3728 *Inorg. Chem.* **1981**, *20*, 3728-3730

Contribution from the Istituto di Chimica Generale ed Inorganica, University of Venice, 30100 Venice, Italy,
and the William Ramsay and Ralph Forster Laboratories, University College London, London, England

Cis Effect of Dimethyl Sulfide and Leaving Group Effect in Reactions of the Cationic Complex Chloro(dimethyl sulfide)(1,2-diaminoethane)platinum(II) Chloride

MASSIMILIANO BONIVENTO,[1] LUCIANO CANOVESE,[1] LUCIO CATTALINI,*[1] GIAMPAOLO MARANGONI,[1]
GIANNI MICHELON,[1] and MARTIN L. TOBE[2]

Received February 2, 1981

The kinetics of the replacement of X from $[Pt(dms)(en)X]^{n+}$ (dms = dimethyl sulfide; en = 1,2-diaminoethane; X = Cl or I ($n = 1$) or H_2O, ($n = 2$)) by a variety of nucleophiles (Br^-, I^-, N_3^-, SCN^-, SO_3^{2-}, NH_3, $SC(NH_2)_2$, H_2O) have been studied in water at 25.0 °C. Good linear relationships have been observed between log $k_2°$ for the 1+ cationic substrates ($k_2°$ is the second-order rate constant at $\mu = 0$) and the index of nucleophilicity, n^+_{Pt}, relative to the standard 1+ cationic substrate $[Pt(NH_3)(en)Cl]^+$. The data obtained have been used, together with data taken from the literature, in order to discuss the kinetic cis effect of dms as compared to that of Me_2SO (Me_2SO dimethyl sulfoxide) and NH_3 and also to discuss the leaving group effect. The data relative to the displacement of water from the aquo complex $[Pt(dms)(en)H_2O]^{2+}$ have been compared with those relative to other bis-cationic aquo species.

Introduction

The understanding of the way in which the nature of the "nonparticipating" ligands affect the reactivity of 4-coordinate planar complexes has been a matter of considerable interest even since the first studies of the kinetics of the reactions of such complexes.[3] It is well established that the reactivity is particularly sensitive to the nature of the ligand trans to the leaving group and that, apart from steric effects, the dependence of reactivity on the nature of the cis ligand is considerably less and much more subtle.

As part of a program comparing the trans and cis effects of a number of uncharged ligands with group 5 and group 6 donors, we have examined the reactions of $[PtLCl_3]^-$ [4,5] and $[Pt(en)LCl]^+$ (en = 1,2-diaminoethane)[6] as representative substrates to measure the trans effect and the cis effect of L, respectively. This paper reports the kinetics of the reactions $[Pt(dms)(en)X]^+ + Y^{n-} \rightarrow [Pt(dms)(en)Y]^{(2-n)+} + X^-$ (X = Cl, I; dms = dimethyl sulfide; Y = H_2O, Br^-, N_3^-, I^-, SCN^-, NH_3, $SC(NH_2)_2$, SO_3^{2-}) together with some data for the displacement of H_2O from the corresponding dicationic $[Pt(dms)(en)H_2O]^{2+}$ species.

Experimental Section

Materials. [Pt(dms)(en)Cl]Cl was prepared by mixing equimolar amounts of *trans*-$[Pt(dms)_2Cl_2]$ and 1,2-diaminoethane in methanolic solution at about 30 °C. The mixture was allowed to stand overnight and the solution evaporated to small volume under vacuum. Addition of diethyl ether precipitated the required material as white crystals which were filtered off, washed with ether, and dried in vacuo for 2 h. Anal. Calcd for $C_4H_{14}N_2Cl_2SPt$: C, 12.38; H, 3.63; N, 7.22; Cl, 18.26; S, 8.26. Found: C, 12.43; H, 3.58; N, 7.38; Cl, 18.07; S, 8.34.

$[Pt(dms)(en)I]^+$ used for the kinetics was prepared in solution by adding an equimolar amount of NaI to an aqueous solution of [Pt(dms)(en)Cl]Cl and allowing the reaction to reach equilibrium. The spectrum of this solution is virtually identical with that observed at the end of the reaction with a considerable excess of iodine ions, indicating that, even with equimolar amounts of reagents, the equilibrium is well in favor of the iodo species. The iodo cation could be precipitated as both the insoluble tetraphenylborate (unsuitable for kinetics because of its insolubility) and the perchlorate by adding $NaB(C_6H_5)_4$ or $NaClO_4$, respectively, to equilibrated equimolar solutions. Anal. Calcd for $C_4H_{14}N_2ClIO_4SPt$: C, 8.84; H, 2.60; N, 5.15; S, 5.89. Found: C, 8.55; H, 2.55; N, 5.02, S, 5.95. Calcd for $C_{28}H_{34}N_2BISPt$: C, 44.05; H, 4.49; N, 3.67; S, 4.20. Found: C, 44.15; H, 4.50; N, 3.75; S, 4.28.

