

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201**Rates of Substitution of Some Diacidobis(ethylenediamine)iridium(III) Complexes**

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The rates of the substitution reactions of the series $trans\text{-Ir}(\text{en})_2\text{X}_2^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $trans\text{-Ir}(\text{en})_2\text{LCl}^+$ ($\text{L} = \text{NO}_2, \text{I}, \text{Br}$) with various nucleophiles have been studied. The reactions were found not to be complicated by catalysis or stereochemical rearrangements, and all were found to be independent of the nature and concentration of incoming nucleophile. The *trans* effect of L was studied and found to increase in the series $\text{NCS}^- < \text{Cl}^- < \text{Br}^- < \text{NO}_2^- < \text{I}^-$. The kinetic *trans* effect was found not to be as pronounced as in the analogous Rh(III) series.

Introduction

The substitution reactions of a series of complexes $trans\text{-Ir}(\text{en})_2\text{LX}^+$ are of considerable interest from a mechanistic point of view and in respect to the operation of the *trans* effect in octahedral complexes. The study of the *trans* effect in octahedral complexes has been limited largely to Pt(IV),¹ Co(III),¹ and Rh(III).² Pt(IV) substitution reactions are complicated by catalysis¹ and Co(III) systems by geometrical rearrangements,³ but an assignment of the *trans* effect has been made in the Rh(III) systems² which do not exhibit either of these complications to a great extent.⁴ Similarly, the *trans*-dihalogenobis(ethylenediamine) complexes of Ir(III) do not exhibit catalysis, and stereochemical *trans* \leftrightarrow *cis* rearrangements are not observed in any of the known complexes.⁵

Experimental Section

The preparation of the diacidobis(ethylenediamine) salts used in this study are described elsewhere.⁵ All complexes were isolated as the perchlorate salts. Sodium halide solutions were prepared by weighing out dry, finely divided reagent grade salts into volumetric flasks.

Ionic chloride was determined in solutions acidified with HClO_4 by titrating with standard AgNO_3 solution. Equivalence points were detected using a Radiometer 25 pH meter as a potentiometer utilizing a silver electrode and a calomel reference electrode.

Visible and ultraviolet spectra were recorded with a Cary Model 14 recording spectrophotometer in 1-cm quartz cells. When it was convenient to study only one wavelength, a Beckman DU spectrophotometer was used to read absorbances of solutions.

Because temperatures higher than the boiling point of water had to be employed, the following apparatus was designed and used in the kinetic studies. The 50-ml solutions to be studied were placed in 100-ml polymer pressure bottles, thick-walled glass bottles with orifices designed to accept beer bottle type caps. The caps employed were designed with two $1/8$ -in. diameter holes in them so that they may accept syringe needles. A rubber gasket was placed in the cap, and the cap was sealed to the bottle with an ordinary bottle capper. This assembly afforded an

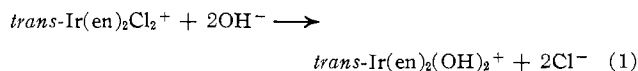
airtight seal which can withstand a 5-atm pressure difference from the inside to the outside of the bottle. A stainless steel syringe needle was pierced through the rubber gasket into the solution and was attached to a two-way stainless steel stopcock with Teflon fittings which also accepted a 5-ml syringe. The polymer pressure bottles were wrapped with aluminum foil and completely immersed in an oil bath kept at constant temperature, $\pm 0.1^\circ$. At the appropriate time intervals a 5-ml syringe was attached to the stopcock, the stopcock was opened, and the reaction solution was allowed to enter the syringe. Samples of 2–3 ml were extracted by this method and cooled to room temperature, and the absorbance was measured, or the concentration of ionic chloride was determined. The substitution reactions studied were so slow at room temperature that the samples could be withdrawn, stored in stoppered tubes, and measured at a later convenience. Sodium perchlorate was used as an inert electrolyte to keep ionic strength constant. No leakage of the reaction vessels was observed within 12 hr at 140° . No visible reaction occurred with the solution and the stainless steel needles or the rubber gasket. Simple calculations show that the amount of solution evaporated to occupy the space of the removed aliquots makes a negligible influence on the concentration of the solution remaining in the reaction vessel.

Rate constants were determined from the equation

$$kt = \ln \left(\frac{A_\infty - A_0}{A_\infty - A_t} \right)$$

where A_0 , A_t , and A_∞ are absorbance readings at zero time, time t , and infinite reaction time, respectively. The A_∞ was usually determined after 7 half-lives of reaction. The rate constants were calculated from the slope of a plot of $\ln [(A_\infty - A_t)/(A_\infty - A_0)]$ vs. t .

