

tion mechanism, k' in eq 7, without opening of the chelate ring. Applying the steady-state approximation to that portion of the reaction which proceeds by path 4, its rate constant $k_{(4)}$ can be represented by eq 5.

$$k_{(4)} = \frac{k_1 k_2 [\text{N}_3^-]}{k_{-1} + k_2 [\text{N}_3^-]} \quad (5)$$

Under the experimental conditions used the reaction goes to completion and therefore k_{-2} is ignored. Also at these conditions the rate of reaction is first order in $[\text{N}_3^-]$, after correcting for k' , which means that $k_{-1} \gg k_2 [\text{N}_3^-]$. Because of this eq 5 simplifies to eq 6. This

$$k_{(4)} = \frac{k_1 k_2 [\text{N}_3^-]}{k_{-1}} \quad (6)$$

means that the values of k_{obsd} in Table IV are related to the rate constants for the over-all reaction by eq 7.

$$k_{\text{obsd}} = k' + \frac{k_1 k_2 [\text{N}_3^-]}{k_{-1}} \quad (7)$$

Mechanisms of this type are fairly common for the removal of chelate ligands from metal complexes.¹⁹

(19) Reference 4, pp 154, 200; R. G. Pearson and D. A. Johnson, *J. Am. Chem. Soc.*, **86**, 3983 (1964).

Furthermore, recent kinetic studies²⁰ show that the reaction of $[\text{Pd}(\text{dien})\text{Cl}]^+$ in acid solution containing chloride ion readily forms $[\text{Pd}(\text{dien})\text{Cl}_2]$ and then more slowly yields PdCl_4^{2-} . This result is analogous to the reaction sequence proposed here for the reaction between $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ and azide ion. Similar qualitative observations were made for the reaction with iodide ion and with thiocyanate ion. The reactions seem to proceed in two steps and to yield the corresponding AuX_4^- complex. That under similar conditions neither chloride nor bromide ions replace the triamine from the complex is because the chloro and bromo complexes of gold(III) are less stable than the analogous azido, iodo, and thiocyanato complexes.

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(20) A. J. Poë, private communication.

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Monohalide Displacements of *trans*- $[\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Cl}_2]$ in Dipolar Aprotic Solvents

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Kinetic data for monohalide displacement of *trans*- $[\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Cl}_2]$ with various nucleophiles in acetone and dimethyl sulfoxide are reported. From a comparison of these rate data with the rates of the corresponding reactions in methanol, it appears that the nucleophilic reactivity order remains the same regardless of the nature of the solvent. The reactivity order parallels the polarizability order of the entering groups. Saturated carbon substrates present a reverse reactivity order as well as a large shift of the reactivity of halide ions in going from protic to dipolar aprotic solvents, depending on the anion solvation. However, in the $\text{S}_\text{N}2$ reactions at soft centers, which generally enhance the polarizability of the nucleophiles, the nucleophilic order and the reactivity are practically unaffected when the solvent is changed. In accordance with the reagent solvation, the nucleophilic discrimination factor of *trans*- $[\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Cl}_2]$ is greater in protic than in dipolar aprotic solvents.

Introduction

Most of the rate measurements on platinum(II) complexes refer to reactions in hydroxylic solvents such as methanol and water. In these solvents the order of reactivity of the entering groups is found to be the same for different Pt(II) substrates.^{1,2} In dipolar aprotic solvents, the only available data concern the chloride exchange of *trans*- $[\text{Pt}(\text{py})_2\text{Cl}_2]$.³

(1) For a review and references see: (a) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 388 (1962); (b) W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964); (c) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

(2) F. Basolo, "Mechanisms of Inorganic Reactions," Summer Symposium of Inorganic Chemistry of the American Chemical Society, Kansas, 1964, p 82.

(3) R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960).

The most important factors recognized to influence the nucleophilic reactivity toward saturated carbon (for which a large amount of data is available) are the following: geometrical factors including steric hindrance⁴ or steric acceleration,⁵ ion aggregation,⁶ M basicity,⁷ M–Y bond strength,⁸ polarizability, and H basicity.⁹ Moreover, it has been recently pointed out

(4) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(5) J. F. Bunnett and T. Okamoto, *J. Am. Chem. Soc.*, **78**, 5363 (1956).

