Inorganica Chimica Acta, 26 (1978) 91–96
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Experimental Evidence for a more Complete Rate Law for Nucleophilic Substitution at Square Planar Metal Complex Centers.
Kinetics and Mechanism of Ligand Replacement in the Complex Cycloocta-1,5-diene-tricyclohexylphosphinechlororhodium(I)

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Received May 20, 1977

The kinetics of the reaction of $(C_8H_{12})(Cl)(P[C_6H_{11}]_3)Rh(I)$ *with the nucleophiles thiocyanate* (2×10^{-4} M *ionic strength), ethylenediamine and NN'-dimethylethylenediamine* (5×10^{-1} M *ionic strength) was investigated by stopped-flow spectrophotometry at 25 °C. The mechanism entails a direct path and a solvent assisted path to a common reaction product. For the amine systems an observed hyperbolic velocity curve provides more kinetic detail for the solvolytic process. A rate limiting value of 5.5* sec^{-1} *was established for this path in three independent studies utilizing the mentioned nucleophiles of vastly different reactivities. Only the direct path is operative at very high chloride ion concentrations.*

Introduction

The classic study on the isotopic chloride exchange reaction [1] of $AuCl_4^-$ gave birth to the so-called two term rate law:

$$k_{obsd} = k_y[Y] + k_s \qquad (1)$$

where Y represents the nucleophile (in this case Cl^-). Numerous kinetic studies that followed [2–5], especially on Pt(II) complexes, proved this rate law to be a fairly general feature of nucleophilic substitution at the square planar metal centre. The association of k_s with a solvent controlled pathway to reaction product is experimentally sound [6, 7]. Since this path is limited by the rate of solvent attack on the substrate, very little can be said about the kinetic properties of the solvent intermediate except that it is very reactive towards the nucleophile Y.

More kinetic detail concerning the solvent path emerges if a rapid equilibrium between the substrate and the solvent complex persists during the course of the reaction from reactants to product. A few examples of the limited number of reactions falling in this category are:

$$\begin{tikzcd}
MCl_4^{2-} + H_2O \arrow[rr, shift left, "K"] \arrow[dr, "k_y(Y)"'] & & MCl_3(H_2O)^- + Cl^- \arrow[ll, shift left, "fast"] \arrow[dl, "k_{sy}(Y)"] \\
& MCl_2(N\text{–}N) &
\end{tikzcd}$$

where M ≡ Pd(II) [8] or Pt(II) [9, 10], and Y ≡ chelating amine. The rate law takes the form:

$$k_{obs} = \left\{ k_y + \frac{k_{sy}K}{[Cl^-]} \right\} [Y] \qquad (2)$$

if the equilibrium constant $K \ll [Cl^-]$.

A study on the kinetics of the interaction of Pd(dien)Br^+ with inosine is the only example reported in the literature [11] where the entering and leaving ligands were found to compete for the solvent intermediate on an equal basis under certain experimental conditions. The present study reports on the kinetics of ligand replacement in $Rh(Cl)(C_8H_{12})(P[C_6H_{11}]_3)$ where a similar phenomenon was observed. Experimental evidence is now available to prove rate laws (1) and (2) as two extreme limiting cases of a more complete rate law.

Experimental

Materials

Reagents

Analytical grade methanol (Merck) was used as the reaction medium. The salts KSCN, LiCl and $LiClO_4$ (*pro analysi* grade) were dried at 100 °C to remove any water. Ethylenediamine and NN'-dimethylethylenediamine were redistilled as a precaution to remove possible decomposition products. Tricyclohexylphosphine (Strem Chemicals) is known to decompose slowly upon exposure to air and was hence stored under nitrogen. The complex cycloocta-1:5-dienetricyclohexylphosphinechlororhodium(I) was prepared by a literature method [12] and characterized by its spectrum (λ = 405 nm; $\epsilon = 7 \times 10^3$ M^{-1} cm^{-1}) and microanalysis: Calc. for $[C_8H_{12}]Rh[Cl][P(C_6H_{11})_3]$: C% = 59.2, H% = 8.6, Cl% = 6.7. Found: C% = 58.9, H% = 8.55, Cl% = 7.0.

