it is assumed that there is no rotational disordering of the methyl groups in the structure. The same consideration, and others, makes it seem difficult to interpret n.m.r. or spectral information.

The higher homologs of trimethylindium do not appear to be associated. Triethylindium melts at $-32,$[17] 120° below trimethylindium. This is not unexpected, since the type of bridges found in trimethylindium are sterically incompatible with higher homologs.

It is somewhat surprising that freezing point depression measurements of trimethylthallium in benzene indicate that it is monomeric.[18] Since the covalent radii of In and Tl are very similar, one might expect it, too, to be associated, especially since its melting point (38°) is relatively high compared to truly monomeric solids such as tetramethyllead. It is, of course, possible that trimethylthallium is tetrameric in the crystal, but that entropy effects lead to dissociation in solution.

Acknowledgments.—The authors are much indebted to Drs. Templeton and Senko of the University of California for I. B. M. 650 programs noted in the text and to Mr. D. R. Fitzwater for a three-dimensional block program as well as help with all our computations on the I. B. M. 650.

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[17] E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 139.

[18] H. Gilman and R. G. Jones, THIS JOURNAL, **68**, 517 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Electron-exchange Reactions between Large Complex Cations[1]

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The rates of the electron-exchange reactions (1) between $Fe(phen)_3^{++}$ and $Fe(phen)_3^{+++}$[2] and (2) between $Os(dipy)_3^{++}$ and $Os(dipy)_3^{+++}$[3] have been investigated both by optical-active and by isotopic-tracer methods, and the rates have been found to be immeasurably large. Limits on the specific reaction rates, calculated with the assumption of second-order kinetics, for reaction 1 are $>10^2$ *M* sec.$^{-1}$ (at 25°) and $>10^5$ *M* sec.$^{-1}$ (at 0°) and for reaction 2 are $>10^3$ *M* sec.$^{-1}$ (at 4°) and $>10^5$ *M* sec.$^{-1}$ (at 0°), the smaller numbers coming from the optical-active measurements, which are free from separation-induced exchange uncertainties. Colorimetric observations led to specific rate limits at 0° of $>3 \times 10^6$ *M* sec.$^{-1}$ for the net reactions between $Os(dipy)_3^{++}$ and $Fe(phen)_3^{+++}$, between $Os(dipy)_3^{++}$ and $Fe(dipy)_3^{+++}$, and between $Fe(phen)_3^{++}$ and $Ru(dipy)_3^{+++}$ and of $>5 \times 10^4$ *M* sec.$^{-1}$ for the net reaction between $Os(dipy)_3^{++}$ and $Ru(dipy)_3^{+++}$. No reduction in the rate of the $Os(dipy)_3^{++}$–$Fe(phen)_3^{+++}$ reaction was observed when resolved rather than racemic reactants were used.

Introduction

The rate of electron exchange between $Os(dipy)_3^{++}$ and $Os(dipy)_3^{+++}$[2] was investigated by Dwyer and Gyarfas[3] by observing the decrease in optical activity with time after mixing *d*-$Os(dipy)_3^{++}$ with *l*-$Os(dipy)_3^{+++}$. They reported that the rate was large but indicated that it was measurable, 95 sec. being required for complete racemization at 5° and 5×10^{-5} *M* reactant concentrations.

Eimer and Medalia[4] used conventional isotopic-tracer methods to investigate the exchange reaction between the tris-(5,6-dimethyl-1,10-phenanthroline) complexes of iron(II) and iron(III). They found complete exchange in 15 sec., indicating either that the rate in 0.5 *f* H_2SO_4 was immeasurably large (specific rate $> 10^3$ *M* sec.$^{-1}$ at 0°) or that complete exchange was induced by the separation methods.

We undertook the measurement of the $Os(dipy)_3^{++}$–$Os(dipy)_3^{+++}$ and $Fe(phen)_3^{++}$–$Fe(phen)_3^{+++}$ exchange rates by the isotopic-tracer method modified to include rapid mixing and quenching techniques, which had made possible measurements of the large rates of exchange between MnO_4^{--} and MnO_4^{-}[5] and between $Fe(CN)_6^{----}$ and $Fe(CN)_6^{---}$.[6] However, since immeasurably large rates were found, we repeated the experiments of Dwyer and Gyarfas[3] and applied a similar optical-active method to the $Fe(phen)_3^{++}$–$Fe(phen)_3^{+++}$ system.

