spectral assignments taken from those for $CuCl_4^{-2}$ (Table VI) are identical with the crystal field assignments[34] for the $CuBr_4^{-2}$ ion.

**Summary.**—It is concluded that the semi-empirical LCAO–MO scheme can be used to give a semiquantitative measure of the ground-state distortions and spectral splittings of transition metal complexes, especially one-electron and one-hole systems. It should be kept in mind that an observed distortion in a crystal does not necessarily result from the so-called Jahn–Teller effect, but may result from packing considerations, such as those giving rise to the trigonal distortion of the $V(OH_2)_6^{+3}$ ion in vanadium alum, which does not appear[3] to arise from Jahn–Teller considerations, even though the ion is in a spatially degenerate $^3T_{1g}$ state if octahedral.[37]

(37) NOTE ADDED IN PROOF.—For new studies of the $NiCl_4^{-2}$ solution spectrum, see N. K. Hamer, *Mol. Phys.*, **6**, 257 (1963). For recent remarks on the $VCl_4$ electronic and vibrational spectra, see E. L. Grubb, F. A. Blankenship, and R. L. Belford, *J. Phys. Chem.*, **67**, 1562 (1963), and E. L. Grubb and R. L. Belford, *J. Chem. Phys.*, **39**, 244 (1963). A private communication from R. B. Johannesen informs us that electron paramagnetic resonance studies suggest that the $VCl_4$ molecule may be distorted in a solid solution of $VCl_4$ in $TiCl_4$, but the amount of the distortion is not clear. Finally, for optical spectra of $Cu^{+2}$ in $Cs_2ZnCl_4$, see D. M. Gruen and R. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963).

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# The Kinetics of the Oxidation of Iron(II) and its Substituted *tris*-(1,10-Phenanthroline) Complexes by Cerium(IV)[1,2]

BY G. DULZ AND N. SUTIN

The kinetics of the oxidation of iron(II) and a number of its substituted tris-(1,10-phenanthroline) complexes by cerium(IV) have been investigated in sulfuric acid using a rapid-mixing and flow technique. The free energies of activation for the latter reactions were found to be related to their standard free energy changes. The rate constant for the oxidation of tris-(1,10-phenanthroline)-iron(II) by cerium(IV) increased with increasing sulfuric acid concentration. The second-order rate constant for the $Fe(phen)_3^{2+}$–Ce(IV) reaction in 0.50 $F$ $H_2SO_4$ is $1.42 \times 10^5$ $F^{-1}$ sec.$^{-1}$ at 25.0° with an activation energy of 6.5 kcal. mole$^{-1}$. The corresponding quantities for the Fe(II)–Ce(IV) reaction are $1.3 \times 10^6$ $F^{-1}$ sec.$^{-1}$ and 9.5 kcal. mole$^{-1}$, respectively. The results are discussed in terms of the Marcus theory of electron-transfer reactions.

There are several examples of linear free energy relationships in electron-transfer reactions.[3–5] For instance, the free energies of activation for the oxidation of ferrous ions by a variety of substituted tris-(1,10-phenanthroline) complexes of iron(III) are linearly related to their standard free energy changes.[5] Such linear free energy relationships are predicted by the Marcus theory of electron-transfer reactions.[6,7]

In order to obtain additional information concerning the relationship between the rates and the free energy changes of oxidation–reduction reactions we have studied the kinetics of the oxidation of iron(II) and a number of its substituted tris-(1,10-phenanthroline) complexes by cerium(IV) in 0.50 $F$ $H_2SO_4$. These studies include reactions with larger standard free energy changes than the $Fe^{2+}$–$Fe(phen)_3^{3+}$ studies.

The results are examined in the light of the Marcus equations[8]

$$k_{12} = (k_1 k_2 K_{12} f)^{1/2} \tag{1}$$

or

$$\Delta G_{12}^* = 0.50\Delta G_1^* + 0.50\Delta G_2^* + 0.50\Delta G_{12}^\circ - 1.15\,RT \log f \tag{2}$$

where

$$\log f = (\log K_{12})^2 / 4 \log (k_1 k_2 / Z^2) \tag{3}$$

In the above expressions $k_{12}$ is the rate constant for the oxidation–reduction reaction, for example, the $Fe^{2+}$–$Fe(phen)_3^{3+}$ reaction, and $K_{12}$ is the equilibrium constant for the same reaction. The rate constants $k_1$ and $k_2$ refer to the corresponding electron exchange reactions; in this instance the $Fe^{2+}$–$Fe^{3+}$ and $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$ exchange reactions. $\Delta G^*$ and $\Delta G^\circ$ are the appropriate free energies of activation and standard free energy changes, respectively, and $Z$ is the collision frequency of two uncharged molecules in solution. It is assumed to have a value of $10^{11}$ l. mole$^{-1}$ sec.$^{-1}$. The above equations are applicable to outer-sphere electron-trans-

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) Based in part on the Ph.D. Thesis submitted by G. Dulz to Columbia University, New York, N. Y., 1962.

