Carbohydrate Research, 56 (1977) 407–410

Note

Complex formation between polyols and periodate anions

Wojciech J. Popiel* and Muhyeddin S. Rustom
Chemistry Department, University of Jordan, Amman (Jordan)

(Received November 10th, 1975; accepted for publication in revised form, October 4th, 1976)

Periodate oxidation of carbohydrates[1] may proceed *via* a charged cyclic intermediate[2]. For 1,2-diol–periodate complexes, Bunton and his co-workers[3] determined the formation constants (K), as well as the rate constants (k) for decomposition into oxidation products. As a general rule, a rise in pH caused an increase in K and a decrease in k. Sugars and sugar alcohols migrate electrophoretically on paper moistened with aqueous sodium metaperiodate at pH 11, giving compact spots with little evidence of oxidation[4], suggesting the formation of comparatively stable, anionic polyol–periodate complexes. We now report further on this phenomenon, especially the stoichiometry and the extent of oxidation during electrophoresis.

On paper electrophoresis in 0.07M periodate at pH 11, the average migration of formate ion was 19.2 cm/h at 20 V/cm, and other mobilities relative thereto were as follows: iodate, 0.76; D-mannitol, 0.82; D-glucose, 0.81; D-ribose, 0.80; *myo*-inositol, 0.76; lactose, 0.75; maltose, 0.73; raffinose, 0.58; methyl α-D-glucopyranoside, 0.41; and sucrose, 0.36. Since the formate ion, and often the iodate ion also, could be separated from the other compounds, the extent of oxidation of the carbohydrates could be estimated from the intensities of the accompanying formate and iodate spots. In a carbonate buffer at pH 11, polyols did not migrate unless previously treated with periodate. The average migration of formate was 30.5 cm/h, and the mobilities of iodate and periodate relative thereto were 0.73 and 0.51, respectively.

During electrophoresis in the presence of periodate at pH 11, oxidation is very slow for raffinose, sucrose, and methyl α-D-glucopyranoside, slightly faster for *myo*-inositol, and more so for D-mannitol. The compact spots detectable with ammoniacal silver nitrate, and having mobilities lower than that of formate, were therefore indicative of anionic periodate–polyol complexes. The complexes formed from raffinose, sucrose, and methyl α-D-glucopyranoside were quite stable, but those from *myo*-inositol and D-mannitol were less so. Evidence of appreciable oxidation was obtained for lactose, maltose, D-glucose, and D-ribose, and, with the exception of D-ribose, the spots detected for the complexes were rather elongated and they

---

*To whom correspondence should be directed. Present address: Chemistry Department, Makerere University, P.O. Box 7062, Kampala, Uganda.

probably involve not the original compounds but products of oxidative degradation.

In the presence of periodate, the optical rotations of raffinose, sucrose, and methyl α-D-glucopyranoside could be enhanced *ca.* 26, 20, and 5%, respectively. Whereas for solutions of methyl α-D-glucopyranoside or raffinose in periodate at pH 11, the optical rotation slowly decreased, that for sucrose remained constant for at least two hours, pointing to a higher stability of the periodate–sucrose complex. At pH 8, the decrease in optical activity was much more rapid and occurred also for sucrose. When the initial specific rotation for each of these carbohydrates was plotted[5] against the periodate-polyol molar ratio, the formation of a 1:1 complex was indicated; the results for raffinose are shown in Fig. 1. The other sugars investigated gave specific rotation-time curves[6] of complicated shapes, which depended on the initial periodate–polyol molar ratio and for which no satisfactory interpretation could be found. Only periodate-ribose mixtures of molar ratios 0.5–5.0 initially gave enhanced optical activities.

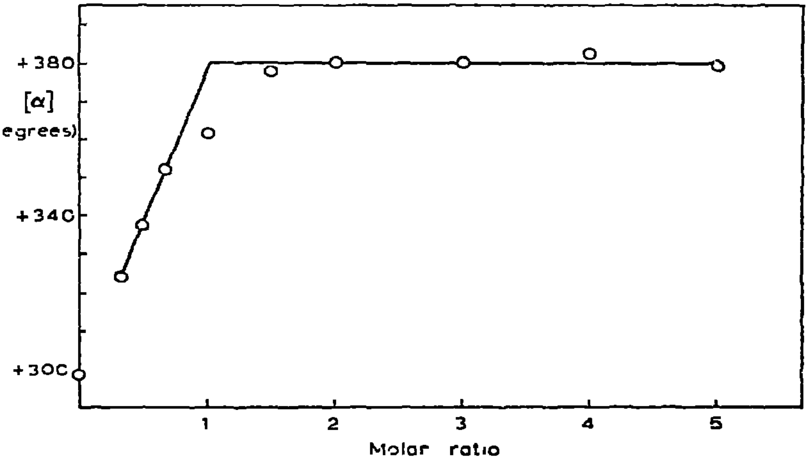

Fig. 1. Effect of molar ratio [0.01M periodate (pH 11)/raffinose pentahydrate] on [α] at 25° and 365 nm.