Experimental

Chemicals.—Mallinckrodt "analytical reagent" grade chemicals were used without purification, with these exceptions: G. F. Smith Co. sodium perchlorate, Eastman Kodak Co. camphorsulfonic acid, and Eimer and Amend *p*-toluenesulfonic acid, while Eastman Kodak Co. Practical dimethyl sulfate was redistilled at atmospheric pressure. Eimer and Amend C.P. nitromethane was purified by the method of Thompson, *et al.*[7] Mallinckrodt U.S.P. potassium tartrate was recrystallized from H_2O.

Stock solutions of $Fe(phen)_3^{++}$ were prepared by dissolving equivalent amounts of $FeSO_4 \cdot 7H_2O$ or $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and 1,10-phenanthroline (G. F. Smith). The $Fe(phen)_3^{+++}$ solutions were prepared immediately before each run by dilution of appropriate amounts of $Fe(phen)_3^{++}$ with dilute sulfuric acid and oxidation with PbO_2. Excess PbO_2 and the product $PbSO_4$ were removed by centrifugation.

Tris-(2,2'-dipyridyl)-osmium(II) chloride was prepared by the method of Burstall, Dwyer and Gyarfas.[8] The compound was purified by recrystallization. Stock solutions of $Os(dipy)_3^{++}$ were prepared from weighed amounts of the compound. The $Os(dipy)_3^{+++}$ solutions were prepared by PbO_2 oxidation of $Os(dipy)_3^{++}$ in dilute H_2SO_4.

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[1] This work was supported by the National Science Foundation. The paper was abstracted from the Ph.D. thesis of Eugene Eichler, Washington University, 1955.

[2] dipy = 2,2'-dipyridyl; phen = 1,10-phenanthroline; en = ethylenediamine.

[3] F. P. Dwyer and E. C. Gyarfas, *Nature*, **166**, 481 (1950).

[4] L. Eimer and A. I. Medalia, THIS JOURNAL, **74**, 1592 (1952).

[5] J. C. Sheppard and A. C. Wahl, *ibid.*, **79**, 1020 (1957); **75**, 5133 (1953).

[6] A. C. Wahl and C. P. Deck, *ibid.*, **76**, 4054 (1954).

[7] C. J. Thompson, H. J. Coleman and R. V. Holm, *ibid.*, **76**, 3445 (1954).

[8] F. H. Burstall, F. P. Dwyer and E. C. Gyarfas, *J. Chem. Soc.*, 953 (1950).

Tris-(2,2′-dipyridyl)-ruthenium(II) chloride was synthesized by the method of Burstall[9] and purified by slow recrystallization at room temperature. Tris-(ethylenediamine)-cobalt(III) chloride and tris-(ethylenediamine)-platinum(IV) chloride were prepared by the methods of Work[10] and Werner,[11] respectively.

$Ni(phen)_3^{++}$ solutions were prepared by dissolution of equivalent amounts of $NiSO_4 \cdot 6H_2O$ and 1,10-phenanthroline.

Radioactivity.—The iron tracer, Fe^{55}, and the osmium tracer, a mixture of Os^{191} and Os^{185}, were obtained from the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission. The Fe^{55} tracer had been purified by Hudis,[12] and it was converted to $Fe(phen)_3^{++}$ in much the same way as the inactive $Fe(phen)_3^{++}$ was made. The osmium tracer was purified by distillation of OsO_4, and converted to $Os(dipy)_3^{++}$ by the method employed for the inactive material.[8]

Radioactive $Fe(phen)_3^{++}$ samples were mounted for counting as the slightly soluble perchlorate salt on filter paper and were counted with an argon–methane proportional counter. All samples were diluted before precipitation to 0.04 mmole with inactive $Fe(phen)_3^{++}$ to ensure equal counting efficiencies for the 5.9 kev. X-rays.

Radioactive $Os(dipy)_3^{++}$ samples were counted in solution, the γ-rays from both Os^{191} and Os^{185} being detected by a stilbene-crystal scintillation counter

Optical Activity.—Dextro- and levorotatory forms of $Fe(phen)_3^{++}$ were prepared according to the procedure of Dwyer and Gyarfas.[13] The active forms of $Os(dipy)_3^{++}$ were resolved by the method of Burstall, Dwyer and Gyarfas.[8]

All rotations were observed with a Rudolph polarimeter. A General Electric Na-1 sodium light served as the light source for the $Fe(phen)_3^{++}$ measurements, and a Hanovia mercury arc with a Baird Associates 3770-5480A interference filter was used for the $Os(dipy)_3^{++}$ work.

