TABLE V

ACTIVATION ENERGIES AND ENTROPIES IN NUJOL SOLUTIONS

Solute	$\Delta F_\epsilon^\ddagger$	$\Delta H_\epsilon^\ddagger$	$\Delta S_\epsilon^\ddagger$	ΔH_v	n
2,2-Dichloropropane[25]	1.77	1.60	−0.6	9.54	0.17
2,2-Dinitropropane[25]	2.20	1.99	−0.7	9.54	.20
d,l-Camphor	2.77	2.42	−1.2	10.5	.23
α-Chloronaphthalene[12]	3.50	3.63	0.5	9.54	.38
Isoquinoline	3.52	4.51	4.0	10.5	.43
4-Bromobiphenyl	5.61	9.00	11.5	10.5	.85
Acridine	5.17	11.0	19.8	10.2	1.1
Acridine (in decalin)	3.39	3.07	−1.1	3.35	0.92

disturbance of the surrounding molecules upon rotation of the elongated molecules. The changes in $\Delta S_\epsilon^\ddagger$ are consistent with this, except for acridine, which has a somewhat larger $\Delta S_\epsilon^\ddagger$ than 4-bromobiphenyl, and for α-chloronaphthalene, which has a very low value. Comparison with solution data for α-chloronaphthalene[12] in *n*-heptane shows that the increase in $\Delta S_\epsilon^\ddagger$ from heptane to Nujol solution is actually large, since the $\Delta S_\epsilon^\ddagger$ in heptane is very low, −4.0 e.u. Thus, the change in $\Delta S_\epsilon^\ddagger$ for α-chloronaphthalene from heptane to Nujol is +4.5 e.u., while for camphor it is $3.2 - 1.4 = 1.8$ only. The $\Delta H_\epsilon^\ddagger$ values increase generally from the spherical molecules to the elongated ones, with 4-bromobiphenyl and acridine having values in the neighborhood of those for $\Delta H_\epsilon^\ddagger$. The ratio n of $\Delta H_\epsilon^\ddagger$ to $\Delta H_\eta^\ddagger$ in Table V goes from 0.16 to about 1.1 as the molecular shape changes. One may consider that only part of the forces acting in viscous flow hinder the dipole rotation and write $\Delta H_\epsilon^\ddagger = n\Delta H_\eta^\ddagger$. By using the rate equations for dielectric relaxation and viscous flow one can derive an empirical relationship $\tau = C\eta^n/T$, which satisfactorily represents the dependence of τ upon viscosity and temperature, C being a constant for each substance. This essentially empirical equation may be of value in the analysis of relaxation time data.

PRINCETON, NEW JERSEY

[25] R. S. Holland, G. N. Roberts and C. P. Smyth, THIS JOURNAL, **78**, 20 (1956).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. XVI.[1] Exchange Reactions of Platinum(II) Complexes in Various Solvents[2]

BY RALPH G. PEARSON, HARRY B. GRAY AND FRED BASOLO

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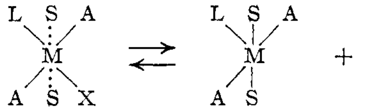
The rate of chloride exchange of *trans*-Py(py)$_2$Cl$_2$ in a variety of solvents depends upon the properties of the solvent in a way consistent with strong interaction of the solvent and metal ion in the rate-determining step. Solvents with empty, or potentially empty, orbitals are particularly effective probably because of π-bonding to the platinum. The term ***biphilic*** reagent is proposed for substances which can simultaneously donate and accept electrons in substitution reactions.

Previous studies[3] on the substitution reactions of planar complexes of platinum(II) showed that a division of nucleophilic reagents (ligands) into two classes could be made. In one class were good reagents, whose reaction rates were high and depended on the concentration of the reagent; in the other class poor reagents with rates independent of concentration and, for a given complex ion, the same rate of reaction. This paper is a study of the mechanism of reaction of the latter class of reagents. As a typical example, chloride ion has been picked since, in a number of cases,[4] the exchange of chloride ion with chloro complex in aqueous solution goes by processes zero order in chloride ion.

A fairly detailed mechanism for the reaction sequence with poor reagents has been proposed.[5] In the absence of strong π-bonding groups, which might favor rearrangement to a trigonal bipyramid intermediate, the mechanism may be described as a "dissociation" with a five-coördinated intermediate which resembles a square pyramid. The mechanism thus assigns a heavy role to the solvent which is considered to occupy coördination sites above and below the square plane.[6] In dissociation of a labile group, two solvent molecules move in from a rather long bonding distance to a shorter one, thus helping to push off the leaving group, *viz.*



(1)

Such a process can serve as a path for chloride exchange with or without the intermediate formation of the solvated complex, MLA$_2$S.

