

of these compounds in the prior literature,<sup>2,3</sup> the present results are regarded as more accurate as well as more extensive. By the application of calibrations based

upon very well-known peaks, the probable error in the present work should not exceed 1 cm.<sup>-1</sup> for regions below 2000 cm.<sup>-1</sup>.

## Nucleophilic Constants and Substrate Discrimination Factors for Substitution Reactions of Platinum(II) Complexes

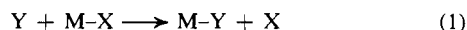
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Contribution from the Chemical Laboratory of Northwestern University, Evanston, Illinois, and the Istituto Chimica Generale, Università di Padova, Padova, Italy. Received July 15, 1964

The kinetics for the substitution reactions of six different platinum complexes of the type *trans*-[PtL<sub>2</sub>Cl<sub>2</sub>] with eighteen different nucleophilic reagents are reported. A set of nucleophilic reactivity constants,  $n_{Pi}$ , are defined for these reagents by selecting *trans*-[Pt(py)<sub>2</sub>Cl<sub>2</sub>] as a standard. Other platinum complexes then obey the equation  $\log k_Y = sn_{Pi} + \log k_S$ , where  $k_Y$  is a second-order rate constant for the nucleophile Y,  $s$  is a nucleophilic discrimination factor, and  $k_S$  is an "intrinsic" reactivity measure which is equal to the first-order rate constant for the reaction in which the solvent is the nucleophile. Complexes with a low intrinsic reactivity have a large value of  $s$ , and complexes which are highly reactive show little discrimination. Strong  $\pi$ -bonding ligands, in the *cis* position, produce low values of  $k_S$  but large values of  $s$ .

### Introduction

The chemical literature contains a large amount of data on rates of bimolecular, nucleophilic substitution reactions.



Here M is an electrophilic atom, which will be a metal in the cases of interest in this paper, Y and X are nucleophilic atoms or groups also called ligands, and M has other inert groups or ligands attached to it. The mechanism is the familiar SN<sub>2</sub> process in which a transition state, or possibly a reactive intermediate, of increased coordination number is formed with both Y and X bound to M. The substrate atoms (M), for which the most data are available,<sup>1</sup> include hydrogen, boron, carbon, nitrogen, oxygen, phosphorus, sulfur, platinum(II), and, more recently, palladium(II)<sup>2</sup> and gold(III).<sup>3</sup>

(1) For a review and references, see J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

(2) (a) R. G. Pearson and D. A. Johnson, *ibid.*, **86**, 3983 (1964); (b) W. H. Baddley, Doctoral Thesis, Northwestern University, Evanston, Ill., 1964.

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

A number of attempts have been made to correlate the rates of eq. 1 with other kinetic and thermodynamic data as Y is varied. These are all based on the principle of linear free-energy relationships.<sup>4</sup> Some of these include the Brønsted relationship,<sup>5</sup> the Swain and Scott equation,<sup>6</sup> and the Edwards equations.<sup>7</sup> The latter are particularly interesting in that the oxidation potential of the nucleophile is taken as one of the parameters.

Recent discussions have emphasized the fact that no one scale of nucleophilic reactivity exists but that the substrate M-X determines the order of effectiveness of various Y groups.<sup>1,8</sup> In particular a simple, useful rule may be formulated. If we define a "hard" acid or base as one of low polarizability and a "soft" acid or base as one of high polarizability, then hard acids combine best with hard bases and soft acids combine best with soft bases.<sup>8</sup> The nucleophilic-electrophilic interaction in the transition state of reaction 1 is, of course, a generalized acid-base reaction. Thus, polarizable metal atoms such as platinum(II) will react rapidly with easily polarizable reagents (which are also those of more positive oxidation potential).

While there is ample evidence to substantiate the above statement,<sup>8,9</sup> there is relatively little evidence as to how changes in the nature of the leaving group X and the inert ligands changes the selectivity of platinum complexes toward a series of nucleophilic reagents. A previous conclusion<sup>9a</sup> that increased negative charge on the complex increases the relative reactivity toward polarizable reagents must be viewed with some caution. The conclusion was based largely on a comparison of rates of reaction with chloride ion and nitrite ion. We

(4) For a general discussion and for details of the various equations proposed, see J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 9.

(5) J. N. Brønsted, *J. Am. Chem. Soc.*, **51**, 428 (1929).

(6) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

(7) J. O. Edwards, *ibid.*, **76**, 1540 (1954); **78**, 1819 (1956); see also D. H. McDaniel and A. Yingst, *ibid.*, **86**, 1334 (1964).