Reaction products

Addition of a ten fold excess of NaSCN to a 1:1 methanol–dichloromethane solvent mixture containing the starting complex afforded a good yield of the SCN-product after stripping the dichloromethane phase under reduced pressure. A microanalysis on the reaction product satisfies the formula $[C_8H_{12}]Rh[P(C_6H_{11})_3][SCN]$: Calc. C% = 59.0, H% = 8.25, N% = 2.55. Found C% = 59.1, H% = 7.9, N% = 2.62. The UV–vis spectrum displays a strong absorption peak at λ_{max} = 412 nm ($\epsilon_{max} = 8.7 \times 10^3$ M^{-1} cm^{-1}).

Reaction of the substrate complex with a ten fold excess of ethylenediamine in a 1:1 dichloromethane–methanol solvent mixture afforded a yellow solution. The reaction product was precipitated by the addition of sodium tetraphenylborate. The complex analysed for $[(C_8H_{12})(N_2H_8C_2)Rh]^+[B(C_6H_5)_4]^-$. H% = 6.5, C% = 65.5, N% = 5.38. An absorption peak is observed at λ_{max} = 380 nm, $\epsilon_{max} = 6.2 \times 10^3$ M^{-1} cm^{-1}.

Solutions used for the kinetic measurements display the same spectral characteristics after completion of the reaction.

Kinetic Experiments

The kinetic data were obtained with a conventional Durrum D110 stopped-flow spectrophotometer. All measurements were carried out at 25 °C and a constant ionic strength (0.5 M for amine systems and 2×10^{-4} M for thiocyanate system). In all cases the complex concentration was kept small enough, approximately 5×10^{-5} M, to assure pseudo first-order conditions. Except for a slight initial curvature excellent linear semi-log plots were obtained for more than 95% of the reaction manifesting a first order loss of the starting complex.

The wavelength of observation was mainly at λ = 415 nm. For the amine systems this amounts to measuring the disappearance of starting complex while measuring the rate of product formation in the thiocyanate study. Kinetic data collected at a few other wavelengths gave identical results.

Results and Discussion

It was initially observed that the pseudo first-order constant, k_{obsd}, was inversely proportional to the complex concentration. This behaviour caused some concern since it would require rather complex mathematics to treat the experimental data by the conventional integration technique. This complication was traced back to a chloride ion effect on the rate of reaction. Fixing the chloride ion concentrations at levels at least ten times higher than the complex concentration produced a rate law: $-d[\text{complex}]/dt = k_{obsd}[\text{complex}]$. The kinetic data could hence be treated in terms of a true pseudo first-order parameter, k_{obsd}.

Experiments designed to elucidate the functional dependence of k_{obsd} on variables such as phosphine, chloride and nucleophile concentrations as well as the ionic strength were carried out. The kinetic results are collected in Table I. Some of the data are represented graphically in Figure 1 for the case where Y represents ethylenediamine. At low chloride ion concentration levels the reaction features different rate laws at low amine (curved region) and high amine (linear region) concentrations. This differentiation is less obvious at intermediate chloride ion concentrations while a mechanism represented by a linear dependence of k_{obsd} *vs.* ethylenediamine concentration prevails at high concentrations of Cl$^-$.

Similar trends were observed for the NN′-dimethylethylenediamine system but with much slower rates of reaction. Only the two extreme chloride concentration levels were studied, namely 0.2 mM and 100 mM. The concentration plot of the former curves continuously towards the amine concentration axis whereas a linear concentration plot through the origin is obtained at high concentrations of chloride ion.

By replacing the chloride ion in the title compound with thiocyanate ion a classical two term rate law was obtained with an intercept value of 5.5 sec^{-1} and a slope value of 320 sec^{-1} M^{-1}. It is significant that the former value is in close agreement with the intercept value obtained by extrapolation of the linear part of plot c in Figure 1 to zero amine concentration.

