on a Hitachi EPS-2U spectrometer, using 2-mm and 0.5-mm quartz cells. A typical spectrum is given in Figure 2. We see there that the spectrum of the "complex" shows no absorption peak at 280 $m\mu$, as is observed characteristic of the complex in *n*-heptane solutions;[18] instead we see the double peak (absorption maxima at 363 and 295 $m\mu$) characteristic of the spectrum of I_3^-.[23] In fact, it seems quite obvious from Figure 2 that the "complex" in dioxane solution has all the iodine present as I_3^-, with practically none present as I_2 complex.[24]

We conclude, therefore, that our studies of the dipole moments of alkylamine complexes of I_2 in dioxane, together with the study of the spectrum, indicate that the predominant species in this solution is the ion pair, not the complex. This possibility has been recognized earlier;[9,22] our studies simply verify it. We do not question the existence of the trialkylamine–iodine complexes in *n*-heptane solution, but in the slightly more polar dioxane solution it is certainly not the dominant species. (It is possible that traces of water cause some reaction to form the ion pairs.) Thus, the theoretically important value of μ for these complexes remains elusive. It is our opinion that this quantity will be quite hard to obtain accurately, since the complexes do not have sufficient solubility in nonpolar solvents such as *n*-heptane, and the ion-pair formation in slightly polar solvents will complicate any studies there. Our question, then, is: "What is the dipole moment for trialkylamine–iodine complexes?"[25]

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[23] A. I. Popov and R. F. Swensen, *J. Am. Chem. Soc.*, 77, 3724 (1955).

[24] This conclusion has been reinforced strongly by a much more complete spectroscopic study of the nature of the species present in solutions of triethylamine and I_2 in dioxane, carried out in this laboratory by Dr. H. D. Bist (to be published). The positive ion has not been established with certainty, but Et_3NH^+ or Et_4N^+ seem possible. It would be desirable, certainly, to attempt to repeat these measurements under more rigorously anhydrous conditions in order to determine which ion is present. However, we have made here normally rigorous attempts to reach these anhydrous conditions.

[25] Professor S. Nagakura has informed us in a private communication that he has answered this question for complexes of I_2 with mono- and dialkylamines (but not for trialkylamines) by a carefully conducted study, which will be published shortly; *e.g.*, he finds for diethylamine–iodine, μ = 7.0 (in dioxane) or 6.2 D. (in benzene). For isopropylamine–iodine, μ = 7.4 (in dioxane) and 6.2 D. (in benzene).

The Kinetics of Hydrolysis of the Dinitrobis(ethylenediamine)cobalt(III) Ion in Various Concentrated Acid Solutions

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Abstract: Hydrolysis rates of *trans*-$[Co(en)_2(NO_2)_2]^+$ were obtained as a function of acid concentration in perchloric, hydrochloric, hydrobromic, sulfuric, and nitric acids at 25°. Values of the parameters in Bunnett's equations are consistent with attack of water on the protonated complex as the rate-determining step. In all acids except perchloric the rate-determining reaction is followed by anation of the nitroaquo intermediate. Arrhenius plots for perchloric acid were linear, with an activation energy of 23.6 ± 0.8 kcal and an activation entropy of 2.9 ± 2.3 eu at the 95% confidence level. For the other acids, curvature increasing with acid concentration and temperature was noted in the Arrhenius plots. This behavior is consistent with two consecutive reactions, the second having the lower activation energy.

Interest in the reactivity of coordination compounds has been so great that several reviews have been written[3] since the classic monograph on the subject.[4] In the hydrolysis reaction, $[Co(en)_2(X)(Y)]^+ + H_2O \rightarrow [Co(en)_2(X)(H_2O)]^{2+} + Y^-$, the nature of the orienting ligand "X" in determining the mechanism of reaction has been emphasized.[3e] Electron-withdrawing groups such as nitrite assist reaction by an S_N2 path, while electron-releasing groups promote S_N1 reactions. At the time this investigation was begun, little information was available on the role of the replaced ligand "Y" except when Y is a halide. Study of the hydrolysis of the dinitro compounds was initiated to show the effect of Y on the rate and to attempt to formulate a mechanism for the hydrolysis.

Since these dinitro complexes are very unreactive, study of the hydrolysis reaction at high acid concen-

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[1] Based on a dissertation by D. Lambert in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Polytechnic Institute, 1965.

