636. *Mechanism of Reactions in the Sugar Series. Part IV.* The Structure of the Carbonium Ions formed in the Acid-catalysed Solvolysis of Glucopyranosides.*

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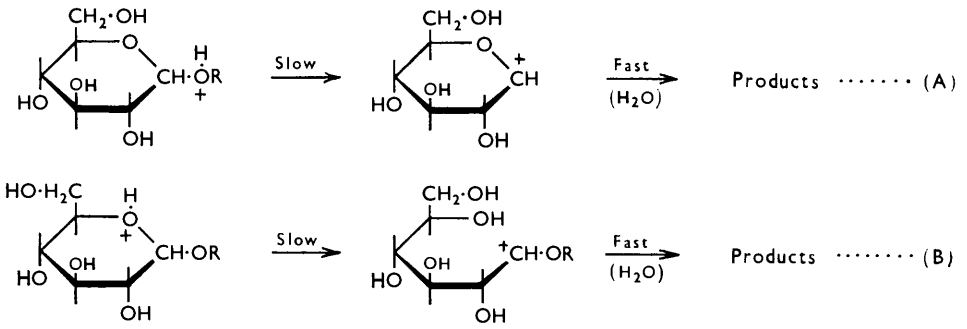
Acid-catalysed methanolysis of phenyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside and of phenyl α- and β-D-glucopyranoside has been found to proceed with predominant inversion. *S*-Phenyl 2,3,4,6-tetra-*O*-methyl-β-D-thioglucopyranoside resists methanolysis in acidic solution. Acid-catalysed hydrolysis of methyl α-D-glucopyranoside is associated with an oxygen isotope effect. These results are consistent with the view that acid-catalysed solvolysis of D-glucopyranosides does not involve ring opening.

Previous work [1] has shown that the acid-catalysed hydrolysis of most glucopyranosides involves hexose–oxygen bond fission and intermediate carbonium ions. Two mechanisms (A) and (B) are possible.



Mechanism (B) involves ring opening in the rate-determining step; mechanism (A) does not. They might be distinguished in two ways. (1) Mechanism (A) which has been unambiguously demonstrated for several D-glucopyranosyl halides,[2,3] should, by analogy with these cases, give high proportions of products with inverted configuration at position 1. Rapid mutarotation of the products renders this criterion useless for hydrolytic reactions but, given a sufficiently reactive glycoside, it is applicable for other solvents (*e.g.*, methanol). (2) Mechanism (A) should be associated with an oxygen isotope effect since the rate-determining step involves rupture of the hexose–oxygen bond: no effect should be observed for mechanism (B).

Both these criteria have been used. Acid-catalysed solvolyses of a number of phenyl D-glucopyranosides in methanol have been studied and the stereochemical compositions of the products determined. The results support the view, previously put forward by Voss and Wachs [4] who based it on semi-quantitative experiments, that methanolysis, in this system, proceeds largely with inversion of configuration at position 1. The oxygen isotope effect has been investigated for acid-catalysed hydrolysis of methyl α-D-glucopyranoside. The evidence points consistently to mechanism (A).

Experimental

Materials.—Methanol was dried as described by Vogel,[5] and then distilled from anhydrous magnesium perchlorate. Commerical methanesulphonic acid was repeatedly distilled *in vacuo*

* Part III, 1961, 412.

Bunton, Lewis, Llewellyn, and Vernon, *J.*, 1955, 4419.
Rhind-Tutt and Vernon, *J.*, 1960, 4637.

[3] Lemieux and Huber, *Canad. J. Res.*, 1955, **33**, 128.

[4] Voss and Wachs, *Annalen*, 1936, **522**, 240.

[5] Vogel, " Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 175.

in an all-glass apparatus. Lithium methanesulphonate was prepared by mixing equivalent solutions, in methanol, of methanesulphonic acid and lithium methoxide; it was recrystallised twice from methanol and dried for 4 hr. at 160°.

Phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside was prepared from glucose penta-acetate, phenol, and toluene-*p*-sulphonic acid;[6] it had m. p. 127°, $[\alpha]_D^{25}$ −30·7° (*c* 1·0 in benzene). Methylation by the method of McClosky and Coleman[7] gave phenyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside, m. p. 77°, $[\alpha]_D^{25}$ −46·8° (*c* 1·96 in $CHCl_3$) (Found: C, 62·3; H, 7·3. Calc. for $C_{16}H_{24}O_6$: C, 61·7; H, 7·7%).

Deacetylation of the tetra-*O*-acetate gave phenyl β-D-glucopyranoside, m. p. 173—174·5°, $[\alpha]_D^{25}$ −70·7° (*c* 2·0 in H_2O).

Phenyl α-D-glucopyranoside was made by deacetylation of the tetra-*O*-acetate. After recrystallisation from water and drying *in vacuo*, it had m. p. 169—170°, $[\alpha]_D^{25}$ +181·1° (*c* 0·65 in H_2O).

Methyl α-D-glucopyranoside, recrystallised several times from ethanol, had m. p. 164—165°, $[\alpha]_D^{25}$ +157·8° (*c* 3·0 in H_2O), +163·3° (*c* 2·0 in MeOH).

Methyl β-D-glucopyranoside, made from acetobromoglucose and recrystallised from ethyl acetate, had m. p. 107—108°, $[\alpha]_D^{25}$ −32·6° (*c* 2·7 in H_2O), −33·9° (*c* 2·1 in MeOH).

t-Butyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside. t-Butyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (40 g.) was heated in acetone (250 ml.) to 45°. 30% Aqueous sodium hydroxide (250 ml.) was added and then dimethyl sulphate (80 g.) with vigorous stirring, during 1 hr. The methylation procedure was then repeated with half the previous quantities of alkali and dimethyl sulphate. The mixture was boiled for 30 min. and excess of alkali neutralised by carbon dioxide. After evaporation of the solvent, ether-extraction gave 15 g. of a pale yellow oil. This was re-methylated as above. Distillation of the final product gave a pale yellow syrup, b. p. 105°/0·4 mm., n_D^{25} 1·4392, $[\alpha]_D^{15}$ −3·2° (*c* 1·4 in $CHCl_3$) (Found: C, 56·0; H, 9·3. Calc. for $C_{14}H_{28}O_6$: C, 57·5; H, 9·6%). The infrared spectrum showed a strong absorption at 11·25 μ. The poor analytical figures might be taken to mean incomplete methylation; however, the infrared spectrum showed no strong absorption in the region 2·5—2·8 μ.

Other materials were prepared as described previously.[2]

Methanolysis of 2,3,4,6-Tetra-O-methyl-α-D-glucopyranosyl Chloride in the Presence of Methanesulphonic Acid.—The kinetic technique was as previously described.[2] Each run yielded good first-order rate coefficients throughout. Solutions of methanesulphonic acid in anhydrous methanol gave constant titres against standard alkali (in either water or anhydrous methanol as medium) for >24 hr. The products were identified as the isomeric methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranosides. Analyses were by the infrared technique previously described.[2] Table 1 summarises the results.

TABLE 1. *Methanolysis of 2,3,4,6-tetra-O-methyl-α-D-glucopyranosyl chloride* (~0·1M) *at 25°.*

Electrolyte and concn. (M)		10^3k_1 (min.$^{-1}$)	Proportion of α-glycoside	Electrolyte and concn. (M)		10^3k_1 (min.$^{-1}$)	Proportion of α-glycoside
—	—	3·58	0·06	$LiClO_4$	0·357	5·00	0·06
$Me{\cdot}SO_3H$	0·612	5·50	0·19	LiOAc	0·605	5·55	0·06
,, ...	1·530	6·52	0·23	LiCl	0·466	6·57	0·31
,, ...	2·62	7·55	0·24	,, ...	0·942	7·15	0·35
,, ...	4·48	9·00	0·24	NaOMe	0·310	6·04	0·06
,, ...	5·35	10·2	0·24				
$Me{\cdot}SO_3Li$	0·748	4·90	0·19				
,, ...	0·848	5·20	0·22				

