[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, NEW YORK, AND WASHINGTON STATE UNIVERSITY, PULLMAN, WASHINGTON]

Kinetics of the Co(II)aq.–Co(III)aq. Isotopic Exchange Reaction

BY N. A. BONNER[1] AND J. P. HUNT[2]

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Additional data are presented on the exchange reaction. The experimental activation energy in 1 *f* $HClO_4$ is 13.2 kcal./mole and the entropy of activation is −13 e.u. A shiny Pt foil surface did not affect the rate. Removal of O_2 from the solutions also produced no change in the rate. The over-all rate is *ca.* one-half as fast in 95% D_2O as in H_2O. Increasing ionic strength appears to increase the reaction rate. There seem to be specific effects due to changing anions from ClO_4^- to NO_3^- or HSO_4^-. The effect of changing (H^+) at constant ionic strength appears to be consistent with either a rate law of the form rate $= (Co(II))(Co(III))[k_1 + k_2/(H^+)]$ or with a linear variation of the logarithm of the activity coefficient function with fraction of $HClO_4$ in $HClO_4$–$NaClO_4$ mixtures. The relative slowness of the ammino system compared to the aquo case appears to be the result of a more negative entropy of activation for the former.

Because of the current interest in oxidation–reduction reactions,[3] data on the "electron transfer" reactions of Co(II)aq. and Co(III)aq. are of interest for comparison with similar reactions.

In a previous communication[4] the authors presented some preliminary findings. The purpose of this article is to report on more detailed information obtained since that time.

Experimental

Radioisotope.—The tracer used was 5.2 yr. Co^{60} obtained from the Oak Ridge National Laboratory in the form of $CoCl_2$ in HCl solution. Radiochemical purity was greater than 99%. This solution was converted to the perchlorate form by repeated fuming with excess $HClO_4$. Activity measurements were made using a solution gamma counter.

Chemicals.—$Co(ClO_4)_2$ was prepared from Mallinckrodt A.r. $CoCl_2$ by fuming with $HClO_4$. Co(III) solutions were made by electrolytic oxidation of acidic $Co(ClO_4)_2$ solutions at 0° using a Pt anode. $HClO_4$ was J. T. Baker Analyzed Reagent 70%. $NaClO_4$ was once recrystallized G. F. Smith reagent. All other chemicals were of reagent grade or better.

Analytical Method.—The Co(III) ethylenediaminetetraacetic acid (EDTA) complex has an absorption peak at 5400 Å. with a molar absorbancy index of 312 at *p*H 5–6. Cobalt analyses were made by measurement of the absorption at this wave length using a Beckman model DU spectrophotometer. This procedure gave results which agreed with standard analytical methods to within 1%.

Co(II) was oxidized to the Co(III) EDTA complex with H_2O_2 in the presence of EDTA in an ammonium acetate buffer (*p*H 5–6).

Quenching–Separation Procedure.—The exchange reaction was stopped by adding the exchange solution to an NH_3–NH_4^+ buffer (*p*H 8–9) containing EDTA. The Co(II) and Co(III) ions form EDTA complexes which exchange extremely slowly under these conditions. The Co(II) could then be extracted into methyl isobutyl ketone (MIBK) as the thiocyanate complex after the solution had been acidified. The Co(III) EDTA complex stayed in the aqueous phase.

The details of the procedure are as follows: 10 ml. of reaction solution was added to 10 ml. of quenching solution at 0° with vigorous stirring. The quenching solution was made by mixing 1 g. of the disodium EDTA salt with 6 ml. of 10 *f* HNO_3 and enough concd. NH_4OH (29%) to give a total volume of 52 ml. The quenched mixture was allowed to stand for 2 hr. at room temperature. It was then put in an ice-bath and kept cold while 10 *f* HNO_3 was added slowly until the *p*H was about 0.5. Methyl violet paper was used as the *p*H indicator.