[2] To whom requests for reprints should be addressed.

[3] (a) F. Basolo in "Survey of Progress in Chemistry," Vol. 2, A. F. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, p 1; (b) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, 3, 1 (1961); (c) C. K. Ingold, "Substitution at Elements Other Than Carbon," Weizmann Science Press, Jerusalem, 1959, Chapter 1; (d) D. R. Stranks, in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers Inc., New York, N. Y., 1960, p 78; (e) M. L. Tobe, *Sci. Progr.*, 48, 483 (1960); (f) R. G. Wilkins, *Quart. Rev.* (London), 16, 316 (1962).

[4] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

trations was possible. For most complexes of the type $[Co(en)_2(X)(Y)]^+$ the rate of hydrolysis is independent of acid concentration provided enough acid has been added to suppress base hydrolysis.[2a] When ligands which are anions of weak acids such as fluoride[5] or azide[6] are present, the simple rate law

$$k_1 = k_0 + k_H(H^+)$$

has been found in low concentrations of acid; k_1 is the first-order rate constant, k_0 and k_H are constants, and (H^+) is the concentration of acid. In contrast, the first-order rate constant for hydrolysis of the dinitro complexes is a complicated function of acid concentration.

While this work was in progress, Staples[7] reported rates of hydrolysis of the $[Co(en)_2(NO_2)_2]^+$ complexes in 3.5 *M* perchloric acid at 25°.

Experimental Section

Preparation of Compounds. All chemicals used were reagent grade. Complexes were dried overnight at 55° *in vacuo* over P_2O_5 before analysis but were used for rate studies after recrystallizing, washing with ethanol, then ether, and drying in air. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Equivalent weights were determined by pipetting a standard solution of complex onto Dowex 50W-X12 ion-exchange resin in the acid form, then titrating the effluent with standardized sodium hydroxide as a function of time. The volume of base was found by extrapolating the two linear portions of the curve of milliliters of base *vs.* time. Results accurate to 0.5% were obtained by this method.

A polarographic study of the *trans* complex gave half-wave potentials which agreed with reported values.[8]

trans-Dinitrobis(ethylenediamine)cobalt(III) nitrate was prepared by the method of Holtzclaw, Sheetz, and McCarty,[9] recrystallized three times from water, washed with ethanol, then ether, and air dried. Extinction coefficients of the product were within 0.1 log unit or better of published values.[10] *Anal.* Calcd for $CoC_4H_{16}N_7O_7$: Co, 17.7; C, 14.4; H, 4.86; N, 29.4; equiv wt, 333. Found: Co, 17.4; C, 14.2; H, 4.60; N, 29.1; equiv wt, 333.

Kinetic Measurements. All kinetic measurements were made spectrophotometrically. The appropriate volume of acid which had been standardized against standard sodium hydroxide was added to the 50- or 100-ml volumetric flasks used as reaction vessels, some water was added, and the flasks were placed in the well-insulated constant-temperature bath; temperatures were accurate to ±0.1°. After 0.5 hr, a solution of complex was added, the flasks were brought to volume with water maintained at the bath temperature, the mixture was shaken, and a portion of the contents of the flask was transferred to the cell of a Beckman DU spectrophotometer equipped with a dual thermospacer set.

Rate constants were usually determined by multiplying the slope of the log $(D - D_\infty)$ *vs.* time plot by 2.303; D is the absorbance of time t and D_∞ is the infinite time absorbance. D_∞ for the slowest reactions was obtained either by heating the solution or by using the infinite time reading from a higher acid concentration. This procedure was checked by using the method of Guggenheim[11] in some cases. All rate constants were reproducible to better than 5%; when sufficient measurements could be made, first-order plots were linear to at least 75% reaction.

During the course of this work the concentration of complex was varied over a wide range with no effect on the first-order rate constant. For example, in 5.890 *M* perchloric acid at 40° the concentration of *trans* complex was varied from 5×10^{-5} to 5×10^{-3} *M*. In units of 10^3 sec^{-1} the rate constants are 2.36 (250); 2.39 (350), 2.45 (400), and 2.35 (440), where the wavelength in millimicrons is given in parentheses.

