Journal of Organometallic Chemistry, 195 (1980) 113—122

SUBSTITUENT EFFECT OF CHELATED COBALT

II *. SAPONIFICATION OF *m*- AND *p*-CARBOMETHOXYPHENYL(LIGAND)COBALOXIMES

KENNETH L. BROWN and ALLAN W. AWTREY

Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019 (U.S.A.)

(Received February 29th, 1980)

Summary

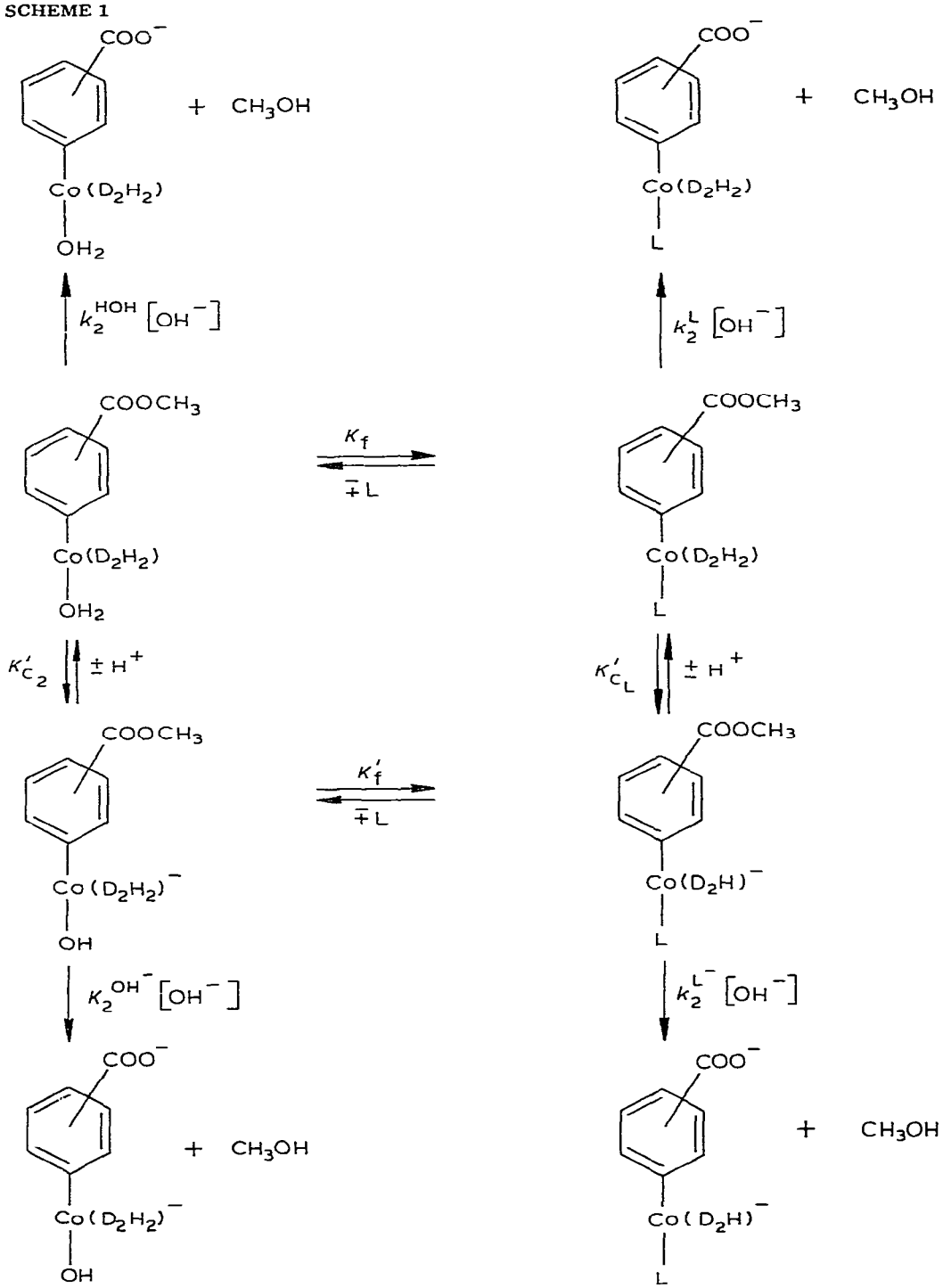
Binding constants for eight axial ligands, including four primary amines, and CN^-, SCN^-, NO_2^-, and N_3^-, to *m*- and *p*-carbomethoxyphenyl(aquo)cobaloxime have been determined in aqueous solution at 25.0°C, ionic strength 1.0 *M*. These constants have been used to establish experimental conditions for the measurement of the second-order rate constants for base-catalyzed hydrolysis of these cobaloxime substituted methyl benzoates. These rate constants have been correlated via the Taft dual substituent parameter equation to provide values for the inductive and resonance substituent constants for the chelated substituents -$Co(D_2H_2)L$. The results show that substantial resonance interaction can occur between these substituents and carbomethoxyphenyl-organic ligands when L is an unsaturated inorganic ligand capable of π-interactions with the cobalt atom. Inductive electron donation by the substituent -$Co(D_2H_2)L$ is found to increase linearly with proton basicity of L for all the inorganic ligands save one, while an unexpected inverse dependence is seen for L = RNH_2.