(3) D. H. Irvine, *J. Chem. Soc.*, 2977 (1959).

(4) N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, **83**, 70 (1961).

(5) M. H. Ford-Smith and N. Sutin, *ibid.*, **83**, 1830 (1961).

(6) R. A. Marcus, *Discussions Faraday Soc.*, **29**, 21 (1960).

(7) R. A. Marcus, *Can. J. Chem.*, **37**, 155 (1959).

(8) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

fer reactions, but not to inner-sphere reactions or to reactions proceeding *via* an atom transfer mechanism.

## Experimental

**Chemicals.**—Either the iron(II) complex or the ligands were obtained from the G. Frederick Smith Chemical Company. In the latter case the iron(II) complex was prepared by adding an equivalent amount of the appropriate ligand to a solution of ferrous sulfate. 3,4,7,8-Tetramethyl-1,10-phenanthroline was purified by recrystallization from benzene (charcoal) and its iron(II) complex purified by precipitation of its sulfate salt. Ceric sulfate (G. Frederick Smith Chemical Co.), ferrous sulfate (Baker Analyzed Reagent), and sulfuric acid (Baker and Adamson) were used without further purification. The solutions for the kinetic measurements were prepared with triple-distilled water and standardized spectrophotometrically.

**Apparatus.**—The apparatus which has been previously described[4] was improved so that reactions with half-times down to about 5 msec. could be studied by means of the stopped-flow technique. The apparatus is shown schematically in Fig. 1.
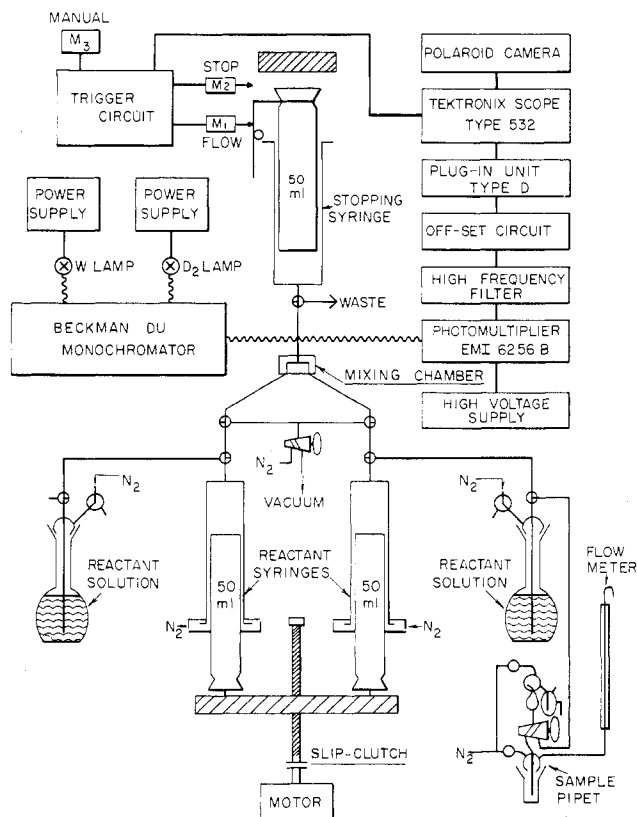


Fig. 1.—Schematic diagram of the flow apparatus.

The pistons of the two reactant syringes were housed in a pushing block which was driven *via* a magnetic slip-clutch by a variable speed, 0.25-horsepower motor (Model NSH-55, Bodine Electric Co.). The reactant syringes were connected to the mixing chamber *via* four three-way stopcocks which could be used to evacuate the system and admit the reactant solutions into the syringes.

