Contribution from the Research School of Chemistry,
Australian National University, Canberra, ACT, Australia

Isomerization and Racemization of the α- and β-Diaquotriethylenetetraminecobalt(III) Ions

G. H. SEARLE and A. M. SARGESON*[1]

Received October 17, 1972

Λ-(*RR*)-α-$[Co(trien)(H_2O)_2]^{3+}$ isomerizes to racemic (*RR*,*SS*)-β-$[Co(trien)(H_2O)_2]^{3+}$; $k_\alpha = k_{1\alpha} + k_{2\alpha}/[H^+]$ in the pH range 1–3, where $k_{1\alpha} = 2.3 \times 10^{-7}$ sec^{-1} and $k_{2\alpha} = 3.0 \times 10^{-7}$ *M* sec^{-1} at 60°, $\mu = 0.1$. Δ-(*RR*)-β-$[Co(trien)(H_2O)_2]^{3+}$ racemizes with a rate law $k_{rac(\beta)} = k_{3\beta}/[H^+]$ in the pH range 1–3 where $k_{3\beta} = 2.75 \times 10^{-7}$ *M* sec^{-1} at 40°, $\mu = 0.1$. Using information from the isomerization (*RR*)-*trans*-diaquo → Δ-(*RR*)-β- + Δ(*RS*)-β-diaquo it is deduced that β-diaquo racemizes by the path Δ-(*RR*)-β-diaquo → (*RR*)-*trans*- → (*RS*)-*trans*- → (*RR*,*SS*)-*trans*- → Δ-(*RR*)-β- + Λ-(*SS*)-β-diaquo. It is also probable that Λ-(*RR*)-α form isomerizes to Δ-(*RR*)-β which then racemizes faster than it isomerizes to α. Both water exchange at the cobalt center and racemization at secondary nitrogen centers appear to govern the processes.

Introduction

The stereochemistry and reactivity of some disubstituted cobalt(III) triethylenetetramine complexes (trien = 1,4,7,10-tetraazadecane) have been discussed extensively in previous articles[2-5] and the features of these studies will not be reiterated here. The present study concerns the isomerization and racemization of the α-diaquo and β-diaquo complexes, Figure 1.[6] By inference some comments can also be made about the intervention of the *trans*-diaquo complexes as probable intermediates.

For the system *cis*- and *trans*-$[Co(en)_2(H_2O)_2]^{3+}$ several thorough studies have been made including isomerization, racemization, and water exchange.[7-9] The α- and β-$[Co(trien)(H_2O)_2]^{3+}$ complexes are analogous to *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ so that the general properties found in the latter system may be applied to the trien complexes. However the three chelate rings coupled about the two asymmetric secondary nitrogen atoms in the trien ligand might be expected to impose some restrictions on the possible stereochemical changes, and in particular racemization of any trien complex requires concomitant inversion of the configurations about the two coordinated secondary nitrogen atoms.

Experimental Section

Complexes. $(+)_{546}$-α- and $(-)_{546}$-β-$[Co(trien)(H_2O)_2](ClO_4)_3$ and $(\pm)$-α-$[Co(trien)CO_3]ClO_4 \cdot H_2O$ were prepared by methods given previously.[3] $(\pm)$-β-$[Co(trien)CO_3]ClO_4 \cdot H_2O$ was precipitated from an aqueous solution of the corresponding crude chloride[3] by addition of $NaClO_4$ followed by ethanol. It was filtered off, washed with ethanol and acetone, and air-dried. Fractional recrystallization from hot water by addition of ethanol gave four fractions having identical visible spectra. *Anal.* Calcd for $(\pm)$-β-$[Co(C_6H_{18}N_4)CO_3]ClO_4 \cdot H_2O$: C, 22.0; H, 5.28; N, 14.6. Found: C, 21.7; H, 5.33; N, 14.6.

Kinetics. Solutions were prepared by adding standardized $HClO_4$ to weighed amounts of the diaquo complexes, and the ionic strength was adjusted in each case (usually to ~0.1) by adding appropriate amounts of $NaClO_4$. α-Diaquo solutions were sealed in Pyrex tubes and immersed in an oil bath (usually at 60°) controlled to ±0.1°. Each tube was removed at appropriate times, cooled in ice, and broken, and the solution was transferred to a spectrophotometer or polarimeter cell jacketed at 25°, then resealed in the tube after each measurement, and replaced in the bath.

