of the hydrogens, as compared to a singlet for compound II under the same conditions. Without this decoupling, the ^{31}P spectrum of III shows only two broad humps, one centered at −2.6 ppm and the other at −11.3 ppm. With broad-band hydrogen decoupling, each of these humps is resolved into four lines apparently of equal areas assignable to a pair of doublets due to P-P splitting. In order to determine the coupling constant, the ^{31}P spectrum of III was run at 24.3 MHz as well as at the usual frequency of 40.55 MHz. This showed that for the upfield as well as the downfield set of four lines, the coupling constant equals 10.7 ± 0.1 Hz at both magnetic field strengths.

Since the phosphorus chemical shift of compound II is +6.6 ppm and the chemical shift for diphenylphosphinyl azide, $(C_6H_5)_2P(O)N_3$, is −28.7 ppm, we assign the hump observed without hydrogen decoupling at −2.6 ppm to the endocyclic phosphorus of compound III and the hump at −11.3 ppm to the exocyclic phosphorus. The broad-band hydrogen decoupling shows that in III there are two kinds of endocyclic phosphorus, δ_{P_A} −2.7 ppm and $\delta_{P_{A'}}$ −2.5 ppm, and two kinds of exocyclic phosphorus, δ_{P_B} −11.5 ppm and $\delta_{P_{B'}} = -11.2$ ppm, with $J_{P_AP_B}$ and $J_{P_{A'}P_{B'}} = 10.7$ Hz.

The presence of A and A′ as well as B and B′ species may be indicative of geometrical isomerism of III. Two factors act to support the concept of an effective geometrical isomerism and simultaneously to complicate its interpretation. First of all, the two perpendicular π orbitals in the phosphorimide bond (usually written $\rightarrow$P=N-) are filled to sufficiently equal amounts[9] so that some rotation about this bond may well occur. Secondly, the cage structure will probably allow[10] electronic short-circuiting across it (*i.e.*, by a through-bond mechanism[11]), thereby enabling the rotational configuration of a diphenylphosphoryl group at one end of the molecule to have an influence on the similar group at the other end. However, we find it difficult to rationalize the essentially equal peak areas of the nmr multiplicity when ascribed to rotational isomerism.

Acknowledgments. We are indebted to Drs. R. K. Howe and M. M. Crutchfield of the Monsanto Chemical Co. for obtaining the ^{31}P nmr spectra at 24.3 MHz. Partial financial assistance from the National Science Foundation (Grant GP-28698X) is gratefully acknowledged.

Registry No. I, 3478-74-8; $C_6H_5N_3$, 622-37-7; $(C_6H_5)_2P(O)N_3$, 4129-17-3; II, 42975-97-3; III, 42975-98-4.

(9) For a somewhat similar situation see I. Absar and J. R. Van Wazer, *J. Amer. Chem. Soc.*, 94, 2382 (1972).

(10) P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 94, 995 (1972).

(11) R. Hoffmann, *Accounts Chem. Res.*, 4, 1 (1971).

Contribution from the Department of Chemistry,
The University of Arizona, Tucson, Arizona 85721

Kinetics of the Reactions of Tetrahalo Complexes of Palladium(II) and Platinum(II) with 1,10-Phenanthroline

John V. Rund

Received May 30, 1973

The rate law for substitution reactions of most platinum(II) and palladium(II) complexes is

$$\text{rate} = k_1[\text{M}] + k_2[\text{M}][\text{L}] \tag{1}$$

where M is the metal complex and L is the entering ligand.[1] The second-order term is attributed to direct attack by L (reaction 2), while the first-order term is the result of a rate-

$$\text{MA}_4 + \text{L} \rightarrow \text{MA}_3\text{L} + \text{A} \tag{2}$$

determining attack by the solvent, S (reaction 3). Recently,

$$\text{MA}_4{}^{2-} + \text{S} \rightarrow \text{MA}_3\text{S} + \text{A} \xrightarrow[+\text{L}]{} \text{MA}_3\text{L} + \text{S} \tag{3}$$