The mixing chambers were based on the designs of Gibson[9] and Chance.[10] Two types of mixing chambers were used. The first type was constructed from a cylinder of Lucite, 25 mm. in diameter and 19 mm. long, and contained eight jets of 0.7-mm. bore which were located in two parallel planes. The jets were tangentially arranged around a 2-mm. hole drilled into one face of the Lucite; the jets in one plane were arranged clockwise

(9) Q. H. Gibson, *Discussions Faraday Soc.*, **17**, 137 (1954).
(10) B. Chance and V. Legallais, *ibid.*, **17**, 123 (1954).

around the hole while the jets in the second plane were arranged counter-clockwise around the hole. An 11-cm. long 2-mm. diameter quartz capillary observation tube was aligned with the hole and cemented into place. The second type was essentially a two-stage mixing chamber. After being mixed in the eight-jet mixing chamber, the flowing solution divided into four jets of 0.7-mm. bore which entered a second mixing chamber of 2-mm. bore. This mixing chamber was aligned with the quartz tube as described above. The two-stage mixing chamber proved more efficient than the one-stage mixing chamber. Solutions of different viscosities, such as water and 1 *F* sulfuric acid, were found to be incompletely mixed at the exit of the one-stage mixing chamber, while no evidence of incomplete mixing of the above solutions was found at the exit of the two-stage mixing chamber.

The light beam from the Beckman DU monochromator traversed the observation tube at a distance of about 10 mm. from the entrance of the mixing chamber. The light beam was collimated by two 1 × 2 mm. slits, which were built into a thermostated metal block which housed the quartz observation tube. The outlet of the observation tube was connected to the stopping syringe *via* a three-way stopcock. The transmitted light beam was detected and amplified by an EMI-6256B photomultiplier. The output of this photomultiplier was connected to the differential preamplifier (type D) of the Tektronix oscilloscope *via* a variable filter for high frequency noise and a zero-suppression circuit. The oscillosope was triggered externally by a trigger circuit, which was connected to three microswitches $M_1$, $M_2$, and $M_3$. $M_1$ and $M_2$ were operated by the stopping syringe while $M_3$ could be operated manually. $M_1$ triggered the oscilloscope shortly after the flow commenced, and $M_2$ just before the flow stopped. The screen of the oscilloscope was photographed with a Polaroid camera loaded with Type 146L transparent film.

The power supply for the tungsten lamp consisted of a 6-volt battery, which was maintained on trickle charge by a stabilized power supply. This procedure reduced the fluctuation in the light intensity during a run to less than 0.01%. The Beckman power supply for the deuterium lamp introduced a considerable amount of 60-cycle noise. This noise was reduced by replacing the a.c. filament supply by a stabilized d.c. power source.

**Procedure.**—The reactant solutions were thermostated for about 1 hr. prior to the runs. Because of the dissociation of the phenanthroline complexes in acid, the complexes were either added to the acid immediately before the runs, or the acid was added to only the cerium(IV) solutions.[11] This latter procedure was followed when the two-stage mixing chamber was being used. The kinetic results obtained by means of the two procedures were identical within the experimental error of the measurements; the rate constants depended only on the acidity of the final mixed solution and were independent of the acidities of the initial reactant solutions.

The reactions were studied by the use of the stopped-flow method. The reactant solutions were drawn into the syringes through the three-way stopcocks and then forced into the mixing chamber through the flow tube and into the stopping syringe. The flow of the reaction mixture was brought to an abrupt halt when the piston of the stopping syringe reached the stopping block. The oscilloscope was triggered just prior to this point by the microswitch $M_2$, and the transmittance of the stationary reaction mixture was recorded as a function of time. In the faster reactions a significant part of the reaction had already taken place before the mixed solution reached the observation point. Under these circumstances the light intensity at zero reaction time was calculated from the transmittances of the reactant solutions.

## Results and Discussion

The reactions were found to be first order with respect to each of the reactants. Plots of log $[b(a -$

(11) The iron(II) complexes are inappreciably dissociated in neutral solutions containing three moles of ligand per mole of metal.

$x)/a(b - x)]$ vs. $t$, where $a$ and $b$ are the initial concentrations of the reactants and $x$ is the concentration of product at time $t$, gave straight lines for all the reactions studied. Values of the rate constants for the Fe(phen)$_3^{2+}$–Ce(IV) reaction determined from the slopes of the appropriate plots are presented in Table I. It will be seen that the rate constants are independent of the initial concentrations of the reactants over a wide concentration range. Values of the rate constants for the Fe(phen)$_3^{2+}$–Ce(IV) reaction as a function of the sulfuric acid concentration are presented in Table II. No attempt was made to keep the ionic strengths of the solutions constant. It will be seen that the rates tend to increase with the sulfuric acid concentrations of the solutions.