Isomerization of the α-diaquo complex was followed spectrophotometrically at the position of the β-diaquo maximum 487 nm (ϵ_β 122, ϵ_α 83), using a Shimadzu QR-50 spectrophotometer. Optical densities (5-cm cell) increased from 0.41 to 0.55. Loss of activity was followed at 546 nm (near the peak of the α-diaquo ORD curve[2]) on a Perkin-Elmer 141 polarimeter (1-dm cell). β-Diaquo solutions, usually measured at 40°, were maintained in a 2-dm cell jacketed to ±0.1° in a polarimeter attachment on a Shimadzu QR-50 spectrophotometer. Decreases in rotations $\alpha°$ were followed at 440 nm (the peak of the β-diaquo ORD curve[2]). For slower runs, aliquots were taken from solutions maintained in thermostated flasks.

Equilibrium Position. The position of the β-diaquo–α-diaquo equilibrium was assessed from the visible spectrum, determined on a Shimadzu RS-27 recording spectrophotometer, of each α-diaquo reactant solution giving 77% β-diaquo and 23% α-diaquo (see Results).

This was checked independently by dissolving $(\pm)$-α- or $(\pm)$-β-$[Co(trien)CO_3]ClO_4 \cdot H_2O$ in 0.1 *M* $HClO_4$ and measuring the spectra of the resulting diaquo solutions[2] (0.006 *M*) after 1 hr on a Cary 14 spectrophotometer thermostated at 25°. Band maxima were as follows: α-diaquo, ϵ_{497} 90, ϵ_{357} 58; β-diaquo, ϵ_{486} 125, ϵ_{357} 88. Another set of solutions 0.001 *M* in α- or β-carbonato complex was prepared in 0.003 *M* $HClO_4$ and 0.093 *M* $NaClO_4$. The resulting diaquo solutions in 0.001 *M* $HClO_4$, $\mu = 0.1$, were equilibrated at 60° for 6 hr when identical spectra were recorded (25°) from either the α or β reactant solutions, maxima ϵ_{488} 116, ϵ_{357} 81. Calculations using all band maxima gave the equilibrium position as 74% β (from band I) and 77% β (from band II).

Equilibrated solutions from all the α-diaquo kinetic runs were also transformed to carbonato complexes by adding excess $NaHCO_3$.[2] For the carbonato mixtures ϵ_{506} was constant at 169, and using ϵ_{507} 178 for β and ϵ_{503} 120 for α, the equilibrium mixture was calculated as 83% β. Since the α- and β-carbonato spectra in water varied slightly with addition of $NaHCO_3$ and $NaClO_4$, this less direct method for estimating equilibrium position was considered less reliable.

Results

The α- and β-diaquo isomers each isomerize and lose activity. The rates of these reactions were measured spectrophotometrically and polarimetrically, respectively, under varying conditions of complex concentration [Co], $HClO_4$ concentration, and temperature. The ionic strength was usually maintained constant at 0.1 by adding $NaClO_4$.

Rate constants, derived from plots of $\log (D_t - D_\infty)$ or of $\log \alpha_t°$ *vs.* time, are listed in Table I for the α isomer and Table II for the β system. All rate plots were linear for at least 3 half-lives.

The compounds each isomerize to an equilibrium mixture of the α- and β-diaquo isomers (>99%, as trans could not be

---

[1] To whom correspondence should be addressed.

[2] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 4, 45 (1965).

[3] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 6, 787 (1967).

[4] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 6, 2172 (1967).

[5] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 6, 1032 (1967).

[6] Λ and Δ refer to the absolute chelate configurations about the metal atom as defined in *Inorg. Chem.*, 9, 1 (1970). The *R* and *S* designations refer to the absolute configurations about the secondary nitrogen centers according to the sequence rules of R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 5, 385 (1966). The normal trigonal secondary nitrogen ("angular" nitrogen) is designated before the central secondary nitrogen of the three coplanar nitrogen atoms ("planar" nitrogen).

[7] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, 6, 1265 (1952).

[8] J. Y. Tong and P. E. Yankwich, *J. Amer. Chem. Soc.*, 80, 2664 (1958).

[9] W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, 83, 1280 (1961).

Table I. Rates of Isomerization and Loss of Activity of α-$[Co(trien)(H_2O)_2]^{3+}$ ([Co] = 0.001 *M*; μ = 0.10 *M*)

$10^3[H^+]$, *M*	Temp, °C	$10^3[NaClO_4]$, *M*	$10^5 k_{rac(\alpha)}$, sec^{-1}	$10^5 k_{isom,obsd}$, sec^{-1}	$10^5 k_{isom(\alpha)}$,[a] sec^{-1}	$10^5 k_{isom(\beta)}$, sec^{-1}
1020	60		0.038[b]			
102	60		0.31	0.43	0.33	0.10
51	60	49	0.60	0.78	0.60	0.18
10.2	40	85	0.060	~0.055	~0.042	~0.02
10.2	60	35	3.60			
10.2	60	85	2.87	4.0	3.1	0.9
10.2	60	72	3.00[c]			
10.2	65	84	7.0	10.7	8.2	2.5
10.2	70	84	16.8	25.8	19.9	5.9
5.1	60	89	5.72	7.5	5.77	1.7
2.04	60	92	14.8	20.3	15.6	4.7
1.02	40	95	0.65	0.78	0.60	0.2
1.02	60	97	28.8	35.7	27.5	8.2
1.02	70	99	112	~150	~115	~35
0.2	60	92	93	121	93	28

