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Solvent Effects in the Reductions of $[Co(en)(ox)_2]^-$ and $[Co(gly)(ox)_2]^{2-}$ by $[Co(en)_3]^{2+}$

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The kinetics of the outer-sphere reductions of $[Co(en)(ox)_2]^-$ and $[Co(gly)(ox)_2]^{2-}$ by $[Co(en)_3]^{2+}$ were examined at 25 °C and 0.10 M ionic strength in water, methanol, ethanol, dimethylformamide, and dimethyl sulfoxide. The rates of both reactions are insensitive to the nature of the solvent, and correlation with a simple dielectric continuum model of the solvent is poor. Chiral induction in the reductions of $[\Delta\text{-}(+)_{546}\text{-}Co(en)(ox)_2]^-$ and $[\Delta\text{-}(+)_{546}\text{-}Co(gly)(ox)_2]^{2-}$ by $[Co(en)_3]^{2+}$ was also investigated in the five solvents mentioned plus formamide and dimethylacetamide. Salt effects on stereoselectivity suggest ion-triplet formation. An empirical method for describing the effect of solvent on the reaction rates and stereoselectivities in terms of donor and acceptor properties is employed, and the correlations have modest predictive power.

Introduction

Studies of the solvent dependence of outer-sphere electron-transfer reactions have been widely reported.[3-8] The model which is most widely used to describe solvent behavior in these processes is an application of dielectric continuum theory.[9] While some reactions show trends in rate which correlate well with the predictions of this model,[10] others do not and suggest the importance of specific solvent–solute interactions.[11] Cross-reactions in particular show poor correlations because specific interactions also affect the driving force for the process.[12]

Recent investigations in these laboratories have focused on a series of electron-transfer cross-reactions which are distinguished by the propensity for hydrogen bonding between the reagents.[13-15] Information on specific interactions such as hydrogen bonding has been deduced primarily from studies of stereoselectivity in the electron-transfer reaction. Effects of hydrogen bonding with the solvent are an inevitable complication; however solvent effects on stereoselectivity have not been widely investigated. Taube and co-workers[16] reported that for the reduction of $[Co(edta)]^-$ by $[Co(en)_3]^{2+}$ the degree of stereoselectivity is strongly solvent dependent and increases in the order water < ethylene glycol < methanol ≈ ethanol ≈ formamide < DMF < DMSO < sulfolane.[17] It was noted that reactions in protic solvents show lower stereoselectivities than those in aprotic solvents, and the proposal was made that the formation of hydrogen bonds between the solvent and the reactants interferes with the hydrogen bonding between the reactants. In this paper a study of solvent effects in two related reactions is reported. The oxidations of $[Co(en)_3]^{2+}$ by $[Co(en)(ox)_2]^-$ and $[Co(gly)(ox)_2]^{2-}$ show significantly different behaviors in aqueous media as a result of differences in hydrogen bonding between the reagents.[18] The roles of the solvents in these two reactions are also found to be quite different.