A stock solution of $[Pt(dms)(en)H_2O]^{2+}$ was prepared by dissolving [Pt(dms)(en)Cl]Cl (77.6 mg, 0.20 mmol) in water (60 cm^3) and adding silver perchlorate (81 mg, 0.39 mmol) and shaking the mixture for 2 days at room temperature in the absence of light. The solution was filtered twice, dilute perchloric acid was added to bring the pH to 4, and the volume was adjusted to 100 cm^3 by the addition of water.

Reagent grade $LiClO_4$, NaOH, NaBr, NaCl, NaI, NaSCN, Na_2SO_3, and $SC(NH_2)_2$ were dried over P_2O_5 in vacuo and used without further purification. AR ammonia solutions were diluted with water and standardized potentiometrically against HCl.

Kinetics. All the reactions with half-lives greater than 10 s were followed spectrophotometrically with use of either a Perkin-Elmer Coleman 575 or a Cary 17D spectrophotometer. The reactions were initiated by mixing equal volumes of a solution of the complex and one of the other reagents previously brought to the reaction temperature, in the spectrophotometer cell. Preliminary experiments indicate that all the involved species closely follow Beer's law. Once the best experimental conditions were determined, the kinetic runs were carried out at a single wavelength. For half-lives shorter than 10 s the reactions were followed with a Durrum D 110 stopped-flow spectrophotometer equipped with a Gould 05-4100 digital storage oscilloscope and a Radiometer REC 61 potentiometric recorder. In all the cases the entering nucleophile was present in concentrations at least 10 times greater than that of the complex in order to ensure pseudo-first-order conditions. Generally, interference from subsequent stages was not serious or could be minimized by a suitable choice of wavelength, and an experimental value for A_∞ taken after 10 half-lives of the reaction could be used. Where this was not possible the standard Guggenheim treatment, with Δt between 2 and 3 half-lives, was used. The reactions with SO_3^{2-} and N_3^- were carried out in the presence of sufficient hydroxide to prevent any significant protonation of the nucleophile, having previously demonstrated that hydroxide does not affect the rate of the reaction. The presence of chloride ion in concentration double that of the cationic iodo species does not give rise to any significant competition under the conditions used.

Results and Discussion

All of the reactions studied were characterized by spectral changes typical of a one stage process with well-defined isosbestic points in many cases. The spectral changes observed for the chloro complex closely resemble those found in the corresponding reaction of $[Pt(Me_2SO)(en)Cl]^+$ [6] (Me_2SO = dimethyl sulfoxide) and, where tested (i.e., for Y = I^-), the final spectrum agreed with that of an independently prepared and characterized sample of $[Pt(dms)(en)I]^+$. The arguments put forward to justify the nature of the reactions of the $[Pt(en)(L)Cl]^+$ complexes apply equally to the reactions reported here, which therefore correspond to $[Pt(dms)(en)X]^+ + Y^{n-}$

---

[1] University of Venice.

[2] University College London.

[3] (a) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967. (b) Cattalini, L. "Inorganic Reaction Mechanisms"; Wiley: New York, 1970. (c) Cattalini, L. *MTP Int. Rev.: Inorg. Chem., Ser. One* 9, 290, 1972.

[4] Romeo, R.; Tobe, M. L. *Inorg. Chem.* **1974**, *13*, 1991.

[5] Kennedy, B. P.; Gosling, R.; Tobe, M. L. *Inorg. Chem.* **1977**, *16*, 1744.

[6] Bonivento, M.; Cattalini, L.; Marangoni, G.; Michelon, G.; Schwab, A. P.; Tobe, M. L. *Inorg. Chem.* **1980**, *19*, 1743.

