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The Kinetics of the Aquation of Iron(III) Chloride. The Role of Water Structure and of the Intermediate $FeOHCl^+$

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The influence of lithium, potassium, and cesium nitrates on the rate of aquation of Fe(III) has been investigated. The acid-independent and the acid-dependent paths are found to be influenced in opposite directions, whereas no specific cationic effects can be expected from the theory of salt effects. The observed effects are tentatively ascribed to the influence of water structure. It is shown that the latter path must proceed *via* $FeOHCl^+$. The formation constant of this compound, *i.e.*, the hydrolysis constant of $FeCl^{2+}$, is estimated from kinetic experiments at low acid concentration and is found to be similar to the hydrolysis constant of Fe^{3+}. Isokinetic relationships are found to hold with $d\Delta H^{\ne}/d\Delta S^{\ne} = 319$ and 305°K for the acid-independent and the acid-dependent paths, respectively.

Introduction

We have recently suggested[2–4] that the rates of reactions in aqueous solution in which water takes part as a reactant should be influenced by factors which influence the properties of water, such as temperature, and structure making or structure breaking solutes. In further pursuance of this topic, we decided to investigate environmental effects on an aquation reaction. We chose iron(III) chloride, because fairly detailed information is available about the kinetics[5,6] and the equilibrium constant of the formation[7–10] of this substance. The rate-determining step in most complex formations is water loss from the inner coordination sphere after an ion pair has been formed.[11,12] The rate of *aquation* is therefore controlled by the *entry* of a water molecule into the inner coordination sphere. The importance of the solvent in reactions of this type has recently been stressed by Caldin.[13]

In the course of the kinetic investigation, we found it necessary to determine also the influence of some electrolytes on the equilibrium constant[14] of $Fe(OH)^{2+}$.

Experimental Section

The kinetic experiments were carried out by the temperature-jump method in an apparatus constructed by the Messanlagenstudiengesellschaft mbH, Göttingen, West Germany. The extent of the jump was ~3.4°; at temperatures which were not very near room temperature, the difference in temperature between the thermostat and the cell was measured as described elsewhere.[4] The reaction was followed spectrophotometrically at 390 nm. The change in absorbance ascribed to the equilibrium under investigation was $(3\text{–}4) \times 10^{-2}$ unit. An initial very rapid increase in the absorbance was ascribed to a shift in the $Fe(OH)^{2+}$–Fe^{3+} equilibrium. Typical oscilloscope traces are shown in Figure 1, where the signal to noise ratio can be seen to be very satisfactory. The relaxation times were evaluated with the aid of a device developed in our department.[15]

For every reaction mixture, about four jumps were carried out. The values of τ exhibited a maximum spread of 10%, but usually much less.

The formal concentrations of Fe(III) and Cl^- were both 0.04 *M* (obtained by mixing $FeCl_3$ and $Fe(NO_3)_3$ in the ratio 1:2), except when otherwise stated. The H^+ was added in the form of nitric acid.

The determination of the formation constant of $Fe(OH)^{2+}$ was carried out in a Cary 14 spectrophotometer using essentially the method of Milburn and Vosburgh.[8]

Results

(a) Methods of Evaluation.—The formation of $FeCl^{2+}$ is known[5,6] to be first order with respect to both reactants. The second-order "rate constant" is composed of an acid-independent term involving Fe^{3+} (path 1) and a term proportional to $1/[H^+]$ (path 2) ascribed to $FeOH^{2+}$ which has a much higher rate constant. If the concentration of the latter species is sufficiently low (see below), the expected expression for $1/\tau$ can be written

$$1/\tau = (k_1 + k_2/[H^+])[1 + ([Fe^{3+}] + [Cl^-])K] \quad (1)$$

where K is the equilibrium constant for the formation of the complex, and the rate constants refer to aquation by reaction paths 1 and 2. If eq 1 is obeyed, a plot of $1/\tau$ *vs.* $1/[H^+]$ should yield a straight line from which the two rate constants can be calculated. (In practice, we usually found it more convenient to plot $(1/\tau)\cdot[1 + ([Fe^{3+}] + [Cl^-])K]^{-1}$ *vs.* $1/[H^+]$.) Because of the comparative weakness of our complex ($K \approx 4\ M^{-1}$ at the ionic strength employed by us) the contribution of the rate of complex formation is smaller than the contribution of its aquation. (The first term in the brackets, due to aquation, is unity, whereas the second, due to formation, is ~0.3 at most.) We therefore considered it sufficient to use the values of K interpolated for our ionic strengths from the results of Rabinowitch and Stockmeyer[7] in the presence of sodium perchlorate and perchloric acid, correcting for different temperatures using[7] $\Delta H = 8.5$ kcal mol^{-1}.