Experimental Section

(a) Materials. $Na[Co(en)(ox)_2]\cdot H_2O$ was prepared by the method of Dwyer[19] but in significantly reduced yield. $(Et_4N)[Co(en)(ox)_2]\cdot H_2O$ was prepared by addition of $AgNO_3$ to precipitate the silver salt, followed by metathesis with Et_4NI. $Na[\Delta\text{-}(+)_{546}\text{-}Co(en)(ox)_2]\cdot 3.5H_2O$ (ϵ_{541} = 109 M^{-1} cm^{-1}, $\Delta\epsilon_{581} = -2.53$ M^{-1} cm^{-1})[20] was prepared[21] using $[(+)_{546}\text{-}Co(en)_2(NO_2)_2]Br$ as a resolving agent. $(Et_4N)[\Delta\text{-}(+)_{546}\text{-}Co(en)(ox)_2]\cdot H_2O$ was prepared by metathesis as described above. $Ba[Co(gly)(ox)_2]\cdot 0.5H_2O$[22] was converted to $Na_2[Co(gly)(ox)_2]\cdot 1.5H_2O$ with Na_2SO_4. $Ba[\Delta\text{-}(+)_{546}\text{-}Co(gly)(ox)_2]\cdot 2.5H_2O$ was prepared[22] using $[(+)_{546}\text{-}Co(en)_2(ox)]I$ and converted using Na_2SO_4 to the more soluble $Na_2[\Delta\text{-}(+)_{546}\text{-}Co(gly)(ox)_2]\cdot H_2O$ (ϵ_{565} = 138 M^{-1} cm^{-1}, $\Delta\epsilon_{581} = -3.08$ M^{-1} cm^{-1}). $(Me_4N)_2[\Delta\text{-}(+)_{546}\text{-}Co(gly)(ox)_2]\cdot 2H_2O$ and $(Et_4N)_2[\Delta\text{-}(+)_{546}\text{-}Co(gly)(ox)_2]\cdot nH_2O$ (very hygroscopic) were prepared by metathesis. Cobalt trifluoromethanesulfonate $Co(CF_3SO_3)_2$ was prepared from $CoCO_3$ and CF_3SO_3H at 80–85 °C, the mixture was filtered, and the solid was isolated and dried by repeated recrystallization from methanol and evaporation under reduced pressure. 1,2-Diaminoethane (Aldrich, 99+%) was distilled over sodium. For the kinetic work, methanol and ethanol were distilled over sodium. DMF and DMSO were vacuum-distilled immediately prior to use. In some experiments, HPLC grade DMF and DMSO (Aldrich) were used as received, with no perceptible effect on the reaction rates. For the stereoselectivity experiments, all of the solvents were dried over molecular sieves and distilled in an atmosphere of nitrogen prior to use. DMF, DMA, and DMSO were distilled under reduced pressure.

(b) Stereoselectivity Experiments. All solutions were purged with N_2 gas for 15 min. In a typical run, 10 mL of 1.14 M ethylenediamine solution, 2 mL of 0.185 M $Co(CF_3SO_3)_2$ solution, and 10 mL of 0.3 M LiCl solution were mixed at 25 °C under a nitrogen atmosphere in a 5.0-cm length × 4.5-cm diameter glass vessel. An 8-mL portion of 5.0

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(17) Abbreviations used in this paper: DMF = dimethylformamide; DMA = dimethylacetamide; DMSO = dimethyl sulfoxide; PC = propylene carbonate; en = 1,2-diaminoethane; gly^- = glycinate(1–); ox^{2-} = oxalate(2–); $edta^{4-}$ = 1,2-diaminoethane-*N,N,N′,N′*-tetraacetate(4–).

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Table I. Solvent Acidity and Basicity Parameters, Dielectric Constants, and Absorption Maxima for the Complexes

	solvent	DN[a]	AN[a]	ϵ	$\bar{\nu}_{max}$ (cm^{-1})[b]	
					$[Co(gly)(ox)_2]^{2-}$	$[Co(en)(ox)_2]^-$
1	water	18.0	54.8	78.5	17 670	18 480
2	methanol	19	41.3	32.6	17 570	18 380
3	ethanol	20	37.1	24.3	17 540	18 320
4	formamide	24	39.8	109.5	17 610	18 420
5	DMF	26.6	16.0	36.7	17 360	18 180
6	DMA	27.8	13.6	37.8	17 330	18 150
7	DMSO	29.8	19.3	46.7	17 420	18 250
8	sulfolane	14.8	19.0	44.0		
9	PC	15.1	18.3	65.1		

[a] Donor number and acceptor number data taken from ref 23. [b] Plots of $\bar{\nu}_{max}$ against acceptor number AN are linear for both complexes. $[Co(en)(ox)_2]^-$ $\bar{\nu}_{max}$ = 18 060 + 7.80AN with a correlation coefficient of 0.947; $[Co(gly)(ox)_2]^{2-}$ $\bar{\nu}_{max}$ = 17 240 + 8.21AN with a correlation coefficient of 0.969. Similar relationships have been noted for $[Co(edta)]^-$.[24]

$\times 10^{-3}$ M Δ-$(+)_{546}$ oxidant was added to the mixture. After completion of the reaction (complete disappearance of the color of the oxidant complex), 6 mL of 4.5 M HCl was added. The solution was diluted with water to 1–1.5 L, and the resulting solution was passed through an SP-Sephadex C-25 column (5.0-cm length × 2.9-cm diameter). After the column was thoroughly washed with 0.07 M HCl, the adsorbed $[Co(en)_3]^{3+}$ oxidation product was eluted with 1.5 M HCl. The absorbance and CD spectra[13] of the solution were recorded using a Jasco Uvidec-320 spectrophotometer and a Jasco J-500 spectropolarimeter.

