purple crystals did not occur until the solutions had stood for about 24 hours. The chloride complex precipitated much more slowly than did the bromide. After recrystallization from 95% ethyl alcohol the chloride melted at 168° and the bromide at 135°.

Anal. Calcd. for $NiC_{15}H_{42}N_6O_3Cl_2$: N, 17.39; Cl, 14.69. Found: N, 17.2; Cl, 14.8. Calcd. for $NiC_{15}H_{42}N_6O_3Br_3$: N, 14.68; Br, 27.95. Found: N, 14.5; Br, 28.0.

Tris-N-methylethylenediamine Ni(II) Bromide, $[Ni(me\text{-}en)_3]Br_2$.—A concentrated absolute ethyl alcohol solution of nickel(II) bromide was treated with an excess of N-methylethylenediamine, the resulting mixture cooled to 0°, and anhydrous ether added until the point of precipitation was just reached. From the clear solution, stoppered at room temperature for about six weeks, very large deep purplish-blue crystals of the tris-complex, $[Ni(me\text{-}en)_3]Br_2$, were slowly deposited.[17]

Anal. Calcd. for $NiC_9H_{30}N_6Br_2$: N, 19.05. Found: N, 19.0.

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anhydrous copper(II) bromide and N-(2-hydroxypropyl)-ethylenediamine in the ratio of 1:2. Dark blue crystals formed within several hours after mixing. The complex, after recrystallization from 95% ethyl alcohol, melted without decomposition at 208–209°. *Anal.* Calcd. for $CuC_{10}H_{28}N_4O_2Br_2$: N, 12.19. Found: N, 12.2. A very small amount of a chloride complex was also isolated. This was presumably the bis-complex inasmuch as the color was identical to that of $[Cu(etol\text{-}en)_2]Cl_2$. No analysis was made.

(17) Fine purplish-blue needles of $[Cu(me\text{-}en)]_2Br_2$ were obtained in an analogous manner. This compound, after recrystallization from 95% ethyl alcohol, melted at 238°. *Anal.* Calcd. for $CuC_6H_{20}N_4Br_2$: N, 15.19. Found: N, 15.1.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

*p*H Change as an Index to Reaction Mechanisms[1]

BY C. H. SORUM, F. S. CHARLTON,[2] J. A. NEPTUNE AND JOHN O. EDWARDS[3]

A preliminary report on the *p*H changes of oxidation–reduction reactions is presented. Several of the observed curves for different types of reactions are included. The Landolt reaction (iodate oxidation of sulfite) is discussed in some detail to show how the *p*H–time curve correlates with the known stoichiometries and rate laws from other investigations.

Introduction

When the experimentally determined *p*H of the unbuffered Landolt reaction[4] (the oxidation of sulfite by iodate in acid solution, in the presence of starch) is plotted as a function of the time, a curve of the form of line 1 in Fig. 1 is obtained. The sharp break in this curve (point C) occurs at the exact time that the blue color appears. When bromate is substituted for iodate in this reaction, curve 2 of Fig. 1 is observed. Where the break in the iodate curve is followed by a pronounced rise in *p*H there is no change in *p*H following the break in the bromate curve. Thus, the *p*H–time curves for these reactions are distinctly different.

For the reaction of iodide with iodate, the *p*H–time curves have the form illustrated in Fig. 2, whereas the bromate–bromide reaction has only a slight change in *p*H under these conditions. The time dependence of the *p*H of the sulfite–permanganate reaction varies with the starting *p*H in the fashion reflected in Fig. 3. A similar sort of dependence on starting *p*H is shown by the nitrite–permanganate, the selenite–permanganate and the arsenite–permanganate reactions, although the last named reaction gives a sudden *p*H drop at all initial *p*H's. In Fig. 4, the *p*H changes in the oxidation of thiosulfate by bromate are presented. The *p*H change is markedly dependent on the initial *p*H and the curves cross, so that one can immediately say that the reaction is complex. Similar curves were found in the iodate–thiosulfate reaction.

The thiosulfate–iodide–hydrogen peroxide reaction is accompanied by very pronounced and striking changes in *p*H (Fig. 5). The regular change in the pattern of *p*H change as the hydrogen ion concentration is varied is noticeable; in addition there is a distinct change in character when the sulfuric acid concentration is greater than 0.0112 *M* for this series of runs.

It is evident from the examples given that oxidation–reduction reactions are, very commonly, accompanied by characteristic *p*H changes. In some reactions these *p*H changes are both pronounced and striking; in others they are small and relatively unspectacular. The question is whether an observation of these *p*H changes can be useful in probing the mechanism of the particular reaction.

