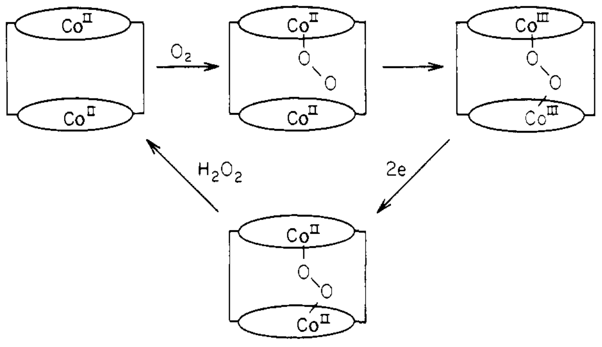
J. Am. Chem. Soc. 1983, 105, 2718-2725

Scheme III



Conclusions

The combinations of observations we have made helps to identify two of the factors that are most important in the catalytic cycle by which the Co$_2$(FTF4) molecule reduces O$_2$ to H$_2$O without release of H$_2$O$_2$: (i) the two cobalt centers must be positioned so that the proposed μ-peroxo complex can be formed; (ii) protonation of the μ-peroxo bridge is required to render it reducible at the potential where it is formed. These two requirements are necessary but apparently not sufficient because the dicobalt cofacial porphyrin with four-atom bridges in the meso position of the porphyrin is not an effective catalyst for reduction of O$_2$ to H$_2$O.[1-3] Furthermore, the electroreduction in acidic media of stable, (μ-peroxo)dicobalt complexes of some other macrocyclic ligands produces cobalt(II) and H$_2$O$_2$, not H$_2$O.[25] Thus, the μ-peroxo group in the complex formed by Co$_2$(FTF4) is apparently unusually reactive toward protonation and further reduction. The combination of steric and electronic constraints imposed simultaneously on the μ-peroxo group and the cobalt centers by the cofacial porphyrin ligand with four atoms in its amide bridges seems of crucial importance to its unique catalytic action. We expect that additional studies of the coordination chemistry of Co$_2$(FTF4), Co$_2$(FTF4*), and Co$_2$(FTF3), including X-ray structural data, will lead to a more thorough understanding of the mechanistic details of their electrocatalytic behavior.

Acknowledgment. This work grew out of a collaborative research effort that also involved the groups of Professors M. Boudart and H. Taube (Stanford University) and Dr. H. Tennent (formerly of Hercules Inc. Research Center). It has been supported by the National Science Foundation. C.S.B. thanks the Venezuelan Council for Scientific and Technological Research (CONITCIT) for her doctoral fellowship.

Registry No. I, 71253-21-9; Co$_2$(FTF6), 71253-22-0; Co$_2$(FTF5), 74452-74-7; Co$_2$(FTF4), 71253-24-2; Co$_2$(FTF4*), 84928-54-1; Co$_2$(FTF3), 84928-53-0; CoH$_2$(FTF4), 84928-51-8; CoFe(FTF4), 84928-55-2; CoMn(FTF4), 84928-50-7; CoAg(FTF4), 84928-49-4; CoAl(FTF4), 84928-48-3; Ag$_2$(FTF4), 84928-52-9; O$_2$, 7782-44-7; H$_2$O, 7732-18-5; H$_2$O$_2$, 7722-84-1; graphite, 7782-42-5.

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Structure-Reactivity Effects in the Hydration of Benzaldehydes

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Abstract: Rate constants have been measured for the approach to hydration equilibrium for seven substituted benzaldehydes [4-Cl, 3-Cl, 4-CF$_3$, 3-NO$_2$, 4-NO$_2$, 3-NO$_2$-4-Cl, 3,5-(NO$_2$)$_2$]. The kinetic method involves the perturbing of the equilibrium position by forming hydrate anion in concentrated sodium hydroxide; addition of acid and buffer results in solutions containing excess hydrate. Hydration equilibrium constants have been calculated by knowing the rate constants in the two directions for the hydroxide ion catalyzed reaction, and a value for the 3,5-(NO$_2$)$_2$ system has been obtained by using a trapping technique. Literature values are also summarized; hydration has a ρ value of +1.7 in the hydration direction. General base catalysis is associated with Brønsted β values around 0.4 and ρ values near zero in the dehydration direction. The β values increase with decreased electron withdrawal, while the ρ values decrease with increased base strength ($\partial\beta/\partial\sigma = -0.06 = \partial\rho/\partial pK_a$). A three-dimensional reaction coordinate diagram is used to show that this behavior is consistent with a class n mechanism—in the dehydration direction, equilibrium deprotonation of the hydrate followed by acid-catalyzed expulsion of OH. The water rates fit the general base correlations, although rate constants at the diffusion limit are required in one step. Two distinct Brønsted plots are observed for general acids, one for RCOOH and a second for RPO$_3$H$^-$, including H$_2$PO$_4^-$. The line for the latter is about 1 log unit above that for the former; this is attributed to an electrostatic interaction and *not* bifunctional catalysis. A significant cross correlation is also found here, with $\partial\alpha/\partial\sigma = -0.12 = \partial\rho/-\partial pK_a$. This is shown to be consistent with a class e mechanism—in the dehydration direction, equilibrium protonation of the hydrate followed by base-catalyzed expulsion of water.

The reversible hydration of alkyl aldehydes has seen considerable investigation.[1] This represents perhaps the most simple example in the important class of carbonyl addition reactions, and the position of the equilibrium and the associated kinetics have been studied in detail for a number of simple aldehydes.[1-6] Aromatic aldehydes, on the other hand, are known not to be hydrated to a significant extent in water, due to the extra resonance stabilization in the unhydrated benzaldehyde. Some measurements or estimates of the extent of hydration have been reported.[7-10] The

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Table I. Observed Catalytic Coefficients for the Dehydration–Hydration of Substituted Benzaldehydes at 25 °C and Ionic Strength 0.6

	k, $M^{-1}\ s^{-1}$						
catalyst	3,5-$(NO_2)_2$	3-NO_2,4-Cl	4-NO_2	3-NO_2	4-CF_3	3-Cl	4-Cl
H_3O^+	12	66	92	110	240	500	1250
H_2O^a	0.15	0.038	0.038	0.037	0.029	0.025	0.021
OH^-	2.4×10^6	4.8×10^5	5.7×10^5	4.8×10^5	3.5×10^5	3.1×10^5	2.0×10^5
$CH_2CNCOOH$	0.52	0.98	1.06	1.63	2.5	3.4	6.3
$CH_2ClCOOH$	0.42	0.77	0.82	1.26	1.65	2.62	4.6
$CH_2OMeCOOH$	0.25	0.36	0.40	0.50	0.77	1.11	2.09
HCOOH	0.165	0.31	0.36	0.42	0.62	0.91	1.36
$Cl(CH_2)_2COOH$	0.149	0.23	0.29	0.33	0.46	0.72	1.18
CH_3COOH	0.089	0.13	0.145	0.179	0.22	0.32	0.48
CH_2CNCOO^-	0.099	0.07	0.04	$-^b$	$-^b$	$-^b$	$-^b$
CH_2ClCOO^-	0.148	0.09	0.062	0.087	$-^b$	$-^b$	$-^b$
$CH_2OMeCOO^-$	0.31	0.20	0.157	0.145	0.09	0.09	$-^b$
$HCOO^-$	0.35	0.28	0.26	0.23	0.21	0.15	0.18
$Cl(CH_2)_2COO^-$	0.51	0.30	0.22	0.41	0.19	0.19	0.15
CH_3COO^-	0.92	0.49	0.47	0.43	0.41	0.38	0.34
$H_2PO_4^-$	0.3	0.43	0.46	0.51	0.66	1.0	1.1
HPO_4^{2-}	9.5	5.2	5.1	4.7	4.5	4.7	5.2

[a] Units of s^{-1}. [b] Not significant.

