The Kinetics of the Hydrolysis of the Dichromate Ion.   VI.   Environmental

Influences on the Acid-Catalyzed Reaction[1]

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The influence of electrolytes, of dioxane, and of temperature on the rate of the acid-catalyzed hydrolysis of the dichromate ion has been investigated by the T-jump method.   Where comparison is possible, the results are in excellent agreement with those reported earlier.   The effect of sodium salts shows only a slight deviation from "classical" behavior.   The apparent energy of activation is 8.92 ± 0.34 and 8.26 ± 0.44 kcal mol^{-1} at an ionic strength of 0.05 and 0.20, respectively.   The influence of dioxane is less pronounced than would be expected from its influence on the dielectric constant.   Tetramethylammonium chloride has a stronger decelerating influence than the sodium salts, at the same time, however, decreasing the apparent energy of activation, especially when temperatures up to 29° are considered.   The influence of water structure is discussed as a possible explanation for the effects of dioxane and of tetramethylammonium chloride.

Introduction

In a previous paper of this series,[2] the activation energy of the hydrolysis of the dichromate ion, *viz.*

$$Cr_2O_7{}^{2-} + H_2O \rightleftharpoons 2HCrO_4{}^- \qquad (1)$$
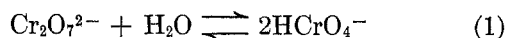
was found to decrease with increasing temperature. Furthermore, the addition of electrolytes was found to enhance the rate of reaction, whereas the addition of dioxane or of tetraethylammoniumbromide was found to decrease the rate. It was suggested that these phenomena might be explained by the reaction taking place more rapidly the more the hydrogen-bonded structure of water has broken down—owing either to an increase in temperature or to the presence of structure-breaking substances.

The present investigation was undertaken in order to find out whether similar effects exist also for the reaction catalyzed by hydrogen ions.

Experimental Section

All our experiments were carried out in a T-jump apparatus.

The stoichiometric concentration of $K_2Cr_2O_7$ was in the range $4-12 \times 10^{-4}$ M, and the wavelength used for detection was 385-405 nm; the lower wavelength, where the extinction coefficient of $Cr_2O_7{}^{2-}$ is higher, was employed for the lower concentrations, and *vice-versa*. The electrolyte necessary to ensure sufficient conductance was either provided by the catalyzing acid itself, or by the electrolyte whose influence was being investigated.

The values of k_{H^+}, the catalytic constant for the reaction in the forward direction (referring, as usual, to the "reaction variable"[3] and measured in M^{-1} sec^{-1}) were obtained from the intercept of plots of $1/\tau$ against five different concentrations of $HCrO_4{}^-$,

calculated from the stoichiometric concentration of $K_2Cr_2O_7$, together with the equilibrium constant of reaction 1 found spectrophotometrically in the presence of various electrolytes.[4]   Each point on a plot was the mean of two to five experiments, exhibiting a maximum spread of $\pm 10\%$, but usually much less.   The intercepts, calculated by the method of least squares, showed a standard deviation of $\sim 9\%$.   The catalytic constant of the back reaction cannot be obtained from these plots; the reason for this is explained elsewhere,[5] where further details on the experimental method are also given.

The changes in absorbance were $6-10 \times 10^{-3}$ unit and enabled a very satisfactory signal to noise ratio to be obtained.   This is exemplified in Figure 1 which shows a typical oscilloscope trace.

The relaxation times were evaluated with the aid of a device developed in our department.[6]

Near room temperature, the temperature in the cell before the T-jump was taken as that of the thermostat from which water was circulated, and which was constant to $\pm 0.1°$.   At other temperatures, the temperature difference between the bath and the T-jump cell had to be taken into account, and was measured with a copper–constantan thermocouple.   The extent of the T-jump, ΔT, was calculated from the known capacity

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

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

(3) See, *e.g.*, A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 9.

(4) B. Perlmutter-Hayman and Y. Weissmann, *Israel J. Chem.*, **6**, 17 (1968).

