

## METAL CARBONYLS CATALYSED REACTION OF ISOCYANATES WITH ALDEHYDES

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### Summary

A novel transition metal-catalysed reaction of isocyanates with aldehydes has been investigated. The reaction is of potential practical interest for the preparation of imines when water-sensitive groups are present. Kinetics and isotope labelling experiments indicate a rather complex mechanism; this implies a determinant insertion of the aldehyde into a preformed isocyanate complex, this true catalytic species being slowly produced through competitive coordination between the two reagents. The mechanism of similar catalysed reactions is discussed in the light of our own results.

### Introduction

Relatively few transition metal-catalysed reactions of isocyanates have been reported in the literature [1 - 4]. As examples, palladium (0) catalysts are efficient for the cycloaddition of phenyl isocyanate onto conjugated diolefins [2], whereas carbodiimides are obtained from isocyanates in the presence of metal carbonyls [3]. The suggested mechanism of this latter reaction involves the formation of an isonitrile complex by evolution of CO<sub>2</sub> from the catalyst and the isocyanate. The fact that the isonitrile complexes that are isolated from the medium [3, 5] appear to be very active in promoting the reaction seems in complete agreement with this hypothesis [3].

On the other hand, the reactions of isocyanates with various metal complexes are well documented [6, 7]. In general, complexes containing sufficiently polarized metal-nitrogen, metal-oxygen, metal-carbon or metal-hydrogen bonds induce insertion-type reactions of the cumulene, either by its C=O or its C=N function [6 - 10]. In all of the other cases, the isocyanate moiety preferably leads to  $\pi$ -bonded [11] or more commonly\*, to doubly  $\sigma$ -bonded [12 - 15] isocyanate complexes.

\*There is some confusion in the literature concerning the so-called ' $\pi$ -bonded' isocyanate complexes. As a matter of fact, a detailed analysis of different reports [12 - 14] reveals that the great majority of these complexes are in reality doubly  $\sigma$ -bonded isocyanate complexes.





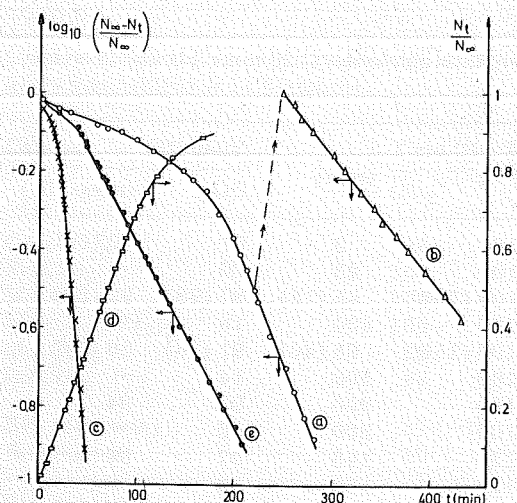


Fig. 1. Kinetics of the reaction of phenyl isocyanate with benzaldehyde in the presence of iron carbonyl catalysts ( $\log_{10} (N_{\infty} - N_t/N_{\infty})$  and  $N_t/N_{\infty}$  vs. time (min)) (see experimental part). (○)  $[R'NCO]_0 = [RCHO]_0 = 0.336 \text{ mol l}^{-1}$ ,  $[Fe(CO)_5]_0 = 6.08 \text{ mmol l}^{-1}$  and  $T = 144.5^\circ\text{C}$ . (△) Addition of the same amount of fresh reagents and solvent to the medium during the reaction; initial conditions are the same as in (○). (×)  $[R'NCO]_0 = 2.712 \text{ mol l}^{-1}$ ,  $[RCHO]_0 = 0.125 \text{ mol l}^{-1}$ ,  $[Fe(CO)_5]_0 = 2.4 \text{ mmol l}^{-1}$  and  $T = 144.5^\circ\text{C}$ . (□)  $[RCHO]_0 = 2.712 \text{ mol l}^{-1}$ ,  $[R'NCO]_0 = 0.120 \text{ mol l}^{-1}$ ,  $[Fe(CO)_5]_0 = 4.6 \text{ mmol l}^{-1}$  and  $T = 144.5^\circ\text{C}$ . (●)  $[RCHO]_0 = [R'NCO]_0 = 0.336 \text{ mol l}^{-1}$ ,  $[Fe(CO)_4(CNC_6H_5)]_0 = 7.7 \text{ mmol l}^{-1}$  and  $T = 129.5^\circ\text{C}$ .

ketones, esters, acid chlorides, dimethyl sulfoxide, N,N-dimethylformamide and aromatic aldehydes bearing strongly coordinating substituents such as  $-N(CH_3)_2$  and  $-NO_2$ . Moreover, isothiocyanates do not react at all, as expected from their different coordinating ability (see discussion).