Table II. Observed Catalytic Coefficients for the Dehydration–Hydration of Substituted Benzaldehydes at 25 °C and Ionic Strength 0.6

catalyst acid form	4-NO_2		3-Cl	
	k_{acid}	k_{base}	k_{acid}	k_{base}
$CCl_3PO_3H^-$	1.18	0.49	3.28	0.25
$CHCl_2PO_3H^-$	0.66	1.04	1.53	1.10
$CH_2ClPO_3H^-$	0.36	2.4	0.78	2.2
$CH_2OHPO_3H^-$	0.22	5.1	0.51	3.6
$CH_3PO_3H^-$	0.17	4.0	0.33	6.4
$(CH_3)_2AsO_2H$	0.07	1.22	0.15	0.93

limited degree of hydration, however, has prevented detailed kinetic studies.

We report here such a kinetic investigation for the hydration equilibration of seven benzaldehydes bearing electron-withdrawing substituents. Our approach is based on the addition of hydroxide ion which has been observed to occur in strongly basic solutions.[7,9,11,12] This reaction provides a way of perturbing the hydration equilibrium, since the adduct formed in base is the ionized hydrate. The initial reaction that will occur on neutralization is the protonation of the adduct, resulting in a solution containing neutral hydrate in excess of its equilibrium concentration. The kinetics associated with the return to the equilibrium position can then be monitored.

Results

In our experimental approach a solution of the aldehyde was prepared in 0.1 M NaOH–0.5 M NaCl. The addition reaction of hydroxide ion is very rapid, the temperature-jump method being required for kinetic study.[9] The above solution was then mixed in a stopped-flow spectrophotometer with solutions containing 0.1 M HCl, buffer, and sufficient NaCl to maintain the ionic strength also at 0.6. The wavelength monitored was the λ_{max} of the benzaldehyde. In all cases an absorbance increase could be observed corresponding to the return to the equilibrium position as the excess hydrate was converted to free aldehyde. Excellent first-order kinetic plots were obtained. The observed rate constants take the expected form[1] as a function of pH and buffer concentration

$$k_{obsd} = k_{H_3O}[H^+] + k_{HA}[HA] + k_{OH^-}[OH^-] + k_{A^-}[A^-] + k_{H_2O} \quad (1)$$

showing catalysis by hydronium ion and hydroxide ion, general

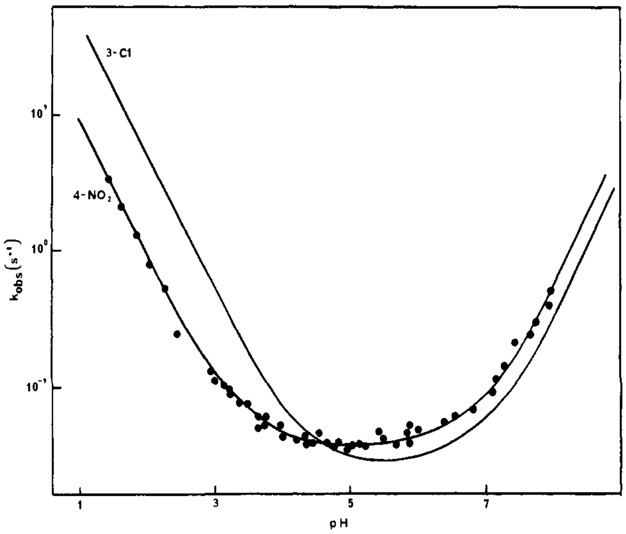

Figure 1. Observed rate constants for the approach to hydration equilibrium for 4-nitrobenzaldehyde and 4-chlorobenzaldehyde. Solid circles represent the experimental points for 4-nitrobenzaldehyde and are based on extrapolation to zero buffer concentration.

Table III. Equilibrium Constants for Addition of Hydroxide Ion to Substituted Benzaldehydes and Concentration of Free Aldehyde in 0.1 M NaOH and in Neutral Solutions

		% free benzaldehyde	
substituent	K_{OH^-}, M^{-1}	0.1 M NaOH[a]	H_2O^b
H	0.18,[c] 0.13[d]	97.9	99.2
4-Cl	0.47,[c] 0.36[d]	95.1	98.4
3-Cl	1.13,[c] 1.20,[d] 1.26[e]	87.6	97.8
4-CF_3	5[f]	64	94.8
3-NO_2	8.3,[c] 9.1,[d] 8.0[e]	50	90
3-NO_2-4-Cl	21,[c] 17[e]	32	85
4-NO_2	13,[c] 16,[d] 18[e]	36	85
3,5-$(NO_2)_2$	10^3 [f]	1	32

[a] $100/(1 + K_{Hyd} + 0.1\ K_{OH^-})$. [b] $100/(1 + K_{Hyd})$. [c] Greenzaid, ref 7. [d] Bover and Zuman, ref 11. [e] Bell and Sørensen, ref 9. [f] Estimated by extrapolation or interpolation.

acids and general bases, and a pH-independent term. Figure 1 shows rate–pH profiles for two aldehydes. Values of the rate coefficients are listed in Tables I and II.

A value of 2.1 ± 0.5 for the hydration equilibrium constant of 3,5-dinitrobenzaldehyde was determined by using the trapping method described by Bell and Sørensen.[9] In this technique, free aldehyde in acetonitrile is added to an aqueous buffer. After attainment of hydration equilibrium, excess hydrogen sulfite is

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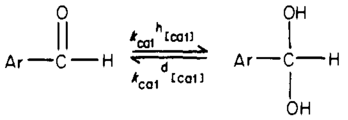
(12) Bover, W. J.; Zuman, P. *J. Am. Chem. Soc.* **1973**, *95*, 2531–2536.

added. A very rapid addition takes place with the free aldehyde, a slower reaction occurring with the hydrate which must dehydrate first. Knowledge of the initial and final absorbance in each experiment provides the equilibrium constant.[9] Considerable error is present in the above number since the required extrapolation to zero time is difficult. In addition, with the two nitro groups present, some of the spectral changes are quite small.

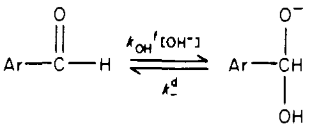
Discussion

Equations 2–4 summarize the equilibria of importance, the



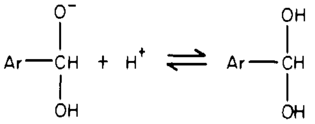
$$\mathrm{Ar{-}C({=}O){-}H} \underset{k_{\mathrm{cat}}{}^{\mathrm{d}}[\mathrm{cat}]}{\overset{k_{\mathrm{cat}}{}^{\mathrm{h}}[\mathrm{cat}]}{\rightleftharpoons}} \mathrm{Ar{-}C(OH)_2{-}H} \qquad (2)$$

$$K_{\mathrm{Hyd}} = [\mathrm{Hyd}]/[\mathrm{Ald}] = k_{\mathrm{cat}}{}^{\mathrm{h}}/k_{\mathrm{cat}}{}^{\mathrm{d}}$$



$$\mathrm{Ar{-}C({=}O){-}H} \underset{k_{-}{}^{\mathrm{d}}}{\overset{k_{\mathrm{OH}}{}^{\mathrm{f}}[\mathrm{OH^-}]}{\rightleftharpoons}} \mathrm{Ar{-}CH(O^-)(OH)} \qquad (3)$$

$$K_{\mathrm{OH}} = [\mathrm{Hyd}^-]/([\mathrm{Ald}][\mathrm{OH}^-])$$



$$\mathrm{Ar{-}CH(O^-)(OH)} + \mathrm{H^+} \rightleftharpoons \mathrm{Ar{-}CH(OH)_2} \qquad (4)$$

$$K_{\mathrm{a}} = [\mathrm{Hyd}^-][\mathrm{H}^+]/[\mathrm{Hyd}] = (K_{\mathrm{OH}}K_{\mathrm{w}})/K_{\mathrm{Hyd}}$$

addition of water and hydroxide ion to the substituted benzaldehydes. Literature values of K_{OH} are given in Table III. The values of Bover and Zuman[11,12] are based on an acidity function approach and are probably more precise in a thermodynamic sense.