data were published[2-16] for some substitution reactions of tetrahalo complexes, $MX_4{}^{2-}$, mostly $PtCl_4{}^{2-}$. Few if any of these reactions were found to have rate laws with first-order terms, perhaps in some cases because aquation of $PtCl_4{}^{2-}$ is fairly rapid, and since water is not very different from chloride either as a leaving group or as a trans labilizing ligand, $Pt(H_2O)Cl_3{}^-$ is similar in reactivity to $PtCl_4{}^{2-}$. Although the product may be formed *via* a solvated intermediate, formation of the intermediate is not the rate-determining step, and the rate law contains two second-order terms[9]

$$\text{rate} = k_2[\text{MX}_4{}^{2-}][\text{L}] + k_2'[\text{MX}_3\text{S}^-][\text{L}] \tag{4}$$

The kinetics of reaction 5 has been examined for M = Pd

$$\text{MX}_4{}^{2-} + \text{AA} \xrightarrow{k_{\text{obsd}}} \text{M(AA)X}_2 + 2\text{X}^- \tag{5}$$

and Pt, AA = 1,10-phenanthroline (phen) and 2,2′-bipyridyl, and X = Cl.[9,14,16] This paper reports an extension of the research to systems M = Pd and Pt, AA = phen, and X = Br and I. The system M = Pt, AA = phen, and X = Cl was reexamined because the supporting electrolyte used in ref 9 was found to affect the rates of some of the reactions. New kinetics constants are reported for this system. The purpose of the research was to find how changing the halide affected the reaction rate and to determine whether other halides gave complexes that behaved like the chloro complexes in not having a first-order term in the rate law.

Experimental Section

Chemicals. Potassium tetrabromopalladate(II) was obtained by twice evaporating a solution of K_2PdCl_4 (10 g) in 48% HBr (150 ml) to the point of crystallization on a steam bath. As the solution cooled, brown needlelike crystals formed, which were filtered out and dried under vacuum; yield 10.1 g (65%). *Anal.* Calcd for K_2PdBr_4: Pd, 21.1; Br, 63.4. Found: Pd, 21.0; Br, 63.3. Potassium tetrabromoplatinate(II) cannot be prepared by the method given above, because platinum(II) is oxidized to platinum(IV) by the bromine in

---

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 377.

(2) L. F. Grantham, T. S. Elleman, and D. S. Martin, *J. Amer. Chem. Soc.*, 77, 2956 (1955).

(3) M. A. Tucker, C. B. Colvin, and D. S. Martin, *Inorg. Chem.*, 3, 1373 (1964).

(4) L. Cattalini, A. Orio, and M. Nicolini, *J. Amer. Chem. Soc.*, 88, 5734 (1966).

(5) C. B. Colvin, R. G. Gunther, L. D. Hunter, J. A. McLean, M. A. Tucker, and D. S. Martin, *Inorg. Chim. Acta*, 2, 487 (1968).

(6) R. M. Milburn and L. M. Venanzi, *Inorg. Chim. Acta*, 2, 97 (1968).

(7) E. D. Smith, J. A. McLean, and J. E. Teggins, *Inorg. Chem.*, 8, 1872 (1969).

(8) R. Pietropaolo, M. Graziani, and U. Belluco, *Inorg. Chem.*, 8, 1506 (1969).

(9) F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, 8, 524 (1969).

(10) J. V. Rund and F. A. Palocsay, *Inorg. Chem.*, 8, 2242 (1969).

(11) J. H. Cawley and J. V. Rund, *J. Inorg. Nucl. Chem.*, 32, 1406 (1970).

(12) G. Dolcetti, R. Pietropaola, and U. Belluco, *Inorg. Chem.*, 9, 553 (1970).

(13) R. A. Reinhardt and W. W. Monk, *Inorg. Chem.*, 9, 2026 (1970).

(14) J. V. Rund, *Inorg. Chem.*, 9, 1211 (1970).

(15) R. Pietropaolo, P. Uguagliati, T. Boschi, B. Crociani, and U. Belluco, *J. Catal.*, 11, 499 (1972).

(16) D. E. Schwab and J. V. Rund, *Inorg. Chem.*, 11, 499 (1972).