Upon plotting the conductivities of the periodate–carbohydrate mixtures against the molar ratios, discontinuities indicating a 1:1 complex were obtained for raffinose, methyl α-D-glucopyranoside, sucrose, D-mannitol, lactose, maltose, and D-ribose, but no clear trend was observed for D-glucose. For the first three compounds, the conductivities of the mixtures were markedly lower than that of periodate, and were constant during 3 h. For *myo*-inositol, a 2:1 periodate-inositol complex was found. It is of interest that Barker[7] showed that *myo*-inositol is rapidly oxidised by periodate at pH 7, with no evidence of complex formation, although *neo*-inositol is known to give a 2:1 complex[7,8]. The conductivities of periodate–*myo*-inositol mixtures increased with time (Fig. 2) The initial conductivities of the mixtures, which were lower than that of periodate, gradually increased during 3 hours, although the break in the graph still occurred at a 2:1 molar ratio. This increase is probably due to the production of formate ions during a slow oxidation process. The conductivities of periodate–D-mannitol mixtures were also initially below that of periodate, but increased substantially, suggesting instability of the 1:1 complex. Conductimetric studies on lactose gave time-dependent results resembling those for mannitol. For maltose and D-ribose, the conductivities measured immediately after mixing were higher than that for periodate alone, although the break at a 1:1 molar ratio was still clearly evident in each case.

The foregoing results confirm that periodate–carbohydrate reactions involve an intermediate anionic complex.

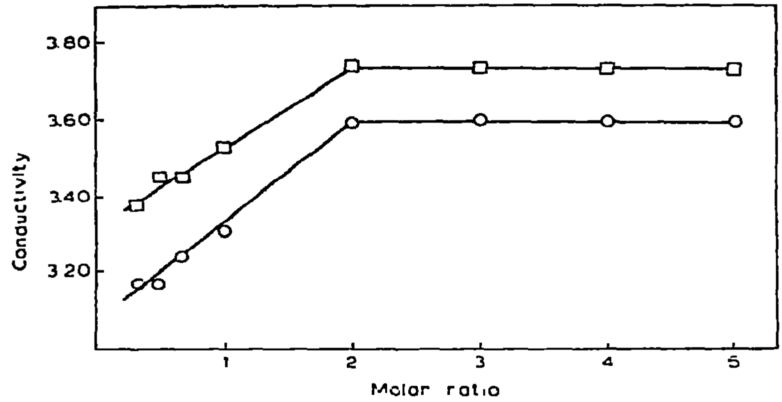

Fig. 2. Conductivity × 10^3 (ohm^{-1} cm^{-1}) against molar ratio (0.025M periodate/*myo*-inositol) at 25° and pH 11: —○—, 5 min after mixing components; —□—, 3 h after mixing. Conductivity of 0.025M periodate is 3.67×10^{-3} $ohm^{-1}.cm^{-1}$.

EXPERIMENTAL

Paper electrophoresis. — Whatman chromatographic paper 31E/1 (57 × 23 cm) was used in a Shandon high-voltage electrophoresis apparatus (model L-24). Owing to the high conductivity of the supporting electrolytes, it was not possible to exceed ~20 V/cm, and there was a temperature rise of 15° → 25° of the cooling water.

Electrophoresis was performed for 1 h in (*a*) 0.07M periodate adjusted to pH 11.0 with sodium hydroxide[4], or (*b*) a sodium hydroxide–sodium hydrogen carbonate buffer at pH 11.0.

For electrophoresis in (*a*), an approximately equal molar quantity of 0.02M sodium formate was spotted alongside each carbohydrate, in order to serve as a standard of comparison for any formate produced by oxidation. After electrophoresis, the dried paper was sprayed with ammoniacal silver nitrate[9] and incubated at 110° until the black formate and polyol spots became sufficiently intense. These spots could then be fixed by immersing the paper in 10% aqueous sodium thiosulphate.

For electrophoresis in (*b*), periodate–carbohydrate mixtures of 2:1 molar ratio were prepared by adding the carbohydrate to a small quantity of 0.04M periodate adjusted to pH 11.0. Aliquots (10 μl) were used for electrophoresis, together with similar volumes of 0.04M sodium periodate, 0.02M sodium formate, 0.02M sodium iodate, and 0.02M carbohydrate as reference standards. Aniline phosphate[6] was used to detect the iodate, periodate, and carbohydrate.

Polarimetry. — A Perkin-Elmer model 141 polarimeter was used together with a jacketed cell of 10-cm path-length maintained at 25°. Test solutions were prepared by adding the solid carbohydrate to a sodium metaperiodate solution of known concentration, adjusted to pH 11.0 with solid sodium hydroxide. The periodate-polyol molar ratios were in the range 0.25–5.00.

Conductimetry. — An M.E.L. conductivity bridge (type E 7566/3) was used, together with a Mullard conductivity cell (E 7591/B).

Test solutions of raffinose were prepared by adding the solid compound to 0.01M sodium metaperiodate, adjusted to pH 11.0 and maintained at 25°, to obtain molar ratios in the range 0.25–5.00. For the other carbohydrates, the initial concentration of periodate was 0.025M.

REFERENCES

1 G. Dryhurst, *Periodate Oxidation of Diol and Other Functional Groups*, Pergamon, London, 1966.
2 G. Hughes and T. P. Nevell, *Trans. Faraday Soc.*, 44 (1948) 941–948.
3 G. J. Buist and C. A. Bunton, *J. Chem. Soc.*, (1954) 1406–1413.
4 B. M. I. Alesofie and W. J. Popiel, *Talanta*, 20 (1973) 251–254.
5 J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Edition*, 16 (1944) 111–115.
6 M. S. Rustom, M.Sc. Thesis, University of Jordan, 1974.
7 G. R. Barker, *J. Chem. Soc.*, (1960) 624–627.
8 S. J. Angyal, D. Greeves, and V. A. Pickles, *Carbohydr. Res.*, 35 (1974) 165–173.
9 L. Hough, *Nature (London)*, 165 (1950) 400.
10 L. Hough, J. K. N. Jones, and W. H. Wadman, *J. Chem. Soc.*, (1950) 1702–1706.