(5) B. Perlmutter-Hayman and R. Koren, *ibid.*, **8**, 1 (1970).
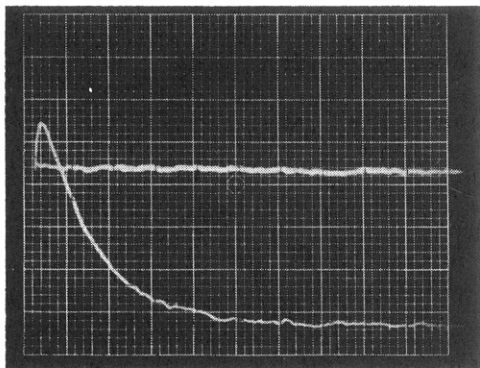
(6) H. J. G. Hayman, *ibid.*, **8**, 603 (1970).

Figure 1. A typical oscillogram; time scale: 5 msec per large scale division; sensitivity of oscilloscope: 5 mV per large scale division. (The horizontal line corresponds to the absorption before the T-jump; the initial rise in the curve has independently been ascertained to follow the time-constant of our high frequency filter and may be ascribed to small changes of the extinction coefficients with temperature.)
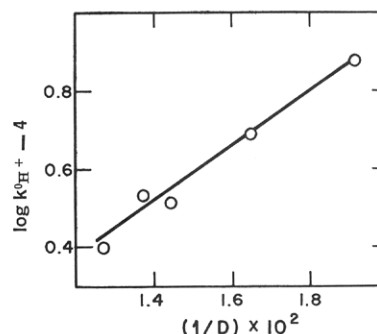

Figure 2. The logarithm of the rate constant, corrected to zero ionic strength, as a function of the reciprocal dielectric constant, in water–dioxane mixtures. (Data for dielectric constant from C. V. King and J. J. Josephs, *J. Amer. Chem. Soc.*, **66**, 767 (1944).)

and voltage of our condenser and the effective volume of the cell, and was between 3.5 and 4.6°. To minimize uncertainties in ΔT, we used the *same* cell throughout the present investigation. We estimate the error in T to be small in comparison with that in k_{H^+}.

Most of our calculations were carried out with the aid of a CTC 6400 computer.

Results

(a) *Influence of Dioxane*. The influence of dioxane was investigated at 24.6° in the presence of 0.044 M perchloric acid at dioxane concentrations up to 30%. Since water takes part in the stoichiometry of our reaction, the rate constants were multiplied by 55.56/[H₂O]. The resulting values of k_{H^+} increased with increasing dioxane concentration. Now, the dielectric constant, D, of the reaction mixture decreases with increasing dioxane concentration; this effect is therefore in the direction expected from classical theory for a reaction between ions of unlike sign. According to this theory, a plot of the logarithm of k^0, the rate constant at zero ionic strength, against $(1/D)$ should yield a straight line with a slope inversely proportional to a, the distance between the reactants in the activated complex.[7] Since our experiments were all carried out at the same ionic strength I, it might at first sight seem justified to use the values of k_{H^+} directly for a plot of this kind. However, at different values of the dielectric constant, the rate constants are differently affected by the ionic strength. Unfortunately, measurements at low ionic strength cannot be carried out by our method. Therefore, again basing ourselves on classical electrolyte theory, we added

$$2|z_A z_B|A_{H_2O}(D_{H_2O}/D_{mixture})^{3/2}\sqrt{\bar{I}}/(1 + \sqrt{\bar{I}})$$

(where A_{H_2O} is the constant of the Debye–Hückel equation in water at 25°, and z_A and z_B are the valencies of the reactants) to the logarithm of k_{H^+} in order to

obtain at least a reasonable approximation to log $k^0_{H^+}$ (see section b). Obviously, the values of $k^0_{H^+}$ increase with increasing dioxane concentration more strongly than do those of k_{H^+}. Nevertheless, the plot of log $k^0_{H^+}$ *vs.* $1/D$, shown in Figure 2, yields $a \sim 7$ Å which is unreasonably high.[7] In other words, even after all corrections are applied, dioxane is found to increase the rate less than would be expected from its influence on the dielectric constant. (For a to have a more realistic value, say 3.5 Å, the rate constant in the presence of 30% dioxane would have to be 3 times higher than our experimental value.)