(b) Dependence on Hydrogen Ions.—In one series of experiments where [Fe(III)] and $[Cl^-]$ were both

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(1) This paper forms part of a thesis to be submitted by R. Koren to the Senate of The Hebrew University, in partial fulfilment of the requirements for a Ph.D. degree.

(2) B. Perlmutter-Hayman, *Isr. J. Chem.*, **9**, 377 (1971).

(3) B. Perlmutter-Hayman and Y. Weissmann, *J. Phys. Chem.*, **71**, 1409 (1967).

(4) B. Perlmutter-Hayman and R. Koren, *ibid.*, **76**, 582 (1972).

(5) R. E. Connick and C. P. Coppel, *J. Amer. Chem. Soc.*, **81**, 6389 (1969).

(6) T. Yasunaga and S. Harada, *Bull. Chem. Soc. Jap.*, **42**, 2165 (1969).

(7) E. Rabinowitch and W. H. Stockmeyer, *J. Amer. Chem. Soc.*, **64**, 335 (1942).

(8) R. M. Milburn and W. C. Vosburgh, *ibid.*, **77**, 1352 (1955).

(9) R. M. Milburn, *ibid.*, **79**, 537 (1957).

(10) H. Olerup, *Sv. Kem. Tidskr.*, **55**, 324 (1943); *Chem. Abstr.*, **40**, 2720 (1946).

(11) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

(12) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965).

(13) H. P. Bennetto, R. Bulmer, and E. F. Caldin in "Hydrogen-Bonded Solvent Systems," A. K. Covington and P. Jones, Ed., Taylor and Francis, London, 1968; H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. A*, 2191, 2198, 2207 (1971).

(14) We shall omit the water molecules of the first hydration shell except in the discussion of the mechanism.

(15) H. J. G. Hayman, *Isr. J. Chem.*, **8**, 603 (1970).

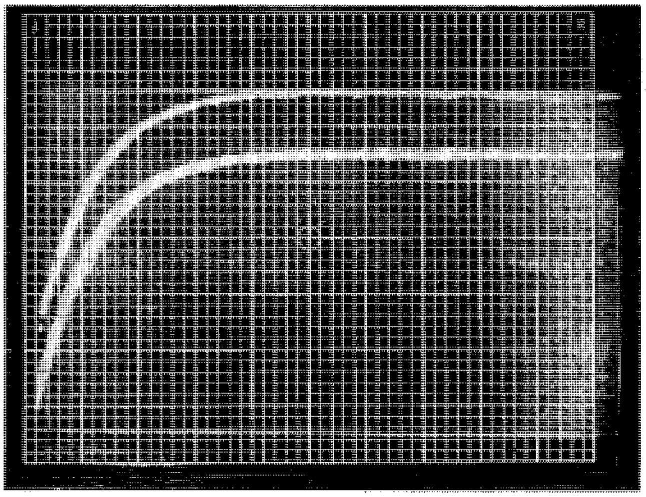

Figure 1.—Typical oscilloscope trace (in duplicate). Sensitivity 20 mV per large scale division; time scale 50 msec per large scale division.