In view of the participation of the solvent postulated in equation 1, a logical test is to study a chloride exchange reaction in a series of solvents to see whether a correlation exists between the coördinating properties of the solvent and the rate of exchange. The reaction selected was

$$trans\text{-Pt(pyridine)}_2\text{Cl}_2 + {}^*\text{Cl}^- \longrightarrow trans\text{-Pt(py)}_2{}^*\text{Cl}_2 + \text{Cl}^- \quad (2)$$

This complex was chosen because it is soluble in a wide variety of solvents although it is insoluble in water. The labeled chloride ion was added in the form of the quaternary salt, *n*-octadecylbenzyldimethylammonium^{36} chloride, or as H^{36}Cl in a few

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[1] Previous paper in this series, R. G. Pearson, R. A. Munson and F. Basolo, THIS JOURNAL, **80**, 504 (1958).

[2] This investigation is partly supported by a grant from the U. S. Atomic Energy Commission under contract AT(11-1)-89-project No. 2.

[3] D. Banerjea, F. Basolo and R. G. Pearson, THIS JOURNAL, **79**, 4055 (1957).

[4] T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., *ibid.*, **81**, 10 (1959).

[5] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 186–190. See also ref. 4, p. 17.

[6] Evidence for groups above and below the plane in "square" complexes is now extensive. See ref. 5, p. 186.

cases. Because of the method of separation used, it was not possible to use amine solvents, since AgCl is rather soluble in such systems. For the same reason the solvent dimethylformamide is not very suitable and the experimental error in this solvent is large.

Experimental and Results

Preparation and Purification of Materials.—*trans*-Dichlorodipyridineplatinum(II) was prepared from tetrapyridineplatinum(II) chloride by heating the solid salt for 30 minutes at 165°. The yellow product was washed with water to remove unreacted salt, filtered, recrystallized from acetone and analyzed.[7]

cis-Dichlorobis-(4-amylpyridine)-platinum(II) was prepared from K_2PtCl_4 and 4-amylpyridine in aqueous acetone following the method of Weiss.[8] The yellow product was purified by recrystallization from aqueous acetone and analyzed.

cis-Dichlorobis-(α-picoline)-platinum(II) was obtained by a method analogous to that of Ramberg.[9] The yellow product, which would not react further with α-picoline, was recrystallized from acetone. *Anal.* Calcd. $Pt(C_6H_7N)_2Cl_2$: Pt, 43.5; C, 31.9; H, 3.1. Found: Pt, 42.74; C, 31.21; H, 3.04.

n-Octadecylbenzyldimethylammonium chloride was obtained from the Rohm and Haas Co. The inactive compound was tagged with radiochloride by passing its alcoholic solution through a strong base resin (Amberlite IRA 400) and neutralizing the hydroxide formed with $H^{36}Cl$. After evaporating to dryness, the product was recrystallized from acetone, m.p. 62°.

Absolute ethanol was used directly; 1-propanol was dried with calcium oxide and fractionated, b.p. 95–96°; *t*-butyl alcohol was dried with lithium aluminum hydride and fractionated, b.p. 82–83°; acetone was dried with potassium carbonate and distilled, b.p. 56.5°; ethyl acetate was washed first with aqueous potassium carbonate, then with water, dried and fractionated from phosphorus pentoxide, b.p. 77°; carbon tetrachloride was dried with calcium chloride and distilled, b.p. 76.7°; ethylene dichloride was washed first with sulfuric acid, then with water, dried with calcium chloride and fractionated, b.p. 83.4–83.7°; benzene was dried with sodium and fractionated, b.p. 80°; dimethyl sulfoxide was distilled, b.p. 86° (21 mm.); nitromethane was washed with aqueous sodium hydrogen carbonate, dried with calcium chloride and fractionated, b.p. 100.8–101.1°; dimethylformamide was dried with calcium oxide and distilled, b.p. 153°; acetonitrile was dried with potassium carbonate and fractionated, b.p. 80–82°; acetic acid was refluxed with potassium permanganate and fractionated, b.p. 117–118°; *m*-cresol was fractionated, b.p. 200–202°; other materials used were reagent grade.