In the case of the reaction



the spectral changes were not large enough to study the reaction spectrophotometrically. Aliquots were removed at equal intervals of time, acidified, and titrated to equivalence. At least 5–10 aliquots were removed during each half-life and the concentration of free chloride at infinity reaction time was estimated by the Guggenheim method.⁶ Infinite points could not be obtained from the reaction solution due to noticeable decomposition of the complex after 3 half-lives. Very good first-order plots were obtained by plotting $\ln [(V_\infty - V_0)/(V_\infty - V_t)]$ vs. t , where V is the total concentration of free chloride ion (or volume of standard AgNO_3 solution used in the titration).

(1) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 331 (1962); F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 1 (1961).

(2) F. Basolo, E. J. Bounsall, and A. J. Poë, *Proc. Chem. Soc.*, 366 (1963); A. J. Poë, K. Shaw, and M. J. Wendt, *Inorg. Chim. Acta*, **1**, 371 (1967), and references therein.

(3) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963).

(4) S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 1741 (1963).

(5) R. A. Bauer and F. Basolo, *Inorg. Chem.*, **8**, 2231 (1969).

(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, N. Y., 1965, p 49.

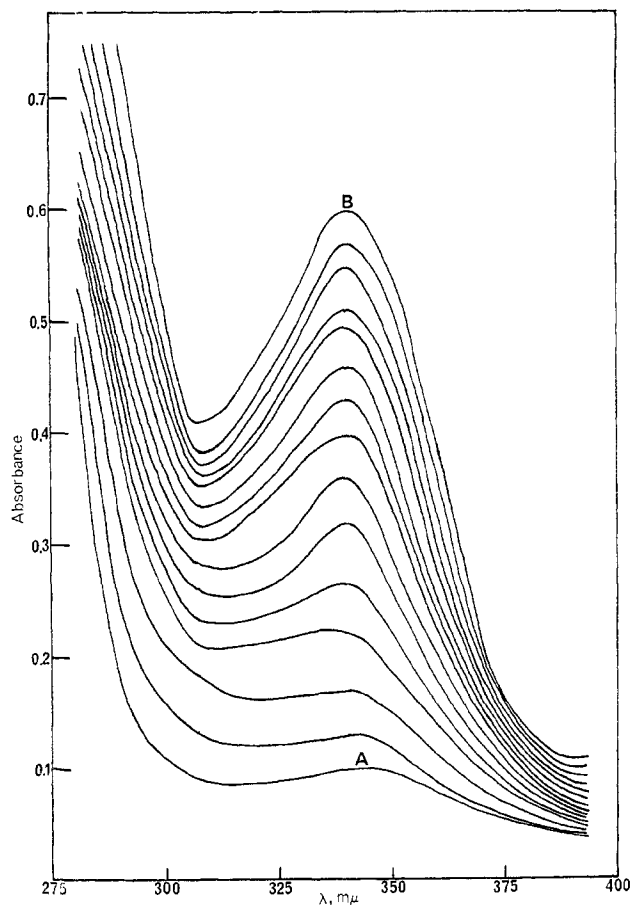


Figure 1.—Spectral changes during the $\text{trans-Ir(en)}_2\text{Cl}_2^+ + \text{N}_3^-$ reaction: (A) initial trace, $\text{trans-Ir(en)}_2\text{Cl}_2^+$, $2.0 \times 10^{-3} M$; (B) final trace, $\text{trans-Ir(en)}_2(\text{N}_3)_2^+$.

Activation enthalpy ΔH^\ddagger and entropy ΔS^\ddagger were calculated from the equation

$$k_r = \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

where k_r is the observed first-order rate constant at Kelvin temperature T , k is the Boltzmann constant, h is the Planck constant, and R is the gas constant. A least-squares analysis of $\log(k_r/T)$ vs. $1/T$ data was used over a temperature range of at least 30° . Standard deviations were also calculated in the analysis assuming that k_r had the same variance at each temperature and that no error was contained in the temperature values.

An attempt was made to observe catalysis by KH_2PO_2 , hydrazine, and Ir(IV) in a kinetic study of the reaction of $\text{trans-Ir(en)}_2\text{Cl}_2^+$ with I^- . In the cases of KH_2PO_2 and hydrazine, 10 mol % of a solution of the reducing agent (prepared by heating an equimolar mixture of reducing agent and K_2IrCl_6) was added to the reaction solution. Iridium(IV) was prepared by adding 10 mol % Ce(IV) to a solution of $\text{trans-Ir(en)}_2\text{Cl}_2^+$. In all cases no catalysis was observed.

