Steric and Electronic Effects of the Alkyl Group on the Activation Parameters of the Water Substitution Reaction of some Cobaloximes

R. DREOS GARLATTI, G. TAUZHER and G. COSTA

Istituto di Chimica, Università di Trieste, P.le Europa 1, 34127 Trieste, Italy

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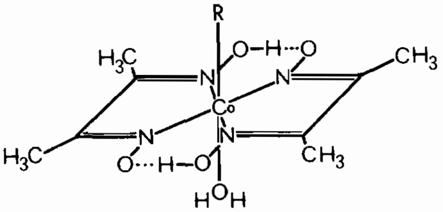
The activation parameters for the water substitution reactions of some organocobaloximes with thiourea in aqueous solution at $I = 1$ M ($NaNO_3$) are reported and discussed. Scatter in an isokinetic plot indicates that more than one interaction mechanism is at play. The ΔH^* values are shown to be influenced by the electron withdrawing power and by the steric bulk of the alkyl group. The influence of these factors on ΔS^* cannot be rationalized.

Introduction

It is well known that the water substitution reactions of the $RCo(DH)_2H_2O$ complexes (I), commonly referred to as organoaquocobaloximes, in aqueous solution involve a dissociative type of activation [1].



The substitution rate has been proved to be strongly dependent on the nature of the R group [2].

For the reaction

$$RCo(DH)_2H_2O + Py \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} RCo(DH)_2Py + H_2O \quad (1)$$

the k_{on} values decrease from 1.49×10^4 M^{-1} s^{-1} for R = i-C_3H_7 to 5.59×10^{-2} for R = CH_2CN, with decreasing electron donor power of R. However, log k_{on} shows a nonlinear dependence on the polar substituent constant σ^*, which is believed to reflect the inductive effect of the alkyl group [3]. The nonlinearity was interpreted as an evidence for the existence of the five coordinate $RCo(DH)_2$ in equilibrium with the hexacoordinate aquocomplex, the ratio of penta/hexacoordinate species being progressively shifted from ~1 to ≪1 with an increasing electron-withdrawing inductive effect through the alkyl substituent. The data for methyl, chloromethyl and iodomethyl deviate from the data of the other substituted alkylcobaloximes on the above free energy correlations, and were not considered. Whether the basis of the deviations were steric or otherwise was unclear.

Steric factors are known to be important in determining geometrical distortions in the structure of the organocobaloximes in the ground state [4, 5]. The observed structural distortions, which are determined by the steric bulkiness of the axial ligands, involve variations in the Co–C and Co–L bond length (L = Py, PPh_3, H_2O), displacement of the cobalt atom out of the plane being defined by the four N atoms of the $(DH)_2$ system, bending between the two individually planar DH units, and deformations of C–Co–N (equatorial) and C–Co–L bond angles. Furthermore, for R = CH_2X, opening of the Co–CH_2–X bond angle has been observed. It is to be expected that all these distortions, and particularly the lengthening of the Co–L bond, may influence the lability of the coordinated water. In order to obtain new insight into the dependence of the reactivity of the organoaquocobaloximes on both electronic and steric factors, we have examined the effect of the variation of the axial R group on the activation parameters of the water substitution reactions.

Experimental

The organoaquocobaloximes were prepared as previously reported [6]. $NaNO_3$ and thiourea were analytical grade and were used without further purification. The thiourea solutions were prepared from a known weight of reagent.

The kinetics were followed by a Durrum Gibson model D 130 stopped flow spectrophotometer. The experimental procedure followed in order to minimize the errors, which may affect the kinetic data obtained by this type of instrument at other than room temperature, has been reported in a previous work [7].

Results

The substitution reactions of the coordinated water of some organocobaloximes with thiourea were

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studied at various temperatures in the range 15.5–42.8 °C. The temperature was maintained constant within ±0.2 °C:

$$RCo(DH)_2H_2O + (NH_2)_2CS \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RCo(DH)_2[(NH_2)_2CS] + H_2O \qquad (2)$$

with R = CH_2Cl, CH_2Br, CH_2I, CH_2CH_3, $CH_2C_6H_5$, CH_2CF_3.

The kinetic experiments were performed in aqueous solution at I = 1 *M* ($NaNO_3$) under pseudo-first order conditions, in the presence of a large excess of incoming ligand. The initial concentration of the complex was 0.2–1.0 × 10^{-3} *M*; the ligand concentrations ranged from 2 × 10^{-3} to 0.35 *M*. The observed pseudo first order rate constants (k_{obs}) were obtained from the linear plots of $\log(A_t - A_\infty)$ *vs.* time, where A_t is the optical absorbance at time t and A_∞ is the final absorbance. The k_{obs} values show a linear dependence on the concentration of thiourea in the range of concentrations examined, according to the expression

$$k_{obs} = k_1[L] + k_{-1} \qquad (3)$$

Values of k_1 and k_{-1}, calculated by linear least squares analysis, are reported in Table I as a function of temperature.