From values of K_{OH} and K_{Hyd} (to be discussed shortly) the percentages of free benzaldehyde in 0.1 M NaOH and in nonbasic aqueous solutions have been calculated and are listed in Table III. The difference between the two represents the change in concentration that occurs in the kinetic experiments. It can be seen that the more electron withdrawing the aromatic substituents, the better the change, although as seen with the 3,5-dinitro compound, there is a limit associated with the requirement that the neutral solution cannot contain significant hydrate. Benzaldehyde itself was not studied since the change is too small. In principle, more concentrated base solutions could be employed to produce greater concentrations of hydrate anion. This proves, however, not practical because of the heat released on neutralization.

Hydration Equilibrium Constants. The rate constants listed in Tables I and II refer to the approach to the hydration equilibrium and therefore represent the sum of coefficients for the dehydration (d) and hydration (h) reactions

$$k_{\mathrm{cat}} = k_{\mathrm{cat}}{}^{\mathrm{h}} + k_{\mathrm{cat}}{}^{\mathrm{d}} \qquad (5)$$

where "cat" refers to any catalyst. These two constants are also related to the equilibrium constant, as in eq 2, so that the individual values can be calculated if the equilibrium constant is known.

Several estimates or measurements have been made of values of K_{Hyd}, and these are summarized in Table IV. Greenzaid[7] arrived at estimates for benzaldehyde itself and for 3-nitrobenzaldehyde using his observed values of K_{OH} for hydroxide ion addition and estimates of the dissociation constant K_{a} of the hydrate (see the relationship in eq 4). The second number for benzaldehyde is based on this approach but using the K_{OH} value of Bover and Zuman.[11] This value agrees with an estimate of Guthrie[10] arrived at through a thermodynamic analysis. The value for 4-chlorobenzaldehyde is based on the γ scale of Sander and Jencks[13] for the addition of a series of nucleophiles to the carbonyl group. Sayer[8] employed three methods for 4-nitrobenzaldehyde—(A) measurement of the absorbance decrease on addition of free aldehyde to aqueous solution, (B) a trapping experiment using semicarbazide as the nucleophile, and (C) NMR spectroscopy. Values of Bell and Sørensen[9] were determined by using a hydrogen sulfite trapping technique. There is a general consistency among the various values, with the one exception that the Bell and Sorenson value for 3-chlorobenzaldehyde seems somewhat out of line with the values estimated for 4-chlorobenzaldehyde and the parent compound. As admitted by these authors,[9] there is a considerable uncertainty in this number since the actual equilibrium concentration of hydrate is so low.

Table IV. Hydration Equilibrium Constants for Addition of Water to Substituted Benzaldehydes

substituent	K_{Hyd} this work	K_{Hyd} literature
H		0.011 (Greenzaid)[a] 0.008 (Greenzaid, modified)[b] *0.008* (Guthrie)[c]
4-Cl		0.016 (Sander, Jencks)[d]
3-Cl	*0.022*[e]	0.01 (Bell, Sørensen)[f]
4-CF_3	(*0.055*)[g]	
3-NO_2	*0.11*[e]	0.08 (Greenzaid)[a]
3-NO_2-4-Cl	*0.18*[e]	0.15 (Bell, Sørensen)[f]
4-NO_2	*0.17*[e]	0.15 (Bell, Sørensen)[f] 0.20 (Sayer, A)[h] 0.30 (Sayer, B)[h] 0.13 (Sayer, C)[h]
3,5-$(NO_2)_2$	*2.1*[i]	

[a] Reference 7. [b] Using the K_{OH} value of Bover and Zuman, ref 11. [c] Reference 10. [d] Reference 13. [e] Based on forward and reverse rate constants. [f] Reference 9. [g] Interpolated value. [h] Reference 8. [i] Hydrogen sulfite trapping.

Another approach can be suggested using rate constants obtained in this study and by Bell and Sørensen.[9] The constants refer to the hydroxide ion catalyzed equilibration reaction for which there can be little mechanistic ambiguity.[6,9] This occurs by the combination of eq 3 and 4, with the hydrate anion as an intermediate. In the hydration direction hydroxide adds to the aldehyde in the rate-determining step, followed by rapid protonation to give the neutral hydrate. The dehydration mechanism is the microscopic reverse, a preequilibrium deprotonation followed by expulsion of hydroxide from the hydrate anion. For our purposes here the key feature is that in the hydration direction the rate constant for hydroxide ion catalysis ($k_{\mathrm{OH}}{}^{\mathrm{h}}$) is the rate constant for hydroxide ion addition ($k_{\mathrm{OH}}{}^{\mathrm{f}}$) and values for this are available through the study of Bell and Sorenson.[9] The relationship of eq 5 still holds, $k_{\mathrm{OH}} = k_{\mathrm{OH}}{}^{\mathrm{h}} + k_{\mathrm{OH}}{}^{\mathrm{d}}$, where k_{OH} is the observed catalytic coefficient listed in Table I. When both k_{OH} and $k_{\mathrm{OH}}{}^{\mathrm{h}}$ are known $k_{\mathrm{OH}}{}^{\mathrm{d}}$ can be determined and then K_{Hyd} as $k_{\mathrm{OH}}{}^{\mathrm{h}}/k_{\mathrm{OH}}{}^{\mathrm{d}}$.

There are four benzaldehydes common to our study and that of Bell and Sorenson for which this can be done. Values of K_{Hyd} calculated in this way show good agreement with the values of other workers, with 3-chlorobenzaldehyde being predicted to be more hydrated. A Hammett plot is shown in Figure 2. By use of the italicized values of K_{Hyd} in Table IV, a ρ value of +1.7 is found. A ρ or ρ^* value near 1.7 seems to be common for the hydration of simple carbonyl compounds, being found also with substituted acetaldehydes,[2] substituted dialkyl ketones,[2] and phenyl-substituted dimethyl benzoylphosphonates.[14] This value also fits well with the ρ value of +2.7 found by Bover and Zuman for hydroxide ion addition (K_{OH}, eq 2). The difference between the values for K_{Hyd} and K_{OH} provides a ρ value of +1.0 for the dissociation constants of the hydrate (K_{a}, eq 4), and this seems reasonable. A value of +1.1 is found for the dissociation of trifluoroacetophenone hydrates.[15]

Equations 6 and 7 express the relationship of the individual

$$k_{\mathrm{cat}}{}^{\mathrm{d}} = k_{\mathrm{cat}}/(1 + K_{\mathrm{Hyd}}) \qquad (6)$$

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(14) Kluger, R.; Chin, J. *J. Am. Chem. Soc.* **1978**, *100*, 7382–7388.

