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Redox Reactions of Metal Carbonyls.
II. *Kinetic Studies on the Disproportionation of $Co_2(CO)_8$ Induced by N-Bases

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The kinetics of the disproportionation reaction of $Co_2(CO)_8$ with triethylamine, benzylamine, cyclohexylamine and diethylamine were investigated employing stopped-flow technique. The kinetic behaviour is suggestive of two competing mechanisms, an amine-independent path involving probably a rate-determining CO dissociation, followed by amine uptake, and an associative mechanism characterized by two or three consecutive attacks of the amine on the substrate, followed by a first-order decomposition of the final intermediate. The reaction rates are sensitive more to the steric characteristics of the entering ligand than to its basicity. Attention is drawn to correlate the reaction mechanism and the different structures of $Co_2(CO)_8$ in solution.

Introduction

There have been several studies published on the disproportionation reaction induced on dicobalt octacarbonyl by hard Lewis bases like N- and O-donors [3]. Its stoichiometry was well established and has the following form:

$$3\,Co_2(CO)_8 + 12\,L \rightarrow 2[CoL_6^{++}] + 4[Co(CO)_4^-] + 8\,CO \qquad (1)$$

The lack of kinetic measurements of reaction (1) prompted us to perform a systematic investigation on it as a part of a wider interest on the redox properties of metal–metal bonds.

In Part I of this series we reported the kinetic behaviour of (1) when L = piperidine. The mechanism is not simple and probably involves several reactive intermediates. In an attempt to gain further information about this reaction we have carried out kinetic studies with a series of N- bases in order to ascertain the effect of the ligand properties on the reaction mechanism.

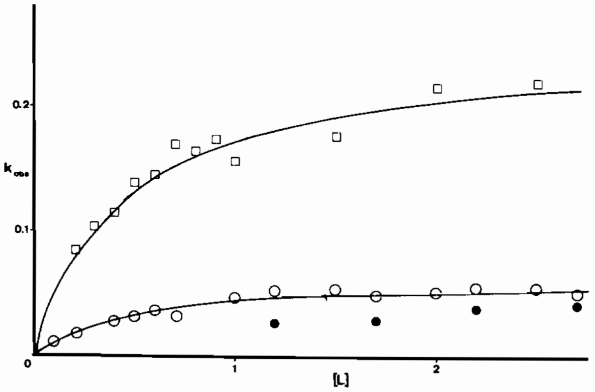

Figure 1. Plots of k_{obs} *vs.* TEA concentration at different temperatures (eq. 3): □ 38.0 ℃; ○ 24.8 ℃; ● 24.8 ℃ under CO.

Results

The reaction of $Co_2(CO)_8$ with triethylamine (TEA) shows that the transmittance of the solution increases to a constant equilibrium value, clearly indicating a single-stage reaction. The values of k_{obs} (Table I) are dependent on the concentration of the ligand whereas, as the concentration increases, they reach a limiting constant value, as shown in Fig. 1. This behaviour can be easily explained by a two-step mechanism, implying a slow dissociation of the substrate, followed by a rapid attack of the ligand on the active intermediate. Several hypotheses could be made on the dissociative rate determining step, which may imply a CO dissociation from the substrate (eq. 2a), as reported for the reaction of $Co_2(CO)_8$ with ^{14}CO [4] or alkynes [5]:

$$Co_2(CO)_8 \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} Co_2(CO)_7 + CO$$
$$Co_2(CO)_7 + L \xrightarrow{k_a} Co_2(CO)_7L \qquad (2a)$$

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*See refs. 1 and 2.