Introduction

In a previous paper [1] we reported a study of the base-catalyzed ester hydrolysis of *m*- and *p*-carbomethoxyphenyl(aquo)cobaloximes according to Scheme 1 (left half). The second-order rate constants, k_2^{HOH} and $k_2^{OH^-}$ for both isomers (Scheme 1) were correlated via the Taft dual substituent parameter

* For Part I, see reference 1. Abbreviations: TFEA, trifluoroethylamine; DEA, dimethoxyethylamine; MEA, methoxyethylamine; nPA, n-propylamine; CAPS, 3-(cyclohexylamine)propanesulfonic acid; BICINE, *N*,*N*-bis(2-hydroxyethyl)glycine.

SCHEME 1



equation (eq. 1) [2] in which k and k^0 are the rate constants for the substituted

$$\log(k/k^0) = \sigma_I \rho_I^i + \sigma_R \rho_R^i \qquad (1)$$

and unsubstituted methyl benzoates, respectively, σ_I and σ_R are position independent inductive and delocalization parameters of the substituent and ρ_I^i and ρ_R^i represent position dependent susceptibilities of the reaction center to inductive and resonance substituent effects, respectively (the superscript i refers to the substituent position, *m* or *p*). From the measured values of the second-order rate constants for base-catalyzed hydrolysis of five *m*- and five *p*-substituted methyl benzoates and the values of σ_I and σ_R for those substituents listed by Ehrenson, et al. [2], the susceptibility parameters (ρ's) for this reaction were calculated by a least-squares fit of the data to eq. 1. This allowed calculation of the substituent parameters for the aquo- and hydroxo-liganded cobaloxime chelated cobalt centers for which the values —0.30 and —0.48, respectively, for σ_I, and —0.05 and —0.07, respectively, for σ_R, were obtained, indicating that there is little or no resonance interaction between this chelated cobalt center and aryl organic ligands.

These results were contrasted to those of Hill, et al. [3] who reported the ^{19}F NMR shifts of *m*- and *p*-$FC_6H_4Co\{(DO)(DOH)pn\}X$, for X = -$CH_3$, *p*-$FC_6H_4$, OCN (or NCO), I, Br, and SCN (or NCS) in CH_2Cl_2 and $(CH_3)_2SO$. Correlation of these NMR shifts via eq. 1 using the ^{19}F NMR shifts of substituted fluorobenzenes in $(CH_3)_2SO$ reported by Taft and co-workers [4] as a basis set gave values of σ_I ranging from —0.54 to —0.03 (for X = CH_3 and X = SCN (NCS), respectively) and σ_R ranging from —0.23 to —0.30 (for X = CH_3 and X = Br, respectively) suggesting substantial resonance interaction of the $Co\{(DO)(DOH)pn\}X$ cobalt center with the fluorobenzene ligand for all X studied. It is not yet clear if these differences mean that the cobalt center's ability to donate π-electron density to aryl ligands is substantially dependent on the nature of its axial and equatorial ligands, or simply that the ability of such chelated cobalt centers to act as π-donating substituents is strongly dependent on the nature of the substituent effect defecting group (i.e. -F or -$COOCH_3$ in the present case) as is the case for a number of other substituents [2]. In order to determine if the ability of cobaloxime chelated centers to interact in resonance fashion with the carbomethoxyphenyl ligand depends upon the nature of the *trans* axial ligand, as well as to determine the dependence of the inductive substituent component upon such axial ligands, we undertook a study of the effect of various axial ligands on the saponification of *m*- and *p*-carbomethoxyphenylcobaloximes, which is the subject of the present report.

