Inorganica Chimica Acta, 23 (1977) L7–L8
© Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Mechanism of Carbonylation of Nitrosyltris(triphenylphosphine) Complexes

G. NAVAZIO

Istituto di Chimica Industriale, Facoltà di Ingegneria, University of Padova

A. MANTOVANI and P. L. SANDRINI

Cattedra di Chimica, Facoltà di Ingegneria, University of Padova

P. UGUAGLIATI

Centro Composti Metallorganici del CNR, Istituto di Chimica Industriale, Facoltà di Ingegneria, University of Padova, Via Marzolo 9, 35100 Padova, Italy

Received March 10, 1977

The carbonylation of nitrosyl tertiary phosphine complexes of Cobalt, Rhodium and Iridium, of type $M(NO)(PPh_3)_3$ [1–3] has been described to proceed to mixed nitrosyl–carbonyl species such as $M(NO)(CO)(PPh_3)_2$ [2–5]. Spectroscopic investigations [2] have shown that in these $M(NO)(PPh_3)_3$ complexes the $M(NO)(PPh_3)_2$ moiety acts as a flexible substrate towards different σ-donor, π-acceptor ligands.

We deemed it worthwhile to study the mechanism of formation of the nitrosyl–carbonyl derivatives from the kinetics of absorption of carbon monoxide by chlorobenzene solutions of the starting nitrosyl–tris(triphenylphosphine) substrates. Preliminary results of these studies for the iridium system will be described herein.

Experimental

Materials and Complexes

The nitrosyl complex $Ir(NO)(PPh_3)_3$ was prepared according to literature methods [2], as was the corresponding carbonylation product $Ir(CO)(NO)(PPh_3)_2$ [2].

Gas chromatography carbon monoxide in stainless steel tanks was used without further purification.

The reagent grade chlorobenzene used as the solvent was repeatedly washed with sulfuric acid and then with a 10% v/v $NaHCO_3$ solution and distilled under reduced pressure.

Kinetic Measurements

The kinetics were studied by measuring the volume of carbon monoxide absorbed in a system containing a weighed quantity of $Ir(NO)(PPh_3)_3$ and known volume of solvent. The gas volumetric apparatus was a modification of that described by Calderazzo and Cotton [6] and measurements were carried out with similar procedures.

Since the gas volumetric apparatus was unfit for measurements at total internal pressures differing significantly from atmospheric pressure, in some runs the partial pressure of carbon monoxide was lowered while maintaining the total gas pressure with an inert diluent gas. To this end, the required mixtures of nitrogen and CO were prepared and used to saturate the solvent and fill the reaction vessel (the relative amount of CO was determined by absorption analysis in a Cu(I) solution [7]).

Pseudo first-order rate constants at various temperatures were measured as the least-squares slopes of initially linear portions of plots of $\ln(C_0/(C_0 - C_t))$ *vs.* time, where C_0 and C_t were the concentrations of substrate $Ir(NO)(PPh_3)_3$ at time zero and t, respectively (see *Discussion*).

The values of pseudo first-order rate constants, k_{obs} (sec^{-1}) are listed in Table I.

The solubility of carbon monoxide in chlorobenzene at various temperatures and partial pressures was measured by gas chromatographic techniques, based on the irreversible adsorption of chlorobenzene on molecular sieves [8]. The values of solubilities at various temperatures are also listed in Table I.

TABLE I. Rate Constants for the Carbon Monoxide Absorption Reactions $Ir(NO)(PPh_3)_3 + CO \rightarrow Ir(NO)(CO)(PPh_3)_2 + PPh_3$ in Chlorobenzene at Various Temperatures and CO Partial Pressures.

t,°C	$10^3[CO]^a, M$	CO Partial Pressure, atm	$10^2 k_{obs}$ s^{-1}	$k_2{}^b$ $M^{-1}s^{-1}$
35	1.79	0.53	0.030	0.15
	3.74	0.78	0.064	
	4.36	0.85	0.067	
40	2.61	0.63	0.076	0.24
	3.56	0.76	0.087	
	4.60	0.88	0.136	
	5.34	0.96	0.130	
	5.88	1	0.153	
50	2.75	0.67	0.258	1.31
	3.31	0.73	0.366	
	5.21	0.67	0.601	
	5.93	0.73	0.65	

^{a}See *Experimental*. ^{b}Slope of plot of k_{obs} *vs* [CO].