To try to find an answer to this question we will examine the results of detailed studies made on one of these reactions, the oxidation of sulfite by iodate. This reaction was probed by the conventional method of varying one factor while holding other factors constant.

Experimental Procedure

The *p*H measurements were made with a Beckman model G *p*H meter; the readings were standardized with a potassium hydrogen phthalate buffer. All chemicals used were of analytical reagent quality. For each reagent, the same batch was used throughout to eliminate any effect of variation in purity. All water was doubly distilled and preserved in CO_2-free air. All reducing solutions were preserved in an atmosphere of nitrogen, and reactions involving reagents susceptible to air oxidation were carried out in a nitrogen atmosphere.

The reactions were carried out in a 300-ml., closed, tall-form beaker with a free flowing pipet suspended overhead. The reaction vessel, the nitrogen gas and the solutions were thermostated at 25°. In the case of the Landolt reaction sulfite solution was measured out in the pipet and was then run into the beaker. Sulfuric acid was added to bring its *p*H to that of the iodate–starch solution. The iodate–starch solution was quickly added, the *p*H noted, the time-clock started and the *p*H–time values recorded.

Discussion of the Landolt Reaction

The presence of starch is necessary to give the sharp, blue end-point characteristic of the Landolt

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[1] Presented at the 117th Meeting of the American Chemical Society, Detroit, April 19, 1950, in the Symposium on the Kinetics of Oxidation–Reduction Reactions.

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[4] H. Landolt, *Ber.*, 249 (1885); 193 (1886); 21 (1887).

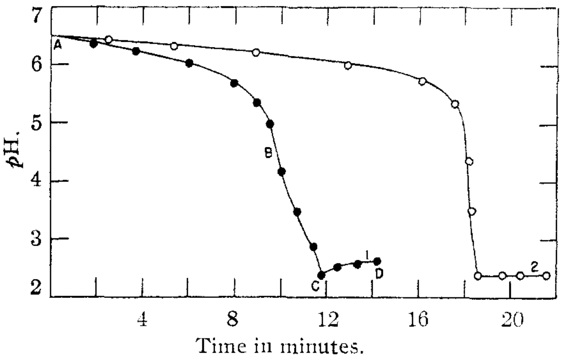

Fig. 1.—*p*H-time curves for sulfite-iodate (1) and sulfite-bromate (2) reactions: 0.054 *N* Na_2SO_3, 0.06 *N* KIO_3, 0.06 *N* $KBrO_3$.

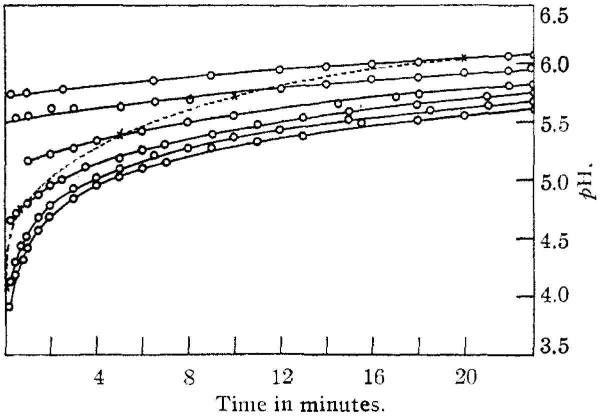

Fig. 2.—Effect of starting RH on the *p*H-time curve for the iodate-iodide reaction: 0.03 *N* KIO_3, 0.012 *N* KI. Broken line shows time of appearance of free iodine.

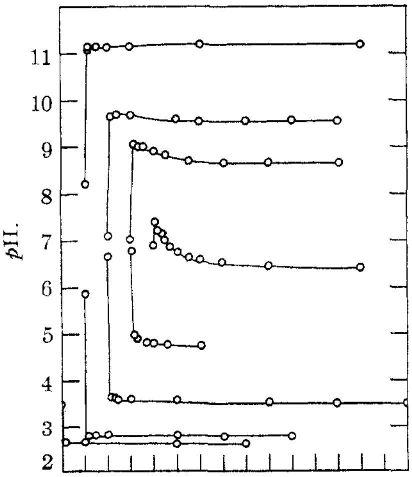

Fig. 3.—Effect of starting *p*H on the *p*H-time curve for the reaction between 0.05 *N* Na_2SO_3 and 0.06 *N* $KMnO_4$. All curves begin at zero time.

reaction. Experiments showed that the starch did not alter the *p*H-time curve of the reaction; therefore the action of the starch is only to give a strong color at the instant some iodine is released.