From a practical point of view, our reaction seems thus limited to the preparation of some imines in high yields, without production of water (as is the case with classical methods). Moreover, the use of difunctional reagents might lead to condensation polymers (polyimines and resulting polyamines upon hydrogenation), without encountering the drawbacks of the classical process [24], since terephthalaldehyde and phenyl isocyanate react indeed quantitatively within 7 min at  $120^\circ\text{C}$  in the presence of a catalytic amount of  $Co_2(CO)_8$  (no reaction is detected after 300 min at  $120^\circ\text{C}$  without catalyst).

#### Kinetic measurements

Reaction (1) is particularly convenient for kinetic studies through volumetric measurements;  $CO_2$  evolution is indeed quantitative and the yield of aldimine is higher than 90% in many cases. The kinetic runs are performed in the presence of  $Fe(CO)_5$  as catalyst, since the more efficient  $Co_2(CO)_8$  (Table 1) gave poorly reproducible results due to the low solubility of the organometallic species.

TABLE 3

Kinetic rate constants of the reaction between phenyl isocyanate and benzaldehyde: determination of order in catalyst

$10^3 \times [Fe(CO)_5]_0$ ( $\text{mol l}^{-1}$ )	$10^3 \times k_{\text{obs}}$ ( $\text{min}^{-1}$ )	$k_{\text{obs}}/[Fe(CO)_5]_0$ ( $\text{l mol}^{-1} \text{min}^{-1}$ )
3.04	7.1	2.3
4.52	9.5	2.1
6.08	14	2.3
7.70	16	2.1

$[RCHO]_0 = [R'NCO]_0 = 0.336 \text{ mol l}^{-1}$ .  $T = 144.5^\circ\text{C}$ . Catalyst =  $Fe(CO)_5$ .

At the very beginning of the reaction, a fast evolution of CO (checked by mass spectroscopy) is detected. Thereafter, an *induction period* is observed under practically every set of conditions (typical example, Fig. 1, curve a). This induction period must correspond to the slow formation of the true catalytic species from the aldehyde and/or the isocyanate as it does not reappear later on further addition of the same amounts of reactants and solvent to the reaction medium (Fig. 1, curve b). It depends also on the presence of an excess of one or the other reagent (Fig. 1, curves c and d), and particularly on the nature of the ligands (Fig. 1, curve e).

After this induction period, the kinetics follow current zero order or first order plots up to at least 80% conversion (see Fig. 1).

#### Partial orders in catalyst and reagents

The reaction is first order in catalyst (Table 3) and in reagents (Fig. 1, curves a, b and e). The determining kinetic step is therefore not dependent on associative equilibria of the metal complexes (e.g. formation of polynuclear species).

When the kinetics are determined with an excess of aldehyde, the curves fit with a current zero order plot and the induction period is almost completely cancelled (Fig. 1, curve d), but the apparent rate constants remain proportional to the initial concentration in isocyanate (Fig. 2, curves a, b and c).

As the addition of aldimine at the beginning of the reaction has only a very slight accelerating effect on the rate\*, the only reasonable interpretation must assume a zero order kinetic step in isocyanate, but also that the total amount of active species produced during the induction period is directly proportional to  $[R'NCO]_0$ .

When the reaction is run with an excess of isocyanate, the kinetics are first order (Fig. 1, curve c) and the induction period is longer than when an

\* $k_{\text{obs}} = 3.72 \times 10^{-5} \text{ mol min}^{-1}$  instead of  $3.52 \times 10^{-5} \text{ mol min}^{-1}$  without imine, if  $[C_6H_5CH=NC_6H_5]_0 = 0.096 \text{ mol l}^{-1}$ ,  $[Fe(CO)_5]_0 = 4.6 \text{ mmol l}^{-1}$ ,  $[C_6H_5NCO]_0 = 0.163 \text{ mol l}^{-1}$ ,  $[C_6H_5CHO]_0 = 2.712 \text{ mol l}^{-1}$  and  $T = 144.5^\circ\text{C}$ .

