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Mechanism of the Reaction of Bis(cyclopentadienyl carbonyl nickel) with Acetylenes

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A re-examination of the kinetic of reaction between $Cp_2Ni_2(CO)_2$ *and diphenylacetylene shows that a second-order mechanism is significant at very high concentration of the ligand, whereas at low concentration a two-stage mechanism is more important.*

It is noted also that the side-reactions, as the complete decomposition or the reaction of $Cp_2Ni_2(CO)_2$ *with CO, do not change significantly the value of the specific rate constant of the main reaction.*

Introduction

In this laboratory we have intensively studied the kinetics and the mechanism of reactions of $Cp_2Ni_2(CO)_2$ (Cp = π-cyclopentadienyl) with monodentate and acetylenic ligands.[1,2]

Monodentate ligands have been found[1] to react with bis(cyclopentadienyl carbonyl nickel) according to (1):

$$Cp_2Ni_2(CO)_2 + 2\,L \rightarrow NiCp_2 + Ni(CO)_2L_2 \quad (1)$$

The rate of the above reaction follows a simple second-order rate law, first order in each reactant:

$$\text{rate} = \varkappa_2\,[Cp_2Ni_2(CO)_2][L] \quad (2)$$

so the rate determining step is simply a direct attack of the incoming ligand on the complex. These results have been substantially confirmed by a report appeared about at the same time.[3]

The reaction of $Cp_2Ni_2(CO)_2$ with acetylenes RC_2R' (3),

$$Cp_2Ni_2(CO)_2 + RC_2R' \rightarrow Cp_2Ni_2RC_2R' + 2CO \quad (3)$$

on the contrary, shows a more complicated kinetic behaviour.[2]

The observed total pseudo-first-order rate constant $k_{obs}{}^{t}$ depends on alkyne concentration and the experimental data are consistent with a two-term rate law given by:

$$\text{rate} = k_{obs}{}^{t}[Cp_2Ni_2(CO)_2] = k_{obs}{}^{I}[Cp_2Ni_2(CO)_2] + k_{II}[Cp_2Ni_2(CO)_2][RC_2R'] \quad (4)$$

in which:

$$k_{obs}{}^{1} = \frac{k_1k_2[RC_2R']}{k_{-1} + k_2[RC_2R']} \quad (5)$$

Two mechanisms appear to be operating simultaneously in this case: a bimolecular associative mechanism, identical to that suggested for the monodentate ligand reactions, and a two-stage mechanism (6) implying a dissociative path as a rate-determining step:

$$\begin{aligned} &Cp_2Ni_2(CO)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cp_2Ni_2(CO)_2{}^{*} \\ &Cp_2Ni_2(CO)_2{}^{*} + RC_2R' \xrightarrow{k_2} \text{products} \end{aligned} \quad (6)$$

By applying the steady-statc approximation on the active intermediate $Cp_2Ni_2(CO)_2{}^{*}$, eq.(5) is obtained. At high alkyne concentration, i.e. when $k_2[RC_2R'] \gg k_{-1}$, $k_{obs}{}^{I}$ is constant and eq. (4) will reduce to eq. (7):

$$k_{obs}{}^{t} = k_I + k_{II}[RC_2R'] \quad (7)$$

from which values of k_I and k_{II} can be easily obtained. The values of $k_{obs}{}^{1}$ are dermined by subtracting from the $k_{obs}{}^{t}$ values the contribution of the associative mechanism, given by $k_{II}[RC_2R']$. Finally, eq. (5) can be rearranged to give eq. (8):

$$\frac{1}{k_{obs}{}^{t}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2[RC_2R']} \quad (8)$$

which enable us to calculate the k_2/k_{-1} values.