Experimental

m- and *p*-$CH_3OOCC_6H_4Co(D_2H_2)OH_2$ were prepared as previously described [1]. Primary amine axial ligands were redistilled and stored under argon except TFEA (obtained as its hydrochloride), which was recrystallyzed from ethanol, dried and stored over P_2O_5. Potassium salts of the inorganic axial ligands were recrystallized and dried and stored over P_2O_5. Buffer components, methanol and KCl were obtained in the highest purity commercially available and used without further purification. Glass distilled deionized water was used throughout.

NMR spectra were recorded on a Varian T-60 NMR spectrometer. Electronic spectra were obtained on a Cary 219 Recording Spectrophotometer and single

TABLE 1

BINDING CONSTANTS, K_f, FOR VARIOUS AXIAL LIGANDS TO *m*- AND *p*-$CH_3OOCC_6H_4Co(D_2H_2)OH_2$ IN AQUEOUS SOLUTION [a]

Ligand	pK_a [b]	Isomer	K_f^{app} (M^{-1})	λ (nm)	pH	α_L [c]	K_f (M^{-1})
TFEA	5.68 ± 0.01 [d]	*p*-	38.1 ± 1.4	445	8.43 ± 0.03	0.998 ± 0.001	38.2 ± 1.4
		m-	44.7 ± 1.0	445	8.42 ± 0.03	0.998 ± 0.001	44.8 ± 1.0
DEA	8.86 ± 0.01 [e]	*p*-	1060 ± 32	440	9.31 ± 0.01	0.738 ± 0.007	1380 ± 50
		m-	1200 ± 110	445	9.47 ± 0.01	0.803 ± 0.005	1490 ± 130
MEA	9.68 ± 0.01 [d]	*p*-	792 ± 73	440	9.61 ± 0.02	0.460 ± 0.013	1720 ± 160
		m-	1530 ± 60	445	9.63 ± 0.02	0.471 ± 0.012	3240 ± 150
nPA	10.80 ± 0.02 [d]	*p*-	239 ± 71	440	9.64 ± 0.01	0.0688 ± 0.0033	3470 ± 290
		m-	280 ± 18	445	9.57 ± 0.01	0.0556 ± 0.0027	5040 ± 400
CN^-	9.00 [f]	*p*-	$2.16 \pm 0.07 \times 10^4$	430, 385	11.75 ± 0.02	—	—
		m-	$2.34 \pm 0.14 \times 10^4$	335, 390	11.79 ± 0.03	—	—
SCN^-	0.85 [g]	*p*-	84.1 ± 4.2	440, 355	8.44 ± 0.01	1.000	84.1 ± 4.2
		m-	79.5 ± 3.1	440, 355	8.42 ± 0.02	1.000	79.5 ± 3.1
NO_2^-	3.29 [g]	p-	69.5 ± 0.8	440	6.73 ± 0.03	1.000	69.5 ± 0.8
		m-	64.7 ± 6.0	440	6.68 ± 0.02	1.000	64.7 ± 6.0
N_3^-	4.72 [g]	*p*-	352 ± 11	340, 365	7.74 ± 0.01	0.999 ± 0.001	352 ± 11
		m-	322 ± 13	350, 360	7.70 ± 0.02	0.999 ± 0.001	322 ± 13

[a] 25.0 ± 0.1°C, ionic strength 1.0 *M* in KCl. [b] pK_a of the conjugate acid of the ligand. [c] Fraction of ligand as the free base at the measurement pH, calculated from eqs. 2 and 3. [d] Ref. 7. [e] Ref. 8. [f] Ref. 9. [g] Ref. 10.

wavelength measurements were made either on a Cary 219 or Gilford Model 250 Spectrophotometer. pH measurements were made with a Radiometer PHM 64 using a type B combined glass electrode at 25.0°C as previously described [5].

Binding constants, K_f (Scheme 1), for axial ligands to the organo(aquo)-cobaloximes were determined from single wavelength absorption measurements of aqueous solutions containing cobaloxime and varying amounts of axial ligand in phosphate, CAPS, or BICINE buffers, ionic strength 1.0 *M* (KCl) by the method which has been previously described [6]. Measurement wavelengths are listed in Table 1. When necessary (primary amines), the apparent binding constants, K_f^{app}, thus obtained were corrected for protonation of the axial ligand at the measurement pH by use of eq. 2

$$K_f = K_f^{app}/\alpha_L \tag{2}$$

where α_L is the fraction of axial ligand as the unprotonated species, calculated from eq. 3

$$\alpha_L = K_a/(K_a + [H^+]) \tag{3}$$

where K_a is the proton dissociation constant of the conjugate acid of the ligand [5,7,8]. When necessary (primary amines) because of poor solubility of the liganded complexes, water jacketed 10 cm pathlength cells were employed.

