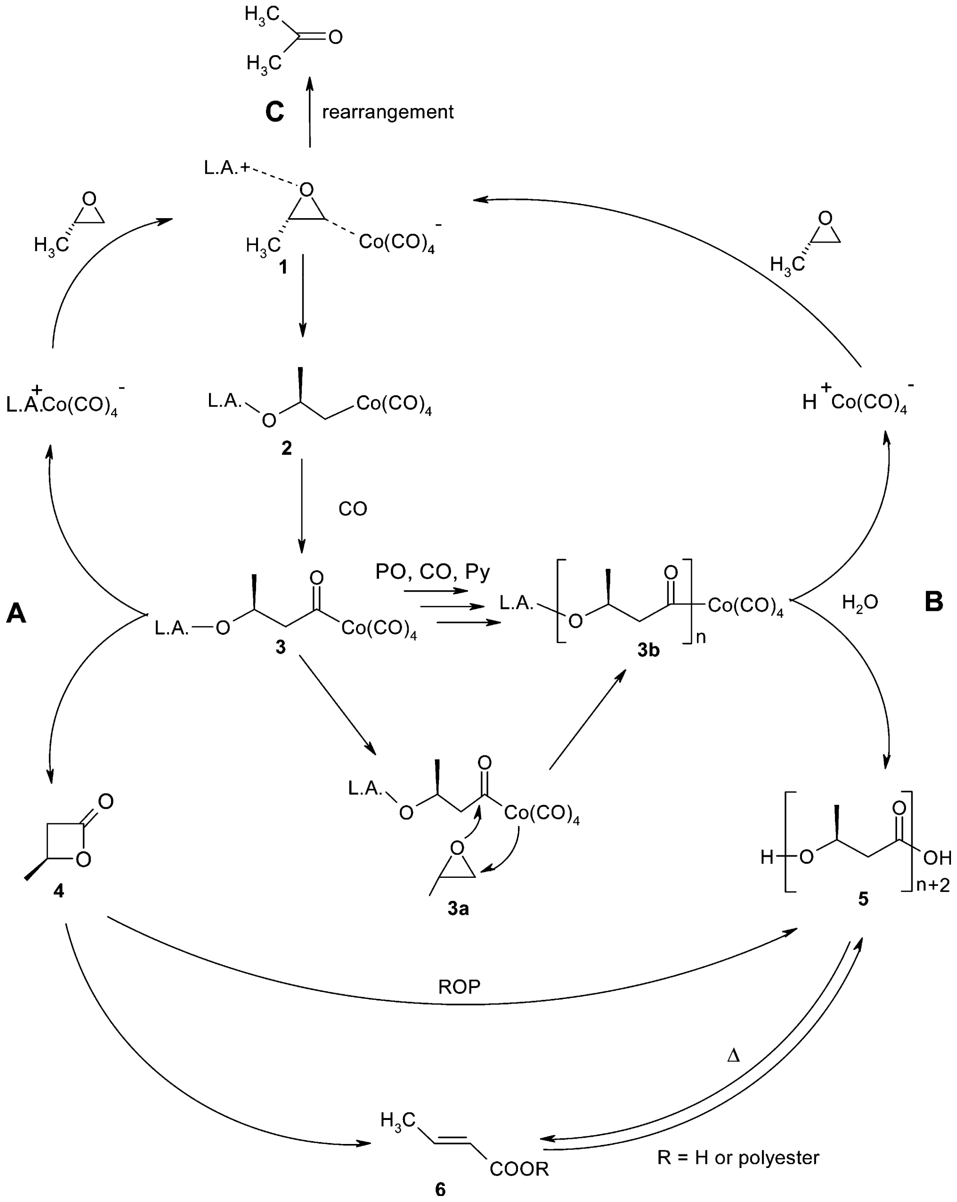


Fig. 7. Reactivity of HO–CH(CH_3)CH_2CO–Co(CO)$_4$ in the presence of excess $Et_4NCo(CO)_4$ and PO. Selective β-butyrolactone formation (1829 cm^{-1}) is observed (PO carbonylation product).