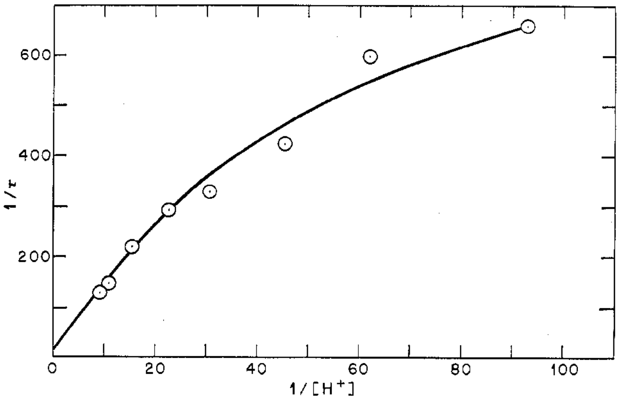

Figure 2.—A plot of $1/\tau$ *vs.* $1/[H^+]$ for experiments at low acidity.

0.05 M and the ionic strength was ~0.4 M, we varied $[H^+]$ between 0.011 and 0.11 M. Figure 2 shows the plot of $1/\tau$ against $1/[H^+]$ to be curved instead of straight; eq 1 is therefore inapplicable in this range.[16] Most experiments were carried out at $[H^+] \geqslant 0.1$, where eq 1 was found to hold, and paths 1 and 2 were found to make comparable contributions to the observed rate.

(c) **Experiments in the Presence of Lithium Nitrate.**—At five temperatures between 10.0 and 33.6°, the concentration of H^+ was varied between 0.13 and 0.43 M; the ionic strength I was kept constant at 0.64 M by the addition of $LiNO_3$ at appropriate concentrations. Values for k_1 and k_2 were calculated from plots of the type of Figure 3. The results are shown in plots of ln (k/T) *vs.* $1/T$ (Figure 4), where one point referring to $I = 0.89$ M and a temperature of 20° is also given. (At the highest temperature, 33.6°, the intercept in Figure 3, *i.e.*, k_1, was too small in comparison with the slope to be considered reliable; the corresponding point is therefore not included in Figure 4.)

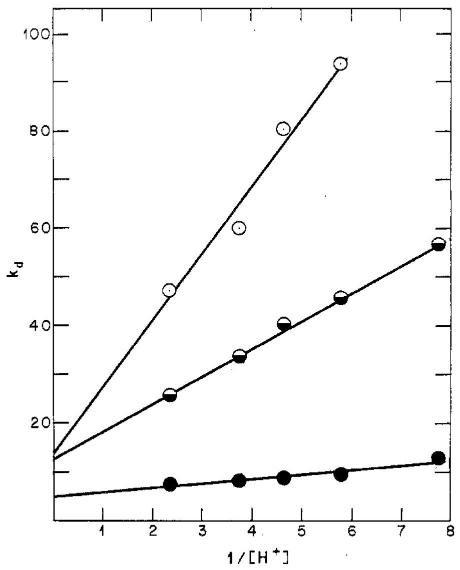

Figure 3.—Typical plots of $k_d \equiv (1/\tau)[1 + ([Fe^{3+}] + [Cl^-]) \cdot K]^{-1}$ *vs.* $1/[H^+]$, in the presenc of 0.64 M $LiNO_3$: ●, 10°; ◒, 25.5°; ○, 34°. The intercept is k_1, and the slope, k_2.

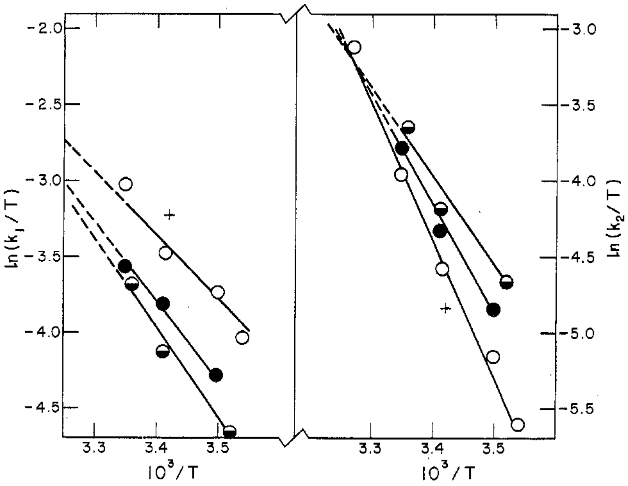

Figure 4.—Plots of ln (k/T) *vs.* $1/T$: ◒, 0.89 M KNO_3; ●, 0.64 M KNO_3; ○, 0.64 M $LiNO_3$; +, 0.89 M $LiNO_3$.