#### TABLE I
DETERMINATION OF THE ORDER OF THE Fe(phen)$_3^{2+}$–Ce(IV)
REACTION IN 0.50 $F$ H$_2$SO$_4$ AT 25.0°

| $10^5$(Ce(IV)), $F$ | $10^5$(Fe(phen)$_3^{2+}$), $F$ | $10^{-5}k$, $F^{-1}$ sec.$^{-1}$ |
|---|---|---|
| 4.10 | 1.55 | 1.44 |
| 7.90 | 2.54 | 1.42 |
| 7.90 | 20.3 | 1.39 |
| 15.8 | 5.08 | 1.43 |
| 39.5 | 12.7 | 1.43 |
| 41.0 | 3.10 | 1.41 |
| 63.2 | 20.3 | 1.41 |
| 94.8 | 30.5 | 1.43 |

#### TABLE II
DEPENDENCE OF THE RATE OF THE Fe(phen)$_3^{2+}$–Ce(IV)
REACTION ON THE SULFURIC ACID CONCENTRATION AT 25.0°
[Fe(phen)$_3^{2+}$] = 5.08 × 10$^{-5}$ $F$; [Ce(IV)] = 1.58 × 10$^{-4}$ $F$

| (H$_2$SO$_4$), $F$ | $k$, $F^{-1}$ sec.$^{-1}$ × 10$^{-5}$ |
|---|---|
| 0.05 | 1.37 |
| .10 | 1.42 |
| .25 | 1.41 |
| .50 | 1.42 |
| .75 | 1.51 |
| 1.00 | 1.61 |

The values of the second-order rate constants for the oxidation of the various iron(II) complexes in 0.50 $F$ H$_2$SO$_4$ at 25.0° are summarized in Table III together with the formal oxidation potentials of the complexes in 0.50 $F$ H$_2$SO$_4$. Individual determinations of the rate constants differed from the mean by less than 10%.

The activation energies for the Fe(phen)$_3^{2+}$–Ce(IV) and Fe(II)–Ce(IV) reactions in 0.50 $F$ H$_2$SO$_4$, calculated from plots of log $k$ vs. $1/T$, were found to be 6.5 and 9.5 kcal. mole$^{-1}$, respectively. The entropies of activation for the above reactions, calculated from the equation $\Delta G^* = \Delta H^* - T\Delta S^*$, are −15.2 and −1 cal. deg.$^{-1}$ mole$^{-1}$, respectively. These energies and entropies of activation may be compared with the values of 0.8 kcal. mole$^{-1}$ and −37.2 cal. deg.$^{-1}$ mole$^{-1}$, respectively, determined for the Fe$^{2+}$–Fe(phen)$_3^{3+}$ reaction in 0.50 $F$ HClO$_4$.[4]

In Fig. 2 values of $[\Delta G_{12}^* - 0.5\Delta G_1^*]$ for the oxidation of the various iron(II) phenanthroline complexes by cerium(IV) are plotted as a function of the

#### TABLE III
SECOND-ORDER RATE CONSTANTS FOR THE OXIDATION OF
IRON(II) COMPLEXES BY CERIUM(IV) IN 0.50 $F$ H$_2$SO$_4$ AT 25.0°

| | $E^0$ of complex, v.[a] | $k$, $F^{-1}$ sec.$^{-1}$ |
|---|---|---|
| Iron(II) | 0.68[b] | 1.3 × 10$^6$ |
| Tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)-iron(II) | .83[c] | 1.6 × 10$^6$ |
| Tris-(5,6-dimethyl-1,10-phenanthroline)-iron(II) | .99[c] | 4.3 × 10$^5$ |
| Tris-(5-methyl-1,10-phenanthroline)-iron(II) | 1.04[c] | 2.2 × 10$^5$ |
| Tris-(1,10-phenanthroline)-iron(II) | 1.08[c] | 1.42 × 10$^5$ |
| Tris-(5-phenyl-1,10-phenanthroline)-iron(II) | 1.10[d] | 1.2 × 10$^5$ |
| Tris-(5-chloro-1,10-phenanthroline)-iron(II) | 1.14[d] | 2.5 × 10$^4$ |
| Tris-(5-nitro-1,10-phenanthroline)-iron(II) | 1.26[e] | 3.9 × 10$^3$ |

