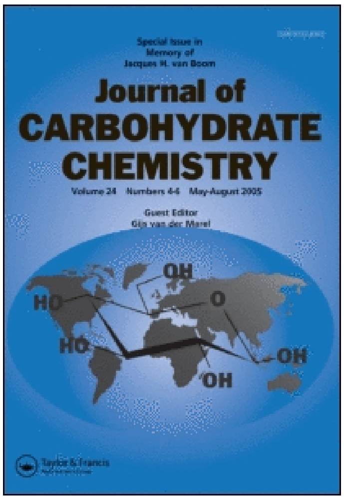

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Kinetics of the Oxidation of Monosaccharides with Acidic Bromate and N-Bromosuccinimide

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COMMUNICATION

KINETICS OF THE OXIDATION OF MONOSACCHARIDES WITH ACIDIC BROMATE AND *N*-BROMOSUCCINIMIDE

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In earlier studies on the oxidation of monosaccharides, we measured the rates of the oxidation of three aldohexoses, two ketohexoses and three aldopentoses with V(V),[1] Ce(IV),[2] Cr(VI)[3] and Mn(VII).[4] We now report on the corresponding oxidations with bromate ion and *N*-bromosuccinimide (NBS) as oxidants. To our knowledge, only kinetic studies of oxidations of ribose with BrO_3^- in aqueous H_2SO_4[5] and aldoses with NBS in 10% AcOH - H_2SO_4[6] have been reported. Because oxidation of carbohydrates is subject to HSO_4^- ion catalysis, $HClO_4$ was used, as in our earlier studies, in the present investigation to minimize the number of different catalyzing species.

Acetoin, MeCOCH(OH)Me, which has a secondary alcohol group, can be considered a model compound for **open-chain** aldosugars ($C_{(1)}$-$C_{(2)}$ complexation and cleavage) and for ketosugars ($C_{(2)}$-$C_{(3)}$ complexation). Previously we had estimated the relative amounts of the open-chain forms of monosaccharides by comparing the rates of the oxidation of monosaccharides with V(V), a reaction which we believe to involve mainly open-chain sugars, with the corresponding rate for acetoin.[7] This communication reports how acetoin can be used to get

TABLE 1. Rate Constants from Oxidation of Monosaccharides and Acetoin with BrO_3^- in 1.00 M $HClO_4$ at 30 °C. $[KBrO_3] = 1.0 \times 10^{-3}$ M, $[Hg(AcO)_2] = 6 \times 10^{-3}$ M.

Substrate	[Substrate] M	$10^5\ k_{obs}$ s^{-1}	$10^4\ k_{obs}/[Substrate]$ $M^{-1}\ s^{-1}$	r
D-Galactose	0.1087	3.60 ± 0.06	3.32 ± 0.06	0.9992
D-Glucose	0.1001	2.54 ± 0.04	2.54 ± 0.04	0.9991
D-Mannose	0.1148	3.76 ± 0.07	3.27 ± 0.06	0.9992
L-Arabinose	0.1198	2.84 ± 0.08	2.37 ± 0.07	0.9977
D-Ribose	0.0997	2.61 ± 0.15	2.62 ± 0.15	0.9920
D-Xylose	0.1194	1.94 ± 0.06	1.62 ± 0.05	0.9974
D-Fructose	0.1004	3.65 ± 0.10	3.64 ± 0.10	0.9979
L-Sorbose	0.0997	2.98 ± 0.11	2.99 ± 0.11	0.9962
Acetoin	0.1004	3.72 ± 0.11	3.71 ± 0.11	0.9984

information about the progress of the oxidation of monosaccharides with oxidants.

For a typical kinetic run, weighed amounts of monosaccharide and $Hg(AcO)_2$ were dissolved in $HClO_4$ solution in a graduated flask and the reaction was started by the addition of $KBrO_3$ solution. $Hg(AcO)_2$ was used to scavenge Br^- and to eliminate the kinetic complexity. After thermostating at 30 °C, samples were added at intervals to a mixture of KI and starch in HCl solution. After incubation for 5 min, the solution was titrated with standardized $Na_2S_2O_3$ solution. The oxidations with NBS were carried out similarly.

The rate constants $k_{obs} = -d\ln[BrO_3^-]/dt$ were determined under pseudo-first-order conditions with monosaccharide in excess and they refer to the oxidation of the first alcohol group ($C_{(2)}$ for aldosugars, $C_{(1)}/C_{(3)}$ for ketosugars).

TABLE 2. Rate Constants from Oxidation of Monosaccharides and Acetoin with NBS in 1.05 M $HClO_4$ at 60 °C. [NBS] = 2.0×10^{-3} M, $[Hg(AcO)_2] = 6 \times 10^{-3}$ M.