For measurement of the saponification rates of the liganded complexes, the amount of ligand necessary to maintain >97% ligation at the measurement pH was calculated by assuming that the binding constant for the axial ligand to the anionic organocobaloxime, K_f' (Scheme 1), had a limiting value of zero. Consequently, a lower limit for the apparent binding constant, K_f^{app}, at any pH, could be calculated from eq. 4

$$K_f^{app} = K_f(1 - \alpha_{cob}) + K_f'\alpha_{cob} \tag{4}$$

where α_{cob}, the fraction of organocobaloxime as the anionic hydroxo-species, was calculated from eq. 5 and the values of K'_{c_2} previously determined for each isomer

$$\alpha_{cob} = K'_{c_2}/(K'_{c_2} + [H^+]) \tag{5}$$

(pK'_{c_2} = 11.41 ± 0.01 for the *p*-isomer and 11.75 ± 0.06 for the *m*-isomer [1]). Since eq. 4 is a monotonically decreasing function of pH, the value of K_f^{app} calculated at the highest pH employed for saponification rate measurements represents an underestimated lower limit for K_f^{app} at all lower pH's. Hence the concentration of ligand thus calculated for >97% ligation at the highest pH employed was also sufficient throughout the saponification pH-rate profiles. No attempt was made to measure either K_f' or $k_2^{L^-}$ (Scheme 1) because of the anticipated low values of the former constants [7,11].

First-order rate constants, k_{obsd}, for base-catalyzed hydrolysis of the cobaloxime substituted methyl benzoates at a given pH (maintained with phosphate, CAPS or nPA buffers) were determined from the time dependence of the UV absorbance at the wavelengths listed in Table 2. Stock solutions of cobaloximes (methanol) contained cobaloxime and sufficient ligand to insure >99% ligation. To initiate the reaction, the stock solution was diluted into samples (in 3 ml

TABLE 2

SECOND-ORDER RATE CONSTANTS, k_2^L, FOR THE BASE-CATALYZED HYDROLYSIS OF *m*- AND *p*-$CH_3OOCC_6H_4Co(D_2H_2)L$ [a]

Ligand	pK_a [b]	Isomer	k_2^L (M^{-1} s^{-1})	λ, nm	σ_I [c]	$\sigma_{R(BA)}$ [c, d]
TFEA	5.68 ± 0.01	*p*-	$6.18 \pm 0.45 \times 10^{-3}$	280	−0.827	−0.011
		m-	$6.72 \pm 0.45 \times 10^{-3}$	255		
DEA	8.86 ± 0.01	*p*-	$2.19 \pm 0.02 \times 10^{-2}$	285	−0.482	+0.032
		m-	$2.07 \pm 0.04 \times 10^{-2}$	245		
MEA	9.68 ± 0.01	*p*-	$1.89 \pm 0.03 \times 10^{-2}$	275	−0.476	−0.013
		m-	$2.02 \pm 0.04 \times 10^{-2}$	245		
nPA	10.80 ± 0.02	*p*-	$1.94 \pm 0.06 \times 10^{-2}$	275	−0.391	−0.084
		m-	$2.50 \pm 0.08 \times 10^{-2}$	260		
CN^-	9.40	*p*-	$1.51 \pm 0.04 \times 10^{-2}$	275	−0.437	−0.115
		m-	$2.12 \pm 0.05 \times 10^{-2}$	230		
SCN^-	0.85	*p*-	$1.13 \pm 0.03 \times 10^{-2}$	285	−0.527	−0.118
		m-	$1.61 \pm 0.04 \times 10^{-2}$	295		
NO_2^-	3.29	*p*-	$1.33 \pm 0.02 \times 10^{-2}$	415	−0.306	−0.274
		m-	$2.85 \pm 0.06 \times 10^{-2}$	420		
N_3^-	4.72	*p*-	$1.75 \pm 0.06 \times 10^{-2}$	290	−0.396	−0.110
		m-	$2.42 \pm 0.05 \times 10^{-2}$	295		
H_2O [e]	−1.7	*p*-	$2.97 \pm 0.11 \times 10^{-2}$	290	−0.297	−0.048
		m-	$3.45 \pm 0.21 \times 10^{-2}$	240		
OH^- [e]	15.7	*p*-	$1.54 \pm 0.04 \times 10^{-2}$	290	−0.477	−0.072
		m-	$1.93 \pm 0.06 \times 10^{-2}$	240		