Determination of the Rate of Chloride Exchange.—Separate solutions of the complex and of $R_4N^{36}Cl$ or $H^{36}Cl$ were prepared in the solvent to be used. The concentration of the complex always was taken as 0.0010 *M* except where the solubility was too slight. This was the case in ethyl, *n*-propyl and *t*-butyl alcohols, ethylene dichloride and carbon tetrachloride. However the concentrations in these solvents were near 0.001 *M* except for CCl_4, 0.0035 *M* and *t*-butyl alcohol 0.00020 *M*. The $H^{36}Cl$ was obtained from the AEC as a concentrated aqueous solution. This was diluted with alcohol and then with the solvent to be used so that about 1% of alcohol and 0.2% of water were actually added as well as the HCl. The separate solutions were mixed and then diluted with the solvent to the required volume and thermostated at 25.1 ± 0.05°. Aliquots of 0.20 ml. were removed at known intervals and the uncomplexed chloride was precipitated by adding 20% excess of the required quantity of alcoholic silver nitrate solution. In solvents in which the solubility of silver chloride is appreciable a larger volume of a more dilute silver nitrate solution was used. The mixture was centrifuged for 4 min. and then an aliquot of the clear supernatant liquid was withdrawn and evaporated on a disc of filter paper in an aluminum tray under strong infrared light. The activity of all these samples was then counted in a Scaling Unit, Model 182A, Nuclear Instruments and Chemical Corporation, Inc. These data were analyzed as described earlier[3] and the rate constants calculated are given in Tables I–VI.

Spectral Studies.—Spectra were taken with a Beckman DK-2 double beam recording spectrophotometer, programmed for maximum resolution (expanded scale and slow scanning) which was in a constant temperature room maintained at 23.5 ± 1°. Freshly prepared solutions 0.010 *M* in K_2PtCl_4 were used in 1-cm. quartz cells. The results are shown in Table VII.

TABLE I

RATES OF CHLORIDE EXCHANGE IN SOLVENTS IN WHICH THE RATE IS INDEPENDENT OF $R_4N^{36}Cl$ AT 25.1°

Solvent	Concn. of $R_4N^{36}Cl$, *M*	k_{obs}, min.$^{-1}$	k, min.$^{-1}$	ϵ (solvent)
H_2O			2.1×10^{-3a}	80
$(CH_3)_2SO$	0.00085	2.38×10^{-2}	2.3×10^{-2}	45
	.00253	(1) 2.24×10^{-2}		
	.00253	(2) 2.30×10^{-2}		
CH_3NO_2	.0010	1.97×10^{-3}	1.92×10^{-3}	39
	.0015	1.92×10^{-3}		
	.0030	1.93×10^{-3}		
	.0070	1.80×10^{-3}		
C_2H_5OH	.00080	8.50×10^{-4}	8.5×10^{-4}	24
	.0013	8.50×10^{-4}		
	.0023	8.40×10^{-4}		
	.0063	7.50×10^{-4}		
	.0076	8.45×10^{-4}		
	.0010	8.10×10^{-4a}		
n-C_3H_7OH	.00108	2.5×10^{-4}	2.5×10^{-4}	20
	.00306	2.5×10^{-4}		

[a] These data refer to *trans*-$Pt(NH_3)_2Cl_2$.

TABLE II

RATES OF CHLORIDE EXCHANGE AT 25.1° IN CH_3NO_2 WITH ADDED CH_3COOH OR CF_3COOH

Concn. of $R_4N^{36}Cl$, *M*	Concn. of CH_3COOH, *M*	Added substance	k, min.$^{-1}$
0.0010		....	2.0×10^{-3}
.0011	2.2	....	2.4×10^{-2}
.00375	2.2	....	3.0×10^{-2}
.00375	2.2	0.0125 *M* NaOAc	3.64×10^{-3}
.00375	4.4	....	14.8×10^{-2}
.0010	Glacial	....	Too fast to measure
.0035	..	3.45 *M* EtOAc	8.1×10^{-4}
.0018	2.2^a	....	2.1×10^{-2}

[a] CF_3COOH.

TABLE III

RATES OF CHLORIDE EXCHANGE AT 25.1° WITH ADDED H_3BO_3[a]

Complex	Concn. of R_4N^{36}-Cl, *M*	Concn. of H_3-BO_3, *M*	Added substances	k, min.$^{-1}$
trans-$Pt(py)_2Cl_2$	0.0076	...	....	8.45×10^{-4b}
	.006	0.075	....	31.2×10^{-4}
	.006	.075	0.2 *M* NaOH	14.3×10^{-4}
	.010	.075	....	32.7×10^{-4}
cis-$Pt(4\text{-ampy})_2Cl_2$	.005	...	....	6.55×10^{-4b}
	.006	.075	....	17.9×10^{-4}
	.006	.075	0.2 *M* NaOH	9.25×10^{-4}
	.010	.075	....	18.2×10^{-4}

[a] The solvent consisted of 90% ethyl alcohol and 10% water. [b] This value for 100% ethyl alcohol.