[a] $k_{isom(\alpha)} = 0.77\ k_{isom,obsd}$. [b] μ = 1.0 *M*. [c] [Co] = 0.003 *M*.

Table II. Rates of Racemization of β-$[Co(trien)(H_2O)_2]^{3+}$

$10^3[H^+]$, *M*	Temp, °C	10^3[Co], *M*	$10^3[NaClO_4]$, *M*	$10^3\mu$, *M*	$10^5 k_{rac(\beta)}$,[a] sec^{-1}
1020	40	1.3		1020	0.138
102	40	1.3		110	0.27
10.2	25	1.3	77	95	0.182
10.2	35	1.3	77	95	1.03
10.2	40	2.6	69	96	2.15
10.2	40	1.3	77	95	2.80
10.2	40	1.3	58	76	2.68
10.2	40	1.3	41	59	2.62
10.2	40	1.3	21	39	2.80
10.2	40	1.3	7	24	3.62
10.2	40	1.3		18	4.83
10.2	50	1.3	7	95	13.1
5.1	40	1.3	82	95	5.5
2.04	40	1.3	85	95	13.7
1.02	40	1.3	85	94	27.3
1.02	40	2.4		16	52
1.02	40	3.0		19	50[a]
0.2	40	1.3	86	94	93

[a] Measured at 578 nm on a Bellingham and Stanley visual polarimeter.

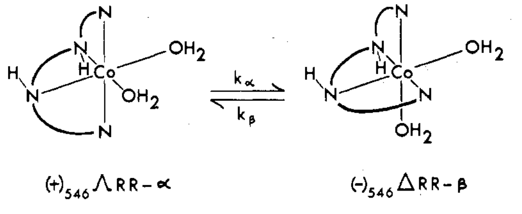

Figure 1. Observed isomerization of the α- and β-$[Co(trien)(H_2O)_2]^{3+}$ isomers.[6]

detected spectrophotometrically) so that the isomerization rate constants are composite values ($k_\alpha + k_\beta$) (Figure 1). The position of the β-diaquo-α-diaquo equilibrium was evaluated from the spectra of the equilibrium solutions. The equilibrium solutions ($\geqslant 8t_{1/2}$) from all runs had the same absorption spectrum with ϵ_{487} 113, and from the molar absorptions of the diaquo species measured under the same conditions and at the same wavelength 487 nm, ϵ_β 122 and ϵ_α = 82, the equilibrium mixture was calculated as 77% β and 23% α. This equilibrium was independent of $[H^+]$ over the acid range studied, 1-10^{-3} *M* $HClO_4$. The composite isomerization rate constants determined for the α isomer (Table I) have been separated into k_α and k_β, and these are also listed in Table I ($k_{isom(\alpha)} = 0.77 k_{isom,obsd}$). The absorption change for the isomerization $\beta \rightarrow (\beta + \alpha)$ equilibrium was too small to make this rate measurement practicable starting from the β isomer.

The α-Diaquo System. It is apparent (Table I) that the rate constants for loss of optical activity of the α isomer, $k_{rac(\alpha)}$, agree closely with those for isomerization k_α over the complete range of temperature and $[H^+]$ studied. The rates of both isomerization and activity loss show little dependence on [Co], but decrease as the ionic strength μ increases. This dependence on μ is due at least partly to the variation of K_a with μ, since the dissociation constant pK_a was found to increase as μ increased.[10] This corresponds to less contribution from the more reactive hydroxoaquo species at higher μ.

A plot of log $k_{rac(\alpha)}$ (at 60°) against log $[H^+]$ was linear in the range 0.1 *M* > $[H^+]$ > 0.001 *M* and the rate constants are represented by the expression

$$k_{rac(\alpha)} = k_{1\alpha} + k_{2\alpha}/[H^+]$$

where $k_{1\alpha} = 2.3 \times 10^{-7}\ sec^{-1}$ and $k_{2\alpha} = 3.0 \times 10^{-7}\ M\ sec^{-1}$ at 60° over the above range of acidity. The acid-independent term $k_{1\alpha}$ is equated to optical activity loss from the diaquo complex and the term inverse in acid is equated to reaction of the hydroxoaquo species (see Figure 2) as in the trans → cis isomerization of $[Co(en)_2(H_2O)_2]^{3+}$.[7] For $[H^+] \leqslant 0.1$ *M* the contribution of the $k_{1\alpha}$ path to the observed rate is considerably less than that of the hydroxoaquo species $k_{2\alpha}/[H^+]$; only at $[H^+]$ = 1 *M* do the contributions from the two paths become comparable. The same rate law is derived from the $\alpha \rightarrow \beta$ isomerization data in Table I.