[a] 25.0 ± 0.1°C, ionic strength 1.0 *M* maintained with KCl. [b] pK_a of the conjugate acid of the ligand, see footnotes to Table 1 for references. [c] Calculated from the values of k_2^L and eq. 1 using the ρ values determined in ref. 1. [d] $\sigma_{R(BA)}$ is the resonance substituent parameter appropriate for "benzoic acid type" reactions and applicable to methyl benzoate hydrolysis rates [2]. [e] Data from ref. 1.

quartz cuvettes) containing buffer, KCl (ionic strength 1.0 *M*) and sufficient excess ligand to maintain >97% ligation at the measurement pH (calculated as described above) which had been previously incubated for 30 min. at 25.0 ± 0.1°C. Absorbance was monitored continuously for at least $6 \times T_{1/2}$ except for samples for which $T_{1/2} > 10$ h in which case measurements were made for ca. 50 h. First-order rate constants were obtained from the slopes of plots of $\ln|A_t - A_\infty|$ (absorbance at time t and $t > 6 \times T_{1/2}$, respectively) vs. t (linear for at least $3 \times T_{1/2}$) except for those for which $T_{1/2} > 10$ h which were analyzed by the method of Guggenheim using ΔT ca. $1 \times T_{1/2}$ [12]. Second-order rate constants, k_2^L, for the saponification of the carbomethoxyphenyl(ligand)cobaloximes were then obtained from least-squares fits of the data to eq. 6

$$k_{obsd} = k_2^L a_{OH^-} \quad (6)$$

where a_{OH^-} was calculated from the measured pH and K_w (1×10^{-14} at 25°C).

Results and discussion

Values for the ligand binding constants, K_f (Scheme 1), to *m*- and *p*-$CH_3OOCC_6H_4Co(D_2H_2)OH_2$ are listed in Table 1 along with the measurement conditions. Among the series of four isosteric primary amine ligands the values of K_f can be seen to be monotonically increasing functions of amine basicity for both cobaloxime isomers as was the case for $CH_3Co(D_2H_2)OH_2$ [7]. For the