(6) S. Winstein, L. G. Svedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, **9**, 24 (1960).

(7) A. J. Parker, *Proc. Chem. Soc.*, 371 (1961).

(8) R. F. Hudson, *Chimia* (Milan), **16**, 173 (1962).

(9) (a) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962); (b) J. O. Edwards, *ibid.*, **76**, 1540 (1954). For a review and references see also: J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1964, p 51; J. F. Bunnett, *Ann. Rev. Phys. Chem.*, **271** (1963); W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 1778 (1960).

that the order of nucleophilic reactivity is largely affected by the solvent.¹⁰ Some of these factors are expected to be more important than others, and two among these appear to be generally predominant: the energy required to remove the fraction of an electron from Y⁻ in solution and the energy corresponding to the fraction of desolvation at the transition state.^{8,10c}

In the case of bimolecular reactions of low-spin d⁸ systems, the entering group reactivity order was identified with the polarizability order of the reagents.^{1,2} However, in the case of reactions at soft centers, such as Pt(II), no attempts have been made, up to now, to distinguish between the solvation of the entering group and the contribution of polarizability to the nucleophile reactivity.

In this work we report the rates of substitutions of *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] with Cl⁻, Br⁻, I⁻, SCN⁻, and thiourea in acetone and in dimethyl sulfoxide. The rate data are compared with the corresponding data of the same substrate in methanol.

Experimental Section

Materials.—The complexes *trans*-[Pt(P(C₂H₅)₃)₂Y₂] (Y = Cl, Br, I, SCN) were prepared by the method of Jensen.¹¹ All other materials used were reagent grade.

Acetone was refluxed with potassium permanganate, dried with potassium carbonate, and fractionated, bp 56.5°; dimethyl sulfoxide (DMSO) was fractionated under reduced pressure in a nitrogen atmosphere.

Kinetics.—The chloride reactions were carried out with two different methods; the first method was described in a previous paper.¹²

With the second method, the solution of the *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] labeled with ³⁶Cl⁻ and that of LiCl or (C₄H₉)₄NCl were mixed in the required volumes and thermostated at 25 ± 0.1°. Aliquots of the mixture (2 ml) were removed at time intervals, and the complex was separated from uncomplexed chloride by making use of an anion-exchange resin, Dowex 1X4 (200–400 mesh), nitrate form.

The resin was washed with several portions of acetone, and the washings were added to the original effluent. The resulting solution was concentrated to a known volume (10.5 ml). The solution activity of the liquid samples (10 ml) was determined by means of an immersion-type Geiger–Müller counter. The reliability of this separation method had been tested by passing through the resin an acetone solution of Li³⁶Cl; the radioactivity was absent in the effluent. It was also found that the radioactivity of the complex was unchanged by passing through the same resin. The time necessary for the separation was negligible as compared to the half-time of the reaction.

The kinetics were analyzed by means of the well-known McKay law for simple exchange reactions involving one atom of each reactant and a negligible kinetic isotope effect.¹³

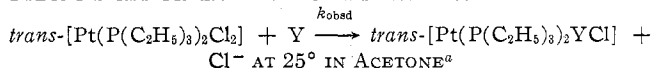
The rate constants obtained with both the methods used were reproducible to within 5%.

Other reactions of *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] with Br⁻, I⁻ (lithium or tetrabutylammonium salts), SCN⁻ (potassium salt), and thiourea were followed spectrophotometrically in the ultraviolet region by using both a Beckman DK-2A recording appara-

tus and a Beckman DU with a cell compartment thermostated at 25 ± 0.1°. The details of the experimental procedure have been given in a previous paper.¹² For these reactions, excess reagent was used in order to avoid unfavorable equilibrium. Thus, pseudo-first-order rate constants, *k*_{obsd} (sec⁻¹), were determined. The rate data are listed in Table I.