(c) **Kinetic Experiments.** The kinetics of reduction of $[Co(en)(ox)_2]^-$ and $[Co(gly)(ox)_2]^{2-}$ by $[Co(en)_3]^{2+}$ were investigated using an excess of reductant. All solutions were prepared immediately prior to use under an atmosphere of argon gas. Typically, oxidant concentrations were (1–2) $\times 10^{-4}$ M and reductant concentrations were (1–100) $\times 10^{-4}$ M, with [en] = 0.4 M. Sufficient electrolyte (LiCl or LiBr) was present in each case to take the ionic strength to 0.10 M. The reaction was monitored at the absorption maximum of the oxidant (Table I) using a Varian Instruments Cary 3 spectrophotometer, equipped with a water-jacketed cell holder, giving temperature control to better than ±0.2 °C. Stopped-flow kinetics were monitored on a Durrum Model 13000 stopped-flow spectrophotometer modified to allow solutions to be handled under rigorously anaerobic conditions, at the expense of temperature control. Stopped-flow rates are quoted at room temperature (23 ± 1 °C). Pseudo-first-order rate constants, k_{obsd}, were calculated by least-squares analysis from plots of $\ln(A - A_\infty)$ against time and are presented in Tables SI and SII, available as supplementary material. The effect of trace water on the reactions was investigated by controlled addition of small amounts of water, and these data are also included in Tables SI and SII.

(d) **Data Analysis.** Data analysis was performed using the program Multiple Linear Regression (Heizer Software) on a MacIntosh personal computer.

Results

(a) **Reaction Products.** In all the solvents examined, the reductions of $[Co(gly)(ox)_2]^{2-}$ and $[Co(en)(ox)_2]^-$ by $[Co(en)_3]^{2+}$ show approximate 1:1 stoichiometry based on recovery of $[Co(en)_3]^{3+}$. The presence of $[Co(en)_3]^{3+}$ as the dominant oxidized product strongly suggests that the reactions are outer-sphere in nature, consistent with eqs 1 and 2. In a few instances, the recovery

$$[Co(gly)(ox)_2]^{2-} + [Co(en)_3]^{2+} \rightarrow [Co(gly)(ox)_2]^{3-} + [Co(en)_3]^{3+} \quad (1)$$

$$[Co(en)(ox)_2]^{-} + [Co(en)_3]^{2+} \rightarrow [Co(en)(ox)_2]^{2-} + [Co(en)_3]^{3+} \quad (2)$$

of $[Co(en)_3]^{3+}$ was substantially smaller than expected, due to the presence of a competing inner-sphere reaction pathway where $[Co(en)_2(ox)]^+$ is the reaction product.[18] Conditions for the solvent comparisons of kinetic and stereoselectivity data were chosen to minimize the effects from this minor pathway.

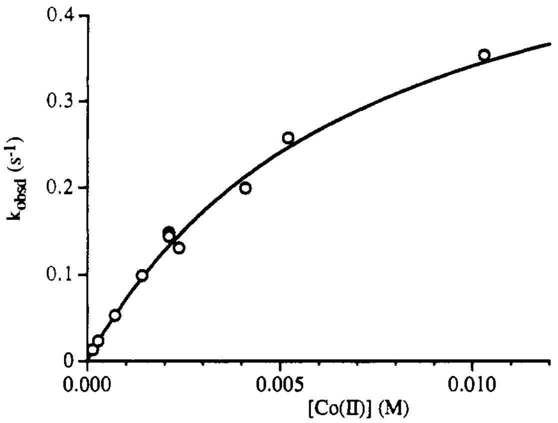

Figure 1. Plot of pseudo-first-order rate constant, k_{obsd}, against $[[Co(en)_3]^{2+}]$ for the reduction of $[Co(gly)(ox)_2]^{2-}$ by $[Co(en)_3]^{2+}$ in ethanol at 0.10 M ionic strength (LiCl) and 25.0 °C.