In all reactions studied, no $\text{trans} \leftrightarrow \text{cis}$ isomerizations occurred. The uv spectra in all cases showed the appearance of only one set of absorptions of the product (Figures 1 and 2). $\text{trans-Ir(en)}_2\text{Cl}_2^+$ is extremely stable in aqueous solution. No change in the ultraviolet spectrum of this compound was noted after heating it at 140° in $0.5 M \text{Cl}^-$ for 5 hr. The base hydrolysis of $\text{trans-Ir(en)}_2\text{Cl}_2^+$ also proceeds with retention of geometry.³

$\text{trans-Ir(en)}_2\text{Cl}_2^+$ does not thermally isomerize to the *cis* isomer at 195° . An aqueous solution of 1 g of $\text{trans-[Ir(en)}_2\text{Cl}_2]\text{Cl}$ was

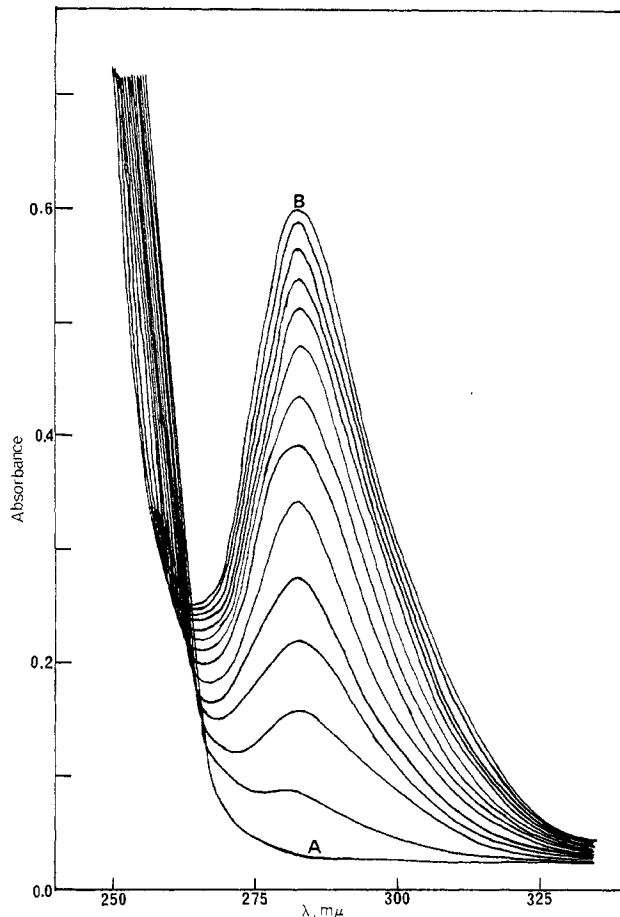
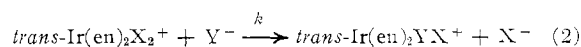


Figure 2.—Spectral changes during the $\text{trans-Ir(en)}_2\text{Br}_2^+ + \text{I}^-$ reaction: (A) initial trace, $\text{trans-Ir(en)}_2\text{Br}_2^+$, $5.0 \times 10^{-3} M$; (B) final trace, $\text{trans-Ir(en)}_2\text{I}_2^+$.

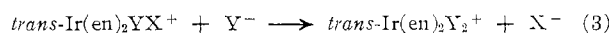
added to 200 ml of ethylene glycol. The solution was refluxed for 20 min at 175° and then allowed to distil until the temperature reached 195° and was then refluxed at that temperature for 30 min. The solution was evaporated under reduced pressure to 50 ml, 10 ml of concentrated HCl was added, and the solution was heated at 80° for 30 min. Upon cooling to 5° for 24 hr, 0.8 g of $\text{trans-[Ir(en)}_2\text{Cl}_2]\text{Cl}$ was recovered. The uv spectrum of the solution showed no *cis* isomer, although slight decomposition to iridium metal occurred during the experiment.

Results

$\text{trans-Ir(en)}_2\text{X}_2^+$.—In most cases the rates of reaction of $\text{trans-Ir(en)}_2\text{X}_2^+$ with different nucleophiles Y^- were followed spectrophotometrically at appropriate wavelengths to record the disappearance of substrate in the reaction



and/or the formation of product in the reaction



The latter could only be used if reaction 3 is fast compared to reaction 2, and this was most often the case for the systems investigated.