TABLE I

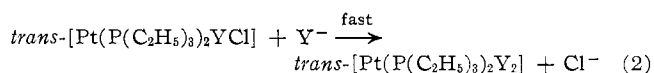
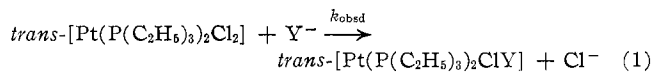
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE REACTIONS:



Nucleophile Y	Nucleophile concn., 10 ² M	10 ³ <i>k</i> _{obsd} , sec ⁻¹	10 ⁴ <i>K</i> ^b
Cl ⁻ (LiCl)	4	0.048	0.027
	1.36	0.016	
	0.68	0.009	
	0.17	0.002	
	0.17	0.002	
((<i>n</i> -C ₄ H ₉) ₄ NCl)	17.5	0.048	22.8
	8.75	0.029	
	4.37	0.017	
	1.05	0.007	
	0.10	0.001	
	0.10	0.001	
Br ⁻ (LiBr)	16.4	1.53	5.22
	13.5	1.28	
	6.7	0.67	
	4.0	0.42	
	1.6	0.16	
((<i>n</i> -C ₄ H ₉) ₄ NBr)	16	1.8	32.9
	13	1.49	
	8	0.96	
	4	0.51	
	2	0.25	
I ⁻ (LiI)	6.4	11.1	69
	3.75	6.7	
	0.65	1.3	
	0.37	0.63	
	0.37	0.63	
((<i>n</i> -C ₄ H ₉) ₄ NI)	6.28	14.45	64.8
	4	10.00	
	3.14	7.00	
	2	4.60	
	1	2.34	
SCN ⁻ (KSCN)	7.8	9.4	38.3
	3.9	4.6	
	1.0	1.46	
	0.5	0.79	
Thiourea	0.25	97.5	
	0.2	80.0	
	0.12	50.5	

^a Complex concentration is about 2 × 10⁻⁴ M. ^b The value of ion-pair dissociation constants, *K*, are taken from ref 6.

The reactions proceed by a slow rate-determining first step (1), followed by a rapid second step (2)



Results and Discussion

The data in Table I show that *k*_{obsd} values depend on the concentration and nature of the reagent.

In the substitutions of Pt(II) complexes in hydroxylic solvents it has always been found that the reactions obey the rate law: *k*_{obsd} = *k*₁ + *k*₂[Y:], where *k*₁ is a pseudo-first-order rate constant for the reaction involving the solvent as entering group and *k*₂ is a second-order rate constant for the direct reaction with Y:.

(10) See ref 6 and: (a) A. J. Parker, *J. Chem. Soc.*, 4398 (1961); (b) E. S. Gould "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959, p 260; (c) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963.

(11) K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **229**, 225 (1936).

(12) U. Belluco, L. Cattalini, and A. Turco, *J. Am. Chem. Soc.*, **86**, 226 (1964).

(13) G. Friedlander and J. Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p 315.

Plots of k_{obsd} vs. $[Y:]$ give straight lines with k_1 as intercept and k_2 as slope.¹⁴

In the case of *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] reacting with different nucleophiles in DMSO, linear plots of k_{obsd} vs. the reagent concentrations were also obtained in accordance with the complete dissociation of the examined salts in this solvent.¹⁵ The extrapolated value of k_1 in this solvent is about 2×10^{-5} sec⁻¹. Complex concentration is about 10^{-4} M. For each entering group, at least four concentrations have been examined, in the range 10^{-3} to 10^{-1} M.

However, for the reactions of *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] in acetone the same plots give smooth curves passing through the origin with the initial slope being equal to k_2 . Only in the reactions with Cl⁻ was a non-zero intercept found. The estimated k_1 value for the *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] in acetone is less than 10^{-6} sec⁻¹, and thus the maximum possible contribution of k_1 to the lowest reaction rate in acetone of the examined reagents is then less than 1% (except for Cl⁻). Consequently, it is possible to apply the treatment of a simple bimolecular reaction after correction of k_{obsd} for the k_1 value.

In Figure 1, the k_{obsd} values of the *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] reaction with bromide in acetone are reported as a function of the initial concentration of the reagents.

It can be seen that the apparent second-order rate constants (slopes of the plots) decrease by increasing the salt concentration. This is interpreted as being due to the occurrence in acetone of free and paired ions having different reactivities toward the substrate. Such a smooth and orderly variation in the apparent second-order rate constants, as shown in Figure 1, has been observed in bimolecular substitutions of alkyl halides with halide ions in liquid sulfur dioxide.¹⁶ The same behavior was also observed in the substitutions of toluenesulfonates in dimethylformamide and was attributed to an association of salts to ion pairs and not to a salt effect or to the ionic strength effect.¹⁷ It is worth noting that salt effects are generally absent in the reaction of ions with neutral molecules;¹⁸ this trait has also been noted in reactions of platinum(II) complexes.^{1c,14}

In this present work, constant ionic strength was avoided since the addition of any salt would exert a buffering effect on the dissociation of the ion pairs.