[a] The formal oxidation potentials of the complexes are in 0.50 $F$ H$_2$SO$_4$. [b] G. F. Smith, Anal. Chem., 23, 925 (1951). [c] W. W. Brandt and G. F. Smith, ibid., 21, 1313 (1949). [d] W. W. Brandt and D. K. Gullstrom, J. Am. Chem. Soc., 74, 3532 (1952). [e] G. F. Smith and W. M. Banick, Talanta, 2, 348 (1959).
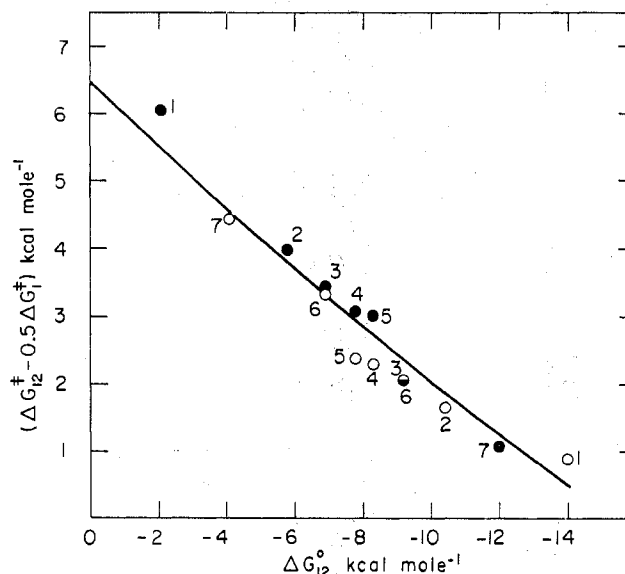


Fig. 2.—Relation between ($\Delta G_{12}^* - 0.5\Delta G_1^*$) and the standard free energy change of the oxidation–reduction reactions at 25.0°: open circles, Fe(phen)$_3^{2+}$–Ce(IV) reactions in 0.50 $F$ H$_2$SO$_4$; closed circles, Fe$^{2+}$–Fe(phen)$_3^{3+}$ reactions in 0.50 $F$ HClO$_4$; 1, tris-(3,4,7,8-tetramethyl-1,10-phenanthroline); 2, tris-(5,6-dimethyl-1,10-phenanthroline); 3, tris-(5-methyl-1,10-phenanthroline); 4, tris-(1,10-phenanthroline); 5, tris-(5-phenyl-1,10-phenanthroline); 6, tris-(5-chloro-1,10-phenanthroline); 7, tris-(5-nitro-1,10-phenanthroline).

standard free energy changes of the various reactions (open circles; $\Delta G_1^*$, the free energy of activation for the cerium(III)–cerium(IV) exchange reaction in 0.50 $F$ H$_2$SO$_4$, is equal to 16.2 kcal. mole$^{-1}$).[12] The appropriate data for the oxidation of Fe$^{2+}$ by the various iron(III) phenanthroline complexes in 0.50 $F$ HClO$_4$ at 25.0° are also plotted in this figure[5] (closed circles; in this case $\Delta G_1^* = 16.3$ kcal. mole$^{-1}$, the free energy of activation for the Fe$^{2+}$–Fe$^{3+}$ exchange reaction).[13]

(12) P. B. Sigler and B. J. Masters, J. Am. Chem. Soc., 79, 6353 (1957).
(13) J. Silverman and R. W. Dodson, J. Phys. Chem., 56, 846 (1952).