For very fast reactions, solid complex was added directly to the acid solution in the spectrophotometric cell, the cell was inverted, and readings were initiated when solution was complete. Since the rate constant was demonstrated to be independent of wavelength, wavelengths were used to give a large difference in absorbance between reactant and product. The products were essentially the *trans* complexes: $HClO_4$, *trans*-nitroaquo; HCl, *trans*-nitrochloro; HBr, *trans*-nitrobromo; HNO_3, *trans*-nitronitrate. For sulfuric acid, the identification of the product is uncertain.

Sources of Water Activity Data. The water activities were read from plots of the data given by Bunnett[12a] for perchloric, sulfuric, and hydrochloric acids below 10 *M*. For hydrochloric acid concentrations above 10 *M*, the equations of Akerlof and Teare[13] were solved. Davis and DeBruin's recent results[14] were used for nitric acid. A graph of H_0 *vs.* activity of water was constructed from the H_0 values listed by Paul and Long;[15] all acids fell on the same curve as was first noticed by Wyatt.[16] The activity of water in hydrobromic acid was read from the graph using tabulated H_0 values[15] for this acid; this procedure is justified by the work of Hogfeldt.[17]

Results

Hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]^+$ in Five Acids at 25°. First-order rate constants were obtained as a function of acid concentration in perchloric, sulfuric, hydrochloric, hydrobromic, and nitric acids at 25°. These rate constants are given in detail elsewhere.[18]

Bunnett[12a] proposed that acid hydrolyses of organic compounds could be described by the equations

$$\log k_1 + H_0 = w \log a_w + C \quad (1)$$

$$\log k_1 - \log (H^+) = w^* \log a_w + D \quad (2)$$

where k_1 is the first-order rate constant at a given acid concentration, H_0 is the value of the Hammett acidity function for that concentration, and a_w is the activity of water in that solution. The parameters w and w^* are the slopes, C and D are the intercepts, of plots of the left side of eq 1 or eq 2, respectively, against log a_w. When protonation is incomplete, the quantity log $(h_0/h_0 + K_a)$, where K_a is the acid dissociation constant of the substrate, must be subtracted from the left side of either equation. At low acid concentrations, observed differences in rate among the acids are due to this factor. In all acids, the data at low acid concentrations were described using approximately the same value for K_a.

Plots of eq 1, which were linear, gave a value of w of +2.3 in all acids with K_a = 5–10. In Figure 1 is shown a graph of the data according to eq 2. Values of w^* determined by the method of least squares[19] are listed in Table I; the uncertainties quoted are 95% confidence intervals.

Examination of Table I shows that w^* values are the same within experimental error for all acids except nitric; the values of the intercept, D, are also the same.

Activation Energy Data for Hydrolysis of *trans*-$[(CO(en)_2(NO_2)_2]^+$ in Five Acids. The first-order rate

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[5] F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4883 (1956).

[6] P. J. Staples, *J. Chem. Soc.*, 745 (1964).

[7] P. J. Staples, *ibid.*, 2534 (1964).

[8] J. G. Mason and Richard L. White, *J. Electroanal. Chem.*, **8**, 454 (1964).

[9] H. F. Holtzclaw, D. P. Sheetz, and B. D. McCarty, *Inorg. Syn.*, **4**, 177 (1953).

[10] F. Basolo, *J. Am. Chem. Soc.*, 72, 4393 (1950).

[11] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

[12] (a) J. F. Bunnett, *J. Am. Chem. Soc.*, 83, 4956 (1961); (b) *ibid.*, **83**, 4958 (1961); (c) *ibid.*, **83**, 4973 (1961); (d) *ibid.*, 83, 4983 (1961).

[13] G. Akerlof and J. W. Teare, *ibid.*, **59**, 1855 (1937).

[14] W. Davis, Jr., and H. J. DeBruin, *J. Inorg. Nucl. Chem.*, **26**, 1069 (1964).

[15] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

[16] R. A. H. Wyatt, *Discussions Faraday Soc.*, **24**, 162 (1957).

[17] K. Hogfeldt, *Acta Chem. Scand.*, **14**, 1627 (1960).

[18] D. G. Lambert, Ph.D. Thesis, Virginia Polytechnic Institute, 1965.

[19] B. Ostle, "Statistics in Research," The Iowa State University Press, Ames, Iowa, 1963, p 163.

