Contribution from the National Chemical Research Laboratory, P.O. Box 395, Pretoria, South Africa

Kinetics of the Reactions of Thiourea with Complexes of the Type $Pt(N\text{-}N)(SCN)_2$

R. J. Mureinik and W. Robb

Received November 10, 1970

The kinetics of the reactions $[Pt(N–N)(SCN)_2]+{}^{*}$*-tn*$\rightarrow[Pt(N–N)(SCN)(tu)]^{+}+SCN^{-}$ *have been investigated for N–N = ethylenediamine (en), N,N'–dimethylethylenediamine (N,N'–Me*$_2$*–en), N,N'–diethylenediamine (N,N'–Et*$_2$*–en) and N,N'–diisopropylethylenediamine (N,N'–iPr*$_2$*–en) in DMF. A second reaction* $[Pt(N–N)(SCN)(tu)]^{+}+tu\rightarrow[Pt(N–N)(tu)_2]^{2+}+SCN^{-}$ *occurs, the kinetics of which were determined for N–N = en and N,N'–iPr*$_2$*–en. Activation parameters are reported and discussed in terms of steric effects. Two effects of bulky groups on activation parameters are described and discussed. A novel linkage isomerization leading to an equilibrium mixture of thiocyanato and isothiocyanatoplatinum(II) complexes has been characterised.*

Introduction

Studies of the influence of steric factors on the rates of reaction of platinum(II) complexes have played a major role in elucidating the nature of the mechanism of substitution reactions for these compounds. In such studies the bulky groups have either been incorporated in the Pt^{II} substrate, or have been part of the incoming ligand itself.

When bulky groups were present in the Pt^{II} substrate close to the site of the reaction, the rate of the reaction was generally found to be retarded if compared to similar substrates containing less bulky groups. This was taken as evidence for an associative mechanism. For example, Basolo *et al.*[1] measured reaction rates for the reaction

$$[Pt(PEt_3)_2LCl]+py\rightleftharpoons[Pt(PEt_3)_2Lpy]^{+}+Cl^{-}$$

where L = phenyl, *o*–tolyl, It was found that the rate decreases sharply as the extent of substitution on the phenyl group is systematically increase. Since this effect is dramatically much more effective for *cis* compounds than for *trans*, the incoming ligand is believed to approach the Pt^{II} substrate along a direction perpendicular to the plane of the complex.

Comparisons of rate-laws for the reactions of $[Pt(dien)Cl]^{+}$ and the highly hindered $[Pt(Et_4dien)Cl]^{+}$ show marked differences.[1,2] The former compound obeys the well-characterised two-term rate law[3,4]

$$k_{sbo}=k_S+k_Y[Y]$$

The latter-type compound, however, with a few recently noted exceptions,[5,6] shows no dependence on [Y], and in fact resembles obtahedral complexes in its kinetic behaviour. In all these studies, only rate constants were determined, and no attempt was made to evaluate activation parameters.

The influence of bulky incoming groups on the rates of reaction of Pt^{II} complexes, has formed the subject of a number of publications.[7-13] Cattalini *et al.* have shown that the reactions of $[Pt(Bipy)Cl_2]$ with pyridines depends on the nature of the pyridine. Pyridine with no α substituents react faster than those with one group in the α position, while 2,6–disubstituted pyridines react slowest of all. Chan and Wong[8] studied the reactions of $[Pt(dien)Br]^{+}$ with various pyridines, and found that the rate retardation for hindered pyridines is principally the result of increased activation enthalpies, ΔH^{*}.

This study constitutes one of the few cases where activation parameters were determined as an integral part of a steric effect study.

Recently, activation parameters for the ligand exchange reaction $[Pt(N–N)(SCN)_2]+{}^{*}SCN^{-}\rightleftharpoons[Pt(N–N)(SCN)(SCN^{*})]+SCN^{-}$ where N–N is ethylenediamine or a substituted ethylenediamine have been reported.[14,15] The observed activation parameters for the k_2 path were interpreted in terms of « orientation-effects » imposed on the incoming ligand. Because of the radioactive tracer technique used, the data obtained was not of sufficient accuracy to be able to assess activation parameters for the observed k_1 path.