The activation parameters were calculated from the $k_{rac(\alpha)}$ data (Table I) at $[H^+]$ = 0.01 *M*, μ = 0.1, to give by regression $E_{a(obsd)} = 40.0 \pm 0.1$ kcal mol^{-1}. A similar value $E_{a(obsd)}$ = 39.3 kcal mol^{-1} calculated from the data at $[H^+]$ = 0.001 *M*, μ = 0.1, accords with the hydroxoaquo reaction path predominating up to 0.1 *M* H^+.

The rate constant $k_{2\alpha}$ may be written as $k_{OH}k_a$, where $k_{OH(\alpha)}$ is the specific rate constant for the α-$[Co(trien)(OH)(H_2O)]^{2+}$ path and k_a is the first acid dissociation constant of the α-diaquo complex. Allowance for the temperature dependence of k_a[10] gives $E_{a(OH)(\alpha)} = 24.8 \pm 4$ kcal mol^{-1}, where the error arises substantially from the errors in the pK_a values.[10] $\Delta S_{OH}^{\ddagger}$ is then calculated as +12 ± 13 cal

---

[10] The first dissociation constants $pK_{a,1}$ as concentration constants of the α and β diaquo isomers are as follows: for (+)-α-$[Co(trien)(H_2O)_2](ClO_4)_3$, 5.80 ± 0.05 (10°), 5.40 ± 0.05 (20°); for (−)-β-$[Co(trien)(H_2O)_2](ClO_4)_3$, 5.60 ± 0.05 (10°), 5.30 ± 0.05 (20°) (μ = 0.10 *M*, $NaClO_4$), as reported by C. J. Hawkins, A. M. Sargeson, and G. H. Searle, *Aust. J. Chem.*, 17, 598 (1964). The $pK_{a,1}$'s for both isomers increased by 0.2 for μ = 0.03 → 0.10 consistent with the equation $pK_0 = pK_a - 2\sqrt{\mu} + \mu$ given by J. N. Bronsted and K. Volquartz, *Z. Phys. Chem., Stoechiom. Verwandschaftslehre*, 134, 97 (1928).

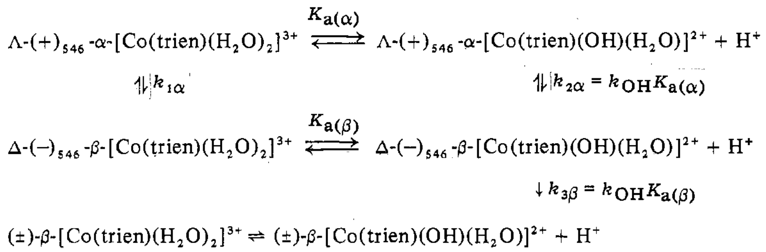

Figure 2. Reaction scheme for isomerization and racemization of the α- and β-[Co(trien)$(H_2O)_2]^{3+}$ isomers.

deg^{-1} mol^{-1} and appears to be positive allowing for the large possible error.

The β-Diaquo System. Plots of log α° against time were linear for at least 3 half-lives and the complex racemized to zero rotation over the wavelength range 350-700 nm. From the rate constants listed for varying conditions of $[H^+]$, μ, and temperature in Table II, several properties emerge.

In the range 0.1 $M > [H^+] > 0.001$ M the data at 40° and $\mu \approx 0.1$ fit a rate law of the form

$$k_{\text{rac}(\beta)} = k_{3\beta}/[H^+]$$

where $k_{3\beta} = 2.75 \times 10^{-7}$ M $\sec^{-1}$ at 40°. The rate constant at $[H^+] = 1.02$ M is sufficiently large to suggest that at high acidities a term first order in $[H^+]$ may exist, as the difference between $k_{\text{obsd}} = 0.138 \times 10^{-5}$ $\sec^{-1}$ ($\mu = 1.02$) and the rate constant calculated from $k_{3\beta}/[H^+]$ at $[H^+] = 1.02$ M ($k_{\text{calcd}} = 0.027 \times 10^{-5}$ $\sec^{-1}$) is probably too large to be attributed to the difference in ionic strength.

