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COORDINATION CATALYSIS OF THE REACTION BETWEEN ANHYDRIDES AND ISOCYANATES

(CATALYSED BY METAL COMPLEXES)

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In a previous note$^{1)}$, we have reported the metal carbonyl-catalysed condensation of aldehydes and isocyanates; we have now observed a similar catalytic effect of $Co_2(CO)_8$ on the formation of imides (III) from anhydrides (I) and isocyanates (II) :

$$(RCO)_2O(I) + C_6H_5NCO(II) \xrightarrow{Co_2(CO)_8} (RCO)_2NC_6H_5(III) + CO_2$$

In general, the reaction proceeds without any catalyst but is definitely slower than in the presence of $Co_2(CO)_8$, particularly in the case of acetic anhydride (Table I). Moreover a detailed study of this catalytic reaction is interesting since in contrast to the reaction of aldehydes and isocyanates$^{1)}$, we have isolated active complexes and got therefore a direct insight into the mechanism of isocyanates activation.

Two complexes were isolated from the reaction mixture : a pink compound (A) cristallized from the solution by cooling, whereas a brown amorphous complex (B) was obtained by evaporation of the excess of anhydride in vaccuo, dissolution of the residue into benzene and reprecipitation by heptane.
Similar complexes could be obtained separately from the reactants : (A) was formed from Ac_2O and $Co_2(CO)_8$ within 20 minutes, whereas the formation of (B) from (A) and phenyl isocyanate required 5 to 7 hours.
A probable mechanism could be drawn from these results in terms of an oxidative addition of acetic anhydride on $Co_2(CO)_8$$^{2)}$ to give (IV); this would be followed by a cis rearrangement (probably rate determining) involving a coordinated molecule of phenyl isocyanate, and CO_2 elimination, giving (VI) e.g. by a reaction scheme similar to :

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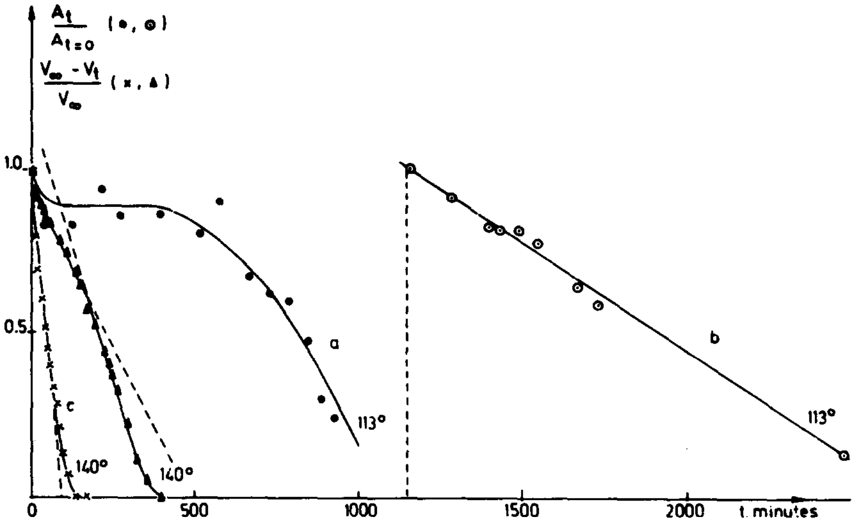
Table I : $(R-CO)_2O$ (I) + Ph(N=C=O) (II)

Conditions : I = 60 mmoles, II = 15 mmoles, $Co_2(CO)_8$ = 0,12 mmoles.

Anhydride	Solvent	$Co_2(CO)_8$	T° C.	t. min.	Yield %[(a)]
Acetic	-	+	140	400	100
	-	0	140	400	27
	-	+	113	1620	91
	-	0	113	1620	0[(b)]
Succinic	-	+	140	160	100
	-	0	140	160	21
	DMSO	+	96	25	83
	DMSO	0	96	150	67
	HMPT	+	96	150	70
	HMPT	0	96	150	51
Glutaric	-	+	60	5	90
	-	0	60	38	83
Pyromellitic	DMSO	+	78	< [1]	90
	DMSO	0	78	< [1]	90
	HMPT	+	78	16	97
	HMPT	0	78	61	85

a) Determined by volumetry of CO_2. The yield of isolated (III) is usually 5-10 % lower than the reported one.

b) The reaction works at 170° C. without catalyst : 72 % after 660 minutes[5)].



Kinetics of the reaction of anhydrides (I) and phenyl isocyanate (II)

Reaction followed by I.R. spectr (-N=C=O at 2125 cm⁻¹)	•	Ac_2O : 60 mmole ; (II) : 15 mmole ; $Co_2(CO)_8$: 0,12 mmole T = 113°C
	⊙	Addition of Ac_2O (60 mmole) and (II)(15 mmole) to the same solution after reaction T = 113°C
Reaction followed by volumetry (CO_2)	▲	Acetic anhydride (Ac_2O) T = 140°C
	×	Succinic anhydride T = 140°C

$$(RCO)_2O + Co_2(CO)_8 \rightarrow RCO - Co^{II} - OOCR^{(IV)} \xrightarrow{PhNCO} (RCO)(RCOO)Co^{II}(PhNCO)L_2^{(V)}$$

$$\rightarrow (RCO)Co^{II}(NPhCOOCOR)L_2 \rightarrow RCO - Co^{II} - (NPhCOR)L_2^{(VI)} + CO_2 \xrightarrow{(RCO)_2O} III + V$$

($L \equiv$ additionnal molecule of phenyl isocyanate).

A similar reaction could occur alternatively by a cis rearrangement of the CH_3CO - group bonded to the metal.

Preliminary analytical and spectrosopical date indicate that IV could correspond to A and VI to B but further studies are in progress to elucidate completely the structure of these intermediates.

Cobalt(II) acetate (Co(II)) is active too, but less than the isolated species : $k^{(b)}_{Co_2(CO)_8} / k_{Co(II)} \simeq 1$, $k_A/k_{Co(II)} = 3$, $k_B/k_{Co(II)} = 30$.

The figure (curve a) shows an induction period in the case of acetic anhydride : a slow formation of the active species, e.g. (VI) from (IV), can explain this phenomenon.

(b) $Co_2(CO)_8$ gave some precipitate during the early stages of the reaction.

The break in curve (a) is not due to an impurity as it did not reappear by adding a fresh mixture of (I) and (II) to the reacted solution (curve b). In opposition, cyclic anhydrides such as succinic anhydride gave a straight line (curve c).

Moreover, high rates were observed in DMSO and HMPT (table I). The catalytic effect of $Co_2(CO)_8$ was still detectable, and the products isolated from the cyclic anhydrides were the imides previously obtained. In contrast, acetic anhydride gave $PhNHCOCH_3$ and $CH_3SCH_2\text{-}OOCCH_3$ 3,4) in DMSO (catalytic : $k_{Co_2(CO)_8}/k_o = 16$), whereas $[(CH_3)_2N]_2PCH_3$ and the new compound $CH_3COON(Ph)CON(CH_3)_2$ were obtained from HMPT.

There reactions are under further investigation, and a paper devoted to mechanistic aspects will be published shortly.

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