In this paper the kinetics of the reaction of thiourea with the series of compounds $[Pt(N–N)(SCN)_2]$ is reported. A more accurate experimental technique is used, which enabled data for the k_1 path to be obtained with reasonable accuracy. In addition acti-

---

* tu = thiourea.

(1) F. Basolo, J. Chatt, H.B. Gray, R.G. Pearson, and B.L. Shaw, *J. Chem. Soc.*, 2207 (1961).

(2) H.B. Gray, *J. Am. Chem. Soc.*, *84*, 1548 (1962).

(3) F. Basolo and R.G. Pearson, «Mechanisms of Inorganic Reactions», 2nd Ed., Wiley, N.Y. (1967), Chap. 5.

(4) C.H. Langford and H B. Gray, «Ligand Substitution Processes», Benjamin, N.Y. (1965), Chap. 2.

(5) J.B. Goddard and F. Basolo, *Inorg. Chem.*, 7, 936 (1968).

(6) J.B. Goddard and F. Basolo, *Inorg. Chem.*, 7, 2457 (1968).

(7) L. Cattalini, A Orio, and A. Doni, *Inorg. Chem.*, 5, 1517 (1966).

(8) S.C. Chan and T.W. Wong, *Austr. J. Chem.*, *21*, 2873 (1968).

(9) W.R. Rimm, D.O. Johnston, C.H. Oestreich, D.G. Lambert, and M.M. Jones, *J. Inorg. Nucl. Chem.*, *29*, 2401 (1967).

(10) L. Cattalini, M. Martelli, and G. Kirschner, *Inorg. Chem.*, *7*, 1488 (1968).

(11) L. Cattalini, M. Martelli, and G. Marangoni, *Inorg. Chim. Acta*, *2*, 2405 (1968).

(12) A.L. Odell and H.A. Raethall, *Chem. Comm.*, 1323 (1968).

(13) A.L. Odell and H.A. Raethall, *Chem. Comm.*, 87 (1969).

(14) W. Robb and R.J. Mureinik, *Inorg. Chim. Acta*, 3, 575 (1969).

(15) R.J Mureinik and W. Robb, *Inorg. Chim. Acta*, 3, 580 (1969).

vation parameters for the k_2 path where thiourea is the incoming group, are reported.

Experimental Section

Materials. The complexes were prepared and characterised as discussed elsewhere.[15-17] Ammonium perchlorate and thiourea were analytical grade and were recrystallised and dried to constant weight before use. The complexes $[Pt(N–N)(tu)_2]Cl_2$ were prepared by the method of Derendyaev,[18] and anaysed satisfactorily. The solvent used, N,N'–dimethyl formamide (DMF) was distilled from CaO before use (B. Pt 144-146°). Infrared spectra were determined on a Perkin Elmer 125 IR Spectrophotometer.

Kinetics. The reactions were followed spectrophotometrically using either a Cary 14 or Cary 15 recording spectrophotometer, fitted with thermostatically controlled sample chambers. Complex and ligand solutions were equilibrated separated at the temperature of teh reaction and mixed in proportions to give the desired concentrations of complex and ligand. The ratio [tu]:[complex] was always such as to ensure pseudofirst order knetics. Ionic strength was maintained constant at $\mu = 0.6$ with ammonium perchlorate. Rate constants were obtained from graphs of log (D_∞–D) against time.