Acid-catalysed Methanolysis of Phenyl D-Glucopyranosides.—Phenol was estimated by means of Folin and Ciocalteu's reagent.[8] Serial aliquot parts (*e.g.*, 0·25 ml.) of a solution, at 25°, of the glucoside (*ca.* 0·05M) in anhydrous methanol containing methanesulphonic acid were run into mixtures of saturated sodium carbonate solution (25 ml.) and water (25 ml.). After addition of the Folin–Ciocalteu reagent (5 ml.), the solutions were shaken for a few minutes, made up to 100 ml. with water, and left for *ca.* 30 min. The colour intensities were then measured on a

[6] Montgomery, Richtmyer, and Hudson, *J. Amer. Chem. Soc.*, 1942, **64**, 690.
[7] McClosky and Coleman, *J. Org. Chem.*, 1945, **10**, 188.
[8] Folin and Ciocalteu, *J. Biol. Chem.*, 1927, **73**, 627.

Spekker photoelectric absorptiometer fitted with a red filter. Phenol concentrations were calculated by reference to a standard curve. Theoretical and experimental infinity values usually agreed to within 2%. Good first-order rate coefficients (k_1) were found for each run. The following details of an experiment with phenyl α-D-glucopyranoside (0·0395M) and 2·375M-methanesulphonic acid at 25° are illustrative:

Reaction (%)	8·8	15·0	23·8	32·0	44·6	48·7	56·5	66·1
10^3k_1 (min.$^{-1}$)	3·61	3·65	3·60	3·57	3·51	3·41	3·46	3·62

Table 2 shows the results obtained (25°) with three phenyl D-glucopyranosides.

The solutions used for the experiments summarised in Table 2 were also used to follow the changes in optical rotatory power accompanying methanolysis. Portions (10 ml.) of freshly made up solutions were placed in a jacketted polarimeter tube (1 dm.). Constant temperature (25°) was maintained by circulation of water from a thermostat-bath.

TABLE 2. *Methanolysis of phenyl* D-*glucopyranosides* (~0·05M) *at* 25°.

Substrate	[Me·SO_3H] (M)	10^3k_1 (min.$^{-1}$)
Ph α-D-glucopyranoside	2·375	3·55
Ph β-D-glucopyranoside	2·330	1·28
Ph tetra-*O*-methyl-β-D-glucopyranoside ...	2·393	0·41

In each experiment the total amount of the products of methanolysis produced at any time (t) can be calculated from the data in Table 2. By assuming that the corresponding methyl pyranosides are the sole reaction products, the proportion (α) in which the α-isomer is present at a time (t) can be calculated from the rotation of the solution at that time. Table 3 shows the results. The following values of $[\alpha]_D^{25}$ (c ~1·0 in MeOH, [Me·SO_3H] *ca.* 2·0M) were used; +158°, −17°, and +163°, −33·9°, for the α- and β-isomers of methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside and for the α- and β-isomers of methyl D-glucopyranoside, respectively.

TABLE 3. *Products* * *of methanolysis of phenyl* D-*glucopyranosides at* 25°.

(*a*) Ph α-D-glucopyranoside: [Me·SO_3H] = 2·375M; $(\alpha)_{t=0}$ 0·10.

Reaction (%)	16·2	23·3	29·9	35·8	41·3	46·3	50·8	55·0	58·8	62·3	68·4	71·1	99·2
α	0·11	0·10	0·10	0·10	0·11	0·14	0·15	0·17	0·17	0·17	0·18	0·18	0·30

(*b*) Ph β-D-glucopyranoside: [Me·SO_3H] = 2·330M; $(\alpha)_{t=0}$ 0·73.