A reaction mechanism that conforms to all of the experimental observations is the following:

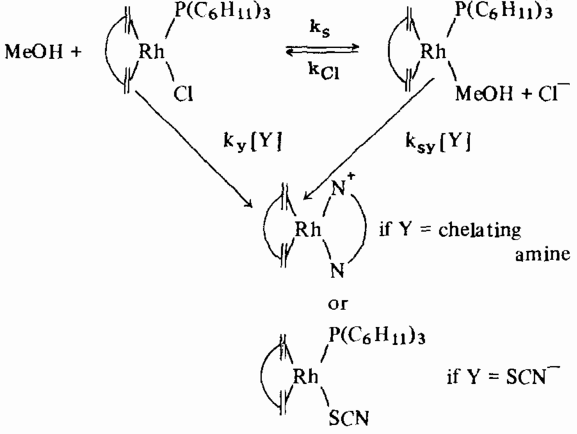

TABLE I. Kinetic Data for the Reaction of $(C_8H_{12})(Cl)(P[C_6H_{11}]_3)Rh(I)$ with Various Nucleophiles in Methanol at 25 °C. Ionic strength is 0.5 *M* for the amine systems and 2×10^{-4} *M* for the thiocyanate system.*

[en], m*M*	k_{obsd}, sec^{-1}					
	(a)	(b)	(c)	(d)	(e)	(f)
1.58	1.30	1.40	0.460	0.130	0.085	0.037
3.12	2.31	2.15	0.853	0.260	0.173	0.082
6.25	3.38	3.2	1.30	0.505	0.35	0.178
12.5	4.30	4.8	2.50	0.97	0.65	0.375
50	6.80	7.0	5.50	3.40	2.61	1.54
100	8.32	8.36	7.60	6.0	4.58	3.0
200	11.10	11.5	10.50	10.50	8.83	6.24
400	17.00	16.8	16.80	16.50	15.80	12.00

[NN'en], m*M*	(a) k_{obsd}, sec^{-1}	(b) k_{obsd}, sec^{-1}	$[SCN^-]$, m*M*	(a) k_{obsd}, sec^{-1}
1.58	0.0312	–	1.56	5.9
3.12	0.0577	–	3.13	6.7
6.25	0.112	–	6.25	7.4
12.5	0.236	0.0045	12.5	9.6
50	0.745	0.0193	25	13.9
100	1.39	0.0375	50	21.7
200	2.38	0.0693		
400	3.38	0.150		

*All measurements were carried out at 1 m*M* of $[P(C_6H_{11})_3]$ except for (b) where the concentration was 10 m*M*. The symbols in brackets refer to the following $[Cl^-]$: (a) 0.2 m*M*; (b) 0.2 m*M*; (c) 1.0 m*M*; (d) 5.0 m*M*; (e) 10 m*M* and (f) 100 m*M*.