Discussion

Experimentally the exchange reactions of *trans*-$Pt(py)_2Cl_2$ with $R_4N^{36}Cl$ in different solvents fall into three groups: (1) those that are first order in

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[7] S. G. Hedin, *Acta Univ. Lundensis*, [II] **22**, No. 3 (1886).

[8] R. N. Weiss, M.S. thesis, Northwestern University, 1958.

[9] L. Ramberg, *Z. anorg. Chem.*, **83**, 33 (1913).

TABLE IV

RATES OF CHLORIDE EXCHANGE IN SOLVENTS IN WHICH THE RATE IS FIRST ORDER IN CHLORIDE AT 25.1°

Solvent	Concn. of $R_4N^{36}Cl$, M	k_{obsd}, min.$^{-1}$	$kK_{eq}^{1/2}$, $M^{-1/2}$ min.$^{-1}$	k, M^{-1} min.$^{-1}$
CCl_4	0.00080	(1) 8.3×10^{-4}	2.80×10^{-2}	10^6
	.00080	(2) 7.2×10^{-4}		
	.00080	(3) 8.6×10^{-4}		
	.0014	10.2×10^{-4}		
	.0016	11.2×10^{-4}		
C_6H_6	.0016	2.5×10^{-4}	6.35×10^{-3}	10^4
	.0023	2.95×10^{-4}		
	.0028	3.29×10^{-4}		
	.0048	4.37×10^{-4}		
	.0085	6.50×10^{-4}		
m-Cresol	.00254	2.82×10^{-4}	5.60×10^{-3}	10^1
	.00328	3.08×10^{-4}		
	.0055	4.22×10^{-4}		
t-BuOH	.00108	13.4×10^{-4}	4×10^{-2}	10^1
	.0012	13.8×10^{-4}		
	.00282	21.0×10^{-4}		
CH_2ClCH_2Cl	.00079	6.45×10^{-4}	2.30×10^{-2}	10^1
	.0010	7.30×10^{-4}		
	.00375	14.20×10^{-4}		
EtOAc	.001075	4.22×10^{-5}	1.3×10^{-3}	1
	.00537	1.49×10^{-4}		
$(CH_3)_2CO$	.00050	1.58×10^{-4}	1.02×10^{-2}	1
	.00068	2.92×10^{-4}		
	.00080	2.98×10^{-4}		
	.0016	4.09×10^{-4}		
	.0018	4.24×10^{-4}		
	.0047	6.87×10^{-4}		
	.0060	8.60×10^{-4}		
$HCON(Me)_2$	.0010	9.2×10^{-4}		10^{-1}
	.0030	16.8×10^{-4}		
CH_3CN	.00085	0.64×10^{-3}		7.6×10^{-1}
	.0016	1.2×10^{-3}		
	.0024	1.82×10^{-3}		

TABLE V

RATES OF CHLORIDE EXCHANGE OF *trans*-$Pt(py)_2Cl_2$ WITH $H^{36}Cl$ AT 25.1°

Solvent	Concn. of $H^{36}Cl$, M	k_{obsd}, min.$^{-1}$
C_6H_6	0.0010	6.90×10^{-5}
	.0050	18.70×10^{-5}
CH_3NO_2	.0010	6.56×10^{-4}
	.0030	20.5×10^{-4}
	.0075	20.0×10^{-4}
CCl_4	.00050	(1) 9.0×10^{-6}
	.00050	(2) 8.5×10^{-6}
	.00250	7.95×10^{-6}
CH_3CN	.00080	7.6×10^{-4}
	.0024	24.7×10^{-4}

TABLE VI

STERIC FACTOR IN EXCHANGE REACTIONS OF Pt(II) COMPLEXES IN ETHANOL AT 25.1°

Complex	Reactant, Y	Concn. of Y, M	k, min.$^{-1}$
cis-$Pt(4\text{-ampy})_2Cl_2$	$^{36}Cl^-(R_4NCl)$	0.0050	6.55×10^{-4}
cis-$Pt(\alpha\text{-pic})_2Cl_2$	$^{36}Cl^-(HCl)$	0.00143	2.88×10^{-5}

TABLE VII

THE SPECTRUM OF K_2PtCl_4 IN VARIOUS SOLVENTS. POSITIONS OF THE PRINCIPAL MAXIMA IN THE NEAR ULTRAVIOLET REGIONS[a]

Solvent	Maxima, mμ
12 M HCl	384, 325
H_2O	390, 329
3% aq. H_3BO_3	391, 331
50% aq. EtOH	391, 332
50% aq. CH_3COOH	392, 333
50% aq. $(CH_3)_2CO$	394, [b]
70% aq. CH_3CN	394, 333
$(CH_3)_2SO$	401,[c] 336

