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**Rates of Substitution Reactions of Square-Planar Platinum(II) Complexes. I. The Reaction of *trans*-Dichloro-bis-(triethylphosphine)-platinum(II) with Radiochloride and Nitrite Ions**

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RECEIVED JULY 22, 1963

Rates of chloride replacement by nitrite and radiochloride in the platinum(II) complex *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] are reported. The results show that both first-order and second-order reactions occur. The first-order rate constant for the reaction with NO<sub>2</sub><sup>-</sup> is obtained by applying a stationary state treatment. The relative reactivities of Cl<sup>-</sup> and NO<sub>2</sub><sup>-</sup> are compared with those of similar amino complexes of platinum(II). The bimolecular reactivity of NO<sub>2</sub><sup>-</sup> decreases in the reaction with *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and this is interpreted in terms of the electrophilic character of the nitrite ion and of the electronic structure of the complex.

The kinetics of nucleophilic substitution in square complexes generally take place according to two simultaneous paths, one of which is first order and the other is second order.<sup>1-13</sup> This results in the general kinetic equation<sup>12</sup>

$$k_{\text{obsd}} = k_1 + k_2[Y]$$

where  $k_{\text{obsd}}$  is a pseudo-first-order constant,  $k_1$  and  $k_2$  are constants of first and second order, and Y is the entering group.

The first-order path of the reaction is generally assumed to involve a nucleophilic displacement by the solvent followed by the coordinated solvent being rapidly replaced by the entering reagent. Hence  $k_1$ , a pseudo-first-order rate constant, is independent of the nature of the reagent.

The second-order path of the reaction, ascribed to  $k_2$ , is interpreted as a direct bimolecular reaction between the complex and the entering group. A comparison of the specific rate constants  $k_2$  for some reactions of Cl<sup>-</sup> and NO<sub>2</sub><sup>-</sup> with Pt(II) complexes has shown that Cl<sup>-</sup> reacts more rapidly than NO<sub>2</sub><sup>-</sup> with positively charged complexes, whereas with negatively charged and neutral complexes the opposite occurs.<sup>13</sup> This leads to the conclusion that the NO<sub>2</sub><sup>-</sup> attack can be partially electrophilic and that of Cl<sup>-</sup> is primarily nucleophilic. This is reasonable if we consider the ability of NO<sub>2</sub><sup>-</sup> to stabilize the transition state by using electrons in the  $\delta d$ -orbitals of Pt(II).<sup>13</sup>

It is generally accepted that filled  $nd$ -orbitals of transition metals are used in the formation of  $\pi$ -bonds with the empty  $3d$ -orbitals of phosphorus.<sup>14</sup> This type of interaction is formally equivalent to transferring some negative charge from the metal to the ligands and hence to render it more "positive." Thus the effectiveness of NO<sub>2</sub><sup>-</sup> as an electrophilic reagent is expected to be reduced in complexes of platinum(II) with tertiary phosphines. Accepting this view as a working hypothe-

sis, we have studied the reactions of Cl<sup>-</sup> and of NO<sub>2</sub><sup>-</sup> with *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]. Similar complexes containing cyclohexylphosphine or phenylphosphine proved to be unsuitable for the present work owing to their limited solubility.

**Experimental**

**Preparation of Materials.**—P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> was prepared as described<sup>15</sup> from PCl<sub>3</sub> and Grignard compound in ether.

*trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] was prepared from H<sub>2</sub>PtCl<sub>6</sub> in water.<sup>16</sup> In order to separate it from the *cis* isomer, the product was treated with ether and purified by recrystallization from ethanol; m.p. 142–143°. *Anal.* Calcd.: Cl, 14.2. Found: Cl, 14.1.

Anhydrous CH<sub>3</sub>OH was obtained by distillation over (CH<sub>3</sub>O)<sub>2</sub>Mg.<sup>17</sup>

Li<sup>36</sup>Cl was obtained from LiCl and H<sup>36</sup>Cl by isotopic exchange and purified by recrystallization from acetone.