Reaction (%)	3·1	6·2	9·2	12·0	14·8	17·5	20·1	22·6
α	0·72	0·73	0·73	0·74	0·72	0·73	0·72	0·71
Reaction (%)	25·0	27·4	29·7	31·9	34·0	36·1	38·1	82·4
α	0·72	0·72	0·72	0·73	0·73	0·73	0·73	0·71

(*c*) Ph tetra-*O*-methyl-β-D-glucopyranoside: [Me·SO_3H] = 2·393M; $(\alpha)_{t=0}$ 0·72.

Reaction (%)	9·5	11·3	12·9	15·4	21·7	43·0	45·5	48·1
α	0·72	0·74	0·73	0·74	0·69	0·70	0·70	0·70

* α = Proportion of α-glycoside.

The stabilities of the α- and β-isomers of methyl D-glucopyranoside and 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside, under the conditions of the experiments described above, were determined by following the changes in optical rotation of solutions containing a particular isomer. Approximate initial first-order rate coefficients were calculated by using, in each case, an infinity value corresponding to complete anomerisation. The values obtained for 10^3k_1 (min.$^{-1}$) at 25° with 2·38M-methanesulphonic acid were, respectively, 0·03, 0·04, *ca.* 0·01 and 0·03.

Acid-catalysed Methanolysis of t-Butyl 2,3,4,6-*Tetra*-O-*methyl*-β-D-*glucopyranoside and of* S-*Phenyl* 2,3,4,6-*Tetra*-O-*methyl*-β-D-*thioglucopyranoside.*—Measurements of the optical rotatory power of a solution of t-butyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (0·2527 g. in 25 ml.) in methanol containing methanesulphonic acid (1·55M) gave the annexed results (40·5°):

Time (min.)	0	8	17	30	42	58	81	105	121
Rotation	0·075°	0·175°	0·268°	0·378°	0·470°	0·558°	0·675°	0·751°	0·820°
Time (min.)	165	256	357	425	740	1430	3660	4500	
Rotation	0·909°	1·606°	1·170°	1·200°	1·310°	1·467°	2·015°	2·275°	

A sample of the solution taken at 14 hr. from zero was found, after neutralisation, not to reduce Fehling's solution. Isolation of the products gave a mixture of the isomeric methyl

2,3,4,6-tetra-*O*-methyl-D-glucopyranosides, which, by infrared analysis,[2] was shown to contain 46% of the α-isomer.

A plot of optical rotation against time gives a curve with (*a*) an initially steeply rising section followed by (*b*) a linear section of small slope. Extrapolation, to time zero, of (*b*), which may be identified as arising from anomerisation of the products, gives the optical rotation of the products before secondary anomerisation (+1·13°, corresponds to 42% of α-isomer). The value +1·13° can also be used as an infinity for the calculation of first-order rate coefficients, whence $k_1 = 0{\cdot}012$ min.$^{-1}$. The product ratio was unaffected by initial addition of lithium methanesulphonate (1·0M). Methanolysis of t-butyl β-D-glucopyranoside under the same conditions led to a similar product ratio (*ca.* 52% of the α-isomer).

The optical rotation of a solution of *S*-phenyl 2,3,4,6-tetra-*O*-methyl-β-D-thioglucopyranoside (0·1436 g. in 10 ml.) in methanol containing methanesulphonic acid (1·55M) was found to change very slowly at 40·5° with time from −0·630° to −0·585° in 55·6 hr. Darkening prevented further observations. Qualitative comparison with an equivalent solution of phenyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside showed that the latter compound is at least 100-fold more reactive.

