Reactivity Patterns in the Base Hydrolysis of Coordinated Aromatic Nitriles

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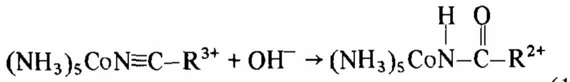
Received May 11, 1982

Two new aromatic organonitrile complexes of pentaamminecobalt(III) have been synthesized, the complexes of 2- and 4-nitrobenzonitrile. The kinetics of their base hydrolysis to coordinated carboxamides have been measured and found to follow a simple second order rate law with rate constants of 180 ± 4 M^{-1} s^{-1} *and 510 ± 90* M^{-1} s^{-1} *at 25 °C and ionic strength 1.0 for the* ortho *and* para *isomers respectively. Rate constants for the hydrolysis of eleven coordinated substituted aromatic nitriles have been found to follow a Hammett type correlation where* $\log k = 1.93\sigma + 1.30$ *at 25 °C and ionic strength 1. Carbon-13 NMR studies indicate that the variation in the slope of these Hammett plots for free and coordinated nitrile hydrolysis rates is a transition state effect rather than a ground state phenomenon.*

Introduction

Coordination compounds with organonitrile ligands are of considerable interest due to the increased reactivity imparted to the coordinated nitrile function and the synthetic versatility this creates [1–11]. The kinetics of base hydrolysis of a number of organonitriles coordinated to pentaamminecobalt(III) have been reported and a rate enhancement of 2 X 10^6 is seen for the nitrile-to-amide conversion (reaction 1 below) upon coordination [9, 10, 12–14]. An early investigation of this reaction utilizing substituted benzonitriles reported a linear free energy relationship (LFER) for 3 nitrile base hydrolysis rates with Hammett σ substituent constants [12]. However, a later study noted an error in one of the σ values which, when corrected, negated the linear correlation [13]. We report here additional base hydrolysis kinetic studies with substituted benzonitriles and the successful application of the Hammett equation. The mechanistic implications of the Hammett equation has, in turn, lead to an NMR study of coordinated aromatic nitriles.



$$(NH_3)_5CoN{\equiv}C{-}R^{3+} + OH^- \rightarrow (NH_3)_5Co\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}R^{2+} \quad (1)$$

Both 2- and 4-nitrobenzonitrile were chosen as our ligand systems for this study for several reasons. First, the σ-*para* value of the nitro group is known quite accurately [15] and lies outside the range of values for substituents employed in previous studies [12, 13]. The 2-nitrobenzonitrile ligand was chosen because *ortho* group participation and unusual reactivity patterns have been reported for coordinated *ortho* substituted benzonitriles [6, 9]. The *ortho* nitro group appeared to be a promising candidate for such effects since the free ligand is known to react with hydroxide in aqueous ethanol to yield benzoic acid and N_2 [16]. The reaction pathway to these products apparently proceeds *via* the stepwise intermediate formation of 2-nitrobenzamide [16], 2-nitrosobenzamide [17] and indazol-3-one [18]. We were interested in determining if the relatively mild conditions for base hydrolysis employed in this study would result in the formation of any of these products beyond the expected 2-nitrobenzamido complex.

Experimental

Materials

All chemicals utilized in this study were reagent grade unless noted otherwise below. The substituted benzonitriles were purchased from Aldrich Chemical Co., Inc. and used as received. Nitrile complexes were prepared by general published procedures for organonitrile complexes of pentaamminecobalt(III) [19, 20]. Solutions were prepared with house-supplied distilled water which was passed through a mixed-bed ion exchange resin before use. Sodium perchlorate solutions, prepared from the anhydrous salt (G. F. Smith Chemical Co.), were standardized as described previously [13]. Standard sodium hydroxide solutions were prepared by serial dilution of stock solutions made from analytical

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concentrates purchased from J. T. Baker Chemical Co.