**Rate of Isotopic Exchange.**—The isotopic exchange experiments were carried out in CH<sub>3</sub>OH and the ionic strength was kept constant by addition of LiNO<sub>3</sub>. The reaction mixture was divided into several portions and sealed in glass ampoules, care being taken to avoid moisture. Ampoules were removed from the constant temperature bath and rapidly cooled to -78°, thus stopping the reaction. The complex which crystallized was separated from the solution by centrifugation and washed with water. The complex was treated with aqueous HNO<sub>3</sub> and AgNO<sub>3</sub>. The AgCl precipitate was then treated with zinc in very dilute nitric acid and the chloride was again precipitated as Hg<sub>2</sub>Cl<sub>2</sub> by adding Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>. Mercurous chloride was transferred to small plastic disks and the specific activity determined by means of an end-window counter, using a calibration plot.

Another procedure involved the separation of the complex from the reaction solution by addition of water. The precipitation was quantitative and the sum of the radioactivity of the complex and of the solution containing Li<sup>36</sup>Cl was found to be equal to the initial activity of the lithium chloride.

**Rate of Reaction with Nitrite Ion.**—Rates of reaction between *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and NO<sub>2</sub><sup>-</sup> have been studied, adding LiNO<sub>3</sub> to maintain the same ionic strength (2.75 × 10<sup>-1</sup> M), keeping the same initial complex concentration (5 × 10<sup>-3</sup> M), and varying that of NaNO<sub>2</sub>. Toluenesulfonic acid was added to avoid the formation of CH<sub>3</sub>O<sup>-</sup>. The reaction mixture was divided into 10-ml. aliquots and the reaction was stopped by rapidly cooling the solution. The displaced chloride was titrated with AgNO<sub>3</sub> (10<sup>-2</sup> N) in CH<sub>3</sub>OH using the dead-stop end-point method for the determination of the equivalence point. The titration results were confirmed by determining, potentiometrically, the concentration of the chloride ion by means of a concentration cell. The reference silver-silver chloride electrode contained a known concentration of Cl<sup>-</sup>, all other reagents being the same as in the reaction solution. A saturated solution of lithium nitrate in methanol was used as a salt bridge.

The reaction of *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] with NO<sub>2</sub><sup>-</sup> in methanol was also followed by measuring changes in optical density in the range from 4200 to 4600 Å. In this range, the absorbancies of *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] are considerably larger than those of *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]. The rate of disappearance of *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] was equal to that calculated from the Cl<sup>-</sup> titrations, according to the equation  $kt = 2.303 \log a/(a - x)$  (where  $a$  = initial concentration of the complex,  $x = 1/2$ [released chlorine]), based on the assumption of the release of two chlorine atoms for each kinetic act. The completeness of the reaction was checked by comparing the spectrum of a solution of *trans*-

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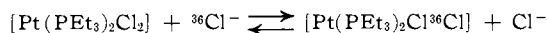
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$[\text{Pt}(\text{PET}_3)_2(\text{NO}_2)_2]$  at the desired concentration with the final spectrum obtained from the reacting solution. Titration of the released chloride also indicated that the reaction had gone to completion.

Spectrophotometric tests showed that no appreciable amounts of *cis* isomer are formed under these experimental conditions. However, the possible formation of trace amounts of the *cis* isomer cannot be excluded. It was found that the nitrate ion does not react with *trans*- $[\text{Pt}(\text{PET}_3)_2\text{Cl}_2]$  under these experimental conditions.

