The inverse dependence of the cerium(IV)-chromium(III) reaction rate upon the concentration of bisulfate ion or upon both the concentration of hydrogen ion and sulfate ion is reasonable. The final products of the reaction are both less cationic and probably less complexed by sulfate ion than are the reactants. As is generally the case under such circumstances, it is energetically profitable for some of the positive charge and sulfate ions to be lost prior to the formation of the transition-state.[21]

[21] E. L. King and M. L. Pandow, THIS JOURNAL, **75**, 3063 (1953).

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The Influence of Ionic Strength and of Temperature on the Rate of Oxidation of D-Glucose by Bromine

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RECEIVED JANUARY 11, 1960

The influence of ionic strength on the rate of oxidation of D-glucose by bromine in aqueous solution has been shown to support the previous assumption that in strongly acid solution molecular bromine reacts with the D-glucose *molecule*, whereas in moderately acid solution, it reacts with the *anion* of D-glucose. The energies of activation for the two reactions have been determined. The high value of the rate constant for the reaction between bromine and the D-glucose anion has been shown to be due to a low energy of activation, the P_Z-factors being practically identical.

We have shown recently[1] that the oxidation of D-glucose in bromine water proceeds *via* molecular bromine and that the *p*H dependence of the rate of reaction is consistent with the assumption that the anionic form of D-glucose is oxidized much faster than D-glucose itself. We thought it desirable to substantiate this assumption by further experiments and therefore investigated the influence of ionic strength in somewhat greater detail and also measured the influence of temperature on the reaction rate.

Methods

The experimental procedure was the same as in our previous work.[1]

The influence of the ionic strength was investigated in solutions containing a mixture of bromine and hypobromous acid. As described in section 4 of our previous paper,[1] this enables the reaction to be carried out at very low buffer concentration and therefore at low ionic strength. We again[1] achieved the *p*H by the addition of sulfuric acid and chose the values of *p*H of 1.5 and 3.03 (at an acid concentration corresponding to a *p*H markedly higher than 3.03, the buffer-capacity of the acid would become insufficient). The rate equation has been shown[1] to be

$$\frac{dx}{dt} = k_{Br_2}\left[(c + x) + \frac{k_{HOBr}}{k_{Br_2}}(e - 2x)\right][\beta\text{-D-glucose}] \quad (1)$$

where *c* and *e* are the initial concentrations of bromine and of hypobromous acid, respectively, and *x* the concentration of the product formed at time *t*. At *p*H 3.03, the second member in the square brackets is negligible; at *p*H 1.5 it is small, and no appreciable error is introduced if we assume k_{HOBr}/k_{Br_2} to be independent of the ionic strength.

The ionic strength was varied by adding the uni-univalent electrolyte sodium nitrate.

The influence of temperature was investigated in solutions containing bromine to which bromide at an initial concentration of 0.187 *M* had been added. Because of the tribromide formed in this mixture (*cf.* section 2 of our previous paper[1]) the reaction is slowed down sufficiently for kinetic measurements at temperatures above 0° to be carried out conveniently. The rate constant was calculated from

$$\frac{dx}{dt} = k_{Br_2}\frac{K_3}{K_3 + [Br^-]}(a - x)[\beta\text{-D-glucose}] \quad (2)$$

where K_3 is the dissociation constant of tribromide (*cf.* equations 1 and 6 of our previous paper[1]).

The values of *p*H were 1.57 which again[1] was achieved by the addition of sulfuric acid, and 4.04 and 4.55 at which acetate buffers were employed.

The temperatures used were 0 and 25° at *p*H 1.57 and 0, 9.4 and 25° at the other two values of *p*H. The temperature control was ± 0.08° or better.

The values of K_3 employed at 0 and 25° were 0.051 and 0.0625, as measured by Jones, *et al.*[2,3] At 9.4°, we assumed K_3 to be equal to 0.053. This was obtained from an interpolation of the log K_3 *vs.* $1/T$ plot (Fig. 1, crosses), in which we inserted also the values of Griffith, McKeown and Winn[4] at 16.5 and 21.5°. As can be seen from the figure, the various values are not entirely consistent with each other. However, the error introduced into k_{Br_2} by a possible error in K_3 is not too serious, since (a) the temperature dependence of K_3 is only slight in comparison with that of the experimental rate constant and (b) expression 2 is less sensitive to changes in K_3 than would be an expression directly proportional to K_3.

Results and Discussion

1. Influence of Ionic Strength.—At *p*H 3.03, a pronounced positive salt-effect was observed. This is illustrated by Fig. 2, where log k_{Br_2} has been plotted against the square root of the ionic strength (circles). On the basis of the assumption that at this *p*H the reaction takes place between bromine and the glucose anion, this can be interpreted as a typical secondary salt-effect, affecting the degree of dissociation of glucose. At constant *p*H, the slope in Fig. 2 should be 0.5 provided the Debye Limiting Law is applicable. Our experimental value is about 0.4 at the lowest concentration amenable to measurement; the difference may well be due to a failure of the Limiting Law at these concentrations. The slope of course decreases further with increasing ionic strength.

On the other hand, at *p*H 1.5 the increase of the rate-constant remained within the limit of experimental error when the ionic strength was changed from 0.03 to 0.28 (see Fig. 2, crosses). This is entirely consistent with the assumption of a reaction between two molecules, *viz.*, glucose and bromine.

2. Influence of Temperature.—In Fig. 1, log k_{Br_2} has been plotted *vs.* $(1/T)$. The lines for *p*H 4.04 and 4.55 are seen to be parallel (half-closed

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[1] B. Perlmutter-Hayman and A. Persky, THIS JOURNAL, **82**, 276 (1960).