The experimental linear dependence of both $k_{obs}{}^{t}$ vs. $[RC_2R']$ (at high alkyne conc.) and $1/k_{obs}{}^{I}$ vs. $1/[RC_2R']$ supports the proposed mechanisms. As expected, k_1 is independent of the nature of RC_2R': its value is quite constant (2.5–3.0×10^{-5} sec^{-1}) for the different alkynes. k_{II} and k_2/k_{-1}, on the contrary, definitely depend on RC_2R' and have be found to increase as increases the electron attracting power of the R and R′ groups.[2] Moreover, the bulkiness of the alkyne can probably explain for the diphenylacetylene and 1-phenylpropyne reactions the values of k_{II} and k_2/k_{-1} smaller than those which could be expected. In a recent report[4] Ellgen has claimed that the kinetics of the reaction (3) cannot give sufficiently accurate results because of (a) the spontaneous decomposition of $Cp_2Ni_2(CO)_2$; (b) the reaction, according to (1), of $Cp_2Ni_2(CO)_2$ with CO evolved in (3); (c) the partial decomposition of $Ni(CO)_4$ produced *via* (1), to give additional free carbon monoxide.

On the basis of the above considerations and of a few experimental data Ellgen has concluded that the rate law of the $Cp_2Ni_2(CO)_2$ reaction with diphenylacetylene is simply expressed by:

$$k_{obs} = k_d + k_r[C_2(C_6H_5)_2] \qquad (9)$$

in which the k_d term is the rate constant for substrate decomposition in the absence of alkyne and the k_r term is twice the second-order rate constant for attack of $C_2(C_6H_5)_2$ on $Cp_2Ni_2(CO)_2$ [assuming that the CO liberated by (3) reacts rapidly and quantitatively with the complex according to (1)].

We think that the previous considerations are in part inaccurate. Actually, (a) the spontaneous decomposition of $Cp_2Ni_2(CO)_2$ is slow compared with the alkyne reaction. Literature reports that in the solid state $Cp_2Ni_2(CO)_2$ decomposes *at 130°* to give $Cp_3Ni_3(CO)_2$[5], whereas in mesitylene solution extrapolation of the decomposition rate to 80° gives an estimate of 0.1×10^{-5} sec^{-1} for the values of the first order rate constant at this temperature[6]. (b) It seems logical to suppose that the carbon monoxide evolved in (3) should be conveniently distributed into the solution and the gas phase. So, if a suitable volume gas/volume solution ratio is used in the reaction vessels, taking into account the low solubility of CO in n-heptane at 80.0°, the probability of the reaction (1) can be so lowered that its contribution to the disappearance of the complex is negligible. In fact, in our experiments only after two or three half-lives have been observed a little absorbance at 2046 cm^{-1} due to the $Ni(CO)_4$ produced[7]. (c) The extent of the thermal decomposition of $Ni(CO)_4$ is small;[8] however the above consideration renders it unimportant.

TABLE I. Values of the pseudo-first-order rate constant for the reaction of $Cp_2Ni_2(CO)_2$ with $C_2(C_6H_5)_2$ in n-heptane at 80.0°.

Ligand concn. *M*	$k_{obs}{}' \times 10^5$ sec^{-1}
–	0.15[a]
0.080	3.29
0.101	4.12
0.126	4.08
0.151	4.27
0.175	5.07
0.199	5.38
0.225	5.72
0.249	6.02
0.275	6.31
0.300	6.44
0.324	6.83
0.350	6.89
0.399	7.38
0.450	8.31
0.500	8.44

[a] Average of three values; uncertainty ± 25%.

Nevertheless, at this point a brief reinvestigation of the reaction (3) with diphenylacetylene has become necessary: the values of the total pseudo-first-order rate constant [eq. (4)] are reported in Table I.

Results and Discussion

First of all it can be noted that the rate constant of the spontaneous decomposition of $Cp_2Ni_2(CO)_2$ at 80.0° in n-heptane is taken in the uncertainty of the rate constant for the reaction with diphenylacetylene: so corrections are unnecessary. Furthermore, the kinetic data indicate that a limiting rate is not reached at very high concentration of diphenylacetylene, but the $k_{obs}{}'$ value increase with increasing $[C_2(C_6H_5)_2]$. Figure 1 shows the dependence of $k_{obs}{}'$ vs. ligand concentration. This behaviour is consistent with the general mechanism proposed for reaction of $Cp_2Ni_2(CO)_2$ with alkynes (eq. 4): so the contributions to the $k_{obs}{}'$ values of both mechanism can be evaluated separately, as described before. The test of the correctness of this interpretation is the linear relationship of $1/k_{obs}{}^{1}$ vs. $1/[C_2(C_6H_5)_2]$ [eq. (8)], as illustrated in Figure 2. The rate constant values are: k_{II} (1.20 ± 0.06) $10^{-4}M^{-1}$ sec^{-1}; $^{k}{}_{1}$ (2.77 ± 0.17) 10^{-5}sec^{-1}; k_2/k_{-1} 123 ± 11 M^{-1} (uncertainties are the standard deviations.