The rate constants for the bimolecular reaction of free anions were estimated by Acree's analysis,¹⁹ which ascribes different reactivities to free ions (k_2) and paired ions (k_p); i.e., $k_{\text{obsd}} = \alpha k_2 C + (1 - \alpha) k_p C$ (C is the initial reagent concentration and α is the degree of

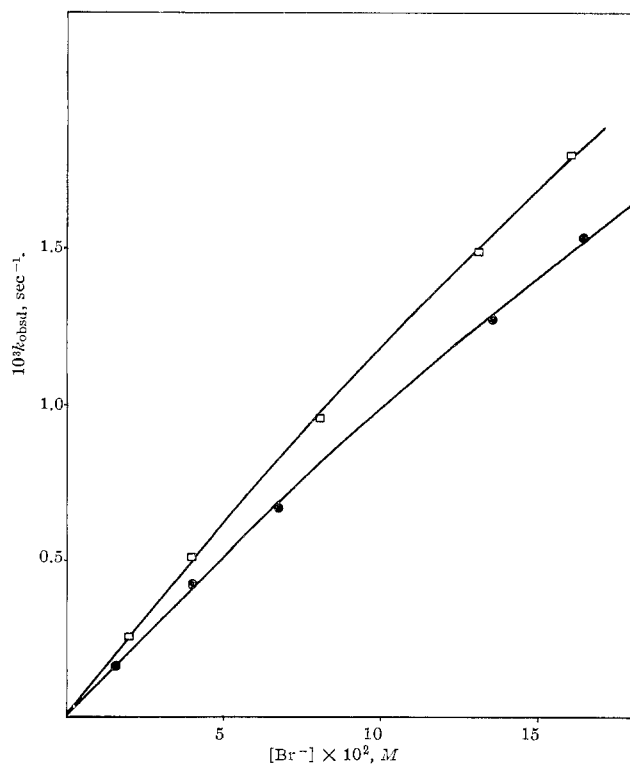


Figure 1.—Rates of reaction, k_{obsd} (sec⁻¹), for the monohalide displacements of *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] at 25° in acetone as a function of the concentration of Br⁻ salts: LiBr, ●; (*n*-C₄H₉)₄NBr, □.

dissociation of the salts). The validity of this analysis is supported by the fact that the k_2 values obtained by this treatment are independent of the nature of the cation. In fact, the lithium and tetrabutylammonium salts lead to the same values of k_2 for the free ions, as shown in Figure 2. The small amount of reactivity data for ion pairs (k_p) or higher aggregates and the lack of unequivocal information regarding their structure in the examined solvents make it difficult to discuss the reactivity of such reagent species.

In bimolecular nucleophilic substitutions toward some saturated carbon substrates, the nucleophilicity order found in protic solvents is I⁻ > Br⁻ > Cl⁻.^{6,20} Winstein, *et al.*,⁶ and, more recently, Weaver and Hutchison,¹⁷ found that the halide reactivity order for the reaction toward alkyl halides or toluenesulfonates is the exact reverse in acetone and dimethylformamide. Thus, in dimethylformamide the relative rates of reaction at 0° of lithium halides with methyl tosylate after ion-pairing correction are¹⁷ Cl⁻ (9.1) > Br⁻ (3.4) > I⁻ (1.0). An opposite order occurs for sodium halides reacting with ethyl tosylate in aqueous dioxane at 50° where the order is²¹ Cl⁻ (0.14) < Br⁻ (0.32) < I⁻ (1.0).

In anhydrous acetone the reactivity order at 25° of lithium halides reacting with *n*-butyl *p*-bromobenzenesulfonate is⁶ Cl⁻ (18.3) > Br⁻ (4.3) > I⁻ (1.0). It is interesting to point out that, in respect to Pt(II) reac-

(14) (a) H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962); (b) H. B. Gray and R. J. Olecott, *Inorg. Chem.*, **1**, 481 (1962). See also ref 1a and 1c.