The spectra of Figures 1 and 2 are typical of spectral changes that accompany the reactions, with good isobestic points indicating quantitative conversion of

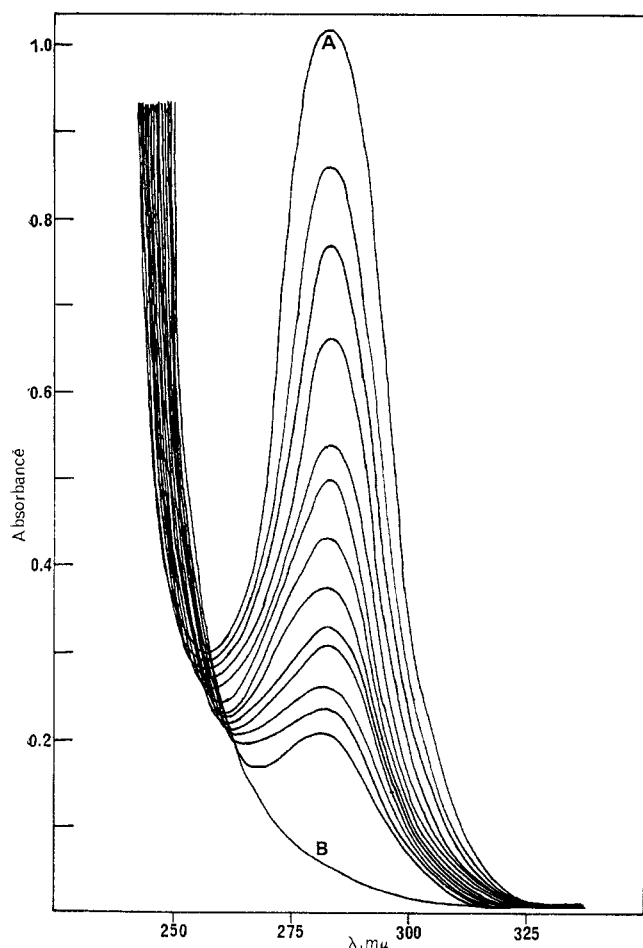


Figure 3.—Spectral changes during the reaction of *trans*-Ir(en)₂I₂⁺ with Cl⁻: (A) initial trace, *trans*-Ir(en)₂I₂⁺, 1.0 × 10⁻⁴ M; (B) final trace, *trans*-Ir(en)₂ICl⁺.

substrate to product. The wavelengths (in mμ) used to follow the reactions with different reagents are as follows: X⁻ = Cl⁻: Y⁻ = Br⁻ (365), I⁻ (398 and 282.5), N₃⁻ (341), NCS⁻ (295); X⁻ = Br⁻: Y⁻ = I⁻ (282.5), N₃⁻ (341); X⁻ = I⁻: Y = Cl⁻ (282.5), Br⁻ (282.5).

The reaction of *trans*-Ir(en)₂Cl₂⁺ with hydroxide ion could not be studied by spectrophotometric methods, because of noticeable decomposition of the glass of the reaction vessel toward the end of the reaction period. In these cases, the kinetics were studied by chloride titration. An Na₂HPO₄ and NaOH buffer at pH 11.5 was used. The pH value was estimated from published data⁷ but cannot be considered valid at all temperatures studied. The rates of reaction with OH⁻ are the same as those obtained with other nucleophiles at these temperatures, and it may be considered that the base hydrolysis is independent of hydroxide ion concentration, although no attempt was made to study concentration ranges. The base hydrolysis of *trans*-Rh(en)₂Cl₂⁺ was also found to be independent of hydroxide ion concentration.⁸

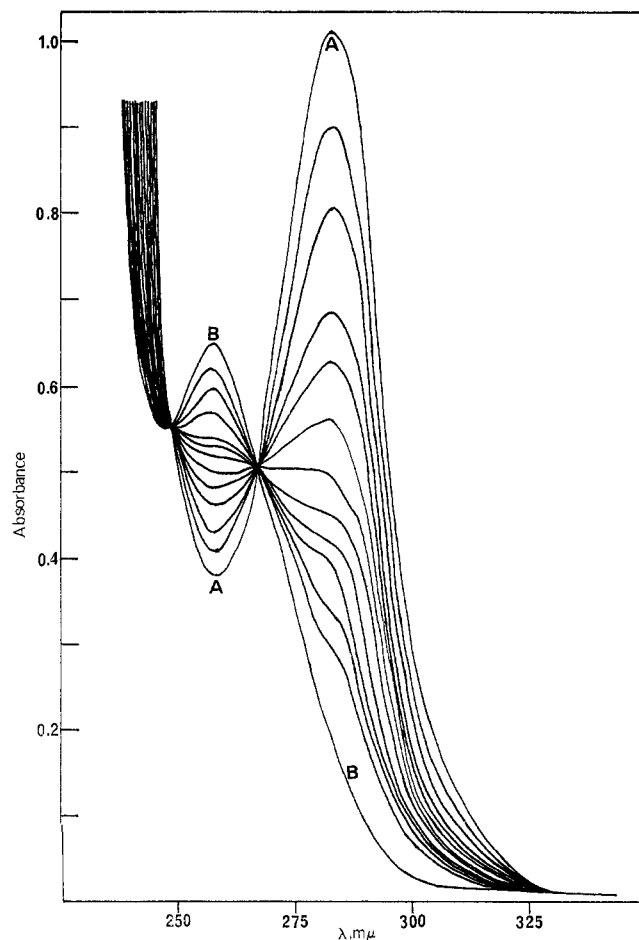
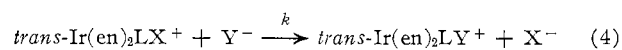