Separation Methods.—The +3 reactant was tagged, and appearance of radioactivity in the +2 form was observed. Reduction of the +3 form was negligible during the course of an experiment. All separations involved removal of the +2 ion from solution. Both precipitation and solvent-extraction separation methods were used for each reaction. Table I indicates the degree of separation for each method.

TABLE I

SEPARATION METHODS

	Reactant:	$Fe(phen)_3^{++}$	$Os(dipy)_3^{++}$
ClO_4^- precipitation method	Carrier:	$Ni(phen)_3^{++}$	$Fe(phen)_3^{++}$
	% Removal of +2 form:	~60	~70
	% +3 form in precipitate:	<1	<5
Solvent extraction method	Reactant:	$Fe(phen)_3^{++}$	$Os(dipy)_3^{++}$
	Solvent:	Dimethyl sulfate and nitromethane	Nitromethane
	Extracting agent:	10-Camphorsulfonic acid	*p*-Toluenesulfonic acid
	% Removal of +2 form:	~60	~90
	% +3 form in organic phase:	<1	<1

Stand-in carriers were necessary for precipitation separations because the reactant concentrations were too small for precipitation. Experimental conditions are given with the results.

Analyses and Specific Activity Determinations.—Both osmium and iron were determined spectrophotometrically. At 5100 Å. $Fe(phen)_3^{++}$ has a molar absorbance coefficient[14] of 1.11×10^4. This value was verified.

The molar absorbance coefficient for $Os(dipy)_3^{++}$ was determined at its spectral maximum, 4800 Å., to be 1.34×10^4. This value was obtained from measurements of solutions prepared from three different compounds, $Os(dipy)_3Cl_2 \cdot 6H_2O$, $Os(dipy)_3Br_2 \cdot 3H_2O$ and $Os(dipy)_3(ClO_4)_2 \cdot H_2O$. The purity of these compounds, with reference to reducing power, was shown to be greater than 98%.

Specific activity determinations involved return of the iron or osmium complex from organic extractant or precipitate to aqueous phase, regeneration of the complex if necessary, observation of the optical density and removal of an aliquot for counting. Back extraction was effected by addition of CCl_4 or benzene to the organic phase. Precipitates were dissolved by boiling in 3 *f* H_2SO_4. This did not destroy $Os(dipy)_3$ but caused disassociation of $Fe(phen)_3^{++}$. Thus, when $Fe(phen)_3^{++}$ was acting as carrier for $Os(dipy)_3^{++}$ it did not interfere in the spectrophotometric determination of $Os(dipy)_3^{++}$. However, when the $Fe(phen)_3^{++}$ was a reactant, it was necessary to regenerate it for spectrophotometric determination by addition of more 1,10-phenanthroline after buffering with sodium acetate and reduction of any Fe^{+++} with hydroxylamine. $Ni(phen)_3^{++}$, which was used as a carrier in many experiments, did not regenerate under these conditions.

Experimental Results

Isotopic Method.—Homogeneous exchange reactions were performed with the $Os(dipy)_3^{++}$–$Os(dipy)_3^{+++}$ and $Fe(phen)_3^{++}$–$Fe(phen)_3^{+++}$ systems. The reactants at approximately equal concentrations were mixed in the rapid mixing device described by Wahl and Deck[6] and delivered directly into the extracting or precipitating solution contained in a 40-ml. centrifuge tube fitted with a stirrer. Reaction times were ~ 0.07 sec. A mixture was stirred for a few seconds and immediately centrifuged for 30 sec. after an extraction or for 4 min. after a precipitation. The usual volume of quenching solution was 5 ml., and 7 to 10 ml. of reaction solution was delivered.

The results are shown in Tables II and III. Each value is an average obtained from three to five separate experiments. It can be seen that within an experimental error of ~ 5% all experiments resulted in complete exchange.