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$$k_{cat}{}^{h} = k_{cat}K_{Hyd}/(1 + K_{Hyd}) \qquad (7)$$

coefficients to k_{cat} and K_{Hyd}. In the following discussions where $k_{cat}{}^{h}$ or $k_{cat}{}^{d}$ is referred to, they are based on the italicized values of K_{Hyd} in Table IV. Since K_{Hyd} is significantly less than unity in all but one case, values of $k_{cat}{}^{d}$ are relatively insensitive to its exact value, while the reverse is true of values of $k_{cat}{}^{h}$. For this reason the majority of our analysis will be based on the dehydration rate constants. It can be noted that Brønsted plots using the observed k_{cat} represent the Brønsted plots for both $k_{cat}{}^{d}$ and $k_{cat}{}^{h}$. This occurs since for a given aldehyde the quantities $1/(1 + K_{Hyd})$ and $K_{Hyd}/(1 + K_{Hyd})$ are constant as the catalyst is varied. These two terms do obviously change as the aldehyde structure is varied so that $k_{cat}{}^{d}$ or $k_{cat}{}^{h}$ must be specifically used in considering substituent effects, as in a Hammett plot.

The individual constants and associated ρ values[16] for the H^+-, OH^--, and water-catalyzed reactions are given in Table V, along with literature values for the decomposition of benzaldehyde methyl hemiacetal[17] and for the H^+-catalyzed hydrolysis of benzaldehyde diethyl acetal.[18] The numbers for the hydrates and hemiacetals are not surprisingly very similar. There is some difference in the ρ values for the hydroxide-catalyzed decompositions, but as seen in the following analysis, this appears to be a real effect. The ρ value for this reaction is a combination of

$$\rho(k_{OH}{}^{d}) = \rho(K_a) + \rho(k_{-}{}^{d}) \qquad (8)$$

ρ values for the two steps—ionization and expulsion of hydroxide or methoxide. As discussed previously, $\rho(K_a)$ for both the hydrate and hemiacetal should be near +1. Bell and Sorenson[9] measured $k_{-}{}^{d}$ for the hydrate anion decomposition and found very little substituent effect, a ρ value of just −0.1 being calculated by using their data for 3-Cl, 3,4-Cl_2, 3-NO_2, and 4-NO_2. Thus, the net positive ρ on $k_{OH}{}^{d}$ found for the hydrate in this study seems reasonable. A temperature-jump study[19] has also been carried out for the reversible addition of methoxide ion in methanol, and here a definite substituent effect on the $k_{-}{}^{d}$ process is apparent, a ρ value of −1.0 being calculated from the data. Taking into account the different solvents the slightly negative net ρ value observed for the hemiacetal[17] does not seem out of place.

General Base Catalysis. Figure 3 displays Brønsted plots for the base-catalyzed equilibration in two systems, with the plot for the 3-chlorobenzaldehyde displaced by 1 log unit. There is in fact very little substituent effect on the base-catalytic coefficients, resulting in a situation where the Brønsted plots for all of the benzaldehydes are almost superimposable on one another. A common Brønsted line is defined by the oxyanion bases, including the singly charged $RCOO^-$ and the doubly charged $RPO_3{}^{2-}$. The rate constant for the pH-independent reaction, when corrected to second-order units, lies very near this line, while being placed considerably above the acid line. The rate constants for the hydroxide ion catalyzed reaction, on the other hand, are about 2 log units above. This pattern of behavior can be seen in other systems. In the decomposition of formaldehyde hydrate and hemiacetals,[6] the water rates were found to fit within a factor of 2 on the Brønsted lines based on carboxylate bases, with the hydroxide rates 2 orders of magnitude above. In the hydration of phthaldehyde[20] and three alkyl aldehydes[5] the water rates again fit on the Brønsted plots for bases. In these cases the hydroxide point is also near this line. From the observations in the formaldehyde systems Funderburk, Aldwin, and Jencks[6] suggested that the water reaction is mechanistically similar to the general base reaction, while the hydroxide reaction is different. Our data support these conclusions, although, as will be discussed, in the water case a rate constant for an individual step very near the diffusion limit seems to be required.

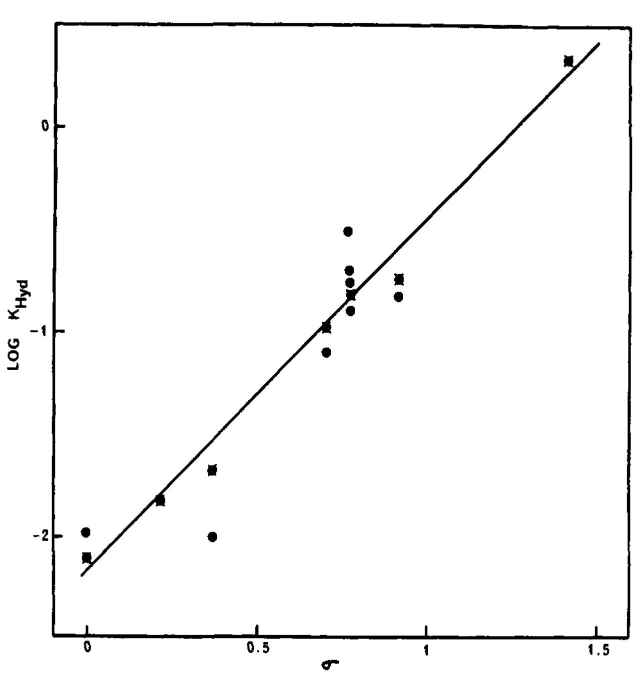

Figure 2. Hammett plot for the hydration equilibrium constants of benzaldehydes. The line drawn has a slope of 1.71 and is the linear regression line for the crossed points.

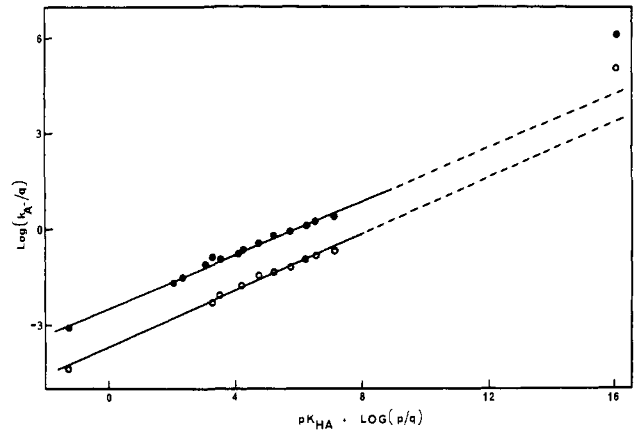

Figure 3. Brønsted plots for the base-catalyzed hydration: dehydration of 4-nitrobenzaldehyde (●) and 3-chlorobenzaldehyde (○). The plot for the latter is displaced downward 1 log unit.

Brønsted β values are listed in Table VI. Some literature values for comparison are 0.24 for formaldehyde,[6] 0.45 for propionaldehyde,[5] and 0.51 for phthalaldehyde.[20] In the present case the values lie around 0.4. There appears a tendency for β to increase with decreasing electron withdrawal in the substituent. A plot of β vs. the Hammett σ constant obeys the relationship $\partial\beta/\partial\sigma = -0.06$. A variation can also be seen in the ρ values, ρ for the dehydration changing from +0.30 for water to +0.06 for acetate to −0.15 for phosphate dianion (Table VII). This represents the same cross correlation[21] since $\partial\beta/\partial\sigma = \partial\rho/\partial pK_a$. The ρ value for hydroxide does not fit this correlation, consistent with the different mechanism by which this catalyst operates.

Two kinetically equivalent mechanisms can be written[1,6] for the base catalysis of hydrate and hemiacetal formation and decomposition.

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(16) The data for 3-nitro-4-chlorobenzaldehyde have been ignored in all ρ value calculations.