Some considerations can be drawn at this point.

a) It seems unambiguously ascertained that the reaction of $Cp_2Ni_2(CO)_2$ with alkynes obeis a mixed-order rate law [eq. (4) and eq. (7)], in which the first-order term k_1 is too greater than the specific rate for the complex decomposition to be mistaken for it. The values of k_d and k_r terms [eq. (9)] in Ellgen's report have no reliable significance, as obtained by means of two different series of data, one of them[1] referring solely to the rate of the reaction (3), the other one[4] referring of both reaction (2) and reaction (3) together.[9]

b) The data indicate that the second-order mechanism as well contributes to the rate of the reaction of $Cp_2Ni_2(CO)_2$ with $C_2(C_6H_5)_2$, which has not been considered in our previous report. Otherwise, it should be noted that, owing the low k_{II} value, this effect is significant at very high diphenylacetylene concentration: e.g. at $[C_2(C_6H_5)_2] = 0.05$ the contribution of the second-order mechanism is less than 20% of the total rate, so that it practically falls in the uncertainty of the observed rate constant value. Really, the corrected rate constants from eq. (5) or from eq. (8) do not differ significantly from the uncorrected values previous reported.[1] Figures 1 and 2 illustrate this well.

c) The absence of the second-order term with $C_2(C_6H_5)_2$ has been ascribed to the bulkiness of the phenyl group, which prevents the direct attack of the ligand. On the light of the new results however, this

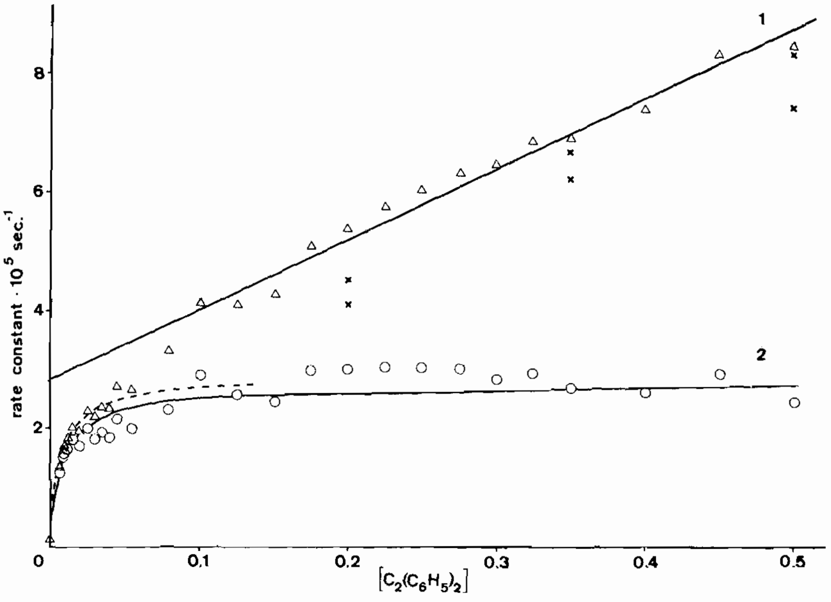

Fig. 1. Plots of the rate constants vs. diphenylacetylene concentrations. Triangles are k_{obs}^{t} values, circles are k_{obs}^{1} values, crosses are half of k_{obs} values from Ref. 4. Values below 0.08 *M* are taken from Ref. 1. Line 1 is the least-squares fit of the k_{obs}^{t} in Table I; line 2 is the best fit of all the k_{obs}^{1} values to eq. (5); dashed line is computed only by the data given in Ref. 1.