(b) *Influence of Electrolytes*. Again at 24.6°, we investigated solutions 0.046 M in nitric acid, and containing sodium or tetramethylammonium chloride at varying concentrations, up to 0.2 M. Experiments at 0.1 M sodium nitrate and perchlorate and a similar concentration of nitric acid were also carried out. Following a procedure first suggested by Guggenheim and Prue,[8] we plotted log $k^{0\prime}_{H^+}$ against the concentration of the added electrolyte. (This quantity is defined by

$$\log k^{0\prime}_{H^+} \equiv \log k_{H^+} + 2.03\sqrt{\bar{I}}/(1 + \sqrt{\bar{I}}) \quad (2)$$

where k_{H^+} is the rate constant measured at ionic strength I, and is thus a rate constant which has been partially corrected for the influence of ionic strength.) If the Guggenheim equation[9] is obeyed, this plot should yield a straight line with a *small* positive slope, corresponding to a suitable combination of the interaction parameters of that equation.[8] The result is shown in Figure 3. We find that though $k^{0\prime}_{H^+}$ indeed changes only slightly with ionic strength, the

(7) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941, pp 430–438.

(8) E. A. Guggenheim and J. E. Prue, "Physico-Chemical Calculations," North Holland Publishing Co., Amsterdam, 1955, p 466; see also B. Perlmutter-Hayman and Y. Weissmann, *J. Phys. Chem.*, **68**, 3307 (1964); B. Perlmutter-Hayman in *Progr. React. Kinet.*, **6**, 239 (1971).

(9) E. A. Guggenheim, "Thermodynamics," North Holland Publishing Co., Amsterdam, 1949, Chapter 9.
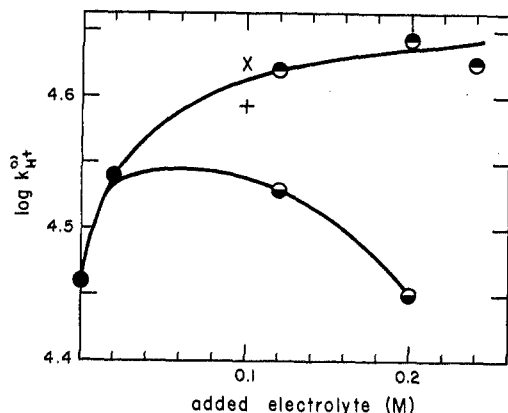
Figure 3. The dependence of log $k^{0'}{}_{H^+}$ (as defined by eq 2) on concentration of added electrolyte, in the presence of 0.046 M acid; ◗, sodium chloride; ✕, sodium nitrate; +, sodium perchlorate; ◒, tetramethylammonium chloride. Straight lines with a small positive slope would correspond to "classical" behavior.

Figure 4. The logarithm of the rate constant as a function of the reciprocal temperature: ○, [HClO₄] $\sim 0.05\ M$; ●, [HClO₄] $= 0.001\ M$ plus [NaClO₄] $= 0.20\ M$; ◒, [HClO₄] $= 0.001\ M$ plus [Me₄NCl] $= 0.20\ M$.

plots are curved instead of straight, especially at low concentrations of added salt. An extrapolation to $I = 0$ was therefore not attempted.

The sodium salts of different anions are seen to fall on or near the same curve which, at the high concentrations, has the expected small positive slope. On the other hand, the points for the tetramethylammonium ion, at concentrations above 0.02 M, begin to diverge in the direction of a stronger decelerating influence, the divergence reaching definite statistical significance at 0.2 M.

(c) *Influence of Temperature.* The influence of temperature was investigated in three series of experiments, in a temperature range from 6.3 (or 8.8) to 45°. In the first series, perchloric acid was $\sim$0.05 M, with no further substances added. In the second and third series, perchloric acid was $2 \times 10^{-3}\ M$ and 0.2 M NaClO₄ or tetramethylammonium chloride were added. Arrhenius plots are shown in Figure 4. For the first two series, straight lines were fitted by the method of least squares which yielded activation energies E_A of 8.92 ± 0.34 (standard deviation) and 8.26 ± 0.44 kcal mol^{-1}, respectively.