The rate constants depend on ionic strength up to $\mu \approx 0.4$ but appear to be essentially constant at higher μ values. There also appears to be a slight dependence of rate on the Co concentration.

The temperature dependence of the rate constants gave $E_{a(\text{obsd})} = 32.9 \pm 0.7$ kcal mol^{-1}. If the inverse acid dependence were to be attributed to reaction of the hydroxoaquo species as with the α system (Figure 2), then $k_{3\beta} = k_{OH}K_a$. After correction for the temperature dependence of K_a,[10] $E_{a(OH)(\beta)} = 22 \pm 5$ kcal mol^{-1} and $\Delta S_{OH}{}^{\ddagger} = +9 \pm 15$ cal deg^{-1} mol^{-1}. The errors in these activation parameters arise from the errors accrued in the pK_a determinations.[10]

Discussion

For both the isomerization of the α-[Co(trien)$(H_2O)_2]^{3+}$ isomer and racemization of the β isomer in the pH range 1-3 the major terms in the respective rate laws are the inverse acid-dependent terms. It is likely therefore that each reaction occurs through the hydroxoaquo species or through a route which involves proton abstraction from the amine as the rate-determining step.

For the α isomer, the close agreement between the rate constants for loss of optical activity $k_{\text{rac}(\alpha)}$ and isomerization $k_{\text{isom}(\alpha)}$ over the range of acidity and temperature studied (Table I) implies that the loss of activity of the α-diaquo compound is due to its isomerization to the β isomer. The β form racemizes more than 100 times faster ($k_{\text{rac}(\beta)}$) than it reverts to the α isomer ($k_{\text{isom}(\beta)}$), so that it is probable that the Λ-α[6] isomer mutarotates to the active Δ-β form, which subsequently racemizes as indicated in Figure 2. It cannot be demonstrated that this actually occurs, however, and the proposal cannot be tested since the β racemization rate constant $k_{\text{rac}(\beta)}$ is ~40 times larger than $k_{\text{rac}(\alpha)}$. There is no hindrance for Λ-α → Δ-β isomerization from the asymmetric centers in the trien chelate since neither center need invert during this process (Figure 1). It seems logical therefore to ascribe the inverse $[H^+]$ dependence of k_α to the isomerization of the hydroxoaquo ion. Each of the α-diaquo and -hydroxoaquo species could then undergo edge displacement by a path where bond breaking substantially leads bond making in a similar manner to that found in the trans → cis isomerization in the $(en)_2$ system.[9]

For the β isomer to racemize, not only is the chelate configuration about the cobalt center required to invert $\Delta \rightarrow \Lambda$,[6] but also both the secondary nitrogen centers must invert $RR \rightarrow SS$.[6] For both these processes to occur it can be argued that the *trans*-diaquo should intervene (Figure 3), since it is clearly not possible to invert the asymmetric "angular" nitrogen center in the β topology unless the apical chelate bridge is first brought into the plane of the other three nitrogen atoms. This stereochemical route parallels the route for the racemization of *cis*-[Co$(en)_2(H_2O)_2]^{3+}$ through the intermediate formation of the inactive *trans*-diaquo isomer.[9] The corresponding step in the trien system would produce the optically active *RR*-trans isomer, however, and clearly inversion of one nitrogen center (along with conformational inversions) would subsequently have to occur to give the inactive meso isomer *RS*-trans (Figure 3), which could then revert to racemic β. This sequence of events is designated route A in Figure 4, but an alternative path, route B, through the Δ-*RS*-β isomer may also be envisaged (Figure 4). These two routes differ in the order in which the edge displacement and nitrogen inversion steps occur to achieve the meso structure.

The isomerization of the active (*RR*)-*trans*-[Co(trien)-$(H_2O)_2]^{3+}$ has been studied previously, and it is known that *RR*-trans isomerizes rapidly, following the rate law $k_{\text{isom(trans)}} = k_{1t} + k_{2t}/[H^+]$, to a mixture of the two Δ-β conformers.[5] The rotatory dispersion curves obtained at different H^+ concentrations show that these two paths lead to the different products, Δ-*RR*-β by the acid-independent path k_{1t} and Δ-*RS*-β by path $k_{2t}/[H^+]$.[5] The Δ-*RS*-β isomer subsequently mutarotates rapidly with an inverse $[H^+]$ dependence, $k_M = k_1' + k_2'/[H^+]$, to the more stable Δ-*RR*-β ion. These isomerizations and the rate constants are included in Figure 4. During these processes no loss of optical activity was detected experimentally, and the observed rate constants $k_{\text{isom(trans)}}$ and k_M are larger by at least an order of magnitude than the β racemization rate constant $k_{\text{rac}(\beta)}$. This implies that the active trans or Δ-*RS*-β isomers would be present only as labile intermediates in low concentration in the racemization of β-[Co(trien)$(H_2O)_2]^{3+}$ by either routes A or B, respectively, consistent with our present results.

