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Transition-metal-mediated activation of arylisocyanates in supercritical carbon dioxide

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Abstract

The reactivity of arylisocyanates in supercritical carbon dioxide ($scCO_2$) was studied using the easily available complexes $CpCo(CO)_2$, $CpCoPPh_3Me_2$ and $Ni(cod)_2$ as catalysts. A study of the solubility of the catalysts in $scCO_2$ was undertaken in all cases. The complex $CpCo(CO)_2$ is very soluble, 1.7×10^{-1} mol kg^{-1}, while $CpCoPPh_3Me_2$ has a lower solubility, 7.2×10^{-3} mol kg^{-1}, and $Ni(cod)_2$ is insoluble in $scCO_2$. For comparison purposes, the reactions were performed in parallel in $scCO_2$, using toluene as a solvent and just with the neat liquid arylisocyanate. Reactions in $scCO_2$ either do not take place at all, when $CpCo(CO)_2$ is used as catalyst, or occur with low yields affording the trimer of the corresponding arylisocyanate when $CpCoPPh_3Me_2$ or $Ni(cod)_2$ act as catalysts. No incorporation of CO_2 into the organic substrate was observed. Better conversions to triarylisocyanate were obtained when the reactions were performed by direct mixture of the liquid arylisocyanate ArNCO (Ar = Ph, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$) and the catalyst. Using toluene as a solvent, the yields of the trimers were lower than those obtained in neat arylisocyanate, and in some cases they were not formed at all. For instance in the reaction of $CpCo(CO)_2$ and tolylisocyanate either under stoichiometric or catalytic conditions the trimer is not obtained, instead the compound $H_2R_3N_3C_2O_2$ (R = $CH_3C_6H_4$), was isolated in low yield. In the reaction of $Ni(cod)_2$/PPh_3 with phenylisocyanate, the trimer was formed but in low yield. The lower yields of the trimers observed when the reactions were performed in $scCO_2$ or in toluene, compared to that observed in neat arylisocyanates, indicates that the decrease in reactivity is due to a decrease in concentration. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Supercritical CO_2; Ni complexes; Co complexes; Arylisocyanates; Cyclotrimerisation

1. Introduction

Recently there has been a considerable growing interest in the use of supercritical carbon dioxide ($scCO_2$) as an environmental friendly reaction medium [1]. CO_2 presents moderate critical constants ($T_c = 31.06°C$, $P_c = 73.825$ bar) and a non-toxic nature, offering many advantages over conventional solvents such as higher selectivity, increased reaction rates and facile separation of reactants, catalyst and products after reaction [2]. All these properties made $scCO_2$ a solvent with the potential to replace conventional organic solvents in different applications such as homogeneous catalysis [3]. $scCO_2$ can also be used as both solvent and reagent in reactions involving activation of the CO_2 molecule. CO_2 can be activated in the presence of transition metals, either by forming metal–CO_2 complexes, or it can be converted into organic products by reaction with the appropriate organic substrates [4]. This strategy has been recently applied in the production of tetraethylpyrone in $scCO_2$ by coupling of 3-hexyne and CO_2 using $Ni(cod)_2$/R_3P as catalyst [5]. Hydrogenation of CO_2 using ruthenium phosphine complexes as catalysts has been reported by Noyori et al. The rates of formic acid production in $scCO_2$ were significantly higher than those found in organic solvents [6].

We report here our first studies exploring $scCO_2$ as a solvent, and simultaneously as reagent, a C_1 building block. For that purpose we have systematically studied

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the reactivity of several unsaturated substrates in scCO$_2$ in the presence of transition-metal complexes. The formal electronic analogy of arylisocyanates with carbon dioxide made them suitable candidates for this study.

Activation of arylisocyanates can be achieved by the use of transition-metal complexes [7]. The complexes dicarbonyl(η^5-cyclopentadienyl)cobalt, CpCo(CO)$_2$, bis(η^4-1,5-cyclooctadiene)nickel, Ni(cod)$_2$ and dimethyltrifenilphosphine(η^5-cyclopentadienyl)cobalt, CpCoPPh$_3$(Me)$_2$ are well known activators of unsaturated organic substrates [8] and a great deal of work involving the reactivity of these complexes towards arylisocyanates has been reported [9].

