any form of desiccator. In the dome-shaped form, the three supports rest on the brass rim; in the commonly used Scheibler pattern, the notches in the under side of the supports bear on a frame of glass rod, similar to that generally used for the platinum triangle, and thus danger of lateral displacement is avoided.

To use the device, one adjusts the screws to impinge on the upper part of the crucible. The latter is thus held firmly but may be released when desired by lowering and withdrawing the holder.

Messrs. Eimer and Amend have taken up the manufacture of the article, which is obtainable at a moderate price. C. W. EASLEY.

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THE MECHANISM OF THE OXIDATION OF GLUCOSE BY BROMINE IN NEUTRAL AND ACID SOLUTIONS.

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I. Introduction.—Glucose is known to be both an acid and a base. At least one of its hydrogens may be replaced by a metal to form a salt. Kullgren[1] states that the dissociation constant of invert sugar is 7.2×10^{-13} and cane sugar, 1.05×10^{-13} at 21°. Osaka[2] has computed the dissociation constant of glucose to be 5.9×10^{-13} at 25°. Glucose is, therefore, a very weak acid and its dissociation as an acid will be diminished by small amounts of strong acids.

The work of Baeyer and Villiger,[3] Cohn,[4] Walden,[5] Walker[6] and others on oxonium salts and the work particularly of Stieglitz[7] on the inversion of the imido esters and cane sugar shows that glucose is also a weak base uniting with acids in its double bonded oxygen of the aldehyde group. As a base it is extremely weak so that even in solutions containing a considerable amount of strong acid there will still be a large amount of hydrolytic dissociation, only a small amount of the glucose salt being present.

We have, therefore, in a neutral or acid solution of glucose the following kinds of glucose particles: $C_6H_{12}O_6$ undissociated; $C_6H_{12}O_6.H_2O$, the free base; $C_6H_{11}O_6^-$; and $C_6H_{13}O_6^+$. These are formed according to the following reactions:

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[1] Kullgren, *Z. physik. Chem.*, **41**, 407 (1902).

[2] Osaka, *Z. physik. Chem.*, **35**, 661 (1900); Cohen, *Ibid*, **37**, 69 (1901).

[3] Bayer u. Villiger, *Ber.*, **35**, 1189 and 3013, (1902); **34**, 2679 and 3612 (1901).

[4] Cohn, *Ibid.*, **35**, 2673 (1902).

[5] Walden, *Ibid.*, **34**, 4185 (1901).

[6] Walker, *Ibid.*, **34**, 4115 (1901).

[7] Stieglitz, *Amer. Chem. J.*, **39**, 29 and 166 (1908).

1. $C_6H_{12}O_6 \rightleftharpoons C_6H_{11}O_6^- \times H^+$.
2. $C_6H_{12}O_6 + HCl \rightleftharpoons C_6H_{13}O_6^+ + Cl^-$.
3. $C_6H_{12}O_6 + H_2O \rightleftharpoons C_6H_{12}O_6H_2O$.

We sought to determine which of these kinds of particles are most easily oxidized by bromine.

To solve the problem we have studied the velocity of oxidation of glucose by bromine in solutions of varying acidity, the rate of oxidation being measured by the rate of disappearance of the bromine, Br_2, from the solution. The velocity of oxidation under these different conditions will show which of these particles are oxidizing. The experimental work has been done entirely by the junior author.

II. Methods.—The bromine solution was made up fresh before each experiment. A few drops of Kahlbaum's pure bromine were dissolved in distilled water, the solution rapidly titrated with 0.01 *N* sodium thiosulphate solution and then diluted with distilled water till its strength was approximately 0.02 *N*. It was practically impossible to get it exactly that strength, as the solution weakened on shaking. A known amount of glucose solution, previously warmed to 25°, was then measured into a tall glass stoppered cylinder and a known (generally an equal) amount of the bromine solution added. The solutions were now rapidly mixed, a sample of 10 cc. drawn into a small Erlenmeyer flask containing 2 cc. of 5 per cent. potassium iodide solution for the determination of the initial titer, and the rest of the solution placed in a thermostat kept at 25°. At intervals varying with the speed of the reaction, samples were drawn and at once titrated with 0.01 *N* sodium thiosulphate solution. The latter was frequently checked and corrected against a standard solution of iodine. Starch and potassium iodide served as indicator, the disappearance of the color being considered the end point. The sugar used was Kahlbaum's purest crystalline glucose.

To simplify conditions by making the reaction practically a monomolecular one, in all the experiments a large excess of glucose was used, the latter being always present in the concentration of a one-half molecular solution.

Our actual procedure was to study the velocity of oxidation under varying conditions of acidity produced by different acids, to formulate various hypotheses and test them by seeing which equations represented our results. We found, as may be seen in Tables I and III (pp. 471 ff.) and the curves in Fig. 1, that the addition of small amounts of acids to the glucose greatly retarded the rate of oxidation, but that after a certain small concentration of H ions was reached, further addition of acid did not slow the reaction further, except when hydrobromic acid and hydrochloric acids were used. A monomolecular formula for the velocity constant gave the values for (K) shown in Tables I and III. It will be observed that (K) was sometimes constant, sometimes not constant. It was first necessary to consider the oxidizing action of the bromine. We then took up the reducing action of the glucose.