(15) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

(16) N. N. Lichtin and K. N. Rao, *J. Am. Chem. Soc.*, **83**, 2417 (1961).

(17) W. M. Weaver and J. D. Hutchison, *ibid.*, **86**, 261 (1964).

(18) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford University Press, London, 1942, pp 128-130.

(19) (a) H. C. Robertson and S. F. Acree, *J. Am. Chem. Soc.*, **37**, 1902 (1915); (b) J. H. Shroder and S. F. Acree, *J. Chem. Soc.*, 2582 (1914); (c) E. K. Marshal and S. F. Acree, *J. Phys. Chem.*, **19**, 589 (1915).

(20) (a) A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962); (b) J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 271 (1963).

(21) H. R. McCleary and L. P. Hammett, *J. Am. Chem. Soc.*, **63**, 2254 (1941).

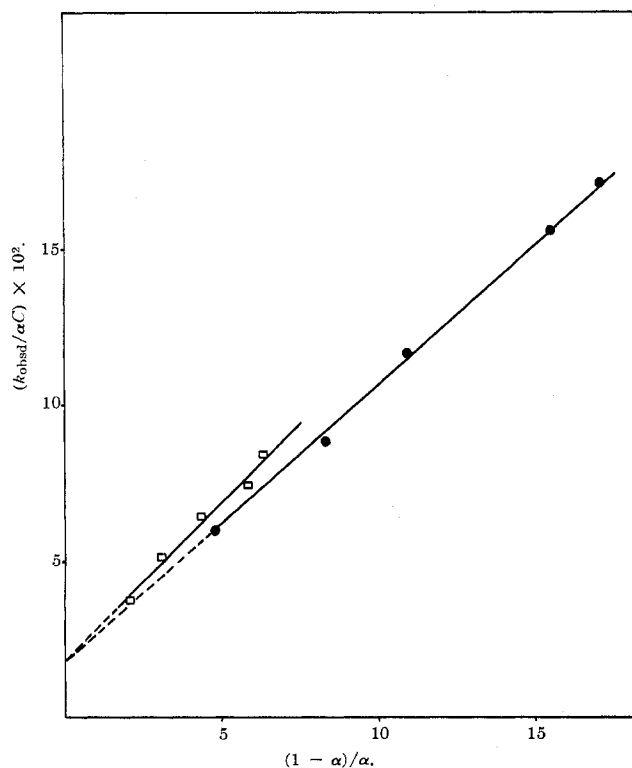


Figure 2.—Acree's analysis for the reaction of *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] at 25° in acetone with LiBr (●) and (*n*-C₄H₉)₄NBr (□).

tions, in S_N2 reactions of methyl chloride²² there is a larger shift (about 100-fold) in the reactivity of halide ions as the solvent changes from water to acetone (Table II).

TABLE II
SOLVENT EFFECT ON S_N2 REACTIONS OF *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] AND OF CH₃Cl

Nucleophile	(CH ₃) ₂ CO (25°)	CH ₃ OH (30°)	<i>k</i> ₂ (CH ₃) ₂ CO/ <i>k</i> ₂ (H ₂ O) Pt(II) (25°), CH ₃ Cl
	10 ³ <i>k</i> ₂ , M ⁻¹ sec ⁻¹	10 ³ <i>k</i> ₂ , M ⁻¹ sec ⁻¹	
Cl ⁻	1.5	0.029	2500
Br ⁻	16	0.93	200
I ⁻	230	263	80

The observed effects of solvents on rates of the S_N2 reactions of methyl chloride were rationalized in terms of solvation differences of the anionic reagents. In protic solvents the retarding effect in the rate of reaction of small anions with high charge density is due to their solvation which is greater than that for the large polarizable ions with lower charge density. In dipolar aprotic solvents, such as acetone and dimethylformamide, the observed reactivity order is expected, owing to the smaller chloride solvation with respect to that of the iodide ion.