The solution at room temperature was made about half saturated with NH_4SCN by adding 13.6 g. of the iron-free salt. The Co(II) was then extracted into 30 ml. of MIBK. The aqueous phase was re-acidified and re-extracted with another 30 ml. of MIBK. The organic phases were discarded because our earlier experiments[4] had shown that measurement of the specific activity of the Co(II) fraction was unnecessary.

The aqueous phase containing the Co(III) was boiled for 20 min. after 20 ml. of 16 *f* NaOH had been added. This treatment destroyed the Co(III) EDTA complex and liberated Co(II). The solution was cooled in an ice-bath and acidified with concd. HCl. Addition of HCl was stopped when the red Fe(III) thiocyanate complex appeared. Enough saturated NaF solution was added to bleach the red color (the iron impurity came from the NaOH. The fluoride prevented extraction of Fe(III), which would have interfered with the subsequent spectrophotometric analysis).

The Co(II) then was extracted with two 20-ml. portions of MIBK. The MIBK extracts were combined and the cobalt back-extracted into 15 ml. of 2.5 *f* HCl. This solution was then treated as described in the "Analytical Method" section to prepare the Co(III) EDTA complex for counting and for cobalt analysis.

It should be pointed out that the above procedure does not have to be quantitative, since the counting and chemical analysis are carried out on the same final sample, and all that is needed is a measure of the specific activity of the cobalt.

Zero-time exchange varied from *ca.* 10–30% depending on the nature of the exchange solution. For a given composition of exchange solution the zero-time exchange was reproducible to ±10% of the average value (*e.g.*, 20 ± 2%). Typical exchange curves are shown in Fig. 1.

Attempts were made to find a more convenient and reproducible quenching procedure. Many common complexing agents are oxidized by Co(III) and cannot be used. Attempts to precipitate one or both Co species with CO_3^{-2}, PO_4^{-3}, $Fe(CN)_6^{-3}$, α-nitroso-β-naphthol and others, including use of various ions as carriers, all failed to give useful results. A few experiments using Amberlite resin IRA-400 also proved fruitless. The procedure finally used was chosen after changing many variables to give the minimum zero-time exchange.

Exchange Procedure.—The Co(III) solution containing $HClO_4$ and other solutes as desired was placed in an opaque Erlenmeyer flask and thermostatted (±0.05°). The Co(II) solution containing tracer was likewise brought to the desired temperature. The Co(II) was rapidly pipetted into the stirred Co(III) solution using a large bore pipet at the proper temperature. Aliquots were removed with a similar pipet and put rapidly into the quenching solution. Pipetting times were *ca.* 2 sec.

Specific activities were measured as (counts/min.)/*f* Co(III), using identical counting volumes, etc., for all samples. The fraction exchange was obtained by division of the specific activities of Co(III) at time *t* by the average specific activity determined for the initial mixture.

Results

It was reported in the earlier publication[4] that: at 0° and 1 *f* $HClO_4$, the rate law $R = k(Co(II))\cdot(Co(III))$ is obeyed, glass beads do not change the rate and that light of ordinary laboratory intensity has no effect.

The experimental activation energy (E exp.)

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[1] University of California Radiation Laboratory, Livermore, California.

[2] To whom inquiries may be addressed: Department of Chemistry, Washington State University, Pullman, Washington.

[3] H. Taube in "Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeleus and A. G. Sharpe, Eds., Academic Press, Inc., New York, N. Y., 1959, pp. 1–53.

[4] N. A. Bonner and J. P. Hunt, THIS JOURNAL, **74**, 1866 (1952).

and the entropy (ΔS^*)[5] were determined in 1 f $HClO_4$. A value of k (3.20°) = 0.98 ± 0.02 f^{-1} sec.$^{-1}$ and values of k (20.3) = 3.79 f^{-1} sec.$^{-1}$ and k (24.93°) = 5.96 f^{-1} sec.$^{-1}$ were used to calculate E exp. = 13.2 ± 0.5 kcal./mole and $\Delta S^* = -13 \pm 2$ cal. mole^{-1} deg.$^{-1}$ for the over-all reaction.