(8) R. G. Pearson, *ibid.*, **85**, 3533 (1963).

(9) (a) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 388 (1962); (b) H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962); (c) H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962).

have now found that nitrous acid in small amounts has a pronounced effect on the reactions of some platinum(II) complexes with nitrite ion. This subject will be reported on in detail at a later date. The rate data of the present paper with nitrite ion were obtained in alkaline solution in order to prevent the presence of  $\text{HNO}_2$ .

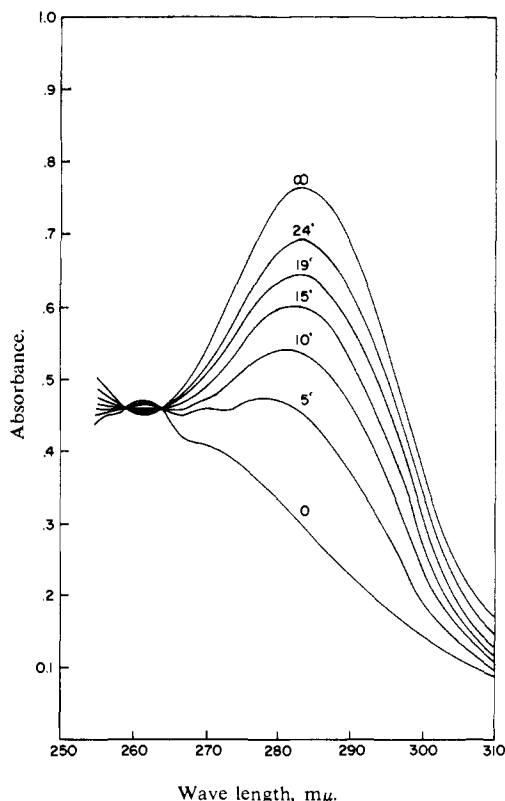


Figure 1. Spectral changes during the reaction in methanol at  $30^\circ$  of  $\text{trans-[Pt(py)}_2\text{Cl}_2]$  (zero time) with  $\text{I}^-$  to yield  $\text{trans-[Pt(py)}_2\text{I}_2]$  (infinite time); complex concentration  $5 \times 10^{-5} M$ .

In this work we report the results of an extensive kinetic study of the substitution reactions of a number of platinum(II) complexes of the type  $\text{trans-[PtL}_2\text{Cl}_2]$  with a variety of nucleophiles. The solvent was usually methyl alcohol and the temperature  $30^\circ$ . The object was, first, to try to order the nucleophiles in terms of relative reactivity and to see what properties made a reagent good, and, second, to observe the effect of changing the substrate platinum complex on the relative reactivities. Finally, it was hoped that a general, quantitative correlation of the rate constants might be found.

## Experimental

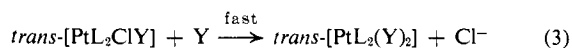
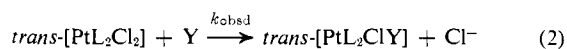
**Materials.** The Pt(II) complexes used in this investigation were all known compounds and were prepared by the methods reported in the literature. Each was characterized by means of a platinum analysis by burning the compound to yield a platinum residue. References to the methods of preparation are as follows<sup>10</sup>:  $\text{trans-[Pt(py)}_2\text{Cl}_2]$ ,<sup>11</sup>  $\text{trans-[Pt(pip)}_2\text{Cl}_2]$ ,<sup>12</sup>

(10) The symbols used are py, pyridine; pip, piperidine; Et, ethyl; s-Bu, *sec*-butyl; en, ethylenediamine; and dien, diethylenetriamine.

$\text{trans-[Pt(PEt}_3)_2\text{Cl}_2]$ ,<sup>13</sup>  $\text{trans-[Pt(AsEt}_3)_2\text{Cl}_2]$ ,<sup>13</sup>  $\text{trans-[Pt(S-(s-Bu)}_2)_2\text{Cl}_2]$ ,<sup>14</sup>  $\text{trans-[Pt(SeEt}_2)_2\text{Cl}_2]$ ,<sup>15</sup>  $[\text{Pt(en)-Cl}_2]$ ,<sup>16</sup> and  $[\text{Pt(dien)Cl}]_2$ .<sup>17</sup>

The solvent methanol was purified by distillation after refluxing over  $\text{Mg(OCH}_3)_2$  to remove water. The other chemicals were all reagent grade commercial materials and were used without further purification.