Route B can be discounted in favor of route A from the magnitudes of all these rate constants. In both the *RR*-trans → β and the β mutarotation studies,[5] the equilibrium positions lie completely toward Δ-*RR*-β since the final rotatory dispersion curve agrees with that of Δ-(*RR*)-β-[Co(trien)-$(H_2O)_2]^{3+}$ obtained from optically pure Δ-(*RR*)-β-[Co(trien)-$CO_3]^+$ to within the limits of measurement.[2,5] Upper limits may thus be estimated for the rate constants k_{-1} and k_{-M} (Figure 4) by taking these as 3% of the measured rate con-

Table III. Rate Constants at 40° for the Reaction Steps for Racemization of β-$[Co(trien)(H_2O)_2]^{3+}$

							$10^4k_{rac(\beta)}$, sec^{-1}	
$[H^+]$, M	$10^4k_{1\beta}$,[a] sec^{-1}	10^4k_{-1},[b] sec^{-1}	$10^4k_{2\beta}/[H^+]$,[a] sec^{-1}	10^4k_M,[c] sec^{-1}	10^4k_{-M}, sec^{-1}	10^4k_B,[b] sec^{-1}	Calcd for route B	Obsd
1.0	71	2.1	6.8	1.7	0.05	0.05	0.0015	0.014
0.1	71	2.1	68	9.1	0.27	0.27	0.008	0.027[e]
0.01	71[d]	2.1	680[d]	84[d]	2.5	2.5	0.074	0.28[e]

[a] Calculated from experimental data at 15°, $\mu = 1.3$, using $\Delta H^{\ddagger} = 28$ kcal mol^{-1} for $k_{1\beta}$ and $\Delta H^{\ddagger} = 10.1$ kcal mol^{-1} for k_2.[5] [b] Upper limit calculated as 3% of $k_{1\beta}$ or k_M. [c] Experimental data at $\mu = 1.3$.[5] [d] Calculated from rate law.[5] [e] $\mu = 0.1$.

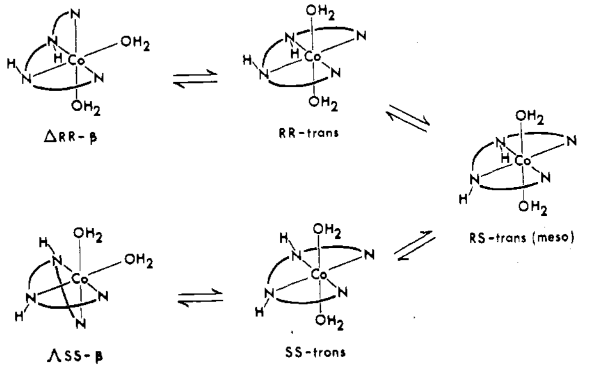

Figure 3. Probable stereochemical route for the racemization of Δ-(RR)-β-$[Co(trien)(H_2O)_2]^{3+}$ isomers.

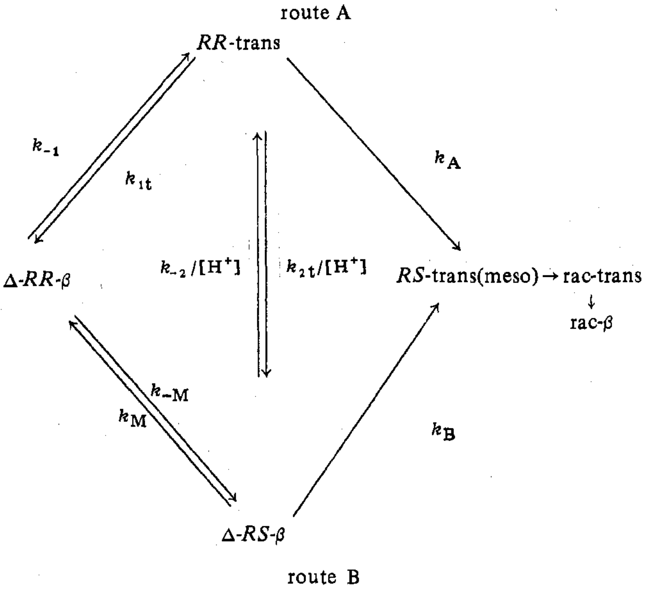

Figure 4. Reaction paths for racemization of Δ-(RR)-β-$[Co(trien)(H_2O)_2]^{3+}$. (k_1 and k_2 are the rate constants used in ref 5.)