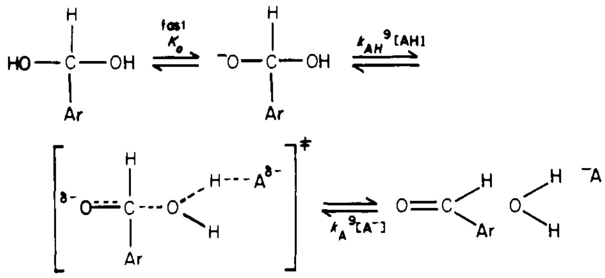
(17) Przystas, T. J.; Fife, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 4884–4890.

(18) Jensen, J. L.; Herold, L. R.; Lenz, P. A.; Trusty, S.; Sergi, V.; Bell, K.; Rogers, P. *J. Am. Chem. Soc.* *1979*, *101*, 4672–4677.

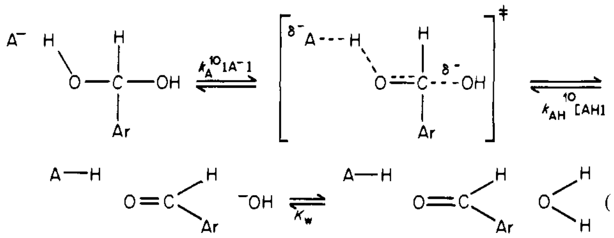
(19) Arora, M.; Cox, B. G.; Sørensen, P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 103–107.

(20) McDonald, R. S.; Martin, E. V. *Can. J. Chem.* **1979**, *57*, 506–516.

(21) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948–7960.



(9)



(10)

Equation 9 is a class n reaction[22] and represents true general base catalysis in the hydration direction and specific base–general acid catalysis in the dehydration direction. Equation 10 is a class e reaction, with true general base catalysis in the dehydration direction and specific base–general acid catalysis in the formation direction. Funderburk, Aldwin, and Jencks presented strong evidence for the class n reaction for formaldehyde hydrate and hemiacetals.

Figure 4 depicts structure–reactivity diagrams for the two base reactions. These have been drawn as is normally done,[6,23,24] with the modification of placing the two reactions on the same diagram since they share a common edge. The class e reaction proceeds in the dehydration direction from A to E to F and has its transition state in the left half of the diagram, while the class n reaction proceeds from A to B to F with a transition state in the right half. The x axis represents the proton transfer coordinate and can be taken as a measure of the β value as indicated on the diagram. The y axis represents C–O bond cleavage and formation. The ρ values indicated at the corners represent the values associated with the equilibria of the species in the corners with the neutral hydrate in corner A. Corner B consists of the hydrate anion, and corners E and F consist of the free aldehyde; the substituent effects of their equilibria with hydrate have been discussed. The zwitterionic hydrate occurs in corner C, and since there is no change in net charge there should be little substituent effect in the equilibrium with hydrate. Corner D represents a protonated benzaldehyde; the ρ of -4 is based on the equilibria of acetophenone ketals with their oxocarbocations.[25] The dashed lines are an approximation of the loci of transition states for reactions which have ρ values of $+0.5$, 0, and -1.0 in the dehydration direction, that is, with respect to neutral hydrate. These have been drawn by using the ρ values at the corners and assuming that ρ is linearly related to distance across the surface.

The two points approximate the possible locations of the actual transition state, being drawn at $\beta = 0.45$ and $\rho = 0$. Since β is not constant, the position of the transition state moves slightly with the substituent. The direction of this movement can be predicted on the basis of the effects of substitutent on the relative energies of diagonal corners.[6,23,24] We will consider a change to a more electron withdrawing substituent. This destabilizes the aldehyde in corner E relative to the hydrate in corner A; this represents motion parallel to the reaction coordinate[24] and causes the transition state to move toward E. The hydrate anion at B is considerably stabilized relative to the oxocarbocation at D; this is motion perpendicular to the reaction coordinate[24] and results in the transition state sliding toward B. With respect to the proton transfer axis both effects operate in the same direction, an increase in the amount of proton transfer at the transition state. The prediction for a class e reaction therefore is an increase in β with increased electron withdrawal and $\partial\beta/\partial\sigma > 0$. For the class n transition state the same substituent change destabilizes F (aldehyde) relative to B (hydrate anion), so that the transition state should move toward F. Corner C (zwitterion) is stabilized relative to E (aldehyde) with a resultant movement toward C. Both effects again operate in the same direction with respect to the x axis, predicting a decrease in the amount of proton transfer and $\partial\beta/\partial\sigma < 0$. This is the observed behavior. We conclude that the class n mechanism is in operation.

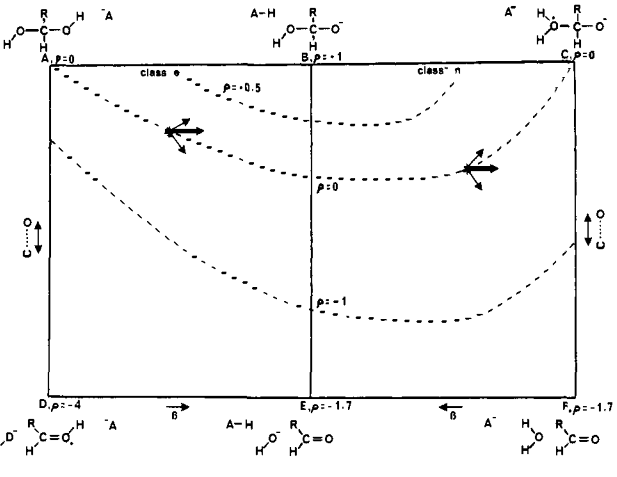


Figure 4. Reaction coordinate diagram for the base-catalyzed hydration of aldehydes, with proton transfer along the horizontal coordinate and C–O bond cleavage and formation along the vertical coordinate. The ρ values given by the dashed lines and at the corners represent the values at these locations relative to corner A, the neutral hydrate. The asterisks represent the location of the two possible transition states, corresponding to $\beta = 0.45$ and $\rho = 0$. The arrows represent the movement of the transition states when there is greater electron withdrawal in a benzaldehyde or for a change R = aryl to R = H. The light arrows depict the motion parallel to and perpendicular to the reaction coordinate and the heavy arrows the net result.

It can also be commented that the significantly smaller β observed for formaldehyde hydrate decomposition[6] also fits the class n mechanism and not class e. In this case the change is R = aryl to R = H in Figure 4. This causes a considerable stabilization of the entire top half of the diagram (A, B, and C) relative to the bottom half (D, E, F) because of the much greater stability of the hydrate form of formaldehyde. The discussion of the movement of the two transition states follows exactly the same arguments as just presented, leading to the same predictions. A class e mechanism requires a greater β for formaldehyde hydrate than for benzaldehyde hydrate, while a class n mechanism requires a smaller β.

The dehydration in the class n mechanism is specific base–general acid catalyzed and the observed rate constants k_A^d are therefore a composite equal to $k_{AH}^9K_a/K_{HA}$ where k_{AH}^9 is the rate constant for the acid-catalyzed step and K_a and k_{HA} are ionization constants of the hydrate and catalyzing acid, respectively. Values of K_a can be estimated from the relationship $k_{OH}^d = K_ak_-^d$ by using the values of k_{OH}^d of Table V and k_-^d values from Bell and Sorenson.[9] Typical numbers are 6×10^{-13} for 3-chlorobenzaldehyde and 8×10^{-13} for 3-nitrobenzaldehyde.[26] The values of k_{AH}^9 required in order to obtain the observed constants can then be calculated and are all found to be less[27] than the value of 10^{10} M^{-1} s^{-1} commonly accepted for a diffusion-limited reaction.[28] The same calculation for water as the catalyst, or H_3O^+ catalyzing the expulsion from hydrate anion, reveals that a rate at the diffusion limit is required, a value of 4×10^{10} M^{-1} s^{-1}, for example, being calculated for 3-chlorobenzaldehyde. This may signify that

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(23) More O'Ferral, R. A. *J. Chem. Soc. B* **1970**, 274–277.