We further considered the reactivity of Hg[Co(CO)$_4$]$_2$ and Zn[Co(CO)$_4$]$_2$. The two components differ in Lewis acidity. Hg[Co(CO)$_4$]$_2$ is a covalent complex of low polarity, while Zn[Co(CO)$_4$]$_2$ has considerable ionic character [20]. Hg[Co(CO)$_4$]$_2$ proved to be inactive for epoxide ring opening and consecutive carbonylation reactions (Table 1, entry 3). In contrast, a PO carbonylation experiment with Zn[Co(CO)$_4$]$_2$ in diglyme resulted in CO and epoxide consumption (^{1}H NMR: 10% PO consumed after 20 h, 75 °C). The product is a mixture of β-butyrolactone, ester oligomers and acetone (Table 1, entry 4).

Recently, we reported that experiments indicating the possibility of a direct alternating copolymerization reaction of epoxides and CO to generate polyesters (Scheme 2, **B**) [16a]. In order to suppress “backbiting” sequences of the acyl-cobalttetracarbonyl species **3** that would afford lactone, the LA–alkoxy oxygen moiety has to be sufficiently unreactive to form the end-group of a growing polyester chain. The compound $Ph_3SiCo(CO)_4$ (Fig. 8) was found to be an excellent catalysts-precursor in this regard [21]. The corresponding acyl-cobalttetracarbonyl complex (Ph_3Si–OCH(CH_3)–CH_2CO–Co(CO)$_4$; Fig. 8, 2107, 2043, 2024, 2005 and 1710 cm^{-1}) is quantitatively



Scheme 2. Catalytic cycle for the organometallic carbonylation of epoxides.

obtained by adding PO to the solution of $Ph_3SiCo(CO)_4$ in toluene[2] (Fig. 7, **A**)[3] [22]. This acyl-species is stable for several hours at 50 °C or at 75 °C in CO atmosphere [23]. Addition of pyridine to this reaction mixture results in the formation of polyhydroxybutyrates. All investigations show that pyridine plays a prominent, not yet fully understood role in the further insertion of epoxide monomers into cobalt–acyl bonds (**3** → **3a** → **3b**) yielding the polyester product (**5**) [24]. Hydrolysis by residual or intermediate water was demonstrated to be a chain-transfer mechanism (**3b** → **5**), and thermal degradation of the formed PHB to crotonic acid derivatives (**6**) influence the molecular weight of the polymer product.

4. Mechanistic considerations

The results of this study are cumulated in Scheme 2. Polarization of the epoxide (**1**) is achieved by interaction of a Lewis acidic species with the epoxide oxygen atom. A strong Lewis acid results in an immediate ring opening of the cyclic ether (Scheme 2, **C**), affording the

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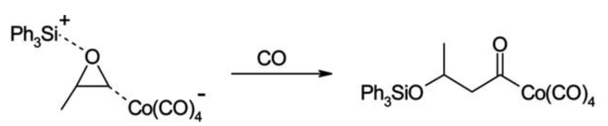
[2] Toluene instead of diglyme was used because $Ph_3SiCo(CO)_4$ is known to react with cyclic and linear ethers.

[3] Alternative methods for the synthesis of acyl- or alkyl-cobalttetracarbonyl complexes were performed by adding $NaCo(CO)_4$ to acyl- or alkyl-chlorides (e.g., ethyl-bromoacetate). Partially, these methods suffer from significant decomposition.