TABLE I. Rate Constants for the Reactions of $Co_2(CO)_8$ with N-bases in n-Heptane

Ligand	t °C	Ligand Conc. *M*	k_{obs} (I) sec^{-1}	k_{obs} (II) sec^{-1}
TEA	10.5	0.11	0.0021	
		0.21	0.0043	
		0.39	0.0051	
		0.71	0.0092	
		1.00	0.0106	
	24.8	0.11	0.012	
		0.21	0.018	
		0.39	0.028	
		0.50	0.032	
		0.59	0.037	
		0.71	0.032	
		1.01	0.047	
		1.20	0.053	
			0.027[a]	
		1.51	0.054	
		1.71	0.049	
			0.029[a]	
		2.01	0.052	
		2.20	0.056	
			0.038[a]	
		2.52	0.055	
		2.75	0.050	
			0.042[a]	
	38.0	0.20	0.096	
		0.30	0.104	
		0.40	0.113	
		0.51	0.139	
		0.61	0.145	
		0.70	0.171	
		0.80	0.164	
		0.90	0.174	
		1.00	0.156	
		1.50	0.176	
		2.00	0.215	
		2.50	0.218	
DEA	24.8	0.58	0.033	
		0.60	0.039	
		0.73	0.042	
		1.02	0.097	
		1.21	0.143	
		1.65	0.38	
		1.84	0.49	
		1.94	0.47	
		2.00	0.45	
		2.14	0.61	
		2.30	0.59	0.150
		2.43	0.62	0.164
		2.86	0.76	0.160
		3.01	0.95	0.152
	38.0	1.21	0.24	
		1.60	0.35	
		2.00	0.40	0.070
		2.30	0.64	0.058
		2.50	0.84	0.075

Ligand	t °C	Ligand Conc. *M*	k_{obs} (I) sec^{-1}	k_{obs} (II) sec^{-1}
		2.70	0.93	0.075
		3.00	1.19	0.070
BZA[b]		0.30	0.45	0.198
		0.40	0.99	0.199
		0.50	1.85	0.173
		0.60	2.80	0.220
		0.71	4.1	
		0.81	6.7	0.261
		0.91	8.7	0.203
		1.00	12.8	
		1.50	37.8	0.268
		2.00	59	
		2.50	75	0.208
		3.46		0.203
	38.0	0.30	0.37	
		0.40	0.78	
		0.50	1.34	
		0.71	3.57	
		0.91	7.3	
		1.00	9.0	
		1.50	24.0	
		2.00	51	
		2.49	80	
CHA	24.8	0.11	0.087	
		0.13	0.131	
		0.17	0.283	
		0.20	0.58	
		0.22	0.86	0.40
		0.28	1.49	0.37
		0.40	4.18	0.35
		0.59	12.5	0.42
		0.60	13.4	0.37
		0.95	56	
		1.10	67	
	38.0	0.20	0.34	
		0.28	0.66	
		0.40	2.09	
		0.60	5.3	
		0.95	24.0	

[a] Under CO atmosphere. [b] In benzene.

or an internal dissociation, without release of CO, giving rise to an active form of $Co_2(CO)_8$ [6]:

$$\begin{aligned} Co_2(CO)_8 &\underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} Co_2(CO)_8^* \\ Co_2(CO)_8^* + L &\xrightarrow{k_a} Co_2(CO)_7L + CO \end{aligned} \qquad (2b)$$

In this light, if the (2a) mechanism holds, the reaction should be retarded by an increase of the CO concentration in solution. Even if the technical apparatus did not allow us a reliable measurement of the effect of the CO concentration on the reaction rate, a qualitative support to this mechanism was obtained by performing some experiments with the reactant solution bubbled by CO. The values of k_{obs} (I) under these conditions were lower, as shown in Fig. 1, than those obtained without dissolved CO. Otherwise, if the CO dissociation is operating, the rate plots of ln(absorbance) *vs.* time should have initial gradient related to the limiting rate constant and should curve as the reaction proceeds and CO is released. Unfortunately this effect could not be evidentiated and the

TABLE II. Specific Rate Constant Values for the Reaction of $Co_2(CO)_8$ with N-bases in n-Heptane.

Ligand	t °C	k_d sec^{-1}	$\frac{k_{-1}k_{-2}}{k_1k_2k_3}$ sec M^3	$\frac{k_{-1}}{k_2k_3}$ sec M^2	$\frac{k_{-1}(k_{-2}+k'_3)}{k_1k_2k_3}$ sec M^2	k_{II} sec^{-1}
TEA	10.5	0.019 ± 0.006				
	24.8	0.065 ± 0.003				
	38.6	0.223 ± 0.015				
DEA	24.8				7.2 ± 1.2	0.157 ± 0.007
	38.6				8.5 ± 1.8	0.070 ± 0.007
BZA[a]	24.8		0.047 ± 0.004	0.045 ± 0.007		0.22 ± 0.03
	38.6		0.059 ± 0.004	0.054 ± 0.007		
CHA	24.8		0.0147 ± 0.0008	0		0.38 ± 0.03
	38.6		0.037 ± 0.002	0		

[a] In benzene.