**Kinetics.** The rates of reaction were followed spectrophotometrically by measuring changes in optical density over a period of time at some selected wave length in the ultraviolet region. The instruments used were either a Beckman DK-2 or a Beckman DU with appropriate attachments to maintain the reaction mixture, contained in a 1-cm. quartz cell, at constant ( $\pm 0.1^\circ$ ) temperature. Each system was characterized at least once by recording the spectral change in the region 230–310  $m\mu$  during the reaction. In most cases, these spectra (Figure 1) showed well-defined isosbestic points which are indicative of only two absorbing species, the substrate and the product. This suggests that the reactions proceed by a slow, rate-determining first step (2) followed by a rapid second step (3). That this supposition is correct is supported by



the isolation and characterization of several of the reaction products. Such a result is understandable, realizing that the *trans* effects<sup>9a</sup> of most of the nucleophiles Y that were used are greater than the *trans* effect of  $\text{Cl}^-$ . This would not be the case for the reactions of  $[\text{Pt(en)Cl}_2]$  or for the reactions of the nucleophiles  $\text{NH}_3$ , py,  $\text{NH}_2\text{OH}$ , and  $\text{NH}_2\text{NH}_2$ . Nevertheless, for these reactions the experimental infinite time optical density was used, and the kinetic plots were linear for at least two half-lives. The method used to investigate the exchange of chloride ion is that described earlier.<sup>18</sup>

The kinetic studies were performed with an excess of reagent present to provide pseudo-first-order conditions. The substrate concentration varied between  $5 \times 10^{-5}$  and  $1 \times 10^{-3} M$  and the reagent concentrations from about  $5 \times 10^{-3}$  to  $10^{-1} M$ . The data obtained were plotted according to the usual first-order rate law. Excellent linear plots were obtained, and the values of the pseudo-first-order rate constants,  $k_{\text{obsd}}$ , were generally reproducible to better than 5%. Some curvature was obtained when an insufficient excess of reagent was used. In these few instances the values of  $k_{\text{obsd}}$  were estimated by considering only the initial points in the curves.

The solvent used was generally methanol, but in some cases it was necessary to use methanol–water (80:20

(11) G. B. Kauffman, *Inorg. Syn.*, 7, 251 (1963).

(12) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955).

(13) K. A. Jensen, *Z. anorg. allgem. Chem.*, 229, 225 (1936).

(14) K. A. Jensen, *ibid.*, 225, 115 (1935).

(15) K. A. Jensen, *ibid.*, 225, 94 (1935).

(16) F. Basolo, J. C. Bailar, Jr., and B. R. Tarr, *J. Am. Chem. Soc.*, 72, 2433 (1950).

(17) F. G. Mann, *J. Chem. Soc.*, 466 (1934).

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

**Table I.** Rates of Reaction<sup>a</sup> for Some Platinum(II) Complexes with Different Nucleophiles in Methanol at 30° and  $\mu = 0.1$

Y	<i>trans</i> -[Pt(py) <sub>2</sub> Cl <sub>2</sub> ]	<i>trans</i> -[Pt(pip) <sub>2</sub> Cl <sub>2</sub> ]	<i>trans</i> -[Pt(AsEt <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	<i>trans</i> -[Pt(PEt <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	<i>trans</i> -[Pt(SeEt <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	<i>trans</i> -[Pt(S(s-Bu) <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ] <sup>b</sup>	[Pt(en)Cl <sub>2</sub> ] <sup>c</sup>
CH <sub>3</sub> OH <sup>d</sup>	1 × 10 <sup>-6</sup>	1.2 × 10 <sup>-6</sup>	e	e	2 × 10 <sup>-6</sup>	1 × 10 <sup>-6</sup>	5 × 10 <sup>-6</sup> <sup>f</sup>
CH <sub>3</sub> O <sup>-</sup>	≤ 0.1	≤ 0.1	...	...	≤ 0.1	≤ 0.1	...
<sup>36</sup> Cl <sup>-</sup>	0.45 <sup>g</sup>	0.925	0.69	0.029	...	0.074	...
NH <sub>3</sub>	0.47	0.6	...	...	...	...	0.5
C <sub>6</sub> H <sub>5</sub> N	0.55	...	...	...	...	...	...
NO <sub>2</sub> <sup>-</sup>	0.68	2.04	0.1	0.027	1.11	...	...
N <sub>3</sub> <sup>-</sup>	1.55	5.30	0.8	0.2	7.5	...	1
NH <sub>2</sub> OH	2.9	...	...	...	...	...	...
H <sub>2</sub> NNH <sub>2</sub>	2.93	...	...	...	...	...	...
Br <sup>-</sup>	3.7	6.16	1.63	0.93	6.35	0.21	1.7
C <sub>6</sub> H <sub>5</sub> SH	5.7	...	...	...	...	...	...
SO <sub>3</sub> <sup>2-</sup>	250 <sup>g</sup>	400	...	...	...	...	...
I <sup>-</sup>	107	...	650	236	1100	1.94	22
SCN <sup>-</sup>	180	399	565	371	675	2.45	40
SeCN <sup>-</sup>	5150	3310	12,300 (ext.)	6950	13,500 (ext.)	...	...
C <sub>6</sub> H <sub>5</sub> S <sup>-</sup>	6000	...	...	...	...	...	...
S=C(NH <sub>2</sub> ) <sub>2</sub>	6000	3500	...	...	22,900 (ext.)	...	170
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	9000	...	...	...	...	...	...