(b) **Kinetic Measurements.** Under the entire range of conditions studied, the reactions show a first-order dependence on the oxidant. The persistence of first-order behavior even at cobalt(II) concentrations comparable with those of the oxidant may be ascribed to rapid regeneration of the reductant following electron transfer (eqs 3 and 4), ensuring constant $[[Co(en)_3]^{2+}]$.

$$[Co(gly)(ox)_2]^{3-} + 3en \xrightarrow{fast} [Co(en)_3]^{2+} + gly^- + 2ox^{2-} \quad (3)$$

$$[Co(en)(ox)_2]^{2-} + 2en \xrightarrow{fast} [Co(en)_3]^{2+} + 2ox^{2-} \quad (4)$$

In the reactions of $[Co(en)(ox)_2]^-$ in all the solvents studied and in the reactions of $[Co(gly)(ox)_2]^{2-}$ in solvents of high dielectric constant, the observed rate constant shows a linear dependence on the concentration of reductant. A significant deviation from this behavior is found in the reduction of $[Co(gly)(ox)_2]^{2-}$ in ethanol, and a plot of the observed first-order rate constant against $[[Co(en)_3]^{2+}]$ is shown in Figure 1. The limiting first-order behavior at high reductant concentrations corresponds to eq 5,

$$k_{obsd} = \frac{k_{et}K_0[[Co(en)_3]^{2+}]}{1 + K_0[[Co(en)_3]^{2+}]} \quad (5)$$

with $K_0 = 139 \pm 23$ M^{-1} and $k_{et} = 0.59 \pm 0.12$ s^{-1}. This expression may also apply to the same reaction in methanol; however the deviations from linear behavior are within experimental error.

The general mechanism proposed for these electron-transfer reactions is presented for $[Co(gly)(ox)_2]^{2-}$ in eqs 6–8, where K_0

$$[Co(gly)(ox)_2]^{2-} + [Co(en)_3]^{2+} \overset{K_0}{\rightleftharpoons} \{[Co(gly)(ox)_2]^{2-},[Co(en)_3]^{2+}\} \quad (6)$$

$$\{[Co(gly)(ox)_2]^{2-},[Co(en)_3]^{2+}\} \xrightarrow{k_{et}} \{[Co(gly)(ox)_2]^{3-},[Co(en)_3]^{3+}\} \quad (7)$$

$$\{[Co(gly)(ox)_2]^{3-},[Co(en)_3]^{3+}\} \xrightarrow{fast} [Co(gly)(ox)_2]^{3-} + [Co(en)_3]^{3+} \quad (8)$$

is an ion association constant and k_{et} represents the rate of electron transfer within the ion pair. With the more highly charged oxidant

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Table II. Second-Order Rate Constants k_{so} for the Reduction of $[Co(gly)(ox)_2]^{2-}$ and $[Co(en)(ox)_2]^-$ by $[Co(en)_3]^{2+}$ at 25.0 °C and Ionic Strength = 0.10 M (LiCl)

	k_{so} (M^{-1} s^{-1})	
solvent	$[Co(gly)(ox)_2]^{2-}$	$[Co(en)(ox)_2]^-$
water[a]	20.0 ± 1.0	0.16 ± 0.01
methanol	31.8 ± 1.8	0.20 ± 0.01
ethanol	81.4 ± 3.1	0.33 ± 0.01
DMF[b]	18.2 ± 0.6	0.37 ± 0.10
DMSO	12.1 ± 0.7	0.060 ± 0.008

[a] KCl media - ref. 18. [b] LiBr media.