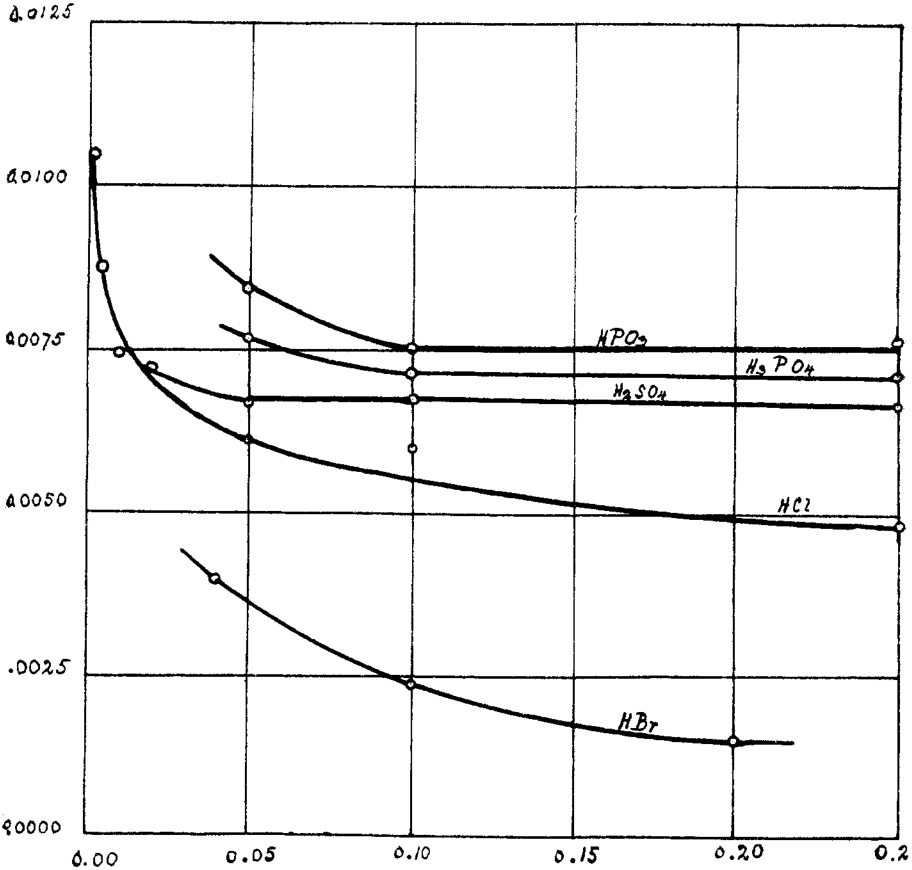

Fig. 1.—Effect of the addition of acids on the rate of oxidation of glucose by bromine. Ordinates = velocity constants by monomolecular reaction formula and common logs. Abscissae = equivalent concentration of acids added.

III. The Oxidizing Action of Bromine.—The reaction may be represented essentially, whatever its intermediate steps, as a transfer of two positive charges of electricity from the bromine to an O or OH ion, and the transfer of this positive oxygen to the glucose. Accordingly the speed of the reaction as far as the Br_2 is concerned must be determined by the concentrations of the OH^- or O ions and of the free Br_2.

We may picture this process in various ways:

4. $Br_2 + 2OH^- = 2OH^+ + 2Br^-$.
5. $C_6H_{13}O_6^+ + OH^+ + Cl^- + Br^- = C_6H_{12}O_6 + HCl + HBr$, or
6. $C_6H_{13}O_6^+ + Br_2 + HOH = C_6H_{12}O_7 + 2HBr_2 + H^+$.

The essential fact is that both free Br_2 and OH^- are involved in the reaction.

The amount of free Br_2 actually present is affected by several secondary reactions.[1] The first and most important of these reactions is that between Br_2 and Br^-.

7. $Br_2 + Br^- = Br_3^-$.

A second reaction leads to the formation of hypobromite and bromate:

8. $Br_2 + HOH \rightleftarrows HBr + HBrO$.

9. $HBrO + 2Br^-O + 2H^+ \rightleftarrows HBrO_3 + HBr + HBr$.

Reactions 7, 8, and 9 are all reversible. Reactions 8 and 9 will not seriously interfere with measurements carried on in a neutral or acid solution[2] in the dark and lasting for only an hour or two as most of ours have done, since the speed of the reaction by which hypobromite is formed is directly proportional to the concentration of the hydroxyl ions present. The conversion into hypobromite under these conditions is, therefore, practically negligible. In an oxidation in slightly alkaline solution however, this reaction would greatly influence the result since bromate and hypobromite ions have little or no oxidizing action.

To what extent the Br^- formed in the course of the reaction, or added at the beginning, will slow the reaction by the formation of Br_3^- thus reducing the amount of free Br_2, may be determined from the equation:

9*a*. $C_{Br_2} \times C_{\overline{Br}} = KC_{\overline{Br_3}}$.