Results

For all the four complexes studied, complete spectral traces were recorded as a function of time, during the reaction. All the complexes show the initial development of well-defined isosbestic points, which gradually disappeared with time. This was interpreted as evidence that two reactions were occurring *viz.,*

$$[Pt(N\text{-}N)(SCN)_2] + tu \rightarrow [Pt(N\text{-}N)(SCN)(tu)]^+ + SCN^-$$

$$[Pt(N\text{-}N)(SCN)(tu)] + tu \rightarrow [Pt(N\text{-}N)(tu)_2]^{2+} + SCN$$

with the second reaction much slower than the first. The isosbestic point corresponds to the two species $[Pt(N–N)(SCN)_2]$ and $[Pt(N–N)(SCN)(tu)]^+$ and its disappearance reflects production of the $[Pt(N–N)(tu)_2]^{2+}$ ion. This phenomenon has been previously documented[19,20] and is probably related to the charge on the substrate. The spectrum after completion of the reaction is identical to that of $[Pt(N–N)(tu_2]^{2+}$ prepared independently.

Kinetic studies are hampered by the fact that large spectral changes occur in regions that are masked by absorption due to thiourea. Best use of the small optical density changes that occur was made by conducting kinetic runs five times for each concentration of ligand, and determining best k_{obs} *vs.* [tu] straight lines by the method of least-squares from a minimum of 20-25 experimental points. This method was edopted for the complexes of en and N,N'–iPr₂–en as well even though fairly large optical density differences are observed for these two compounds.

For the complexes of N'–Me₂–en and N,N'–Et₂–en, traces of optical density with time at a wave-length chosen to give maximum optical density changes, show an increase to a peak value, followed by a fall in optical density to a value intermediate to the starting value and the peak value. This was interpreted as due to the reactions mentioned above. The change in optical density from the peak value to the final value is too small to use for kinetic measurements, but rough calculations show that it is complete in times very much longer (often by a factor of 20 or more) than the time taken for the change from the initial value of the optical density to the « peak » value. This was taken as justification for the assumption that the second reaction was sufficiently slower than the first for the « peak » value to be used as « D_∞ » for the first reaction. Plots of log (« D_∞ »–Dt) against time are linear, and were used to obtain values of k_{obs}.

For the reactions of the en and N,N'–iPr₂–en complexes, the optical density decreases monotically and plots of log (D_t–D_∞) gainst time are curved in the early stages of reaction. Use of « stripping » technique[21] enabled kinetic data for both reactions to be obtained, and it was found that for these two compounds, rate constants for the second reaction were smaller than those for the first by a factor of at least 10. This was taken as further justification for the assumption made above regarding the second reaction of the N,N'–Me₂–en and N,N'–Et₂–en compounds.

Kinetic data for the two reactions of the en and

Table I. Kinetic data for the reaction of thiourea with $[Pt(en)(SCN)_2]$ (a) first reaction:
$[Pt(en)(SCN)_2] + tu \rightarrow [Pt(en)(tu)(SCN)]^+ + SCN^-$
$[Pt(en)(SCN)_2] = 0.002\ M$
$\mu = 0.6$ $\lambda = 350\ m\mu$

[tu] (*M*)	35.0°C	10^4k_{obs} (sec^{-1}) 42.0°C	47.0°C
0.05	2.21	3.43	4.19
0.10	3.99	4.59	7.00
0.15	5.06	6.77	9.89
0.20	5.91	8.77	10.58
0.25	7.97	10.70	12.73

Table II. Kinetic data for the reaction of thiourea with $[Pt(en)(SCN)_2]$ (b) second reaction:
$[Pt(en)(tu)(SCN)]^+ + tu \rightarrow [Pt(en)(tu)_2]^{2+} + SCN^-$
$[Pt(en)(SCN)_2] = 0.002\ M$
$\mu = 0.6$ $\lambda = 350\ m\mu$

[tu] (*M*)	35.0°C	10^6k_{obs} (sec^{-1}) 42.0°C	47.0°C
0.05	2.35	3.09	3.99
0.10	4.06		5.69
0.15	5.56	6.68	
0.20	6.85	8.54	10.28
0.25	7.43	9.97	12.97

---

(16) R.J. Mureinik and W. Robb, *Spectrochim. Acta, 24A,* 837 (1968).
(17) R.J. Mureinik and W. Robb, *Spectrochim. Acta, 26A,* 811 (1970).
(18) S.P. Derendyaev, *Russ. J. Inorg. Chem., 9,* 733 (1964).
(19) F. Basolo, W H. Baddely, and J.L. Burmeister, *Inorg. Chem., 3,* 1202 (1964).
(20) A. Sabatini and I. Bertini, *Inorg. Chem., 4,* 1665 (1965); 5, 1025 (1966).
(21) G. Friedlander, J.W. Kennedy, and J.M. Miller, «Nuclear and Radiochemistry», 2nd Ed., Wiley, N.Y. (1964).