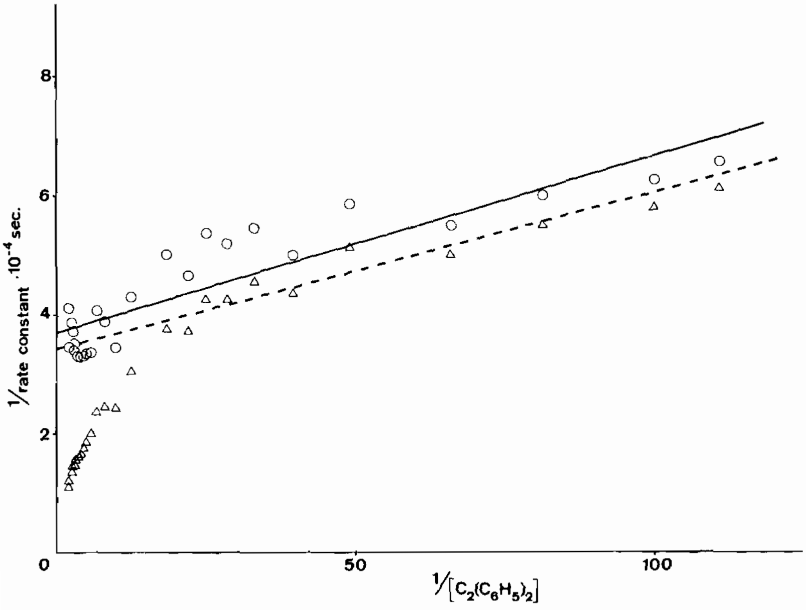

Fig. 2. Plots of the reciprocal of the rate constants vs. the reciprocal of the diphenylacetylene concentrations. Symbols have the same meaning as in Fig. 1. Solid line is the least-squares fit of all the $1/k_{obs}^{1}$ data to eq. (8); dashed line is computed only by the data given in Ref. 1.

assumption can be mantained whereas the k_{II} and k_2/k_{-1} values for $C_2(C_6H_5)_2$ are much lower than those which can be expected, in relation to the inductive properties of the phenyl group.[2]

Experimental

Compounds and Solvent

Bis(π-cyclopentadienyl carbonyl nickel) (Alfa Inorganics) and diphenylacetylene (Fluka AG) were dissolved in n-heptane under nitrogen and crystallized at –20°.

The reagent grade n-heptane was dried, distilled and stored under nitrogen according to standard techniques.[10]

High purity N_2 was dried on $CaCl_2$–silica gel columns before use.

Kinetic Measurements

Reaction rates were studied by following changes in the infrared spectra of the reaction mixture. The disappearance of the carbonyl stretching band at 1859 cm^{-1} in the complex was measured to obtain total pseudo-first-order rate constant. Plots of $\ln(A_t - A_\infty)$ vs. time were linear to at least 70% completion. The average deviation of the rate constant was about 5%. The experimental procedure and the method of treating the data have been described in the earlier paper.[1]

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7 In our experimental conditions the complex concentration was 1.0 m*M*, the volume of the vials was about 200 ml; that of solution 20 ml. The value 0.56 M^{-1} sec^{-1} of $\varkappa_2$ for reaction (1) with CO at 80.0° and the value ~ 2.0 m*M* of the CO solubility in n-heptane at the same temperature[2] enable us to calculate the contribution of reaction (1) with CO evolved in (3) to the total rate. E.g., after one half-life k_{obs} for (1) is. 0.3×10^{-5} sec^{-1}, i.e. practically negligible with respect to the k_{obs}' values (see Table I).

8 F. Calderazzo, E. Ercoli and G. Natta in "Organic Syntheses via Metal Carbonyls", Vol. I, p. 44, I. Wender and P. Pino (Eds.), Interscience, New York, N.Y., 1968.

9 The Ellgen values are in good accordance with ours (see Fig. 1), differences being probably ascribed to the fact that $Cp_2Ni_2(CO)_2$ does not completely react with CO under the experimental conditions. Indeed, the least-squares fit to the values from Ref. 4 only gives $k_d = 1.8 \times 10^{-5}$ sec^{-1} and $k_r = 2.9 \times 10^{-4}$ M^{-1} sec^{-1}, which agree with k_I and $2k_{II}$ respectively.

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