Exploring the reactivity of arylisocyanates with the above-mentioned complexes, we have found them excellent catalysts for the cyclotrimerisation reaction, when the reactions are carried out in neat arylisocyanate. The cyclotrimerisation of arylisocyanates to give triaryl isocyanurates is a well documented reaction [10], the trimers have useful applications such as activators in the synthesis of Nylon 6 and enhancing the thermal and

chemical resistance of polyurethanes and quite recently some new catalysts for this reaction have been published [11].

In this paper, we describe the reactivity of several arylisocyanates in scCO$_2$ using CpCo(CO)$_2$, Ni(cod)$_2$ and CpCoPPh$_3$Me$_2$ as catalysts. In Table 1 the solubility of the catalysts in scCO$_2$ is presented. Tables 2 and 3 summarise the results obtained.

2. Experimental

2.1. General

All reactions and manipulations of solutions were performed under an argon atmosphere using Schlenck techniques. Solvents were reagent grade and were dried according to literature methods, arylisocyanates were purchased from Aldrich and they were used as supplied. CpCo(CO)$_2$ [12], CpCoPPh$_3$Me$_2$ [13], and Ni(cod)$_2$ [14], were prepared as reported previously.

Table 1
Data for the solubility of the catalyst in scCO$_2$

Catalyst	T (°C)	P (CO$_2$) (bar)	d (CO$_2$) (g cm^{-3})	Solubility (mol kg^{-1})
CpCo(CO)$_2$	40	84	0.36	1.4×10^{-1}
CpCoPPh$_3$Me$_2$	40	150	0.78	7.2×10^{-3}

Table 2
Data for the cyclotrimerisation of aryl isocyanates to yield triarylisocyanurates in neat isocyanate

Entry	Catalyst	R-NCO	Ratio of R-NCO/catalyst	Conditions	Yield (%)
1	CpCo(CO)$_2$	p-CH$_3$C$_6$H$_4$	25:1	50°C, 24 h	42
2[a]	CpCo(CO)$_2$	p-CH$_3$C$_6$H$_4$	25:1	40°C, 24 h[b]	53
3[a]	CpCo(CO)$_2$	C$_6$H$_5$	25:1	90°C, 24 h[b]	21
4	Ni(cod)$_2$	p-CH$_3$C$_6$H$_4$	42:1	60°C, 24 h	62
5	Ni(cod)$_2$	p-CH$_3$OC$_6$H$_4$	42:1	60°C, 24 h	56
6	Ni(cod)$_2$	C$_6$H$_5$	42:1	60°C, 24 h	13
7	Ni(cod)$_2$/PPh$_3$	C$_6$H$_5$	42:1	20°C, 12 h	Complete
8	PPh$_3$	C$_6$H$_5$	42:4	20°C, 12 h	0
9	CpCoMe$_2$PPh$_3$	C$_6$H$_5$	65:1	20°C, 12 h	Complete

[a] Reaction carried out using a visible lamp (200 W).

Table 3
Data for the cyclotrimerisation of aryl isocyanates to yield triarylisocyanurates in a solvent

| Entry	Catalyst	R-NCO	Ratio of R-NCO/catalyst	Solvent	Conditions	Yield (%)
1	CpCo(CO)$_2$	p-CH$_3$C$_6$H$_4$	25:1	scCO$_2$	50°C, 140 bar, 24 h	0
2[a]	CpCo(CO)$_2$	p-CH$_3$C$_6$H$_4$	25:1	scCO$_2$	100°C, 140 bar, 24 h	0
3[a]	CpCo(CO)$_2$	p-CH$_3$C$_6$H$_4$	25:1	Toluene	40°C, 24 h	0
4[a]	CpCo(CO)$_2$	C$_6$H$_5$	25:1	Toluene	90°C, 24 h	0
5	Ni(cod)$_2$/PPh$_3$	C$_6$H$_5$	42:1	scCO$_2$	40°C, 228 bar, 24 h	9
6[b]	Ni(cod)$_2$/PPh$_3$	C$_6$H$_5$	42:1	Toluene	40°C, 12 h	17
7	CpCoMe$_2$PPh$_3$	C$_6$H$_5$	124:1	scCO$_2$	40°C, 125 bar, 24 h	19