TABLE II

THE $Os(dipy)_3^{++}$–$Os(dipy)_3^{+++}$ ISOTOPIC EXCHANGE REACTION

(Reaction time, 0.07 sec.; 0°)

Sum of reactant concn., *M*	(H_2SO_4), *f*	Stirring time, sec.	Fraction exchange
	Extraction separation[a]		
1×10^{-5}	3.0	2	1.05
2	3.0	2	1.03
8	3.0	2	1.00
8	3.0	1	1.06
8	3.0	None	1.03
11	3.0	1	0.98[b]
11	3.0	1	1.01[b,c]
	Precipitation separations[d]		
10×10^{-5}	3.0	None	0.97
10	0.1	3	1.01
7.5	1×10^{-3}	3	1.02
10	2×10^{-4}	3	0.95

[a] 0.2 *M* *p*-toluenesulfonic acid in nitromethane; 10^{-3} *M* $Ni(phen)_3^{++}$ and 10^{-3} *M* $Pt(en)_3^{++++}$ stand-in carriers in the reaction solution. [b] 1.7×10^{-4} *M* $Fe(phen)_3^{++}$ [c] Nitromethane solution at −15°. [d] 1.0 *f* $NaClO_4$ precipitating reagent; 5×10^{-4} *M* $Fe(phen)_3^{++}$ stand-in carrier reaction solution.

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(9) F. H. Burstall, *J. Chem. Soc.*, 173 (1936).

(10) J. B. Work, "Inorganic Syntheses," Vol. II, W. C. Fernelius (Editor), McGraw–Hill Book Co., Inc., New York, N. Y., 1946, p. 221.

(11) A. Werner, *Vierteljahrsschr. Naturforsch. Ges. Zurich*, 555 (1917).

(12) J. Hudis and A. C. Wahl, THIS JOURNAL, **75**, 4153 (1953).

(13) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc., N.S. Wales*, **83**, 263 (1949).

(14) W. W. Brandt and D. K. Gullstrom, THIS JOURNAL, **74**, 3532 (1952).

TABLE III

THE $Fe(phen)_3^{++}$–$Fe(phen)_3^{+++}$ ISOTOPIC EXCHANGE REACTION

(Reaction time, 0.07 sec.; 0°; 3.0 *f* H_2SO_4)

Sum of reactant concn., *M*	Stirring time, sec.	Fraction exchange
Extraction separation[a]		
2×10^{-5}	3	1.05
1	None	1.04[b]
0.5	3	0.98[b]
0.5	3	0.94[b,c]
20	None	1.07[d]
20	None	0.98[e]
0.5	2	1.09[f]
1	2	1.04[f,g]
Precipitation separation[h]		
20×10^{-4}	None	1.00
0.5	2	0.95[i]

[a] 0.1 *M* 10-camphorsulfonic acid in dimethyl sulfate; 5×10^{-4} *M* $Ni(phen)_3^{++}$ stand-in carrier in the reaction solution. [b] At 25°. [c] 5×10^{-4} *M* $Os(dipy)_3^{+++}$. [d] 5×10^{-3} *M* $Ni(phen)_3^{++}$ in the dimethyl sulfate. [e] No stand-in carrier. [f] 0.017 *M* 10-camphorsulfonic acid in nitromethane as extracting agent; 5×10^{-4} *M* $Ni(phen)_3^{++}$ stand-in carrier in nitromethane. [g] 2.5×10^{-4} *M* $Ni(phen)_3^{++}$ and 1×10^{-8} *M* $Co(en)_3^{+++}$ in the reaction solution. [h] 0.5*f* $HClO_4$ precipitating agent. [i] 5×10^{-4} *M* $Ni(phen)_3^{++}$ stand-in carrier in reaction solution.

Since exchange could have occurred during the separation processes, exchange studies of the processes were made.

(1) **Heterogeneous-exchange Reactions.**—The +2 reactant was placed in the non-aqueous phase (*i.e.*, extracted into the organic phase or coprecipitated with $Ni(phen)_3(ClO_4)_2$) and immediately mixed with the +3 reactant in sulfuric acid solution. The mixtures were stirred 1, 2 or 3 sec. and then centrifuged as in the homogeneous exchange experiments. For the $Fe(phen)_3^{++}$–$Fe(phen)_3^{+++}$ reaction, ~50% exchange occurred for both heterogeneous systems, so all of the exchange observed in the homogeneous exchange reactions could not have occurred during the stirring and centrifugation steps—extensive exchange must have occurred either in the homogeneous solution or as the precipitate formed or extraction occurred.