(24) Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705–718.

(25) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238–8248.

(26) Greenzaid[7] estimated a K_a value of 10^{-12} for 3-nitrobenzaldehyde.

(27) The largest value required is 10^8 M^{-1} s^{-1} for cyanoacetate-catalyzed decomposition of 3-nitrobenzaldehyde.

(28) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1–19.

Table V. Rate Constants[a] for the Formation and Decomposition of Benzaldehyde Hydrates

	$k_H{}^d$	$k_H{}^h$	$k_O{}^d$	$k_O{}^h$	$k_{OH}{}^d$	$k_{OH}{}^h$
4-Cl	1230	20	0.021	3.3×10^{-4}	2.0×10^5	3.1×10^3
3-Cl	489	11	0.024	5.3×10^{-4}	3.0×10^5	6.6×10^3
4-CF_3	227	13	0.027	1.5×10^{-3}	3.3×10^5	1.8×10^4
3-NO_2	99	11	0.033	3.7×10^{-3}	4.3×10^5	4.8×10^4
4-NO_2	79	13	0.032	5.5×10^{-3}	4.9×10^5	8.3×10^4
3-NO_2-4-Cl	56	10	0.032	5.8×10^{-3}	4.1×10^5	7.3×10^4
3,5-$(NO_2)_2$	3.9	8	0.048	0.10	7.7×10^5	1.6×10^6
3-Cl, hemiacetal[b]	197		0.018		2.0×10^6	
3-Cl, acetal[c]	11.5					
ρ, hydrates	−2.0	−0.3	+0.30	+2.1	+0.5	+2.3
ρ, hemiacetal[b]	−1.9		+0.35		−0.3	
ρ, acetals[c]	−3.2					

[a] k_O units = s^{-1}. k_{OH} and k_H units = M^{-1} s^{-1}. Hydrate data at 25 °C, $\mu = 0.6$. Hemiacetal data at 30 °C, $\mu = 0.1$. Acetal data at 25 °C, $\mu = 0.5$. [b] Benzaldehyde methyl hemiacetal, ref 16. [c] Benzaldehyde diethyl acetal, ref 17.

Table VI. Brønsted β and α Values for Benzaldehyde Hydration–Dehydration

	β	α_{RCOOH}	$\alpha_{RPO_3H^-}$
3,5-$(NO_2)_2$	0.39	0.35	
3-NO_2-4-Cl	0.43	0.40	
4-NO_2	0.42	0.38	0.28
3-NO_2	0.44	0.44	
4-CF_3	0.45	0.46	
3-Cl	0.44	0.46	0.32
4-Cl	0.46	0.50	

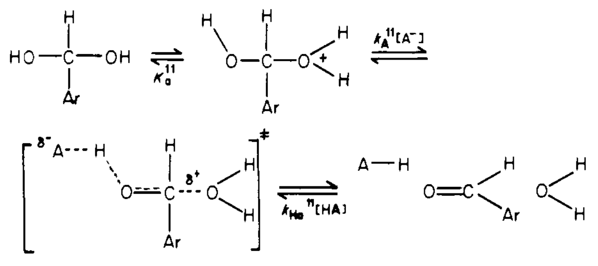
Table VII. Hammett ρ Values for Decomposition of Benzaldehyde Hydrates

catalyst	ρ^a
OH^-	+0.48
$HPO_4{}^{2-}$	−0.15
CH_3COO^-	+0.06
$HCOO^-$	+0.05
H_2O	+0.30
H_3O^+	−2.04
$CH_2CNCOOH$	−1.33
$CH_2ClCOOH$	−1.29
$CH_2OMeCOOH$	−1.33
HCOOH	−1.15
$Cl(CH_2)_3COOH$	−1.15
CH_3COOH	−1.00
$H_2PO_4{}^-$	−0.85

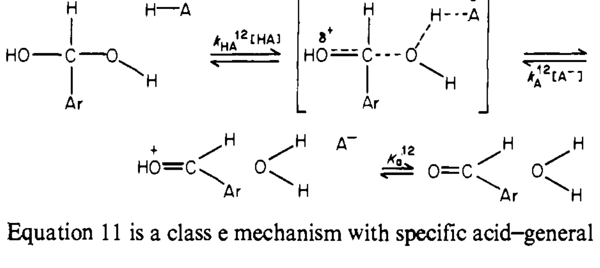
[a] Based on 4-Cl, 3-Cl, 4-CF_3, 3-NO_2, 4-NO_2, and 3,5-$(NO_2)_2$ with 3,5-$(NO_2)_2$ being given a 50% weighting.

the water reaction is not completely analogous to the other base reactions, although it does seem to fit other correlations.

General Acid Catalysis. Two kinetically equivalent mechanisms can also be written for the general acid catalyzed reactions.[1,6]



(11)



(12)

Equation 11 is a class e mechanism with specific acid–general base catalysis in the dehydration direction. Equation 12 is a class n mechanism with true general acid catalysis in the dehydration. Funderburk, Aldwin, and Jencks[6] favored the class e mechanism for formaldehyde hydrate and hemiacetals.

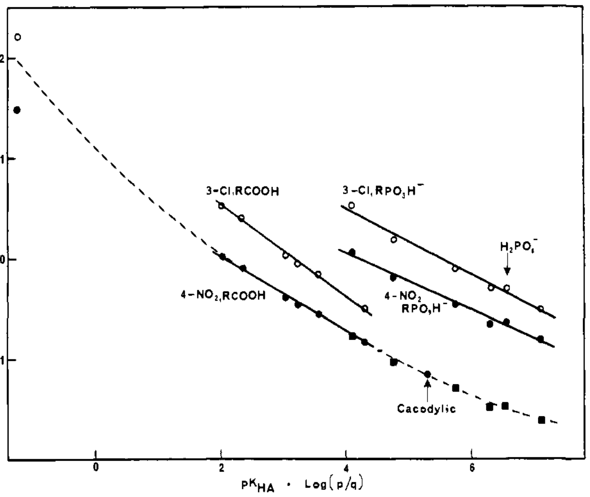
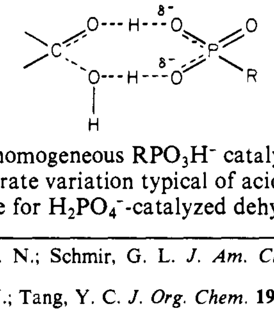


Figure 5. Brønsted plots for the acid-catalyzed hydration: dehydration of 4-nitrobenzaldehyde (●) and 3-chlorobenzaldehyde (○). Linear regression lines are drawn based on RCOOH and RPO_3H^- points. The points (■) represent the 4-nitro data for RPO_3H^- artificially lowered by a log factor of 0.85. The dashed line represents a curved Brønsted plot for 4-nitrobenzaldehyde.

Figure 5 depicts Brønsted plots for two benzaldehydes with catalysis by a series of oxyacids. Unlike the case in the base reaction, a common Brønsted relationship is clearly not observed. There are two quite distinct Brønsted lines, one for neutral carboxylic acids and one for alkyl hydrogen phosphonate anions. Dihydrogen phosphate is included with the latter; the point for H_3O^+ lies close to the former. For a comparison involving acids of the same acidity, the anionic phosphonates are about an order of magnitude more reactive.

Enhanced catalytic reactivity associated with $H_2PO_4^-$ has been observed in a number of cases,[29] including aldehyde hydration–dehydration.[5,20] Some form of bifunctional catalysis is usually invoked,[5,29] with a proton being simultaneously transferred to and from the catalyst. This cannot be the explanation here, however.