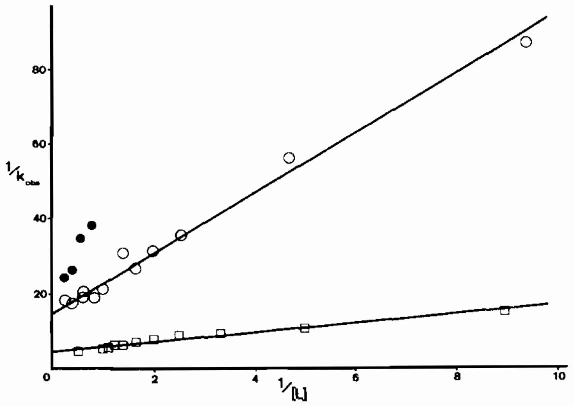


Figure 2. Reciprocal of k_{obs} *vs.* the reciprocal of the TEA concentration at different temperatures (eq. 4): symbols from Fig. 1.

observed rate constants, reported in the Table I, refer to the linear trend of the above plots. Anyway, whatever mechanism is operating, if the steady-state condition applies to the concentration of the active intermediate, similar expressions are obtained:

$$k_{obs} = \frac{k_d[L]}{k_{-d}[CO] + k_a[L]} \tag{3a}$$

$$k_{obs} = \frac{k_d[L]}{k_{-d} + k_a[L]} \tag{3b}$$

Their rearrangement gives rise to the equations:

$$\frac{1}{k_{obs}} = \frac{1}{k_d} + \frac{k_{-d}[CO]}{k_dk_a}\frac{1}{[L]} \tag{4a}$$

$$\frac{1}{k_{obs}} = \frac{1}{k_d} + \frac{k_{-d}}{k_dk_a}\frac{1}{[L]} \tag{4b}$$

which show a linear dependence of $1/k_{obs}$ *vs.* $1/[L]$, as the experimental data clearly confirm (Fig. 2).

The limiting rate constant k_d is obtained from the intercept of the straight line (eq. 4a, 4b) by the least-squares treatment. Its values at different temperatures and the relevant activation parameters are reported in Table II and III respectively. The error is the standard deviation.

The reaction with other ligands is much more complicated as it appears strictly similar to that previously reported with piperidine [2]. Three consecutive stages are observed. The first one (increase of transmittance) shows an high rate-dependence on the ligand concentration: the order is 2 in the case of diethylamine (DEA), 3 in the case of cyclohexylamine (CHA), lying between 2 and 3 in the case of benzylamine (BZA) and piperidine (PIP). The second stage is characterized by a decrease of the solution transmittance and its rate is independent of the concentration of the ligand in all cases. The transmittance varies randomly during the third stage, according to the [L] values, indicating probable and complicate competition between two or more different reaction paths.

We proposed for the first stage with piperidine the following mechanism:

$$Co_2(CO)_8 + L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Co_2(CO)_8L \tag{5a}$$

$$Co_2(CO)_8L + L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Co_2(CO)_8L_2 \tag{5b}$$

$$Co_2(CO)_8L_2 + L \xrightarrow{k_3} Co_2(CO)_7L_3 + CO \tag{5c}$$

If the concentration of the active intermediates $Co_2(CO)_8L$ and $Co_2(CO)_8L_2$ remains nearly constant during the reaction, the rate has the following expression:

TABLE III. Activation Parameters for the Reaction of $Co_2(CO)_8$ with N-bases in n-Heptane.