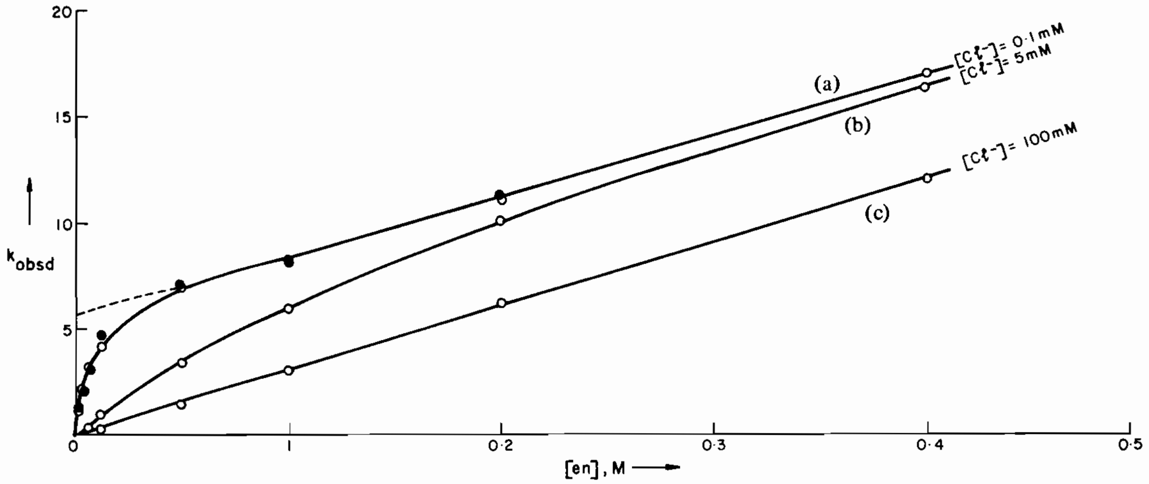

Figure 1. Concentration Plots of k_{obsd} against ethylenediamine concentration at various chloride ion concentration levels. Conditions: t = 25 °C, I = 0.5 *M*, $[(C_8H_{12})(Cl)(P[C_6H_{11}]_3)Rh]$ = 0.05 m*M*. Open circles refer to 5 m*M* phosphine added and closed circles to 0.1 m*M* phosphine added. Solid lines represent theoretical curves drawn through experimental points (circles) calculated from equation (3) where $k_s = 5.5\ sec^{-1}$, $k_y = 30\ sec^{-1}\ M^{-1}$ and $k_{Cl}/k_{sy} = 21.0$.

The theoretical rate law takes the form:

$$k_{obsd} = \frac{k_s k_{sy}[Y]}{k_{Cl}[Cl^-] + k_{sy}[Y]} + k_y[Y] \qquad (3)$$

assuming steady state kinetics for the solvent intermediate.

Despite numerous kinetic studies on substitution reactions of square planar metal complexes the hyperbolic characteristics of the solvolytic term of rate law (3) have always eluded experimental observation. The substitution reaction of the title compound with ethylenediamine represents one of the few reactions [11] to disclose these characteristics.

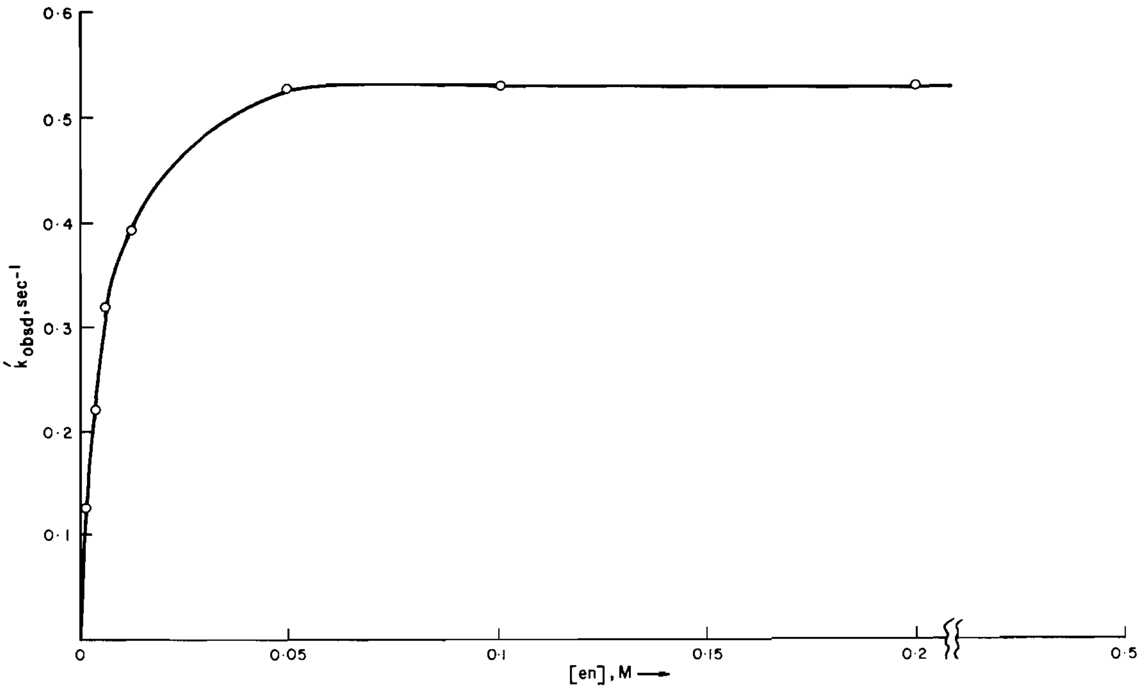

Figure 2. Solvent path for the ethylenediamine system, t = 25 °C, I = 0.5 *M*, [complex] = 0.05 m*M*, [Cl^-] = 0.2 m*M*.

The linear region of plot (c) of Figure 1 can be rationalized in terms of the classical two term rate law producing specific rate constants of $k_s = 5.5$ sec^{-1} and $k_y = 30$ sec^{-1} M^{-1} calculated from the intercept and slope values respectively.