Physical Measurements

Spectroscopic data were obtained on the following instruments: infrared (KI pellets, 4000–200 cm^{-1}), Perkin-Elmer Model 599; ^1H NMR (in Me_2SO-d_6 *vs.* internal Me_4Si), Hitachi Perkin-Elmer Model R-600 60 MHz FT NMR; ultraviolet–visible, Cary 17. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Ga. ^{13}C NMR studies were performed on a Varian FT80A multinuclear instrument in Me_2SO-d_6 solutions, using the center of the Me_2SO multiplet (39.5 ppm *vs.* Me_4Si) as the shift reference.

Kinetic Studies

The kinetics of base hydrolysis were followed at 370 nm for both complexes (appearance of product). Kinetic measurements were made on a stopped flow-temperature jump apparatus (SF/TJ) operating in the SF mode. The SF/TJ was constructed by Dr. John Simplicio based upon the design of Erman and Hammes [21] and was equipped with a Forma Scientific Model 2095 refrigerated–heating water bath and circulator which controlled the temperature to better than ±0.1 °C. Kinetic studies were performed under pseudofirst order conditions using a 10 fold or greater excess of hydroxide over complex. Complex concentrations were 2.5×10^{-4} *M* and sodium hydroxide concentrations ranged between 2.5×10^{-3} *M* and 2.5×10^{-2} *M*. Ionic strength was controlled to 1.00 *M* with sodium perchlorate. Rate constants were extracted from absorbance *vs.* time traces as described previously [13] and at least three traces were obtained at each concentrations of hydroxide employed.

Characterization of Complexes

(4-nitrobenzonitrile)pentaamminecobalt(III) perchlorate, $[(NH_3)_5Co(4\text{-}NO_2C_6H_4CN)](ClO_4)_3\cdot 2H_2O$

Typical yields of this complex by the procedure described in ref. 19 were 45%. Water content of the solid material was variable from one preparation to another and did not seem to be a function of either drying time or desiccant. The complex was normally stored *in vacuo* over anhydrous calcium chloride. A typical analysis follows. *Anal.* Calcd. for $CoC_7H_{19}N_7O_{14}Cl_3\cdot 2H_2O$: C, 13.41; H, 3.86; N, 15.65. Found: C, 13.30; H, 3.76; N, 15.50. IR: ν(CN), 2310 cm^{-1} (complex); 2240 cm^{-1} (free ligand). UV–visible λ_{max} (0.1 *M* $HClO_4$): 465 nm (ϵ 81). ^1H NMR: δ 3.52 (*cis* NH_3's); 3.97 (*trans* NH_3); 8.22, 8.37, 8.55, 8.70 (aromatics).

(2-nitrobenzonitrile)pentaamminecobalt(III) perchlorate, $[(NH_3)_5Co(2\text{-}NO_2C_6H_4CN)](ClO_4)_3\cdot 3.5H_2O$

As with the *para* isomer above, water content varied from one preparation to another. Typical yields of 40% were obtained. *Anal.* Calcd for $CoC_7H_{19}N_7O_{14}Cl_3\cdot 3.5H_2O$: C, 12.87; H, 3.97; N, 15.01. Found: C, 12.86; H, 4.16; N, 15.00. IR: ν(CN), 2315 cm^{-1} (complex): 2240 cm^{-1} (free ligand). UV–visible λ_{max} (0.1 *M* $HClO_4$): 464 nm (ϵ 69). ^1H NMR: δ 3.59 (*cis* NH_3's); 3.98 (*trans* NH_3); (8.28 aromatics, center of multiplet).

(4-nitrocarboxamidobenzene) pentaamminecobalt(III) perchlorate

This complex and its *ortho* isomer below analyzed as a mixture of protonated (3+) and deprotonated (2+) salts as has been observed with other amido complexes [10, 14, 19]. However, salts of each isomer gave satisfactory C/N ratios. IR: $\nu(NO_2)$, 1520 (asym.); 1350 (sym.). UV–visible (0.1 *M* NaOH): 480 nm (ϵ 89). ^1H NMR: δ 3.43 (*cis* and *trans* NH_3's); 5.79 (amido H); 7.92, 8.06, 8.26, 8.41 (aromatics). C/N calcd: 0.858. Found: 0.860.