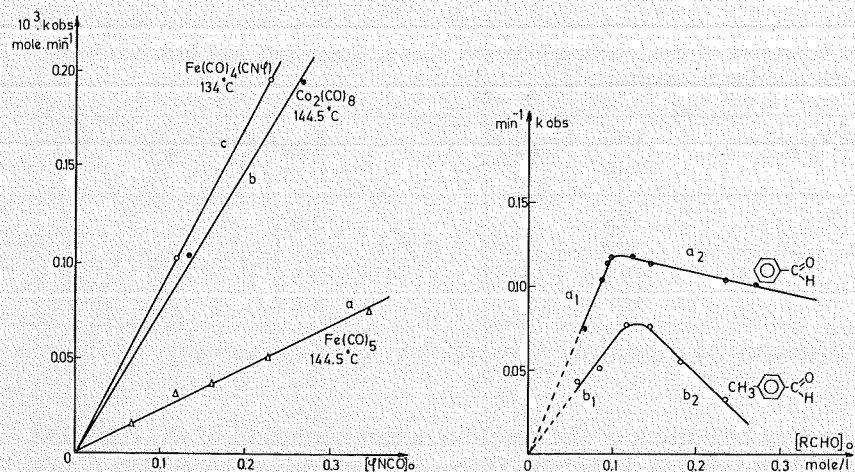


Fig. 2. Dependence of the apparent rate constant on the initial isocyanate concentration. ( $\Delta$ )  $[\text{C}_6\text{H}_5\text{CHO}]_0 = 2.712 \text{ mol l}^{-1}$ ,  $\text{R}'\text{NCO} = \text{C}_6\text{H}_5\text{NCO}$ ,  $[\text{Fe}(\text{CO})_5]_0 = 4.6 \text{ mmol l}^{-1}$  and  $T = 144.5^\circ\text{C}$ . ( $\bullet$ ) catalyst =  $\text{Co}_2(\text{CO})_8$ ; other conditions are the same as in ( $\Delta$ ). ( $\circ$ ) catalyst =  $\text{Fe}(\text{CO})_4(\text{CNC}_6\text{H}_5)$ ,  $T = 134^\circ\text{C}$ ; other conditions are the same as in ( $\Delta$ ).

Fig. 3. Dependence of the apparent rate constant on the initial aldehyde concentration. ( $\bullet$ )  $[\text{C}_6\text{H}_5\text{NCO}]_0 = 2.712 \text{ mol l}^{-1}$ ,  $\text{RCHO} = \text{C}_6\text{H}_5\text{CHO}$ ,  $[\text{Fe}(\text{CO})_5]_0 = 4.6 \text{ mmol l}^{-1}$  and  $T = 144.5^\circ\text{C}$ . ( $\circ$ )  $\text{RCHO} = \text{p-CH}_3\text{C}_6\text{H}_4\text{CHO}$ ; other conditions are the same as in ( $\bullet$ ).

excess of aldehyde is present (see Fig. 1, curves d and c). Moreover, plots of apparent rate constants *versus* initial aldehyde concentration show a maximum for the two different aldehydes investigated (Fig. 3, curves a and b). This means that the rate-determining step is first order in aldehyde, but that this reactant can act also as an inhibitor or a promoter of the formation of the true catalytic species, depending on its relative concentration. The inhibiting effect of the aldehyde becomes predominant as soon as the  $[\text{RCHO}]_0$  to  $[\text{R}'\text{NCO}]_0$  ratio becomes higher than  $5 \times 10^{-2}$  under our conditions (see Fig. 3, curves a and b).

The data in Fig. 2 (curves a, b and c) and in Fig. 3 (curves a and b), obtained at constant temperature and catalyst concentration, also show clearly that both reagents are required to promote the formation of the true active sites. On the other hand, Fig. 3 (curves a and b) also indicates that the relative importance of the promotion (slopes of  $a_1$  and  $b_1$ ) and of the inhibition (slopes of  $a_2$  and  $b_2$ ) processes due to the aldehyde depends much on the electronic density at the aldehydic group level. The inhibiting effect of the aldehyde is much more important for the para-methyl benzaldehyde than for the unsubstituted derivative ( $a_2:b_2 = 0.25$ ), whereas the opposite is observed as far as the promoting effect is concerned ( $a_1:b_1 = 1.7$ ).

#### Influence of preheating on catalyst efficiency

When the catalyst is preheated at the reaction temperature in the presence of the solvent and one of the reagents (prior to the addition of the

TABLE 4

Influence of preheating (10 min) two reactants prior to the addition of the third one

	Last reactant <sup>a</sup>	$10^3 \times k_{\text{obs}}$ ( $\text{min}^{-1}$ )	Induction time (min)
$\text{Fe}(\text{CO})_5$	$\text{C}_6\text{H}_5\text{NCO}$	2.9 (0) <sup>b</sup>	190 (0) <sup>b</sup>
	$\text{Fe}(\text{CO})_5$	3.9	230
	$\text{C}_6\text{H}_5\text{CHO}$	5.8 (4.2) <sup>b</sup>	130 (0) <sup>b</sup>
$\text{Fe}(\text{CO})_4(\text{CNC}_6\text{H}_5)$	$\text{Fe}(\text{CO})_4(\text{CNC}_6\text{H}_5)$	11	40
	$\text{C}_6\text{H}_5\text{CHO}$	14	30

$[\text{RCHO}]_0 = [\text{R}'\text{NCO}]_0 = 0.336 \text{ mol l}^{-1}$ .  $[\text{Catalyst}]_0 = 7.7 \text{ mmol l}^{-1}$ .  $T = 129.5^\circ\text{C}$ .

<sup>a</sup>Last component introduced into the reactor heated at  $129.5^\circ\text{C}$ .