[a] Extinction coefficients independent of solvent except as indicated in footnote *c*. [b] Solvent absorbs in this region. [c] Very weak.

both complex and R_4NCl; (2) those that are first order in complex and half order in R_4NCl; (3) those that are first order in complex and zero order in R_4NCl. If we assume that the chloride ion is the reagent, group 2 can be combined with (1) into a category of reactions first order in both complex and chloride ion. This follows from the fact that in most of the group 2 solvents the R_4NCl is present as an ion pair in equilibrium with free single ions

$$R_4N^+Cl^- \rightleftarrows R_4N^+ + Cl^- \qquad (3)$$

$$[Cl^-] = K_{eq}^{1/2}\,[R_4N^+Cl^-]^{1/2}$$

The situation is undoubtedly more complicated in solvents of very low dielectric such as C_6H_6. Kraus[10] has summarized the state of electrolytes in C_6H_6 and finds that for quaternary chlorides there is considerable aggregation even at 10^{-4} molar con-

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(10) C. A. Kraus, *J. Chem. Ed.*, **35**, 330 (1958).

centration. However, Hughes, *et al.*,[11] have done a detailed conductance study on quaternary chlorides in C_6H_6 and find that although triple ions carry the major portion of the current at 10^{-3} *M* R_4NCl concentration, it so happens that the concentration of free chloride ions is proportional to the square root of the concentration of R_4NCl. This is quite consistent with our experimental data if we assume single chloride ions are the active reagents in the exchange. A plot of $\sqrt{R_4NCl}$ *vs.* *k* for C_6H_6 is shown in Fig. 1. From the slope of this plot a value of $kK_{eq}^{1/2}$ can be calculated, where *k* is a second-order rate constant.

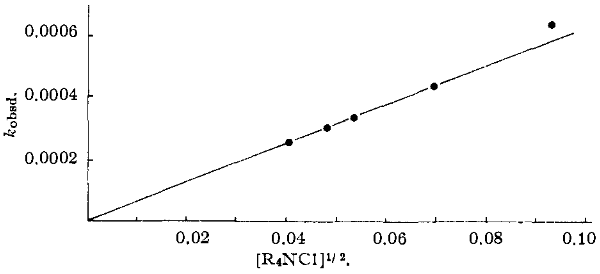

Fig. 1.—Observed rate constant for chloride exchange as a function of the concentration of R_4NCl in benzene.

Table I lists all the solvents in which the exchange is independent of chloride. The order of the rates of exchange is the same as that of the dielectric constants of the solvents except in the case of $(CH_3)_2SO$, which is a better solvent for reactions of Pt(II) than its dielectric constant indicates. Nitromethane, which is a non-hydrogen-bonding solvent and a very poor solvent for the reactions of octahedral Cr(III) complexes,[12] also appears unusually good for reactions of Pt(II). Another solvent which probably belongs in Table I is glacial acetic acid. It was found that the rate of exchange in this case was too fast to measure. However by adding acetic acid to nitromethane it was possible to study the effect of the acid on the rate (Table II). The complex was too insoluble in methyl borate to use it as a solvent. The exchange reaction in a mixture of methyl borate and nitromethane was slower than in pure nitromethane. However, the effect of adding boric acid and sodium borate on the rate of exchange in water–alcohol is shown in Table III.

Table IV lists the solvents in which the exchange appears to be first order in chloride ion. It should perhaps be emphasized that the possible reaction of ion pairs or higher aggregates is not completely excluded. Such reactions, however, are not needed to explain our data. In DMF and acetonitrile the quaternary chloride may be considered completely ionized in agreement with the behavior of other salts in these solvents.[13] Accordingly the rates should be first order in added salt. The large experimental error in the case of DMF prevents this conclusion from being checked. In the other solvents, the product of a rate constant and an equilibrium constant is obtained. While the value of K_{eq} is not known for our salt, R_4NCl, in any of these solvents, values for quite similar salts have been measured for most of them.[14] Accordingly estimates have been made of the magnitude of K_{eq} for all the solvents in Table IV, using the rough[15] guide

$$\log K_{eq} = A - B/\epsilon \qquad (4)$$

where *A* and *B* are constants and ϵ is the dielectric constant, for solvents where no data were available. This procedure enables an approximate value of the rate constant *k* to be calculated so that all solvents can be compared on the same basis. These values of *k* are given in the last column of Table IV.