(2-nitrocarboxamidobenzene) pentaamminecobalt(III) perchlorate

IR: $\nu(NO_2)$, 1530 (asym.); 1355 (sym.). UV–visible (0.1 *M* NaOH): 480 nm (ϵ 69). ^1H NMR: δ 3.39 (*cis* and *trans* HN_3's); 5.95 (amido H); 7.83 (aromatics, center of multiplet). C/N calcd: 0.858. Found: 0.866.

Purity of the perchlorate salts of the other nitrile complexes used in the ^{13}C NMR studies was verified by visible spectroscopy using published molar absorptivities [12, 13, 19].

Results and Discussion

The spectral characteristics of the nitrobenzonitrile complexes verify coordination to Co(III) *via* the nitrile group nitrogen. Among these are the frequencies for the nitrile stretches at *ca.* 2300 cm^{-1} for the complexes *vs. ca.* 2240 cm^{-1} for the free ligands, the positions and extinction coefficients of the visible peak maxima, and the shifts of these maxima upon addition of dilute sodium hydroxide [19]. A nitrobenzonitrile complex of pentaamminecobalt(III) has previously been reported [22] but the particular isomer (2, 3 or 4 nitro) was not specified. However, the visible spectral parameters agree closely with our 4-nitrobenzonitrile complex.

The products of the base hydrolysis reaction are formulated as the carboxamidopentaamminecobalt(III) complexes based upon spectral parameters. Foremost among these are the disappearance of the nitrile group stretching frequency peak in the infra-