Some miscellaneous results are reported in Table I. These show that the presence of shiny Pt foil (2.7 cm.^{2}/ml. of solution) and removal of O_2 from the system by bubbling pure N_2, followed by maintaining a N_2 atmosphere, had no effect on the rate. In greater than 95% D_2O, however, the over-all rate was decreased by *ca.* a factor of 2. It would also appear that NO_3^- and HSO_4^- increase the rate over ClO_4^-. A trace of Cl^- (which probably does not persist) appears to have no effect.

TABLE I

MISCELLANEOUS RATE DATA

(Co(II) + Co(III)) *ca.* $10^{-3} f$, ClO_4^- anion except as noted

Conditions	$k(f^{-1}$ min.$^{-1})$ ± 5%
3.2°, 1.0 f $HClO_4$ only, Pyrex container	59
As above, but 2.7 cm.^{2}/ml. shiny Pt present	57
As first item, with oxygen removed	57
3.2°, $HClO_4$ 0.12 f, $NaClO_4$ 0.40 f, H_2O solvent	84
As preceding run but greater than 95% D_2O solvent	35
0.0°, 1.0 f $HClO_4$ only	43
0.0°, 0.85 f HNO_3 + 0.15 f $HClO_4$	53
0.0°, 0.85 N H_2SO_4 + 0.15 f $HClO_4$	369
0.0°, 0.1 f $HClO_4$	33
0.0°, 0.1 f $HClO_4$ + $10^{-4} f$ Cl^-	31

The effect of H^+ concentration was studied at constant ionic strength (μ) using $NaClO_4$–$HClO_4$ mixtures. In Fig. 2 are shown the results of these experiments. It is seen that a reasonably good straight line is obtained when k is plotted *vs.* 1/(H^+). Such results usually are interpreted as indicating a rate law of the form Rate = [Co(II)]·[Co(III)] [$k_1 + k_2/(H^+)$]. The values at 3.2° are: for $\mu = 3$, $k_1 = 64 f^{-1}$ min.$^{-1}$, $k_2 = 21$ min.$^{-1}$; for $\mu = 1$, $k_1 = 50 f^{-1}$ min.$^{-1}$, $k_2 = 8.3$ min.$^{-1}$; for $\mu = 0.5$, $k_1 = 39 f^{-1}$ min.$^{-1}$, $k_2 = 5.3$ min.$^{-1}$. The rate constants appear to increase as μ increases.

Results of some experiments with varying $HClO_4$ concentrations (not at constant μ) are given in Table II. Taking into account experimental error, there appears to be a gradually increasing rate as perchloric acid concentration increases.

TABLE II

EFFECT OF ($HClO_4$) ON k

Temp. 0.0°; Total (Co) *ca.* $10^{-3} f$

($HClO_4$) f	k f^{-1} min.$^{-1}$ ± 5%
0.1	33
.3	32
.4	33
.5	38
.6	40
1.0	43
3.0	54

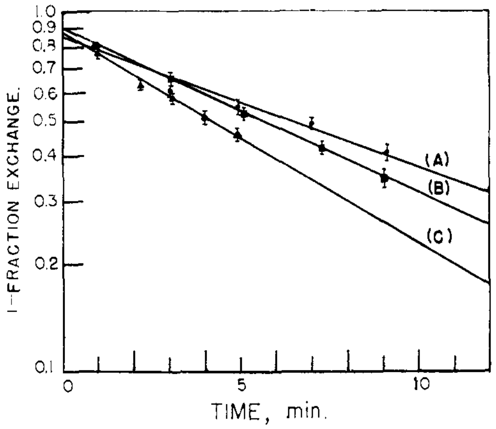

Fig. 1.—Typical exchange curves-conditions: 3.20°, [Co(II) + Co(III)] = *ca.* 1.7 × $10^{-3} f$, ionic strength adjusted to 0.50 with $NaClO_4$: Curve (A), 0.50 f H^+, $t_{1/2}$ 8.6 min.; Curve (B): 0.24 f H^+, $t_{1/2}$ 6.6 min.; Curve (C): 0.17 f H^+, $t_{1/2}$ 5.2 min. The errors shown correspond to ±0.02 in the 1-fraction exchange values.