In most systems, as quoted, "the solvation is one of the most important factors controlling nucleophilicity, and hence the two factors affecting nucleophilic order cannot be separated."¹⁸

For reactions of *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] the rate data in Table III show that the reactivity order of free ions is

TABLE III
SECOND-ORDER RATE CONSTANTS OF FREE IONS FOR THE MONOHALIDE DISPLACEMENTS OF *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] IN VARIOUS SOLVENTS

Nucleophile Y	Acetone ^a	Dimethyl sulfoxide ^a	Methanol ^b	<i>n</i> ^o Pt ^c
	10 ³ <i>k</i> ₂ , M ⁻¹ sec ⁻¹	10 ³ <i>k</i> ₂ , M ⁻¹ sec ⁻¹	10 ³ <i>k</i> ₂ , M ⁻¹ sec ⁻¹	
Cl ⁻	1.5	0.7	0.029	3.04
Br ⁻	16	5.8	0.93	4.18
I ⁻	230	160	263	5.42
SCN ⁻	180	246	371	5.65
Thiourea	40,000	15,200		7.17
Acetone ^d	~10 ⁻⁶	
DMSO ^d	...	2 × 10 ⁻⁵	...	
CH ₃ OH ^d	~10 ⁻⁷	0

^a Temperature 25°. ^b Data from ref 1c. Temperature 30°. ^c Nucleophilic reactivity constants, *n*^oPt = log (*k*₂/*k*^o₂), for the reaction of *trans*-[Pt(py)₂Cl₂] in methanol at 30° with different nucleophiles (see ref 23). ^d Values of *k*₁ in sec⁻¹.

the same in protic and aprotic solvents. It clearly appears that the nucleophilic reactivity parallels the polarizability of the reagents.

As shown in Table IV, the difference of reactivities on Pt(II) displacements in the two classes of solvents is that the nucleophilic discrimination factor²³ is greater in protic than in aprotic solvents, as a consequence of the relative reagent solvations in the considered solvents.^{20a} Of course, the transition state structure for these reactions is assumed to be the same in different solvents.

TABLE IV
NUCLEOPHILIC DISCRIMINATION FACTORS OF *trans*-[Pt(P(C₂H₅)₃)₂Cl₂] IN DIFFERENT SOLVENTS AT 25°

Solvents	Nucleophilic discrimination factors
Methanol ^a	1.43
Acetone	1.04
Dimethyl sulfoxide	1.06

^a Data at 30° (ref 1c).

It is of interest to note that no relevant solvent effect was found on the leaving group in reactions of some Pt(II) complexes.^{3, 24}

Moreover, in the present case the possibility of a strong interaction between Pt(II) and the dipolar solvent in the rate-determining step is reduced, owing to the presence of two strong π-bonding ligands coordinated to the metal ion.³

It must be pointed out that differentiation of the reaction rates of single reagents and, consequently, the study of the solvent effect have been possible with the complex chosen because its nucleophilic discrimination is sufficiently high in all of the solvents used.

(23) The nucleophilic discrimination factors (*s*) are calculated by use of the least-squares analysis on the linear free energy relationship: log *k*₂ = *s**n*^oPt + log *k*₂^o. The nucleophilic reactivity constants, *n*^oPt, are defined as log (*k*₂/*k*₂^o) for the reaction of each nucleophile Y: with the *trans*-[Pt(py)₂Cl₂] in methanol at 30° selected as standard conditions. *k*₂, M⁻¹ sec⁻¹, is the second-order rate constant for the nucleophile Y; and *k*₂^o, M⁻¹ sec⁻¹, is the second-order constant for the reaction in which the methanol is the entering group. The *k*₂^o value was computed from the pseudo-first-order rate constant *k*₁, sec⁻¹, of *trans*-[Pt(py)₂Cl₂] in CH₃OH at 30° by simply dividing by the "concentration" of the solvent. See ref. 1c; U. Belluco, "Coordination Chemistry Reviews," Elsevier Publishing Co., New York, N. Y., in press; ref 14b; R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964).

(24) U. Belluco, unpublished data.

One general conclusion which can be drawn is that, when the electrophilic center enhances the contribution of the polarizability of the reagent in SN2 reactions, then the nucleophilic order and the reactivity are little influenced by the nature of the solvent. In other words, in the reactions at soft centers such as Pt(II), in which the polarizability of the nucleophile exerts an important role, the nature of the solvent becomes relatively less important.

In these reactions, it is therefore possible to distinguish the contribution of solvation from that of the reagent polarizability, owing to the fact that the solvation effect is a relatively small one in comparison to the contribution from the polarizability of the reagents.