The activation parameters ΔH* and ΔS* were calculated by fitting the k_1–T data to the Eyring equation in the exponential form

$$k_1 = \frac{kT}{h} e^{-\Delta H^*/RT} e^{\Delta S^*/R} \qquad (4)$$

by a nonlinear least squares analysis, each value of k_1 being weighted as $1/\sigma_{k_1}{}^2$. Initial parameter estimates for this analysis were determined from the slope and the intercept of the linear form of the Eyring equation

$$\ln\frac{k_1}{T} = \ln\frac{k}{h} - \frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R} \qquad (5)$$

The ΔH* and the ΔS* values are reported in Table II. All errors reported in this work are standard deviations. The computer program used was SPSS (Statistical Package for Social Sciences) version 8.3, May 82, Vogelback Computing Center, Northwestern University.

Discussion

The relationship between log k_1 and σ* for the water substitution reactions of the organocobaloximes with thiourea is nonlinear (Table II), as previously observed for the analogous reactions with pyridine [2]. Kallen *et al.* [2] suggest that the deviation from linearity provides a line of evidence for

TABLE I. Rate Constants for the Reaction $RCo(DH)_2H_2O$ + Thiourea at I = 1 *M* ($NaNO_3$) at Various Temperatures.

R	t (°C)	k_1 ($M^{-1}s^{-1}$)	k_{-1} (s^{-1})
CH_2CH_3	15.5	897 ± 34	13.5 ± 0.2
	20.1	1349 ± 73	21.4 ± 0.5
	25.0	2201 ± 130	33.6 ± 0.9
	30.5	3003 ± 311	52.8 ± 2.1
	35.0	4403 ± 941	76.1 ± 7.4
$CH_2C_6H_5$	16.2	725 ± 30	3.00 ± 0.20
	20.4	1050 ± 36	4.92 ± 0.25
	25.2	1448 ± 31	8.55 ± 0.20
	30.9	2119 ± 58	16.37 ± 0.37
	37.0	3681 ± 124	30.23 ± 0.87
CH_2CF_3	16.8	0.38 ± 0.02	
	23.0	0.72 ± 0.01	
	25.2	0.91 ± 0.03	
	31.5	1.78 ± 0.04	
	39.2	3.73 ± 0.05	
CH_2Cl	15.6	8.51 ± 0.26	0.13 ± 0.04
	22.2	14.95 ± 0.42	0.20 ± 0.07
	28.9	29.25 ± 0.53	0.26 ± 0.08
	35.3	53.87 ± 0.88	1.04 ± 0.14
	42.6	100.24 ± 2.26	1.87 ± 0.34
CH_2Br	16.6	5.04 ± 0.27	0.25 ± 0.04
	17.7	5.41 ± 0.09	0.08 ± 0.02
	22.0	7.53 ± 0.25	0.10 ± 0.04
	22.8	8.57 ± 0.17	0.06 ± 0.03
	28.8	15.44 ± 0.40	0.03 ± 0.07
	29.8	15.78 ± 0.22	0.17 ± 0.04
	35.2	27.58 ± 0.52	0.08 ± 0.09
	42.8	52.70 ± 1.02	0.61 ± 0.17
CH_2I	17.7	4.35 ± 0.10	0.04 ± 0.02
	22.5	6.92 ± 0.11	0.04 ± 0.02
	29.8	13.86 ± 0.19	0.06 ± 0.03
	35.3	21.60 ± 0.52	0.34 ± 0.07
	43.6	39.12 ± 0.57	0.74 ± 0.10

TABLE II. Activation Parameters for the Reaction $RCo(DH)_2H_2O$ + Thiourea.

	σ^{*a}	log k_1 at 25 °C^b	ΔH* kcal/mol	ΔS* (e.u.)
C_2H_5	−0.10	3.31	14.32 ± 0.71	4.62 ± 2.41
$CH_3{}^c$	0.0	2.12	14.62 ± 0.50	0.21 ± 1.09
$CH_2C_6H_5$	0.215	3.16	12.81 ± 0.66	−1.11 ± 2.20
CH_2I	0.85	0.95	14.80 ± 0.42	−4.56 ± 1.39
CH_2CF_3	0.92	−0.04	18.01 ± 0.13	1.68 ± 0.42
CH_2Br	1.00	1.02	16.01 ± 0.33	−0.15 ± 1.09
CH_2Cl	1.05	1.31	16.30 ± 0.32	2.13 ± 1.05

[a] From ref. 3. [b] Interpolated from the rate constants determined at temperatures other than 25 °C. [c] From ref. 7.

the existence of a pre-equilibrium (see Introduction). On the other hand, the source of the failure in the LFE relationships is often the operation of a number of different factors simultaneously influencing substituent effects [3]. The hypothesis that interaction mechanisms other than the purely polar effects of the substituent occur in this case is supported by the lack of correlation between the ΔH^* and the ΔS^* values (Table II). Scatter in an isokinetic plot indicates that more than one interaction mechanism is at play, but does not suggest the causes of the scatter [3]. However, inspection of the data of Table II may provide some indications.