The structurally homogeneous RPO_3H^- catalysts,[30] with $H_2PO_4^-$ included, show a rate variation typical of acid catalysts; there is a negative ρ value for $H_2PO_4^-$-catalyzed dehydration and this is

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(29) See Lee, Y. N.; Schmir, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 3026–3035.

(30) Kresge, A. J.; Tang, Y. C. *J. Org. Chem.* **1977**, *42*, 757–759.

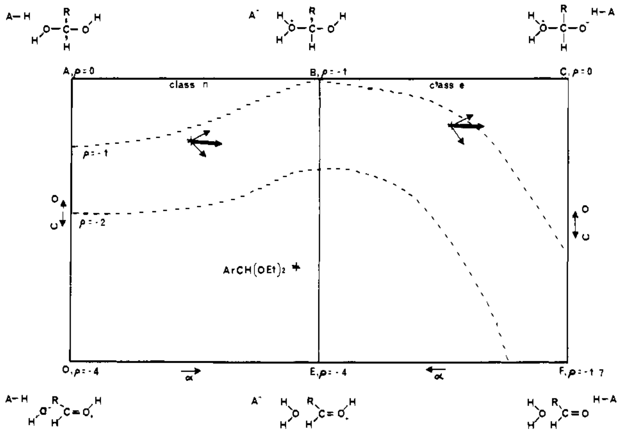

Figure 6. Reaction coordinate diagram for the acid-catalyzed hydration of aldehydes, with proton transfer along the horizontal coordinate and C–O bond cleavage and formation along the vertical coordinate. The ρ values given by the dashed lines and at the corners represent the values at these locations relative to corner A, the neutral hydrate. The asterisks represent the location of the two possible transition states corresponding to $\rho = -1.1$ and $\alpha = 0.46$. The arrows represent the movement of the transition state when there is greater electron withdrawal in a benzaldehyde or for a change R = aryl to R = H. The light arrows depict the motion parallel to and perpendicular to the reaction coordinate; the net result is shown by the heavy arrows. The dagger represents the actual position of the transition state in the class n portion of the diagram, as determined for benzaldehyde acetal hydrolysis.

also typical of acid catalysts (Table VII).

The observation of different Brønsted relations for different acid types is not uncommon.[31-33] The explanation[32] recognizes that there are different charges in the two sets of catalysts, resulting in an electrostatic interaction in the transition state with differing degrees of stabilization. Such an interaction is present in both the class e and class n transition states of eq 11 and 12. In each case a partial positive charge is present somewhere in the substrate molecule, for example, on the entering or leaving H_2O in the class e reaction. With a carboxylic acid catalyst this charge is offset by an equal partial negative charge on the catalyst. The same interaction is also present with the phosphonic acid catalysts but is augmented by the full negative charge already present. There is more stabilizing interaction in the latter case, so that for a comparison of acids of the same strength, the transition state is of lower energy and the phosphonate is a more effective catalyst.

A second notable feature of the Brønsted plots is the significant dependence of the Brønsted slope on the aromatic substituent (Table VI), α increasing with decreasing electron withdrawal with $\partial\alpha/\partial\sigma = -0.12$. This corresponds to an increase in ρ with increased acid strength, where again a significant effect is seen (Table VII). A reaction coordinate diagram is shown in Figure 6. This is drawn in a manner similar to the base diagram of Figure 4. In the acid diagram the class n reaction proceeds in the dehydration direction from A → E → F, and the class e reaction from A → B → F. The dashed lines approximate the positions of transition states which would correspond to ρ values of −1 and −2 for the dehydration reaction, these lines being drawn on the basis of the ρ values associated with equilibration of the neutral hydrate and the five other corners. These have been discussed in conjunction with the analysis of Figure 4, with the exception of the value at corner B. We assume that since the ionization of hydrate is associated with a ρ of +1, its protonation should have a ρ near −1.

The two points represent the location of transition states with $\rho = -1.1$ and $\alpha = 0.46$, or approximately the transition state for the 3-chloro system with formic acid as the catalyst. We again consider the movement of the transition state in two situations, for a change to a more electron withdrawing substituent and for a change to formaldehyde. The α value for dehydration of formaldehyde hydrate is 0.29,[6] so that each substitution is resulting in a decrease in the α value. The lines drawn in Figure 6 represent the direction that the transition state will tend to move with these substituent changes. For the class n reaction, the transition state tends to move toward corner E, the protonated aldehyde, since this is destabilized relative to A, the neutral hydrate, and it tends to move toward B, the protonated hydrate, since this is stabilized (less destabilized) relative to D, the protonated aldehyde. The class e transition state has a small tendency to move toward F, the free aldehyde, since this is more destabilized than the protonated hydrate at B (compare ρ values); there should also be significant movement toward C, the zwitterion, which is stabilized relative to the protonated aldehyde. With respect to the proton transfer axes, the prediction is a net increase in α for a class n mechanism and a net decrease for a class e mechanism. The latter is observed, and again our data provide strong support for the mechanistic conclusion of Funderburk, Aldwin, and Jencks.[6]

The class n mechanism can be ruled unlikely on other grounds. A model[6] for this mechanism is the acid-catalyzed oxocarbocation forming step of an acetal hydrolysis. Benzaldehyde acetal hydrolysis is characterized by $\rho = -3.2$ and $\alpha = 0.9$,[18] so that the true transition state in the class n half of Figure 6 must lie very near corner E, the protonated aldehyde or oxocarbocation. Moreover, the rates for these acetals are significantly slower than the corresponding rates for hydrate decomposition (Table V), suggestive again that the acetal mechanism is a poor model.

With the same aldehyde different α values are observed for the catalysis by RCOOH and RPO_3H^- (Table VI). A possible explanation for this is that the overall Brønsted plot is curved, and the two lines which have been drawn through the two acid sets merely represent approximate straight line segments. A curved correlation is pictured for 4-nitrobenzaldehyde in Figure 5. This has been obtained by artifically lowering[34] the phosphonic acid points by a constant factor such that a continuous curve is obtained with the carboxylic acid points. Support for such an operation can be seen in the fit of the cacodylic acid rate to the curve which is obtained. This catalyst in its charge type is like a carboxylic acid, and yet it shows a small poisitive deviation from the straight line drawn through this set. The question of H_3O^+ is also interesting. The electrostatic arguments would suggest a diminished reactivity due to an unfavorable δ^+–δ^+ interaction in the transition state. The H_3O^+ point, however, is slightly above the extrapolated straight line based on RCOOH. As indicated in Figure 5, this may be accidental. The inherent position in the absence of the electrostatic effect may be higher because of the curved relationship.

A curved Brønsted relation is a direct correlation[21] representing the effect of a substituent in a reacting group (the acid) on a first derivative coefficient (α or $\partial k/\partial pK_{HA}$). The curvature in Figure 5 is unusual since α is increasing with decreasing pK_{HA} or a stronger acid is resulting in a greater amount of proton transfer at the transition state. In terms of Figure 6 an increase in acid strength raises the right-hand side (CF) of the class e reaction coordinate relative to the left-hand side (BE). This results in a movement parallel to the reaction coordinate toward F and a movement perpendicular to the reaction coordinate toward E. With respect to the proton transfer coordinate these two effects operate in the opposite direction. A greater importance for the perpendicular movement is required for the curvature which we are suggesting.[35]

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(31) Bell, R. P. "Acid-Base Catalysis"; Oxford University Press: London, 1941.

(32) Kresge, A. J.; Chiang, Y. *J. Am. Chem. Soc.* **1973**, *95*, 803–806.