With k_y known the kinetic behaviour of the solvent assisted pathway can be illustrated more explicitly by rearranging equation (3) to:

$$k'_{obsd} = k_{obsd} - 30[en] = \frac{k_s k_{sy}[en]}{k_{Cl}[Cl^-] + k_{sy}[en]} \qquad (4)$$

and plotting the rate of the solvolytic path, k'_{obsd}, as a function of [en] as depicted in Figure 2. It is clear that the solvolytic term can take different forms depending on the relative contribution by the two terms in the denominator. Fixing the chloride ion concentration at a very low level of 0.2 m*M* the complete spectrum of the various kinetic patterns is revealed, namely,

(i) a limiting rate of $k'_{obsd} = k_s$ at very high [en].

(ii) a curved plot of k'_{obsd} *vs.* [en] at intermediate [en] with k'_{obsd} becoming progressively less than the limiting rate k_s the more effective Cl^- can compete with amine for the solvent intermediate.

(iii) at very low [en] the rate of chloride ion attack on the solvent complex is much faster than attack by amine and a continuously maintained equilibrium defined by $K = k_s/k_{Cl^-}$ exists during the course of the reaction from reagents to product. Rate law (4) changes to $k'_{obsd} = k_{sy}K[en]/[Cl^-]$ and represents the tangent to the plot of Figure 2 passing through the origin.

Conditions (i) and (iii) thus represent two extreme cases of a more complete rate law (equation 3).

A mass retarding effect is operative with the addition of chloride ions to the reaction solution. The kinetic data are best treated by inverting equation (4)

$$\frac{1}{k'_{obsd}} = \frac{1}{k_s} + \frac{k_{Cl}[Cl^-]}{k_s k_{sy}[en]} \qquad (5)$$

Good linear plots of $1/k'_{obsd}$ *vs.* 1/[en] are obtained, the slopes of which are linearly dependent on chloride ion concentration. Phosphine concentration had no effect on the reaction rate. It can be concluded that chloride ion serves as the leaving group in the rate determining activation process with the phosphine being replaced in a consecutive rapid ring closing step. A concurrent solvent pathway involving a rate limiting replacement of phosphine by solvent will manifest itself as curved plots of equation (5), which was not observed.

By gradually increasing the chloride ion concentration level a stage will eventually be reached where the chloride ions scavenge the solvent intermediate completely, hence rendering the solvent assisted pathway inoperative as is borne out by the kinetic data portrayed in plot (a) of Figure 1.

A critical test for rate law (3) is that k_s should be independent of the nature and reactivity of Y. Thiocyanate and NN′-dimethylethylenediamine were chosen as nucleophiles for this purpose.

TABLE II. Specific Rate Constants Calculated at 25 °C.

Y	k_y, sec^{-1} M^{-1}	k_s, sec^{-1}	k_{Cl}/k_{sy}^{a}	Ionic Strength
en	30.0	5.5	21.0	5×10^{-1}
NN'en	0.38	5.5	1458	5×10^{-1}
SCN^-	320	5.5	–	2×10^{-4}

^{a}Ratio value calculated by substituting the values of k_y and k_s in equation (3).

It can be predicted that thiocyanate which is traditionally very reactive towards "soft" transition metal atoms [13] would scavenge the solvent intermediate very efficiently and hence cause equation (3) to approximate to the classical two term rate law. This was verified experimentally. The rate parameters appear in Table II.

The k_y value for the NN'-dimethylethylenediamine system was obtained from a concentration plot constructed at a high chloride ion concentration level of 100 m*M* where the solvolytic process is known to be fully suppressed. With the k_y value known the contribution of the solvent assisted pathway can be evaluated at a lower chloride ion concentration level where this pathway is more prominent. The variation of k'_{obsd} with [NN'en] at 0.2 m*M* chloride ion concentration is depicted graphically in Figure 3. It is apparent that a limiting rate is not reached within experimental range of [NN'en] used because of the much lower reactivity of the substituted amine compared to chloride ion (Table II). The method developed by Eisenthal and Cornish-Bowden [14] was used to obtain the limiting rate as the conventional technique of obtaining limiting rates with the aid of reciprocal plots (equation 5) failed to produce an accurate value (intercept too close to the origin because of a very steep slope). They disclosed a certain property of hyperbolic velocity curves namely that straight lines drawn through the corresponding [NN'en] values plotted on a negative concentration axis and the corresponding k'_{obsd} values plotted on the vertical axis, intersect at the limiting rate (Figure 3).

