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Acid Hydrolysis of Salicylaldehydato Chromium(III) Complexes: Substituent Effects on Rate

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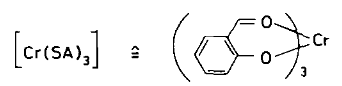
Introduction

It was shown previously [1] that the acid hydrolysis of$[Cr(SA)_3]$ takes place stepwise and can be described as a sequence of 3 pseudo first order



consecutive reactions of decreasing rate:

$$[Cr(SA)_3] \rightarrow [Cr(SA)_2(H_2O)_2]^+ \rightarrow$$
$$\rightarrow [Cr(SA)(H_2O)_4]^{2+} \rightarrow Cr^{3+}_{aq} \qquad (1)$$

The rate law for the hydrolysis of the three species $[Cr(SA)_3]$, $[Cr(SA)_2(H_2O)_2]^+$, and $[Cr(SA)(H_2O)_4]^{2+}$ was found to be first order in complex, with the observed rate constant k_{obs} in each case being composed of an acid independent path and an acid dependent path according to (2) [1, 2]:

$$k_{obs} = k_0 + k'[H^+] \qquad (2)$$

It has been suggested [1b, 2] that the acid dependent path results from the addition of a proton to a lone electron pair of the phenolic oxygen (fast equilibrium, K_1) followed by the rate determining rupture of the Cr–O bond (k_1) and loss of the bidentate ligand. For the condition $K_1[H^+] \ll 1$ this interpretation leads to (3):

$$k_{obs} = k_0 + k_1K_1[H^+] \qquad (3)$$

The present study deals with the effect of substituents X^5 in 5-position of the salicylaldehyde ring on the rate of the acid hydrolysis of the cationic species *I* = $[Cr(SA\text{-}X^5)_2(H_2O)_2]^+$ and *II* = $[Cr(SA\text{-}X^5)(H_2O)_4]^{2+}$. It was undertaken (i) to prove the expected dependence of the parameter k_1K_1 on the electron density at the phenolic oxygen as determined by the *para*-substituent X^5 (= H, Br, NO_2, Me, MeO) and (ii) to correlate k_1K_1 with Hammett's substituent parameters σ [3] on the basis of LFE relationships.

Experimental

The ligands salicylaldehyde (Merck) and 5-methoxy-salicylaldehyde (EGA-Chemie) were used without further purification. 5-Bromosalicylaldehyde [4], 5-nitro-salicylaldehyde [5], and 5-methylsalicylaldehyde [6] were prepared by methods described in the literature. The complexes $[Cr(SA\text{-}X^5)_3]$ were prepared according to a procedure described elsewhere [2]. Their analytical data and melting points are compiled in Table I.

The cationic complexes *I* = $[Cr(SA\text{-}X^5)_2(H_2O)_2]^+$ and *II* = $[Cr(SA\text{-}X^5)(H_2O)_4]^{2+}$ were separated by cation exchange chromatography as described previously [2].

The acid hydrolysis of *I* and *II* was studied in aqueous solution with $[HClO_4]$ = 0.5–2 *N*, I = 2 *M* $[NaClO_4)$, T = 41 °C and with $[HClO_4]$ = 0.1–3 *N*, I = 3 *M* $(NaClO_4)$, T = 80 °C, respectively. The spectrophotometric measurements and the determination of k_{obs}, k_0, and k_1K_1 have been described [1, 2].

TABLE I. Analytical Data for the Complexes $[Cr(SA\text{-}X^5)_3]$.

X^5	M.p. (°C)	C(%)		H(%)		N(%)		Cr(%)	
		calc.	found	calc.	found	calc.	found	calc.	found
H	225–228	60.73	60.38	3.64	3.61	–	–	12.52	12.45
MeO	178–180	57.03	56.61	4.19	4.24	–	–	10.29	9.44
Me	255	63.01	63.92	4.63	4.71	–	–	11.36	10.77
Br	288–290	38.68	37.93	1.85	1.79	–	–	7.97	7.94
NO_2	210 (dec.)	45.83	45.74	2.20	2.30	7.63	7.53	9.45	not det.

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TABLE II. Parameter k_1K_1 for the Acid Dependent Path of the Acid Hydrolysis of *I* and *II*.