[a] Reaction carried out using a visible lamp (300 W).
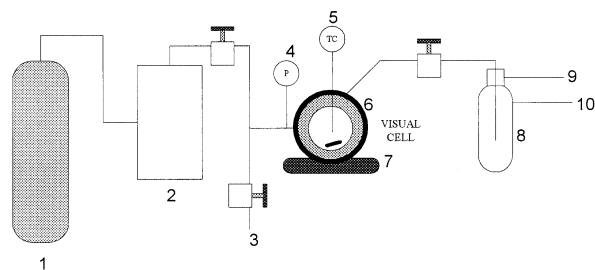
Fig. 1. 1, CO_2 cylinder; 2, pneumatic liquid pump; 3, vacuum line; 4, pressure transducer; 5, temperature controller; 6, heating tape; 7, stir plate; 8, Schlenck tube; 9, vent line; and 10, argon line.

2.2. Physical methods

Infrared spectra were recorded as mulls on NaCl plates using an ATI Mattson Genesis FTIR spectrometer.

Elemental analyses were performed at the microanalytical laboratory of the Universidade Técnica de Lisboa, Portugal.

Mass spectra were recorded on VG Autospec EI technique, at the Instituto de Ciencias de Materiales de Aragon, Zaragoza, Spain. ^{1}H-, and ^{13}C-NMR spectra were recorded on a Bruker ARX 400 spectrophotometer. ^{1}H-NMR spectra were recorded using TMS as internal reference and ^{13}C-NMR spectra were referenced using the ^{13}C resonance of the solvent as internal standard.

2.3. Reactions in supercritical CO_2

The reactions and the solubility measurements in $scCO_2$ were carried out in a 30 ml stainless steel high-pressure cell. Two sapphire windows allow full observation of the inside. The cell is described elsewhere [15]. A schematic diagram of the experimental apparatus is shown in Fig. 1.

All reagents and catalysts are charged into the cell under argon, then the reactor is evacuated under vacuum and refilled with argon. The cell is then placed in the high-pressure apparatus. CO_2 (purity 99.9999% from Carburos Metálicos) is transferred into the cell using a pneumatic liquid pump. The cell is heated to the desired temperature through a heating tape wrapped around the cell. The temperature is measured by a thermocouple inside the cell connected to a temperature controller. A digital transducer measures the pressure. The cell is on a stir plate inducing the magnetic Teflon bar inside the cell to undergo irregular movements, being a simple and effective mixing device. After reaction the cell is depressurised using an Schlenck tube as a trap. The contents of both, the cell and Schlenck tube are analysed.

2.4. Solubility measurements of the catalysts in supercritical CO_2

The solubility of the catalysts was visually determined by observing the CO_2 pressure at which the solid dissolved completely. The solubility values were calculated on the basis of the amount of solid and the calculated amount of CO_2 in the cell at the reported pressure.

2.4.1. Solubility of $Co(\eta^5-C_5H_5)(CO)_2$
The complex (0.28 g, 1.56 mmol) was loaded into the view cell with a syringe under dry, oxygen-free argon atmosphere. The reactor was then evacuated under vacuum and refilled with argon. Finally the reactor was heated to 40°C and the CO_2 was slowly introduced. The complex was totally dissolved in CO_2 when a pressure of 84 bar was reached, producing a red solution. The solubility was 1.4×10^{-1} mol of complex per kilogram of CO_2.

2.4.2. Solubility of $CpCo(CH_3)_2(PPh_3)$
$CpCo(CH_3)_2(PPh_3)$ (0.07 g, 0.17 mmol) were charged into the cell under argon. The cell was heated at 40°C and the CO_2 was introduced. A total dissolution of the complex in CO_2 was observed at 150 bar, forming an orange single phase. The solubility was 7.2×10^{-3} mol of complex per kilogram of CO_2.

2.4.3. Solubility of $Ni(cod)_2$
The measurement of the solubility of this complex in $scCO_2$ was previously carried out [5a]. We have repeated this measurement using the view cell and we have found no sign of dissolution even at high pressure of CO_2. However, it was found that the complex dissolved somewhat when it was mixed with excess of phenylisocyanate.