(d) **Experiments in the Presence of Potassium Nitrate.**—Experiments were carried out at three temperatures between 11 and 25° in a way analogous to that described under (b), except that potassium was substituted for lithium. The results are again shown in Figure 4. It can be seen that the effect on k_1 of replacing Li^+ by K^+ is the opposite of that on k_2.

(e) **Experiments in the Presence of Cesium Nitrate.**—Because of the low solubility of cesium nitrate, we had to content ourselves with determining its influence at low concentrations. This is shown in Figure 5, for $[H^+] = 0.13$ M, where results with $LiNO_3$ are shown for comparison. We see that, at low temperatures, the two salts have almost the same decelerating effect. At high temperatures, where path 2 predominates, the two salts differ considerably in their effect.

(f) **Activation Parameters.**—The activation parameters obtained from Figure 4 are summarized in Table I. Plots of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ (for path 1, including all four entries) give straight lines, with slopes of 320 ± 18 and 305 ± 2°K and correlation coefficients of 0.997 and 0.999 (rather better than can be expected from the ex-

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[16] At acid concentrations below 0.1 M, an additional, slower relaxation process was observed which depended on $[H^+]$ and on $[Cl^-]$ but persisted also in the absence of chloride. These features are characteristic of the dimerization of $Fe(OH)^{2+}$, as is the range of relaxation times (*e.g.*, $\tau \approx 0.4$ sec at $[H^+] = 0.02$ M and $[Cl^-] = 0.05$ M): B. A. Sommer and D. W. Margerum, *Inorg. Chem.*, **9**, 2517 (1970). Furthermore, the amplitude of this relaxation process decreased with increasing acidity, as it must when $[FeOH^{2+}]$ becomes lower and lower.

TABLE I

ACTIVATION PARAMETERS AND THEIR STANDARD DEVIATIONS

I, M	Added salt	$\Delta H_1^{\ddagger}$, kcal mol^{-1}	$\Delta H_2^{\ddagger}$, kcal mol^{-1}	$\Delta S_1^{\ddagger}$, eu	$\Delta S_2^{\ddagger}$, eu
0.64	$LiNO_3$	8.5 ± 1.0	18.0 ± 0.9	−25.0 ± 3.9	5.6 ± 0.3
0.64	KNO_3	9.4 ± 0.8	14.2 ± 1.8	−22.6 ± 2.4	−7.0 ± 1.0
0.89	KNO_3	12.0 ± 1.8	11.7 ± 3.1	−14.0 ± 2.6	−15.0 ± 4.9
1.0[a]	$NaClO_4$	10.0		−21	

[a] Reference 6.

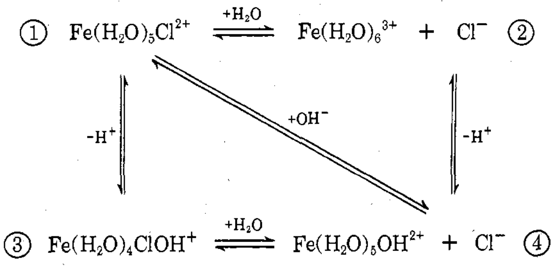
perimental precision!) for paths 1 and 2, respectively. This means that the data follow an isokinetic relationship.[17] In accordance with this,[18] the three lines for path 2 in Figure 4 cut at $1/T \approx 1/305$, whereas those for path 1 cut outside the graph at $1/T \approx 1/315$ to 1/324.