0020-1669/81/1320-3728$01.25/0 © 1981 American Chemical Society

Table I. Rate Constants for the Reaction $[Pt(dms)(en)X]^+ + Y^{n-} \rightarrow [Pt(dms)(en)Y]^{(2-n)+} + X^-$ [a]

X	Y	10^3k_2, M^{-1} s^{-1}	$10^3k_2°$, M^{-1} s^{-1}	log $k_2°$	log $k_2°$ for $[Pt(NH_3)(en)Cl]^{\bullet}$ [c]
Cl	H_2O	0.001 05 [b]	0.001 05	−5.978	−6.05
	NH_3	2.2 ± 0.3	2.2	−2.657	−3.022
	Br^-	6.07 ± 0.08 [d]	12.5	−1.903	−2.638
	N_3^-	4.4 ± 0.3 [e]	10.2	−1.991	−2.569
	I^-	304 ± 20 [f]	535	−0.272	−1.114
	SCN^-	462 ± 40 [g]	954	−0.020	−0.886
	$SC(NH_2)_2$	1135 ± 135	1135	0.055	−0.735
	SO_3^{2-}	590 ± 40 [h]	1823	0.261	−0.511
I	H_2O	0.001 26 [b]	0.001 26	−5.899	−6.05
	Br^-	14.8 ± 0.6 [i]	39.2	−1.406	−2.638
	SCN^-	2523 ± 400 [j]	5520	0.742	−0.886
	$SC(NH_2)_2$	9690 ± 2900	9690	0.986	−0.735

[a] In water at 25 °C. [b] $k_1/55.5$. [c] From ref 6. [d] $\mu = 0.20$ ($LiClO_4$). [e] $\mu = 0.30$ ($LiClO_4$). [f] $\mu = 0.10$ ($LiClO_4$). [g] $\mu = 0.20$ (NaOH). [h] $\mu = 0.10$ (NaOH). [i] $\mu = 0.50$ ($LiClO_4$). [j] $\mu = 0.25$ (NaOH).

Table II. Rate Constants for the Reaction $[Pt(dms)(en)H_2O]^{2+} + Y^{n-} \rightarrow [Pt(dms)(en)Y]^{(2-n)+} + H_2O$ [a]

Y	k_2, M^{-1} s^{-1}	$k_2°$, M^{-1} s^{-1}	log $k_2°$	log $k_2°$ $[Pt(dien)H_2O]^{2+}$ [b]	$k_2°$, M^{-1} s^{-1} $[Pt(dien)H_2O]^{2+}$ [c]
Cl^- [d]	1.18 ± 0.2	3.65	0.562	0.29	1.44
Br^- [d]	8.64 ± 1.5	26.7	1.427	1.16	10.7
Br^- [e]	9.12 ± 2.4	28.2	1.450	1.16	10.7
$SC(NH_2)_2$ [e]	56.3 ± 10	56.3	1.750	1.61	30.7
SCN^- [e]	76.7 ± 9	237	2.375	2.23	125
I^- [e]	219 ± 15	677	2.830	2.40	185

[a] In water at 25.0 °C, $\mu = 0.1$ ($NaClO_4$), pH 4 ($HClO_4$). [b] Data from ref 12 at 30.0 °C in water. [c] Extrapolated to 25 °C with use of $\Delta H^{\ddagger} = 10$ kcal/mol.[12] [d] Data obtained with the usual spectrophotometric technique. [e] Data obtained with the stopped-flow technique.

$\rightarrow [Pt(dms)(en)Y]^{(2-n)+} + X^-$ (X = Cl, I).

The plots of ln $(A_t - A_\infty)$ against time (A_t and A_∞ being the absorbances at a suitable wavelength at times t and at the end of the reaction) were linear, and the first-order rate constants, k_{obsd}, were the slopes of these lines. Plots of k_{obsd} against $[Y^-]$ were linear, and the values of the slopes k_2, obtained by a linear least-squares regression, are collected in Table I. The contribution from the nucleophile independent (k_1) term was generally small under the experimental conditions used to determine k_2 so that the error in determining the intercept (k_1) in this analysis was too large to give reliable values. The value of k_1 was therefore determined by the now well-established method of displacing X in the presence of OH^-. The rate constant obtained is independent of $[OH^-]$, indicating, as expected, that deprotonation of 1,2-diaminoethane does not occur to any significant extent under the experimental conditions used. Since the substrate was charged, it was necessary to make correction for primary salt effects when the entering nucleophile was also charged. Kinetics were generally carried out at constant ionic strength, and since the data for the standard reaction have been transferred to $\mu = 0$, the second-order rate constants have been extrapolated to zero ionic strength by using the standard relationship $\log k_2 = \log k_2° + 1.02 z_a z_b \mu^{1/2}(1 + \mu^{1/2})^{-1}$, where z_a and z_b are the charges on the substrate and nucleophile, respectively. The values for $k_2°$ and log $k_2°$ are also collected in Table I.