N,N′–iPr₂–en complexes and for the first reactions of the N,N′–Me₂–en and N,N′–Et₂–en complexes are listed in Tables I-VIII and the activation parameters are listed in Tables IX and X. For comparison activation parameters for the exchange reaction $[Pt(N\text{–})(SCN)_2] + {}^*SCN^- \rightleftharpoons [Pt(N\text{–}N)(SCN)(SCN^*)] + SCN^-$ are listed in Table XI.

TableI II. Kinetic data for the reaction of thiourea with $[Pt(N,N'\text{–}Me_2\text{–}en)(SCN)_2]$:
$[Pt(N,N'\text{–}Me_2\text{–}en)(SCN)_2] + tu \rightarrow [Pt(N,N'\text{–}Me_2\text{–}en)(tu)(SCN)]^+ + SCN^-$
$[Pt(N,N'\text{–}Me_2\text{–}en)(SCN)_2] = 0.001$ *M*;
$\mu = 0.6$; $\lambda = 346$ mμ

[tu]		10^3k_{obs} (sec^{-1})	
(*M*)	20.3°C	29.8°C	34.8°C
0.05	1.16	2.20	2.94
0.10	2.01	4.54	6.30
0.15	3.00	6.40	8.57
0.20	4.10	9.46	
0.25	5.05	11.19	12.90

Table IV. Kinetic data for the reaction of thiourea with $[Pt(N,N'\text{–}Et_2\text{–}en)(SCN)_2]$:
$[Pt(N,N'\text{–}Et_2\text{–}en)((SCN)_2] + tu \rightarrow [Pt(N,N'\text{–}Et_2\text{–}en)(tu)(SCN)]^+ + SCN^-$
$[Pt(N,N'\text{–}Et_2\text{–}en)(SCN)_2] = 0.002$ *M*;
$\mu = 0.6$; $\lambda =$ mμ

[tu]		10^3k_{obs} (sec^{-1})	
	19.2°C	24.9°C	29.9°C
0.05	0.63	1.35	1.54
0.10	1.36	2.57	4.04
0.15	1.88	2.96	3.53
0.20	2.43	3.53	4.77
0.25		4.65	5.65

Table V. Kinetic data for the reaction of thiourea with $[Pt(N,N'\text{–}iPr_2\text{–}en)(SCN)_2]$ (a) first reaction:
$[Pt(N,N'\text{–}iPr_2\text{–}en)(SCN)_2] + tu \rightarrow [Pt(N,N'\text{–}iPr_2\text{–}en)(tu)(SCN)]^+ + SCN^-$
$[Pt(N,N'\text{–}iPr_2\text{–}en)(SCN)_2] = 0.002$ *M*;
$\mu = 0.06$; $\lambda = 345$ mμ

[tu]		10^4k_{obs} (sec^{-1})	
(*M*)	35.2°C	40.6°C	45.8°C
0.05	6.10	7.67	12.03
0.10	9.05	12.42	15.83
0.15	12.66	16.99	
0.20	15.02		26.80
0.25	18.83	23.60	

Table IV. Kinetic data for the reaction of thiourea with $[Pt(N,N'\text{–}iPr_2\text{–}en)(SCN)_2]$ (b) second reaction:
$[Pt(N,N'\text{–}iPr_2\text{–}en)(tu)(SCN)]^+ + tu \rightarrow [Pt(N,N'\text{–}iPr_2\text{–}en)(tu)_2]^{2+} + SCN^-$
$[Pt(N,N'\text{–}iPr_2\text{–}en)(SCN)_2] = 0.002$ *M*;
$\mu = 0.6$; $\lambda = 345$ mμ

