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Note

Kinetic study of the oxidation of D-galactose by *N*-bromosaccharin in aqueous acetic acid

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Halogens[1–3] and their derivatives[4,5] are the most important oxidants used in the fields of carbohydrates. The most widely investigated carbohydrates are the aldoses. We report here the oxidation of D-galactose with a new haloimide, *N*-bromosaccharin (NBSA), in aqueous acetic acid in the presence of mercuric acetate as a scavenger for Br^-.

EXPERIMENTAL

Materials and methods. — *N*-Bromosaccharin[6] was prepared by bromination of saccharin in alkaline solution at 0°, and a solution of it in acetic acid was used. The solution so obtained was standardised by an iodometric method[7]. A fresh aqueous solution of D-galactose (Loba chemie) was prepared. A stock solution of mercuric acetate was prepared in 1:1 (v/v) acetic acid–water. Other chemicals used were of standard grade.

The mixture was equilibrated in a thermostat (±0.1°) at the desired temperature. Kinetics of the reaction were monitored by estimating unreacted NBSA iodometrically at different intervals.

STOICHIOMETRY AND PRODUCT ANALYSIS

A mixture containing an excess of NBSA over galactose in the presence of mercuric acetate was kept at a fixed temperature. When the reaction was complete, the residual NBSA was determined iodometrically. Several determinations indicated 1:1 stoichiometry. Further, under kinetic conditions, the value of the second-order rate-constant was found similar to that obtained in the stoichiometric runs, which establishes the 1:1 stoichiometry. The product (galactonic acid) was

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TABLE I

EFFECT OF VARYING [NBSA] ON REACTION RATE[a]

[NBSA] (10^3M)	10^3k_1 (min^{-1})
1.00	24.40
1.25	24.29
2.00	24.35
3.33	24.37
5.00	24.36

[a] [Galactose], 0.1M; [$Hg(OAc)_2$], 10.0mM; [HOAc], 20% (v/v); temperature, 60°.

identified by paper chromatography[8]. Similar end-products have been reported for the bromine oxidation of aldoses[3].

The oxidation studies employed large excess of galactose and mercuric acetate over the oxidant. The constant values for the pseudo-first-order rate constants obtained from the slopes of linear plots of $\log(a - x)$ versus time, and the integrated first-order rate-equation are in good agreement, confirming the first-order dependence in NBSA (Table I).

An increase in [galactose] increases the reaction rate. The plot of $\log k_1$ versus log[galactose] is linear, with a slope less than unity (slope = 0.58), indicating fractional-order dependence in galactose. This dependence of rate on [galactose] makes the formation of an intermediate complex prior to the rate-limiting step likely; this presumption was also confirmed by the linearity and positive intercept of the double-reciprocal plot of k_1 and [galactose] as shown in Fig. 1. Added perchloric acid enhances the rate. For example, when [$HClO_4$] increases from 1.0 to 5.0M, the value of 10^3 k_1 min^{-1} increases from 34.08 to 70.40 under the

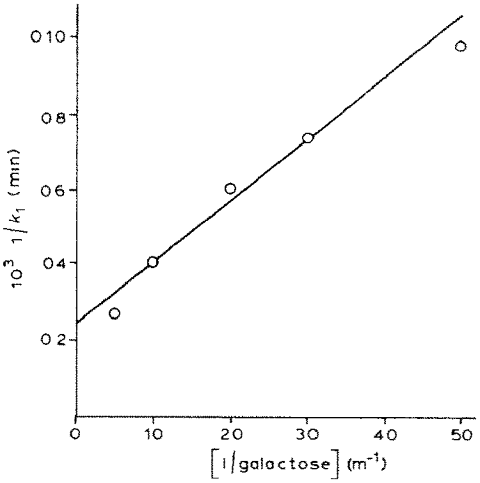


Fig. 1. Plot of $1/k_1$ vs 1/[galactose]; [NBSA], 3.33mM; [$Hg(OAc)_2$], 10.0mM, [HOAc], 20% (v/v); temperature 60 ±0.1°.

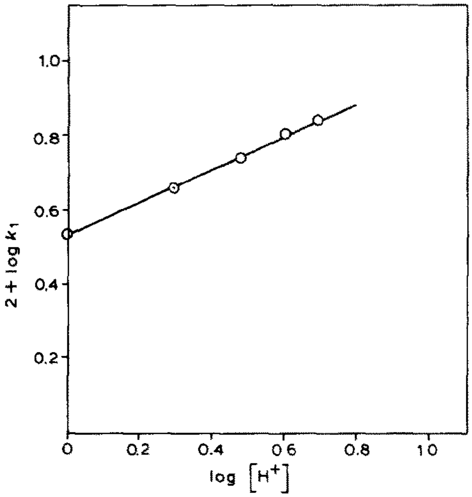


Fig. 2. Plot of logk_1 *vs.* log$[H^+]$; [NBSA], 3.33mM; [HOAc], 20% (v/v); [galactose], 0.1M; $[Hg(OAc)_2]$, 10.0mM; temperature, 60 ±0.1°.

conditions: [galactose], 0.1M; [NBSA], 3.33mM; $[Hg(OAc)_2]$, 10.0mM; [HOAc], 20% (v/v); and temperature 60°. The plot of log k_1 versus log$[H^+]$ gives a slope of 0.5, indicating fractional order in H^+ (Fig. 2).