In most cases of SN2 reactions at saturated carbon centers, the extent of bond formation realized at the transition state is relatively small.⁸ In the case of displacements on Pt(II) complexes, however, one can conclude that bond formation at the transition state is

the driving force of the reaction,²⁵ whereas solvation exerts a secondary effect. This assumption is supported by the fact that stable five-coordinated complexes of d⁸ ions have recently been prepared.²⁶ Furthermore, Pt(II) reactions are accompanied by relatively small activation enthalpies and by rather negative values of activation entropies; this is consistent with a net increase in bonding at the transition state.²⁷

Acknowledgments.—This work was supported by the Italian Consiglio Nazionale delle Ricerche (CNR, Rome).

(25) For a discussion on the platinum-nucleophile bond see R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963), and ref 1a and 9a.

(26) For a recent review see L. M. Venanzi, *Angew. Chem., Intern. Ed. Engl.*, **3**, 453 (1964); see also R. O. Cramer, R. V. Lindsey, C. T. Prewitt, and V. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965); C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1963); C. M. Harris and R. S. Nyholm, *ibid.*, 63 (1957); J. W. Collier, F. G. Mann, D. G. Watson, and H. R. Watson, *ibid.*, 1803 (1964); P. C. Westland, *ibid.*, 3060 (1965).

(27) U. Belluco, R. Ettore, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

CONTRIBUTION NO. 1821 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

Kinetics and Mechanism of Electron Exchange between Chromium(II) and Monoamminepentaquo chromium(III)¹

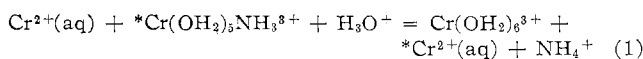
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Chromium(II) catalyzes replacement of ammonia by water in the complex $\text{Cr}(\text{H}_2\text{O})_5\text{NH}_3^{3+}$; the rate law is $-d[\text{CrNH}_3^{3+}]/dt = (k_0 + k_{-1}/[\text{H}^+])[\text{Cr}^{2+}][\text{CrNH}_3^{3+}]$, with $k_0 = 2.5 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ and $k_{-1} = 5.9 \times 10^{-9} \text{ sec}^{-1}$ at 25.0° and 2.0 M ionic strength. Kinetic measurements have been made from 25 to 70°, and activation parameters have been calculated for each rate constant. The reaction is formulated in terms of a chromium(II)-chromium(III) electron-exchange reaction, and it is inferred indirectly that the reaction proceeds by an inner-sphere mechanism with H₂O and OH⁻ bridging ligands. Radiotracer experiments on *Cr²⁺ and the ammine complex establish that chromium exchange, with accompanying NH₃ transfer, does not take place rapidly, compared to the rate at which chromium(II) catalyzes ammonia release.

Introduction

Anderson and Bonner² have studied the kinetics of the relatively slow electron exchange between the aquo ions of chromium(II) and -(III) in acidic perchlorate solutions. We report here the results of a study of the electron exchange between aquochromium(II) and the inert monoammine complex of chromium(III).



The principal feature distinguishing this reaction from the aquo ion exchange² is that net chemical change—replacement of the ammonia molecule by water in the primary coordination sphere of chromium(III)—accompanies electron transfer. It is just this aspect, rather incidental to the main electron-transfer process of interest here, that allows us to follow the rate of

reaction 1 by conventional spectrophotometric techniques without recourse to isotopic substitution.

The possibility of electron transfer *without* loss of coordinated NH₃ (*i.e.*, NH₃ ligand transfer accompanying electron transfer) has been examined by use of isotopically labeled chromium. This study also provides information on the role of ligands, such as NH₃, which cannot act as efficient electron-transfer bridges.

Experimental Section

Reagents.—Two independent preparations of chloride-free chromium(II) solutions were used: chromium(III) perchlorate solutions were reduced electrolytically at a mercury cathode, and high-purity chromium metal was dissolved in dilute perchloric acid. The preparations, handling, and analyses of these solutions have been described in detail previously.³ The ion⁴ CrNH_3^{3+} was prepared by reaction of chromium(II) and hydrazoic

(1) Work was performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission.

(2) M. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

(3) (a) J. H. Espenson, *Inorg. Chem.*, **3**, 968 (1964); (b) *ibid.*, **4**, 1025 (1965).

(4) In general, coordinated solvent molecules will be omitted in formulas for complex ions unless necessary for clarification.