X^5	$k_1K_1 \times 10^4$ (s^{-1}) for I^a	$k_1K_1 \times 10^5$ (s^{-1}) for II^b
MeO	6.08 ± 0.75	10.30 ± 0.08
Me	4.57 ± 0.90	8.10 ± 0.07
H	5.52 ± 0.39	6.83 ± 0.14
Br	4.69 ± 0.46	5.97 ± 0.18
NO_2	1.53 ± 0.08	1.78 ± 0.02

^{a}T = 41 °C, I = 2 *M*. ^{b}T = 80 °C, I = 3 *M*.

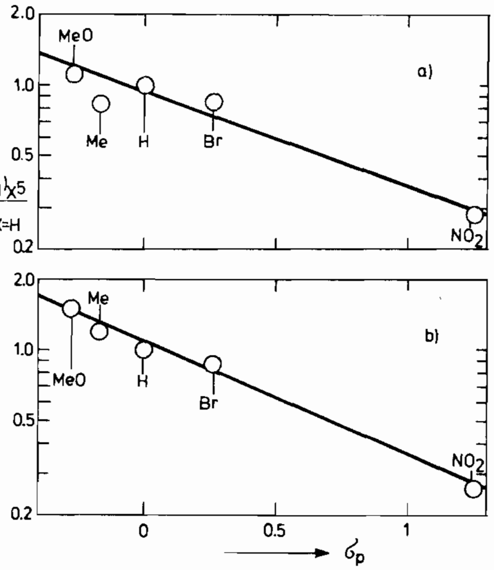

Fig. 1. Hammett plot for the parameter k_1K_1 on the basis of the substituent constant σ_p; (a) refers to $I = [Cr(SA\text{-}X^5)_2(H_2O)_2]^+$ and b) to $II = [Cr(SA\text{-}X^5)(H_2O)_4]^{2+}$; the value of $\sigma_p = 1.25$ for $X^5 = NO_2$ refers to σ_p^- [3]).

Results and Discussion

One would expect that there are substituent effects on k_0 as well as on k_1K_1. Rate constant k_0, however, is determined by extrapolation and its relatively large limits of error do not allow to claim any substituent effects convincingly. Table II summarizes the values found for k_1K_1 upon acid hydrolysis of *I* and *II* as a function of substituent X^5. The average limits of error obtained for k_1K_1 in the case of *I* are approx. ±11% as compared to approx. 1.6% only in the case of *II*. This relatively large difference in error is due to the fact that k_{obs} for *I* has to be determined by a subtraction procedure whereas k_{obs} for *II* is obtained directly ($II \rightarrow Cr^{3+}_{aq}$ is the last step in (1)).

As can be seen from Table II there is a small but distinct dependence of k_1K_1 on the nature of X^5. It follows from a plot (see Fig. 1) of the logarithm of $(k_1K_1)_{X^5}/(k_1K_1)_{X^5} = H$ *versus* Hammett's substituent constant σ_p [3] that the relationship is linear in both cases (the correlation coefficients are 0.959 for *I* and 0.995 for *II*). The reaction constant ρ is negative and one finds $\rho = (-0.38 \pm 0.13)$ for *I* and $\rho = (-0.48 \pm 0.03)$ for *II*.

The result of the reaction constant ρ being negative and the fact that ρ_I and ρ_{II} agree within the limits or error support the mechanistic interpretation for the acid dependent part of the hydrolysis of *I* and *II* as presented earlier [1b, 2]. The protonation of the complex takes place at the phenolic oxygen and not at the carbonyl oxygen of the salicylaldehydato ligand since plotting of the data *versus* Hammett's substituent constant σ_m (instead of σ_p) does not yield linear relationships (the correlation coefficients are 0.836 for *I* and 0.876 for *II*).

The higher the electron density at the phenolic oxygen is (see X^5 = MeO, Me, *e.g.*) the faster the reaction becomes. This is in agreement with the interpretation given earlier: increased electron density leads to an increase in K_1, the protonation constant and, hence, to a correspondingly higher concentration of the protonated complex which is believed to be the intermediate for the acid dependent path (the direct proportionality between K_1 and the concentration of the protonated complex is valid as long as the condition $K_1[H^+] \ll 1$ is fulfilled). It is an open question as to what extent there are substituent effects on k_1, the rate constant for the rupture of the Cr–O bond.

Acknowledgements

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