Figure 4.—Spectral changes during the reaction of *trans*-Ir(en)₂I₂⁺ with Br⁻: (A) initial trace, *trans*-Ir(en)₂I₂⁺, 1.0 × 10⁻⁴ M; (B) final trace, *trans*-Ir(en)₂IBr⁺.

The reaction of *trans*-Ir(en)₂Cl₂⁺ with thiocyanate ion is the only reaction studied in which only one chloride ion was released, indicating that chloride has a higher *trans* effect than thiocyanate. No evidence for the formation of the dithiocyanate complex was observed in the ultraviolet spectrum. On a preparative scale, only *trans*-[Ir(en)₂Cl(NCS)]ClO₄ was isolated from this reaction.⁵

In the reaction of *trans*-Ir(en)₂I₂⁺ with chloride and bromide ions only step 1 was observed, yielding the mixed iodochloro and iodobromo complexes, respectively. The spectral changes for these two reactions are shown in Figures 3 and 4. The spectrum at infinity reaction time with bromide ion is that of *trans*-Ir(en)₂IBr⁺ (Figure 4) and the isosbestic points indicate that reaction step 3 was too slow to be observed.

trans-Ir(en)₂LX⁺.—The rate of release of X⁻ from the mixed complexes was studied by following the disappearance of substrate or appearance of product in the reaction



The reactions were followed spectrophotometrically at the following wavelengths (mμ): L = I, X = Cl, Y = I (282.5); L = I, X = Cl, Y = Br (255); L = I,

(7) R. G. Bates, *J. Res. Natl. Bur. Std.*, **A66**, 172 (1962).

(8) S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962).

TABLE I
 RATES OF REACTION 2 OF $trans\text{-Ir}(\text{en})_2\text{Cl}_2^+$
 WITH VARIOUS NUCLEOPHILES, Y^-

Temp, °C	Y^-	$[\text{Y}^-]^a, M$	$10^4 k, \text{sec}^{-1}$
80	I^-	0.10	0.48
	I^-	0.20	0.52
	I^-	0.30	0.52
105	I^-	0.04	5.5
	I^-	0.20	6.1 ^b
	N_3^-	0.50	5.7
	N_3^-	0.10	5.8 ^c
	OH^-	<i>d</i>	6.0
110	I^-	0.05	9.2
	I^-	0.10	9.4 ^c
120	I^-	0.04	32
	I^-	0.02	29
	OH^-	<i>d</i>	18
125	N_3^-	0.50	33
	N_3^-	0.10	32 ^c
130	I^-	0.05	76
	I^-	0.10	70
	I^-	0.50	68
	OH^-	<i>d</i>	71
	Br^-	0.05	69
	Br^-	0.10	68
	Br^-	0.50	73
140	I^-	0.05	170
	I^-	0.10	170
	I^-	0.50	170
	OH^-	<i>d</i>	170
	Br^-	0.05	160
	Br^-	0.10	150
	Br^-	0.50	160
	N_3^-	0.50	180
	NCS^-	0.50	180

^a Ionic strength 0.50. ^b Ionic strength 0.20. ^c Ionic strength 0.10. ^d $\text{Na}_2\text{HPO}_4\text{-NaOH}$ buffer at pH 11.5. See text.

 TABLE II
 RATES OF REACTION 2 OF $trans\text{-Ir}(\text{en})_2\text{Br}_2^+$ WITH Y^-

Temp, °C	Y^-	$[\text{Y}^-]^a, M$	$10^4 k, \text{sec}^{-1}$
105	I^-	0.04	1.6
	I^-	0.08	1.5
120	I^-	0.04	6.0
	I^-	0.08	6.2
125	N_3^-	0.50	9.7
130	I^-	0.04	14
	I^-	0.08	13
140	N_3^-	0.50	33
	I^-	0.04	37
	I^-	0.08	39

^a Ionic strength 0.50.