[tu]		10^6k_{obs} (sec^{-1})	
	35.2°C	40.6°C	45.8°C
0.05	2.49	3.25	5.92
0.10	5.87	9.21	13.25
0.15	7.63	17.17	22.60
0.20	13.98		33.34
0.25		31.26	45.02

Table VII. Rate constants for the reaction:
$[Pt(N\text{–}N)(SCN)_2] + tu \rightarrow (Pt(N\text{–}N)(tu)(SCN)]^+ + SCN^-$

(N–N)	Temp (°C)	10^4k_S (sec^{-1})	10^4k_Y (M^{-1}sec^{-1})
en	35.0	0.90	28.70
	42.0	1.36	36.59
	47.0	2.34	39.40
N,N′–Me₂–en	20.3	1.02	197.69
	29.8	6.07	401.74
	34.8	10.23	474.89
N,N′–Et₂–en	19.2	1.02	118.2
	24.9	5.40	160.3
	29.9	9.64	189.6
N,N′–iPr₂–en	35.2	2.92	62.87
	40.6	4.04	81.98
	45.8	6.62	98.96

Table VIII. Rate constants for the reaction:
$[Pt(N\text{–}N)(tu)(SCN)^+ + tu \rightarrow [Pt(N\text{–}N)(tu)_2]^{2+} + SCN^-$

(N–N)	Temp (°C)	10^5k_S (sec^{-1})	10^5k_Y (M^{-1}sec^{-1})
en	35.0	1.34	25.74
	42.0	1.42	34.80
	47.0	1.49	45.03
N,N′–iPr₂–en	35.2		7.25
	40.6		14.18
	45.8		19.54

Table IX. Activation parameters for the reaction:
$[Pt(N\text{–}N)(SCN)_2] + tu \rightarrow [Pt(N\text{–}N)(tu)(SCN)]^+ + SCN^-$

	k_S path		k_Y path	
(N–N)	Δ_Y^* (Kcal/mole^{-1})	ΔH_S^* (e.u.)	ΔH_S^* (Kcal/mole^{-1})	Δ_Y^* (e.u.)
en	14.1	–31	5.6	–52
N,N′–Me₂–en	27.9	19	10.8	–29
N,N′–Et₂–en	36.2	47	6.9	–44
N,N′–iPr₂–en	13.4	–31	7.1	–49
estimated errors	±1.5	±2	±1	±1.5

Table X. Activation parameters for the reaction:
$[Pt(N\text{–}N)(tu)(SCN)]^+ + tu \rightarrow [Pt(N\text{–}N)(tu)_2]^{2+} + SCN^-$

	k_S path		k_Y path	
(N–N)	ΔH_S^* (Kcal/mole^{-1})	ΔH_S^* (e.u.)	ΔH_Y^* (Kcal/mole^{-1})	ΔH_Y^* (e.u.)
en	unreliable values obtained		8.2	–49
N,N′–iPr₂–en			16.6	–23
estimated errors			±1.5	±3

Table XI. Activation parameters for the reaction:
$[Pt(N\text{–}N)(SCN)]_2 + S^*CN^- \quad [Pt(N\text{–}N)(SCN)(S^*CN)] + SCN^-$

	k_S path		k_Y path	
(N–N)	ΔH_S^* (Kcal/mole^{-1})	ΔH_S^* (e.u.)	ΔH_Y^* (Kcal/mole^{-1})	ΔH_Y^* (e.u.)
en	10.6	–50	23.4	–2
N.N′–Me₂–en			16.8	–16
N,N′–Et₂–en			20.1	–6
N,N′–iPr₂–en			16.5	–19
pn	8.0	–55	23.4	–3
stien	20.0	–16	14.0	–30
estimated error	±1.5	±2	±1.5	±2