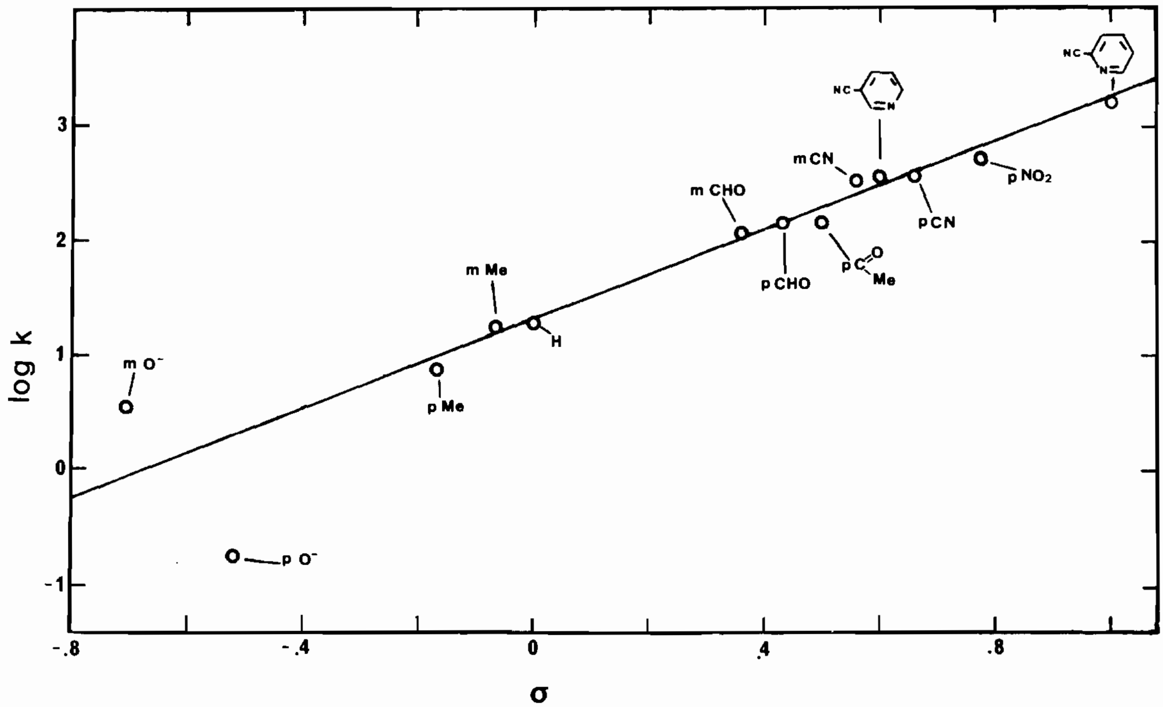

Fig. 1. Hammett plot of base hydrolysis rate constants for aromatic nitriles coordinated to the pentaamminecobalt(III) moiety at 25 °C and ionic strength 1.0.

TABLE I. Summary of Kinetic Data for Coordinated Nitrile Hydrolysis.

Nitrile	T, °C	k, M^{-1} s^{-1} [a]
2-nitrobenzonitrile	14.4	96
	23.9	172
	33.3	283
4-nitrobenzonitrile	23.9	500
	33.3	758
	46.7	1820

[a] Ionic strength, 1.0 ($NaClO_4$).

red, the positions and extinction coefficients of the visible peak maxima, and the appearance of broad carboxamido nitrogen bound proton resonances in the nmr [19]. In particular, the 2-nitrobenzonitrile complex product of hydroxide attack is formulated as the 2-nitrocarboxamidobenzene complex rather than any of the previously described products (see Introduction) associated with base attack on the free ligand. This is indicated not only because of the spectral characteristics described above, but also because of the retention of the nitro group asymmetric and symmetric stretches in the infrared, the carbonyl stretch at 1665 cm^{-1} due to the carboxamido function, and the elemental analysis (see Experimental).

Kinetic studies of the nitrile-to-amide base hydrolysis reaction verify a rate law of the form shown in equation 1.

$$-\frac{d[\text{Co(III) nitrile complex}]}{dt} = k[\text{Co(III)nitrile}]\,[OH^-] \qquad (1)$$

Table I summarizes the results of these kinetic investigations at several temperatures. Eyring plots of the rate constants yield $\Delta H^{\ddagger}$ = 9.4 ± 0.3 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −16.6 ± 0.9 cal deg^{-1} mol^{-1} for the 2-nitrobenzonitrile complex with a rate constant at 25.0 °C of 180 ± 4 M^{-1} s^{-1}. The 4-nitrobenzonitrile complex hydrolysis reaction is characterized by $\Delta H^{\ddagger}$ = 10.2 ± 1.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −12 ± 4 cal deg^{-1} mol^{-1} and k at 25.0 °C of 510 ± 90 M^{-1} s^{-1}.

A Hammett plot of rates of Co(III) coordinated aromatic nitrile hydrolysis rates is presented in Fig. 1. With the exception of the two phenoxybenzonitrile data points, an 'excellent' [23] linear correlation is obtained for the remaining 11 points, satisfying equation 2. The correlation coefficient for the least squares line defined by these 11 points is 0.993. We feel that elimination of the 2 points for the phenoxy substituents is justified considering the specific reservations expressed by Jaffe concerning their σ values [24]. All σ values used in the plot

TABLE II. Nitrile Carbon ^{13}C Chemical Shifts of 4-Substituted Benzonitriles and Their Pentaamminecobalt(III) Complexes.

p-Substituent	δ (free ligand)^a	δ (complex)^a	$\Delta\delta$
–H	118.6	129.5	10.9
$-CH_3$	118.8	129.7	10.9
–CHO	117.9	128.4	10.5
$-COCH_3$	117.9	128.6	10.7
–C≡N	117.5	128.0	10.5
$-NO_2$	117.2	127.8	10.6

^{a}Shift in ppm from Me_4Si (δ = 0), solvent Me_2SO-d_6.