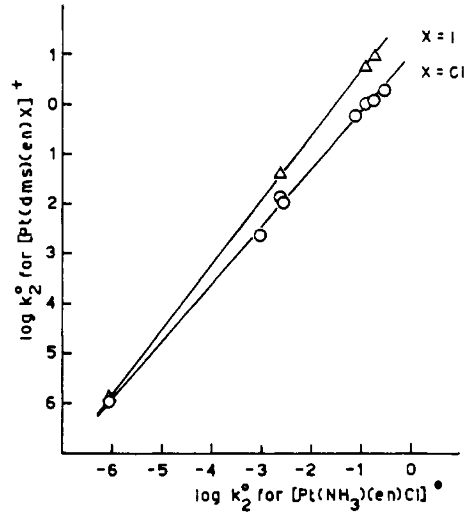

Figure 1. log $k_2°$ for $[Pt(dms)(en)X]^+ + Y^{n-} \rightarrow [Pt(dms)(en)Y]^{(2-n)+} + X^-$ (X = Cl (○), X = I (△)) in water at 25 °C plotted against log $k_2°$ for the analogous reactions of the standard $[Pt(NH_3)(en)Cl]^+$.

In all cases, for a particular nucleophile, the reactivity of the $[Pt(dms)(en)Cl]^+$ complex lies between that of the standard substrate, $[Pt(NH_3)(en)Cl]^+$, and that of $[Pt(Me_2SO)(en)Cl]^{+6}$, and plots of log $k_2°$ for the reactions of the $[Pt(dms)(en)Cl]^+$ against the corresponding log $k_2°$ values for the standard complex in Figure 1 show that there is a reasonably good linear relationship (slope = 1.14 ± 0.05). This slope is considerably smaller than that of the Me_2SO complex (1.26) and suggests that the cis effect of dms in terms of nucleophilic discrimination is considerably less than that of Me_2SO, which also has the greater trans effect.[4,5,7] At this time the only studies of the relation of the trans effect to nucleophilic discrimination are concerned with the rate dependence upon the basicity of an entering amine. The reactions of $[PtLCl_3]^-$ with stronger nucleophiles are fast and require stopped-flow spectrophotometry, possibly even at low temperature. There does not seem to be any extensive relationship between the trans labilizing effect of a ligand in $[PtLCl_3]^-$ and its effect upon the nucleophilic discrimination of $[Pt(en)(L)Cl]^+$, where it is cis to the leaving group. Preliminary studies of the case where L = PEt_3[8] suggest that the nucleophilic discrimination of the cis cationic complex is not significantly greater than that of the complex where L = Me_2SO, even though the trans effect of the former is considerably greater than that of the latter. Detailed discussion

---

(7) Elding, L. I.; Gröning, O. *Inorg. Chem.* **1978**, *17*, 1872.

(8) Annibale, G.; et al., private communication.

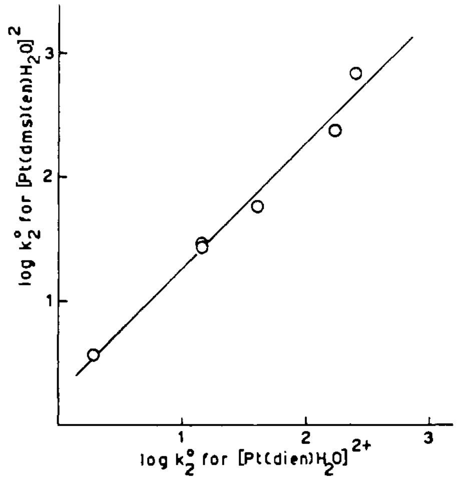

Figure 2. log $k_2°$ for $[Pt(dms)(en)H_2O]^{2+} + Y^{n-} \rightarrow [Pt(dms)(en)Y]^{(2-n)+} + H_2O$ in water at 25 °C plotted against data for analogous reactions of $[Pt(dien)H_2O]^{2+}$ in water at 30 °C.

must await the completion of this work.