Discussion

Although the reactions were not all studied at the same temperature, the reactivity order of the various complexes appears to be N,N'–Me_2–> N,N'–Et_2–en> N,N'–iPr_2–en> en for the substitution of the first thiocyanate group in the series [Pt(N–N)$(SCN)_2$] *via* the k_2 path. This is the same order as was observed for the exchange reactions of the series of complexes with labelled thiocyanate.[15] Once again the dangers in drawing mechanistic conclusions from rate data for a single temperature should be pointed out. Decrease in rate of reaction with increased steric hindrance has been taken as evidence for an associative mechanism, while increase in rate for highly hindered compounds has been used as a diagnostic test for dissociative mechanism.[4]

Comparison of the rates of reaction with thiourea for [Pt(en)$(SCN)_2$] and [Pt(N,N'–Me_2–en)$(SCN)_2$] would therefore lead to the conclusion that a dissociative mechanism is operative. The impasse is removed by recalling the fact that slopes of graphs of log k against 1/T contain the activation energy of the reaction. Where these differ considerably between reactions, the graphs of log k against 1/T can cross, and comparison of relative reactivities is reduced to the rather fortuitous choice of working temperature. In such cases the only comparisons that may be validly drawn are between the activation parameters of the various reactions.

Generally it was found that k_Y for the reaction with thiourea were much larger than the corresponding value with thiocyanate as the incoming group. This is in accordance with the values of their relative nucleophilic reactivity constants, n_{Pt}° values (tu: 7.17; SCN^-: 6.65).[22] However ΔH_Y^* and ΔS_Y^* do not obey the same trends for Y = tu, as was observed for Y = SCN^-. In addition, with the exception of the N,N'–iPr_2–en compound whose value appears to be anomalous, activation parameters for the k_1 path show trends opposite to those expected on the basis of the exchange reaction study. The values of k_1 for the N.N'–iPr_2–en complex are unexpectedly different from the rest and in view of this, and its anomalous activation parameters, it seemed possible that the observed k_1 was not a single rate constant, but actually a composite value containing more than one term.

In view of the fact that sterically hindered thiocyanato complexes of Pt^{II} have been shown to prefer the Pt–N bonding mode to the Pt–S form,[19,23] the possibility of linkage isomerisation was investigated. In the starting product [Pt(N,N'–iPr_2–en)$(SCN)_2$], the thiocyanato groups are bound through sulphur, as determined by the infrared spectrum[16,20] ($\nu_{CN} = 2130$ cm^{-1}). After recovery from a solution maintained at 48° for 48 hr in addition to the ν_{CN} peak of the S–bonded species, a small peak of position and shape characteristic of the N–bonded species appears at 2077 cm^{-1}. This peak is weak, and does not increases in intensity if kept at 48° for 72 hr. Extent of conversion is estimated at 5-7%. The isomerisation was not detected for the exchange reaction due to the fact that a much higher concentration of complex (0.01 *M* as opposed to 0.001 *M*) was used, and hence equilibrium is reached in much less than 48 hr. The fact that no increase in intensity of the infrared band due to the N–bonded species is observed, implies that an equilibrium is established with its position well over to the S–bonded species. This represents the first reported case where an equilibrium mixture of the two species is recovered from solution.

For the N,N'–iPr_2–en complex the full mechanism therefore is as follows

$$\begin{tikzcd}
{[Pt(N,N'\!-\!iPr_2\!-\!en)(SCN)_2]} \arrow[r, "tu", "k_{Y_1}"'] \arrow[d, shift left] \arrow[d, leftarrow, shift right, "K_{isom}"'] \arrow[dr, "k_S"] & {[Pt(N\!-\!N)(tu)(SCN)]^+} \arrow[r, "tu", "k_{Y_2}"'] & {[Pt(N\!-\!N)(tu)_2]^{2+}} \\
{[Pt(N\!-\!N)(SCN)(NCS)]} & {[Pt(N\!-\!N)(tu)(SCN)]^+} &
\end{tikzcd}$$