The first feature emerging from these data is that, according to the expectation for a dissociative mechanism, the activation enthalpies generally increase with increasing electron withdrawing power of R. Two relevant exceptions to the general trend are present, for $R = CH_2CF_3$ and $CH_2C_6H_5$.

i) The activation enthalpy of the 2,2,2-trifluoroethyl derivative is higher than expected on the basis of its σ^* value (Table II), in agreement with the low value of the rate constant k_1. A similar behavior is shown by this complex in the reaction with pyridine [2] and NH_3 [8]. Structural data of $CF_3CH_2Co(DH)_2PPh_3$ [4] show that the Co–P bond length in this complex is shorter than that in CH_2Br and $CH_2CNCo(DH)_2PPh_3$ complexes. As the increase in the Co–L bond length generally parallels the increasing donor power of R, a longer Co–P bond should be expected for the 2,2,2-trifluoroethyl derivative ($\sigma^* = 0.92$ for $R = CH_2CF_3$, 1.00 for $R = CH_2Br$ and 1.3 for $R = CH_2CN$). The observed structural distortions for this complex [4] suggest that the CH_2CF_3 group has a steric hindrance smaller than expected, owing to the large deformations in the bond lengths and angles within the alkyl group. The relatively small steric hindrance results in shorter Co–P and Co–C bonds. On the basis of the structural data an order of increasing steric bulk $CH_2CN < CH_2CF_3 < CH_2Br$ is suggested. The substitution of PPh_3 with Py does not alter the general trend [4]. It is very probable that the trend is also the same for the aquocomplexes. Thus the inertness of the 2,2,2-trifluoroethyl derivative may be due to a relatively short $Co–H_2O$ bond in the ground state, which is in turn ascribed to steric effects. It should be noted that in the three complexes ($R = CH_2Br$, CH_2CF_3, and CH_3) for which structural data are available for comparison with reactivity data, the decrease in the Co–L bond lengths parallels the decrease in ΔH^*. However, we wish to point out that the relationships between reactivity and structural data do not take into account the effect on the reactivity of the structure of the transition state, which may be considerably different for various R groups. Therefore only a rough accord in these structure–reactivity relationships should be expected.

ii) The activation enthalpy of the benzyl derivative is lower than expected on the basis of its σ^* value, in agreement with the high reactivity of this complex (Table II). The benzyl derivative exhibits an anomalously high reactivity also in the water substitution reactions of the structurally related $RCo[(DO)(DOH)pn]H_2O^+$ complexes (where an O–H–O group is replaced by a $-(CH_2)_3-$ group)[†]. Unfortunately, structural data for this complex are not available, but the hypothesis that the relatively bulky phenyl group provokes geometrical distortions similar to those observed in other sterically-hindered complexes, and the consequent labilization of the complex, seems reasonable.

Hence in the present case the ΔH^* values appear to be affected both by the electron withdrawing power and by the steric bulk of the R group. The influence of these factors on ΔS^* cannot be rationalized. In the light of these facts a nonlinear relationship between $\log k_1$ and σ^* should be expected, even in the absence of pre-equilibria.

Finally, it appears from the data of Table II that the variations in the reaction rates are due mainly to the ΔH^* changes[¶], but that when the activation enthalpies are not very dissimilar, the trend of the rate constants may be determined by entropic effects. This consideration is relevant in the case of the halomethyl derivatives, for which the rate constants decrease in the order $CH_2Cl > CH_2Br > CH_2I$. A similar trend has been observed in the substitution reactions with pyridine [2], and in the base exchange reactions in non-aqueous solvents [11]. This sequence is opposite to that expected on the basis of the electronegativity and of the size of the R groups. Various explanations have been proposed [11, 12]. Since for these three complexes, the sequence of the activation enthalpies is that expected, the inversion in the trend of k_1 is determined by entropic effects. In this case, the variation of ΔH^* with the structure appears to be more regular than the variation of $\log k_1$.

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[†] For the reaction $RCo[(DO)(DOH)pn]H_2O^+ + NH_3 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} RCo[(DO)(DOH)pn]NH_3^+ + H_2O$ in aqueous solution at I = 1 *M* ($NaNO_3$) and 25 °C, the k_2 values are 7.05 $M^{-1}\ s^{-1}$ for $R = CH_3$ [9], 1.07×10^2 $M^{-1}\ s^{-1}$ for $R = CH_2CH_3$ [9], and 44.6 $M^{-1}\ s^{-1}$ for $R = CH_2C_6H_5$.

[¶] We recall that a change of ΔS^* of 4.6 e.u. causes a 10-fold change in the reaction rate, if ΔH^* remains constant; if ΔS^* remains constant the rate changes by a factor of 10 for a change of ΔH^* of 1.36 kcal/mol at 25 °C [10].

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