Ligand		$\Delta H^{\ddagger}$ Kcal/mol	$\Delta S^{\ddagger}$ cal/mol deg.
TEA		15 ± 1	– 13 ± 5
DEA	I stage	2 ± 4	– 50 ± 10
	II stage	–10 ± 2	–100 ± 6
PIP[a]	I stage (slope)	–1.1 ± 0.8	– 74 ± 3
	I stage (intercept)	10.5 ± 4.0	– 31 ± 13
	II stage	13 ± 5	– 15 ± 16
BZA[b]	I stage (slope)	2.5 ± 1.7	– 56 ± 4
	1 stage (intercept)	2.1 ± 3.0	– 58 ± 7
CHA		11.6 ± 1.2	– 28 ± 3

[a] From Ref. 2. [b] In benzene.

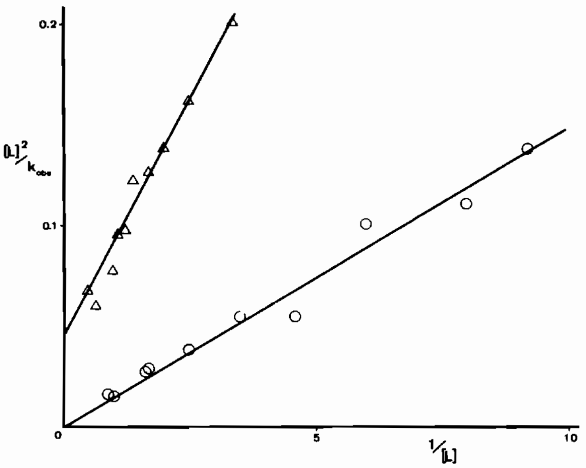


Figure 3. Plots of $[L]^2/k_{obs}$ *vs.* $1/[L]$ (eq. 8) at 24.8 °C: △ BZA; ○ CHA.

$$\text{rate} = k_{obs}(I)[Co_2(CO)_8] = \frac{k_1k_2k_3[Co_2(CO)_8][L]^3}{(k_{-1}+k_2[L])(k_{-2}+k_3[L]) - k_2k_{-2}[L]} \qquad (6)$$

Equation (6) is a good basis to rationalize the experimental results. If the following condition holds, as seems reasonable:

$$k_{-1} \gg k_2[L] \qquad (7)$$

eq. 6 transforms into eq. 8:

$$\frac{[L]^2}{k_{obs}(I)} = \frac{k_{-1}k_{-2}}{k_1k_2k_3}\,\frac{1}{[L]} + \frac{k_{-1}}{k_1k_2} \qquad (8)$$

which fits very well with the data of BZA reaction, as illustrated in Fig. 3.

If we apply to eq. 6 the same restriction and/or the similar one:

$$k_{-2} \gg k_3[L] \qquad (9)$$

we obtain the following relationship:

$$k_{obs}(I) = \frac{k_1k_2k_3}{k_{-1}k_{-2}}[L]^3 \qquad (10)$$

which accounts for the kinetic behaviour or CHA, as shown in Fig. 3.

The DEA reaction can be rationalized by a slight modification of the mechanism (5), *i.e.* by substituting eq. (5c) with eq. (5c′):

$$Co_2(CO)_8L_2 \xrightarrow{k_3'} Co_2(CO)_7L_2 + CO \qquad (5c')$$

The steady state condition applied to 5a, 5b and 5c′ gives rise to the following modification of eq. (6):

$$\text{rate} = k_{obs}(I)[Co_2(CO)_8] = \frac{k_1k_2k_3'[Co_2(CO)_8][L]^2}{(k_{-1}+k_2[L])(k_{-2}+k_3') - k_2k_{-2}[L]} \qquad (6')$$

If condition (7) holds, eq. (6′) can be rearranged as follows:

$$k_{obs}(I) = \frac{k_1k_2k_3'}{k_{-1}(k_{-2}+k_3')}[L]^2 \qquad (11)$$

Fig. 4 shows the agreement between the experimental data and eq. (11).

Table I collects all the values of the k_{obs} (I); Table II lists the rate constant values obtained from the slope and intercept of equations (8), (10) and (11); Table III shows the activation parameters.

In the same Tables are reported the experimental data referring to the second stage of the reaction. Be-

TABLE IV. Kinetic and Activation Parameters for the Dissociative Reaction of $Co_2(CO)_8$.