$[Co(gly)(ox)_2]^{2-}$ in the low dielectric constant solvent ethanol, K_0 is large and kinetically detectable amounts of the ion pair are formed.[25] In other solvents and with the lower-charged oxidant, $[Co(en)(ox)_2]^-$, $1 \ll K_0[[Co(en)_3]^{2+}]$ and eq 5 simplifies to $k_{obsd} = k_{so}[[Co(en)_3]^{2+}]$. Values for the second-order rate constants k_{so} ($=k_{et}K_0$) are collected in Table II. The rate constants are relatively insensitive to changing solvent and for each oxidant are contained within a single order of magnitude. Rates for reactions of $[Co(gly)(ox)_2]^{2-}$ are 2 orders of magnitude faster than those for $[Co(en)(ox)_2]^-$, principally a reflection of the increased driving force for the former reaction.[18]

The effect of trace amounts of water (<3% by volume) on the rates of the reaction in nonaqueous solvents was examined. In the protic solvents, ethanol and methanol, the effect is negligible (<20%); however in aprotic solvents significant changes are observed. The reductions of $[Co(en)(ox)_2]^-$ in DMSO and DMF and of $[Co(gly)(ox)_2]^{2-}$ in DMF are retarded by the presence of water, whereas the reduction of $[Co(gly)(ox)_2]^{2-}$ in DMSO is accelerated. Interpretation of these observations is difficult, but they may indicate that there are differences between the two oxidants regarding the role of water in solvating the transition state for electron transfer.

(c) Stereoselectivity Measurements. Stereoselectivities in the reduction of $[\Delta\text{-}(+)_{546}\text{-}Co(gly)(ox)_2]^{2-}$ range from 8% to 50% in the different solvents and show a consistent ΔΛ preference (Table III), paralleling the behavior reported by Taube[16] for $[\Delta\text{-}(+)_{546}\text{-}Co(edta)]^-$ (Table IV). Stereoselectivities in the reduction of $[\Delta\text{-}(+)_{546}\text{-}Co(en)(ox)_2]^-$ are much smaller and vary from a ΔΛ preference to a ΔΔ preference depending on conditions.

Changes in the ionic medium have an effect on the stereoselectivity measurements. The effect of changing LiCl (or KCl) salt concentrations on the stereoselectivity of the reduction of $[\Delta\text{-}(+)_{546}\text{-}Co(gly)(ox)_2]^{2-}$ by $[Co(en)_3]^{2+}$ in water, formamide, and DMSO is negligible, and replacing LiCl with LiBr or $LiClO_4$ also has little effect. This lack of a dependence on the salt concentration is consistent with the participation in the reaction (eq 6) of a neutral ion pair, where ion-triplet formation is unlikely. However, in the reduction of $[\Delta\text{-}(+)_{546}\text{-}Co(en)(ox)_2]^-$ by $[Co(en)_3]^{2+}$, the corresponding ion pair, $\{[Co(en)_3],[Co(en)(ox)_2]\}^+$, is charged and ion-triplet formation is more likely. In water, formamide, and DMSO, an increase in the chloride ion concentration leads to an increase in the preference for ΔΔ, especially in formamide, where stereoselectivity inverts from a ΔΛ preference to a ΔΔ preference. As shown by studies in DMSO, the magnitude of the change varies with different anions, decreasing with increasing radius in the order $Cl^- > Br^- > I^- \approx ClO_4^-$. The simplest explanation is that the ion pair $\{[Co(en)_3],[Co(en)(ox)_2]\}^+$ has a ΔΛ preference while the ion triplet $\{[Co(en)_3],[Co(en)(ox)_2],X\}$ ($X^- = Cl^-, Br^-, I^-$, or ClO_4^-) has a ΔΔ preference. Previous observations[27] on the effects of anions on the reactions of $[Co((\pm)\text{-}chxn)_3]^{2+}$ reveal that Cl^- induces a change in chelate ring conformation, and this has been shown to favor ΔΔ interactions in reactions of $[\Delta\text{-}(+)_{546}\text{-}Co(edta)]^-$ with $[Co((\pm)\text{-}chxn)_3]^{2+}$.[28] Similar considerations may be operating in the present reaction.