<sup>a</sup> Values of  $10^3 k_Y$  in  $M^{-1} \text{sec}^{-1}$  and  $k_S$  in  $\text{sec}^{-1}$ . <sup>b</sup> 55°. <sup>c</sup> 35°, water solvent. <sup>d</sup> Values of  $k_S$  in  $\text{sec}^{-1}$ . <sup>e</sup> Value was too small to measure. <sup>f</sup> Value for H<sub>2</sub>O. <sup>g</sup> Estimated from the data on *trans*-[Pt(pip)<sub>2</sub>Cl<sub>2</sub>].

v./v.) in order to be able to dissolve sufficient reagent. Duplicate runs for the reaction of *trans*-[Pt(py)<sub>2</sub>Cl<sub>2</sub>] with I<sup>-</sup> and with thiourea show that the rates of reaction in these two solvents are almost the same. Whenever possible, the ionic strength was maintained at 0.1 by the addition of either LiClO<sub>4</sub> or LiNO<sub>3</sub>. Difficulties with precipitation or with low transmission of light prevented maintenance of the ionic strength in about one-fourth of the runs. However, the effect of ionic strength is small judging from a study of the rates of reaction of *trans*-[Pt(py)<sub>2</sub>Cl<sub>2</sub>] with I<sup>-</sup> at various ionic strengths. Reactions with NO<sub>2</sub><sup>-</sup> were carried out with added OH<sup>-</sup> (the concentration of OH<sup>-</sup> being <sup>1</sup>/<sub>10</sub> that of NO<sub>2</sub><sup>-</sup>) to prevent the formation of HNO<sub>2</sub>.

## Results

The rates of the reactions investigated follow the two-term rate law (4) that is well recognized for substitution reactions of platinum(II) complexes.<sup>9</sup> The rate constant  $k_1$  is for the solvent path, and  $k_2$  is for the

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{reagent}] \quad (4)$$

direct reagent path. For reaction 2, an excess of reagent was used, and the pseudo-first-order rate constant,  $k_{\text{obsd}}$ , was determined. This experimental rate constant is related to  $k_1$  and  $k_2$  as given by eq. 5. For

$$k_{\text{obsd}} = k_1 + k_2[Y] \quad (5)$$

each reaction, the values of  $k_{\text{obsd}}$  were determined at about five different concentrations of nucleophile, Y. Linear plots (Figure 2) of  $k_{\text{obsd}}$  vs. [Y] were obtained as is predicted by eq. 5. The extrapolated values of  $k_1$  (at zero [Y]) and the calculated values of  $k_2$  (slopes of the plots) are reported in Table I.

## Discussion

The assumption will be made that all the substitution reactions reported in this paper proceed by an S<sub>N</sub>2 mechanism. The evidence for this assumption

is ample and has been summarized elsewhere.<sup>19</sup> The experimental rate law contained in eq. 4 and 5 may now be rewritten as

$$k_{\text{obsd}} = k_S + k_Y[Y] \quad (6)$$

that is,  $k_1$  is interpreted as a pseudo-first-order constant for a bimolecular nucleophilic reaction of the solvent,