[2] Grinnell Jones and M. L. Hartman, *Trans. Am. Electrochem. Soc.*, **30**, 295 (1916).

[3] Grinnell Jones and S. Baeckström, THIS JOURNAL, **56**, 1517 (1934).

[4] R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 107 (1932).

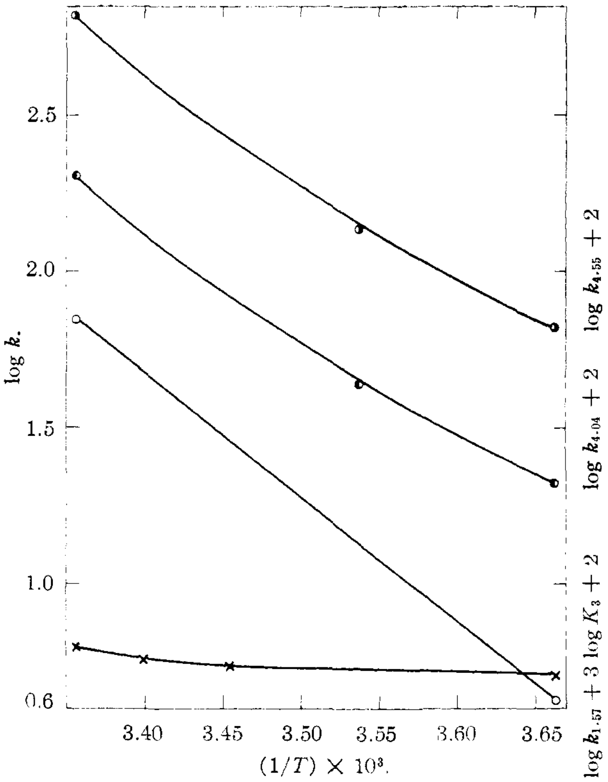

Fig. 1.—The dependence on the reciprocal of the absolute temperature of (a) the logarithm of the dissociation constant of tribromide (crosses) and (b) the logarithm of the rate constant: open circles: *p*H 1.57; half-closed circles: *p*H 4.04 and 4.55 (◐ and ◑, respectively).

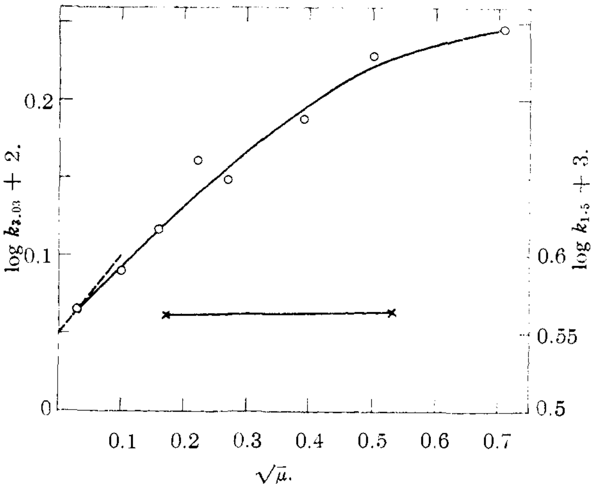

Fig. 2.—The dependence of the logarithm of the rate constant on the square root of the ionic strength: crosses, *p*H 1.5; circles, *p*H 3.03.

circles) and less steep than the line for *p*H 1.57 (open circles). From the latter we can directly calculate the energy of activation for the reaction between the D-glucose and bromine molecules and get

$$E_G = 18.32 \text{ kcal. mole}^{-1}$$

This leads to a frequency factor of 2.7×10^{10} l. mole^{-1} sec.$^{-1}$, a value which seems very reasonable for a reaction of this kind.

At the higher values of *p*H, the situation is somewhat more complicated, since k_{Br_2} is now a composite constant, *viz.*

$$k_{Br_2} = k_{G^-}K_G/[H^+]$$

where K_G is the dissociation constant of D-glucose, and k_{G^-} is the specific rate of the D-glucose anion (*cf.* equation 9 of our previous paper[1]). Therefore, the slope in Fig. 2 yields the sum of E_{G^-}, the activation energy for the reaction between the bromine molecule and the D-glucose anion, and ΔH_G, the heat of dissociation of D-glucose. The increase of the slope with increasing temperature appears at both values of *p*H, and is larger than the experimental error. It may be due to an increase in either E_{G^-} or ΔH_G or both. We shall get a reasonably accurate mean value for E_{G^-} if we employ ΔH_G as calculated from Thamsen's[5] measurements of K_G at 0 and 18°, assuming that the change in ΔH_G between 18 and 25° is not significant. This yields

$$E_{G^-} = 5.01 \text{ kcal. mole}^{-1}$$

and a frequency factor of 2.6×10^{10} l. mole^{-1} sec.$^{-1}$

We note that the extremely high value[1] of k_{G^-} ($k_{G^-} = 10^8$ l. mole^{-1} min.$^{-1}$ at 0°) is caused by a low energy of activation, and not by an abnormally high frequency factor. Since both in the oxidation of the glucose *molecule* and the glucose *ion* the pyranose ring is attacked by bromine essentially at the same point, the similarity in the frequency factors for the two reactions is consistent with the proposed mechanism. On the other hand, the agreement between the two values to within less than 4% is almost certainly fortuitous.

Summarizing, we may say that our experiments further confirm the assumption that the reaction path in strongly acid solution is different from that in moderately acid solution. The dependence on ionic strength confirms the contention that these reaction paths involve a molecule, and the anion of a weak acid, respectively, and the dependence on the temperature leads to reasonable values for the energies of activation and frequency factors for the two reactions.

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(5) J. Thamsen, *Acta Chem. Scand.*, **6**, 270 (1952).