It seems evident that the rate constants calculated in this way are in agreement with the expected solvent properties. Thus in a poor solvent for ions such as CCl_4, the chloride ion has a high reactivity and *k* is large. In a good solvent such as DMF, acetone or acetonitrile, the chloride ion is rather stable and *k* is small. In the latter three cases the question arises as to why these solvents do not appear in Table I, particularly in the case of CH_3CN where it is known[16] that two molecules of solvent are held strongly in position above and below the plane of the complex. In view of the postulated mechanism shown in (1), it would be expected that such strong interaction would facilitate the displacement of chloride ion from the complex. Hence external chloride ion as a reagent would not be necessary.

The structure of the species $[Pt(NH_3)_4(CH_3CN)_2Cl_2]$ as determined by X-ray studies[17] suggests an explanation for the kinetic behavior. The acetonitrile molecules lie with their axes parallel to the plane of the platinum complex and a distance of 3 Å. compared to a normal Pt–N distance of about 2 Å. The bonding is between the triple bond of the C≡N group and the Pt atom, similar to the platinum–olefin complexes. Such bonding may be strong but the parallel arrangement of the CH_3CN molecule does not permit a closer distance of approach because of steric repulsion between the CH_3 group and the groups lying in the plane. Hence the displacement shown in (1) may not be possible. It then becomes necessary to assume that acetone and DMF also coördinate to the complex through their carbonyl double bonds. Benzene and *m*-cresol may also assume a planar arrangement above and below the complex.

In Table V are the results of the exchange reaction of *trans*-$Pt(py)_2Cl_2$ with HCl. Since HCl is probably completely dissociated in CH_3CN at the concentrations used, the exchange rate is the same as that with R_4NCl. In CH_3NO_2 and C_6H_6 the reaction with HCl is similar to the one with R_4NCl. The fact that the results with HCl in C_6H_6 and CCl_4 are so different probably is evidence of π-type complexing of C_6H_6 and HCl.[18] Chloride ion prob-

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(11) E. D. Hughes, C. K. Ingold, S. Patai and Y. Pocker, *J. Chem. Soc.*, 1206 (1957).

(12) A. W. Adamson, THIS JOURNAL, **80**, 3193 (1938).

(13) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1958, pp. 703–705.

(14) Reference 13, pp. 293–295 and 703–705.

(15) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **79**, 3304 (1957).

(16) L. Tschugaeff, *Compt. rend.*, **161**, 563 (1915).

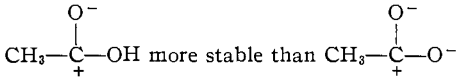
(17) C. M. Harris and N. C. Stephenson, *Chemistry and Industry*, **14**, 426 (1957).

(18) H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

ably can dissociate from this complex and react, but HCl is completely associated in CCl_4. Hence the concentration of free chloride ion is so small that some other mechanism involving the solvent as a displacing agent takes over.

Considering again the solvents where the rate of exchange does not depend on the chloride ion, it is necessary to explain the high reactivity of solutions in dimethyl sulfoxide and nitromethane. Also it appears from Tables II and III that acetic acid and boric acid are extremely "fast" solvents.[19] It is clear that the order of reactivity of the solvent does not parallel the usual kind of coördinating ability toward metal ions. This property would place water first, ethyl alcohol next and nitromethane last. However it is just the solvents which are fast for exchange reactions of platinum(II) which have available potentially vacant orbitals of a type capable of bonding with the filled d_{yz} or d_{xz} orbitals of the platinum atom. These are the orbitals which project above and below the plane of the complex. Figure 2 shows how such π-bonding may permit these solvent molecules to approach so that their basic oxygen atoms are very close to Pt and in a good position to displace Cl^- from the complex. Alternatively, one may say the transition state is stabilized by π-bonding.

It is of importance that acetate ion does not have the accelerating ability of molecular acetic acid.[20] In fact Table II shows inhibition of chloride exchange by acetate ion. Table III also shows that converting boric acid to borate ion destroys its accelerating effect. These are reasonable results since the empty orbital is less available in these anionic forms, *i.e.*



$$CH_3-\overset{\overset{O^-}{|}}{\underset{+}{C}}-OH \text{ more stable than } CH_3-\overset{\overset{O^-}{|}}{\underset{+}{C}}-O^-$$

The failure of methyl borate and ethyl acetate to behave as the acids do may be due to one of two causes. In the case of the esters there is steric crowding in forming the structure shown in Fig. 2; hydrogen-bonding between the acid proton and one of the chlorine atoms of the complex may stabilize the transition state.

The low reactivity in *m*-cresol, which could also hydrogen bond to chlorine, indicates that solvation of the leaving chloride ion by this process is not of great importance. This is also borne out by the failure of HCl to show any large increases in rate compared to chloride ion.