$\text{X} = \text{Br}$, $\text{Y} = \text{I}$ (282.5); $\text{L} = \text{I}$, $\text{X} = \text{Br}$, $\text{Y} = \text{Cl}$ (255); $\text{L} = \text{Br}$, $\text{X} = \text{Cl}$, $\text{Y} = \text{Br}$ (365); $\text{L} = \text{NO}_2$, $\text{X} = \text{Cl}$, $\text{Y} = \text{Br}$ (280). The rates of the reaction at various temperatures are listed in Tables I-VI. A temperature dependence study on the rate of reaction of $trans\text{-Ir}(\text{en})_2(\text{NO}_2)\text{Cl}^+$ with bromide ion was not made. The rates of this reaction at 105° were found to be 1.1×10^{-4} and $1.0 \times 10^{-4} \text{ sec}^{-1}$ at 0.1 and 0.2 *M* bromide ion concentration, respectively. In both cases the ionic strength was 0.5.

Discussion

In all the substitution reactions of $trans\text{-Ir}(\text{en})_2\text{XY}^+$ studied, the rates were found to be independent of the

 TABLE III
 RATES OF REACTION 2 OF $trans\text{-Ir}(\text{en})_2\text{I}_2^+$ WITH Y^-

Temp, °C	Y^-	$[\text{Y}^-]^a, M$	$10^4 k, \text{sec}^{-1}$
90	Cl^-	0.20	1.1
	Cl^-	0.50	1.1
	Br^-	0.20	1.1
	Br^-	0.50	1.1
105	Cl^-	0.20	5.4
	Cl^-	0.50	6.0
	Br^-	0.20	5.8
	Br^-	0.50	5.5
125	Cl^-	0.20	40
	Cl^-	0.50	43
	Br^-	0.20	43
	Br^-	0.50	39

^a Ionic strength 0.50.

 TABLE IV
 RATES OF REACTION 4 OF $trans\text{-Ir}(\text{en})_2\text{ICl}^+$ WITH Y^-

Temp, °C	Y^-	$[\text{Y}^-]^a, M$	$10^4 k, \text{sec}^{-1}$
80	I^-	0.04	1.4
	Br^-	0.02	1.3
95	I^-	0.05	5.0
	I^-	0.02	5.6
	Br^-	0.05	5.1
105	Br^-	0.02	5.0
	I^-	0.05	14
	I^-	0.02	14
	Br^-	0.05	18
115	Br^-	0.02	18
	I^-	0.05	42
	I^-	0.02	41
	Br^-	0.05	39
	Br^-	0.02	41

^a Ionic strength 0.50.

 TABLE V
 RATES OF REACTION 4 OF $trans\text{-Ir}(\text{en})_2\text{IBr}^+$ WITH Y^-

Temp, °C	Y^-	$[\text{Y}^-]^a, M$	$10^4 k, \text{sec}^{-1}$
80	I^-	0.04	0.65
	Cl^-	0.04	0.61
95	I^-	0.05	3.5
	I^-	0.02	3.7
	Cl^-	0.04	3.7
	Cl^-	0.02	3.7
105	I^-	0.05	9.8
	I^-	0.02	12
	Cl^-	0.05	11
	Cl^-	0.02	11
115	I^-	0.05	29
	I^-	0.02	24
	Cl^-	0.05	27
	Cl^-	0.02	28

^a Ionic strength 0.50.

nature or concentration of nucleophile, and no change of rate was observed over a fivefold increase in ionic strength. This suggests that the reactions proceed by a rate-determining step (eq 5) followed by the rapid replacement of water (eq 6).

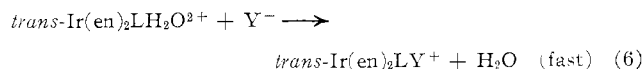
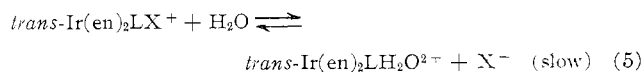


TABLE VI
RATES OF REACTION 4 OF *trans*-Ir(en)₂BrCl⁺ WITH Br⁻
AT IONIC STRENGTH 0.5

Temp. °C	[Br ⁻], M	10 ⁶ k, sec ⁻¹
105	0.20	0.92
	0.50	0.89
125	0.10	5.7
	0.40	5.3
	0.50	6.0
140	0.10	25
	0.50	20

For the complexes used and at the conditions of our experiments, equilibrium 5 lies almost entirely to the left. The results of our experiments do not permit a distinction between a dissociation (SN1) and displacement (SN2) mechanism for substitution. However, it appears that there is more assistance by the entering group for substitution reactions of Rh(III) complexes than for corresponding Co(III) systems.^{4,9} Thus it seems reasonable that bond making in the transition state for substitution reactions of Ir(III) complexes may be more important than it is in analogous reactions of Co(III) and Rh(III) compounds.