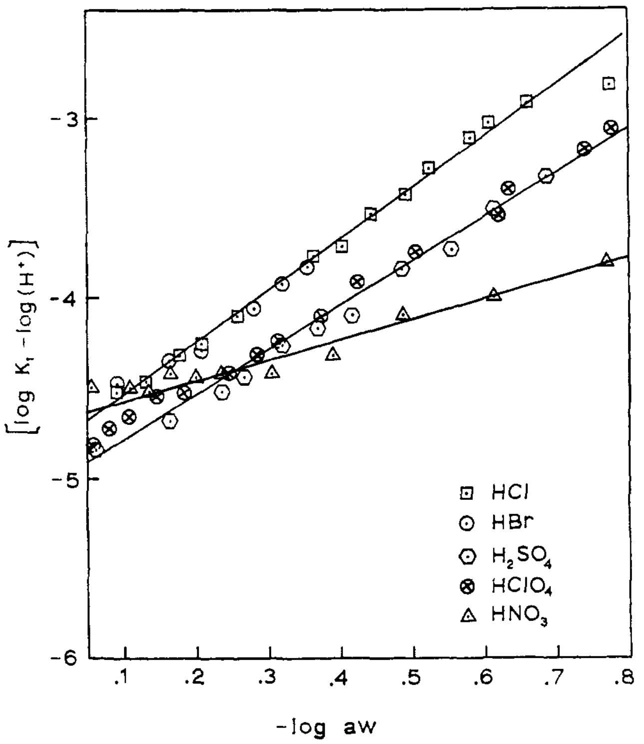

Figure 1. Hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]^+$ in five acids at 25°; log k_1 − log (H^+) *vs.* log a_w.

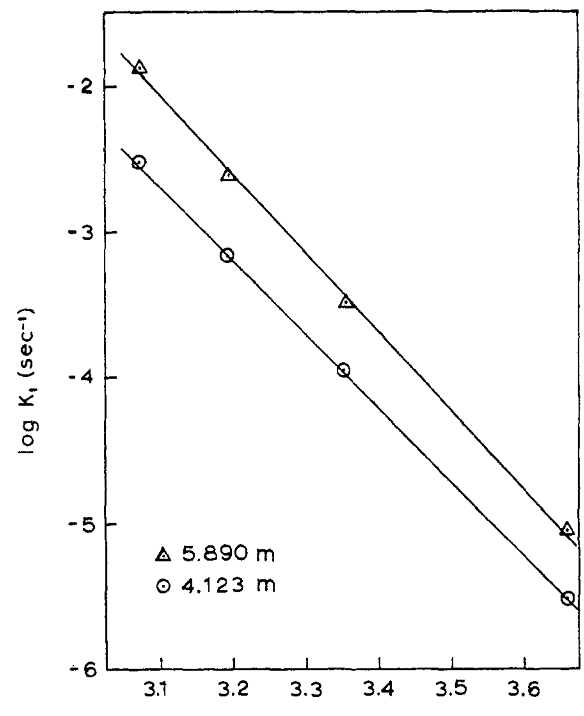

Figure 2. Arrhenius plot for the hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]^+$ in perchloric acid.

constant was determined as a function of temperature at two concentrations of perchloric acid. These data are listed in Table II and the Arrhenius plot is shown in Figure 2.

Table I. w^* for Hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]^+$ in Five Acids at 25°

Acid	Concn range, *M*	w^*	*D*	n^a
Nitric	3.074–15.37	−1.03 ± 0.19	−4.64 ± 0.19	11
Perchloric	2.358–8.247	−2.42 ± 0.12	−4.96 ± 0.05	15
Sulfuric	2.575–8.585	−2.49 ± 0.18	−5.08 ± 0.13	11
Hydrobromic	3.547–7.097	−2.55 ± 0.58	−4.48 ± 0.54	6
Hydrochloric	2.621–11.88	−2.74 ± 0.30	−4.84 ± 0.26	15

[a] Number of observations.

Table II. Variation of k_1 with Temperature for Hydroysis of *trans*-$[Co(en)_2(NO_2)_2]^+$ in Perchloric Acid

Temp, °C	$k_1 \times 10^4$, sec^{-1}	
	4.123 *M*	5.890 *M*
0.0	0.0306	0.0910
25.0	1.08	3.28
40.0	6.83	24.0
55.0	31.2	135

From the Arrhenius plot, activation energies of 22.7 kcal for 4.123 *M* acid and 23.6 kcal for 5.890 *M* acid are obtained, with an 0.9-kcal 95% confidence interval.