(33) (a) Harron, J.; McClelland, R. A.; Thankachan, C.; Tidwell, T. T. *J. Org. Chem.* **1981**, *46*, 903–910. (b) The reaction of this study, the reversible ring opening of two cyclic benzaldehyde hemiacetals, obviously bears a close relation to the benzaldehyde dehydration, and similar Brønsted plots were in fact observed.

(34) Chwang, W. K.; Eliason, R.; Kresge, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 805–808. Chiang, Y.; Chwang, W. K.; Kresge, A. J.; Robinson, L. H.; Sagatys, D. S.; Young, C. I. *Can. J. Chem.* **1978**, *56*, 456–460.

(35) We suggested a similar curved Brønsted relation with the hemiacetals of ref 33. Our interpretation there was in terms of competing class e and class n reactions. We feel that this cannot be the explanation with the benzaldehyde hydrates and is probably wrong also with the hemiacetals.

In summary, we can conclude that the three-dimensional energy surface for acid-catalyzed hydration–dehydration is such that relatively small variations in structure can result in significant changes in the position of the transition state. The same reaction mechanism, however, is in operation whether the aldehyde has a large tendency to hydrate, as with formaldehyde, or little tendency to hydrate, as with benzaldehydes.

Experimental Section

3,5-Dinitrobenzaldehyde was a gift of Professor P. Yates. All other aldehydes were commercially available. The hydration equilibrium constant for 3,5-dinitrobenzaldehyde was measured by using the method of Bell and Sorenson.[9]

Rate constants were measured by using a Durrum-Gibson stopped-flow spectrophotometer. The aldehyde dissolved in 0.1 M NaOH–0.5 M NaCl was mixed in the spectrophotometer with solutions containing 0.1 M HCl, buffer, and NaCl such that the total ionic strength was also 0.6. The wavelength maximum of the aldehyde was monitored. The photomultiplier output was digitized and the digital data were transferred to a Tektronix 4050 minicomputer. A total of 118 data points were obtained in each kinetic run. First-order rate constants were calculated by using the infinity method [ln $(A_\infty - A_t)$ vs. t] in most cases, with the Guggenheim method being used for runs with a half-life greater than 5 s. For each solution, five to nine separate kinetic runs were carried out, and the rate constnats were calculated as the average of these.

Acknowledgment. Continued financial support from the Natural Sciences and Engineering Research Council of Canada is greatefully acknowledged.

Registry No. H_3O^+, 13968-08-6; H_2O, 7732-18-5; OH^-, 14280-30-9; $CH_2CNCOOH$, 372-09-8; $CH_2ClCOOH$, 79-11-8; $CH_2OMeCOOH$, 625-45-6; HCOOH, 64-18-6; $Cl(CH_2)_3COOH$, 627-00-9; CH_3COOH, 64-19-7; CH_2CNCOO^-, 23297-32-7; CH_2ClCOO^-, 14526-03-5; $CH_2OMeCOO^-$, 20758-58-1; $HCOO^-$, 71-47-6; $Cl(CH_2)_3COO^-$, 75974-45-7; CH_3COO^-, 71-50-1; $H_2PO_4^-$, 14066-20-7; HPO_4^{2-}, 14066-19-4; $CCl_3PO_3H^-$, 59641-42-8; $CHCl_2PO_3H^-$, 57556-34-0; $CH_2ClPO_3H^-$, 54947-16-9; $CH_2OHPO_3H^-$, 62305-76-4; $CH_3PO_3H^-$, 39863-50-8; $(CH_3)_2AsO_2H$, 75-60-5; hydrogen sulfite, 15181-46-1; 3,5-dinitrobenzaldehyde, 14193-18-1; 4-chloro-3-nitrobenzaldehyde, 16588-34-4; 4-nitrobenzaldehyde, 555-16-8; 3-nitrobenzaldehyde, 99-61-6; 4-(trifluoromethyl)benzaldehyde, 455-19-6; 3-chlorobenzaldehyde, 587-04-2; 4-chlorobenzaldehyde, 104-88-1; 4-chlorobenzaldehyde hydrate, 54365-48-9; 3-chlorobenzaldehyde hydrate, 85152-57-4; 4-(trifluoromethyl)benzaldehyde hydrate, 85152-58-5; 3-nitrobenzaldehyde hydrate, 85152-59-6; 4-nitrobenzaldehyde hydrate, 55649-04-2; 4-chloro-3-nitrobenzaldehyde hydrate, 85152-60-9; 3,5-dinitrobenzaldehyde hydrate, 85152-61-0.

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(36) The mathematical analyses suggested by Jencks and Jencks[21] are difficult here since ρ is not proportional to carbon–oxygen bond formation and cleavage. An important parameter is also missing, the direct correlation coefficient $\partial\rho/\partial\sigma$. A nonzero value for this corresponds to a curved Hammett plot. We feel that the substituent range is not sufficiently large to determine if such curvature exists.

N,N′-Dinitrosation of Pt(IV)-Coordinated 1,2-Ethanediamine: Crystal and Molecular Structure of Chloronitro(bipyridyl)(*N*,*N*′-dinitroso-1,2-ethanediaminato)platinum(II) Hemihydrate

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Contribution from the Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680. *Received August 9, 1982*

Abstract: A Pt(IV) complex of the previously unknown ligand, the dianion of *N*,*N*′-dinitroso-1,2-ethanediamine, was synthesized by nitrosation of coordinated 1,2-ethanediamine and characterized by X-ray crystallography and ^{13}C NMR spectroscopy. $[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]$ gives monoclinic crystals with a = 11.739 (4) Å, b = 7.332 (2) Å, c = 19.423 (6) Å, and β = 102.55 (2)° in space group $P2_1/c$. The structure was solved by the heavy atom method and refined by least-squares methods to a conventional R factor of 0.058 for 2268 observed data. In the crystal, one of the *N*-nitroso groups is syn and the other is anti to the carbon atoms of the five-membered en chelate ring, and the N–O distances in the N-coordinated nitro group differ greatly (1.278 (20) Å and 1.130 (19) Å). In the ^{13}C NMR spectrum, every carbon atom gives a different signal.

Primary amines coordinated to Pt(IV) can be N-nitrosated by treatment in aqueous solution with alkali metal nitrites,[1-3] an interesting reaction that has not been extensively studied. Complexes of this type may be of special interest because of the notorious carcinogenicity of many *N*-nitrosamines. This paper reports the N,N′-dinitrosation of Pt(IV)-coordinated 1,2-ethanediamine (en). The result is a complex of the new ligand $(ONNCH_2CH_2NNO)^{2-}$.

Experimental Section

Synthesis. *trans*-Dichloro(bipyridyl)(1,2-ethanediamine)platinum(IV) chloride pentahydrate, $[Pt(bpy)(en)Cl_2]Cl_2 \cdot 5H_2O$, was prepared from $[Pt(bpy)(en)]Cl_2$ according to the method of Morgan and Burstall.[4] Two grams (3.11 x 10^3 mol) of it was dissolved in 20 mL of boiling water. To this was added 0.794 g (9.33 x 10^3 mol) of KNO_2 dissolved in 10 mL of boiling water. There was an immediate precipitation of an orange solid. The mixture was kept on the steam bath for 3 h. After the mixture cooled to room temperature, the precipitate was filtered off and washed with hot water, ethanol, and then ether. It was dissolved in boiling *N*,*N*′-dimethylformamide and recrystallized by cooling and evaporation. It decomposed explosively at 210 °C. Yield: 1.45 g (84%). Anal. Calcd for $[Pt(C_{10}H_8N_2)(C_2H_4N_4O_2)ClNO_2] \cdot 0.5H_2O$: C, 25.84; H, 2.35; N,

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