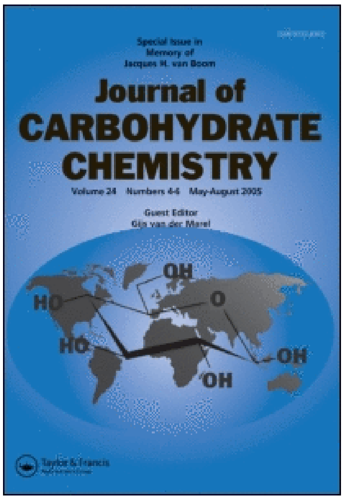

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KINETICS OF THE OXIDATION OF MONOSACCHARIDES WITH BROMAMIDE-T

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ABSTRACT

The kinetics of the reaction of eight monosaccharides and the model compound acetoin with sodium salt of *N*-bromo-*p*-toluenesulfonamide in hydrochloric acid solutions was studied at 25 °C. The low value of the ratio of the second-order rate constants k_2 (Acetoin)/k_2 (Glucose) and the low reactivity of ketosugars relative to that of aldosugars indicate that the ring forms of the aldosugars are involved in the oxidations. A mechanism consistent with the experimental observations is proposed. The configurations and reactivities of aldosugars are compared.

INTRODUCTION

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] Mn(VII),[4] BrO_3^- [5] and NBS (*N*-bromosuccinimide).[5] The oxidation of aldoses with bromine including the pioneering studies of the 1930's by Isbell and his co-workers has been reviewed by Capon.[6] We now report on the corresponding oxidations with *N*-bromo-*p*-toluenesulfonamide, or bromamide-T (BAT). The kinetics of the oxidations of four hexoses with BAT[7] have earlier been investigated in highly alkaline media. To allow comparison of our new and our earlier results, and because monosaccharides may undergo epimerization in alkaline solutions,[8] strongly acidic aqueous solutions were used throughout the present investigation.

RESULTS AND DISCUSSION

The rate constants $k_{obs} = d\ln[BAT]/dt$ 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). The reactions are first order with respect to [BAT], but the second-order rate constants $k_2 = k_{obs}/[\text{Substrate}]$ tend to decrease with increasing [Substrate]. Representative data are given in Tables 1 and 2.

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. For the reversible pseudo-first-order reaction

$$\alpha\text{-Glucose} \Leftrightarrow \beta\text{-Glucose} \qquad (1)$$

the observed rate constant $k_{obs} = k_\alpha + k_\beta = k_o + k_{H^+} \times [H^+] = 9.90 \times 10^{-4} + 3.28 \times 10^{-2} \times 0.51\ s^{-1} = 1.77 \times 10^{-2}\ s^{-1}$ in 0.51 M HCl at 35.21 °C.[9] Comparing this value with the values of k_{obs} for the oxidations in Tables 1 and 2, one can see that in our experimental conditions mutarotation is fast compared to the oxidation.

Acetoin, MeCOCH(OH)Me, can be considered a model compound for open-chain aldosugars ($C_{(1)}$ -$C_{(2)}$ complexation and cleavage) and for open-chain ketosugars ($C_{(1)}$-$C_{(3)}$ complexation). For example, for the oxidation of D-glucose with V(V),[1] a reaction which we believe to involve mainly open-chain sugar, the ratio of the rate constants k_2(Acetoin)/k_2 (Glucose) at 25 °C is 2500, but for BrO_3^- oxidation,[5] where the reacting species of monosaccharides are the ring forms, the ratio is only 1.5.

In the present work, for BAT oxidation the ratio is 6 indicating that the main reacting species are the ring forms. This conclusion is supported by the slow reactivity measured for D-fructose and L-sorbose. In clear contrast with aldosugars, hydrogen abstraction is not possible at the hemiacetal carbon of the ring forms of ketosugars.