The heterogeneous exchange between $Os(dipy)_3^{++}$ (in nitromethane) and $Os(dipy)_3^{+++}$ (aq) was essentially complete.

(2) **Competitive Reactions.**—To approximate conditions existing during formation of a precipitate, the exchange and precipitation reactions were run in competition. The +3 reactant was dissolved in ClO_4^- solution, and the +2 reactant was made up as usual in dilute H_2SO_4. The two solutions were mixed rapidly by ejection of the +2 solution into the +3 solution being stirred. Incomplete exchange, ~85%, was observed for both the iron and the osmium systems. The conditions were the same as for the eighth entry of Table II and the last two entries of Table III.

Since the conditions were similar to those existing during the separation process in a homogeneous exchange reaction, it might reasonably be assumed that the competitive exchange is a measure of the zero-time exchange[15] in the homogeneous reaction. Making this assumption, the fraction exchange *F* occurring during the 0.07 sec. reaction time is

$$F = \frac{F_a - F_0}{1 - F_0} = \frac{>0.95 - <0.90}{1 - <0.90} = >0.5$$

F_a and F_0 being the observed fraction exchange and the zero-time exchange, respectively.[15] If in addition it is assumed that the exchange reactions obey second-order rate laws, limits for the specific rate constants may be calculated from the <0.07 sec. half-time, $t_{1/2}$.

$$k = \frac{(\ln 2)}{(t_{1/2})\ (\text{sum of reactant concn.})}$$

$$k = \frac{(0.7)}{(<0.07)(\leqslant 10^{-4})} = >10^5\ \text{M}^{-1}\ \text{sec.}^{-1}$$

The Optical-activity Method.—$Os(dipy)_3^{++}$–$Os(dipy)_3^{+++}$.—The very large electron-exchange rate indicated by the isotopic measurements just described is inconsistent with the measurable rate indicated by the optical-activity measurements of Dwyer and Gyarfas.[3] Therefore, we repeated their experiment at 4°, *p*H 5, and 1×10^{-4} *M* total reactant concentration. They reported complete racemization of a *d*-$Os(dipy)_3^{++}$–*l*-$Os(dipy)_3^{+++}$ mixture after 95 sec.; we observed complete racemization after 15 sec., the time required to mix the reactants with the rapid mixer, to place the reaction mixture in the polarimeter, and to observe the matched fields. We obtained the same result at 4°, 0.1 *f* H_2SO_4, and 5×10^{-5} *M* total reactant concentration. (The initial rotation was kept the same, −0.1°, by replacement of the 10-cm. polarimeter tube with a 20-cm. tube.)

The cause of the discrepancy is not known. We found the measurement a difficult one because the intense coloration of the reactants limited the length of the light path and the concentrations of the reactants so that the initial rotation was only −0.1°, and rotations of this magnitude were difficult to measure quickly with fields of low luminosity. Also, the term "complete racemization" is rather indefinite. Dwyer and Gyarfas did not state the limits of completeness for their observations; we estimate for ours that complete racemization means rotations of 0.0 ± 0.05°. (A 0.1° rotation was quickly and certainly distinguishable from zero rotation.)

The <15 sec. half-time for racemization from our measurements corresponds to a second-order rate constant for the electron-exchange reaction of $>10^3\ M^{-1}\ \text{sec.}^{-1}$.

$Fe(phen)_3^{++}$–$Fe(phen)_3^{+++}$.—Application of the above method to this system was not feasible because of the rapid racemization of resolved $Fe(phen)_3^{+++}$ ($t_{1/2}^{III} = 44 \pm 9$ sec. at 25° in 3 *f* H_2SO_4). Resolved $Fe(phen)_3^{++}$ also racemizes, but more slowly ($t_{1/2}^{II} = 25 \pm 5$ min. at 25° in 3 *f* H_2SO_4). These values were the same at various reactant concentrations, confirming the first-order rate laws, and they are consistent with other re-

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[15] O. E. Myers and R. J. Prestwood, "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Bonner (Editors), John Wiley and Sons, Inc., New York, N. Y., 1951, p. 16.

ported values[16,17] determined for different acid media.