The kinetics of isomerisation of an S–bonded palladium(II) thiocyanato complex to its N–bonded isomer, $[Pt(Et_4die)(SCN)]^+ \rightarrow [Pt(Et_4dien)(NCS)]^+$, have been reported.[24]

The reaction is zero order in any ligand and appears to go *via* a solvent-assisted intermolecular interchange process. If a similar mechanism applies here, then the observed term zero order in thiourea will contain terms from the forward and reverse isomerisation reactions as well as the usual k_S term. The isomerisation is too slow and the equilibrium too far to one side to be conveniently studied, and so k_S for the reaction of thiourea with [Pt((N,N'–iPr_2–en)-$(SCN)_2$] cannot be obtained. The values of ΔH_S^* and ΔS_S^* do not therefore apply to the solvent path and in the following discussion are not referred to further.

For the other three complexes, ΔH_S^* and ΔS_S^* both increase through the series en <N,N'–Me_2–en<N,N'–Et_2–en. This is the opposite trend to that observed in the k_Y path for Y = SCN^-.

It appears that increasing steric hindrance makes it more difficult for the incoming solvent molecule to approach the complex and activate it, and the value of the activation enthalpy thus increases. The activation entropy also becomes more positive with increased steric hindrance, perhaps due to the fact that the reacting species cannot approach each other closely enough for the « orientation-effect » that obtains where Y = SCN^-, to apply. The degree of association of the solvent molecule with the substrate in the transition state probably also decreases.

Thus there appears to be two possible ways in which steric hindrance may affect the activation parameters.

Effect A. The incoming group is subjected to orientation effects and can only approach the substrate along certain directions. The value of ΔS^* tends to be highly negative, while ΔH^* correspondingly is low since activation is easily attainable with an incoming group, that having been preorientated, is in a suitable position for reaction.

Effect B. With increasing steric hindrance, the incoming group experiences increasing difficulty in ap-

---

[22] U. Belluco, L. Cattalini, F. Basolo, R G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, *87*, 241 (1965).

[23] J.L. Burmeister, *Coord. Chem. Rev.*, *1*, 205 (1966).

[24] F. Basolo, W.H. Baddley, and K.J. Weidenbaum, *J. Am. Chem Soc.*, *88*, 1576 (1966).

proaching the reactive site of the substrate. Values of ΔH^* rise because increased steric repulsion oppose formation of the transition state. ΔS^* tends to increase as a result of the lower degree of orientation in the transition state, and as a result of a smaller degree of association in the transition state which can be ascribed to the « setting free » of solvent molecules to attain the transition state.

The small incoming groups, where despite steric hindrance, the group can reach the complex and activate it, effect A predominates. Where the incoming group is itself large, so that appreciable steric repulsions are experienced well before the incoming group reaches the site of reaction, effect B predominates.

For $Y = SCN^-$, effect A can be expected to predominate. The ligand is small, and activation can easily occur without serious perturbations of the substrate. This is confirmed by experiments with molecular models.

In the solvent path, DMF, a large molecule is the incoming group. Tests with molecular models show that serious steric interactions occur at a distance considerably greater than the probably approximate bonding distance, as the DMF molecule approaches the complex. Effect B can therefore be expected to predominate.

For $Y = tu$, the incoming group has steric requirements intermediate between those of « small » SCN^- and « large » DMF. Intermediate behaviour may therefore be expected. Comparison of ΔS_Y^* and ΔH_Y^* values for the en and N,N'–Me_2– complexes show that a type B effect appears to operate. ΔH^* for the N,N'–Et_2–en and N,N'–iPr_2–en complexes are approximately equal and less than for the N,N'–Me_2–en compound. Either orientation effects are of importance or more likely, as far as the incoming group is concerned, less bulk is « seen » due to the CH_3 groups of ethyl and isopropyl being removed a C–C bond length distant. The bulkiness encountered by the incoming tu group is thus actually less for the longer chain alkyls than for methyl. The amino group of tu may be subject to orientation effects as well, although this is not clear from the molecular models. For the N,N'–iPr_2–en compound ΔS_Y^* is less than for the N,N'–Et_2–en compound, and this may suggest that orientation effects play a role.