Reference	Solvent	k_d 10^{-3} sec^{-1} (at 25 °C)	$\Delta H^{\ddagger}$ Kcal/mol	$\Delta S^{\ddagger}$ cal/mol deg
This Work	n-Heptane/TEA	65	15 ± 1	−13 ± 5
4	Toluene	62[a]	23 ± 2	13 ± 4
5	"	9.4	16 ± 2	−14 ± 7
7	"	11	22	4[a]

[a] Calculated from the available data.

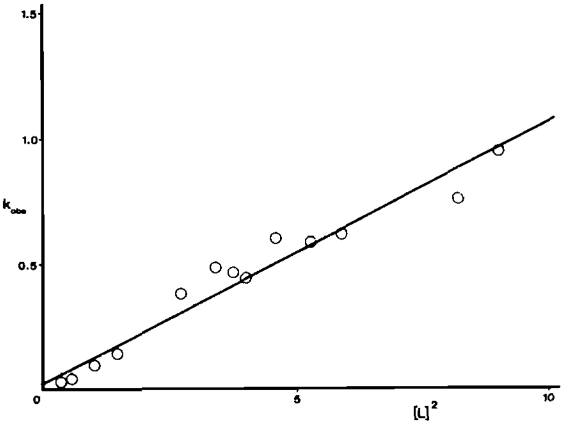


Figure 4. Plots of k_{obs} *vs.* $[L]^2$ for DEA at 24.8 °C (eq. 11).

cause the rate is independent of the ligand concentration, the specific rate constant k_{II} is calculated as the average of the observed rate constant values k_{obs} (II).

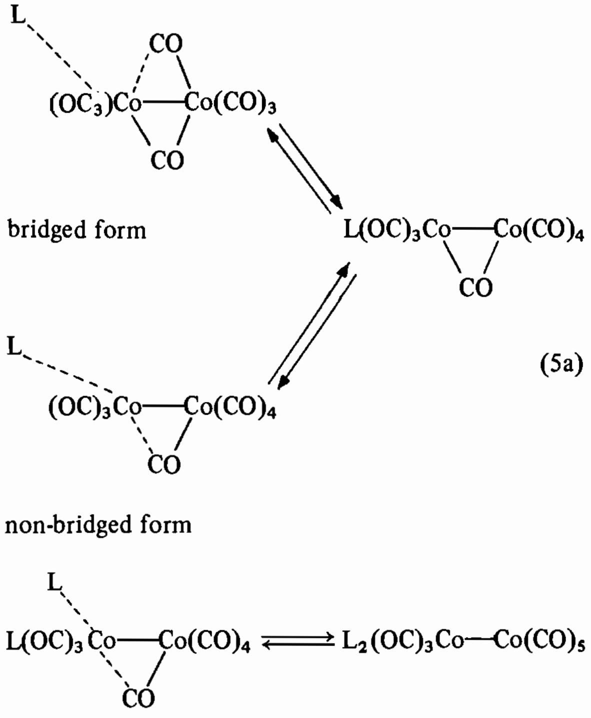
Discussion

$Co_2(CO)_8$ is known to react via first-order mechanism in several reactions, in which CO dissociation [4, 5] or Co–Co bond breaking [7] were proposed to be the rate determining step. For a comparison all the kinetic and thermodynamic data are reported in Table IV.

The agreement is not very good, even if it could be partly ascribed to the different experimental techniques. The similarity between and Basolo's rate constant values and ours is probably fortuitous, as Ellgen suggested that the rate of the CO exchange is probably increased by a simultaneous exchange of the intermediate $Co_2(CO)_7$. In our case the solvent can play a significant role, because the more polar TEA/n-heptane mixture could favour the dissociation with respect to toluene. There is a surprisingly good agreement between the activation parameter values found by us and by Ellgen, in particular for the low value of $\Delta S^{\ddagger}$, which is unexpected in a dissociative process. Even if the fact could be tentatively ascribed to the presence of two isomeric forms of $Co_2(CO)_8$ and/or to a simultaneous structural rearrangement of the intermediate $Co_2(CO)_7$, it remains substantially unclear. Anyway, in view of the relatively large uncertainties in the determined activation entropies, it would seem unwise to attempt any more detailed interpretation.