Empirically it was found that the data up to 4.7 *M* perchloric acid could be fitted to the equation

$$k_1 = A(HClO_4)^2 \qquad (3)$$

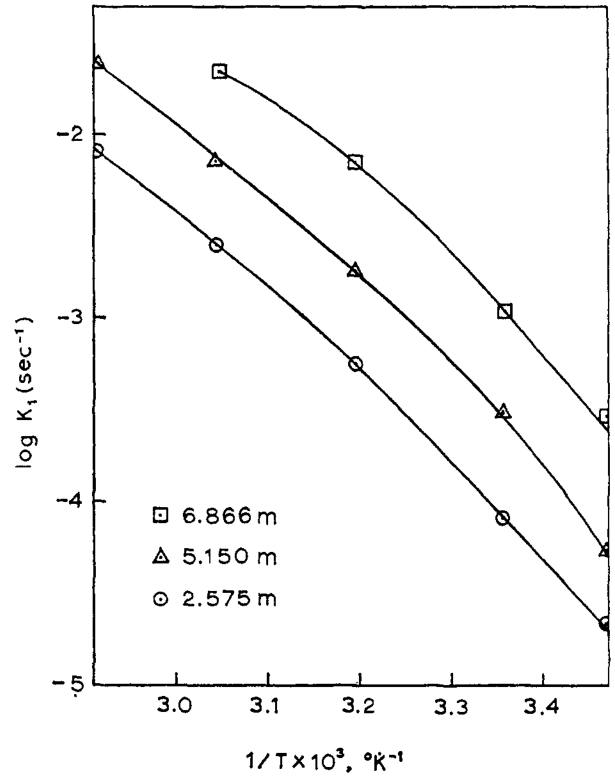

Figure 3. Arrhenius plot for the hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]^+$ in sulfuric acid.

where $(HClO_4)$ is the concentration of perchloric acid. From the values of *A* in eq 3 determined by least squares from the nine observations at 25° and the seven observations at 40°, the activation energy is 23.6 ± 0.8 kcal and the activation entropy is 2.9 ± 2.7 eu at the 95% confidence level. Staples[7] lists 24.9 kcal and 2.0 eu for these parameters in 3.5 *M* perchloric acid.

Arrhenius plots in all the other acids appear to be curved toward lower activation energies as the temperature or concentration of acid is increased. The data for hydrobromic, sulfuric, and nitric acids are given in Table III and the Arrhenius plot for sulfuric acid is shown in Figure 3.

Table III. Variation of k_1 with Temperature for the Hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]^+$ in Three Acids

Concn of acid, M	$k_1 \times 10^4$, sec^{-1} 15°	25°	40°	55°	70°
Hydrobromic					
3.547	...	1.19	7.98	37.9	120
4.965	...	2.19	14.9	51.2	...
6.383	...	5.53	35.1	91.2	213
Sulfuric					
2.575	0.214	0.746	5.60	24.9	79.8
4.292	...	1.76	11.2	45.3	...
5.150	0.549	3.12	18.2	73.6	244
6.866	2.95	11.1	69.3	224.	...
Nitric					
3.074	...	0.983	4.66	21.1	...
6.148	0.597	2.37	10.5	44.7	166
9.222	1.05	4.47	23.4	68.6	...
12.30	2.65	9.89	55.4	134	...

Discussion

In the previous study of the acid-catalyzed aquation of *trans*-$[Co(en)_2(NO_2)_2]^+$, Staples[7] proposed the following mechanism as the most reasonable.

$$[Co(en)_2(NO_2)_2]^+ + H^+ \rightleftharpoons [Co(en)_2(NO_2)(NO_2H)]^{2+} \text{ (equilibrium)} \quad (4)$$

$$[Co(en)_2(NO_2)(NO_2H)]^{2+} + H_2O \longrightarrow [Co(en)_2(NO_2)(H_2O)]^{2+} + HNO_2 \text{ (rate-determining)} \quad (5)$$

For the reactions under discussion here, an additional step, anation, is required for all acids except perchloric

$$[Co(en)_2(NO_2)H_2O]^{2+} + Z^- \longrightarrow [Co(en)_2(Z)(NO_2)]^+ \quad (6)$$

which appears not to be rate determining (*vide infra*).