### Results and Discussion

The values of  $k_{\text{obsd}}$  obtained for the isotopic exchange



are given in Table I. A typical run is shown in Fig. 1. The  $\log(1 - F)$  plots indicate that the two chlorine

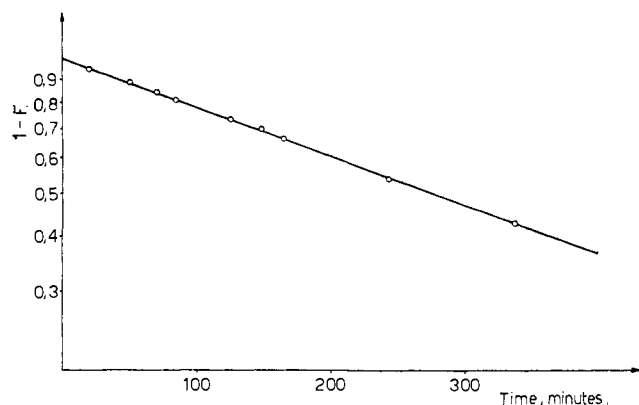


Fig. 1.—Chloride exchange; temperature  $55^\circ$ ; concn. complex,  $0.005 M$ ; concn.  $\text{Li}^{36}\text{Cl}$ ,  $0.06 M$ ; typical experiment.

atoms are equivalent, in accordance with the structure of the complex. The values of  $k_1$  and  $k_2$  have been obtained graphically from the diagram shown in Fig. 2. The intercept gives the value of  $k_1$  and the slope gives the value of  $k_2$ .

TABLE I

RATES OF REACTION OF *trans*- $[\text{Pt}(\text{PET}_3)_2\text{Cl}_2]$  COMPLEX WITH  $^{36}\text{Cl}^-$  IN  $\text{CH}_3\text{OH}$  AT  $55^\circ$

Complex concn. *trans*- $[\text{Pt}(\text{PET}_3)_2\text{Cl}_2] = 0.005 M$

Reactant, concn. ( $M$ ) $^{36}\text{Cl}^- (\text{LiCl})$	Added substance, $M \text{ LiNO}_3$	$k_{\text{obsd}} \times 10^5, \text{sec.}^{-1}{}^a$
0.03	0.07	5.78
.06	0.04	7.08
.10	..	8.72

${}^a k_{\text{obsd}} = R/\text{trans}-[\text{Pt}(\text{PET}_3)_2\text{Cl}_2]$ .

A pseudo-first-order plot for the reaction



is shown in Fig. 3. The marked departure from linearity can be attributed to the competition between  $\text{NO}_2^-$  and the  $\text{Cl}^-$  ion formed during the course of reaction. This was proved by carrying out some experiments in the presence of variable amounts of  $\text{LiCl}$ . Increase of chloride concentration results in a decrease in  $k_{\text{obsd}}$ .

Gray<sup>12</sup> found, for the reaction between  $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$  and pyridine, that the value of  $k_1$  was smaller than the values obtained with other nucleophilic reagents. He attributed this difference to a competitive

reaction between  $\text{Br}^-$  and pyridine. When  $\text{Br}^-$  is absent (at the beginning of the reaction using  $[\text{Pt}(\text{dien})\text{Br}]\text{NO}_3$ ), the values of  $k_1$  agree with those obtained with other reagents.

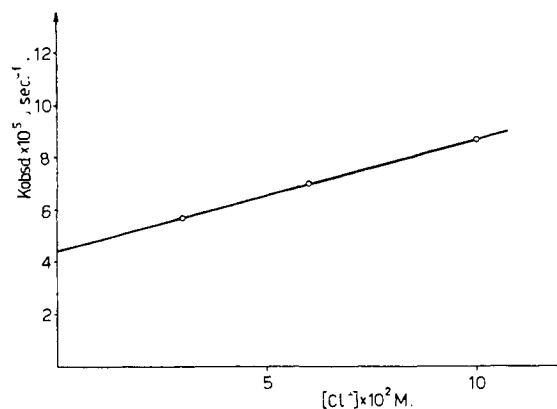


Fig. 2.—Dependence of  $k_{\text{obsd}}$  on concentration of  $\text{Cl}^-$ .