<sup>b</sup>Value obtained when the first two reagents have been heated together for 4 h prior to the addition of the third one.

second one), the apparent rate constants are clearly modified. As shown in Table 4, preheating  $\text{Fe}(\text{CO})_5$  in phenyl isocyanate for 10 min increases the number of active species ( $10^3 k_{\text{obs}} = 5.8 \text{ min}^{-1}$  *versus*  $3.9 \text{ min}^{-1}$  without preheating), whereas the reverse is observed when the aldehyde is added first ( $10^3 k_{\text{obs}} = 2.9 \text{ min}^{-1}$ ). On the other hand, a longer preheating time (4 h) decreases the rate in both cases. The irreversible production of inactive species takes place therefore in the presence of both reactants, but the inhibition is particularly important in the presence of the aldehyde since only this last reactant leads to complete inactivation ( $10^3 k_{\text{obs}} = 0$ ). This is in complete agreement with the results reported in the preceding section.

#### Arrhenius' parameters

The activation parameters have been calculated from the kinetics of the benzaldehyde-phenyl isocyanate reaction at different temperatures (catalyst:  $\text{Fe}(\text{CO})_5$ ),  $E_a = 24 \pm 2 \text{ kcal mol}^{-1}$  and  $\Delta S_{134.5^\circ\text{C}} = -11 \pm 2 \text{ eu}$  (see Fig. 4).

#### Influence of the aldehyde substituents

In opposition to classical organic reactions, catalytic processes such as the one reported here do not always allow simple conclusions to be drawn from Hammett-type correlations, since the coordinative interactions often wipe out the steric and electronic effects of the substituents, and sometimes also have a direct influence on the production of catalytic centers. This is particularly true in our case: the rate accelerating effect of the ortho-methyl substituent on benzaldehyde (as compared to the para-substituted isomer (see Fig. 5, data within the frame)) indicates indeed that steric hindrance decreases mainly the inhibiting effect of the aldehyde (of course, with the more encumbered 2, 4, 6-trimethyl derivative, the kinetic step itself is influenced). It follows that the positive  $\rho$  value ( $\rho = 1.4$  from Fig. 5) should not necessarily correspond to an electrophilic attack by the aldehyde during



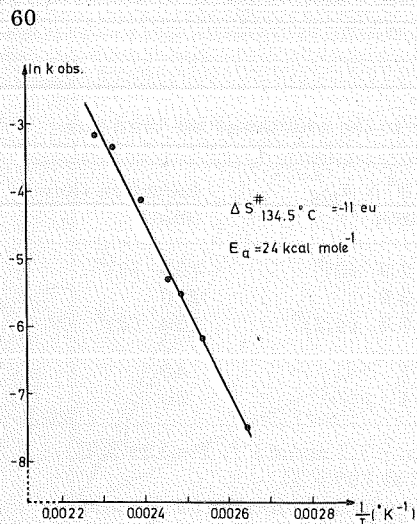


Fig. 4. Dependence of apparent rate constant on temperature (plot of  $\ln k_{\text{obs}}$  vs.  $1/T$  (K)).  $[\text{C}_6\text{H}_5\text{CHO}]_0 = [\text{C}_6\text{H}_5\text{NCO}]_0 = 0.336 \text{ mol l}^{-1}$  and  $[\text{Fe}(\text{CO})_5]_0 = 7.7 \text{ mmol l}^{-1}$ .

the rate-determining step, but rather to a decrease of the inhibition efficiency of this latter during the induction period.

#### Labelling experiments and isotopic effects

By using a  $^{13}\text{C}$  labelled aldehydic group it was possible to prove that  $\text{CO}_2$  is not formed from this carbonyl, as the label is quantitatively recovered in the imine (III). Moreover, the substitution of the aldehydic hydrogen by deuterium decreased the rate only slightly ( $k_{\text{obs H}}/k_{\text{obs D}} = 1.20$ ). It is therefore highly unlikely that the cleavage of the C-H aldehydic bond would be involved in the rate-determining step, as the observed variation is within the range of secondary isotopic effects [25].

#### Experimental

Microanalyses were performed by the Centre Interservice d'Analyses Organiques (University of Liège) and Dr. A. Bernhardt (Mülheim).

Infrared spectra were taken using a Perkin-Elmer model 21 instrument. Nuclear magnetic resonance spectra were recorded on a Varian T60 spectrometer using tetramethylsilane as internal reference. Molecular weight determinations were made in toluene at  $45^\circ\text{C}$  on a Dampdruck Osmometer Knauer instrument. Melting points (uncorrected) were determined using a Leitz Wetzlar microscope. Mass spectra were recorded by Dr. R. Weber (University of Liège) and Dr. J. Pecher (University of Brussels).

All experiments were normally carried out under nitrogen atmosphere.