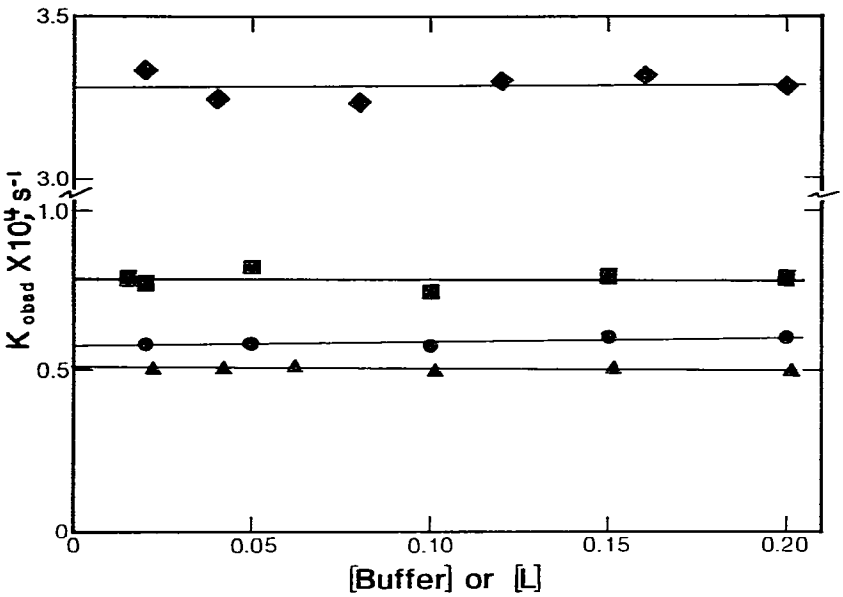


Fig. 1. Representative plots of k_{obsd} for carbomethoxyphenyl(ligand)cobaloxime saponification vs. buffer or added axial ligand concentration: ●, *p*-$CH_3OOCC_6H_4Co(D_2H_2)OH_2$ vs. phosphate buffer concentration, pH 11.42 ± 0.02 (slope = 1.55 ± 0.61 X 10^{-5} M^{-1} s^{-1}, intercept = 5.75 ± 0.07 X 10^{-5} s^{-1}); ■, *m*-$CH_3OOCC_6H_4Co(D_2H_2)OH_2$ vs. phosphate buffer concentration, pH 11.42 ± 0.02 (slope = —1.15 ± 16.9 X 10^{-6} M^{-1} s^{-1}, intercept = 7.85 ± 0.19 X 10^{-5} s^{-1}); ◆, *m*-$CH_3OOCC_6H_4Co(D_2H_2)$DEA vs. [DEA], pH 12.33 ± 0.01 (slope = 4.08 ± 32.0 X 10^{-6} M^{-1} s^{-1}, intercept = 3.28 ± 0.04 X 10^{-4} s^{-1}); ▲, *p*-$CH_3OOCC_6H_4Co(D_2H_2)CN^-$ vs. [CN^-], pH 11.41 ± 0.01 (slope = —3.68 ± 4.20 X 10^{-6} M^{-1} s^{-1}, intercept = 5.09 ± 0.05 X 10^{-5} s^{-1}).

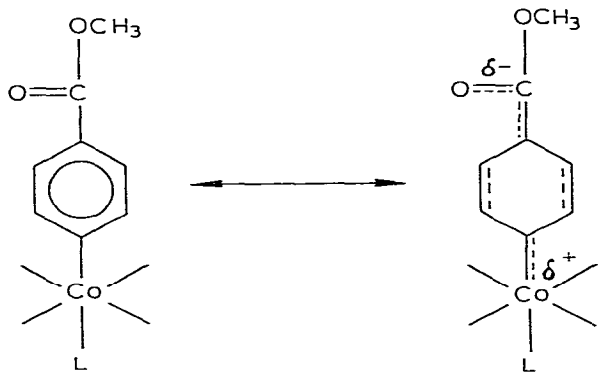
inorganic ligands, CN^- shows the typical hyperaffinity for the cobalt center, while the affinities of the other inorganic ligands are more in line with their proton basicities. Plots of log K_f vs. primary amine basicity (not shown) were reasonably linear and gave least squares slopes of 0.39 ± 0.04 (*p*-isomer) and 0.42 ± 0.05 (*m*-isomer), in excellent agreement with the previously determined value of 0.38 ± 0.01 for $CH_3Co(D_2H_2)OH_2$ [7]. These results indicate that the selectivity of the organocobaloxime cobalt center for purely σ donating primary amine ligand does not depend significantly upon the electron inductive effect of the *trans* organic ligand ($\sigma^* = 0$ for CH_3- [13] and 0.85 and 0.90 for *m*- and *p*-$CH_3OOCC_6H_4$-, respectively [14]).

Figure 1 shows the results of selected experiments designed to determine if either the buffers or axial ligands employed in the saponification experiments could act as either general-base or nucleophilic catalysts for the saponification reaction. As seen in this figure, changes in phosphate buffer concentration over the range 0.02 to 0.20 *M* had no effect on the rate of base-catalyzed hydrolysis of either ester. Similarly, changes in the concentration of DEA and CN^- over a similar concentration range (>97% saturation is maintained at all concentrations in this range) also had no experimentally significant effect on the observed rates. We concluded that no such catalysis by buffer salts or axial ligands occurs.

Figure 2 shows representative pH-rate profiles for the saponification of

various *m*- and *p*-carbomethoxyphenyl(ligand)cobaloximes, all of which are satisfactorily linear over the pH range investigated. From these and other similar data (not shown) the values of k_2^L (Scheme 1) listed in Table 2 were derived as described in the Experimental section. These values were used in conjunction with eq. 1 and the previously determined ρ values [1] to calculate the values for the inductive and resonance substituent constants for the -Co(D_2H_2)L centers which are also listed in Table 2.

As seen in Table 2, none of the cobaloxime cobalt centers with primary amine axial ligands (with the possible exception of nPA) show any substantial ability for resonance interaction with the carboxymethoxyphenyl- organic ligand, as was also the case with the purely σ-donating axial ligands OH_2 and OH^- previously investigated. However, all of the inorganic, anionic ligands which are at least potentially capable of π-interactions with the cobalt center give cobalt substituents which are moderately, but significantly, π donating. Since $\sigma_{R(BA)}$-type resonance interactions require some stabilization of positive charge on the substituent [2] this effect could possibly be ascribed to the presence of an anionic axial ligand acting as a sink for positive charge placed on the cobalt as shown below.



