## Note

# Oxidation of D-glucose by a mixture of chromic and perchloric acids

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Oxidation of carbohydrates by such oxidizing agents as ceric perchlorate[1], periodates[2], and a mixture of chromic acid and sulfuric acid[3] has been widely used in carbohydrate chemistry. We now describe a study of the kinetics of the oxidation of D-glucose by a mixture of chromic and perchloric acids at a constant ionic strength and in the temperature range of 20–50°.

*Materials.* — All the reagents used were in the purest form available. D-Gluconic acid was donated by Sigma Chemical Company, St. Louis, Missouri, U. S. A.

*Method.* — The order of the reaction with respect to chromic acid was determined by the method used by Chatterji and co-workers[4]. The concentration of chromic acid in the reaction mixture was kept very low in comparison with that of the other reactants, and the amount of unreacted chromic acid was determined at various time-intervals.

The rate of reaction ($dx/dt$) is given by

$$-\frac{dx}{dt} = k[A]^{n_1}\,[B]^{n_2}\,[C]^{n_3}, \tag{1}$$

where A, B, and C are the concentrations of chromic acid, D-glucose, and perchloric acid, respectively, and $n_1$, $n_2$, and $n_3$ are the orders with respect to these reactants. As the concentration of chromic acid was very low, equation 1 may be written as:

$$-\frac{dx}{dt} = k_0[A]^{n_1}, \tag{2}$$

where $k_0 = k[B]^{n_2}[C]^{n_3}$. (3)

Equation 2 shows that the order of the reaction with respect to chromic acid and the velocity constant $k_0$ can be determined from the above-mentioned observations.

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Now, if the concentration of D-glucose is changed to B′, and the concentrations of the other two reactants are kept the same, the value of the velocity constant will be changed to $k'_0$, and

$$k'_0 = k[B']^{n_2}[C]^{n_3} \quad (4)$$

From equations 3 and 4,

$$\log k_0 - \log k'_0 = n_2(\log [B] - \log[B']) \quad (5)$$

The order of reaction with respect to D-glucose, $n_2$, can be obtained from equation 5.

By determining $k_0$ for reaction mixtures having different concentrations of D-glucose and the same concentrations of chromic and perchloric acids (chromic acid always having a concentration considerably lower than those of the other two reactants), the order with respect to D-glucose was obtained. The order with respect to perchloric acid was obtained as for D-glucose.

Sodium perchlorate was used in all experiments to keep the ionic strength constant at 0.4M.

The temperature coefficient, the energy of activation, and the frequency factor were calculated by determining, for different temperatures, the total velocity constant $k$, given by the equation

$$k_0 = k[\text{D-glucose}]^{n_2}\,[\text{perchloric acid}]^{n_3},$$

where $n_2$ and $n_3$ are the orders with respect to D-glucose and perchloric acid, respectelvely.

## RESULTS AND DISCUSSION

With respect to chromic acid, D-glucose, and perchloric acid, the reaction was found to be zero-, first-, and second-order (see Tables I and II). On summing up the

TABLE I

ORDER OF REACTION WITH RESPECT TO CHROMIC ACID, FOR THE OXIDATION OF D-GLUCOSE BY A MIXTURE OF CHROMIC AND PERCHLORIC ACIDS[a] AT 30°

| *Time* (*min*) | *Molarity of chromic acid* $\times 10^3$ | $k_0 \times 10^6$ ($mol.min^{-1}$) |
|---|---|---|
| 0 | 2.000 | |
| 10 | 1.895 | 10.50 |
| 20 | 1.776 | 11.20 |
| 30 | 1.660 | 11.33 |
| 40 | 1.550 | 11.25 |
| 50 | 1.433 | 11.34 |
| 60 | 1.327 | 11.22 |
| | Mean | 11.14 |

[a]Molarity of reactants: chromic acid, 0.002; perchloric acid, 0.3469; and D-glucose, 0.16. As constant values of the velocity constant are obtained by using the equation for the zero-order reaction, the order is zero with respect to chromic acid. $k_0 = x/t$.