The oxidation of monosaccharides with Ce(IV)[2] proceeds by Michaelis-Menten kinetics in which the dissociating complex is formed between Ce(IV) and the ring form of a monosaccharide.[10] From the values in Table 2 and the equation

$$\frac{1}{k_{obs}} = \frac{1}{k_{diss}K_{ass}} \times \frac{1}{[Glu]} + \frac{1}{k_{diss}} \qquad (2)$$

the following equation is derived

$$\frac{1}{k_{obs}}/s = (8.07 \pm 0.27) \times 10^2 \times \frac{1}{[Glu]}/M^{-1} \pm (1.82 \pm 0.64) \times 10^3 \qquad (3)$$

TABLE 1. Rate Constants for the Oxidation of Monosaccharides and Acetoin with BAT in 0.51 M HCl at 25 °C. [BAT] = 2.2 x 10^{-3} M.

Substrate	[Substrate] M	$10^4 k_{obs}$ s^{-1}	$10^4 k_{obs}$/[Substrate] $M^{-1} s^{-1}$	r
D-Galactose	0.0407	1.03 ±0.02	25.4 ±0.5	0.9990
D-Glucose	0.0338	0.369±0.011	10.9 ±0.3	0.9979
D-Mannose	0.0406	0.155±0.003	3.81±0.06	0.9993
L-Arabinose	0.0428	1.10 ±0.02	25.7 ±0.5	0.9990
D-Ribose	0.0440	0.295±0.007	6.70±0.15	0.9987
D-Xylose	0.0428	0.411±0.010	9.61±0.23	0.9985
D-Fructose	0.7846	0.304±0.014	0.387±0.017	0.9950
L-Sorbose	0.7809	0.236±0.007	0.302±0.008	0.9980
Acetoin	0.0538	3.58 ±0.20	66.5±3.7	0.9920

TABLE 2. Effect of [Glucose] on the Rate Constant of the Oxidation of D-Glucose with BAT in 0.51 M HCl at 25 °C. [BAT] = 2.2 x 10^{-3} M.

[D-Glucose] M	$10^5 k_{obs}$ s^{-1}	$10^4 k_{obs}$/[Glucose] $M^{-1} s^{-1}$	r
0.0221	2.67 ± 0.05	12.1 ± 0.2	0.9993
0.0338	3.69 ± 0.11	10.9 ± 0.3	0.9979
0.0641	6.97 ± 0.12	10.9 ± 0.2	0.9992
0.0823	8.62 ± 0.21	10.5 ± 0.3	0.9988
0.1011	9.96 ± 0.18	9.85 ± 0.18	0.9992
0.1983	19.2 ± 0.7	9.70 ± 0.37	0.9964

with a correlation coefficient of 0.9978. From equation (3) we obtain the values K_{ass} = 2.3 M^{-1} for the formation constant of the complex and k_{diss} = 5.5 x 10^{-4} s^{-1} for its dissociation constant. The corresponding values for the Ce(IV)-oxidation are K_{ass} = 34 M^{-1} and k_{diss} = 0.72 s^{-1}. It may be that the oxidation of monosaccharides with BAT proceeds by an S_N2 mechanism in which con-

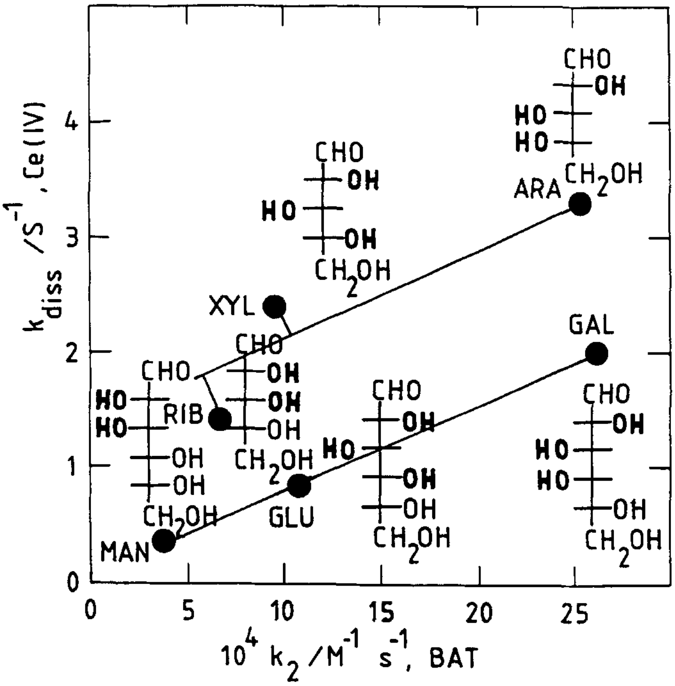

Fig. 1. Comparison of the rate constants of the oxidation of aldosugars with BAT and Ce(IV).