(g) The Formation Constant of $Fe(OH)^{2+}$.—At $[Fe(III)] = 2 \times 10^{-4}\ M$, the reciprocal of the apparent absorption coefficient ϵ_{app} ($\epsilon_{app} \equiv A/[Fe(III)]d$; d (path length) = 10 cm; A is absorbance) was plotted against $[H^+]$, for acid concentrations $(1\text{–}5) \times 10^{-3}$ M, in the presence of $LiNO_3$ and KNO_3 at $I = 1\ M$, at 18°. For the sake of comparison with data given in the literature,[8] the influence of $NaClO_4$ was also measured. Straight lines were obtained. This shows that at this low concentration of Fe(III), dimerization is negligible at the values of $[H^+]$ employed.[8] From the common intercept of these lines, together with some results at other temperatures, we get $\epsilon_{Fe(OH)^{2+}}$ 433 ± 20 at 360 nm, in reasonable agreement with previous results.[19] The equilibrium constant is calculated from the slope. The value of K_{OH} was found to change from $(2.6 \pm 0.2) \times 10^{-3}\ M$ in the presence of $LiNO_3$ *via* $(1.8 \pm 0.3) \times 10^{-3}\ M$ in the presence of KNO_3 to $(1.2 \pm 0.1) \times 10^{-3}\ M$ in the presence of $NaClO_4$.[20]

Discussion

(a) The Role of the Intermediate $FeOHCl(H_2O)_4^+$.—Since both Fe^{3+} and $Fe(OH)^{2+}$ undergo reaction with chloride, we have to consider Scheme I for aquation.

SCHEME I



The reaction ① → ② is our path 1. The vertical equilibria may be assumed to be very fast proton-transfer reactions between water and $Fe(H_2O)_5Cl^{2+}$ or $Fe(H_2O)_6^{3+}$, respectively. The only direct way from ① to ④, however, would be an exchange reaction of OH^- for Cl^-. This would give to k_2 of eq 1 the meaning $k_2 = k_{14}K_W$, where K_W is the ionization product of water. Since $k_2 \approx 10$, this would make k_{14} quite impossibly high. The system must therefore proceed from ① to ④ *via* ③. The meaning of k_2 now becomes $k_2 = k_{34}K_4$, where $K_4 = [FeClOH^+][H^+]/[FeCl^{2+}]$.

The existence of $FeOHCl^+$ as an intermediate has been assumed before for our[6] and for analogous[21,22] reactions, but nothing seems to be known about K_4. Some information about this quantity can be obtained from our experiments at low acid concentration where $1/\tau$ *vs.* $1/[H^+]$ is no longer linear. When $[FeOH^{2+}]$ and $[FeOHCl^+]$ are no longer negligibly small in comparison with $[Fe^{3+}]$ and $[FeCl^{2+}]$, respectively, eq 1 must be replaced by

$$1/\tau = [(k_1 + k_{34}K_4/[H^+])/(1 + K_4/[H^+])] \times [1 + (\Sigma[Fe^{3+}] + [Cl^-])K_{app}] \quad (2)$$

where $\Sigma[Fe^{3+}]$ is the sum of the total uncomplexed Fe(III), *viz.*, $[Fe^{3+}] + [FeOH^{2+}] + {}^1/_2[Fe_2(OH)_2{}^{4+}]$, and the apparent equilibrium constant K_{app} is

$$K_{app} = \frac{[FeCl^{2+}] + [FeOHCl^+]}{\Sigma[Fe^{3+}][Cl^-]} = \frac{K(1 + K_4/[H^+])}{(1 + K_{OH}/[H^+])(1 + K_dK_{OH}[Fe^{3+}]/2[H^+])} \quad (3)$$

where K_d is the dimerization constant[19] of $FeOH^{2+}$.

Assuming k_1 to be known from the experiments at $[H^+] \geqslant 0.1\ M$, we can transform eq 2 into

$$\frac{1/[H^+]}{(1/\tau)[1 + (\Sigma[Fe^{3+}] + [Cl^-])K_{app}]^{-1} - k_1} = \frac{1}{K_4(k_{34} - k_1)} + \frac{1}{(k_{34} - k_1)[H^+]} \quad (4)$$

Taking a trial value for K_{app} in which $K_4 = 0$, we can evaluate the left-hand side of eq 4 and plot it against $1/[H^+]$. From the slope and intercept we get a value for K_4 which enables us to calculate a better value for K_{app}, and so on. After two iterations the change in K_4 was within the limit of experimental error. This is because the expression on the left-hand side is not very sensitive to the exact value of K_{app}. We obtain $K_4 = 1.2 \times 10^{-2}$, with a standard error of $\pm 0.2 \times 10^{-2}$, at $I \approx 0.4\ M$. The actual accuracy may be considerably worse than suggested by the standard error, owing to systematic errors. There seems no doubt, however, that K_4 is of similar magnitude as K_{OH}, though somewhat higher.