In the presence of tetramethylammonium chloride, however, the result is different. The best straight line through the experimental points yields $E_A = 7.59 \pm 0.81$, but this is not the best representation of the data. Without wishing to attach theoretical significance to any particular mathematical form, we fitted a quadratic equation to our points. This is the line shown in Figure 4. The coefficient of $(1/T)^2$ is 6 times its standard deviation; according to the t-test, this means that the change of activation energy with temperature is significant on a 99% level. When only the temperature range up to 29° is considered, we may say that E_A $\sim$ 5.9 kcal mol^{-1}.
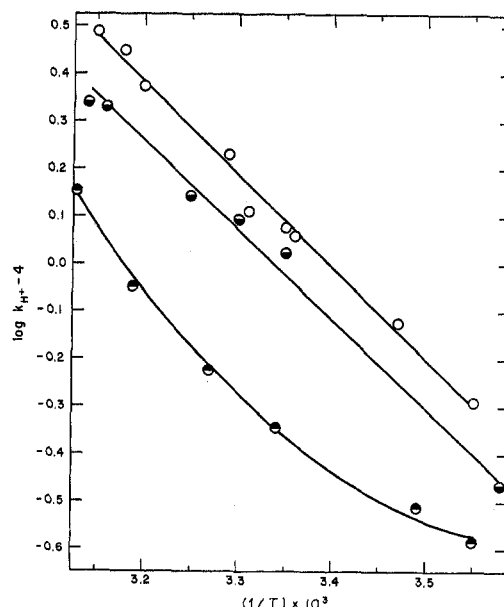
Discussion

Our present values of $k_{H^+} = 1.14 \times 10^4$ and $1.05 \times 10^4\ M^{-1}$ sec^{-1} at $I = 0.046$ and 0.2, respectively, are in excellent agreement with our previous results (where a stopped flow apparatus was employed for measurements in the presence of perchloric acid,[10] and ordinary mixing[10] or mixing with a rapid mixing syringe[11] for measurements in the presence of suitable buffers).

The influence of sodium salts on the reaction rate, though not exactly following classical behavior—the line in Figure 3 is curved instead of straight—may be considered essentially normal for a reaction of this charge type. This is further emphasized by the fact that the curve in Figure 3 corresponding to the sodium salts continues smoothly to the value calculated from Espenson's result[12] at $I = 1.0$, made up of lithium perchlorate and perchloric acid.

Similarly, the change of 0.66 kcal in activation energy as we pass from $I = 0.05$ to $I = 0.2$, though almost within the limit of experimental error, is in the direction expected from classical theory. (Employing the expression given in the literature[13] for the dependence of E_A on ionic strength and modifying it for

(10) B. Perlmutter-Hayman, *J. Phys. Chem.*, **69**, 1736 (1965).

(11) R. Baharad, B. Perlmutter-Hayman, and M. A. Wolff, *J. Phys. Chem.*, **73**, 4391 (1969).

(12) J. R. Pladziewicz and J. H. Espenson, *Inorg. Chem.*, **10**, 634 (1971); we should like to thank Professor Espenson for making his manuscript available to us before publication.

(13) E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, London 1947, Chapter 4. (The expression given for dE_A/dT at nonzero ionic strength is incorrect. Consequently the theoretical value for dE_A/dT is slightly smaller than that predicted on the basis of this reference.)

use at higher ionic strength by dividing through by $(1 + \sqrt{I})$, a slightly smaller change, viz. ~ 0.20 kcal mol^{-1}, may be predicted. Both a change of 0.20 and the difference between 0.66 and 0.20 kcal mol^{-1} are practically within the limit of experimental error.) Furthermore, our value of E_A at $I = 0.2$ lies midway between the two values obtained by Espenson, et al.,[12] at $I = 1.0$, on two slightly different assumptions concerning the equilibrium constant.