Table IV

COMPARISON OF OBSERVED AND CALCULATED RATE CONSTANTS AT 25.0°

| Reaction | $k_1$,ᵃ $F^{-1}$ sec.⁻¹ | $k_2$,ᵃ $F^{-1}$ sec.⁻¹ | $k_{12}$ obsd.,ᵇ $F^{-1}$ sec.⁻¹ | $k_{12}$ calcd.,ᶜ $F^{-1}$ sec.⁻¹ |
|---|---|---|---|---|
| Fe(II)–Ce(IV) | $4.0^d$ | $4.4^e$ | $1.3 \times 10^6$ | $6 \times 10^{5}$ ᶠ |
| Cr(II)–Fe(III) | $\leqslant 2 \times 10^{-5}$ ᵍ | $4.0^d$ | $\sim 8 \times 10^{3}$ ʰ | $\leqslant 6 \times 10^5$ |
| V(II)–Fe(III) | $1.0 \times 10^{-2}$ ⁱ | $4.0^d$ | $> 10^5$ ʲ | $9 \times 10^5$ |
| Eu(II)–Fe(III) | $\leqslant 1 \times 10^{-4}$ ᵏ | $4.0^d$ | $> 10^5$ ʲ | $\leqslant 2 \times 10^6$ |
| Cr(II)–Co(III) | $\leqslant 2 \times 10^{-5}$ ᵍ | $\sim 5^l$ | $> 3 \times 10^2$ ʲ | $\leqslant 1 \times 10^{10}$ |
| V(II)–Co(III) | $1.0 \times 10^{-2}$ ⁱ | $\sim 5^l$ | $> 3 \times 10^2$ ʲ | $\sim 2 \times 10^{10}$ |
| $Cr^{2+}$–$V^{3+}$ | $\leqslant 2 \times 10^{-5}$ ᵍ | $1.0 \times 10^{-2}$ ⁱ | .... | $\leqslant 2 \times 10^{-2}$ |
| $Fe^{2+}$–$Co^{3+}$ | $4.0^d$ | $\sim 5^l$ | $42^j$ | $\sim 6 \times 10^6$ |

ᵃ Except for the Ce(III)–Ce(IV) reaction, the rate constants refer to the $M^{2+}$–$M^{3+}$ exchange reactions. The rate constant for the Ce(III)–Ce(IV) reaction was determined in 0.4 $F$ $H_2SO_4$ at 25.0°. ᵇ The rate constant for the Fe(II)–Ce(IV) reaction was determined in 0.50 $F$ $H_2SO_4$, while the rate constants for the Cr(II)–Fe(III), V(II)–Fe(III), Eu(II)–Fe(III), Cr(II)–Co(III), and V(II)–Co(III) reactions were determined in 1 $F$ $HClO_4$. ᶜ The following $E^0$ values, taken from E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1949, and from W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, were used to calculate the equilibrium constants for the electron transfer reactions: Eu(II)–Eu(III), −0.43 v.; Cr(II)–Cr(III), −0.41 v.; V(II)–V(III), −0.21 v.; Fe(II)–Fe(III), 0.73 v.; Ce(III)–Ce(IV), 1.44 v.; Co(II)–Co(III), 1.82 v. ᵈ Reference 13. ᵉ Reference 12. ᶠ The rate constant for the $Fe^{2+}$–$Fe^{3+}$ exchange, and the oxidation potential of the $Fe^{2+}$ ion in perchloric acid, were used in the calculation of $k_{12}$. The above quantities should, to a good approximation, be the same in sulfuric and perchloric acids. ᵍ A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954). ʰ G. Dulz and N. Sutin, to be published. ⁱ K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 5921 (1958). ʲ L. E. Bennett and J. C. Sheppard, *J. Phys. Chem.*, **66**, 1275 (1962). ᵏ D. J. Meier and C. S. Garner, *ibid.*, **56**, 853 (1952). ˡ N. A. Bonner and J. P. Hunt, *J. Am. Chem. Soc.*, **82**, 3826 (1960).

The rate constants for the reduction of the phenyl- and tetramethylphenanthroline complexes of iron(III) in 0.50 $F$ $HClO_4$ were calculated from the rate constants in 0.50 $F$ $H_2SO_4$ on the assumption that the rates are a factor of 7.9 slower in 0.50 $F$ $HClO_4$.[5]

**Comparisons with the Marcus Theory.**—It is apparent from eq. 3 that $f \rightarrow 1$ as $K_{12} \rightarrow 1$. Under these conditions eq. 1 and 2 reduce to

$$k_{12} = (k_1 k_2 K_{12})^{1/2} \qquad (4)$$

and

$$\Delta G_{12}^* = 0.50 \Delta G_1^* + 0.50 \Delta G_2^* + 0.50 \Delta G_{12}^\circ \qquad (5)$$

In Fig. 2 a line of slope 0.50, as required by eq. 5, has been drawn through the data for those reactions for which $\Delta G_{12}^\circ$ is close to zero. It is apparent from Fig. 2 that deviations from eq. 5 begin to occur when $\Delta G_{12}^\circ$ becomes more negative than about 5 kcal. mole⁻¹. The intercept of Fig. 2 gives 13.0 kcal. mole⁻¹ as the average value of the free energy of activation for the various Fe(phen)₃²⁺–Fe(phen)₃³⁺ exchanges in 0.50 $F$ acid; this corresponds to a value of $k_2$, the average rate constant for the exchanges, of $2 \times 10^3$ $F^{-1}$ sec.⁻¹ at 25.0°. The remainder of the curve in Fig. 2 was calculated from eq. 2 by substitution of the above estimate of $k_2$ in the expression for $f$. It will be seen that the experimental data satisfy the requirements of the Marcus theory reasonably well.[14]