The value of K has been determined by Roloff[3] and Worley[4] to be about 0.05 at 25°, depending somewhat upon the relative amounts of Br^- and Br_2 present. If much Br_2 is present compared with Br^-, a small amount of some higher compounds such as Br_5 are formed. For the sake of simplicity we have supposed that only Br_3^- is formed. This can be done without much error since in many of our experiments the amount of Br_2 was small compared to the Br^- and accordingly the amount of Br_5^- was negligibly small; and in any case the Br_5^- is small compared to Br_3^-.

IV. The Mechanism of the Reaction.—Our first guess was that reaction 1, page 465, was taking place and that only the negative ion was being oxidized. The velocity of the reaction, or *dx/dt*, may be expressed as follows:

10. $dx/dt = K'C_6H_{11}O_6^- \times C_{\text{Free Br}_2} \times C_{\overline{OH}}$;

that is, the velocity of the reaction will be directly proportional to the

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[1] T. W. Richards and W. N. Stull, "Velocity and Nature of Reaction of Bromine and Oxalic Acid," *Z. physik. Chem.*, 41, 544 (1902).

[2] Jakowkin, *Ber.*, 30, 518 (1897). Kretzschmar, *Z. Elektrochem.*, **10,** 789 (1904). Foerster and Müller, *Ibid.*, **8,** 921 (1902).

[3] Roloff, *Z. physik. Chem.*, 13, 353 (1894).

[4] Worley, Transactions, *J. Chem. Soc.*, **87,** 1107 (1905).

concentration of the sugar ion, free Br_2 and OH ions.[1] Now from equation 1,

$$C_6H_{12}O_6 = C_6H_{11}O_6^- + H^+.$$

11. $$K''C_{C_6H_{12}O_6} = C_{\overset{-}{C_6H_{11}O_6}} \times C_{\overset{+}{H}}.$$

12. $$C_{\overset{-}{C_6H_{11}O_6}} = K''C_{C_6H_{12}O_6}/C_{\overset{+}{H}}.$$

Since the sugar is very little dissociated, the total sugar concentration may be used for $C_6H_{12}O_6$ without appreciable error. We may write for $C_{\text{Free Br}_2}$ in equation 10, α ($C_{\text{Total Br}_2}$), where the total Br_2 is all Br_2 titrated with thiosulphate and α is the per cent. of this total which is present as free Br_2. α may be computed from equation 9*a*.

$$C_{\overset{-}{Br_3}} = C_{\text{Total Br}_2} - C_{\text{Free Br}_2},$$

Substituting this value of $C_{\overset{-}{Br_3}}$ in 9*a*, we get:

$$C_{\text{Free Br}_2} \times C_{\overset{-}{Br}} = 0.05\ C_{\text{Total Br}} - 0.05\ C_{\text{Free Br}_2}.$$

$$C_{\text{Free Br}_2}(0.05 + C_{\overset{-}{Br}}) = 0.05C_{\text{Total Br}_2}.$$

13. $$\alpha = C_{\text{Free Br}_2}/C_{\text{Total Br}_2} = 0.05/(0.05 + C_{\overset{-}{Br}}).$$

Substituting 11 and 12 in 10 we obtain

14. $$dx/dt = K'K'' \times C_{C_6H_{12}O_6} \times 0.05. \times C_{\text{Total Br}_2} \times C_{\overset{-}{OH}}/C_{\overset{+}{H}}(0.05 + C_{\overset{-}{Br}}).$$

In 14 $C_{\overset{-}{OH}} = K^{H_2O}/C_{\overset{+}{H}}$; substituting this gives 15.

15. $$dx/dt = K'K''K^{H_2O}\ C_{C_6H_{12}O_6} \times C_{\text{Total Br}_2} \times 0.05/C^2_{\overset{+}{H}}(0.05 + C_{\overset{-}{Br}}),$$

let $K_4 = K'K''K^{H_2O}C_{C_6H_{12}O_6}$.

x = Amount of Br_2 used up in time t,
A = Concentration of total Br_2 at start,
$A - x$ = Concentration of total Br_2 at time t,
$B + 2x$ = Concentration of H ions after time t,
B = Concentration of H ions at the start.

Equation 15 becomes then:

16. $$dx/dt = K_4\,0.05(A - x)/[(B + 2x)^2(0.05 + C_{\overset{-}{Br}})].$$

Equation 16 states that the velocity of the reaction must be inversely proportional to the square of the concentration of the hydrogen ions. Our results show that though there is an initial rapid slowing by acid, yet after a very small addition of H ions no further addition has any effect in slowing the reaction further. Our hypothesis that the oxidation of the negative sugar ion is the only oxidation taking place is obviously incorrect. We made, therefore, a second hypothesis.

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[1] There is a certain weakness in the argument at this point owing to our ignorance of the exact reaction between the free Br_2 and water. We were uncertain whether one or two hydroxyl ions took part in the reaction at once. We adopted the hypothesis that the hydroxyls were reacting by their first power, because no other assumption we could think of would agree with our results. We recognize the fact that this point, which is really vital to the argument which follows, is still insecure.

We assumed that only the positive sugar ion was oxidized by the bromine according to equation 6, page 466.