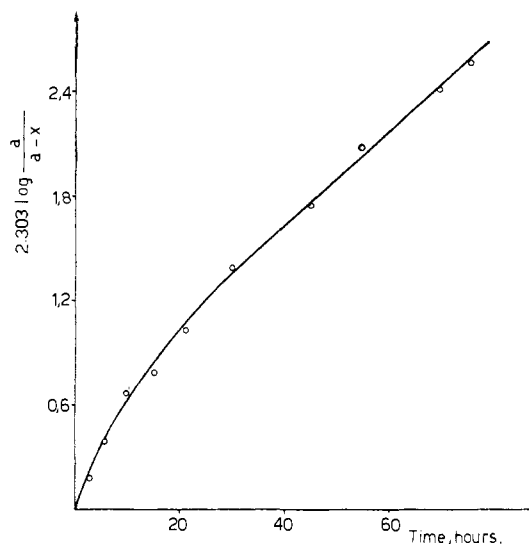
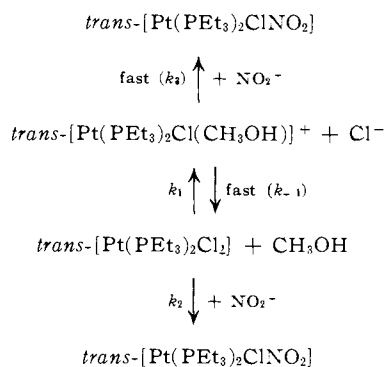


Fig. 3.—First-order plot for the reaction of *trans*- $[\text{Pt}(\text{PET}_3)_2\text{Cl}_2]$  with  $\text{NO}_2^-$  in  $\text{CH}_3\text{OH}$  at  $55^\circ$ :  $a = 0.005 M$  concn. complex;  $x = 0.5[\text{Cl}^-]$  determined; concn.  $\text{NO}_2^- (\text{NaNO}_2) = 0.10 M$ ; typical experiment.

The product of the reaction between *trans*- $[\text{Pt}(\text{PET}_3)_2\text{Cl}_2]$  and  $\text{NO}_2^-$  is  $[\text{Pt}(\text{PET}_3)_2(\text{NO}_2)_2]$ . However, the rate-determining stage must be the replacement of the first  $\text{Cl}^-$  of the complex, leading to the formation of the intermediate species  $[\text{Pt}(\text{PET}_3)_2\text{ClNO}_2]$ . Displacement of the second  $\text{Cl}^-$  must occur at a much higher rate in accord with the greater *trans* effect of  $\text{NO}_2^-$  compared to  $\text{Cl}^-$ . It was not possible to detect the presence, in solution, of the chloronitro complex. Spectrophotometric studies showed that the rate of appearance of the chloride ion is twice that of the consumption of the dichloro complex, thus showing that no other absorbing species is formed in appreciable concentration during the course of the kinetics. The compound  $[\text{Pt}(\text{PET}_3)_2\text{ClNO}_2]$  is expected to absorb in the range  $4200\text{--}4600 \text{ \AA}$ . used in the present investigation (shorter wave lengths are useless owing to the strong absorption of  $\text{NO}_2^-$ ) considering that the absorption curve of  $[\text{Pt}(\text{PET}_3)_2(\text{NO}_2)_2]$  and that of *trans*- $[\text{Pt}(\text{PET}_3)_2\text{Cl}_2]$  start at  $\sim 3600$  and  $\sim 5000 \text{ \AA}$ ., respectively.

The over-all reaction may be summarized as



The rate constants  $k_2$  were calculated from the slopes of the curves obtained by plotting  $k_{\text{obsd}}$  (Table II) vs. nitrite concentration.