(14) Equation 5 may be rationalized by considering, for example, the Fe²⁺–Fe(phen)₃²⁺ reaction and assuming, in the first instance, that the standard free energy change of the reaction is zero [N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 319 (1962)]. Under these conditions 0.50ΔG₁*, which is half the free energy of activation for the Fe²⁺–Fe³⁺ exchange, is approximately equal to the free energy required for the reorganization, etc., of the Fe²⁺ ion (and is assumed to be the same in the Fe²⁺–Fe³⁺ and Fe²⁺–Fe(phen)₃²⁺ reactions). Similarly 0.50ΔG₂*, which is half the free energy of activation for the Fe(phen)₃²⁺–Fe(phen)₃³⁺ exchange, is approximately equal to the free energy required for the reorganization, etc., of the Fe(phen)₃²⁺ ion (and is assumed to be the same in the Fe(phen)₃²⁺–Fe(phen)₃³⁺ and Fe²⁺–Fe-(phen)₃²⁺ reaction). However, ΔG₁₂° for the Fe²⁺–Fe(phen)₃³⁺ reaction is not zero but has a negative value. This will tend to lower the free energy of activation for the Fe²⁺–Fe(phen)₃²⁺ reaction by 0.50ΔG₁₂° provided the slopes of the potential energy curves representing the reactants and products are not too different at their point of intersection.

For a somewhat more accurate comparison with the Marcus theory, it is necessary to correct the free energies of activation for the amount of work required to bring the reactants together. However, it is likely that the electrostatic contributions to this work are small at the ionic strengths used in these studies. It is of interest that the estimate of the rate constant for the Fe(phen)₃²⁺–Fe(phen)₃³⁺ exchange lies below the lower limit established for this exchange by isotopic labeling and n.m.r. studies.[15,16] Marcus has suggested that this disagreement could perhaps arise from the noncancellation of the nonelectrostatic contributions to the work required to bring the various pairs of reactants together.[5] This may arise in the above comparisons since the cross reactions involve the reactions of an ion containing hydrogen bonding ligands [Fe(H₂O)₆²⁺ or Ce(IV)] with one containing organic ligands [Fe(phen)₃²⁺ or Fe(phen)₃³⁺].

The latter complication does not arise in the Fe(II)–Ce(IV) reaction. The various electron exchange rates for this system are all known and both reactants are hydrogen bonding. Values of the observed and calculated rate constants for this reaction are presented in Table IV, which also contains data for some other oxidation–reduction reactions. The calculation of the rate constant for the Fe(II)–Ce(IV) reaction requires additional comment. Since iron(II) is but weakly complexed in sulfuric acid it is likely that Fe²⁺ is the predominant iron(II) species present in the solutions under the conditions used in the kinetic measurements. The iron(III) species produced in the outer-sphere oxidation of an uncomplexed Fe²⁺ ion will be an uncomplexed Fe³⁺ ion. Therefore, although iron(III) is strongly complexed in sulfuric acid, the rate constant for the Fe²⁺–Fe³⁺ exchange and the oxidation potential of the Fe²⁺ ion in perchloric acid were used in the calculation of the rate constant for the Fe(II)–Ce(IV)

(15) E. Eichler and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 4145 (1958).
(16) M. W. Dietrich and A. C. Wahl, *J. Chem. Phys.*, **38**, 1591 (1963).

reaction. It will be seen that the rate constant for the Fe(II)–Ce(IV) reaction calculated in this manner is in good agreement with the observed value and that the rate constants for the Cr(II)–Fe(III), V(II)–Fe(III), Eu(II)–Fe(III), Cr(II)–Co(III), and V(II)–Co(III) reactions are consistent with the observed values. On the other hand, there is a large difference between the observed and calculated rate constants for the $Fe^{2+}$–$Co^{3+}$ reaction. The reason for this discrepancy is not known. It may lie in the complexity of Co(III)

solutions or it may be that different spin restrictions obtain in the $Fe^{2+}$–$Co^{3+}$ and $Co^{2+}$–$Co^{3+}$ reactions. It is also possible that the $Fe^{2+}$–$Co^{3+}$ reaction or the $Co^{2+}$–$Co^{3+}$ reaction, or both, involve an atom transfer mechanism; the Marcus equations are not applicable to such reactions.