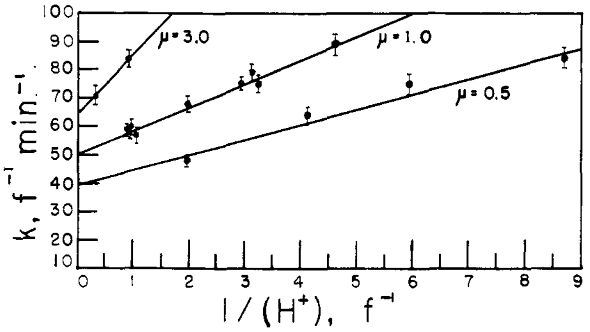

Fig. 2.—Hydrogen-ion dependence of rate-conditions: 3.20°, [Co(II) + Co(III)] = *ca.* 1.7 × $10^{-3} f$, ionic strength adjusted with $NaClO_4$. The errors shown correspond to ±4% in k.

Since the various data suggest that medium effects may be quite important, the constant μ data were also treated in the following manner. The usual equation relating k to medium effects is $k = k_0 f_A f_B / f^*$ or $k = k_0 F$. The terms f_A, f_B, f^* are the activity coefficients of reactants and activated complex, respectively, and F is the ratio $f_A f_B / f$. Following Güntelberg[6] and others[7] one can write $\log F = \alpha X + \beta$ where X is the ratio ($HClO_4$)/($HClO_4$) + ($NaClO_4$). This implies a linear relation between the logarithm of the activity coefficient function and the composition of the mixture. We then obtain the relation $\log k = C + X$, where C is $\log k_0 + \beta$. In Fig. 3 is shown such a plot for the $\mu = 0.5$ data. The straight line obtained here is as good as for the 1/(H^+) plot. A similar curve for the $\mu = 1.0$ data does not fit as well, although by increasing the error in k to ±7% a reasonable fit is obtained. The values of α and C are: for $\mu = 0.5$, $\alpha = -0.31$, $C = 1.98$; for $\mu = 1.0$, $\alpha = -0.21$, $C = 1.98$; for $\mu = 3.0$, $\alpha = -0.11$, $C = 1.96$. In view of the highly charged ions involved,

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(5) S. Glasstone, K. S. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, N. Y., 1941, p. 417.

(6) E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y. 1958, Chap. 14.

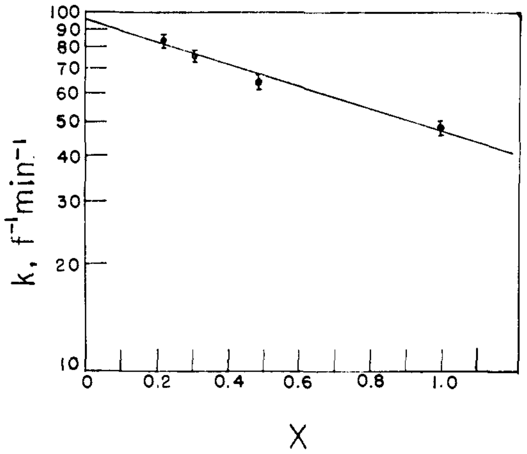

Fig. 3.—Effect of the fraction $(HClO_4)/(HClO_4) + (NaClO_4)$ on the rate-conditions as in Fig. 2.

it is hard to say whether these values are reasonable or not.

Discussion

A complete treatment of the (H^+) data in terms of the usual two term rate law requires data on the hydrolysis of Co^{+3}. There appears to be considerable question as to the actual state of affairs[8,9] so that no discussion can be given at this time. The possibility that only a medium effect is involved warrants further investigation in view of the data obtained.