It is clear that the nature of the rate determining dissociative mechanism of $Co_2(CO)_8$ is still a problem and probably $Co_2(CO)_8$, owing to the complexity of its structure and the presence of two (or three [8]) isomeric forms, can react via different first-order mechanisms, according to the nature of the ligand and the experimental conditions. So, if there is some experimental evidence that renders the CO dissociation the most probable mechanism in the reaction with TEA, other mechanisms cannot certainly be excluded. The reaction product is indicated as $Co_2(CO)_7TEA$. Even if there is no experimental evidence, this formulation seems to be the most probable one according to the fact that the reaction of $Co_2(CO)_8$ with $P(C_6H_5)_3$ under mild conditions gives rise to $Co_2(CO)_7P(C_6H_5)_3$, as the initial product [9].

The reaction mechanism with BZA, CHA, DEA strictly resembles that of PIP, as reported before [2]. The high dependence on the ligand concentration of the rate of the first stage strongly suggests the consecutive attack of two or three molecules of the ligand on the substrate (eq. 5a, 5b, 5c or 5c′). It is probable that all the ligand molecules coordinate on the same Co atom, as suggested by the fact that the disproportionation gives rise as final product to a ligand-free cobalt carbonyl anion and to a carbonyl-free cation and that quite stable intermediates like $[Co(CO)_3L_2^+][Co(CO)_4^-]$ with L = phosphines are reported [10]. Probably the ligand coordination can promote a polarization of the metal–metal bond, such as $L \rightarrow Co^+ \rightarrow Co^-$, as a step toward the final ionic breaking, and so it can favour the subsequent attack on the same atom. It is evident that ligand coordination ought to be accompanied by internal rearrangements of the carbonyl groups on the substrate to avoid too strong steric hindrance. Besides, the presence of the two isomeric forms of $Co_2(CO)_8$, at virtually equal concentration [11], should be taken into account, as the probability of attack of the ligand on one isomer rather than on the other one



Scheme 1

cannot be very different. We suggest the following mechanism for eq. 5a and 5b:

which clearly shows CO displacement from bridging to terminal position (or *viceversa*), according to the reactive isomer. In this way both isomers give rise to the same active intermediate, which undergoes the successive reactions. The possibly different reactivities of the two isomers have no kinetic significance, provided that the equilibrium reaction between them is very fast with respect to the ligand reaction. This seems to be the case [12].

The coordination ability of the various N-bases appears to follow the order: CHA > BZA ≅ PIP > DEA >> TEA. TEA is the least reactive ligand, as it is unable to coordinate directly on the substrate; it is significant also that in a comparatively long time of reaction only a monosubstituted product is formed. In this light the relative positon of DEA is justified by its capacity to coordinate only two molecules before decomposition of the intermediate occurs, whereas with the preceding ligands three subsequent attacks are displayed. CHA appears the most nucleophilic one on the basis of its $\Delta H^{\ddagger}$ value, much greater than those of BZA and PIP. This suggests that the CHA enthalpy related to the k_1, k_2 and k_3 steps is lower, so the nucleophilicity is greater as these steps represent the attack of the ligand on the substrate. This order does not agree with the values of the dissociation constant pK_a (PIP (11.12) > TEA (11.01) > CHA (10.66) > DEA (10.49) > BZA (9.33)) nor with the values of dielectric constant (PIP (5.8) > CHA (5.4) > DEA (3.6) > TEA (2.4)), indicating that neither the basicity nor the polarity of the ligands play a significant role in their reactivity. Thus, the discriminating factor is more probably the steric hindrance of the groups bonded to the nitrogen, as it is expected that two and, in particular, three ethyl groups are so bulky to make difficult or even to prevent the coordination. In the other cases the groups are certainly more compact and less cumbersome.