6. $C_6H_{13}{}^+O_6 + Cl^+ + Br_2 + HOH = C_6H_{12}O_7 + 2HBr + HCl.$

The velocity equation will be as before:

17. $$dx/dt = K'''C_{C_6\overset{+}{H}_{13}O_6} \times C_{Br_2} \times C_{\overline{OH}}.$$

From equation 2

18. $$C_{C_6H_{12}O_6} \times C_{\overset{+}{H}} = K^{IV}C_{C_6\overset{+}{H}_{13}O_6}.$$

19. $$C_{C_6\overset{+}{H}_{13}O_6} = C_{C_6H_{12}O_6} \times C_{\overset{+}{H}}/K^{IV}.$$

Substituting this value in 17 and also the value for the free Br_2 as already obtained, we have:

20. $$dx/dt = K'''\, C_{C_6H_{12}O_6} \times C_{\overset{+}{H}} \times C_{\overline{OH}} \times 0.05 \times C_{\text{Total } Br_2}/[K^{IV}(0.05 + C_{\overline{Br}})].$$

$$C_{\overline{OH}} \times C_{\overset{+}{H}} = K^{H_2O};\ C_6H_{12}O_6 \text{ is constant so that}$$

$$K^V = K'''K^{H_2O}C_{C_6H_{12}O_6}/K^{IV}.$$

21. $$dx/dt = K^V\, 0.05(A - x)/(0.05 + C_{\overline{Br}}).$$

Equation 21 states that the velocity of the reaction will be independent of the concentration of the hydrogen ions. It is plain that the second hypothesis also fails to agree with the facts, for while it agrees with the observation that after the addition of a small amount of acid no further addition will slow the velocity more, it fails to account for the slowing at the outset.

As a third hypothesis we assumed that only the undissociated sugar is oxidizing. In that case the velocity equation becomes

22. $$dx/dt = K^{VI}C_{C_6H_{12}O_6} \times C_{\overline{OH}} \times C_{\text{Free } Br_2}.$$

According to this equation the velocity will run inversely proportional to the concentration of the H ions, which is again contrary to fact as already pointed out for the first guess. The well-known fact that the sugars are most stable when in neutral solution, when the undissociated particles are present in largest amounts and that they break up rapidly in alkaline and also in acid solutions, shows that the undissociated molecule is the most stable; the negative ion the least stable; and the positive ion intermediate in stability. The hypothesis that the undissociated sugar was oxidizing at anything more than a very slow rate, if at all, was therefore abandoned.

Since the first hypothesis of the oxidation of the negative ion explained the rapid fall of the rate on the addition of a little acid and the second hypothesis of the oxidation of the positive ion explained why the addition of more acid produced no further effect, we made a fourth hypothesis that both the negative and the positive ions were oxidizing but the negative more rapidly. We therefore assumed that both these ions were being oxidized by the bromine and that there were two reactions mutually independent proceeding side by side. In the first, the velocity varied inversely with the square of the concentration of the hydrogen ions; the second proceeded independent of changes in acidity, Reactions 21 and 16 may be assumed to be taking place simultaneously. At the start of the reaction in a neutral solution reaction 16, that is, the oxidation of the negative $C_6H_{11}O_6^-$ ion, predominates, but owing to the formation of hydrobromic acid by the oxidation, the dissociation of the sugar is pushed back and after a certain amount of acid has been formed the number of $C_6H_{11}O_6^-$ ions is so small that this oxidation becomes negligible compared to the other. From this point on the oxidation is practically that of the $C_6H_{13}O_6^+$ ion.

Assuming then that these two reactions are taking place side by side the velocity equation becomes:

$$23.\quad dx/dt = K_4\, 0.05(A - x)/[(B + 2x)^2(0.05 + C_{\overline{Br}})] + K^V\, 0.05\, (A - x)/(0.05 + C_{\overline{Br}}) = [0.05(A - x)/(0.05 + C_{\overline{Br}})]\, [K^V + K_4/(B + 2x)^2].$$

This equation as it stands we were unable to integrate since $C_{\overline{Br}}$ is itself a function of $A - x$ and the substitution of the proper value for it gives rise to a complex expression. We have, therefore, adopted the simplifying assumption that $C_{\overline{Br}}$ remains constant for short intervals of time using for this interval the mean of the value of $C_{\overline{Br}}$ at the beginning and the end of the period. When much Br^- is present at the start, this assumption accords pretty strictly with the facts, since then $C_{\overline{Br}}$ actually remains practically constant throughout, for at the most 0.01 NBr^- can be formed by the transformation of all the Br_2 into Br^-.

If, now, we add a considerable quantity of hydrobromic acid to our solution, α becomes, as just stated, practically a constant and the first reaction, that of the oxidation of the $C_6H_{11}O_6^-$ ion becomes negligible; hence, the velocity of oxidation will be that of the second reaction only or

$$dx/dt = K^V\, 0.05\, (A - x)/(0.05 + C_{\overline{Br}}.)$$

Integrating, this becomes

$$24.\quad (C_{\overline{Br}} + 0.05)\log (A - x'/A - x'')/(0.05\,(t'' - t')) = K^V \text{ or}$$

$$(C_{\overline{Br}} + 0.05)\,[\log (A/A - x)]/0.05\,t = K^V.$$

This relationship was tested by the data acquired from the addition of varying quantities of hydrobromic acid and other acids to the glucose solution. The computation of K^V was first made from those cases where HBr had been added, since here α was more constant. The results obtained for successive intervals of time were as follows:

TABLE I.