Addition of $NaClO_4$, Na_2SO_4, and NaOAc shows a marginal positive effect. The effect of variation of the acetic acid–water ratio was examined and it was found that the values of k_1 increase with decrease in dielectric constant (*D*) of the medium. A positive slope from the linear plot of log k_1 versus 1/*D* and the results of salt effects indicate that the reaction is of an ion–dipole type. A retardation of rate with the addition of saccharin was observed (Table II).

The oxidation was studied at different temperatures (50–70°). The values of the thermodynamic parameters were calculated from the Arrhenius-dependence plot and the values of *E*, *A*, and ΔS are 14.56 ±0.93 kcal mol^{-1}, 1.22 ±0.5 × 10^6 sec^{-1}, and −30.92 ±0.90 e.u. These values are qualitative, based on the kinetic

TABLE II

EFFECT OF VARYING [SACCHARIN] ON REACTION RATE[a]

[Saccharin] (mM)	*10^3k_1 (min^{-1})*
0.00	24.37
1.66	20.93
2.00	17.65
2.50	12.53
3.33	10.47
4.00	7.90

[a] [NBSA], 3.33mM; [Galactose], 0.1M; $[Hg(OAc)_2]$, 10.0mM; [HOAc], 20% (v/v); temperature, 60°.

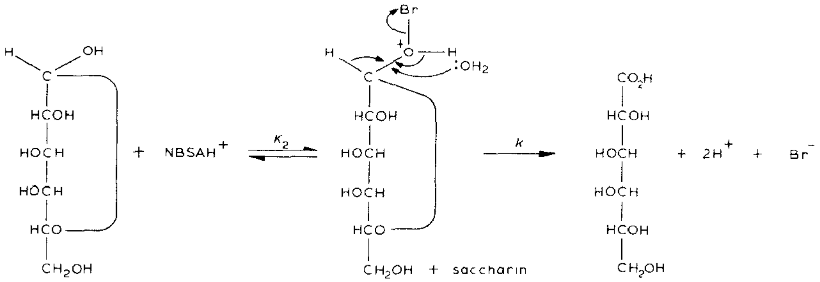
results. High value of the energy of activation suggests that the reaction should be slow at room temperature. Similar values have been obtained in the oxidation of glucose by potassium bromate[9], chromic acid[10], and chromium peroxydichromate[11]. The value of the entropy of activation is consistent with that of C–H bond fission[12].

MECHANISM AND RATE LAW

The dependence of rate on [H$^+$] suggests the protonation of one of the reactants. Protonation of the oxidant is more plausible, as with other haloimides (Eq. *1*).

$$\text{NBSA} + \text{H}^+ \overset{K_1}{\rightleftharpoons} \text{NBSAH}^+ \qquad (1)$$

Furthermore, NBSAH$^+$ may be presumed to form an intermediate complex with galactose. Waters[13] and Stewart[14] have pointed out that, with heterolytic oxidants, the oxidation of alcohols generally proceeds via esterification or by hydride transfer. In both the mechanisms, the rate-determining step involves C–H bond fission. Overend *et al.*[1] also suggested the formation of an intermediate hypobromite ester in the oxidation of α- and β-D-glucose with bromine. Consistent with the results of the present investigation, we propose an ester mechanism.



The plot of log k_1 against $-H_0$ is linear with slope 0.13. A linear plot with a slope value (ω) of +3.2 is obtained if drawn between (log k_1 + H_0) and log a_{H_2O}. The ω value suggests that water molecule is acting as nucleophile[15].

Applying steady-state kinetics, the rate expression is obtained as:

$$k_{obs} = \frac{K_1K_2k\,[\text{galactose}]\,[\text{H}^+]}{[\text{saccharin}]\,\{1 + K_1[\text{H}^+]\} + K_1K_2\,[\text{galactose}]\,[\text{H}^+]}$$

$$\frac{1}{k_{obs}} = \frac{[\text{saccharin}]\,\{1 + K_1[\text{H}^+]}{K_1K_2k\,[\text{galactose}]\,[\text{H}^+]} + \frac{1}{k}$$

According to the foregoing equation, plots of $1/k_{obs}$ against [saccharin] and $1/k_{obs}$ versus 1/[galactose] should be linear. This has been found to be so. Retardation of rate with the addition of saccharin suggests that the pre-equilibrium process involves a step in which saccharin is one of the products.

In the proposed mechanism, the intermediate ester is less polar than the reactants because of dispersal of charge, and hence decreasing the polarity of the solvent is expected to stabilize the hypobromite ester in preference to the reactants, thereby enhancing the rate. Such a solvent influence has actually been observed.

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