Table III. Stereoselectivities Expressed as Percent Enantiomeric Excess in the Reduction of $[\Delta\text{-}(+)_{546}\text{-}Co(gly)(ox)_2]^{2-}$ and $[\Delta\text{-}(+)_{546}\text{-}Co(en)(ox)_2]^-$ by $[Co(en)_3]^{2+}$ at 25 °C

solvent (electrolyte)	mean % recovery	ionic strength, M			
		0.04	0.14	0.54	1.04
	$[\Delta\text{-}(+)_{546}\text{-}Co(gly)(ox)_2]^{2}$				
water (KCl)[a]	94		9.0 ΔΛ	8.4 ΔΛ	8.0 ΔΛ
methanol (LiCl)[b]	88		17.1 ΔΛ		
ethanol (LiCl)[c]	86		19.7 ΔΛ		
formamide (LiCl)[c]	94		22.2 ΔΛ	20.7 ΔΛ	20.0 ΔΛ
DMF ($LiClO_4$)	81		43.5 ΔΛ		
DMF (LiBr)	99		45.7 ΔΛ		
DMA (LiCl)	100		39.8 ΔΛ		
DMSO (LiCl)	93	34.0 ΔΛ	50.2 ΔΛ	49.1 ΔΛ	49.3 ΔΛ
DMSO ($LiClO_4$)	86		47.5 ΔΛ		
DMSO (LiBr)	95		50.2 ΔΛ		
	$[\Delta\text{-}(+)_{546}\text{-}Co(en)(ox)_2]^-$				
water (KCl)[a]	71		3.6 ΔΛ	2.5 ΔΛ	1.6 ΔΛ
methanol (LiCl)	100		0.49 ΔΛ		
ethanol (LiCl)[c]	112		0.18 ΔΛ		
formamide (LiCl)	82		1.3 ΔΛ	0.31 ΔΛ	0.84 ΔΔ
DMF (LiBr)	114		2.4 ΔΔ		
DMSO (LiCl)	95	0.82 ΔΛ[d]	1.5 ΔΔ	6.2 ΔΔ	7.9 ΔΔ
DMSO ($LiClO_4$)	*d*		1.9 ΔΛ	1.5 ΔΛ	0.4 ΔΔ
DMSO (LiBr)	94		0.3 ΔΛ[d]	1.3 ΔΔ	2.6 ΔΔ
DMSO (NaI)	*d*		0.9 ΔΛ	0.5 ΔΛ	0.4 ΔΛ

[a] Reference 15. [b] $[Me_4N]^+$ salt of the oxidant. [c] $[Et_4N]^+$ salt of the oxidant. [d] Lower recoveries than expected due to interference from an inner-sphere process and/or precipitation.

Table IV. Stereoselectivities Expressed as Percent Enantiomeric Excess in the Reduction of $[\Delta\text{-}(+)_{546}\text{-}Co(edta)]^-$ by $[Co(en)_3]^{2+}$ at 0.04 M Ionic Strength and 25 °C in Various Solvents

solvent	stereoselectivity[a]	solvent	stereoselectivity[a]
water	9.0 ΔΛ	DMF	27.9 ΔΛ
methanol	16.9 ΔΛ	DMSO	34.5 ΔΛ
ethanol	17.4 ΔΛ	sulfolane	44.9 ΔΛ
formamide	17.3 ΔΛ	PC	46 ΔΛ[b]

[a] Data taken from ref 16. [b] Reference 26.

Discussion

The reactions of $[Co(gly)(ox)_2]^{2-}$ and $[Co(en)(ox)_2]^-$ with $[Co(en)_3]^{2+}$ show two interesting features. First, in neither case is there a strong dependence of the second-order rate constant for electron transfer, k_{so}, on solvent. Second, the stereoselectivities for the reactions differ markedly both in magnitude and in their dependence on solvent. Previously it was shown that subtle differences in the reactivity of these oxidants with $[Co(en)_3]^{2+}$ in aqueous solution correlate with differences in the hydrogen-bonding arrangement between the reactants.[18] Consideration of the solvent effects provides insight into the role of solvation in these reactions.