siderable amount of complex is formed. The Michaelis-Menten limit in which all BAT is complexed is not reached because the large amount of [Sugar] needed is not experimentally possible.

The reactivities of aldohexoses decrease in the order D-galactose > D-glucose > D-mannose for both BAT and Ce(IV) oxidations. As seen in FIG. 1, the rate constants k_2 for BAT oxidation correlates linearly with the rate constant k_{diss} for Ce(IV) oxidation. Likewise the reactivities of the aldopentoses decrease in the same order for both oxidations L-arabinose > D-xylose > D-ribose. Interestingly, as seen from the Fischer projections in FIG. 1, the configurations and reactivities change in a similar way for both aldohexoses and aldopentoses.

In acidified BAT solutions the following equilibria are possible[10]

$$RNBr^-Na^+ \Leftrightarrow RNBr^- + Na^+ \quad (4)$$

$$RNBr^- + H_3O^+ \Leftrightarrow RNHBr + H_2O \quad (5)$$

$$2\,RNHBr \Leftrightarrow RNH_2 + RNBr_2 \quad (6)$$

$$RNBr_2 + H_2O \Leftrightarrow RNHBr + HOBr \quad (7)$$

The possible oxidizing species in acidified BAT solutions are therefore RNHBr, $RNBr_2$ and HOBr. The possibility that $RNBr_2$ functions as an oxidant can be ruled out because from equation (6) the rate law would predict a second-order dependence on [BAT], which is contrary to experimental observation. Moreover, if HOBr were involved as oxidant, a retardation of the rate upon addition of RNH_2 would be expected, but no such effect was observed. It is likely therefore that the oxidant is RNHBr. Addition of acrylamide to the reaction mixture did not influence the rate and no polymer formation was observed. The existence of free radicals is therefore unlikely.

On the basis of the above, the following mechanism can be proposed for aldohexoses:

$$C_6H_{12}O_6 + RNHBr \overset{K_{ass}}{\Leftrightarrow} \{C_6H_{12}O_6{\cdot}RNHBr\} \qquad \text{(fast)} \qquad (8)$$

$$\{C_6H_{12}O_6{\cdot}RNHBr\} \overset{k_{diss}}{\Leftrightarrow} C_6H_{11}O_6Br + RNH_2 \qquad \text{(slow)} \qquad (9)$$

$$C_6H_{11}O_6Br + H_2O \Leftrightarrow C_6H_{12}O_7 + HBr \qquad \text{(fast)} \qquad (10)$$

in which $C_6H_{12}O_7$ is an aldonic acid.

The total concentration of unreacted RNHBr in D-glucose solutions is

$$[RNHBr]_T = [RNHBr] + K_{ass}[RNHBr][Glu] \qquad (11)$$

and

$$[RNHBr] = \frac{[RNHBr]_T}{1 + K_{ass}[Glu]} \qquad (12)$$

$$\text{Rate} = k_{diss}[C_6H_{12}O_6{\cdot}RNHBr] \qquad (13)$$

$$= \frac{k_{diss}K_{ass}[RNHBr]_T[Glu]}{1 + K_{ass}[Glu]} = k_{obs}[RNHBr]_T \qquad (14)$$

and

$$\frac{1}{k_{obs}} = \frac{1 + K_{ass}[Glu]}{k_{diss}K_{ass}[Glu]} = \frac{1}{k_{diss}K_{ass}} \times \frac{1}{[Glu]} + \frac{1}{k_{diss}} \qquad (15)$$

which is identical to equation (2).