Concentration of acid.	No. of cc. of 0.01 *N* $Na_2S_2O_3$ for 10 cc. of mixture.	Time from beginning.	$K=1/t \log_{10} A/A\text{-}x$.	K^V (Nat. logs)
0.04 *N* HBr	10.02	0	....	......
	9.05	10	0.00442	0.0183
	8.28	20	0.00414	0.0173
	7.38	35	0.00380	0.0159
	5.72	65	0.00375	0.0159
	4.10	100	0.00381	0.0166
0.1 *N* HBr	10.80	0	....	......
	9.61	20	0.00253	0.0175
	8.60	40	0.00247	0.0172
	7.31	70	0.00242	0.0169
	5.95	105	0.00246	0.0172
	4.88	145	0.00238	0.0167
	3.60	200	0.00239	0.0168
0.2 *N* HBr	0.90	0	....	......
	9.21	20	0.00157	0.0181
	8.50	45	0.00148	0.0170
	7.68	75	0.00147	0.0169
	7.02	100	0.00149	0.0172
	6.47	125	0.00140	0.0177
	5.49	175	0.00146	0.0179
	5.04	200	0.00147	0.0182
0.5 *N* HBr	10.45	0	....	......
	10.00	25	0.000765	0.0194
	9.18	85	0.000662	0.0168
	8.90	115	0.000607	0.0154
	8.68	125	0.000645	0.0163
	8.65	130	0.000631	0.0160
0.01 *N* HBr	9.90	0	....	......
	8.48	10	....	0.0186
	7.31	20	....	0.0183
	6.45	30	....	0.0174
	5.54	40	....	0.0178
	4.82	50	....	0.0178
0.02 *N* HBr	9.69	0	....	......
	8.51	10	....	0.0180
	7.65	20	....	0.0165
	6.71	30	....	0.0174
	6.07	40	....	0.0167
	5.45	50	....	0.0166
0.05 *N* HBr	9.75	0	....	......
	8.91	10	....	0.0180
	8.21	20	....	0.0172
	7.00	40	....	0.0168
	4.29	100	....	0.0167

TABLE I—(*Continued*).

Concentration of acid.	No. of cc. of 0.01 *N* $Na_2S_2O_3$ for 10 cc. of mixture.	Time from beginning.	$K = 1/t \log_{10} A/A-x$.	K^V (Nat. logs).
0.1 *N* HBr	9.80	0	....	......
	8.79	20	....	0.0163
	7.42	50	....	0.0167
	5.67	100	....	0.0167
0.01 *N* H_2SO_4	14.88	0	....	......
	11.39	15	0.00774	0.0180
	8.09	35	0.00680	0.0166
	6.40	50	0.00733	0.0181
	5.40	60	0.00734	0.0183
	5.00	65	0.00729	0.0183
0.02 *N* H_2SO_4	17.82	0	....	......
	16.49	5	0.00674	0.0155
	15.00	10	0.00748	0.0177
	10.79	30	0.00726	0.0177
	7.80	50	0.00718	0.0180
	5.04	80	0.00686	0.0177
	3.70	100	0.00693	0.0182
	2.93	115	0.00682	0.0181
0.05 *N* H_2SO_4	7.71	0	....	......
	6.77	10	0.00565	0.0130
	5.72	20	0.00648	0.0152
	4.81	30	0.00683	0.0160
	4.14	40	0.00675	0.0160
	3.41	50	0.00709	0.0160
	2.90	60	0.00708	0.0171
0.1 *N* H_2SO_4	8.30	0	....	......
	7.20	10	0.00618	0.0142
	6.19	20	0.00637	0.0148
	5.13	30	0.00696	0.0163
	4.35	40	0.00701	0.0168
	3.70	50	0.00702	0.0168
	3.11	60	0.00710	0.0169
0.25 *N* H_2SO_4	13.10	0	....	......
	10.28	15	0.00709	0.0165
	8.00	30	0.00714	0.0168
	5.90	50	0.00693	0.0168
	4.41	70	0.00675	0.0168
	3.14	95	0.00653	0.0164
	1.71	135	0.00654	0.0166
	1.45	150	0.00637	0.0146
0.25 *N* H_3PO_4	8.10	0	....	......
	6.40	15	0.00682	0.0159

TABLE I—(*Continued*).