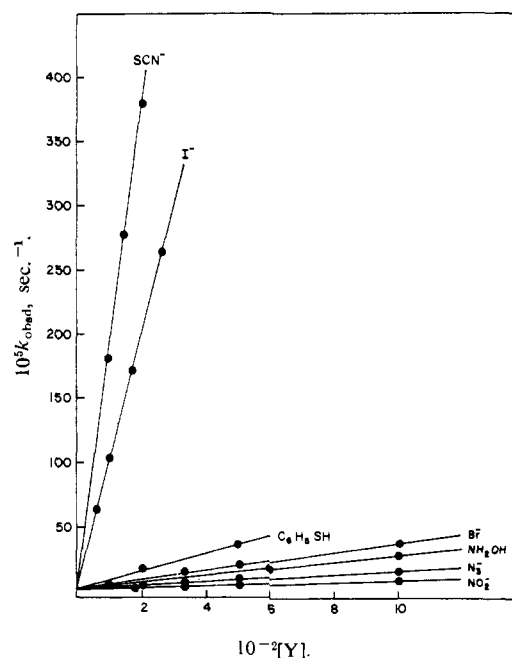
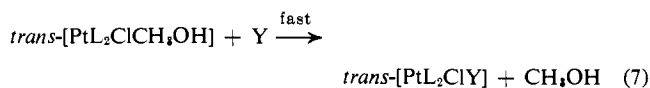


Figure 2. Rates of reaction of *trans*-[Pt(py)<sub>2</sub>Cl<sub>2</sub>] in methanol at 30° as a function of the concentrations of different nucleophiles.

$k_S$ , and  $k_2$  as a bimolecular constant for the nucleophilic reagent,  $k_Y$ . The methanol complex is known to

(19) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 4; see also ref. 9.

react rapidly with Y so that the product is the same for both the  $k_S$  and  $k_Y$  paths.



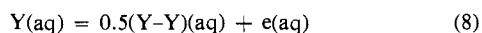
Quantitative evaluation of the nucleophilic properties of various reagents generally brings in their basicities toward the proton and a characteristic which may be loosely defined as polarizability or electronegativity. The nature of the electrophilic substrate determines which of the properties makes the greatest contribution. It is already known<sup>1</sup> that platinum(II) forms substrates in which basicity is of little importance. This is borne out by the present work as is shown by the kinetic data of Table I and the  $pK_a$  values of the nucleophiles listed in Table II.

Table II. Some Properties of Different Nucleophiles

Y	$E^\circ$ <sup>a</sup>	$pK_a$ <sup>a</sup>	$pK_{\text{CH}_3\text{Hg}^+}$ <sup>b</sup>	$n_{\text{Pt}}$
H <sub>2</sub> O	-2.60	-1.7	...	0 <sup>c</sup>
C <sub>6</sub> H <sub>5</sub> N	-1.40	5.3	4.8	1.74
Cl <sup>-</sup>	-1.36	(-4)	5.45	1.65 <sup>d</sup>
NH <sub>3</sub>	-0.76	9.5	8.4	1.67
Br <sup>-</sup>	-1.09	(-7)	6.7	2.79
N <sub>3</sub> <sup>-</sup>	-1.02	4.7	...	2.19
OH <sup>-</sup>	-0.95	15.7	9.5	≤ 1 <sup>c</sup>
NO <sub>2</sub> <sup>-</sup>	-0.87	3.4	...	1.83
SCN <sup>-</sup>	-0.77	(-0.7)	6.1	4.26
I <sup>-</sup>	-0.54	(-10)	8.7	4.03
SeCN <sup>-</sup>	(> -0.54) <sup>e</sup>	...	...	5.71
SO <sub>3</sub> <sup>2-</sup>	-0.03	9.1	8.16	4.40 <sup>d</sup>
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	+0.30 <sup>f</sup>	1.9	10.95	5.95
C <sub>6</sub> H <sub>5</sub> S <sup>-</sup>	(+0.3)	(7)	(19.7)	5.78
S=C(NH <sub>2</sub> ) <sub>2</sub>	+0.42	0.4	...	5.78
C <sub>6</sub> H <sub>5</sub> SH	...	...	...	2.75
NH <sub>2</sub> OH	...	9.8 <sup>g</sup>	...	2.46
H <sub>2</sub> NNH <sub>2</sub>	...	7.9 <sup>g</sup>	...	2.47

<sup>a</sup> Data from ref. 7. Values of  $E^\circ$  are for  $\text{Y(aq)} = 0.5(\text{Y}-\text{Y})(\text{aq}) + \text{e(aq)}$  <sup>b</sup> R. B. Simpson, *J. Am. Chem. Soc.*, **83**, 4711 (1961); M. Schellenberg and G. Schwarzenbach, Proceedings of the Seventh International Conference on Coordination Chemistry, Stockholm and Uppsala, Sweden, June 25-29, 1962, p. 157. <sup>c</sup> Value for CH<sub>3</sub>OH and CH<sub>3</sub>O<sup>-</sup>. <sup>d</sup> Estimated from the rates of reaction of *trans*-[Pt(pip)<sub>2</sub>Cl<sub>2</sub>]. <sup>e</sup> T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 466. <sup>f</sup> B. V. Ptitsyn and V. A. Kozlov, *Zh. Anal. Khim.*, **2**, 259 (1947). <sup>g</sup> F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 250-253.