#### Materials

##### Reagents

The aldehydes and the isocyanates are all commercial products. They were purified by distillation or recrystallization just before use. The deuteriated benzaldehyde  $\text{C}_6\text{H}_5\text{CDO}$  was synthesized with an isotopic yield of 89% (determined by mass spectroscopy) by the procedure of Cohen and Song [26]. Benzaldehyde-(carbonyl)- $^{13}\text{C}$ , of isotopic purity (checked by mass spectroscopy) 18.4%, was prepared in 78% yield from a mixture of benzoic acid and benzoic acid-(carboxyl)- $^{13}\text{C}$  (Merck, Sharp and Dohm Ltd) by reduction of the acid chloride according to a modification of the method of Rosenmundt [27].

##### Catalysts

$\text{Co}_2(\text{CO})_8$  and  $\text{Cr}(\text{CO})_6$  (Alfa Inorganics),  $\text{W}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$  (Climax Molybdenum Company), and  $\text{Fe}(\text{CO})_5$  (Fluka) were used as received.  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  [28] and  $\text{Fe}(\text{CO})_4(\text{CNC}_6\text{H}_5)$  [29] were synthesized as reported.  $\text{BF}_3$  (etherate) was purified by the method of Zweifel and Brown [30].

##### Solvents

All the solvents were of reagent-grade quality.

The solvents for kinetic studies were carefully dried and degassed immediately before use.

#### Preparations and reactions

##### General procedure

Unless otherwise stated, the aldehyde (120 mmol), the isocyanate (30 mmol) and the catalyst (0.24 mequiv) were heated pure under nitrogen at the reported temperature until complete evolution of  $\text{CO}_2$ . After cooling, the excess of reagent was distilled off and the residue was purified by distillation, crystallization or column chromatography. The simple aromatic imines are classical compounds [31 - 37]. They were characterized by the presence of the typical infrared absorption of the C=N group in the range  $1600 - 1630 \text{ cm}^{-1}$  [37 - 39].

##### Cinnamylidene-*n*-butylamine

(III,  $\text{R} = \text{C}_6\text{H}_5\text{CH}=\text{CH}$ ,  $\text{R}' = n\text{-C}_4\text{H}_9$ ) was isolated by distillation. B.p. =  $91 - 93^\circ\text{C}/0.5 \text{ mm}$ . Found: C, 83.1; H, 9.1; N, 7.6%;  $M$ , 198. Calculated for  $\text{C}_{13}\text{H}_{17}\text{N}$ : C, 83.4; H, 9.1; N, 7.5%;  $M$ , 187. IR (liquid film):  $\nu = 1622$  (C=C) and  $1665$  (C=N)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CS}_2$ ):  $\delta = 7.8$  (m, 1H, CH=N), 7.4 - 6.9 (m, 5H,  $\text{C}_6\text{H}_5$ ), 6.7 (m, 2H, CH=CH), 3.4 (m, 2H,  $\text{CH}_2\text{N}$ ) and 1.6 - 0.7 (m, 7H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ) ppm.

##### Crotonylideneaniline

(III,  $\text{R} = \text{CH}_3\text{CH}=\text{CH}$ ,  $\text{R}' = \text{C}_6\text{H}_5$ ) was distilled under vacuum. B.p. =  $62 - 64^\circ\text{C}/0.1 \text{ mm}$ . Found: C, 82.75; H, 7.7; N, 9.6%;  $M$ , 140. Calculated for

$C_{10}H_{11}N$ : C, 82.75; H, 7.6; N, 9.65%;  $M$ , 145. IR (liquid film):  $\nu = 1600$  (C=C) and  $1640$  (C=N)  $cm^{-1}$ .  $^1H$  NMR ( $CCl_4$ ):  $\delta = 7.9$  (m, 1H, CH=N),  $7.4 - 6.9$  (m, 5H,  $C_6H_5$ ),  $6.3$  (m, 2H, CH=CH) and  $1.9$  (d, 3H,  $CH_3$ ) ppm.

#### 2-(*n*-butyl)-2-octenyldeneaniline (IV)

Hexanal (80 mmol), phenyl isocyanate (160 mmol) and  $Co_2(CO)_8$  (0.5 mmol) were heated at  $140^\circ C$  for five hours in *o*-xylene (20 ml) as solvent. After cooling,  $N,N'$ -diphenylurea (49 mmol) was filtered off and the solvent was evaporated. Distillation of the residue *in vacuo* afforded (IV) (22 mmol, 55%). B.p. =  $121 - 124^\circ C/0.5$  mm. Found: C, 83.7; H, 10.6; N, 5.4%;  $M$ , 265. Calculated for  $C_{18}H_{27}N$ : C, 84.0; H, 10.6; N, 5.4%;  $M$ , 257. The hydrolysis of (IV) in dilute hydrochloric acid (pH 3) for 30 min at  $40^\circ C$  yielded the expected 2-(*n*-butyl)-2-octenal in 70% yield after extraction with ether and distillation. B.p. =  $68 - 72^\circ C/0.5$  mm. IR (liquid film):  $\nu = 1685$  (C=O) and  $1640$  (C=C)  $cm^{-1}$ . M.p. observed for the 2,4-dinitrophenylhydrazone =  $132^\circ C$ ; reported [40] =  $131.5^\circ C$ .