It follows that the rate of aquation of the chloride complex is enhanced by the hydrolysis to a similar extent as is the rate of its formation. This is borne out by the value of $k_{34} = (8.1 \pm 1.0) \times 10^2$ obtained from the slope.

(b) Comparison with Previous Results.—Our results, in common with previous results concerning

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[17] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, Chapter 9.

[18] B. Rosenberg, *Discuss. Faraday Soc.*, **51**, 190 (1971).

[19] B. Behar and G. Stein, *Isr. J. Chem.*, **7**, 827 (1969).

[20] The formation of $FeOH^{2+}$ has served to demonstrate the principle of specific effects of ions of opposite sign: A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1322 (1949). It is interesting to note that at higher concentrations, specific effects of cations also appear. These effects cannot be explained on the basis of electrostatic considerations.

[21] D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

[22] F. P. Cavasino and M. Eigen, *Ric. Sci., Parte 2: Sez. A*, **34**, 509 (1964).

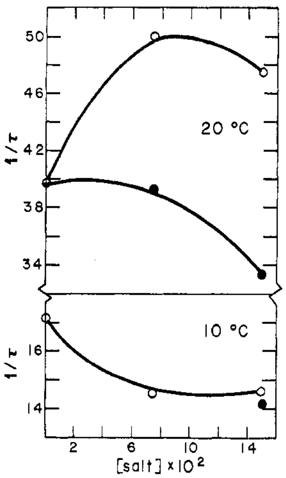

Figure 5.—Influence of $CsNO_3$ on $1/\tau$, at two different temperatures: ○, $CsNO_3$; ●, $LiNO_3$ for comparison.

FeCl (and most other complexes of Fe^{3+}!) pertain almost directly to the *dissociation* reaction. The constants for the rate of *formation* which are given and discussed in the literature depend strongly on the value which has been used for the equilibrium constant. All data given in the literature refer to $I = 1\ M$, achieved by the addition of $NaClO_4$ and perchloric acid. Therefore, comparison is difficult. Nevertheless, our extreme values of k_1 at 25° ($k_1 = 3.9 \pm 0.4$ in the presence of KNO_3, and $k_1 = 10 \pm 1.0$ in the presence of $LiNO_3$, both at $I = 0.89\ M$) include those of previous authors within their range, whereas those of k_2 ($k_2 = 4.0 \pm 0.4$ and $2.0 \pm 0.2\ M^{-1}\ \text{sec}^{-1}$ under conditions as above) are only slightly lower. Similar remarks hold for the $\Delta S^{\ne}$ and $\Delta H^{\ne}$ values (see Table I); in particular, it should be noted that the point ($\Delta S_1^{\ne}$; $\Delta H_1^{\ne}$) of Yasunaga and Harada[6] lies on the same straight line as the points measured by us.

Our value of K_{OH}, under identical conditions, differs from that given in the literature[8] by no more than 9% which is within one standard deviation.

(c) **The Effect of Supporting Cations.**—Our previous results[3,4] concerning reactions in which water is an active participant lead us to expect that here, too, structure breaking should enhance the reaction rate. This expectation is fulfilled by the behavior of k_2; the rate is faster in the presence of KNO_3 than in the presence of $LiNO_3$, the difference becoming more pronounced the higher the concentration of supporting salt. Furthermore, Cs^+, even at the low concentration employed, has a marked accelerating effect.

However, we know k_2 to be a composite quantity, *viz.*, $k_2 = k_{34}K_4$. The effect we have just discussed operates on the rate of hydrolysis, *i.e.*, on k_{34}. It should be stressed that this effect does not arise from the fact that $Fe(H_2O)_4ClOH^+$ is an ion. Existing theories on ionic effects would predict a very small effect for our reaction, taking place between an ion and a dipolar molecule. The same is not true for K_4, which, classically, should increase with increasing ionic strength, irrespective of the nature of the cation. The possibility of specific effects has however also to be considered. Unfortunately, our method described under (a) is not sufficiently sensitive for changes in K_4 to be determinable with any confidence. We may expect, however, that K_4 should exhibit some parallelism with the analogous K_{OH}, which we have found to be higher in the presence of $LiNO_3$ than in the presence of KNO_3, at the same ionic strength. We conclude that the influence on K_4 is outweighed by that on k_{34} in the product which makes k_2.