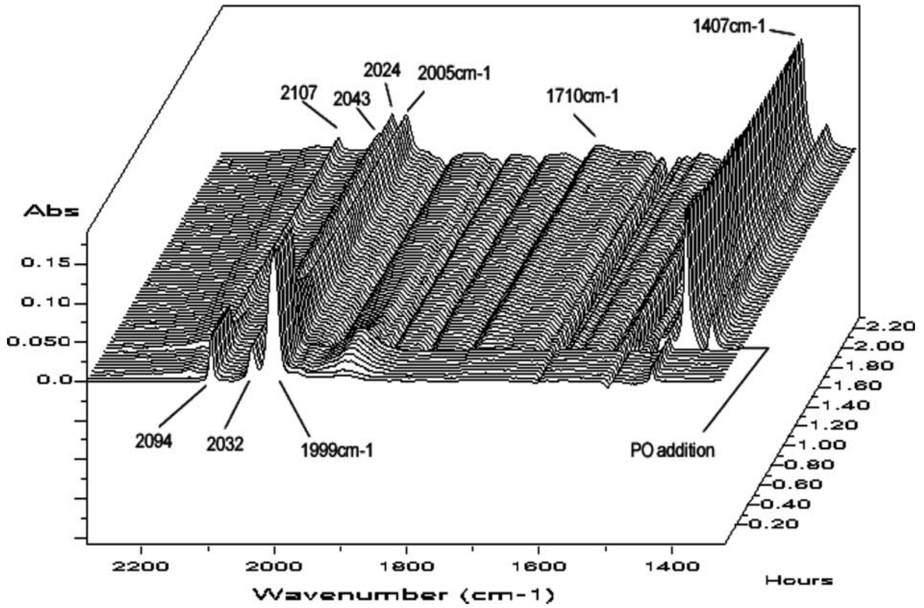


Fig. 8. Stack plot for the reaction of $Ph_3SiCo(CO)_4$ (2094, 2032, 1999 cm^{-1}) in toluene with PO (1407 cm^{-1}; addition after 0.6 h) under CO-atmosphere. Product is the acyl complex $Ph_3Si–OCH(CH_3)–CH_2CO–Co(CO)_4$ (2107, 2043, 2024, 2005, 1710 cm^{-1}).

propylene oxide isomer acetone or inducing a ring opening polymerization (ROP) reaction of the epoxide to polyethers. Less acidic fragments activate the epoxide substrate and an alkyl-cobalttetracarbonyl species (Scheme 2, **2**) is formed after backside attack of the $Co(CO)_4^-$-nucleophile. Carbon monoxide is subsequently inserted to yield the corresponding acyl-cobalttetracarbonyl species (**3**), which is stable under CO atmosphere. The intermediate **3** can now react according to two different routes, depending on the Lewis acid cocatalyst to produce lactone (**4**) or polyester (**5**) products after the addition of pyridine. A backbiting reaction of the alkoxy oxygen on the acyl moiety of **3** results in a lactone formation process provided that the LA–oxygen entity is labile enough. In addition, the catalyst ([Lewis acid]$^+$[$Co(CO)_4$]$^-$) is re-generated (**A**) if the lactone effectively de-coordinates from the Lewis acid. ROP of the lactone intermediate gives secondary polyester products or rearrangement to crotonic acid derivatives (**6**), feasible reactions in the presence of a Lewis acid [25].

5. Conclusions

In situ ATR-IR spectroscopy has proven to be a powerful tool to gain insight in cobalt carbonylate catalyzed carbonylation reactions of propylene oxide at elevated pressure and temperature. It became clear, that the Lewis acidity of the cocatalyst is of eminent importance. Several reaction channels are accessible for the reactive epoxides, ranging from isomerization or polyether formation with potent Lewis acids, fast ring opening and formation of stable cobalt acylium β-alkoxy complexes with Lewis acids of intermediate strength, or catalytic lactone formation with even weaker acidic species to complete interactivity. Polyester is formed under the action of pyridines on unreactive cobalt acylium species. It may be anticipated, that pyridine induces the formation of Lewis acid after reaction with the cobalt acyl compound. The exact reaction pathway is still under investigation. A comprehensive reaction scheme (Scheme 2) shows the whole of the currently established reaction modes.

6. Experimental

Racemic propylene oxide (rac-PO) was supplied by BASF AG (water <15 ppm). Diglyme was purchased water free from Fluka, degassed before use. $NaCo(CO)_4$ [26], $Et_4NCo(CO)_4$ and $PPNCo(CO)_4$ [15a], Hg-$[Co(CO)_4]_2$ [27], $Zn[Co(CO)_4]_2$ [28] and $Ph_3SiCo(CO)_4$ [29] were synthesized according to literature procedures.

The applied ReactIR1000™ from Mettler Toledo is based on mid-infrared Fourier transform (FTIR) spectrometer. The sampling system includes a dipper, connected to the autoclave, equipped with a choice of DiComp™ (diamond sensor for highest chemical resistance) or SiComp™ (silicon sensor) ATR insertion probes.

General carbonylation procedure. Reactions were conducted in a 250-ml Büchi reactor equipped with the ReactIR1000™ for in situ ATR-IR measurements under high-pressure conditions. For the preparation of the catalyst mixture, 60 ml of diglyme were transferred to the autoclave. The system was cooled to 0 °C and the catalyst-precursors (3.47 mmol of $Co(CO)_4^-$-anion salt) were added. HBF_4 and propylene oxide (30 ml) were transferred to the autoclave through a pressure burette with a carbon monoxide pressure pulse. The carbonylation reactions were carried out at 75 °C for periods of 2–20 h while pressurizing the reactor with 60 bar CO. The carbonylation reaction was quenched by cooling the ATR-IR-reactor setup to ambient temperature and ventilation of the gaseous components. Yields were determined by online-IR and by NMR analysis of the resulting solutions.

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