#### Terephthalylidenedianiline

( $C_6H_5N=CH-C_6H_4-CH=NC_6H_5$ ) was prepared from terephthalaldehyde (15 mmol), phenyl isocyanate (60 mmol) and  $Co_2(CO)_8$  (0.12 mmol). After reaction, the excess of isocyanate was distilled off and the diimine (14.3 mmol, 95%) was purified by recrystallization from benzene-ethanol. M.p. observed =  $163^\circ C$ ; reported [37] =  $161.5 - 163^\circ C$ .

### Kinetics

#### General procedure

The kinetic runs were followed by volumetry with the apparatus and in accordance with the general procedure described by Monagle and coworkers [41]. The solvents used were *o*-xylene for reactions run at a temperature under  $144.5^\circ C$ , and tetraline in the other cases. Unless otherwise stated, the catalysts (pure for  $Fe(CO)_5$ , in *o*-xylene solution for  $Fe(CO)_4(CNC_6H_5)$ , or in phenyl isocyanate for  $Co_2(CO)_8$ ) were delivered last of all to the reaction flask, the time  $t_0$  being taken at the end of the addition.

#### Treatment of data

The volume of gas released at time  $t$  was measured at  $20^\circ C$  and corrected to STP before being converted to the corresponding mole number  $N_t$ . In all cases,  $N_\infty$  was calculated from the weights of aldehyde and isocyanate introduced into the reactor. The values so obtained were then plotted according to the kinetic relationships that gave the best straight lines, and the apparent rate constants ( $k_{obs}$ ) were determined from the slope of these plots.

The Arrhenius' parameters  $A$  and  $E_a$  were obtained from the plot of  $\ln k_{obs}$  versus  $1/T$  (K), whereas the Hammett  $\rho$  value was determined from the plot of  $\log_{10} k_{obs}$  versus  $\sigma$  values [42]. The entropy of activation (at  $134.5^\circ C$ ) was calculated from the equation [43]

$$\Delta S^\ddagger = 1.99 \ln \left( \frac{A}{T} \right) - 49.2$$

#### Isotopic labelling experiments

Experiments with benzaldehyde-(carbonyl)- $^{13}C$  were run as described in the preceding sections. The tracer recovery yield in the products was determined by mass spectrometry at the end of the reaction. The results were benzylideneaniline 97% and carbon dioxide 0%.

#### Kinetic isotopic effects

The kinetics of the reactions between phenyl isocyanate ( $2.712 \text{ mol l}^{-1}$ ) and (carbonyl)-deuteriated or non-deuteriated benzaldehyde ( $0.146 \text{ mol l}^{-1}$ ) in the presence of  $Fe(CO)_5$  ( $4.6 \text{ mol l}^{-1}$ ) were followed as above at  $T = 144.5^\circ C$ . The measured apparent rate constants were  $k_{obs} = 11.3 \times 10^{-2} \text{ min}^{-1}$  for  $C_6H_5CHO$  and  $9.4 \times 10^{-2} \text{ min}^{-1}$  for  $C_6H_5CDO$  ( $k_{obs} H/k_{obs} D = 1.20$ ).

### Discussion

Two different important stages (see Scheme 1) can be distinguished in the kinetic complexity of this reaction.

#### (1) The formation of the catalytic species

Several observations lead to the assumption that both the aldehyde and the isocyanate can act as promoters of the true catalytic species formation depending on their relative initial ratio, while the inhibition due to the aldehyde becomes predominant as soon as the  $[RCHO]_0$  to  $[R'NCO]_0$  ratio is higher than  $5 \times 10^{-2}$  (Fig. 3). These observations are the modifications of

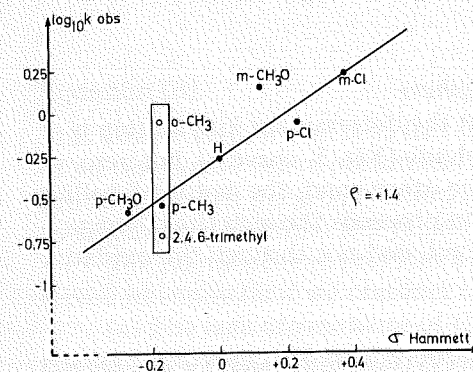


Fig. 5. Dependence of apparent rate constant on aldehydic substituents (plot of  $\log_{10} k_{obs}$  vs.  $\sigma$  values).  $[C_6H_5NCO]_0 = 7.31 \text{ mol l}^{-1}$ ,  $[C_6H_4CHO]_0 = 1.83 \text{ mol l}^{-1}$ ,  $[Fe(CO)_5]_0 = 35 \text{ mmol l}^{-1}$  and  $T = 131.5^\circ C$ .



the induction period with the reaction conditions (Fig. 1 and Table 4), as well as the variations of the apparent rate constants with the initial reagent concentrations (Figs. 2 and 3), the steric and electronic effects at the aldehydic group level (Figs. 3 and 5) and the influence of the order in which the reactants are added (Table 4).