The most widely used analysis for discussing solvent effects in outer-sphere electron-transfer reactions is the dielectric continuum model,[9] which predicts a simple correlation between ln k_{so} and $(1/\epsilon_o - 1/\epsilon)$, where ϵ_o is the optical dielectric constant and ϵ is the bulk dielectric constant of the solvent. For the reductions of $[Co(gly)(ox)_2]^{2-}$ and $[Co(en)(ox)_2]^-$ by $[Co(en)_3]^{2+}$ the correlations are very poor, with correlation coefficients of 0.452 and

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(25) An alternative interpretation involves the ion pair as an unreactive assembly and electron transfer by a parallel second-order pathway:

$$[Co(gly)(ox)_2]^{2-} + [Co(en)_3]^{2+} \xrightarrow{k_{so}} [Co(gly)(ox)_2]^{3-} + [Co(en)_3]^{3+}$$

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Table V. Donor Number (DN) and Acceptor Number (AN) Description of the Solvent Effect on Second-order Rate Constants and Stereoselectivities

oxidant	Q_0	$\alpha\ (\bar{\alpha})^a$	$\beta\ (\bar{\beta})^a$	r^2
		$\log((k_{so})_{calc}) = Q_0 + \alpha DN + \beta AN$		
$[Co(gly)(ox)_2]^{2-}$	4.7 ± 2.1	–0.11 ± 0.06 (59)	–0.03 ± 0.02 (41)	0.640
$[Co(en)(ox)_2]^-$	3.7 ± 1.5	–0.14 ± 0.05 (53)	–0.04 ± 0.01 (47)	0.821
		$\log(k_{\Delta\Lambda}/k_{\Delta\Delta}) = Q_0 + \alpha DN + \beta AN$		
$[Co(gly)(ox)_2]^{2-}$	–0.02 ± 0.3	0.019 ± 0.009 (56)	–0.004 ± 0.003 (44)	0.939
$Co(en)(ox)_2]^-$	–0.09 ± 0.02	0.0016 ± 0.0006 (24)	0.0016 ± 0.0002 (76)	0.985
$[Co(edta)]^-$	0.72 ± 0.09	–0.010 ± 0.003 (27)	–0.009 ± 0.001 (73)	0.875

[a] Percentage contribution from DN and AN given by $\bar{\alpha} = 100\alpha'/(\alpha' + \beta')$ and $\bar{\beta} = 100\beta'/(\alpha' + \beta')$ where α' and β' are the partial regression coefficients $\alpha' = |\alpha|[\Sigma(DN_i - \overline{DN})^2/\Sigma(Q_i - \bar{Q})^2]^{1/2}$ and $\beta' = |\beta|[\Sigma(AN_i - \overline{AN})^2/\Sigma(Q_i - \bar{Q})^2]^{1/2}$.

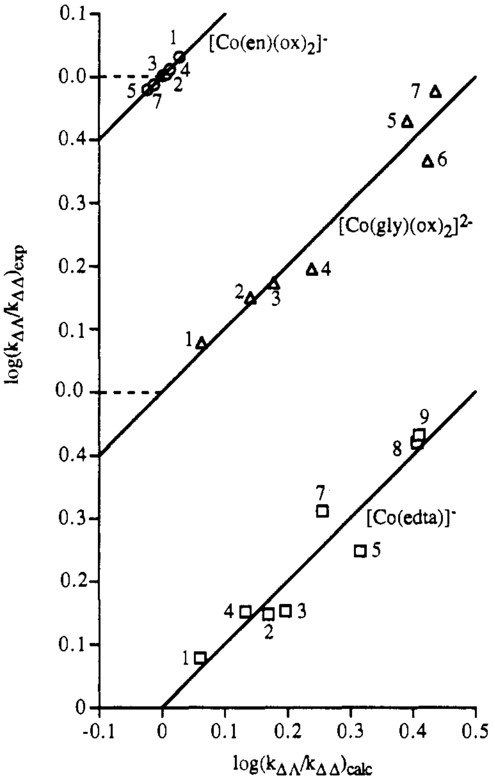

Figure 2. Plots of $\log((k_{\Delta\Lambda}/k_{\Delta\Delta})_{exp})$ against $\log((k_{\Delta\Lambda}/k_{\Delta\Delta})_{calc})$ evaluated from eq 9 for the oxidations of $[Co(en)_3]^{2+}$ by $[\Delta\text{-}(+)_{546}\text{-}Co(en)(ox)_2]^-$ (circles), $[\Delta\text{-}(+)_{546}\text{-}Co(gly)(ox)_2]^{2-}$ (triangles), and $[\Delta\text{-}(+)_{546}\text{-}Co(edta)]^-$ (squares). Solvents are numbered according to Table I.