However, the small value of $-\sigma_{R(BA)}$ for the "hard" ligand OH^- (Table 2) would seem to suggest that charge interactions alone are not sufficient to explain the effect, and that π-interactions of the axial ligand are required for substantial resonance interaction of the cobalt center with "benzoic acid type" aryl ligands. Since two of the unsaturated ligands undoubtedly must act as π-electron sinks (SCN^- and N_3^- may act either as π-donors or π-acceptors to cobalt) [15], we have the interesting conclusion that π-electron withdrawal from the cobalt atom by the axial ligand seems to engender π-electron donation from the cobalt atom to a "benzoic acid type" aryl group. Hence, electron depletion of the cobalt atom by π-electron removal seems to be synergistic with respect to the two axial ligands rather than antagonistic.

Figure 3 shows a plot of $-\sigma_I$ for the -Co(D_2H_2)L cobalt centers vs. the pK_a of the conjugate acid of the ligand, L. Among the inorganic ligands (except SCN^-) there is a clear, relatively linear trend toward increasing inductive electron donation with increasing proton basicity of the ligand. A least-squares fit to the data (excepting SCN^-, $N = 5$) provides the values of 0.0113 ± 0.0025 for the slope and 0.313 ± 0.022 for the intercept, showing a perhaps surprisingly

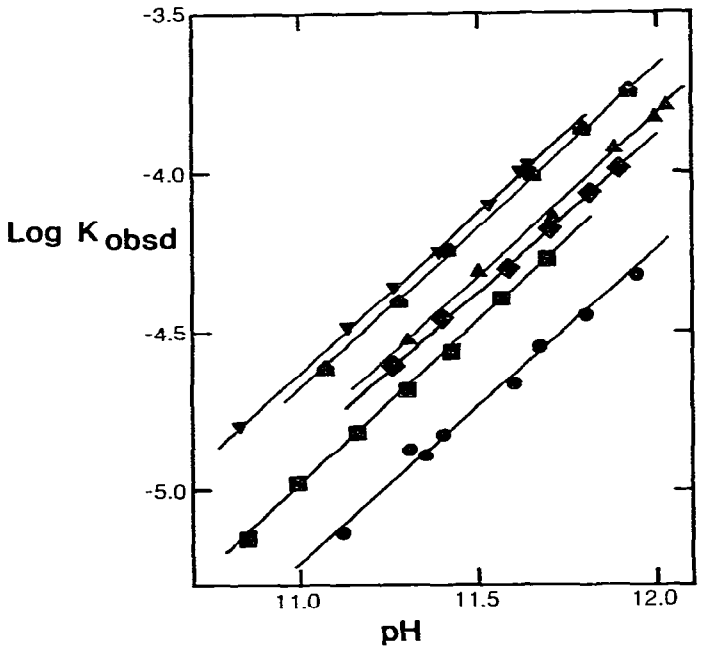


Fig. 2. Representative plots of log k_{obsd} vs. pH for the base-catalyzed hydrolysis of *m*- and *p*-$CH_3OOCC_6H_4Co(D_2H_2)L$, 25.0 ± 0.1°C, ionic strength 1.0 *M*. ●, *para* isomer, L = TFEA; ■, *para* isomer, L = SCN^-; ◆, *para* isomer, L = NO_2^-; ▲, *para* isomer, L = CN^-; ●, *meta* isomer, L = CN^-; ▼, *meta* isomer, L = N_3^-.