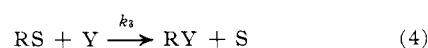
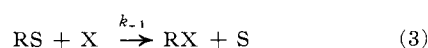
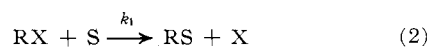
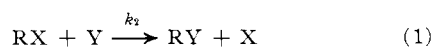
TABLE II

RATES OF REACTIONS OF *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] COMPLEX WITH NaNO<sub>2</sub> IN CH<sub>3</sub>OH AT 55°  
Complex concn. *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] = 0.005 M

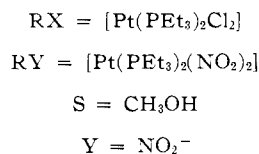
Reactant, concn. M	Added substance	$k_{\text{obsd}} \times 10^5$ , sec. <sup>-1</sup>
0.10	0.165 M LiNO <sub>3</sub>	3.62
	.01 M toluenesulfonic acid	
.15	.11 M LiNO <sub>3</sub>	4.15
	.015 M toluenesulfonic acid	
.20	.055 M LiNO <sub>3</sub>	4.55
	.02 M toluenesulfonic acid	
.25	.025 M toluenesulfonic acid	5.10

The best values of  $k_2$  obtained from experiments with the highest nitrite concentration were used in order to calculate the rate constant  $k_1$ . This was obtained by using the following mathematical treatment suggested by Tobe.<sup>18</sup>

The general equations 1, 2, 3, and 4 can be written ignoring for the moment the fact that there are two replaceable chlorines (but this must be remembered later on).



where



Since steps 3 and 4 are known to be much faster than 1 and 2, the concentration of RS is always very small. Then

$$d\text{RY}/dt = -d\text{RX}/dt = dx/2dt \equiv \text{"rate"}$$

$$\text{"rate"} = \{k_3[\text{RS}] + k_2[\text{RX}]\}[\text{Y}]$$

Since [RS] is always small we can apply a stationary state treatment so that

$$d\text{RS}/dt = k_1[\text{RX}] - k_{-1}[\text{RS}][\text{X}] - k_3[\text{RS}][\text{Y}] \equiv 0$$

$$[\text{RS}] = k_1[\text{RX}]/(k_{-1}[\text{X}] + k_3[\text{Y}])$$

Then

$$\text{"rate"} = \left\{ \frac{k_1 k_3 [\text{Y}]}{k_{-1} [\text{X}] + k_3 [\text{Y}]} \right\} [\text{RX}] + k_2 [\text{RX}] [\text{Y}]$$

If Y is in large excess [Y] remains constant for a particular experiment and we can write

$$k_2[\text{Y}] = k_2'; \quad k_3[\text{Y}] = k_3'$$

So for a particular concentration of Y

$$\text{"rate"} = \left\{ \frac{k_1 k_3'}{k_{-1} [\text{X}] + k_3'} + k_2' \right\} [\text{RX}]$$

Obviously this is not a simple first-order process. If we write the rate in terms of  $x$

$$\frac{dx}{2(a - 1/2x)dt} = \frac{k_1 k_3'}{k_{-1} [\text{X}] + k_3'} + k_2'$$

$$\frac{dx}{2(a - 1/2x)dt} = \frac{-d \ln(a - 1/2x)}{dt}$$

Therefore

$$-\frac{d}{dt} \log(a - 1/2x) = \frac{1}{2.303} \left\{ \frac{k_1 k_3'}{k_{-1} [\text{X}] + k_3'} + k_2' \right\}$$

If we plot  $\log(a - 1/2x)$  against time, the slope is not constant but is equal to

$$-\frac{1}{2.303} \left\{ \frac{k_1 k_3'}{k_{-1} [\text{X}] + k_3'} + k_2' \right\}$$

The rate constant  $k_1$  can be calculated with the following expression, by measuring the slope at various times and knowing the value of [X] at the same times

$$-\frac{1}{2.303 \text{"slope"} + k_2'} = \frac{k_{-1} [\text{X}]}{k_1 k_3'} + \frac{1}{k_1}$$

Plotting  $-1/(2.303 \text{"slope"} + k_2')$  against  $x$  one should have a straight line of intercept  $1/k_1$ .