Results and Discussion

The kinetics of carbon monoxide absorption by chlorobenzene solutions of $Ir(NO)(PPh_3)_3$, according to the reaction

$$Ir(NO)(PPh_3)_3 + CO \rightarrow Ir(NO)(CO)(PPh_3)_2 + PPh_3 \quad (1)$$

are first order in $Ir(NO)(PPh_3)_3$ at constant CO pressure, as shown by the fact that plots of $\ln(C_0/(C_0 - C_t))$ *vs.* time are linear up to approximately 40–60% of conversion. The plots tend to level off at higher percent conversions (see further). The pseudo-first order rate constants, $k_{obs}(sec^{-1})$, calculated from the slopes of these initially linear plots, are set forth in Table I for various temperatures. Through each run the manostatic device allowed us to maintain a constant pressure and hence concentration of carbon monoxide in solution, so that pseudo-first order conditions prevailed throughout.

The CO concentration in solution was made to vary in a limited range as described in the *Experimental*, and the dependence of k_{obs} on the CO concentration could be obtained.

The k_{obs} values fit the second order rate law (2):

$$k_{obs} = k'[CO] \qquad (2)$$

The values of second order rate constants, k_2 (M^{-1} sec^{-1}), resulting from a least-squares fit of eqn. 2, are listed in Table I. The appropriate concentrations of CO were obtained by separate measurements of CO solubilities by gas chromatographic methods. The activation parameters for CO absorption (eqn. 1) were calculated from a weighted linear least-squares fit of $\ln(k_2/T)$ to $1/T$, with the weighting scheme $w_i = (k_i/\sigma_i)^2$, where σ_i is the estimated standard error for k_i. The ensuing values are $\Delta H^{\neq} = 29 \pm 3$ kcal/mol, $\Delta S^{\neq} = +33 \pm 8$ e.u. (uncertainties are estimated standard errors).

A single run in the presence of excess free triphenylphosphine was found to proceed at a much slower rate under comparable conditions. Moreover, the enthalpy of activation is unusually high and the entropy of activation is oddly positive for a simple ligand displacement reaction.

These findings indicate the following stepwise mechanism:

$$Ir(NO)L_3 \underset{-S,k_{-1}}{\overset{+S,k_1}{\rightleftharpoons}} Ir(NO)(S)L_2 + L$$

$$(S = \text{solvent}) \qquad (3)$$

$$Ir(NO)(S)L_2 + CO \xrightarrow[-S]{k_2} Ir(NO)(CO)L_2$$

Under steady-state conditions and at constant L concentration the pseudo first-order rate constant, k_{obs}, will fit the general rate law (4)

$$k_{obs} = \frac{k_1 k_2[CO]}{k_{-1}[L] + k_2[CO]} \qquad (4)$$

which reduces to the observed second order rate law 2 when $k_2[CO] \ll k_{-1}[L]$ (which appears to be the case for the range $(1.8–5.9) \times 10^{-3}$ M of CO concentrations examined).

Therefore, the apparent second order rate parameter k' in eqn. 2 should be a composite of k_1, k_2, k_{-1} rate constants and of the particular value of [L] at which single runs are carried out:

$$k' = k_1 k_2/k_{-1}[L] \qquad (5)$$

Of course, eqns. 4 and hence 5 can only be valid if the concentration of L is held constant throughout each run – a condition which, in the absence of excess added L, cannot be met but for the earlier stages of the overall reaction, when the concentrations of L generated are still too low to affect the kinetics. The levelling off in the rates of CO absorption that sets in as the reaction progresses is likely to be due to the rate-depressing presence of increasing concentrations of free L.

We are now carrying out a complete kinetic study in the presence of excess free L for this as well as for the analogous Cobalt and Rhodium systems, in order to determine the separate kinetic parameters k_1 and k_2/k_{-1} in detail.

When these data become available we will be in a position to provide a rationale for the observed activation parameters which, according to eqn. 5, must also be a composite function of those pertaining to the single steps of the mechanism in eqn. 3.

References

1 J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 2947 (1970).

2 C. A. Reed and W. R. Roper, *J. Chem. Soc. A*, 3054 (1970).

3 G. La Monica, G. Navazio, P. L. Sandrini and S. Cenini, *J. Organometal. Chem.*, *31*, 89 (1971).

4 G. La Monica, S. Cenini, G. Navazio and P. L. Sandrini, unpublished results.

5 C. B. Ungermann and K. G. Caulton, *J. Am. Chem. Soc.*, *98*, 3862 (1976).

6 F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, *1*, 30 (1962).

7 W. W. Scott, "Standard Methods of Chemical Analysis", 5th Ed., D. Van Nostrand, New York, N.Y., p. 2349.

8 N. Brenner, E. Cieplinski, L. S. Ettre and V. J. Coates, *J. Chromatog*, *3*, 230 (1960).