Concentration of acid.	No. of cc. of 0.01 *N* $Na_2S_2O_3$ for 10 cc. of mixture.	Time from beginning.	K=1/*t* $\log_{10}$ A/A-*x*.	K^V(Nat. logs).
	5.00	30	0.00698	0.0164
	3.75	45	0.00743	0.0176
	2.98	60	0.00724	0.0173
	2.30	75	0.00729	0.0176
	1.80	90	0.00726	0.0176
	1.45	105	0.00711	0.0175
0.05 *N* H_3PO_4	10.22	0	....	......
	8.70	10	0.00699	0.0160
	7.15	20	0.00776	0.0184
	5.95	30	0.00783	0.0188
	4.93	40	0.00791	0.0189
	4.15	50	0.00783	0.0190
	3.25	65	0.00776	0.0188
	2.10	90	0.00774	0.0188
0.1 *N* H_3PO_4	11.11	0	....	......
	9.60	10	0.00634	0.0149
	8.04	20	0.00702	0.0166
	6.69	30	0.00734	0.0170
	5.61	40	0.00742	0.0178
	3.61	65	0.00751	0.0179
	2.36	90	0.00747	0.0181
0.05 *N* HPO_3	11.50	0	....	......
	8.49	15	0.00879	0.0204
	6.40	30	0.00848	0.0200
	4.75	45	0.00853	0.0200
	3.63	60	0.00835	0.0198
	2.10	90	0.00820	0.0198
0.1 *N* HPO_3	13.17	0	....	......
	10.14	15	0.00750	0.0174
	7.60	30	0.00792	0.0186
	6.00	45	0.00766	0.0182
	4.77	60	0.00733	0.0174
	3.61	75	0.00748	0.0178
	2.30	100	0.00757	0.0183
0.25 *N* HPO_3	9.30	0	....	......
	7.15	15	0.00761	0.0177
	5.39	30	0.00789	0.0184
	4.15	45	0.00787	0.0185
	3.21	60	0.00770	0.0182
	2.50	75	0.00760	0.0180
	2.09	90	0.00720	0.0174

TABLE II.—MEAN VALUE OF K^V.

(0.01 N HBr	0.0180)
0.02 “	0.0170
0.04 “	0.0168
0.05 “	0.0172
0.1 “	0.0171
0.2 “	0.0171
0.5 “	0.0168
(0.01 N H_2SO_4	0.0179)
0.02 “	0.0175
0.05 “	0.0161
0.1 “	0.0167
0.25 “	0.0168
(0.05 N H_3PO_4	0.0184)
(0.1 “	0.0175)
0.25 “	0.0171
(0.05 N HPO_3	0.0199)
(0.1 “	0.0179)
(0.25 “	0.0180)

Mean (omitting 0.01 N and more dilute acids; 0.05 and 0.1 N H_3PO_4 and HPO_3) = 0.0169.

It will be seen from the figures of Table II that when the concentration of the strong acid added is 0.02 N or greater the equation gives a constant within the limits of error of the observations, for while there are some marked deviations here and there from the mean value of the constant, these deviations are evidently, from their sporadic nature, due to observational errors, the small time intervals taken, the rapid oxidation and in some cases the small differences in concentration to be measured making such errors easy. The constant is too high in the phosphoric and metaphosphoric acids, except in strong solutions, owing to the small dissociation of these acids not giving hydrogen ions enough entirely to suppress the oxidation of the negative sugar ion. We could not find the dissociation of metaphosphoric acid, but a 0.1 N H_3PO_4 solution contains only about 0.008 N hydrogen ions.

The results obtained after the addition of hydrochloric acid were at first glance abnormal, since the constant continues to fall with each increase in the concentration of the acid. The reason for this is that a reaction takes place between the Br_2 and the Cl^- which removes some of the Br_2 from the solution active state. We have been unable to find a determination of the constant of the reaction $Br_2 \times Cl^- = KCl^-Br_2$, but from our results it may be computed to be about 0.55, or about eleven times the constant of the similar reaction with Br^-.

Assuming that 0.55 is the constant of the above reaction the computation of K^V from the hydrochloric acid results gave the values in Table III;

when α[1] = Free Br_2/Total Br_2 = $0.55/(0.55 + 11\,Br^- + Cl^-)$, and when the above value of α was substituted in equation 24.

TABLE III.

Concentration of acid.	No. of cc. of 0.01 *N* $Na_2S_2O_3$ for 10 cc. of the mixture.	Time from beginning.	$K = 1/t \log_{10} A/A-x$.	K^V (Nat logs).
0.005 *N* HCl	9.48	0	....	......
	8.62	5	0.00826	......
	7.71	10	0.00898	......
	7.00	15	0.00878	......
	6.30	20	0.00887	......
	5.70	25	0.00884	......
0.010 *N* HCl	10.80	0	....	......
	9.90	5	0.00756	......
	8.39	15	0.00731	......
	7.72	20	0.00729	......
	7.10	25	0.00729	......
	6.50	30	0.00735	......
	5.53	40	0.00766	......
0.02 *N* HCl	10.10	0	....	......
	9.30	5	0.00717	0.0172
	8.60	10	0.00698	0.0169
	7.90	15	0.00711	0.0173
	7.19	20	0.00738	0.0180
	6.69	25	0.00716	0.0176
	6.12	30	0.00725	0.0179
0.05 *N* HCl	10.65	0	....	......
	9.24	10	0.00617	0.0157
	7.95	20	0.00635	0.0163
	6.95	30	0.00618	0.0160
	6.12	40	0.00602	0.0157
0.1 *N* HCl	7.50	0	....	......
	6.10	15	0.00598	0.0163
	4.96	30	0.00599	0.0165
	3.73	50	0.00607	0.0171
	2.70	75	0.00592	0.0168
	1.80	105	0.00590	0.0168
0.25 *N* HCl	16.21	0	....	......
	13.75	15	0.00477	0.0162
	10.21	40	0.00502	0.0175
	9.75	45	0.00490	0.0171
	3.05	157	0.00462	0.0168

Mean value of K^V.