The rate of the second stage is independent of the ligand concentration in all cases and the values of the rate constants are quite similar. We tentatively suggest that this stage represents an internal dissociation of the final product of the first stage, *i.e.* the complete ionic breaking of the Co–Co bond. According to the different formulation of this intermediate with DEA and with the other ligands, we propose two different mechanisms, that with CHA, BZA and PIP implying a simultaneous loss of a molecule of CO:

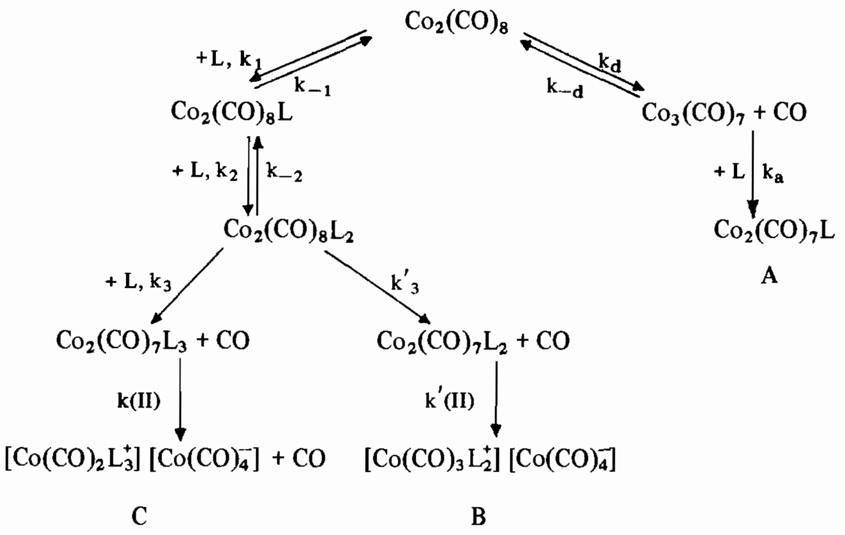
$$Co_2(CO)_7L_3 \xrightarrow{k(II)} [Co(CO)_2L_3^+][Co(CO)_4^-] + CO \qquad (5d)$$

$$Co_2(CO)_7L_2 \xrightarrow{k'(II)} [Co(CO)_3L_2^+][Co(CO)_4^-] \qquad (5d')$$

It is not surprising in this light that the activation parameters for this stage are so different in the two cases. The negative value of $\Delta H^{\ddagger}$ for the DEA mechanism is justified by observing that this value is the sum of $\Delta H^{\ddagger}$ associated to the Co–Co breaking (>0) an of $\Delta H^{\ddagger}$ (<0) related to the interaction between the ions and the molecules of the ligand. This interaction is probably so strong as to exceed the effect of the Co–Co scission; besides, Edgell has pointed out the strength of the interaction of $[Co(CO)_4^-]$ ion with polar solvents like piperidine or tetrahydrofuran [13]. If the enthalpy effect is similar with piperidine we obtain in this case $\Delta H^{\ddagger} \cong 23$ Kcal/mol for the cobalt–carbonyl breaking, which is reasonable for such kind of reaction [14]. The strong ion–solvent interaction clearly implies a sensible loss of degrees of freedom during the reaction, greater with DEA than with the other ligands, where the compensating effect of the loss of CO is operating: the values of $\Delta S^{\ddagger}$ in both cases strongly support the proposed mechanism.

In summary, we propose for the reaction of $Co_2(CO)_8$ with N-bases the following overall mechanism (scheme 2), in which the paths A, B and C represent the preferential reaction pathways for TEA, DEA and the other ligands respectively.

It is conceivable that all ligands can follow simultaneously all the reaction pathways. Therefore, the rate of path A is under our experimental conditions too low to be revealed in the presence of the much faster paths B and C, except in the case of TEA, in which mechanisms B and C are hindered by the



Scheme 2

bulkiness of the ligand. Only if the concentration of the ligand is low, can the rate of A become competitive with the rate of B and C. At low concentrations the values of the specific rate for DEA, CHA *etc.* do not longer obey to eqs. 8, 10, 11, but are higher than expected, probably indicating the superimposition of the contribution of the dissociative path.

Experimental

Reactants and solvents were purchased commercially and were purified by standard methods. Benzene was used in the BZA reaction, owing to the incomplete miscibility of benzylamine with n-heptane.

The kinetic measurements were performed by the stopped-flow technique. The experimental conditions and the treatment of the data were described in full details in Part I of this series.

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