stants $k_{1\beta}$ and k_M, respectively (Table III). In a similar manner, since no loss of optical activity was detected during measurement of the mutarotation (detection limit <3%),[5] k_B for the step Δ-RS-$\beta \rightarrow$ meso-trans may be conservatively estimated as 3% of k_M (Table III). Assuming a steady-state concentration of Δ-RS-β in the formulation

$$\Delta\text{-}RR\text{-}\beta \underset{k_M}{\overset{k_{-M}}{\rightleftharpoons}} \Delta\text{-}RS\text{-}\beta \xrightarrow{k_B} RS\text{-trans}$$

as an approximation, the overall rate constant for racemization of Δ-RR-β by this route is then given by $k_{rac(\beta)(calcd)} = k_{-M}k_B/k_M$. The values of the rate constants so calculated as upper limits (Table III) are clearly too small to account for the observed β racemization rates at three different acid concentrations, so that route B is improbable. If the equilibrium constants are smaller than the upper limits used, then this path becomes even less likely.

By comparison with route B, route A involves faster rates for the formation of RR-trans by k_{-1} and for the disappearance of this species with full retention of optical activity by paths $k_{1\beta}$ and $k_{2\beta}/[H^+]$ (Table III). The observed racemization rate constants $k_{rac(\beta)}$ are an order of magnitude smaller than the above rate constants so that essentially no measurable loss of activity by step k_A need occur in the time for measurement of the $k_{2\beta}/[H^+]$ and k_M steps. Using the formulation

$$\begin{tikzcd}
 & & RS\text{-trans} \\
\Delta\text{-}RR\text{-}\beta \arrow[r, shift left, "k_{-1}"] & RR\text{-trans} \arrow[l, shift left, "k_{1t}"] \arrow[ur, "k_A"] \arrow[dr, "k_{2t}/[H^+]"'] & \\
 & & \Delta\text{-}RS\text{-}\beta
\end{tikzcd}$$

the values of 10^4k_A which would be required to give the observed rate constant

$$k_{rac(\beta)} = \frac{k_{-1}k_A}{k_{1t} + k_A + k_{2t}/[H^+]}$$

are calculated to be 0.5, 1.7, and 110 at 1.0, 0.1, and 0.01 M H^+, respectively. While the proposed route A, Δ-RR-$\beta \rightleftharpoons$ RR-trans $\rightarrow$ RS-trans, can account satisfactorily for the observed results in the acidity range considered, the initial acid-independent equilibrium step k_{-1} to form RR-trans will become less important relative to the acid-dependent steps

$$\Delta\text{-}RR\text{-}\beta \xrightarrow{k_{M-1}} \Delta\text{-}RS\text{-}\beta \xrightarrow{k_{-2}/[H^+]} RR\text{-trans}$$

at higher pH levels. The contribution from these steps may therefore become significant at pH >3.

The probable route A deduced above requires that the inverse acid dependence of the observed rates $k_{rac(\beta)}$ is associated with the nitrogen inversion step RR-trans $\rightarrow$ RS-trans. The formation of the active trans form by the acid-independent path k_{-1} is proposed to involve water exchange[5] as in the $(en)_2$ system, and the rate constants for these two steps require that water-exchange rates in both the Δ-(RR)-β- and (RR)-*trans*-diaquo ions exceed the nitrogen inversion rates. Although the water-exchange rates in these trien-diaquo complexes are not yet known, it is becoming clear that topological changes in multidentate chelate systems are determined largely by the rates of secondary nitrogen exchanges and inversions, so that exact correlations with ethylenediamine systems need not be expected.

The measured equilibrium position in acid solutions clearly demonstrates that the β structure is favored over the α isomer for the diaquo compounds by ~1 kcal mol^{-1}, and this contrasts with the apparent preference for α in the dichloro- and dinitro-trien complexes.[3] It is possible that the β-diaquo structure might allow a more favorable balance between nonbonded atomic H-H interactions and intramolecular hydrogen bonding between the cis aquo ligands than does the α isomer, although a complete energy minimization analysis would be necessary to check this. The isomerization $\alpha \rightarrow \beta$

has been observed also in the complexes of the trien ligand methylated at the secondary nitrogen atoms, α-$[Co(4,7\text{-}Me_2\text{-}trien)Cl_2]^+ \rightarrow \beta$-$[Co(4,7\text{-}Me_2 trien)CO_3]^+$,[11] but on the basis of the above mechanistic proposals the active β compounds of this methylated ligand should be extremely inert to racemization and this aspect is currently being examined.

[11] G. H. Searle and F. R. Keene, to be submitted for publication.