HBr. Instead, platinum sponge (10 g) was dissolved in hot aqua regia (55 ml). Concentrated HBr (100 ml) was very cautiously added to the solution, which was then boiled down to a volume of about 30 ml. When four successive 100-ml portions of HBr had been added and evaporated, the solution was filtered and diluted to 100 ml with water. Potassium bromide (15 g dissolved in a little water) was added, whereupon red-orange crystals of K_2PtBr_6 precipitated; yield 37.4 g (97%). Conversion to K_2PtBr_4 was carried out by the method of Biilmann.[17] *Anal.* Calcd for K_2PtBr_4: Pt, 32.9; Br, 54.0. Found: Pt, 33.4; Br, 53.7. A more efficient method of converting K_2PtBr_6 into K_2PtBr_4 has been published by Livingstone.[18] Preparations of the chloro complexes have been given elsewhere.[9,14]

Salts of MI_4^{2-} complexes have not been isolated. The complexes or their aquation products are supposed to result when K_2MCl_4 or MI_2 are dissolved in concentrated, aqueous KI solution.[19] Stock solutions were prepared in this way for use in kinetics runs, and their metal contents were determined.

The reaction products $M(phen)X_2$ were identified by elemental analysis. Their physical properties will be included in a subsequent paper.

Platinum content of the compounds was obtained by ignition to the metal. Palladium was determined gravimetrically as the dimethylglyoximate complex. Halogen analyses were carried out by Huffman Laboratories, Inc., Wheatridge, Colo.

Kinetics. Reactions were carried out with equal concentrations (5×10^{-4} *M*) of metal complex and phenanthroline, at an ionic strength of 0.278 *M* and a pH of 3.2. The background electrolyte was KBF_4 for palladium and KNO_3 for platinum. The pH was adjusted by addition of standardized nitric acid. It was found to be constant during the course of the reaction. Reactions were carried out in a constant-temperature bath that was controlled to better than 0.1°. Temperatures and halide concentrations are given in the table of rate constants. Reaction progress was monitored by determining the amount of uncomplexed phenanthroline present in the reaction. At regular intervals, portions of the reaction mixture was pipetted into solutions containing Fe^{2+}. Unreacted phenanthroline was rapidly converted into the red, inert $Fe(phen)_3^{2+}$ complex, which was assayed spectrophotometrically. Procedural details have been given in ref 9. Values of k_{obsd} were determined by plotting the reciprocal of the absorbance as a function of time. Ten to twenty points were obtained for each graph. Standard deviations quoted in the rate constant table are calculated from different values of k_{obsd} for three or four independent reactions run under the same set of conditions. All reactions were second order.

Rate measurements for the Pt–I system were difficult because $Fe(phen)_3I_2$ precipitated. Several alternative methods were examined, including direct spectrophotometry of the reaction mixture, development with $SnCl_3^-$, and precipitation of I^- with Ag^+. No method gave very satisfactory results, but at 5° and $[I^-] = 0.278\ M$, k_{obsd} was about $10\ M^{-1}\ sec^{-1}$. The problem did not arise for palladium, since under the same conditions, no unreacted phenanthroline was found in the first sample removed from the reaction. If reasonable allowances are made for the delays in sampling and quenching, a lower limit of about $600\ M^{-1}\ sec^{-1}$ may be placed on k_{obsd}.

Results and Discussion

Table I presents calculated and observed rate constants for various systems involving phenanthroline as the attacking ligand. The reactions of the chlorides and bromides were second order. Since the conditions were chosen to give the maximum opportunity of detecting a first-order term in the rate law,[9] such a term, if it exists, must be very much less important than it is in most reactions of platinum(II) and palladium(II). The rates varied with halide concentration as if MX_4^{2-} complexes were in equilibrium with $M(H_2O)X_3^-$ complexes and phenanthroline reacted with both (see eq 6).

$$\begin{tikzcd} MX_4^{2-} + H_2O \arrow[r, shift left] \arrow[d, "k_X"', "+\text{phen}"] & M(H_2O)X_3^- + X^- \arrow[l, shift left] \arrow[dl, "k_{H_2O}"', "+\text{phen}"] \\ M(\text{phen})X_2 + 2X^- + H_2O & \end{tikzcd} \qquad (6)$$