Equation (4) is a neutralization reaction. The pK_a of RNHBr, however, is so high, 4.95,[11] that, under the present conditions, [RNHBr] = [$RNBr^-$] and the rate is independent of acidity at constant ionic strength. This was experimentally verified by using solvents obtained by partially neutralizing 3 M HCl with

NaOH to maintain a constant ionic strength. In the range 1 - 3 M HCl, at 25 °C, a constant value of $(2.83 \pm 0.16) \times 10^{-4}$ M^{-1} s^{-1} was obtained for k_{obs}/[Glu]. If the ionic strength was allowed to vary, the rate decreased with increasing [HCl] showing a negative ionic strenght effect.

For 0.5 M HCl and 0.036 M D-glucose solutions at different temperatures, the values 73.0 ± 1.0 kJ mol^{-1} for the enthalpy of activation and -57.0 ± 3.3 J K^{-1} mol^{-1} for the entropy of activation were evaluated from the plot of $\ln[(k_2/T)/M^{-1}$ s^{-1} $K^{-1}]$ vs. $(1/T)/K^{-1}$. The sign and magnitude of $\Delta S^{\#}$ as observed suggest that the complex formed is more compact than the reactants.

EXPERIMENTAL

In a typical kinetic run, weighed amounts of monosaccharide were dissolved in aqueous 0.51 M HCl solution in a darkened graduated flask and the reaction was started by the addition of aqueous BAT solution. After thermostating at 25 °C, samples were added at intervals to a mixture of KI and starch in HCl solution. After incubation for 5 min, the solutions were titrated with standardized $Na_2S_2O_3$ solution.

The reaction products were analyzed by TLC using silica gel 60 F_{254} from E. Merck as the stationary phase, acetonitrile-water (4:1) as the mobile phase and 1,3-naphthalenediol as the spraying reagent. Glucose, which behaved characteristically, first was oxidized to gluconolactone. Gluconic acid was subsequently formed by hydrolysis and identified by TLC. No arabinose was detected.

REFERENCES

1. P. O. I. Virtanen, S. Kurkisuo, H. Nevala and S. Pohjola, *Acta Chem. Scand.*, **A40**, 200 (1986); P. O. I. Virtanen and S. Kurkisuo, *Carbohydr. Res.*, **138**, 215 (1985); P. O. I. Virtanen, H. Nevala and S. Pohjola, *Finn. Chem. Lett.*, **15**, 109 (1988); P. O. I. Virtanen, E. Oikarinen and A. Yli-Pyky, *Finn. Chem. Lett.*, **15**, 139 (1988), *ibid.*, **16**, 53 (1989).

2. P. O. I. Virtanen, R. Lindroos, E. Oikarinen and J. Vaskuri, *Carbohydr. Res.*, **167**, 29 (1987).

3. P. O. I. Virtanen and R. Lindroos-Heinänen, *Acta Chem. Scand.*, **B42**, 411 (1988).

4. R. Lindroos-Heinänen and P. O. I. Virtanen, *Finn. Chem. Lett.*, **15**, 117 (1988).

5. A.-M. Kiviniemi and P. O. I. Virtanen, *J. Carbohydr. Chem.*, **11**, 195 (1992).

6. B. Capon, *Chem. Rev.*, **69**, 407 (1969).

7. R. N. Singh and O. Prakash, *Indian J. Chem.*, **21A**, 616 (1982).

8. R. N. Guthrie and J. Honeyman, *An Introduction to the Chemistry of Carbohydrates*, 2nd ed.; Clarendon Press: Oxford, pp 44-47; N. R. Williams, *Carbohydrate Chemistry*, Vol. 20, The Royal Society of London, pp 11-12.

9. N.M. Ballash and E.B. Robertson, *Can. J. Chem.*, **51**, 556 (1973).

10. R. Lindroos-Heinänen, R. Oilunkaniemi, P. O. I. Virtanen and T. Rauma, *Acta Chem. Scand.*, **45**, 543 (1991).

11. F. E. Hardy and V. J. Johnson, *J. Chem. Soc. Perkin Trans. 2*, 742 (1973).