Bunnett[12b] proposed on empirical grounds that the parameters w and w^* (see eq 1 and 2) have mechanistic significance. His proposals are (1) if w is negative, water is not involved in the rate-determining step, (2) if w is between 0 and 3, water is acting as a nucleophile, and (3) if w is greater than 3, water is acting as a proton-transfer agent. The observed w value of 2.3 is consistent with water acting as a nucleophile. Similarly, if w^* is less than -2, water acts as a nucleophile. The values of w^* of -2.5 for all acids except nitric are consistent with this proposal. The experimental data and the interpretation presented here support the mechanism of Staples for this reaction.

Arrhenius Plots. Hulett[20] has recently reviewed reasons for deviations from the Arrhenius equation. Medium effects have been observed to give curved Arrhenius plots in the hydrolysis of neutral organic compounds. These effects have been discussed in detail.[21] If a preequilibrium is involved and the rate depends upon the concentration of a species formed, a curved Arrhenius plot may be obtained. This curvature would be due to the variation of the equilibrium constant with temperature.

If two consecutive reactions occur, the second having the lower activation energy, the Arrhenius plot is concave downward in the region where the two rates are comparable.

As shown in Figure 3, the Arrhenius plots for sulfuric acid exhibit considerable curvature as a function of concentration. As shown in Figure 2, the Arrhenius plot for perchloric acid appears to be linear. For the other acids, the data suggest curvature but are not adequate to establish unequivocally the reality of such curvature. Unfortunately, it is for sulfuric acid that the product composition remains unspecified.

Neither medium effects nor variation of the equilibrium constant with temperature seem to be adequate explanations of the curvature in the hydrolysis of $[Co(en)_2(NO_2)_2]^+$. If they were significant, Arrhenius plots for the perchloric acid system should be nonlinear.

It appears then that the curvature may be due in part to a contribution from the consecutive anation reaction.

In principle, if the anation reaction were to become rate determining or competitive at higher temperatures, then some buildup of the nitroaquo intermediate would be expected with resulting curvature in the individual kinetic plots. No such curvature was observed at least to 75% reaction. At the wavelengths used, the possibility exists that such an effect was not spectrophotometrically detectable.

Competition between water and the acid anion as nucleophiles would lead to opposite curvature of the Arrhenius plots than that observed.

The Bunnett Treatment. Bunnett[12c] showed that the parameters w and w^* can be related to changes in hydration if one assumes that activity coefficient ratios are medium independent. For example, w^* is $(t - s - n)$, where t is the hydration of the transition state, s the hydration of the substrate, and n the hydration of the proton. In Table I, w^* is seen to be the same for all acids but nitric. Different w^* may be related to the idea[22] that nitric acid is less hydrated than perchloric or sulfuric acids.

Bunnett plots have been used to determine when a change in mechanism occurs in study of the isomerization of chalcones[23] and in the study of the decomposition of hyponitrous acid.[24] Sharp changes in w were observed which could be related to the changing role of water with change in acid concentration. No test of the theoretical foundations of the Bunnett equations seems to have been made, but their usefulness cannot be denied.

The Bunnett treatment of hydrolysis reactions has been reviewed recently;[25] both reviewers express doubts about the general applicability of the equations. Although caution still is necessary, it is satisfying that application of Bunnett's equations to the hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]^+$ gives results consistent with nucleophilic participation of water in the rate-determining step. This result would have been predicted from the theory that since the orienting ligand ("X") is the electron-withdrawing nitrite group, an SN2 reaction with water should be observed.

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(20) J. R. Hulett, *Quart. Rev.* (London), **18**, 227 (1964).

(21) K. T. Leffek, R. E. Robertson, and S. E. Sugamori, *J. Am. Chem. Soc.*, **87**, 2097 (1965).

(22) E. Hogfeldt, *Acta Chem. Scand.*, 17, 765 (1963).

(23) D. S. Noyce and M. J. Jorgenson, *J. Am. Chem. Soc.*, **85**, 2420, 2427 (1963).

(24) J. R. Buchholz and R. E. Powell, *ibid.*, **84**, 509 (1963).

(25) (a) H. Zollinger, *Ann. Rev. Phys. Chem.*, **13**, 391 (1962); (b) K. E. Howlett, *Sci. Progr.*, **53**, 297 (1965).