TABLE III

CALCULATED FIRST-ORDER RATE CONSTANTS  
Complex concn. = 0.005 M

Reactant concn., M	$k_1$ , sec. <sup>-1</sup> × 10 <sup>5</sup>
0.10	3.45
.15	4.00
.20	5.45
.25	6.25

The calculated rate constants  $k_1$  are presented in Table III. Figure 4 shows that a good linear relation is obtained for the curves at various nitrite ion concentrations. The extrapolated values of  $1/k_1$  for  $[\text{Cl}^-] \rightarrow 0$  are not exactly the same. However, they can be considered satisfactory, except perhaps for the value at the highest nitrite concentration. This may result from the fact that at highest nitrite concentrations most of the reaction goes by the  $k_2$  path so that the errors in  $k_1$  become appreciable. The average  $k_1$  in Table IV has

{18} M. L. Tobe, private communication.

been calculated neglecting the value obtained for the highest nitrite ion concentration. It can be seen that the agreement between the  $k_1^{\text{NO}_2^-}$  and  $k_1^{\text{Cl}^-}$  is extraordinarily good. If the neglected value at highest  $[\text{NO}_2^-]$  were also used, then the average  $k_1$  becomes  $5.05 \times 10^{-5}$ , which is still a very satisfactory value.

TABLE IV

RATES CONSTANTS FOR THE REACTION OF *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] WITH <sup>36</sup>Cl<sup>-</sup> AND NO<sub>2</sub><sup>-</sup> IN CH<sub>3</sub>OH AT 55°

Reactant	$k_1, \text{sec.}^{-1} \times 10^5$	$k_2, M^{-1} \text{sec.}^{-1} \times 10^4$
<sup>36</sup> Cl <sup>-</sup>	4.5	4.20
NO <sub>2</sub> <sup>-</sup>	4.47	0.97

The kinetic data for several Pt(II) complexes in water indicate that the effectiveness of NO<sub>2</sub><sup>-</sup> as a reagent, as compared to Cl<sup>-</sup>, is much greater for the neutral and anionic complexes, e.g., [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and [PtCl<sub>4</sub>]<sup>2-</sup>, than for cationic complexes. Indeed, for [Pt(dien)H<sub>2</sub>O]<sup>2+</sup> the reactivity order is inverted. A comparison of  $k_2$  values between the substitution and chlorine exchange reactions is given in Table IV. The ratio  $k_2^{\text{NO}_2^-}/k_2^{\text{Cl}^-}$  is of the order of magnitude found for positively charged complexes in water.<sup>13</sup>

That NO<sub>2</sub><sup>-</sup> can act as an electrophilic agent can easily be understood if one considers that it has an empty antibonding  $\pi$ -orbital where charge can be transferred from the metal atom. If 14 of the 18 outer shell electrons of the nitrite ion are put in its bonding orbitals and lone pair orbitals, there are 4 electrons left for occupation of three  $\pi$ -orbitals. These are orbitals arising from the combination ( $p_{z_1} + p_{z_2}$ ) +  $\lambda p_{zN}$  (bonding, filled),  $p_{z_1} - p_{z_2}$  (nonbonding, filled), and  $\lambda(p_{z_1} + p_{z_2}) - p_{zN}$  (antibonding, empty), written in order of increasing energy. The antibonding orbital is probably of too high an energy to combine with the  $\pi$ -platinum orbitals. However, the drift of electrons in the N → Pt  $\sigma$ -bond will cause the energy of the antibonding or-