A specific influence of tetraalkylammonium salts is found in many other reactions involving ions,[14] and may be formally ascribed to the unusual magnitude and often negative sign of the interaction coefficients between these bulky cations and many anions.[15] Although the reason for this behavior is still being discussed,[15] it is agreed to be connected with the interaction of these cations with the solvent water, an interaction which is usually termed "structure making."

The validity of the Born equation, which forms the basis of our treatment of the influence of dioxane, has often been questioned.[16] Factors other than the bulk dielectric constant clearly have to be considered. In our case, the latter factor seems to be partly counterbalanced by another, decelerating one. (This is in contrast with the acetate-catalyzed hydrolysis of dichromate[2] where the value of a obtained from a plot of the type of our Figure 2 is a very reasonable one.) We suggest that this, again, might be connected with the fact that dioxane profoundly influences the structure of water—according to most criteria (though not all![17]) in the direction of structure promotion.

As far as we are aware, the influence of tetraalkylammonium salts on energies of activation has not been reported. In the present case, in spite of its decelerating effect, the tetramethylammonium ion significantly decreases the activation energy—at least at temperatures up to 29°. Moreover, the activation energy increases with increasing temperature. This effect, although in the direction expected for a reaction between ions of unlike sign,[13] is much higher than can be accounted for on this basis, and, furthermore, should be more pronounced the lower the ionic strength.

A possible explanation[18] for a positive dE_A/dT is the operation of two different parallel mechanisms, the one with the higher activation energy becoming predominant as the temperature increases. This possibility cannot be ruled out, but is made improbable by the fact that the effect appears only in the presence of tetramethylammonium ion.

The influence of proton tunnelling on the apparent energy of activation has recently been reviewed.[19] This leads to a positive dE_A/dT, the effect becoming noticeable, however, only at temperatures well below those employed by us.

We shall now analyze the possibility that our hydrolysis should indeed be influenced by the structure of water, proceeding at different rates with the hydro-

gen bonded, (1), and the broken-down, unstructured, (2), forms. We have recently developed formulas for the apparent energy of activation, and for dE_A/dT for such a situation,[20] and have discussed the applicability of our formulas to the two forms of water.[20,21] We have shown that

$$E_A = E_{(1)} - \frac{K}{K + 1} \Delta H + \frac{Kk_{(2)}/k_{(1)}}{1 + Kk_{(2)}/k_{(1)}} (\Delta H - \delta E)$$

(3)

with $\delta E \equiv E_{(1)} - E_{(2)}$, where $E_{(1)}$ and $E_{(2)}$ are the "true" activation energies of the two reaction paths, $k_{(1)}$ and $k_{(2)}$ their rate constants, and K and ΔH refer to the equilibrium between (1) and (2).

There are some difficulties[21,22] in assigning numerical values to K and to ΔH. If we consider the number of hydrogen bonds broken divided by the number of hydrogen bonds intact as an adequate measure for K, it turns out—according to some modern estimates[22,23]—that $K > 1$. On the other hand, assuming the tetramethylammonium ion to be structure promoting (i.e., to cause K to decrease), we conclude from its specific decelerating influence that $k_{(2)} > k_{(1)}$, whereas we conclude from its influence on E_A that $\delta E < 0$ (the decelerating influence being due to a decrease in entropy of activation which outweighs the decrease in energy of activation). Now, it can easily be verified from eq 3 that, when the three above inequalities hold simultaneously, then a decrease in K can lead to a decrease in E_A. This is in accordance with our experimental finding.

The dependence of E_A on temperature can also be explained on this basis. Differentiation of eq 3 with respect to temperature shows dE_A/dT to be composed of a negative and a positive term (see eq 9 of reference 20). We have discussed elsewhere[20] the conditions which can lead to positive values of dE_A/dT. These conditions are further illustrated in Figure 5 which is designed to emphasize high positive values. In this figure dE_A/dT is shown as a function of $\delta E/RT$, for

(14) A. Indelli, J. Phys. Chem., 65, 972 (1961); E. S. Halberstadt and J. E. Prue, J. Chem. Soc., 2234 (1952).