Polarizability, on the other hand, seems to play a major role, and the only difficulty is to find a suitable set of numbers to assess quantitatively the polarizability or electronegativity effect. Edwards<sup>7</sup> has had success with the use of electrode potentials to estimate nucleophilic reactivities. It is very desirable to be able to use such extrakinetic data to predict rates of reaction. The disadvantage is that  $E^\circ$  values are not known for many common reagents, since the coupled product Y-Y is often incapable of existence in reaction 8. Table II gives the  $E^\circ$  values listed by Edwards<sup>7</sup>



for a number of cases. Several of these, such as for NH<sub>3</sub>, N<sub>3</sub><sup>-</sup>, and NO<sub>2</sub><sup>-</sup>, are only estimated. Figure 3

shows a plot of  $\log k_Y$  values vs.  $E^\circ$  values for the case of *trans*-[Pt(py)<sub>2</sub>Cl<sub>2</sub>]. There is indeed a rough correlation, similar to what has been noted before.<sup>1</sup> It is possible that some of the deviations are due to incorrect  $E^\circ$  values.<sup>20</sup> The other platinum(II) complexes give results similar to Figure 3 when plotted.

A number of attempts were made to find methods of correlating the rate data of Table I. One was to use the value of  $\lambda_{\text{max}}$  for the charge-transfer spectra of the complexes [Co(NH<sub>3</sub>)<sub>3</sub>X]<sup>2+</sup> where X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, N<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NH<sub>3</sub>. Such charge-transfer bands are a measure of the ease of transfer of an electron to the metal from the ligand.<sup>21</sup> While some correlation existed, no quantitative relationship could be found. This was also the case for the attempted correlation of rates with  $E^\circ - 0.5D$ , where  $D$  is the bond-dissociation energy of Y-Y in electron volts.

Since platinum(II) is a typical soft acid, it was thought that perhaps a series of equilibrium constants for some other, standard, soft acid could be used as a reference. This would parallel the use of  $pK_a$  values to correlate nucleophilic reactivity in the case of typical hard acid substrates (the Brønsted relationship). Table II shows a number of  $pK$  data for the formation constants of various bases with CH<sub>3</sub>Hg<sup>+</sup>, a soft acid (eq. 9). A  $\log k_Y - \log K_{\text{CH}_3\text{Hg}^+}$  plot shows about



as good a correlation as does Figure 3 for *trans*-[Pt(py)<sub>2</sub>Cl<sub>2</sub>] and the other platinum complexes studied. Hydroxide ion, or methoxide ion in methanol, is badly off again since at equilibrium it is bound fairly strongly to CH<sub>3</sub>Hg<sup>+</sup>, whereas it was not found to be a nucleophilic reagent for any of the platinum complexes. It is also known that hydroxide ion is bound strongly at equilibrium for platinum(II) complexes.<sup>22</sup>

Since none of the above attempts was satisfactory, it was finally decided to use the rate constants for the complex *trans*-[Pt(py)<sub>2</sub>Cl<sub>2</sub>] with various nucleophiles as standards. This complex was selected because data were available for the largest number of reagents. The procedure is essentially that of Swain and Scott<sup>6</sup> except that a different reference substrate is used. Methyl bromide, the reference used by Swain and Scott, gives constants which are correlated well by oxidation-reduction potentials.<sup>7</sup> Hydroxide ion would be assigned a fairly large nucleophilic constant in disagreement with the results for platinum(II).

We define a set of nucleophilic reactivity constants,  $n_{\text{Pt}}$ , by the equation

$$\log \left( \frac{k_Y}{k_S} \right)_0 = n_{\text{Pt}} \quad (10)$$

where  $k_Y$  and  $k_S$  refer to the rate constants for the reaction of *trans*-[Pt(py)<sub>2</sub>Cl<sub>2</sub>] in methanol at 30°. Table

(20) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, p. 54, has given a corrected value of  $E^\circ$  for NH<sub>3</sub> which fits the rate data much better. This value does not come from oxidation-reduction data but from other rate data, however.

(21) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962, Chapter 7.

(22) Reference 9a, p. 401; I. Leden and J. Chatt, *J. Chem. Soc.*, 2371 (1956); T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **80**, 536 (1958).