Table I. Observed and Calculated Rate Constants for the Reaction $MX_4^{2-} + \text{phen} \rightarrow M(\text{phen})X_2 + 2X^-$

[X], *M*	k_{obsd}, M^{-1} sec^{-1}	k_{calcd} M^{-1} sec^{-1}
System 1: M = Pd, X = Cl, *T* = 5°		
2.75×10^{-1}	0.56 ± 0.02	0.55
2.07×10^{-1}	0.62 ± 0.02	0.62
1.37×10^{-1}	0.76 ± 0.02	0.75
6.91×10^{-2}	1.16 ± 0.06	1.10
3.48×10^{-2}	1.71 ± 0.08	1.69
1.76×10^{-2}	2.44 ± 0.11	2.54
9.08×10^{-3}	3.64 ± 0.08	3.59
4.79×10^{-3}	4.62 ± 0.08	4.56
System 2: M = Pd, X = Br, *T* = 5°		
2.75×10^{-1}	0.60 ± 0.02	0.61
2.07×10^{-1}	0.67 ± 0.01	0.69
1.37×10^{-1}	0.91 ± 0.02	0.87
6.91×10^{-2}	1.34 ± 0.06	1.34
3.48×10^{-2}	2.20 ± 0.05	2.18
1.76×10^{-2}	3.3 ± 0.4	3.5
9.08×10^{-3}	5.9 ± 0.9	5.3
System 3: M = Pd, X = I, *T* = 5°		
2.78×10^{-1}	>600	
System 4: M = Pd, X = Cl, *T* = 25°		
2.75×10^{-1}	3.1 ± 0.1	3.2
2.07×10^{-1}	3.5 ± 0.1	3.5
1.37×10^{-1}	4.2 ± 0.1	4.1
6.91×10^{-2}	5.9 ± 0.1	5.7
3.48×10^{-2}	8.7 ± 0.1	8.8
1.76×10^{-2}	13.5 ± 0.2	14.1
9.08×10^{-3}	22.3 ± 1.0	22.1
4.79×10^{-3}	32.7 ± 0.7	32.2
System 5: M = Pd, X = Br, *T* = 25°		
2.75×10^{-1}	3.1 ± 0.1	3.2
2.07×10^{-1}	3.6 ± 0.2	3.7
1.37×10^{-1}	4.8 ± 0.2	4.6
6.91×10^{-2}	7.3 ± 0.3	7.2
3.48×10^{-2}	12.6 ± 0.3	12.2
1.76×10^{-2}	21.9 ± 1.6	21.3
9.08×10^{-3}	36.1 ± 1.1	36.5
4.79×10^{-3}	59.3 ± 1.0	59.1
[X], *M*	10^3k_{obsd}, M^{-1} sec^{-1}	10^3k_{calcd}, M^{-1} sec^{-1}
System 6: M = Pt, X = Cl, *T* = 55°		
2.78×10^{-1}	1.98 ± 0.03	2.00
2.08×10^{-1}	2.34 ± 0.12	2.25
1.39×10^{-1}	2.76 ± 0.08	2.70
6.98×10^{-2}	3.81 ± 0.06	3.81
3.52×10^{-2}	5.30 ± 0.29	5.36
1.79×10^{-2}	7.18 ± 0.20	7.12
9.30×10^{-3}	8.96 ± 0.30	8.70
5.12×10^{-3}	9.80 ± 0.23	9.83
System 7: M = Pt, X = Br, *T* = 55°		
2.78×10^{-1}	2.8 ± 0.2	2.7
2.08×10^{-1}	3.1 ± 0.2	3.2
1.39×10^{-1}	4.0 ± 0.2	4.2
6.98×10^{-2}	7.2 ± 0.1	7.2
3.52×10^{-2}	13.4 ± 0.5	13.2
1.79×10^{-2}	23.9 ± 0.9	24.0
9.30×10^{-3}	41.1 ± 3.4	42.3
5.12×10^{-3}	68.2 ± 1.7	68.4
System 8: M = Pt, X = I, *T* = 5°		
2.78×10^{-1}	*Ca.* 10^4	

Reaction constants are related to the observed rate constant by the expression

$$k_{obsd} = \frac{k_{H_2O}K + k_X[X^-]}{K + [X^-]} \qquad (7)$$

Here it is necessary to assume that the aquation reaction is much faster than substitution by phenanthroline so that the

---

(17) E. Biilmann and A. C. Andersen, *Ber. Deut. Chim. Ges.*, 36, 1566 (1903).