The solvents, dimethyl sulfoxide, nitromethane, acetic acid and boric acid, have the same properties as those reagents that were found to be good nucleophiles for platinum(II), such as NO_2^-, allyl alcohol, trialkylphosphine and thiourea.[8] That is, they can both donate electrons to the metal atom and accept electrons from the metal atom. It is proposed that the name *biphilic* reagent be used to describe such ions and molecules.

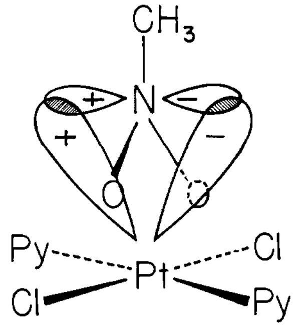


Fig. 2.—π-Bonding (metal to ligand) in the interaction of solvent molecules with platinum (II).

The importance of solvation above and below the plane in determining the rates of certain reactions of platinum(II) may be shown by blocking these positions by groups attached to the ligands in the plane. An example is given in Table V. The rate of dissociation of *cis*-Pt-(α-pic)$_2$Cl$_2$ is 1/25 that of *cis*-Pt(4-ampy)$_2$Cl$_2$ in ethanol. This is believed to result from the methyl groups of the picoline partially blocking access of solvent to the metal atom. A number of similar examples, some of them very striking, have been found and will be published separately.[21]

Spectral Studies.—A brief study of the effect of various added substances on the positions of the principal maxima in the visible and near ultraviolet spectrum of $PtCl_4^{2-}$ was made after the kinetic work was finished. The study was prompted by the interesting paper of Harris, Livingstone and Reece[22] on the visible and ultraviolet spectra of $PtCl_4^{2-}$ and $PdBr_4^{2-}$ in various solvents. These authors found that the solvents could be arranged in the order $H_2O > CH_3CN > CH_3OH >$ acetone $> CH_3NO_2 >$ acetic anhydride $> C_6H_5NO_2$, as far as the effect of shifting the maxima to shorter wave lengths is concerned. They then concluded that this was also the order of decreasing interaction of the solvents with the complex in the positions above and below the plane. Since 10 *M* HCl affected the spectrum of $PdCl_4^{2-}$ more than that of $PtCl_4^{2-}$, it was concluded that solvent interactions with Pd(II) were greater than for Pt(II).

This conclusion is probably correct, but it may be seen from Table VII that considerable interaction with Pt(II) does occur. The shifts observed are of the same magnitude as for those of Pd(II). Interestingly, evidence for interaction with HCl occurs only in concentrated solution (10–12 *M*) where a high activity of molecular HCl exists. It is likely that it is the molecule which adds above and below the plane as opposed to the case of Pd(II) where it is the chloride ion.[22] In these concentrated solutions of HCl, oxidation to $PtCl_6^{2-}$ readily occurs,[23] and we have observed that it happens even in an argon atmosphere. Presumably molecular hydrogen is evolved

$$[PtCl_4 \cdot 2HCl]^{2-} \longrightarrow PtCl_6^{2-} + H_2\uparrow \qquad (5)$$

The second point concerning the spectral studies is that it is by no means clear in which direction a

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[19] The order of effectiveness of the various solvents does not parallel their behavior toward organic halides for reactions of either S_N1 or S_N2 types. See E. M. Kosower, THIS JOURNAL, **80**, 3253 (1958); S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

[20] In a preparative sense, it is much easier to make acetato complexes of platinum(II) in glacial acetic acid than from even high concentrations of quaternary ammonium acetate, H. B. Gray, unpublished observations.

[21] H. B. Gray, to be published.

[22] C. M. Harris, S. E. Livingstone and I. H. Reece, *J. Chem. Soc.*, 1505 (1959).

[23] A. V. Babaeva, *Doklady Akad. Nauk, S.S.S.R.*, **40**, 61 (1943).

strong axial interaction with the central metal atom will shift the spectrum of either platinum(II) or palladium(II) complexes. Thus in the paper by Chatt, Gamlen and Orgel[24] on the spectra of platinum(II) complexes, the bands of $PtCl_4^{2-}$ with maxima at 3895 and 3290 Å. in water are assigned to the transition $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, respectively. In the case of the corresponding bands of Pt(di-amylamine)$_2$Cl$_2$ it was found that the first band was unaffected and the second was shifted to longer wave lengths in going from the solvent hexane to ethanol. Certainly the interaction with hexane is weaker than with ethanol, yet the shift in the spectrum is *opposite* in direction to the shifts found by Harris, Livingstone and Reece.[22] According to theory then, one could invert the order of solvent interactions given by them and say that $C_6H_5NO_2$ interacts most strongly and H_2O least strongly. Unfortunately the theory is not well enough established for such a statement, since it does not explain why both bands are shifted by approximately the same amount in the case of both the Pt(II) and Pd(II) halide complexes. Accordingly the interpretation of these spectra in terms of solvent interactions must be viewed with caution at present.