Substrate	[Substrate] M	10^4 k_{obs} s^{-1}	10^4 k_{obs}/[Substrate] M^{-1} s^{-1}	r
D-Galactose	0.1990	1.39 ± 0.08	7.00 ± 0.41	0.9932
D-Glucose	0.2005	1.14 ± 0.04	5.68 ± 0.19	0.9977
D-Mannose	0.1999	0.97 ± 0.05	4.85 ± 0.24	0.9940
L-Arabinose	0.2000	1.64 ± 0.06	8.19 ± 0.29	0.9963
D-Ribose	0.2003	1.90 ± 0.09	9.49 ± 0.43	0.9949
D-Xylose	0.1999	1.18 ± 0.04	9.92 ± 0.18	0.9973
D-Fructose	0.2001	2.47 ± 0.13	12.4 ± 0.6	0.9946
L-Sorbose	0.1997	1.98 ± 0.08	9.15 ± 0.38	0.9955
Acetoin[a]	0.0505	8.60 ± 1.20	170 ±24	0.9545
D-Glucose[a]	0.0499	0.18 ± 0.01	3.65 ± 0.16	0.9949

a. At 40 °C.

The oxidations are first order with respect to both BrO_3^- and substrate although the second-order rate constants $k_2 = k_{obs}$/[Substrate] tend to decrease with increasing [Substrate]. Representative data are given in Table 1.

The monosaccharides studied in this work exist in solution mainly in pyranose and furanose ring forms and only in small amount in open-chain forms. The magnitudes of $k_2 = k_{obs}$/[Substrate] for monosaccharides and for acetoin are of the same order. Monosaccharides can therefore be considered to react with BrO_3^- mainly in their ring forms. This is in contrast to V(V)-oxidation, in which the sugar reacts in the open-chain form. For example, for the oxidation of D-glucose, the ratio of the rate constants k_2(Acetoin)/k_2(Glucose) at 25 °C is 2500 for V(V)-oxidation but only 1.5 for BrO_3^--oxidation.

The effect of [$HClO_4$] was studied by partially neutralizing 3.5 M $HClO_4$ with NaOH to maintain a constant ionic strength. At 30 °C the correlation for glucose is given by

$$k_2/M^{-1}\,s^{-1} = (6.64 \pm 0.17) \times 10^{-4}[HClO_4]^2/M^2 + (1.21 \pm 1.13) \times 10^{-4} \qquad (1)$$

with a correlation coefficient of 0.9991. This result implies that the oxidant may well be $H_2BrO_3^+$ since

$$BrO_3^- + 2H_3O^+ \rightleftharpoons H_2BrO_3^+ + 2H_2O \qquad (2)$$

The following, simplified mechanism explains the present data:

$$\text{Substrate} + H_2BrO_3^+ \rightleftharpoons [\text{Substrate}, BrO_2]^+ + H_2O \qquad \text{(fast)} \qquad (3)$$

$$[\text{Substrate}, BrO_2]^+ + H_2O \rightleftharpoons \text{Product} + HBrO_2 + H_3O^+ \qquad \text{(slow)} \qquad (4)$$

The kinetic results for NBS oxidation are given in Table 2. The reactions are of first order with respect to [NBS] but of zero order with respect to [Substrate]. This result implies that monosaccharides are not involved in the rate-determining step or that their reactivities are similar.

The reactions are acid-catalyzed and first order with respect to [$HClO_4$]. Uncatalyzed reaction occurs as well. In the range 1.05 - 3.57 M $HClO_4$ at 60 °C, at constant ionic strength of 3.59 M, the correlation for glucose follows the equation

$$k_{obs}/s^{-1} = (4.35 \pm 0.22) \times 10^{-5}[HClO_4] + (3.56 \pm 0.53) \times 10^{-5} \qquad (5)$$

with a correlation coefficient of 0.9975. The following mechanism, taking aldohexose as an example, can account for the results:

$$C_4H_4O_2NBr + HX \rightleftharpoons C_4H_4O_2NH + XBr \qquad (6)$$

$$C_6H_{12}O_6 + XBr \rightleftharpoons \text{Complex} \rightleftharpoons C_6H_{11}O_6Br + HX \qquad (7)$$

$$C_6H_{11}O_6Br + H_2O \rightleftharpoons C_5H_{10}O_5 + HCO_2H + HBr \qquad (8)$$

HX is proposed to be $HClO_4$ or water.

The model compound acetoin reacts about 50 times faster than glucose. Therefore the rate-determining step must be (7) rather than (6). The experimental results can be explained by supposing that reaction (7) proceeds by Michaelis-Menten kinetics. The pseudo-first-order rate in [Monosaccharide] is the result of the high complex forming ability of XBr; the increase in [Substrate] does not increase the rate because no more complex can form. The ring form monosaccharide complexes decompose at approximately the same rate, while the open-chain acetoin complex decomposes about 50 times faster.

In summary, by comparing the oxidation rate of acetoin with the rates of monosaccharides, the following conclusions can be drawn:

(1) With vanadium(V) the reacting species of monosaccharides are the open-chain forms;

(2) With bromate ion the reacting species of monosaccharides are the ring forms;

(3) The cerium(IV) complexes of acetoin and glucose decompose by Michaelis-Menten kinetics at approximately the same rate and therefore the ring forms of monosaccharides are involved;[8]

(4) With NBS the mechanism is complex but the reactions (6) - (8) explain the experimental data.

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