A mixture of the same optical-active forms of Fe(phen)$_3^{++}$ and Fe(phen)$_3^{+++}$ will racemize at two independent rates, one characteristic of each species, if there is no electron exchange between the species. If electron exchange is rapid, the species, being in equilibrium, will racemize at the same rate, the half-time $t_{1/2}$ being an average of the racemization half-times of the individual species weighted for their concentrations, (II) and (III).

$$\frac{(\text{II}) + (\text{III})}{t_{1/2}} = \frac{(\text{II})}{t_{1/2}^{\text{II}}} + \frac{(\text{III})}{t_{1/2}^{\text{III}}}$$

(A similar expression is derived in Eichler's thesis.[1])

Experimentally, a portion of *l*-Fe(phen)$_3^{++}$ in solution was oxidized rapidly[18] by Ce$^{\text{IV}}$, the mixture was allowed to stand at 25° for the desired time, Fe$^{\text{II}}$ was added to reduce rapidly[18] the Fe(phen)$_3^{+++}$, and the optical rotation of the resulting solution was measured. Racemization times were varied, and the results were compared with curves calculated for fast and slow electron exchange as illustrated in Fig. 1.

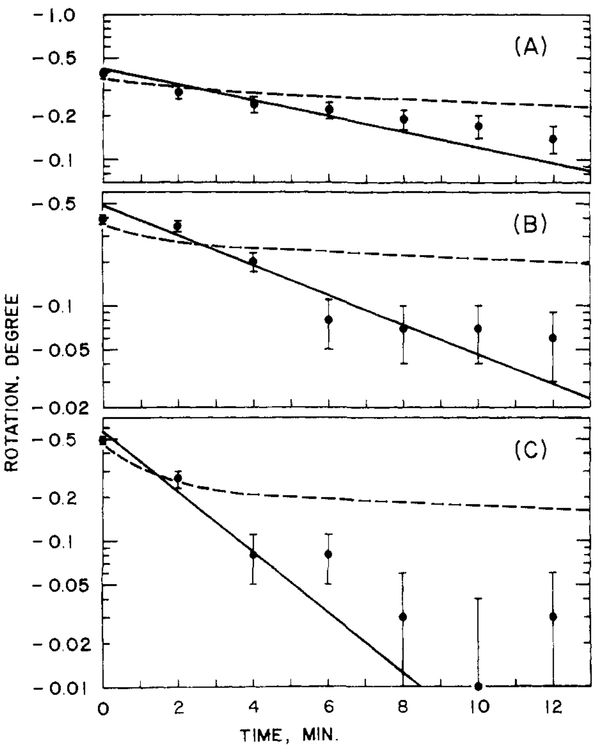

Fig. 1.—Racemization of *l*-Fe(phen)$_3^{++}$–*l*-Fe(phen)$_3^{+++}$ mixtures in 3 *f* H$_2$SO$_4$ at 25°. Solid curves calculated for rapid electron exchange; broken curves for no electron exchange. Indicated errors are due to estimated ±0.03° uncertainty in polarimeter readings.

	(Fe(phen)$_3^{++}$)	(Fe(phen)$_3^{+++}$)
(A)	8.6 × 10^{-5} *M*	1.0 × 10^{-5} *M*
(B)	8.2	2.4
(C)	10.0	9.3

Since the data agree best with the curves for rapid electron exchange, we take the rate of electron exchange to be greater than the largest racemization rate, *i.e.*, that for Fe(phen)$_3^{+++}$. Assuming a second-order rate law for the electron-exchange reaction, a lower limit may be calculated for the specific rate constant *k*.

$$k[\text{Fe(phen)}_3^{++}][\text{Fe(phen)}_3^{+++}] > k_{\text{rac.}}[\text{Fe(phen)}_3^{+++}]$$

$$k > \frac{\ln 2}{44\ \text{sec.}} \times \frac{1}{(10^{-4}\ M)} = 160\ M^{-1}\ \text{sec.}^{-1}$$

Net Oxidation–Reduction Reactions.—Net oxidation–reduction reactions between Os(dipy)$_3^{++}$ and Fe(phen)$_3^{+++}$, Fe(dipy)$_3^{++}$, or Ru(dipy)$_3^{+++}$, and between Fe(phen)$_3^{++}$ and Ru(dipy)$_3^{+++}$ were performed. The intense colors of the +2 forms of the reactants made visual observation of the progress of the reactions possible. The reactants were mixed in the rapid-mixing device described by Gordon and Wahl,[19] and colors were observed in the reaction tube close to the mixing chamber. Comparison tubes containing standards whose intensity of color represented 50 and 100% reaction were used to aid in estimating when a reaction was half, or more, complete.