2.4.4. A typical reaction
A mixture of $CpCo(CH_3)_2(PPh_3)$ (0.021 g, 0.05 mmol) and PhNCO (0.74 g, 6.2 mmol) was charged in the high-pressure cell. CO_2 was transferred into the cell using a pneumatic pump and the cell was heated immediately at 40°C. When the final temperature was reached additional CO_2 was added up to a final pressure of 125 bar. The sapphire windows allow confirmation of a single fluid phase and of complete dissolution of the catalyst and reagent in the reaction mixture. After 24 h, CO_2 was vented and the surplus was extracted with CH_2Cl_2. The extract was filtered, evaporated under reduced pressure and the solid residue was washed with 20 ml of n-pentane. 0.14 g (19% yield) of the trimer was isolated as a white solid. Mass spectrum (EI$^+$) m/z: 358. The spectroscopic data agree with those reported in the literature [11].

2.5. Reactions carried out in neat arylisocyanates

2.5.1. Cyclotrimerisation of arylisocyanates using $CpCo(CO)_2$ as catalyst

A mixture of $CpCo(CO)_2$ (0.10 g, 0.55 mmol) and p-$CH_3C_6H_4NCO$ (1.89 g, 14.2 mmol) was heated at 50°C. A solid precipitated out of the red solution. After 24 h, 20 ml of n-pentane was added to remove the unreacted isocyanate. The white solid was washed with 10 ml of n-pentane for two repetitions and dried under reduced pressure to give 0.87 g (41% yield) of (p-$CH_3C_6H_4NCO)_3$.

The reaction was repeated using visible light (200 W). Yield: 1.12 g (53%).

^{1}H-NMR (CHCl$_3$-d, δ ppm): 7.30–7.26 (m, 12, CH, Ph), 2.40 (s, 9, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, CHCl$_3$-d, δ ppm): 149.0 (s, CO), 139.4, 131.2, 130.1, 128.2 (s, CH), 21.1 (s, CH$_3$). Mass spectrum (EI +) m/z: 400. Anal. Found: C, 72.19; H, 5.22 N, 10.68. Calc. for $C_{24}H_{21}N_3O_3$: C, 72.18; H, 5.26; N, 10.50%.

The cyclotrimerisation of PhNCO using the same procedure described above gave the corresponding trimer (PhNCO)$_3$ (yield: 21%). Spectroscopic data are in agreement with those reported in the literature [11].

2.5.2. Cyclotrimerisation of arylisocyanates using $Ni(cod)_2$ as catalyst

A mixture of $Ni(cod)_2$ (0.06 g, 0.22 mmol) and PhNCO (1.1 g, 9.2 mmol) was stirred at 60°C for 24 h. Using the same procedure described above, a solid was obtained corresponding to (PhNCO)$_3$ (yield: 0.14 g, 13%).

Reaction of $Ni(cod)_2$ (0.025 g, 0.09 mmol) and p-$CH_3OC_6H_4NCO$ (0.58 g, 3.9 mmol) afforded the corresponding trimer as a white solid. Mass spectrum (EI +) m/z: 448. Yield: 0.32 g (56%). Spectroscopic data are in agreement with those reported in the literature [11].

When the cyclotrimerisation reaction of PhNCO with $Ni(cod)_2$ as catalyst was repeated adding four equivalents of PPh$_3$, after 24 h at room temperature (r.t.), a total conversion to the trimer was observed. If toluene is used as solvent, after 24 h at 40°C only a 17% yield of trimer was formed.

No formation of trimer was achieved when a solution of PPh$_3$ (0.23 g, 0.88 mmol) and PhNCO (1.1 g, 9.2 mmol) was stirred at r.t. for 24 h.

2.5.3. Cyclotrimerisation of arylisocyanates using $CpCo(CH_3)_2(PPh_3)$ as catalyst

$CpCo(CH_3)_2(PPh_3)$ (0.017 g, 0.04 mmol) and PhNCO (0.31 g, 2.52 mmol) were mixed and stirred at r.t. After 24 h, all the initial PhNCO had trimerised to give (PhNCO)$_3$. The reaction was worked out using the same procedure described in Section 2.4.1.