0.02 *N* HCl	0.0175
0.05 "	0.0160
0.1 "	0.0167
0.25 "	0.0169

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[1] This value of α is obtained in the same manner as that given on page 468 for the determination of α when only Br ions are present.

The value of K^V of the oxidation of the positive sugar ion is, therefore, 0.0169 computed by natural logarithms.

Having thus found the value of the second constant we proceeded to test the hypothesis that the oxidation involved the negative sugar ion also.

V. The Oxidation of the Negative Sugar Ion.—The equation with which we started was:

$$23.\quad dx/dt = (A - x)[K_4/(B + 2x)^2 + K^V]0.05/(0.05 + Br^-).$$

On integration this becomes:

$$25.\quad (2A + B)^2 \log (A/A - x) - [K_4\{\log [(K_4 + K^V(B + 2x)^2)/(K_4 + K^VB^2)]\}/2K^V] + (\sqrt{K_4}(2A + B)/\sqrt{K^V})[\tan^{-1}(\sqrt{K^V}B/\sqrt{K_4}) - \tan^{-1}(\sqrt{K^V}(B + 2x)/\sqrt{K_4}) = \alpha t[K_4 + K^V(2A + B)^2].$$

Let $K_4/K^V = K^{VII}$; $K_4 = K^{VII}K^V$. Substituting these values and transposing 25, we have:

$$26.\quad ((2A + B)^2/\alpha tK^V) \log (A/A - x) - (2A + B)^2 = K^{VII} + (K^{VII}/2\alpha tK^V) \log \{[K^{VII} + (B + 2x)^2]/(K^{VII} + B^2)\} + \{[\sqrt{K^{VII}}(2A + B)]/\alpha tK^V\}\{\tan^{-1}[(B + 2x)/\sqrt{K^{VII}}] - \tan^{-1}(B/\sqrt{K^{VII}})\}.$$

This equation is in an awkward form to test the theory, although K^V is known. To get an approximation of the value of K_4 we made use of the differential equation 23. We assumed that $B + 2x$ was constant for small intervals of time and had the value of the mean of the extremes of these intervals. Integrating the equation on this assumption we had:

$$27.\quad \{(C_{Br}^{-} + 0.05)\{\log [(A - x')/(A - x'')]\}/(0.05(t'' - t')) - K^V\}C^2_{H'} = K_4.$$

With this formula values were obtained for K_4 given in Table IV:

TABLE IV.

	No. of cc. $Na_2S_2O_3$ for 10 cc. of mixture.	$t''-t'$.	Mean $C_{H'}$ during $t''-t'$.	K_4.
No acid added	13.05	0	....	....
	11.00	5	0.00102	0.19×10^{-7}
	9.45	5	0.00282	1.12
	8.40	5	0.00412	1.41
	6.78	10	0.00546	1.95
	5.70	10	0.00681	1.25
$0.001\ N\ H_2SO_4 + 0.25\ N$ NaBr	7.48	0	....	....
	6.92	5	0.00128	1.25×10^{-7}
	6.70	5	0.00167	0.61
	6.15	10	0.00205	1.45
	5.77	10	0.00252	1.36
	5.19	20	0.00300	1.34

From the results in Table IV it is obvious that the value of K_4 is a little less than 1.4×10^{-7} and that K_4 is really constant, as the hypothesis demanded. The determination of K_4 made in the presence of 0.001 *N* H_2SO_4 and 0.25 *N* NaBr was the more accurate since the addition of the bromide rendered α constant and the determinations were made with especial care. The deviations noted are unavoidable in working with such small time intervals and measuring such small quantities. In some of the readings an error of 0.02 cc. in reading the burette would have sufficed to more than double the constant K_4. In the case where no acid was added the value of K_4 in the first five minutes was far too low. This is owing to the fact that the titration was made immediately after mixing when by the rapid oxidation some of the bromine had already disappeared and acid had appeared. The first interval of 5 minutes is, therefore, to be disregarded.

Having found the approximate value of K_4 by this method the value of K^{VII} was found by trial which would satisfy equation 26 and from these values the real value of K_4 was computed. The results are given in Table V, where K_4 is shown to be 1.2×10^{-7}.

The addition of acid to the oxidizing mixture slows the first reaction, therefore, for the reason that the acid reduces the ionization of the glucose, and the number of OH ions in the water.

TABLE V.

Readings of the burette as in Table IV.

	Time from beginning. min.	K^{VII}.	K_4.
No acid added	0[1]	....	....
	5	0.0000068	1.16×10^{-7}
	10	0.0000071	1.22
	20	0.0000085	1.44
	30	0.0000074	1.25
0.001 *N* H_2SO_4	0	....	....
+	5	0.0000073	1.23
0.25 *N* NaBr	10	0.0000056	0.95
	20	0.0000069	1.17
	30	0.0000070	1.18
	50	0.0000071	1.22
Mean			1.20×10^{-7}

VI. Conclusions.—The differential equation

$$dx/dt = \alpha(A-x)\ [K^V + K_4/(B + 2x)^2],$$

in which $\alpha(A-x)$ is the concentration of the active Br_2, $(B + 2x)$ the concentration of the hydrogen ions, and K_4 and K^V constants of two reactions, has been found to represent quantitatively the course of the

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[1] The beginning of the experiments was taken as at the end of the first five minutes.

oxidation of glucose by Br_2 under varying conditions of acidity when the glucose is present in excess.