Although some *cis*-Ir(en)₂X₂⁺ complexes have been prepared,⁵ the mixed *cis*-Ir(en)₂LX⁺ complexes are unknown. It is unfortunate that the rates of reactions of *cis*-Ir(en)₂LCl⁺ with various nucleophiles are not known, as it would be of interest to see if the effect of L in *trans*-Ir(en)₂LCl⁺ is truly a *trans* effect and not merely a general effect which would produce the same results regardless of which position it occupies on the octahedron. However, from a purely semantics point of view one can speak of the *trans* effect of L simply because it is *trans* to the leaving group, regardless of what *cis* effect it might have. There is a definite kinetic *trans* effect in these systems as is shown in Table VII. The corresponding thermal parameters for the *trans*-Rh(en)₂LX⁺ complexes are listed in Table VIII for comparison.

TABLE VII
THERMAL PARAMETERS FOR THE REPLACEMENT
OF X IN *trans*-Ir(en)₂LX⁺

L	X	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal mol ⁻¹ deg ⁻¹	10 ⁶ k, sec ⁻¹ (105°)
Cl	Cl	29.2	-6	5.9
Br	Cl	27.1	-9	9.0
I	Cl	25.3	-4	159
NO ₂	Cl	107
Br	Br	27.2	-9	14.5
I	Br	27.1	-5	104
I	I	28.7	-3	58.0

Although the rate constant for the replacement of Cl⁻ in *trans*-Ir(en)₂(NCS)Cl⁺ is not available, preliminary studies at 105° show that it is much less than 10⁻⁶ sec⁻¹. The increasing *trans* effect in *trans*-Ir(en)₂LCl⁺ is then in the order: L = NCS < Cl < Br < NO₂ < I. Examination of Table VIII shows that the same order was found in the corresponding rhodium-

TABLE VIII
THERMAL PARAMETERS FOR THE REPLACEMENT
OF X IN *trans*-Rh(en)₂LX⁺ ^a

L	X	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal mol ⁻¹ deg ⁻¹	10 ⁶ k, sec ⁻¹ (50°)
Cl	Cl	24.7	-9	1.49
Br	Cl	23.2	-12	3.94
I	Cl	21.1	-7	825
NO ₂	Cl ^b	21.7	-9	184
Br	Br	25.2	-5	5.3
I	Br	23.1	-3	474
I	I	25.1	1	124

^a Data from ref 2. ^b Data from ref 10.

(III) complexes^{2,10} This is the ordering quite generally found in octahedral and square-planar complexes.¹¹ It should be pointed out that the position of the thiocyanate ion in this *trans*-effect order is inconsistent with the ordering in the Pt(II) systems due to the thiocyanate ion being S bonded in most Pt(II) complexes¹¹ and N bonded in the octahedral *trans*-M(en)₂(NCS)X⁺ complexes (M = Co(III),¹¹ Rh(III),⁸ Ir(III)⁵).

In the series *trans*-Ir(en)₂LX⁺ when X = Cl the rate constants at 105° increase by factors of 3, 36, and 54 (allowing for statistical effects) when L changes from chloride to bromide, to nitrite, and to iodide ions, respectively. Activation enthalpies decrease by 2 kcal/mol when L changes from chloride to bromide and to iodide ions in each case.

Considering the rates of release of X⁻ from the series *trans*-Ir(en)₂IX⁺, rate constants at 105° decrease by factors of about 6 and 4 (allowing for statistical effects) when X changes from chloride to bromide and to iodide ions, respectively. Activation enthalpies increase by about 2 kcal/mol in each case. These two trends show that not only do the complexes become thermodynamically more inert as the ligands change from chloride to bromide to iodide ions, but they become kinetically more inert as well. Since the stability increases with the softness or polarizability of the ligands, Ir(III) in the complexes *trans*-Ir(en)₂LX⁺ may be considered to be a soft Lewis acid¹² or a class b metal.¹³ However, Co(III) in similar complexes is kinetically and thermodynamically class a or hard. It has been argued that the difference in character of the softness of the Lewis acid moiety M(en)₂L²⁺ of Co(III) and Rh(III) lays chiefly in the lower effective charge of Rh(III) and hence in the ability of the central metal atom to accept changes in electron density more readily.²

Examination of Table IX reveals the surprising result that although the *trans* effect of L is in the same order for *trans*-Rh(en)₂LCl⁺ and *trans*-Ir(en)₂LCl⁺, the effect seems to decrease from rhodium to iridium. This result was not expected because it was felt that the third-row transition metal iridium, being more polarizable, would respond more to the *trans* effect of the ligands

(10) U. Klabunde, Doctorate Thesis, Northwestern University, 1967.