(Fig. 1) were taken from references 15, 23 and 25. Rate constants came from references 12, 13, 26 and this work.

$$\log k = 1.93\sigma + 1.30 \qquad (2)$$

The slope, ρ = 1.93, of this plot is notably smaller than that obtained for uncoordinated nitriles where ρ = 2.31 [27], which is consistent with a stabilized transition state due to charge dispersion of the imino anion formed upon attack of hydroxide ion at the nitrile carbon as previously proposed for reaction 1 [13]. However, the reduced influence of ring substituents on the nitrile hydrolysis rate in the complexes could also be due, in whole or in part, to a reduction in effectiveness of these ring substituents at transmitting electronic effects in the reactant nitrile complexes.

In order to explore the ground state influences of ring substituents on aromatic nitrile complexes of pentaamminecobalt(III), we have investigated the ^{13}C NMR spectra of several nitrile complexes. In particular, we have concentrated on the chemical shifts induced in the nitrile group carbon upon coordination since this carbon is the site of attack by hydroxide ion for the base hydrolysis reaction. The results of this study are summarized in Table II.

We see from Table II that the effect of coordination on the nitrile carbon chemical shift is constant within the anticipated accuracy of our measurements, $\Delta\delta$ = 10.7 ± 0.2 ppm. Thus, the inductive effect of the pentaamminecobalt(III) unit on the nitrile carbon is constant for a variety of substituents and any Hammett plot ρ variations between bound and free aromatic nitriles is a transition state phenomenon rather than a ground state effect.

The *para*/*ortho* rate ratio of 2.8 for the nitrobenzonitrile systems seems reasonable if one assumes a degree of steric blocking of hydroxide attack at the nitrile carbon by an *ortho* nitro group.

TABLE III. Summary of Coordinated *ortho vs. para* Substituted Benzonitrile Base Hydrolysis Rate Constants.^{a}

Substituent	k_{ortho}	k_{para}	k_{ortho}/k_{para}	References
$-CH_3$	3.6	7.8	2.2	26, 27
–CN	1050	369	0.35	9, 13
$-NO_2$	180	510	2.8	this work

^{a}25 °C, ionic strength 1.0 ($NaClO_4$).

Such steric hindrance has been noted previously for the hydrolysis of tolunitriles coordinated to the pentaamminerhodium(III) moiety [27]. However, we would note that neighboring group participation can completely overwhelm any steric effects as reported previously for the *ortho* carboxamide function [9]. If we employ equation 2 to calculate a rate constant for a 4-cyanobenzamide complex hydrolysis reaction, we obtain a *para*/*ortho* ratio of 5×10^{-5} for the carboxamide substituent.

In the absence of an anchimeric assistance, those effects normally associated with *ortho* group effects [28] seem to account, at least qualitatively, for rate trends. The available *ortho* and *para* rate comparisons are presented in Table III. The trends in steric blocking potential for these three Table III substituents in the *ortho* position are $CN < CH_3 \ll NO_2$ while *ortho* inductive effects vary as $CH_3 \ll CN \sim NO_2$ [28]. Thus, the *ortho* nitro group introduces a large rate retardation due to steric blocking (*vs.* a *para* nitro group), but compensates for this somewhat by a positive inductive effect. The inductive effect is similar for an *ortho* cyano group, but the steric effect is very much smaller. Hence, we see that the 1,2-dicyanobenzene complex is hydrolyzed faster than the 1,4-dicyanobenzene complex. An *ortho* methyl group introduces a moderate rate retardation due to steric effects, but an almost insignificant inductive effect leading to an *ortho* rate approximately half that of the *para* isomer.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. R. L. is an American Chemical Society-Petroleum Research Fund Fellow. W. R. E. acknowledges the receipt of a Robert E. Maytag fellowship administered by The University of Miami. The Camille and Henry Dreyfus Foundation is acknowledged for a grant enabling the purchase of the Varian FT80A NMR. The authors acknowledge helpful discussions with Drs. Robert E. Gawley and Keith M. Wellman concerning Hammett plots.

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