Let us now consider k_1. Again, from classical considerations this quantity, referring to a reaction between an ion and a dipolar molecule, should exhibit only a weak ionic effect. Instead, we found a pronounced specific influence, this time in the opposite direction.

The rate of formation of Fe^{3+} complexes is known to proceed at a higher rate the more basic the ligand X^-. This can be explained when the reaction is assumed to take place not between Fe^{3+} and X^-, but rather between $FeOH^{2+}$ and HX, the two mechanisms being kinetically indistinguishable.[11,12,21,23-26] The rate constants thus obtained are all within the range which is "normal" for substitution on $FeOH^{2+}$. Less attention has been devoted to the rate of *aquation* of these complexes. When we compare the rate constants of complexes with highly basic ligands[23,24] with those of, say, chloride and bromide complexes, a similar, though far less pronounced, dependence on ligand basicity becomes apparent for the rate of aquation. For substituted phenolates as ligands, a linear free energy relationship between basicity and rate of aquation has actually been found to hold by Cavasino, *et al.*;[24] this has been attributed[24] to the fact that $Fe(H_2O)_4OH^{2+}\cdot HX$ is formed from $Fe(H_2O)_5X$ more easily the more basic the ligand, an effect which, according to these authors, outweighs the increase in binding power between the ligand and the central ion.

According to the principle of microscopic reversibility, the rate-determining step should be the entry of a water molecule into the inner coordination sphere, while the ligand is already in the outer sphere. Such a mechanism is hinted at by Eigen and Wilkins.[12] The assumption that the tendency of a complex to dissociate in this way should be greater when it can form $Fe(H_2O)_4OH^{2+}\cdot HX$ rather than $Fe(H_2O)_5{}^{3+}\cdot X^-$ is in line with Cavasino's ideas. In addition, the entry of water into the former compound might be expected to be faster than the entry into the latter. Now, with our weakly basic ligand Cl^- the pathway *via* $Fe(H_2O)_4OH^{2+}\cdot HX$ can hardly be assumed; in this case, however, the rate of hydrolysis may increase with the ability of a neighboring *water* molecule to accept a proton, in a kind of "internal hydrolysis" (suggested originally by Eigen[27] to explain the abnormally fast reactions between Fe^{3+} and basic ligands). This would labilize the ligand (as borne out by the fact that $k_{34} > k_1$) and thus facilitate its exchange for a water molecule which, itself, has not been involved in internal hydrolysis. Thus two solvent molecules could play the role of the two amine groups of a polyamine in Rorabacher's "internal conjugate base effect."[28]

Therefore, our results can be explained if we assume

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[23] F. Accascina, F. P. Cavasino, and E. di Dio, *Trans. Faraday Soc.*, **65**, 489 (1969).

[24] F. P. Cavasino and E. di Dio, *J. Chem. Soc. A*, 1151 (1970).

[25] H. A. Espenson and J. R. Helzer, *Inorg. Chem.*, **8**, 1051 (1969).

[26] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 199.

[27] M. Eigen in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1971, p 379.

[28] D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

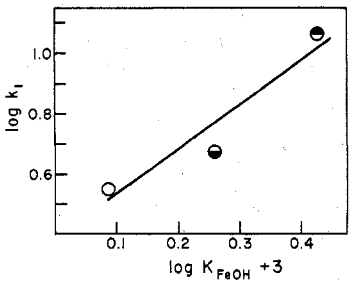

Figure 6.—Linear free energy relationship between k_1 and K_{FeOH}: ○, $NaClO_4$ (1 *M*); ◒, KNO_3 (1 *M* for K_{FeOH} and 0.89 *M* for k_1); ◓, $LiNO_3$ (1 *M* for K_{FeOH} and 0.89 *M* for k_1).