The assumption that solutions of glucose in water ionize and form the ions $C_6H_{11}O_6^-$ and $C_6H_{13}O_6^+$ in the manner indicated on page 465 and that these two ions are the active particles oxidized by bromine has thus been found to agree quantitatively with all the facts of observation. We have tested the hypothesis under very diverse conditions by measuring the rate of oxidation when no acid had been added and after the addition of varying quantities of hydrobromic, hydrochloric, sulphuric and phosphoric acids up to a concentration of 0.5 *N* and with and without the addition of sodium bromide and found that the formula covers all cases investigated. We have tested it under conditions when most of the oxidation was presumably that of the negative ion and also under conditions which presumably suppressed this reaction and left the whole of the oxidation going by the other reaction. We conclude, therefore, that this hypothesis of the mechanism of the oxidation of glucose by bromine accounts satisfactorily for all the facts observed.

The question naturally arises whether the oxidation of the negative ion gives rise to the same or different products from those formed from the positive ion. It is well known that a great number of acids are formed in the oxidation of glucose. It seems not unlikely that some of these are derived from the negative and others from the positive ion, since it is probable that the molecule will be unstable at a different point when it is positively charged, from that when it is negatively charged. The oxidation of glucose by bromine in a neutral or acid solution yields gluconic acid to a very large extent.[1] The solution, even though neutral at the start, must in such oxidations rapidly become acid by the formation of hydrobromic acid if means are not taken to neutralize this. Hence, in the oxidation by bromine as generally conducted, the first reaction, that of the negative ion, will be quickly suppressed and the reaction of the second only will take place. These facts indicate that the oxidation of the positive ion leads to gluconic acid. Whether gluconic acid may be formed also from the anion $C_6H_{11}O_6^-$ or from the undissociated molecule cannot be definitely stated.

The rate of the oxidation of the positive ion is the same, according to the theory, in alkaline and acid solutions. Some gluconic acid should be formed, therefore, in alkaline oxidations of the sugars. On the hypothesis that gluconic acid comes only from the oxidation of the cation, $C_6H_{13}O_6^+$, it is difficult to account for the large amount of gluconic acid recovered by Nef[2] in oxidations of hexoses by Fehling's solution, for

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[1] Ruff, *Ber.*, **32**, 2273 (1899). He obtained 75 per cent. of the glucose as gluconic acid.

[2] Nef, *Liebig's Ann.*, **357**, 214 (1907).

from 114 grams of glucose he got about 30 g. of hexone acids, largely gluconic acid, that is, one-fourth of the oxidation took this direction. It seems not improbable on the basis of these facts, that gluconic acid may be derived also from some other source than the positive ion.

The products of oxidation of the anion $C_6H_{11}O_6$ are possibly those which have been carefully studied by Nef[1] and the further mechanism of the oxidation he has largely elucidated.

THE ACTION OF NITRIC ACID UPON BENZOYL CHLORIDE IN THE PRESENCE OF ACETIC ANHYDRIDE.

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Claus and Schmidt,[1] Orton,[2] Schwalbe,[3] Tingle and Blanck,[4] and many others, have shown that acetic acid and acetic anhydride, when used as solvents and diluents in the nitration of aromatic compounds, exert a more or less marked influence upon the character of the products formed. Pictet and Genequand,[5] and Pictet and Khotinsky[6] have shown that under these conditions the real nitrating agent is probably either diacetylorthonitric acid, or acetyl nitrate, or both. In the general action of these reagents towards aromatic compounds there seems to be, on the whole, a slight tendency to form ortho in preference to para or meta derivatives. Toward aromatic amines they sometimes act as nitrating and sometimes as acylating agents. This behavior is similar to that of benzoyl nitrate.[7] It does not appear, however, that acylation ever takes place in the nucleus, as may nitration, but always in the side chain in connection with hydroxyl, amino, and other similar groups.

In this paper are described a few experiments and the results obtained by the action of mixtures of various proportions (1) of nitric anhydride and acetic anhydride, and (2) of fuming nitric acid and acetic anhydride, upon benzoyl chloride.

In the first set of experiments the conditions are such that the active nitrating agent is acetyl nitrate diluted with more or less acetic anhydride, $(CH_3CO)_2O + N_2O_5 = 2CH_3COONO_2$. When benzoyl chloride, acetic anhydride and nitric anhydride are mixed in a flask at 0° no reaction takes place until they are heated to about 60° when a rather vigorous reaction occurs with evolution of oxides of nitrogen. After the nitrous

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[1] *Ber.*, **19**, 1425.

[2] *J. Chem. Soc.*, **81**, 806. *Ber.*, **40**, 370.

[3] *Ber.*, **35**, 3301.

[4] *Amer. Chem. J.*, **36**, 605.

[5] *Ber.*, **35**, 2526; **36**, 2225.

[6] *Compt. rend.*, **144**, 210.

[7] Francis, *Ber.*, **39**, 3798; Butler, *Ibid.*, **39**, 3804.