TABLE II

ORDER OF REACTION IN OXIDATION OF D-GLUCOSE BY MIXTURES OF CHROMIC AND PERCHLORIC ACIDS AT 30°

| *Order-determining reactant* | *Molarity* | *Molarity of the other reactants*[a] | | | *Mean value of* $k_0 \times 10^6$ *(mol.min*$^{-1}$*)* | *Order* |
|---|---|---|---|---|---|---|
| | | *A* | *B* | *C* | | |
| D-Glucose | 0.24 | 0.3469 | | | 16.368 | — |
| | 0.16 | | | | 11.141 | 0.943 |
| | 0.08 | | | 0.002 | 5.464 | 1.020 |
| | 0.04 | | | | 3.145 | 0.869 |
| | 0.02 | | | | 1.537 | 1.023 |
| Perchloric acid | 0.3469 | | | 0.002 | 11.141 | — |
| | 0.2891 | | 0.16 | | 8.065 | 1.772 |
| | 0.2313 | | | | 5.596 | 1.638 |
| | 0.1734 | | | | 3.255 | 1.880 |
| | 0.1156 | | | | 1.683 | 1.628 |

[a]Key: A, perchloric acid; B, D-glucose; and C, chromic acid.

orders, the total order of the reaction was calculated to be three. It is interesting that, although chromic acid is continuously consumed during the course of the reaction, the order with respect to it is zero. The temperature coefficient, the energy of activation, and the frequency factors were also calculated (see Table III). The value of the temperature coefficient decreased with increase in temperature, as found by earlier workers[5] for oxidations with chromic acid.

TABLE III

TEMPERATURE COEFFICIENT, ENERGY OF ACTIVATION, AND FREQUENCY FACTOR FOR OXIDATION OF D-GLUCOSE BY CHROMIC AND PERCHLORIC ACIDS[a]

| *Temperature (degrees)* | $k_0 \times 10^6$ | $k \times 10^4$ | *Temperature coefficient* | *E (kcal.)* | $A \times 10^6$ |
|---|---|---|---|---|---|
| 20 | 2.530 | 2.955 | | | |
| 30 | 5.596 | 6.537 | 2.21 | | |
| 40 | 11.455 | 13.380 | 2.05 | 13.45 | 3.23 |
| 50 | 21.446 | 25.050 | 1.87 | | |

[a]Molarity of reactants: chromic acid, 0.002; perchloric acid, 0.2313; and D-glucose, 0.16.

On studying the effect of various salts on this reaction, it was found that, in the presence of acetate ions, the rate of the reaction is lowered considerably (see Table IV). Paper chromatography of the reaction products revealed that gluconic acid was one of the products. On the basis of these studies on only one sugar, a reaction mechanism cannot as yet be suggested. Study of the oxidation of a few other hexoses under similar conditions will be necessary.

TABLE IV

EFFECT OF DIFFERENT SALTS ON THE OXIDATION OF D-GLUCOSE BY A MIXTURE OF CHROMIC AND PERCHLORIC ACIDS[a]

| *Salt added* | *Molarity* | *Velocity constant,* $k_0 \times 10^6$ *(mol. min*$^{-1}$*)* |
|---|---|---|
| None | — | 11.141 |
| Sodium chloride | 0.10 | 8.924 |
| Sodium sulfate | 0.05 | 8.462 |
| Lithium chloride | 0.10 | 9.441 |
| Lithium sulfate | 0.05 | 8.811 |
| Magnesium chloride | 0.05 | 9.317 |
| Calcium chloride | 0.05 | 9.863 |
| Calcium nitrate | 0.05 | 9.423 |
| Magnesium acetate | 0.05 | 6.429 |
| Sodium acetate | 0.10 | 6.036 |

[a]Molarity of reactants: chromic acid, 0.002; perchloric acid, 0.3469; and D-glucose, 0.16. Temperature 30°.

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