Moreover, the preheating experiments (Table 4) showed that each of the two reactants is also potentially able to *irreversibly* interact with the metal carbonyl to generate inactive species. The inactivation due to the isocyanate is again a less important factor than the inactivation due to the aldehyde (since this last reagent only leads to complete inhibition in our conditions (see Table 4)).

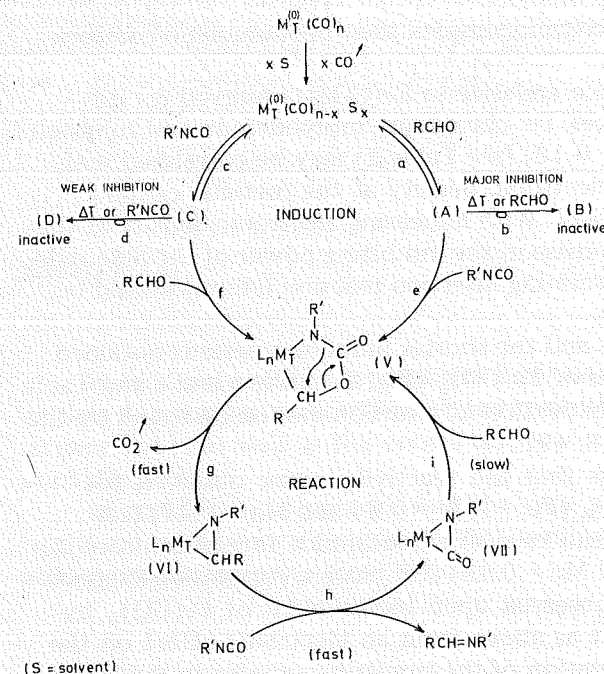
It follows that the induction process is best explained by considering (see induction part of Scheme 1) that in the presence of a large excess of R'NCO ( $[RCHO]_0 : [R'NCO]_0 < 5 \times 10^{-2}$ ), the metal carbonyl preferentially reacts with the cumulene to give an entity (C) which is itself potentially able to *irreversibly*\* interact with the aldehyde or with a second molecule of cumulene to produce either the *active* 'template type' complex (V) or the *inactive* organometallic species (D) respectively. The same is true with the 'aldehyde' complexes (A) (steps b and e of Scheme I) as soon as the  $[RCHO]_0$  to  $[R'NCO]_0$  ratio becomes higher than  $5 \times 10^{-2}$ .

Unfortunately, it was not possible to isolate the postulated intermediates. Nevertheless, it is probable that the "aldehyde" complexes (A) and (B) result from the coordination of the aldehyde lone electron pairs [44]. The fact that the stability of such complexes normally increases with the electronic density at the carbon-oxygen double-bond level [45] would be indeed in complete agreement with the steric and electronic requirements of the aromatic ring substituents (see 'substituent effects'). Under these conditions, the lower coordinating ability of the isocyanate during the induction period might only be explained by assimilating (C) to a thermodynamically unfavoured isocyanate complex such as the Kolomnikov's dative bond complex [12]. Once formed, (C) might then react with a second molecule of cumulene to generate an inactive urylene complex (D) according to the scheme of Monica and coworkers [16].

## (2) The reaction within the coordination sphere

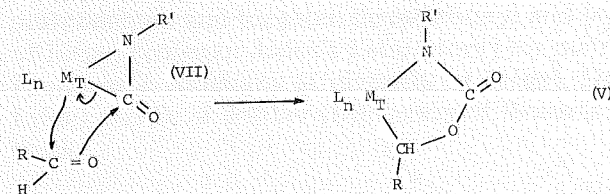
The current reaction orders show that the determinant kinetic step is first order in catalyst (Table 3) and in aldehyde (Fig. 1, curve c), but zero order in isocyanate (Fig. 1, curve d). On the other hand, the isotope labelling experiments demonstrated that the reaction proceeds through the cleavage of the aldehydic carbon-oxygen double bond, and not through the oxidative

\*The irreversible production of (B), (D) and (V) (steps b, d, e and f) is assumed in order to account for the constancy of the reaction orders and rate constants up to at least 80% of reaction. In fact, the irreversible formation of (B) and (D) (steps b and d) has been established during the study of the preheating effects (Table 4).