2.6. Reactions carried out in toluene: preparation of $H_2R_3N_3C_2O_2$ ($R = CH_3C_6H_4$) (**4**)

p-$CH_3C_6H_4NCO$ (1.89 g, 14.2 mmol) was added to a toluene (15 ml) solution of $CpCo(CO)_2$ (0.10 g, 0.55 mmol). The resulting red solution was stirred at 50°C for 24 h and the toluene was then removed under vacuum. The red oil was washed with n-pentane and the resulting solid was extracted with diethyl ether. Cooling the solution at -20°C afforded the compound **4** as a white crystalline solid. Yield: 0.12 g (7%). No presence of the trimer was observed.

When the reaction was repeated at the same conditions, but heated at 85°C for 24 h, 0.17 g of **4** was obtained (yield: 10%).

^{1}H-NMR (CHCl$_3$-d, δ ppm): 8.92 (sa, 2, NH), 7.39–7.11 (m, 12, CH, Ph), 2.46 (s, 3, CH_3), 2.32 (s, 6, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, CHCl$_3$-d, δ ppm): 153.8 (s, CO), 140.0, 134.8, 134.1, 134.0, 131.2, 129.6, 120.8 (s, CH), 21.1 (s, CH$_3$), 20.6 (s, CH$_3$). Mass spectrum (EI +) m/z: 374. Anal. Found: C, 73.92; H, 6.26; N, 11.05. Calc. for $C_{23}H_{23}N_3O_2$: C, 73.93; H, 6.17; N, 11.26%.

3. Results and discussion

The solubility test of the catalyst consists in the visual inspection through the sapphire windows of the high-pressure cell. A known amount of catalyst was placed inside the cell under inert conditions, then it was connected to a high-pressure line and CO_2 was transferred into the cell using a pneumatic pump. The temperature of the cell was kept constant at 40°C. When a single phase (total disappearance of the solid) was observed inside the cell, a measure of the pressure was taken, and the solubility calculated in mole per kilogram. The complex $CpCo(CO)_2$ is very soluble, giving a beautiful red colour, $CpCoPPh_3Me_2$ is moderately soluble, whereas the complex $Ni(cod)_2$, as it was previously reported by Kreher et al. [5a], is practically insoluble. However, when $Ni(cod)_2$ is mixed with an excess of arylisocyanate in scCO_2, a light yellow mixture is formed, showing that the arylisocyanate acts as a co-solvent giving rise to a small solubility of the complex. After these measurements, the starting compounds were recovered in all cases, no reaction with CO_2 was observed for any of the compounds.

In order to compare the results obtained using scCO_2 as reaction medium, the reactions of the arylisocyanates ArNCO (Ar = Ph, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$) and the catalysts ($CpCo(CO)_2$, $CpCoPPh_3Me_2$ or $Ni(cod)_2$) were performed, in the first place, simply by direct mixture of the catalyst with the neat liquid arylisocyanate, without the use of a solvent (these results are presented in Table 2). Trimers of the corresponding

arylisocyanate were obtained in all cases (see Eq. (1)), with yields ranging from the lowest, 13%, in the case of $Ni(cod)_2$ and PhNCO, to completed reaction, obtained, for instance, with the same reagents but with addition of PPh_3 in a 1:4 ratio ($Ni(cod)_2$: PPh_3). To see whether PPh_3 would catalyse the trimerisation by itself, a reaction was carried out with just PPh_3 and phenylisocyanate and no sight of the trimer was observed. A completed reaction was also observed when $CpCoPPh_3Me_2$ was used as catalyst.
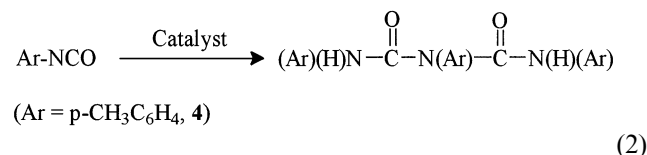
$$\text{Ar-NCO} \xrightarrow{\text{Catalyst}} \quad (1)$$