(18) S. E. Livingstone, *Syn. Inorg. Metal-Org. Chem.*, 1, 1 (1971).

(19) E. Pietsch, Ed., "Gmelins Handbuch der anorganischen Chemie," Vol. 65, Verlag Chemie, Berlin, 1942, p 317.

Table II. Values of the Constants in Reaction 6

System: M, X, *T*	k_X, M^{-1} sec^{-1}	k_{H_2O}, M^{-1} sec^{-1}	*K*, *M*
Pd, Cl, 5°	0.34	6.7	9.4×10^{-3}
Pd, Br, 5°	0.34	13	6.0×10^{-3}
Pd, Cl, 25°	2.2	71	3.7×10^{-3}
Pd, Br, 25°	1.9	210	1.8×10^{-3}
Pt, Cl, 55°	1.2×10^{-3}	1.17×10^{-2}	2.3×10^{-2}
Pt, Br, 55°	1.08×10^{-3}	2.98×10^{-1}	1.5×10^{-3}

equilibrium between MX_4^{2-} and $M(H_2O)X_3^-$ is maintained throughout the kinetic run. When comparisons can be made with known aquation rates, the assumption has been shown to be justified.[9] A few kinetic runs showed small deviations at the very beginning as the equilibrium was being established. Reaction constants were calculated from the observed rate constants and their corresponding halide concentrations. Initially, two values of k_{obsd} at small $[X^-]$ were substituted into eq 7 to solve for k_X, neglecting the $k_{H_2O}K$ term. Crude values for k_{H_2O} and K were then obtained from two values of k_{obsd} at large $[X^-]$ and the number that had been calculated for k_X. These values were used to improve the calculation of k_X, and so on. A few such cycles of calculation gave a convergent solution. Minor adjustments in the reaction constants were then made by trial and error to provide the nearest correspondence between k_{obsd} and k_{calcd} throughout the range of $[X^-]$. Reaction constants are given in Table II. A number of comparisons may be made among the reaction constants. When adjusted to 55°, palladium reactions were faster than corresponding platinum reactions by factors of 2×10^4 to 10^5. Other workers[20] find similar factors and ascribe them to weaker palladium bonds. $M(H_2O)X_3^-$ complexes were more reactive then MX_4^{2-} complexes, probably because water, a better leaving group than halide,[21] was expelled in the $M(H_2O)X_3^-$ reactions. Among the reactions of $M(H_2O)X_3^-$, those with X = Br were faster than those with X = Cl, because of the greater trans effect of bromide.[22] The similar MX_4^{2-} rates were the result of two opposing effects: bromide was a better trans labilizer but a poorer leaving group then chloride.

The equilibrium constants calculated from kinetics data may be compared with those derived by more direct measurements. No attempt was made to force the calculations of *K* to agree with published values. The constant for the first aquation step of $PtCl_4^{2-}$ at 55° is 2.5×10^{-2} *M* by an equilibrium method[9] and 2.3×10^{-2} *M* from kinetics. The constants at 25° for $PdCl_4^{2-}$ are 4×10^{-3} *M* (equilibrium,[23] corrected to $\mu = 0.278$ *M*) and 3.7×10^{-3} *M* (kinetics). An attempt to measure the equilibrium constant for $PtBr_4^{2-}$ was not successful. In general it may be concluded that the bromide complexes follow the pattern of the chlorides in having a second-order solvent route to the product.

Very little can be concluded about the iodide complexes. Their reactions were much faster than those of chloride or bromide, but the form of the complex existing in solution was uncertain. The very insoluble $M(phen)I_2$ complexes seemed to precipitate more slowly than the rate at which phenanthroline was used up, suggesting that the initial substitution product might have been something like $M(H_2O)(phen)I^+$.