On changing the leaving group to iodide, it is observed that the reactivity of the complex increases, expecially in the reactions with the strongest nucleophiles. In the plot of log $k_2°$ against log $k_2°$ for the reaction with the standard, this is seen as a marked increase of the slope to 1.29 ± 0.06 (Figure 1). An effect of similar magnitude has been observed in the reactions of $[Pt(dien)X]^+$[9,10] and $[Pt(Medien)X]^+$[11] (dien = 1,5-diamino-3-azapentane; Medien = 1,5-diamino-3-methyl-3-azapentane) except that in these cases the lines actually cross and the rate constant for the solvolysis of the iodo complex is less than that for the chloro complex. In the case of the dms complex the two solvolytic rate constants are virtually identical. As in the case of the Medien complex, the increased nucleophilic discrimination of the iodo complex is ascribed to the greater ability of the iodo complex to make use of the nucleophile to lower the energy of the rate-determining transition state.

It has also been possible to study the kinetics of the displacement of water from the dicationic aquo complex $[Pt(dms)(en)H_2O]^{2+}$. For the more reactive nucleophiles this required the use of stopped-flow spectrophotometry, but the entry of chloride and bromide could be followed conveniently by conventional techniques if concentrations were held low enough. The plots of k_{obsd} against $[Y^-]$ were linear and, apart from the reaction with SCN^- where the scatter was larger than usual, passed through the origin. Values of the slope, k_2, are collected in Table II. The ionic strength correction was applied where necessary to give log $k_2°$ values, which are also reported in Table II and compared with the standard for the dicationic scale, log $k_2°$, for the analogous reactions of $[Pt(dien)H_2O]^{2+}$ at 30 °C, taken from the work of Romeo and Cusumano.[12] The plot of log $k_2°$ for $[Pt(dms)(en)H_2O]^{2+}$ against that of the standard is reasonably linear, as shown in Figure 2, although the points are somewhat scattered. This indicates that the concept of a nucleophilicity scale that depends only upon the charge of the complex is valid for the complex $[Pt(dms)(en)H_2O]^{2+}$ as well as for $[Pt(Medien)H_2O]^{2+}$ and $[Pt(dien)(Me_2SO)H_2O]^{2+}$,[12] even though in the first case we are replacing a nitrogen donor by sulfur. The range of nucleophilicity over which the slope is determined is fairly small and the error consequently large, and so it is unwise to discuss whether the absence of change of nucleophilic discrimination (represented by a slope significantly different from unity) is a significant observation. Nevertheless, the $[Pt(dms)(en)H_2O]^{2+}$ complex is consistently more reactive than the $[Pt(dien)H_2O]^{2+}$ standard (apart from SCN^- the ratio lies between 2 and 3 times more reactive), and this must be taken as a measure of the slightly greater cis effect of the thio ether compared to that of an amine.

Acknowledgment. We thank the Italian Council for Research (CNR, Rome) and the British Council for financial support in a bilateral research project.

Registry No. $[Pt(dms)(en)Cl]^+$, 60927-59-5; $[Pt(dms)(en)I]^+$, 78109-36-1; $[Pt(dms)(en)H_2O]^{2+}$, 78109-37-2; $[Pt(dms)(en)Cl]Cl$, 64408-20-4; $[Pt(dms)(en)I]ClO_4$, 78109-38-3; H_2O, 7732-18-5; NH_3, 7664-41-7; Br^-, 24959-67-9; N_3^-, 14343-69-2; I^-, 20461-54-5; SCN^-, 302-04-5; $SC(NH_2)_2$, 62-56-6; SO_3^{2-}, 14265-45-3; Cl^-, 16887-00-6; $[Pt(dms)(en)I]BPh_4$, 78109-39-4; *trans*-$[Pt(dms)_2Cl_2]$, 17457-51-1.

Supplementary Material Available: A listing of k_{obsd} as a function of $[Y^{n-}]$ (3 pages). Ordering information is given on any current masthead page.

---

[9] Gray, H. B. *J. Am. Chem. Soc.* **1962**, *84*, 1548.

[10] Belluco, U.; Ettorre, R.; Basolo, F.; Pearson, R. G.; Turco, A. *Inorg. Chem.* **1966**, *5*, 591.

[11] Annibale, G.; Canovese, L.; Cattalini, L.; Marangoni, G.; Michelon, G.; Tobe, M. L., submitted for publication in *Inorg. Chem.*

[12] Romeo, R.; Cusumano, M. *Inorg. Chim. Acta* **1981**, *49*, 167.