Scheme 1

addition of the aldehyde. It follows that the rate-determining step (step i of Scheme 1) probably corresponds to a nucleophilic attack [44] of the aldehydic carbon atom by the metallic center of a doubly  $\sigma$ -bonded isocyanate complex similar to Collman's complexes [13b]:



Equation (3)

This kinetic step, which is in fact formally similar to the postulated insertion of an isocyanate into a preformed acetylene complex [46], would then be followed by fast decarboxylation (step g) and substitution (step h) reactions to regenerate the initial isocyanate complex (VII).

The above scheme provides a satisfactory explanation for all of the observed phenomena if we consider the following:

(a) The lack of reactivity of the isothiocyanates (see 'Synthetic aspects') results from their different coordinating ability, which makes them less able to produce complexes analogous to (VII) [14].

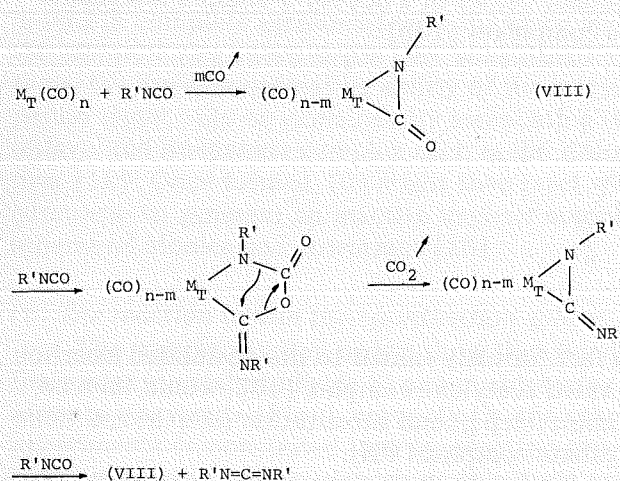
(b) The medium negative value of the activation entropy ( $\Delta S_{134.5}^\ddagger = -11$  eu) should indicate only that the rate determining condensation step

(step i) leads to a less rigid transition complex than the cumulene complex (VII).

(c) The reactivity sequence (relative to  $\text{Fe}(\text{CO})_5$ ) observed for different metal carbonyl complexes, *i.e.* chromium, molybdenum and tungsten ( $W = 0.94$ ,  $\text{Mo} = 0.47$  and  $\text{Cr} = 0.18$ ) (see Table 1) may be correlated with the fact that the increase of electronic density at the metallic centers parallels the atomic numbers [47]. With increasing electronic density at the metal, should correspond a decrease in the inhibiting power of the aldehyde (step b), whereas the rate-determining insertion reaction (step i) should be facilitated.

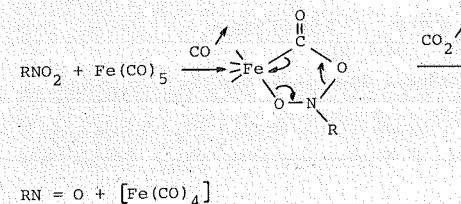
Similarly, the higher rates and the shorter induction periods obtained with  $\text{Fe}(\text{CO})_4(\text{CNC}_6\text{H}_5)$  instead of  $\text{Fe}(\text{CO})_5$  (Fig. 2, curves a and c and Table 4) may be explained by the substitution of a carbon monoxide ligand by the weaker  $\pi$ -acceptor isonitrile [48, 49].

Finally, one should stress that the reactivity order observed for  $\text{Fe}(\text{CO})_5$ ,  $\text{W}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$  ( $\text{Fe} = 1$ ,  $W = 0.94$  and  $\text{Mo} = 0.47$ ) (see Table 1) is similar to Ulrich's sequence for carbodiimide formation from isocyanates ( $\text{Fe} = 1$ ,  $W = 0.53$  and  $\text{Mo} = 0.18$ ) [3]. Such a correlation suggests that the increased reactivity, observed upon replacement of  $\text{Fe}(\text{CO})_5$  by  $\text{Fe}(\text{CO})_4(\text{CNC}_6\text{H}_5)$ , must result as above from an electronic effect on the metal and not from the participation of the isonitrile complex in the reaction scheme as postulated by these authors (see Introduction). Accordingly, we propose that their reaction could be explained by a mechanism similar to ours (Scheme 2):



Scheme 2

It is probable that metallocyclic complexes analogous to (V) are also involved in the catalytic production of nitroso compounds from nitro derivatives [50]:



Equation (4)

In fact such cyclic intermediates have also already been postulated to explain the copper carbonyl catalysed reduction of nitro compounds to oximes [51], as well as the cobalt carbonyl catalysed deoxygenation of epoxides [52].

In conclusion, it appears that the type of mechanism discussed here might indeed be a very general one in coordination activation of organic substrates containing heterodouble bonds.

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