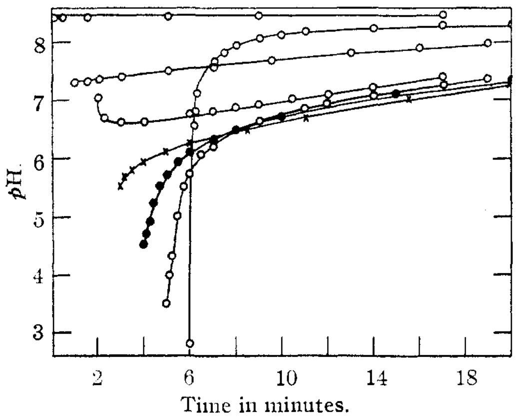

Fig. 4.—The effect of starting *p*H on the reaction between 0.05 *N* $Na_2S_2O_3$ and 0.06 *N* $KBrO_3$. All curves begin at zero time.

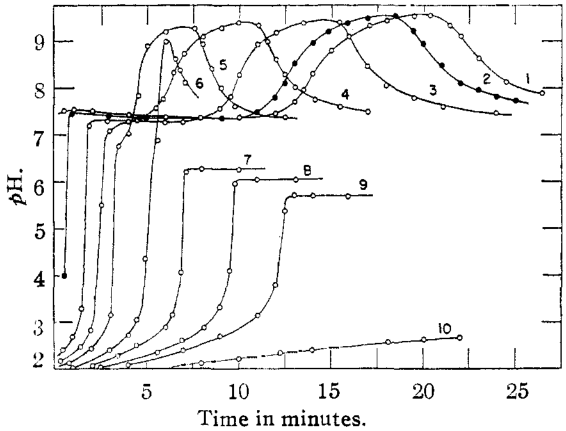

Fig. 5.—Effect of acid concentration on the *p*H-time curve for the iodide-thiosulfate-hydrogen peroxide reaction: 0.03 *M* KI, 0.024 *M* $Na_2S_2O_3$, 0.06 *M* H_2O_2. Concentration of H_2SO_4: (1) 0.0000 *M*, (2) 0.0014 *M*, (3) 0.0045 *M*, (4) 0.0068 *M*, (5) 0.0090 *M*, (6) 0.0112 *M*, (7) 0.0135 *M*, (8) 0.0158 *M*, (9) 0.0180 *M*, (10) 0.0225 *M*.

The initial *p*H has a marked influence on the rate of the reaction. With a reaction mixture containing 0.054 *N* sodium sulfite and 0.06 *N* potassium iodate the end-point fell at 39, 16 and 4 minutes when the initial *p*H values were 6.8, 6.5 and 6.0, respectively. Increases in iodate concentration, though always in excess to the sulfite concentration, cause decreases in the time to the end-point, in similar fashion to those found with increases in hydrogen ion concentration.

With an excess of iodate ion and an initially constant *p*H, it was observed that marked decreases in the end-point time occur when the sulfite concentration is increased. It would be expected that the initial consumption rate would be faster as the sulfite increased in concentration, but the end-point should not be reached sooner since there is more to be oxidized. From these data, it is possible to state that other significant reactions are present.

An examination of curve 1, Fig. 1, reveals that the *p*H-time curve can be broken down into three parts. Part A–B corresponds to the first half of any ordinary titration curve; it undoubtedly is due to a single reaction. Point B represents the incidence of a new reaction; this reaction proceeds at increasing speed to point C where it ends abruptly and a final reaction comes into predominance. The shape of the C–D curve indicates that this reaction slows down as the *p*H increases.

Detailed studies by Eggert,[5] Skrabal,[6] Thiel[7] and others indicate that the over-all Landolt reaction may be represented by the following stoichiometric equations

$$IO_3^- + 3HSO_3^- \longrightarrow I^- + 3SO_4^= + 3H^+ \quad (1)$$
$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \quad (2)$$
$$I_2 + HSO_3^- + H_2O \longrightarrow 2I^- + SO_4^= + 3H^+ \quad (3)$$

where (1) and (2) are measurably slow reactions and (3) is essentially instantaneous. Since (3) will consume the iodine formed in (2) and since it will go on as long as HSO_3^- is present, the starch–iodine color will not appear until all of the sulfite has been consumed. This is the basis for the "clock" feature of the Landolt reaction.

The rate law for reaction (1)[6] is

$$-\frac{d[HSO_3^-]}{dt} = k_1[IO_3^-][HSO_3^-][H^+]$$

and for reaction (2) it probably is

$$-\frac{d[IO_3^-]}{dt} = k_2[IO_3^-][I^-]^2[H^+]^x$$

where x is either 2 or 3, since conclusive results are not at hand[8] in the *p*H range under consideration.