The results, given in Table IV, show that the rate of electron-exchange between the complex cations is large. This is consistent with our conclusions concerning the Fe(phen)$_3^{++}$–Fe(phen)$_3^{+++}$ and Os(dipy)$_3^{++}$–Os(dipy)$_3^{+++}$ exchange reactions and with the observations of George and Irvine[18] that the reactions between Fe(dipy)$_3^{++}$ and Fe(phen)$_3^{+++}$ and between Fe(dipy)$_3^{++}$ and Ru(dipy)$_3^{+++}$ are very fast ($k_{18°} > 10^5\ M^{-1}$ sec.$^{-1}$). No reduction in the rate was observed when resolved rather than racemic reactants were used.

TABLE IV

NET OXIDATION–REDUCTION REACTIONS

(Reactant concn., 10^{-4} *M*; 0°)

Reactants	(H$_2$SO$_4$), *f*	Half-time, sec.	*k*,[a] M^{-1} sec.$^{-1}$
Os(dipy)$_3^{++}$ + Fe(phen)$_3^{+++}$	3.0	<0.004	>2.5 × 10^6
	0.1	< .003	>3 × 10^6
	3.0	< .003	>3 × 10^{6b}
l-Os(dipy)$_3^{++}$ + *d*-Fe(phen)$_3^{++}$	3.0	< .004	>3 × 10^{6c}
l-Os(dipy)$_3^{++}$ + *l*-Fe(phen)$_3^{++}$	3.0	< .004	>3 × 10^{6c}
Os(dipy)$_3^{++}$ + Fe(dipy)$_3^{+++}$	3.0	< .004	>2.5 × 10^6
Os(dipy)$_3^{++}$ + Ru(dipy)$_3^{+++}$	0.1	< .2	>5 × 10^{4d}
Fe(phen)$_3^{++}$ + Ru(dipy)$_3^{+++}$	0.1	< .003	>3 × 10^6

[a] Second-order rate law assumed. [b] 23°. [c] 8 × 10^{-5} *M* reactant concentrations. [d] Colors of +2 ions appeared very similar in 1-mm. capillary of rapid mixer, so reaction was observed in 40-ml. centrifuge tube.

Discussion

We conclude from our experimental results that the rates of electron exchange between the large complex cations, Fe(phen)$_3^{++}$, Fe(phen)$_3^{+++}$, Os(dipy)$_3^{++}$ and Os(dipy)$_3^{+++}$, are at least as large and very probably are much larger than the rates of electron exchange between the large anions, MnO$_4^{--}$, MnO$_4^-$, Fe(CN)$_6^{----}$ and Fe(CN)$_6^{---}$ (specific rates ~10^3 *M* sec.$^{-1}$ at 0°).[5,6,20] Admittedly, there is some uncertainty in this conclusion because the rate laws could not be determined, because our *d*-Os(dipy)$_3^{++}$–*l*-Os(dipy)$_3^{+++}$

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(16) N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **49**, 180 (1953); **50**, 820 (1954).

(17) F. Basolo, J. C. Hayes and H. M. Neumann, THIS JOURNAL, **76**, 3807 (1954).

(18) P. George and D. H. Irvine, *J. Chem. Soc.*, 587 (1954).

(19) B. M. Gordon and A. C. Wahl, THIS JOURNAL, **80**, 273 (1958).

(20) C. F. Deck, Ph.D. thesis, Washington University, 1956.

racemization data do not agree with those of Dwyer and Gyarfas,[3] and because for the immeasurably rapid isotopic-exchange reactions there is the ever-present possibility of complete separation-induced exchange. However, we did present evidence that the separation-induced exchanges were incomplete, and for the net chemical reactions, for which separations were not involved, there is no question but that the reaction between $Os(dipy)_3^{++}$ and $Fe(phen)_3^{+++}$ is much more rapid than the reaction between MnO_4^{--} and $Fe(CN)_6^{---}$ (specific rate, ~10^4 *M* sec.$^{-1}$ near 0°[5]).