(Ar = Ph, **1**; p-CH_3C_6H_4, **2**; p-CH_3OC_6H_4, **3**)
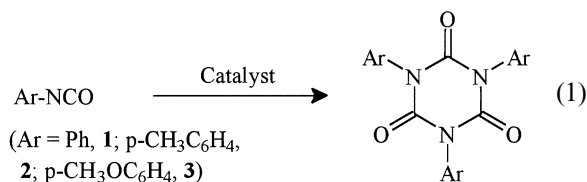
The trimers $(PhNCO)_3$ (**1**), $(p\text{-}CH_3C_6H_4NCO)_3$ (**2**), and $(p\text{-}CH_3OC_6H_4NCO)_3$ (**3**), obtained as white solids, were characterised by infrared spectroscopy, ^{13}C- and ^{1}H-NMR, mass spectrometry, and in some cases by elemental analysis, and compared with the data reported in the literature [11].

The reactions chosen to be performed in $scCO_2$ were those presenting higher yields in neat arylisocyanates. They were performed as reported in Section 2 (see Fig. 1) and the results are summarised in Table 3. The catalyst and the arylisocyanate were placed in a high-pressure cell with sapphire windows (for observation purposes), charged with CO_2 to the required pressure and heated at the reaction temperature, giving, in all cases, a fully homogenous single-phase reaction. After reaction, CO_2 was carefully vented through a cold trap leading to the precipitation of a white solid inside the cell. In all cases the only isolated products were the arylisocyanate trimers. The incorporation of CO_2 into the organic substrate was not observed in any case and no other organic products were isolated.

In all cases the yields for the cyclotrimerisation reactions were lower than in the analogous reactions carried out in neat arylisocyanates. For instance, in the reaction of $CpCo(CO)_2$ with $p\text{-}CH_3C_6H_4NCO$, even under quite drastic conditions, no traces of the trimer were found and the reagents were recovered unreacted. In the case of $Ni(cod)_2/PPh_3$ and $CpCoPPh_3Me_2$, the trimer was obtained in a low yields. The decrease in reactivity in $scCO_2$, compared to that observed in neat arylisocyanates, could be due to the decrease in concentration. In order to study the concentration effect, selected reactions were carried out in toluene.

In the reactions performed using $CpCo(CO)_2$ as catalyst using toluene as a solvent (the results are summarised in Table 3), either under stoichiometric or catalytic conditions, the trimer was not obtained at all. When the reaction was done with tolylisocyanate, the compound $H_2R_3N_3C_2O_2$ $(R = CH_3C_6H_4)$ (**4**) (see Eq.

(2)) was isolated instead, in low yield. The formation of this compound, which was characterised by ^{13}C- and ^{1}H-NMR, IR, mass spectrometry and elemental analyses, is not clear. Hoberg [9a] described the formation of the similar compound $H_2R_3N_3C_2O_2$ $(R = C_6H_5)$ in the reaction of Ni[0] complexes and phenylisocyanate, obtained by protolisis of a six membered nickelacycle. In the reaction of $Ni(cod)_2$–PPh_3 with phenylisocyanate using toluene as a solvent the trimer was formed in low yield.

$$\text{Ar-NCO} \xrightarrow{\text{Catalyst}} (Ar)(H)N-\overset{\overset{\displaystyle O}{\|}}{C}-N(Ar)-\overset{\overset{\displaystyle O}{\|}}{C}-N(H)(Ar)$$

(Ar = p-CH_3C_6H_4, **4**)

$$(2)$$

Therefore, we conclude that the complexes $CpCo(CO)_2$, $Ni(cod)_2$ and $CpCoPPh_3Me_2$, cannot simultaneously activate arylisocyanate and CO_2 when the reactions are performed in $scCO_2$, instead, the arylisocyanate trimers are obtained in low yield. Much better yields for the cyclotrimerisation are obtained when the reactions are carried out in neat arylisocyanate. In toluene, similar to the reactions in $scCO_2$, the yields of the trimers are very low, indicating that the decrease in reactivity in $scCO_2$ and toluene compared to that observed in neat arylisocyanates is due to the decrease in concentration.

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