0.198, respectively. Implicit in the dielectric continuum model are the assumptions that there are no changes in either driving force or the extent of ion association (K_0) in the different solvents. The reduction potential of $[Co(en)_3]^{3+}$ has been shown to be solvent dependent,[29] and while similar data are not available for the oxidants $[Co(en)(ox)_2]^-$ and $[Co(gly)(ox)_2]^{2-}$, it is likely that these reduction potentials are also solvent dependent. In addition, estimates of the extent of ion association are liable to considerable uncertainty since the interactions between the reactants include hydrogen bonding besides the more readily estimated electrostatic attractions. It can be concluded that these reactions are poorly suited to analysis by the dielectric continuum model.

An empirical analysis[30] which may have some merit describes the effect of solvent on a physicochemical property, Q, measured in solution as a linear function of the Gutmann donor number (DN) and acceptor number (AN),[23] eq 9, where α and β are

$$Q = Q_0 + \alpha DN + \beta AN \qquad (9)$$

regression coefficients and Q_0 is a constant which is independent of solvent.[31] The reduction potential of $[Co(en)_3]^{3+}$ shows a linear correlation with DN.[29] Since rates of outer-sphere electron-transfer reactions show a strong dependence on the driving force,[32] solvent effects due to factors associated purely with electron transfer may be masked by this thermodynamic component. In such cases, it seems appropriate to look for correlations of the rate data with donor and acceptor numbers.

Analysis of the rate data according to eq 9 yields the best fit parameters in Table V. The correlations of the experimentally determined values, $\log((k_{so})_{exp})$, with calculated values, $\log((k_{so})_{calc})$, for $[Co(gly)(ox)_2]^{2-}$ and $[Co(en)(ox)_2]^-$ have coefficients 0.636 and 0.802, respectively. These coefficients are low, and while they show a significant improvement over the dielectric continuum model, it must be remembered that they include an additional variable. The physical significance of the parameters is not clear, but it is noted that α and β receive approximately equal weight in the analysis, and as might be predicted, the dominant term is solvent independent.

A rationalization of the effects of solvent on chiral induction has not previously been attempted although the analysis should be simpler than for absolute rate measurements since the driving forces for the ΔΔ and ΔΛ processes are identical. For the analysis, the stereoselectivities are best expressed by a rate ratio, $k_{\Delta\Lambda}/k_{\Delta\Delta}$, rather than percent enantiomeric excess as shown in Tables III and IV. The best fit parameters for the reductions of $[Co(en)(ox)_2]^-$, $[Co(gly)(ox)_2]^{2-}$, and $[Co(edta)]^-$ by $[Co(en)_3]^{2+}$ are presented in Table V, and plots of $\log((k_{\Delta\Lambda}/k_{\Delta\Delta})_{exp})$ against $\log((k_{\Delta\Lambda}/k_{\Delta\Delta})_{calc})$ are shown in Figure 2. In each case the empirical fit found with the stereoselectivity data is better than that obtained for the absolute rate data. The interpretation of the best fit parameters remains obscure, but the analysis has some merit in providing a means for prediction of the magnitudes of stereoselectivity in different solvents. For example, analysis of the data of Taube and co-workers[16] for the reduction of $[Co(edta)]^-$ by $[Co(en)_3]^{2+}$ leads to a prediction of 42% ΔΛ for the stereoselectivity in propylene carbonate.[33] The measured value is 46% ΔΛ,[26] in very good agreement.

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Supplementary Material Available: Lists of pseudo-first-order rate constants, Tables SI and SII (2 pages). Ordering information is given on any current masthead page.

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(29) Mayer, U.; Kotocova, A.; Gutmann, V.; Gerger, W. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *100*, 875–883.

(30) Krygowski, T. M.; Fawcett, W. R. *J. Am. Chem. Soc.* **1975**, *97*, 2143–2148.

(31) A similar expression used in ref 11 includes a parameter for the polarizability of the solvent, π^*. Significantly poorer fits were obtained when this expression was used.

(32) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155–196.

(33) The data from ref 16 yield the expression $\log(k_{\Delta\Lambda}/k_{\Delta\Delta}) = 0.67(13) - 0.0085(44)DN - 0.0083(16)AN$.