For the second reaction

$$[Pt(N{-}N)(SCN)(tu)]^+ + tu \rightarrow [Pt(N{-}N)(tu)_2]^{2+} + SCN^-$$

the substrate is slightly more bulky than the original $[Pt(N{-}N)(SCN)_2]$ compound. It is perhaps significant that a type B–effect appears to operate here, as would be expected.

Of interest is the fact that for all cases ΔS_Y^* is more negative for $Y = tu$ than for $Y = SCN^-$. Thiourea is biphilic and for substrates containing ligands that do not delocalise charge from the central metal atom, the electrophilic nature of thiourea can be expected to be important. This must impose a certain orientation on the tu incoming group as compared to SCN^-, since it must approach the complex in such a way that its π^* system associated with $>C=S$ linkage can overlap with a fill d_π orbital. Basolo *et al.*[25] have reported that if « stringent stereochemical requirements exist in the transition state, then its formation is accompanied by a decrease in entropy ». Cattalini *et al.*[26] have similarly observed that for the reaction of gold(III) with biphilic NO_2^-, ΔS^* is more negative than for reactions with anions that do not show electrophilic character.

Nicolini *et al.*[27] have recently published kinetic data on the reaction of *trans*–$[Pt(SeEt_2)_2I_2]$ in methanol with pyridine, piperidine and 3,4-dimethylpyridine. At 20°, the reaction with 3,4-dimethylpyridine is faster than that with piperidine, but at 40° this reactivity order is reversed. Activation parameters are given for the reactions with piperidine ($\Delta H_Y^* = 7.5$ Kcal/mole^{-1}; $\Delta S_Y^* = -6.5$ e.u.) and for 3,4-dimethylpyridine ($\Delta_Y^* = 9.5$ Pcal/mole^{-1}; $\Delta S_Y^* = -32$ e.u.). The lower reactivity of piperidine relative to 3,4-dimethylpyridine is described as being due to a much higher ΔH^*. Activation parameters are not given for the pyridine reaction, but may be calculated from the rate data given. It transpires that for the reaction with pyridine, which is the fastest of the three, at all temperatures quoted, ΔH_Y^* is the highest of all three ($\Delta H_Y^* = 24$ Kcal/mole^{1-}; $\Delta S_Y^* = +23.8$ e.u.). These rather anomalous results provide an opportunity of applying the ideas suggested in this paper to previously published data.

In the transition state for the reactions of amines with *trans*–$[Pt(SeEt_2)_2I_2]$, the two seleno-ether groups occupy the apical positions of the trigonal bipyramid, with the amine and two iodide groups in the trigonal plane. The four large extended ethyl groups which have considerable steric requirements are *cis* to the leaving group and can be expected to interact with bulky incoming groups. Molecular models of the trigonal bipyramidal intermediate show that for *this* reaction a « steric requirement » order can be assigned py < pip < 3,4–Me_2py. With the latter compound, the intermediate can only be comfortably formed if the amine approaches with its plane parallel to the plane of the incipient trigonal bipyramid. Deviation from this plane by a few degrees produces marked steric interference between the 3–methyl group and the ethyl groups. Less stringent orientation is required of the piperidine molecule and even less of the pyridine group.

This thus constitutes a case where a type-A effect applies to the incoming group, and all the activation features of an A effect are observed.

(25) F. Basolo and W.H. Baddley. *Inorg. Chem.*, 3, 1087 (1964).

(26) L. Cattalini, A. Orio, and M. Tobe, *J.. Am. Chem. Soc.*, *89*, 3130 (1967).

(27) M. Nicolini. M. Giustiniani, and A. Palazzi, *J. Inorg. Nucl Chem.*, *31*, 2899 (1969).