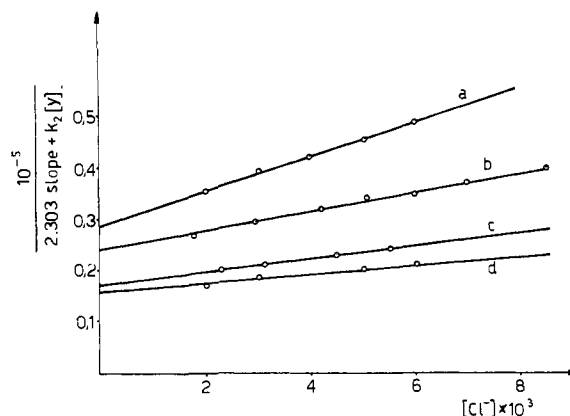


Fig. 4.—Graphical derivation of  $k_1$  using stationary state treatment ( $Y = \text{NO}_2^-$ ): a,  $[Y] = 0.1$ ; b,  $[Y] = 0.15$ ; c,  $[Y] = 0.2$ ; d,  $[Y] = 0.25$ .

bit to be lowered, becoming thus accessible for bond formation with platinum. This empty orbital must be more localized on the less electronegative nitrogen atom. In this way the electrophilic nature of the nitrite ion may arise from a sort of synergic  $\text{O}_2\text{N} \overset{\sigma}{\rightleftharpoons} \overset{\pi}{\text{Pt}}$  interaction. However, when the platinum atom is bonded to strong  $\pi$ -electron acceptor ligands, the energy of its  $\pi$ -electrons will be lowered and the  $\pi$ -attack of the nitrite ion will become less favorable.

The results presented here are consistent with the assumption made that  $\pi$ -bonding may be of importance in determining the effectiveness of NO<sub>2</sub><sup>-</sup> as an electrophilic reagent.

**Acknowledgments.**—We thank Professor F. Basolo for helpful discussions and for his interest in this work, Professor R. G. Pearson for helpful suggestions, and Dr. M. L. Tobe for stimulating discussions. This work was supported by the Italian Council for Research (C.N.R. Rome).

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE, AMHERST, MASS.]

## Anation of the *trans*-Aquanitrobis-(ethylenediamine)-cobalt(III) Ion in a Tetramethylene Sulfone–Water Mixture<sup>1</sup>

BY C. H. LANGFORD AND M. P. JOHNSON

RECEIVED AUGUST 26, 1963

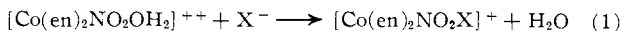
The rates of entry of the anions Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SCN<sup>-</sup> into *trans*-[Co(en)<sub>2</sub>NO<sub>2</sub>OH<sub>2</sub>]<sup>++</sup> (en = ethylenediamine) were found to differ by no more than a factor of four in the solvent 7.8% aqueous tetramethylene sulfone. The reactions were nearly zero order in the anion concentration. Conductance data on a model system strongly suggest that the observed reactions take place within outer-sphere complexes. The insensitivity of the rate to changes in the nature of the entering group suggests no more than weak bonding of the entering group to cobalt in the transition state.

### Introduction

Hydrolysis reactions of Co(III) amine complexes have been the subject of intensive study,<sup>2</sup> but the reverse reaction, "anation," has received much less attention. Yet anation has not only its intrinsic in-

terest but also offers information about the transition state of the hydrolysis process through application of the principle of microscopic reversibility.

The kinetics of reaction 1 in aqueous solution using the *cis* isomer were investigated by Basolo, Stone,



Bergmann, and Pearson.<sup>3</sup> They found that the reaction was first order in the complex, first order in the

(1) From a thesis by M. P. J. submitted in fulfillment of a requirement for the B.A. degree with honors, Amherst College, 1963. This work was supported by a grant from the Research Corporation and presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 8–13, 1963.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

(3) F. Basolo, B. D. Stone, J. G. Bergmann, and R. G. Pearson, *J. Am. Chem. Soc.*, **76**, 3079 (1954).