(11) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.

(12) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(13) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev. (London)*, **12**, 265 (1958).

TABLE IX
RELATIVE RATES OF RELEASE OF Cl⁻ FROM
trans-M(en)₂LCl⁺ (M = Rh, Ir)

L	Ratio of rates (L/Cl)	
	Rh ^b (50°)	Ir (105°)
Cl ^a	1	1
Br	5.3	3
I	1100	54
NO ₂	250 ^c	36

^a Divided by 2 for statistical effect. ^b From ref 2. ^c From ref 10.

than would the second-row transition metal rhodium. Certainly, this appears to be the case for substitution reactions of square-planar complexes where the *trans* effect in complexes of platinum(II) is larger than for corresponding palladium(II) and nickel(II) systems. Even this statement may not be entirely justified be-

cause of the scarcity of data in the latter two systems. Furthermore, the *trans* effect in octahedral systems may operate quite differently from that in square-planar complexes.

An important effect which is operating to diminish the relative kinetic *trans* effects is the high temperature (105°) at which the rates of substitution with different ligands in the *trans*-Ir(en)₂LX⁺ complexes are compared. The slopes of the activation energy plots are such that the kinetic *trans* effect decreases with increasing temperature, and the rates of the analogous Rh(III) complexes shown in Table IX are compared at a much lower temperature (50°).

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The Reaction between 1,10-Phenanthroline and Platinum(II) Compounds.

II. The Reaction of Potassium Tetrachloroplatinate(II) in Water-Ethanol and Other Mixed Solvents

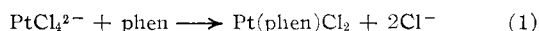
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The reaction of K₂PtCl₄ and 1,10-phenanthroline to give Pt(phen)Cl₂, which is slow and second order in water, proceeds at a fast, nearly constant rate in aqueous ethanol solution. The rate is independent of the concentration of phenanthroline but depends on the concentration of ethanol and on the initial (but not the instantaneous) concentration of K₂PtCl₄. Potential catalysts that might be formed by K₂PtCl₄ in water-ethanol are tested for catalytic activity. Of these, only ethylene has a pronounced effect on the rate, but one that is too small to explain the kinetics. The role of solvolysis in promoting the reaction is examined. Several solvents produce the same kind of reaction as ethanol. The presence of phenanthroline is not necessary for a pseudo-zero-order reaction to occur. When added to an ethanolic solution of K₂PtCl₄ which has stood for some time, phenanthroline will immediately disappear to the same extent as if it had been present from the beginning of the reaction. It appears that a platinum compound which reacts rapidly and irreversibly with phenanthroline is formed at a constant rate as the result of three consecutive, pseudo-first-order solvolysis reactions. This labile intermediate is most likely of the form PtS₂(OH)Cl (S = solvent).

Introduction

In the previous paper¹ we reported that reaction 1 (phen = 1,10-phenanthroline) was slow and second order in water solution. During the investigation, we



found that if the reactants were mixed in 50% aqueous ethanol, the same product was formed much more rapidly. At 45°, a typical reaction in water with millimolar concentrations of reactants took some 10 days to come to 75% completion. The same reaction in 50% ethanol required only 3 hr. Furthermore, it proceeded at a nearly constant rate. This paper describes the kinetics of the ethanolic reaction, an investigation of

possible catalysts formed by ethanol and K₂PtCl₄, and the role of solvolysis in promoting the fast reaction.

Experimental Section

The method of following reaction 1 spectrophotometrically has been described.¹ Aliquots of the reaction mixture were pipetted into iron(II) solutions. Red Fe(phen)₃²⁺ formed rapidly, and the solution absorbance at 510 mμ was used to determine the concentration of phenanthroline that had not reacted with platinum. The reaction product was identified by comparison of its infrared spectrum with that of an authentic sample of Pt(phen)Cl₂ and by elemental analysis. *Anal.* Calcd for Pt-(C₁₂H₈N₂)Cl₂: Pt, 43.72; C, 32.27; H, 1.79; Cl, 15.89. Found: Pt, 43.90; C, 32.22; H, 1.85; Cl, 15.92. The yield, beginning with 1 mmol each of K₂PtCl₄ and phenanthroline in 2 l. of 50% ethanol, was 431 mg (97%).

The solvolysis of K₂PtCl₄ was studied in a similar way. The reaction was found to give an intermediate which reacted immediately and irreversibly with phenanthroline. The progress