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[24] J. Chatt, G. A. Gamlen and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

[CONTRIBUTION FROM THE RALPH G. WRIGHT LABORATORY, SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Isotopic Exchange Reactions. VI. Halogen Exchange in the System BCl_3–$POCl_3$[1,2]

BY ROLFE H. HERBER

RECEIVED SEPTEMBER 26, 1959

The isotopic halogen exchange between $POCl_3$ and BCl_3 has been investigated with the use of Cl^{36} labelled reactants. While a rapid (complete within one minute) exchange is noted at 0° when $POCl_3$ is present in excess, as well as in an equimolar mixture of the two components, no halogen exchange is observed in an excess of BCl_3. These data are interpreted on the basis of a structure previously proposed for the addition compound in which the bonding is through the phosphoryl oxygen. A mechanism for the rapid halogen exchange in $POCl_3$ rich systems is suggested, which does not necessitate the formation of a free tetrachloroborate anion as proposed in earlier studies of halogen exchanges in BCl_3.

In a previous paper[3] in this series it has been pointed out that isotopic halogen exchange between BCl_3 and other chlorine containing chemical species should be observed under conditions when the tetrachloroborate anion can be formed as a reaction intermediate in kinetically significant concentrations. It was also suggested that the formation of this anion occurred in the system BCl_3–$(CH_3)_4NCl$ and gave rise to the rapid halogen exchange which was observed. In the present study, the halogen exchange between BCl_3 and $POCl_3$ has been investigated with a view toward elucidating the nature of the bonding in the addition compound formed from these two components.

The formation of a crystalline 1:1 addition compound with a melting point of ~71–73° obtained from BCl_3 and $POCl_3$ has been amply reported in the literature,[4] with however little agreement on the nature of the chemical bonding which is involved in its formation. Thus the early work of Gutmann[5] suggests that electron deficient compounds such as $AlCl_3$ form anions in $POCl_3$ and then undergo ionic metathesis, so that under these conditions the addition compound may be expected to have the structure $POCl_2^+ \; BCl_4^-$. Similarly, Greenwood and Wade[6] consider the formation of the addition compound between $POCl_3$ and $GaCl_3$ to occur by coördinate bond formation involving one of the phosphoryl chloride chlorine atoms as the donor. Further, these authors cite evidence that at equilibrium, some 99.5% of the reactants are present as the covalent addition complex and about 0.5% as a $POCl_2^+GaCl_4^-$ ion pair formed by chloride ion transfer from the former to the latter.

On the other hand the recent work of Sheldon and Tyree,[7] on the donor properties of $POCl_3$ and related compounds, suggests rather strongly that addition compound formation with solvates such as $AsCl_3$, $SnCl_3$ and $TiCl_4$ occurs *via* bonding through the oxygen atom. This view is supported by the observation that the P–O stretching frequency is shifted some 50–100 cm.$^{-1}$ relative to its value in the pure solvent, when compound formation is observed. Clearly, while the interpretation of this shift is not unambiguous, it suggests strongly that electron pair donation by the oxygen atom is probably taking place. This proposed bonding through the oxygen atom also has been suggested by Groene-

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[1] The experimental portions of this research were carried out under contract AT(11-1)-67, Project 19, between the U. S. Atomic Energy Commission and the University of Illinois in the W. A. Noyes Laboratory of Chemistry, University of Illinois.

[2] Presented in part as paper No. 610 at the XVIIth Congress of the International Union of Pure and Applied Chemistry, Munich, Germany, 1959.

[3] R. H. Herber, THIS JOURNAL, **80**, 5080 (1958).

[4] (a) Gustavson, *Z. Chem.*, **7**, 417 (1871); *Ber.*, **4**, 975 (1871); (b) A. B. Burg and M. K. Ross, THIS JOURNAL, **65**, 1637 (1943); (c) The formation of a crystalline addition compound between PCl_5 and BCl_3 has been reported by M. A. Stieber, *Compt. rend.*, **116**, 1524 (1893). However, this system has been investigated carefully from −78° to room temperature by R. R. Holmes (private communication) who finds no evidence for compound formation over this temperature range, so that Stieber's compound is probably the $POCl_3 \cdot BCl_3$ compound cited earlier by Gustavson.

[5] V. Gutmann, *Monatsh. Chem.*, **83**, 279 (1952); *Z. anorg. u. allgem. Chem.*, **270**, 179 (1952).

[6] N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1516 (1957).

[7] J. C. Sheldon and S. Y. Tyree, Jr., THIS JOURNAL, **81**, 2290 (1959).