the hydrogen-bonded form of water to accept a proton from $FeCl(H_2O)_5^{2+}$ not only with more rapidity[4] but also to a larger extent than does the non-hydrogen-bonded form. This would explain why substituting the structure-breaking potassium nitrate for lithium nitrate causes the reaction rate to decrease. (With cesium, at low temperatures, where paths 1 and 2 make comparable contributions, the effect on k_2 (see above) seems to cancel that on k_1 when τ is measured.) The effect of enhanced proton transfer thus outweighs the accelerating effect which makes a water molecule in broken-down surroundings more reactive.

The argument is further strengthened by the fact that k_1 is influenced in a similar way as is K_{OH} which is rather analogous to the hydrolysis constant of $Fe(H_2O)_5Cl^{2+}$. In Figure 6 we show a linear free energy relationship plot between K_{OH} and k_1, taking K_{OH} from our measurements at 18°, k_1 in the presence of $LiNO_3$ and KNO_3 from our measurements at 19.6°, and k_1 in the presence of $NaClO_4$ from the results of Yasunaga and Harada[6] at 25°, using their value of $\Delta H^{\ddagger}$ to correct to 19.6°. The parallelism of the influences on the two constants is obvious, the rate constant being affected by the change of supporting cation more strongly than is K_{OH}.

The slopes of the $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ plots lie in a range encountered for many reactions where solvent effects in aqueous media have been studied.[17,29] This, again, agrees well with our above interpretations.

Whereas the evidence presented in this paper is insufficient to prove our suggestion, the explanation of the observed effects in terms of water structure thus seems to present a consistent picture.

Acknowledgment.—The authors thank S. de Groot for carrying out the spectrophotometric measurements.

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[29] R. Lumry and S. Rajander, *Bioyolymers*, **9**, 1125 (1970).

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An Investigation of Iodine–Nitrile Complexes in Different Solvents

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The formation equilibrium constants, *K*, for the molecular complexes formed between iodine and a series of aliphatic nitriles were studied in several solvents and values of $\Delta H°$ and $\Delta S°$ determined. The variation in *K* with nitrile was small but consistent with the Taft σ^* values of the nitriles. The values of *K* increased in the order aceto- < propio- < butyro- < valero- < pivalonitrile in the solvent carbon tetrachloride. Any change in the thermodynamic parameters with nitrile was masked by the experimental uncertainty and no variation could be detected. The same general behavior was found in *n*-heptane. In addition, *K*, $\Delta H°$, and $\Delta S°$ were determined for the butyronitrile–iodine complex in several other solvents. In these solvents, *K* increased in the order tetrachloroethylene < carbon tetrachloride ≈ carbon disulfide < cyclohexane ≈ *n*-hexane < *n*-heptane. This variation could not be ascribed to any systematic change in either $\Delta H°$ or $\Delta S°$. There is a compensation between $\Delta H°$ and $\Delta S°$ in that solvents in which $\Delta H°$ is large also have large values of $\Delta S°$. The value of *K* appears to be more a function of solvent type than any specific solvent parameter.

Introduction

The molecular complexes formed between iodine and a variety of bases have been investigated extensively. Attempts have been made to correlate the stabilities of the complexes with the nature of the base using such parameters as the Taft σ^* value of the base,[1] its ionization potential,[2] Hammett σ values,[3] and more complex parameters such as those proposed by Drago and coworkers.[4] In addition to the nature of the base, the solvent has been found to have an effect on the stability of a particular complex.[5] Although the variation in complex stability with base can be adequately accounted for using one of the above parameters, the influence of solvent is not well understood. To date, very few complexes have been studied in a sufficient number of solvents to allow much correlation. In addition, the reliability of the equilibrium constant *K* determined by spectrophotometric measurements has been questioned. The determined values of *K* for a number of complexes have been found to exhibit rather drastic variations with wavelength. These variations have been attributed to either the formation of termolecular complexes[6] or deviations from Beer's law.[7] Some of the differences in the values of *K* ascribed to changes in solvent or base may be due in part to the fact

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