It is of interest to speculate about the cause(s) for the apparent greater rate of electron exchange between the large complex cations than between the large anions. In addition to the difference in sign of the ionic charges, the complex cations differ from the anions in being larger and in having aromatic-type chelating groups. Although any or all of the factors may be significant, the apparent greater rate of electron exchange could be due entirely to the greater size of the cations. We estimate the radii of the cations to be 7 Å. from bond distances given by Pauling.[21] Marcus[22] estimated 2.8_6 Å. for the radii of MnO_4^{--} and MnO_4^- and 4.5 Å. for the radii of $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$. The greater the sizes of the reactants, the smaller will be both the coulombic repulsion between them and the Franck–Condon restrictions due to differences in their hydration spheres.[23] Using the radii given above we have calculated from the Marcus theory[22] of electron transfer that the rate of electron exchange should be ~10^4 greater between the complex cations than between the anions.

(21) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 158–176. Fe^{II} covalent radius, 1.23 Å.; Os^{II} covalent radius, 1.33 Å.; N radius, 0.70 Å.; N to C distance across the ring (taken equal to C to C distance across benzene), 2.78 Å.; C–H distance (taken same as in benzene) 1.08 Å.; H van der Waals radius 1.2 Å.

(22) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); **26**, 867 (1957).

(23) W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

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The Preparation of Tetraborane and Pentaborane-11[1]

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A hot-cold tube technique has been devised which quantitatively converts diborane into a mixture of tetraborane and pentaborane-11. The yield of tetraborane under the reported conditions varies from 80–95%. Pentaborane-11 may be prepared from tetraborane in 70% yield by suitable adjustment of the operating conditions.

The chemistry of tetraborane and pentaborane-11 has received very little attention, primarily because the laboratory preparation of these two materials is exceedingly difficult.[2-9] Unless these compounds are prepared in a system which produces them in a relatively pure state, they are difficult to purify and the presence of impurities makes them highly unstable. Therefore, it was considered very desirable to devise a convenient laboratory method for the preparation of these two compounds.

Because of the instability of tetraborane and pentaborane-11, it was decided to use a hot-cold tube reactor as an approach to their syntheses. Koski, Maybury and Kaufman[10] have used this type of approach for the preparation of pentaborane-9, in that they pyrolyzed diborane in a glass vessel, one end of which was heated to 180°, while the other end was cooled to −80°. Their technique, while entirely satisfactory for a relatively stable compound such as pentaborane-9, was not useful for the preparations of tetraborane or pentaborane-11.

The method of preparation described below gives better yields than have ever been reported and employs a very simple apparatus that can be used repeatedly without frequent cleaning.

Experimental

Design of the Hot-Cold Tube Reactor.—The reactors consisted of two concentric test-tubes connected by a Dewar seal at the top. The outside of the reactor was surrounded by the cold bath. The temperature of the cold bath was determined by two factors. It had to be high enough so that the reactant or reactants would have a fair vapor pressure, and low enough so that the desired product would have a very low vapor pressure. The inner tube was then adjusted to the desired reaction (hot) temperature by placing a knife heater in a suitable heating liquid inside the inner tube. The annular space, 10 mm., was made very small so that the product could diffuse rapidly from the hot wall to the cold wall with minimum thermal decomposition. The reactor was made as long as was practical to give maximum heating and cooling surfaces. The dimensions of the two reactors in this study are given in Table I.

TABLE I

HOT-COLD TUBE REACTOR DIMENSIONS

	Height, cm.	Diameter, cm.		Volume, cc.
		Hot tube	Cold tube	
Reactor I	30	6	8	337
Reactor II	27	8	10	550

Preparation of Tetraborane.—The diborane supply was obtained from the Callery Chemical Company, and was

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 131st meeting of the American Chemical Society, Miami, Florida, April, 1957.

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(3) A. Stock, E. Wiberg and H. Martini, *ibid.*, **63B**, 2927 (1930).

(4) A. Stock and W. Mathing, *ibid.*, **69B**, 1456 (1936).

(5) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933.

(6) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **55**, 4009 (1933).

(7) A. B. Burg and F. G. A. Stone, *ibid.*, **75**, 228 (1953).

(8) A. Stock and E. Pohland, *Ber.*, **59**, 2223 (1926).

(9) T. Wartik, M. Linevsky and H. Bowkley, "Thermodynamic Properties of Boron and Aluminum Compounds," Progress Report No. 3, March 1, 1955, Contract No. AF 18(600)-311.

(10) W. S. Koski, P. C. Maybury and J. J. Kaufman, *Anal. Chem.*, **26**, 1992 (1954).