Comparison of the results obtained here with the similar reaction for $Co(NH_3)_6(II)$–$Co(NH_3)_6(III)$ is of interest.[10] For the latter case E exp. is 13.5 kcal./mole and ΔS^* is calculated to be -41 e.u. The relative slowness compared to the aquo case seems to be due to the ΔS^* term (-41 e.u. compared to -13 e.u.). It should be pointed out, however, that in the ammine case the path $Co(NH_3)_6^{+2}$–$Co(NH_3)_5(NH_2)^{+2}$ is postulated.

The effect of D_2O is about the same as found in the Fe(II)–Fe(III) case. An unambiguous explanation of this effect has not yet been given.

Data under strictly comparable conditions for purposes of comparison are rather scarce. In Table III are given some numbers concerning rates for aquo ions. The values of k are for the rate law term $k[M(H_2O)_x^{+2}][M(H_2O)_y^{+3}]$ and are obtained from plots similar to those in Fig. 2. The value in the cobalt case is an estimate involving the assumption that the over-all activation energy would be close to that for the single path involved.

TABLE III

Comparison of Exchange Data at 25°

System	k (f^{-1} sec.$^{-1}$)	E(kcal./mole)	ΔS^* e.u.	μ
V(II)–V(III)[a]	1×10^{-2}	13.2[d]	−25[d]	2.0
Fe(II)–Fe(III)[b]	4.2	9.9	−25	0.5
Co(II)–Co(III)	*ca.* 5	13.2[d]	−13[d]	1
Cr(II)–Cr(III)[c]	Less than 2×10^{-5}	...	...	1

[a] K. V. Krishnamurty and A. C. Wahl, This Journal, **80**, 5921 (1958). [b] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952). [c] A. Anderson and N. A. Bonner, This Journal, **76**, 3826 (1954). [d] Values are for over-all reaction.

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(8) J. H. Baxendale and C. F. Wells, *Trans. Faraday Soc.*, **53**, 800 (1957).

(9) D. W. Weiser, Ph.D. Thesis, University of Chicago, 1956.

(10) N. S. Biradar, D. R. Stranks, M. S. Vaidya, G. J. Weston and D. T. Simpson, *Trans. Faraday Soc.*, **55**, 1268 (1959).

[Contribution from the Institute of General Chemistry, the University of Palermo, Palermo, Italy]

Thermochemical Studies. I. Thermodynamic Functions of Solutions of Pyridine Bases in Water[1]

By L. Sacconi, P. Paoletti and M. Ciampolini

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The heats of solution of pyridine, picolines, lutidines, piperidine and pyrrolidine in water at 25° have been determined by direct calorimetric measurements, using a non-isothermic calorimeter. By combining the values so obtained with the known values of free energy changes the entropies of solution have been calculated. The thermodynamic functions of hydration have been calculated on the basis of the heat of vaporization values. The data so obtained favor the hypothesis of hydrogen bonding between the bases and the water molecules. The affinity of the bases toward water appears to be essentially an entropy effect. The anomalous values of the heats of solution for 2-substituted picolines and lutidines afford further evidence for the existence of hydrogen bonding between the molecules of the base.

As is well known, the ionization of organic acids and bases is very suitable for obtaining useful information on the structural parameters of the molecules and for investigating the interionic effects in solution.[2] The pyridine bases, on the other hand, are very suitable for studying the relation between physical properties and molecular structure.

While the values reported in the literature on the dissociation constants of pyridine bases in water are numerous,[3] very few data are available on the heats and entropies of neutralization of such bases.

On this account we thought it important to measure calorimetrically the enthalpies of neutralization in water of these pyridine bases in order to obtain all the thermodynamic functions associated with the neutralization. On the other hand, such functions depend largely on the amount of hydration of the bases because neutralization is accom-

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(1) Presented at the 8th National Congress of the Società Chimica Italiana held jointly with the Society of Chemical Industry, Turin, May 1958 (Abstracts of Communications, Division of Physical Chemistry, p. 87).

(2) H. C. Brown, D. H. McDaniel and O. Häfliger, in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 567.

(3) "Stability Constants," Part I, Special Publication No. 6, The Chemical Society, London, 1957.