II gives values of  $n_{Pt}$  for a number of nucleophilic reagents. A plot of  $\log k_Y$  for other platinum complexes against  $n_{Pt}$  gives reasonably good straight lines in all cases. Figure 4 provides examples. This suggests the linear free energy relationship

$$\log k_Y = sn_{Pt} + \log k_S \quad (11)$$

The intercepts of plots such as Figure 4 are fairly close to the values of  $k_S$  for each substrate in those cases where  $k_S$  was measurable. For the  $PtEt_3$  and  $AsEt_3$  systems, the intercepts give predicted values of  $k_S$  which are small, in agreement with the observation that the rates are too slow to measure (Table I). It is also convenient that methoxide ion no longer is a problem, since its rate constant is immeasurably small for all complexes.

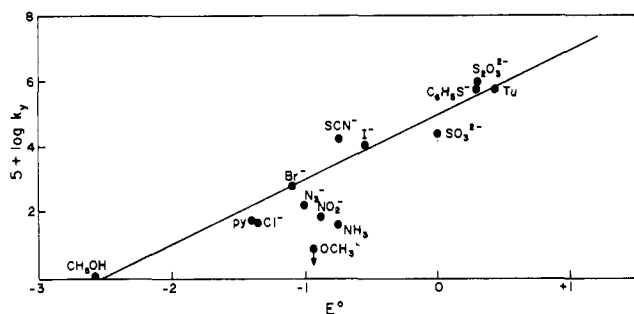


Figure 3. Rates of reaction of  $trans$ -[Pt(py) $_2$ Cl $_2$ ] in methanol at 30° with different nucleophiles as a function of their  $E^\circ$  values.

The constant  $s$  is dependent on the nature of the complex. It is a nucleophilic discrimination factor. A large value of  $s$  means that the complex is very sensitive to changes in the nature of the nucleophilic reagent. Table III gives values of  $s$  and  $\log k_S$  for several

Table III.<sup>a</sup> Nucleophilic Discrimination Parameters,  $s$ , and Intercepts,  $\log k_S$ , for Several Platinum(II) Complexes

Complex	$\log k_S^b$	Std. dev. of $\log k_S$	$s$	Std. dev. of $s$
$trans$ -[Pt(PEt $_3$ ) $_2$ Cl $_2$ ] <sup>c</sup>	-6.83 (-) <sup>d</sup>	0.35	1.43	0.10
$trans$ -[Pt(AsEt $_3$ ) $_2$ Cl $_2$ ] <sup>c</sup>	-5.75 (-) <sup>d</sup>	0.42	1.25	0.12
$trans$ -[Pt(S( <i>s</i> -Bu) $_3$ ) $_2$ Cl $_2$ ] <sup>e</sup>	-4.95 (-5.00)	0.05	0.57	0.02
$trans$ -[Pt(SeEt $_2$ ) $_2$ Cl $_2$ ] <sup>c</sup>	-4.67 (-4.70)	0.19	1.05	0.05
$trans$ -[Pt(pip) $_2$ Cl $_2$ ] <sup>c</sup>	-4.56 (-4.92)	0.13	0.91	0.04
[Pt(en)Cl $_2$ ] <sup>f</sup>	-4.33 (-4.30)	0.09	0.64	0.03
[Pt(dien)Br] <sup>g, h</sup>	-4.06 (-3.92)	0.21	0.75	0.07
[Pt(dien)Cl] <sup>g, i</sup>	-3.61 (-3.70)	0.25	0.65	0.06
[Pt(dien)H $_2$ O] <sup>2+, j</sup>	-0.44 <sup>k</sup>	0.37	0.44	0.12

<sup>a</sup> The intercepts,  $\log k_S$ , and slopes,  $s$ , for different nucleophiles,  $Y$ , were determined by the method of least squares using eq. 11. <sup>b</sup> Values in parentheses are the experimental values taken from Table I or from the literature. <sup>c</sup> Methanol solution at 30°. <sup>d</sup> Value was too small to determine experimentally. <sup>e</sup> Methanol solution at 55°. <sup>f</sup> Water solution at 35°. <sup>g</sup> Water solution at 25°. <sup>h</sup> From ref. 9b; eight nucleophiles. <sup>i</sup> From ref. 2b; four nucleophiles. <sup>j</sup> From ref. 9c; five nucleophiles. <sup>k</sup> This should equal the rate of water exchange, which is not known.

platinum(II) complexes. These are found from the slopes and intercepts of straight lines such as Figure 4 by the use of a least-squares analysis. Included are

not only the results in methanol but a few cases studied in water as the solvent. Some of these data are taken from the literature.