The k_s values obtained from three independent studies are in excellent agreement despite the vastly different reactivities of the nucleophiles Y (Table II) and lends support to the correctness of the proposed reaction mechanism. In addition pathway k_s is independent of the ionic strength as might have been anticipated for a reaction step involving reaction between two neutral reactants.

Conclusion

Rate law (3) will come more to its right in kinetic studies to follow if more emphasis is placed on the

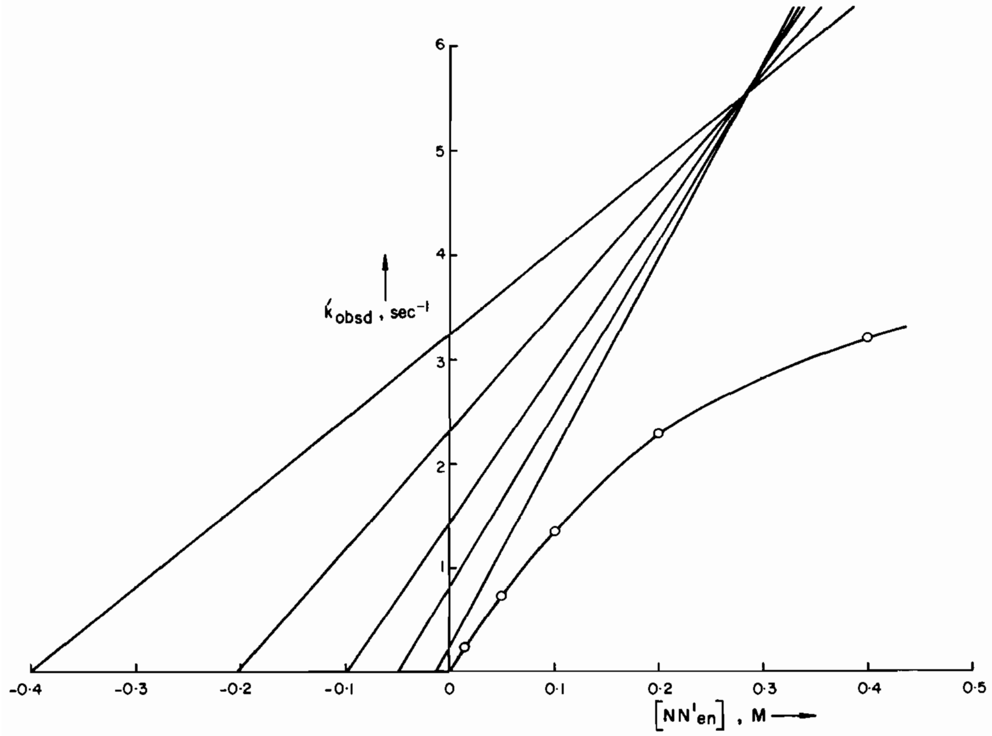

Figure 3. Solvent path for the NN'-en system. t = 25 °C, I = 0.5 *M*, [complex] = 0.05 m*M*, $[Cl^-]$ = 0.2 m*M*.

experimental conditions. These conditions can be met by manipulating reactivities and concentrations such that both terms in the denominator of the solvolytic term of rate law (3) make a significant contribution to the overall rate of reaction.

The reason why the classical two term rate law has featured so prominently in the vast majority of kinetic studies reported is because the concentration of the leaving group was not considered as a possible reaction rate variable. The classical two term rate law emerges merely because the nucleophile scavenges the solvent intermediate rapidly and completely as the nucleophile is usually present in at least a forty fold excess (to assure pseudo first order conditions) to the leaving group with the only source of the latter being the partial solvolysis of the substrate complex. By increasing the concentration of the leaving group systematically a stage must be reached where competiton for the solvent intermediate sets in and the characteristics of rate law (3) should show up. Systems where the leaving group is more reactive than the nucleophile have the best chance of success.

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