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# Acidodiethylenetriaminegold(III) Complexes: Preparation, Solution Chemistry, and Electronic Structure

BY W. H. BADDLEY,[1] FRED BASOLO,[1] HARRY B. GRAY,[2] CLARITA NÖLTING,[3] AND A. J. POË[4]

The preparation of acidodiethylenetriaminegold(III) salts with the general formula [Au(dien)X]X$_2$ (dien = NH$_2$C$_2$H$_4$NH-C$_2$H$_4$NH$_2$ and X = Cl$^-$, Br$^-$) is reported. The complexes are acids in aqueous solution, ionizing a proton from one of the amine nitrogen atoms. The resulting conjugate bases, [Au(dien-H)X]X (dien-H = dien less one proton and X = Cl$^-$, Br$^-$, I$^-$), have been isolated. Equilibrium constants for (N–H) ionization and for the hydrolysis are given. Electronic spectra of the [Au(dien)X]$^{2+}$ and [Au(dien-H)X]$^+$ complexes are assigned using a molecular orbital level classification.

## Introduction

Square-planar acidoammine complexes of the type $[M(amine)_nX_{4-n}]^{(n-2)+}$ (X = Cl$^-$, Br$^-$, etc.) where M = Pt$^{2+}$ and Pd$^{2+}$ are quite common and have played an important role in the experimental and theoretical development of coordination chemistry. However, there have been relatively few reports of compounds of this type for Au$^{3+}$.[5–12]

This paper reports the general synthesis of complexes of Au$^{3+}$ with the tridentate ligand diethylenetriamine, which is abbreviated dien. An investigation of the aqueous solution chemistry of these compounds is discussed. The electronic structures of the $[M(dien)X]^{n+}$ (M = Pd$^{2+}$, Pt$^{2+}$, or Au$^{3+}$) complexes are discussed in terms of molecular orbitals. Electronic spectra are assigned using a molecular orbital energy level scheme.

## Experimental

**Materials.**—The gold-containing starting material for the synthetic work was tetrachloroauric acid, which was freshly made for each preparation. In a typical experiment, 0.5 g. of fine gold powder (Engelhard Industries, Inc.) was added to a mixture of 5

ml. of concentrated HCl and 3 ml. of concentrated HNO$_3$. The gold dissolved in a minute or so to give an orange solution. This solution was evaporated to 1–2 ml., 5 ml. of concentrated HCl was added, and the evaporation repeated. Again, 5 ml. of HCl was added and the evaporation repeated. Upon cooling, the solution crystallized to a solid mass of tetrachloroauric acid.

Diethylenetriamine (Union Carbide, technical grade) was distilled once, b.p. 204–208°. Other chemicals used were reagent grade.

**Analyses.**—The gold content was determined from the weight of the residue obtained by the ignition of a few hundredths of a gram of the compound in a microcrucible. Using this procedure, determination of gold in two of the compounds, [Au(dien-H)X]X (X = Cl$^-$, Br$^-$), gave poor results because these particular compounds tended to spatter when heated. This spattering was prevented by decomposing the compounds with a few drops of 30% hydrogen peroxide prior to ignition. The gold content was also determined by Miss H. Beck of the Chemistry Department, Northwestern University, who carried out the carbon and hydrogen elemental analyses. Several analyses were done by Microtech, Skokie, Ill.

**Preparation of Complexes.**—Each of the complexes reported was synthesized several times. Although some gold compounds are light-sensitive, most of these preparations were carried out under ordinary laboratory fluorescent lighting conditions. After preparation, the compounds were stored in the dark.

No attempt was made to ascertain the structures of these compounds. We make the reasonable assumption that they are square-planar complexes, as are the great majority of Au$^{3+}$ compounds. This assumption will be implied in the notation that is used throughout this paper. For example, the compound which analyzes as AuC$_4$H$_{13}$N$_3$Cl$_3$ will be referred to as [Au(dien)Cl]Cl$_2$.

**Synthesis of [Au(dien)Cl]Cl$_2$ and the Conjugate Base, [Au(dien-H)Cl]Cl.**—Tetrachloroauric acid was prepared from 6 g. of gold powder (30.5 mmoles). This was dissolved in 5 ml. of anhydrous ether and put in an ice bath. Thirteen ml. of dien (126 mmoles) was added to 20 ml. of anhydrous ether and also

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