It can be seen that quite a reasonable spread of  $s$  values is found, from 0.44 to 1.43. Of course, two different solvents are involved and temperatures ranging from 25 to 55°, and  $s$  is expected to be a function of both temperature and solvent. The difference between water and methanol is not apt to be large, however, and only the data for the *sec*-butyl sulfide complex are at a temperature more than 5° different from 30°.

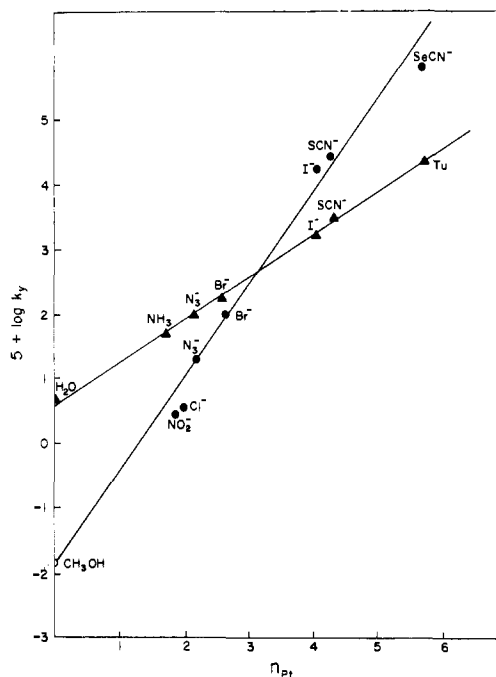


Figure 4. Correlation of the rates of reaction of Pt(II) complexes with the standard  $trans$ -[Pt(py) $_2$ Cl $_2$ ] for different nucleophiles: ●,  $trans$ -[Pt(PEt $_3$ ) $_2$ Cl $_2$ ] in methanol at 30°; ▲, [Pt(en)Cl $_2$ ] in water at 35°.

Ignoring this last case, there is a strong inverse correlation between  $s$  and  $k_S$ . A large value of  $s$  goes with a very small value of  $k_S$ .<sup>23</sup> Such a result is entirely reasonable if we interpret  $k_S$  as a measure of the "intrinsic" reactivity of the platinum complex; that is, it is the rate constant for the poorest nucleophilic reagent whose effect can be measured in any solution.<sup>24</sup> With such a poor nucleophile, the greatest burden is put on the complex to reach the activated complex for reaction. Now a complex of high intrinsic reactivity, such as [Pt(dien)H $_2$ O]<sup>2+</sup>, will not be very discriminating in reacting with different nucleophiles, and  $s$  will be small.<sup>25</sup>

The arsine and phosphine complexes show the largest discrimination between various reagents and the lowest intrinsic reactivity. It is probably sig-

(23) This statement may not always apply for reactions involving different leaving groups. Thus, the  $s$  values for [Pt(dien)Cl]<sup>+</sup> and [Pt(dien)H $_2$ O]<sup>2+</sup> differ less than might be expected on the basis of their large difference in  $k_S$ .

(24) If any nucleophile, such as ClO $_4^-$ , has a rate constant less than the solvent, its kinetic effect will never be measurable.

(25) The limiting case of such a reactive species with low discrimination would be a high energy species of reduced coordination number, such as the carbonium ion in organic chemistry. Compare the discussion in C. G. Swain, C. B. Scott, and K. H. Lohmann, *J. Am. Chem. Soc.*, 75, 135 (1953).

nificant that these two complexes are generally believed to be capable of the largest amount of metal-to-ligand  $\pi$ -bonding. Such  $\pi$ -bonding is probably small in the ground state but becomes quite large in the transition state.<sup>26</sup> It is a variable which can respond to satisfy a demand. Thus, if the more reactive reagents donate electrons more strongly to the platinum atom in the transition state, then more  $\pi$ -bonding can occur to remove excess charge from the metal. It should be recalled that the primary bonding interaction between soft acids and soft bases is believed to be covalent in character.<sup>8</sup>

(26) L. E. Orgel, *J. Inorg. Nucl. Chem.*, 2, 137 (1956); D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964); C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, p. 7 and Chapter 9.

One final point of interest is that  $n_{Pt}$  for  $NH_2NH_2$  and  $NH_2OH$  is appreciably larger than for  $NH_3$ , pyridine,  $NO_2^-$ , and  $N_3^-$ . This suggests that the  $\alpha$ -effect<sup>1</sup> is responsible for their greater reactivity compared to other nucleophiles in which the donor atom is nitrogen.

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