Registry No. Phen, 66-71-7; $PdCl_4^{2-}$, 14349-67-8; $Pd(phen)Cl_2$, 14783-10-9; $PdBr_4^{2-}$, 14127-70-9; $Pd(phen)Br_2$, 41876-11-3; PdI_4^{2-}, 16182-47-1; $Pd(phen)I_2$, 41876-12-4; $PtCl_4^{2-}$, 13965-91-8; $Pt(phen)Cl_2$, 18432-95-6; $PtBr_4^{2-}$, 14493-01-7; $Pt(phen)Br_2$, 42847-12-1; PtI_4^{2-}, 14349-66-7; $Pt(phen)I_2$, 42847-13-2.

(20) Reference 1, p 414.

(21) Reference 1, p 383.

(22) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, p 25.

(23) H. A. Droll, B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, 61, 1000 (1957).

Contribution from the William Rand Kenan, Jr.,
Laboratories of Chemistry, University of North Carolina,
Chapel Hill, North Carolina 27514

Unusual Magnetic Properties of Polymeric Cobalt(II) Monoglycerolate, a Compound Containing Alkoxo-Bridged Cobalt(II) Ions

Richard P. Eckberg, William E. Hatfield,* and D. Bruce Losee

Received July 16, 1973

Complex compounds of various transition metal ions with glycerine have been known for several years.[1] The structure of one of these, cobalt(II) monoglycerolate, $[Co(C_3H_6O_3)]_n$, has been found[2] to be a two-dimensional polymer. The magnetic moment observed at room temperature for this complex, 3.94 BM,[1] is lower than usually observed for high-spin cobalt(II). This fact, coupled with the unusual magnetic properties which are often characteristic of polymeric transition metal complexes, have made cobalt(II) monoglycerolate a subject of interest for low-temperature magnetic susceptibility studies. The results of our measurements in the temperature range 1.6–50°K are described in this note.

Experimental Section

The compound was prepared by heating a mixture of 10.0 g of cobalt(II) acetate in 100 ml of 96% glycerine (U. S. Pharmacopoeia grade) with constant stirring, to a temperature of 165° for 60 hr. The crude product was filtered from the resulting suspension, washed repeatedly with water, ethanol, and ether, and dried *in vacuo* at 110° for 24 hr. The resulting product was a deep magenta, finely divided powder which was insoluble in all common solvents.

Anal. Calcd for $[Co(C_3H_6O_3)]_n$: C, 24.18; H, 4.06; Co, 39.55. Found: C, 24.33; H, 3.95; Co, 39.77.

Attempts to obtain crystals large enough for single-crystal susceptibility measurements have thus far been unsuccessful. The insolubility of the material in all solvents tested ruled out crystal growth *via* slow evaporation from solution. Crystal growth in a silica gel[3] has been attempted but the high temperature required for reaction between glycerine and cobalt acetate has to date prevented the slow dispersion of the reactants along the gel–aqueous interface from producing the desired crystalline product at temperatures low enough to prevent evaporation of the aqueous phase. Therefore, magnetic susceptibility measurements have been confined to powder specimens. The magnetic susceptibility measurements were made with a PAR vibrating-sample magnetometer[4] which is capable of operating over a wide range of field strengths. The magnetometer was calibrated with $HgCo(NCS)_4$,[5] and temperatures were measured using a calibrated gallium arsenide diode.

Although epr *g* values have been reported for Co(II) in a five-coordinate environment at 77°K,[6] all attempts at observing an epr signal at 77°K failed for cobalt monoglycerolate.

(1) E. W. Radoslovich, M. Raupach, P. G. Slade, and R. M. Taylor, *Aust. J. Chem.*, 23, 1963 (1970).

(2) P. G. Slade, E. W. Radoslovich, and M. Raupach, *Acta Crystallogr., Sect. B*, 27, 2432 (1971).

(3) H. K. Henisch, "Crystal Growth in Gels," Pennsylvania State University Press, University Park, Pa., 1970

(4) S. Foner, *Rev. Sci. Instrum.*, 30, 548 (1959).

(5) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(6) C. Busetto, F. Cariati, P. Fantucci, D. Galizzioli, F. Morazzoni, and V. Valenti, *Gazz. Chim. Ital.*, 102, 1040 (1972).