(15) J. E. Prue, A. J. Read, and G. Romeo, Trans. Faraday Soc., 62, 420 (1971); A. D. Pethybridge and J. E. Prue, Annu. Rep. Progr. Chem. Sect. A, 65, 145 (1968).

(16) R. G. Bates in "Hydrogen Bonded Solvent Systems," A. K. Covington and P. Jones, Ed., Taylor and Francis, London, 1968, p 49; D. Feakins and C. M. French, J. Chem. Soc., 2581 (1957).

(17) F. Franks in ref 16, p 34.

(18) J. R. Hulett, Quart. Rev. Chem. Soc., 18, 227 (1964).

(19) E. Caldin, Chem. Rev., 69, 130 (1969).

(20) R. Koren and B. Perlmutter-Hayman, J. Phys. Chem., 75, 2372 (1971).

(21) B. Perlmutter-Hayman, Israel J. Chem., 9, 377 (1971).

(22) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford University Press, London, 1969, pp 176–179.

(23) G. Némethy and H. A. Scheraga, J. Chem. Phys., 36, 3382 (1962); K. Arakawa and K. Sasaki, Bull. Chem. Soc., Jap., 42, 303 (1969).
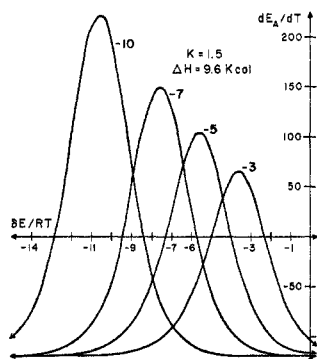
Figure 5. The calculated dependence of dE_A/dT on $\delta E/RT$, for various values of $\delta\Delta S^\dagger/R$, indicated by a number alongside the appropriate curve (where δE and $\delta\Delta S^\dagger$ are the differences in activation energy and activation entropy of two reactant forms[20]).

various values of $\delta\Delta S^\dagger/R$ (where $\delta\Delta S^\dagger$ is the difference in activation entropy of the two forms).[20] It is seen that a given value of dE_A/dT can be obtained with quite a variety of combinations of δE and $\delta\Delta S^\dagger$. If we had chosen a different value of ΔH—for instance a lower value, assuming fewer hydrogen bonds to be involved[21]—the same value of dE_A/dT could be explained, but on the basis of higher values of $|\delta E|$ and $|\delta\Delta S^\dagger|$. Similarly, a shift in K would have shifted the picture without altering it fundamentally. Under the conditions which we believe to obtain in our experiments, a decrease in K will increase the absolute value of the positive term in dE_A/dT more strongly than that of the negative one; this may explain why we found a positive dE_A/dT only in the presence of tetramethylammonium chloride.

Since we are dealing with a hydrolysis reaction, it is very plausible that the structure of water should play some role in the kinetics.[24] We have previously suggested[11] that the rate determining step in the acid catalysis should be the protonation of the bridging oxygen of the dichromate ion, facilitating the heterolytic fission of a chromium–oxygen bond in a "fast" following reaction. It has further been suggested[11] that this fission might be aided by the addition of an OH^- from a neighboring water molecule. The catalyzing acid—which in the present case is H_3O^+—is thus regenerated. It seems probable that this should occur *via* one or more intervening water molecules. Such a mechanism may well be facilitated when the water molecules involved are hydrogen-bonded and are thus present in just the right spatial configuration. This path may have a lower energy of activation, but at the same time a lower probability factor than a reaction path involving randomly oriented water molecules, both paths thus contributing to the observed rate.

We can thus assign to the structure of water a role which, qualitatively, explains our experimental findings. Too many uncertain parameters are however involved for a quantitative comparison to be possible between experiment and a theory which we consider, at present, to be only tentative.

(24) R. E. Robertson, *Progr. Phys. Org. Chem.*, 4, 213 (1967).