Registry No. $(+)_{546}$-α-$[Co(trien)(H_2O)_2](ClO_4)_3$, 14267-03-9; $(-)_{546}$-β-$[Co(trien)(H_2O)_2](ClO_4)_3$, 15154-95-7; $(\pm)\beta$-$[Co(trien)CO_3](ClO_4) \cdot H_2O$, 38531-78-1.

Contribution No. 3083 from the Department of Chemistry,
University of California, Los Angeles, California 90024

A Model for Predicting the Photoreactions and Relative Quantum Yields of Transition Metal and Organometallic Complexes. II. Cobalt(III) and Rhodium(III)

JEFFREY I. ZINK

Received July 28, 1972

The photoreactions of low-spin complexes of the d^6 metals cobalt(III) and rhodium(III) are shown to depend on the spectrochemical splitting parameter Dq and on the energies of the donor orbitals of the ligands and the metal d orbitals in a simple and predictable way. The molecular axis which is photolabilized is predicted by considering bonding changes which occur when the lowest triplet and singlet excited states of the complex are populated. The relative quantum yields of solvation of the two ligands on the labilized axis are interpreted from a simple analysis of the energies of their donor orbitals. It is shown that the "radical pair" model proposed by Adamson may be incorporated into the analysis in order to predict the wavelength dependence of the quantum yield ratio of the two ligands. The total solvation quantum yield of ligands on the labilized axis is shown to depend on the crystal field parameter Dt.

Introduction

The photochemistry of transition metal complexes has been described as the chemistry of excited electronic states.[1] Although the nature of these excited states may be deduced from ligand field theory,[2] no connection between a complex's excited states and its photoreactions had heretofore been made. We recently developed a model of transition metal photochemistry based on the known antibonding properties of the excited states in the exact symmetry caused by the donor atoms of the complex and applied it to the photochemistry of the extensively studied chromium(III) complexes.[3] The model successfully predicted the photoreactions and relative quantum yields for chromium(III) complexes and led to an understanding of Adamson's important empirical rules.[4]

It was of interest to extend the successful model to other metal systems where no empirical trends have been elucidated. Cobalt and rhodium were chosen for this study for two reasons. First, the extent of the photochemically studied complexes is second only to that of chromium.[5-7] Second, there seemed to be no rational order or reason to the photoreactions. The latter reason provided the primary impetus for this study since a major result of our previous work on chromium(III) was a simple, logical, and general model for organizing existing data and for predicting photoreactions in terms of spectroscopic properties.

The empirical rules of Adamson summarized most of the photoreactions of chromium(III). The rules are[4] (1) the axis having the weakest average crystal field will be the one labilized and (2) if the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates. The photoreactions of the d^6 complexes considered in this paper may exhibit reduction of the metal in addition to ligand replacement. When ligand replacement occurs, rule 1 is usually obeyed but rule 2 is often violated.

In this paper we interpret in detail the photoreactions of cobalt and rhodium. It is shown that the general model may be used to explain and predict the redox and ligand replacement reactions. The validity of rule 1 is explained in terms of our ligand field model. The identity of the ligand on the labilized axis which is replaced is shown to depend in a predictable fashion on the orbital energies of the metal and the ligands. The explanation of the redox behavior is contained in the above arguments. Finally, the relative quantum yields in a series of complexes are predicted by considering π-bonding changes resulting from excitation.

d-Orbital Orderings

The correlation diagram for low-spin d^6 complexes is given in Figure 1. The ordering of the excited electronic states under C_{4v} or D_{4h} geometry depends upon the nature of the ligands. Figure 1 illustrates the splitting for weak axial ligands $(Ds, Dt > 0)$. The actual ordering of the excited states of a particular complex may be determined from analysis of polarized single-crystal spectra[8] or by fitting a theoretically calculated spectrum to one experimentally determined. The latter method has been the most widely used following the pioneering work of Wentworth and Piper.[9]

The ground state of the low-spin complexes, $^1A_{1g}$, corresponds to the strong-field $(t_{2g})^6$ configuration. The singlet and the triplet excited states shown in Figure 1 all arise from a $(t_{2g})^5(e_g)^1$ configuration. The electrostatic crystal field

---

[1] A. W. Adamson, *Coord. Chem. Rev.*, 3, 169 (1968).

[2] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.

[3] J. I. Zink, *J. Amer. Chem. Soc.*, 94, 8039 (1972).

[4] A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967).

[5] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

[6] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, 68, 541 (1968).

[7] A. W. Adamson, *Pure Appl. Chem.*, 20, 25 (1969).

[8] W. Moffitt and C. J. Ballhausen, *J. Inorg. Nucl. Chem.*, 3, 178 (1956).

[9] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 4, 709 (1965).