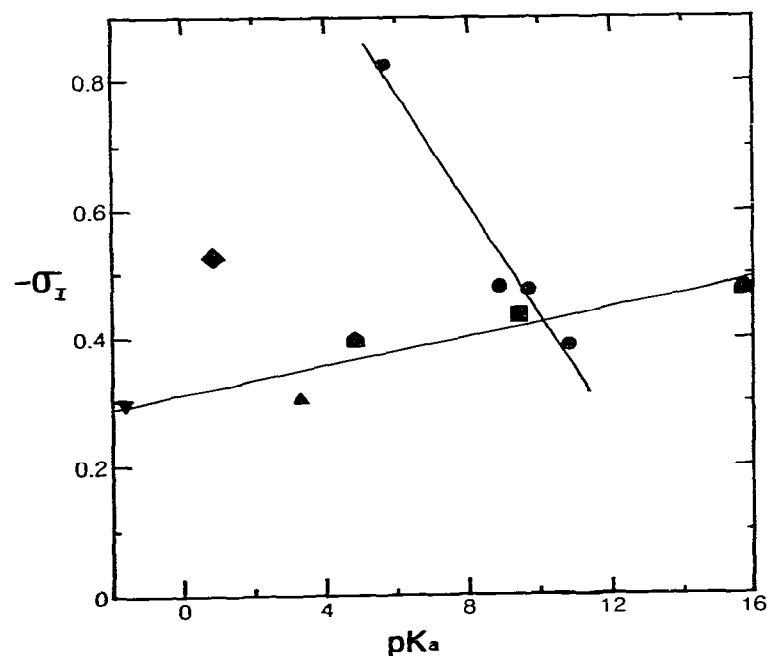


Fig. 3. Plot of $-\sigma_I$ for the -$Co(D_2H_2)L$ substituent vs. the pK_a of the conjugate acid of L. ●, L = RNH_2; ■, CN^-; ◆, SCN^-; ▲, NO_2^-; ●, N_3^-; ▼, OH_2; ■, OH^-. The solid lines are least-squares fits to the values for L = RNH_2 (intercept = 1.30 ± 0.10, slope = −0.0864 ± 0.0115) and for the inorganic ligands (except SCN^-) (intercept = 0.313 ± 0.022, slope = 0.0113 ± 0.0025).

small dependence of $-\sigma_I$ on axial ligand basicity. The exceptional behavior of the cobalt substituent for L = SCN^- may well be due to the formation of both N- and S- liganded complexes with this ligand for which there is NMR evidence for the case of the fluorophenylcobaloximes [16].

The behavior of the cobalt substituents with primary amine axial ligands is strikingly different. Here a sharp decrease in electron donating ability with increasing ligand proton basicity is seen (slope = -0.0864 ± 0.0115). This observation is not only counter to expectations but is in apparent disagreement with the results of Ingraham, et al. [17] who have shown that the ^1H NMR chemical shifts of the cobalt-bound methyl group of $CH_3Co(D_2H_2)L$, for L = 4-substituted pyridines, was directly proportional to the ^1H NMR chemical shifts of *N*-methylpyridinium ions with the same substituents, and that both chemical shifts were directly proportional to the Hammett σ constants for the pyridine substituents. Any attempts to rationalize the observed inverse dependence of $-\sigma_I$ for $-Co(D_2H_2)H_2NR$ on primary amine proton basicity must await confirmation of this strange result. Currently, two experimental systems are under investigation which will provide independently determined values of σ_I for chelated cobalt substituents.

Acknowledgement

This research was supported by the Robert A. Welch Foundation, Houston, Texas, grant number Y-749.

References

1 K.L. Brown, A.W. Awtrey and R. LeGates, J. Amer. Chem. Soc., 100 (1978) 823.
2 S. Ehrenson, R.T.C. Brownlee and R.W. Taft, Prog. Phys. Org. Chem., 10 (1973) 1.
3 H.A.O. Hill, K.G. Morallee, F. Cernivez and G. Pellizer, J. Amer. Chem. Soc., 94 (1972) 277.
4 R.W. Taft, E. Price, I.R. Fox, I.C. Lewis, K.K. Anderson and G.T. Davis, J. Amer. Chem. Soc., 85 (1963) 709, 3146.
5 K.L. Brown and R.G. Kallen, J. Amer. Chem. Soc., 94 (1972) 1894.
6 K.L. Brown, Inorg. Chim. Acta, 37 (1979) L513.
7 K.L. Brown, D. Chernoff, D.J. Kelio and R.G. Kallen, J. Amer. Chem. Soc., 94 (1972) 6697.
8 K.L. Brown and A.W. Awtrey, Inorg. Chem., 17 (1976) 111.
9 W.W. Reenstra and W.P. Jencks, J. Amer. Chem. Soc., 101 (1979) 5780.
10 W.P. Jencks and J. Regenstein in Handbook of Biochemistry, Chemical Rubber Co., Cleveland, 1970, pp. J187—J226.
11 K.L. Brown, D. Lyles, M. Pencovici, R.G. Kallen, J. Amer. Chem. Soc., 97 (1975) 7338.
12 E.A. Guggenheim, Philos. Mag., 2 (1926) 538.
13 R.W. Taft in M.S. Newman (Ed.), Steric Effects in Organic Chemistry, Wiley, New York, 1956, Chapt. 13.
14 Y. Nagai, H. Matsumoto, T. Nakano and H. Watanabe, Bull. Chem. Soc. Jpn., 45 (1972) 2560.
15 F. Basolo and R.G. Pearson, Mechanism of Inorganic Reactions, Wiley, New York, 1968, pp. 167—177.
16 K.L. Brown and L. Lu, unpublished results.
17 J.P. Fox, R. Banninger, R.T. Proffitt and L.L. Ingraham, Inorg. Chem. 11 (1972) 2379.