Reaction (1) accounts for part A–B of the *p*H–time curve, for the rate of change of *p*H with time increases as the concentrations of the reactant species increase. The blue color of the Landolt reaction appears when all of the sulfite is used up; therefore, the only reaction that can occur after the point C is the oxidation of iodide by iodate. As expected, the shape of the *p*H–time curve for this reaction (Fig. 2) correlates well with the C–D section of the Landolt reaction curve. In Fig. 6, curves of *p*H against time and sulfite concentration against time are presented. When iodate is in excess, the *p*H rises after point C, whereas when sulfite is in excess the *p*H does not change after the end point is reached. This observation is further proof that the C–D portion of the curve results from the iodate oxidation of iodide when all the sulfite has been used up.

The autocatalytic nature of this reaction is markedly demonstrated by the change in sulfite concentration with time and by the *p*H–time curve (Fig. 1). This increase in reaction rate is the result of two factors. Since iodide ion is generated by reaction (1) and since it is rapidly oxidized in acid solution, a large share of the increase in rate can be attributed to its presence. The other factor lies in the generation of hydrogen ions by the reaction which is catalyzed by acids. Since the Landolt reaction in its over-all stoichiometry generates hydrogen ions and since both reactions (1) and (2) are catalyzed by acids, the rate of the reaction increases as was shown in the effect of initial *p*H on the reaction curve. As a final result, the over-all reaction rushes to its spectacular climax at point C.

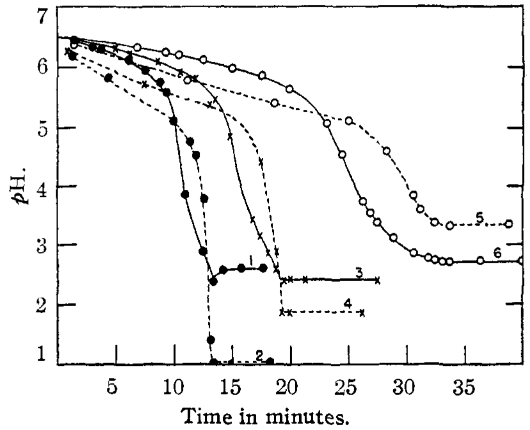

Fig. 6.—The effect of excess sulfite on the *p*H–time curve (solid lines) and the sulfite concentration–time curves (broken lines) for the iodate–sulfite reaction: (1) and (2), 0.05 *N* Na_2SO_3, 0.06 *N* KIO_3; (3) and (4), 0.05 *N* Na_2SO_3, and 0.045 *N* KIO_3; (5) and (6), 0.05 *N* Na_2SO_3, 0.03 *N* KIO_3, *p*H 6.5.

Other Reactions.—The change in *pH* as a reaction proceeds is dependent on two factors, the stoichiometry and the rate law order in hydrogen ion concentration. The direction of the *p*H change is, of course, determined by the stoichiometry of the reaction or reactions which are taking place. The shape of the curve is dependent on the order, if the reaction proceeds with one rate law throughout the observed *p*H range.

The iodate–iodide, iodate–thiosulfate and bromate–thiosulfate reactions proceed at measurable velocity and take up hydrogen ions as the reaction proceeds. The bromate–sulfite and iodate–sulfite reactions release protons to the solution at a measurable rate. The permanganate–sulfite reaction proceeds very rapidly, but the effect of the individual species H_2SO_3, HSO_3^- and $SO_3^=$ may be seen from the *p*H change.

Further studies of more quantitative nature on these reactions and others are to be published in the future.

MADISON, WIS.

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[5] J. Eggert, *et al.*, *Z. Elektrochem.*, **23**, 8 (1917); **27**, 455 (1921); **30**, 501 (1924); *Z. anorg. allgem. Chem.*, **139**, 310 (1924); *Ber.*, **54B**, 2521 (1921); *J. Chem. Soc.*, **112**, 11 (1917).

[6] A. Skrabal, *et al.*, *Z. Elektrochem.*, **28**, 222 (1922); **30**, 109 (1924); **33**, 42 (1927).

[7] A. Thiel, *et al.*, *Chem. Zentr.*, **83**, II, 2017 (1912); *Z. anorg. allgem. Chem.*, **127**, 125 (1924); *Z. Elektrochem.*, **34**, 113 (1928).

[8] O. E. Meyers and J. W. Kennedy, THIS JOURNAL, **72**, 897 (1950).