Oxygen Isotope Effect in the Hydrolysis of Methyl α-D-Glucopyranoside.—A solution (1 l.) of methyl α-D-glucopyranoside (200 g.) in aqueous 2·02N-sulphuric acid was prepared. A portion (900 ml.) was kept at 73° ± 1° for 2½ hr. Measurement of the optical rotation showed that 7·5% of the substrate had been hydrolysed. After an excess of sodium hydroxide had been added (cooling), the solution was distilled and the first 300 ml. of distillate were collected. This fraction was refractionated through a spinning-band column (70 cm.) and gave, as middle cut, methanol (1·1 g.), b. p. 64·5°. The remainder of the original solution was kept at 73° until reaction was complete. Methanol was then isolated as described above. The methanol samples were treated with potassium tetrafluorobromate(III) in a fixed reactor.[9] The recovery of oxygen under these conditions was not quantitative. The ratio $^{18}O/^{16}O$ was determined by using an isotope-ratio mass spectrometer. The samples were measured between samples of normal oxygen, obtained from local (Illinois) water by reaction with bromine trifluoride. The results in Table 4, show that methanol taken towards the beginning of the hydrolysis has a significantly lower content of ^{18}O (*ca.* 3%).

TABLE 4. *Oxygen isotope effect in hydrolysis of methyl α-D-glucopyranoside.*

Source of O_2:	Water	CH_3·OH, 7·5% reaction	Water	CH_3·OH, 100% reaction	Water
$10^2[^{18}O/^{16}O]$	0·209	0·203	0·210	0·209	0·209

DISCUSSION

Esterification of the solvent, producing water, complicates the study of acid-catalysed reactions in methanol. With glucosides this complication is particularly serious since, in the presence of water, free aldohexoses may be formed and give a variety of secondary products. In the present work this difficulty has been largely avoided by using methanesulphonic acid, which appears to esterify methanol only very slowly, and by the use of relatively low temperatures (25°) and reactive substrates.

We found that the isomeric composition of the products produced by methanolysis of phenyl D-glucopyranosides under our experimental conditions could not be determined by analysis at complete reaction because, first, the rates of anomerisation of the appropriate products were not negligibly slow compared with the overall reaction rates and, secondly, secondary changes arising from esterification of the solvent occurred over the relatively long time required. Consequently, we estimated the ratio in which the isomeric products were formed from each substrate, using results obtained, in each case, during about one half-life. Certain assumptions are necessary: (*a*) that there is no anomerisation of the substrate and (*b*) that the products are methyl D-glucopyranosides and not methyl D-glucofuranosides. Our justification for these is essentially that calculations based on them lead, for each substrate, to values of α (the proportion of product having α-configuration) which

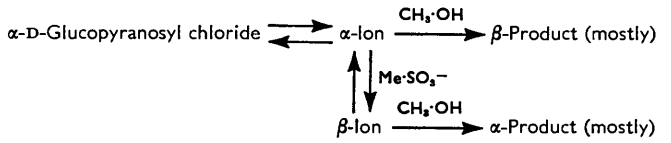
[9] Sheft and Katz, *Analyt. Chem.*, 1957, **29**, 1322.

are reasonable and constant over about one half-life (*i.e.*, over times in which the disturbing factors discussed above are not important). Trial calculations showed that if, at any time during the first half-life of a reaction, compounds other than the original substrate and the isomeric methyl D-glucopyranosides had been present, the values of α would not, in general, have been constant and would, in some cases, have been unphysical (*i.e.*, outside the range 0—1·0).

The following particular considerations also support the correctness of our assumptions: (i) With phenyl α-D-glucopyranoside the tendency of α (initially 0·10) to increase after *ca.* 50% reaction is as expected since approximate measurements of the rates of anomerisation of the methyl D-glucopyranosides show that, under our experimental conditions, the proportion of α-isomer present at equilibrium is *ca.* 0·7. Consistently, the values of α (0·72) found for phenyl β-D-glucopyranoside show no such tendency. (ii) With phenyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside, which cannot form furanoside products, the observed value of α is, within experimental error, the same as that found for the unmethylated compound.

We conclude, therefore, that methanolysis of the three compounds studied, under the specified experimental conditions, gives pyranoside products and proceeds with a high degree of inversion at the position 1 (90% and 72% of inverted product with substrates of α- and β-configuration, respectively).

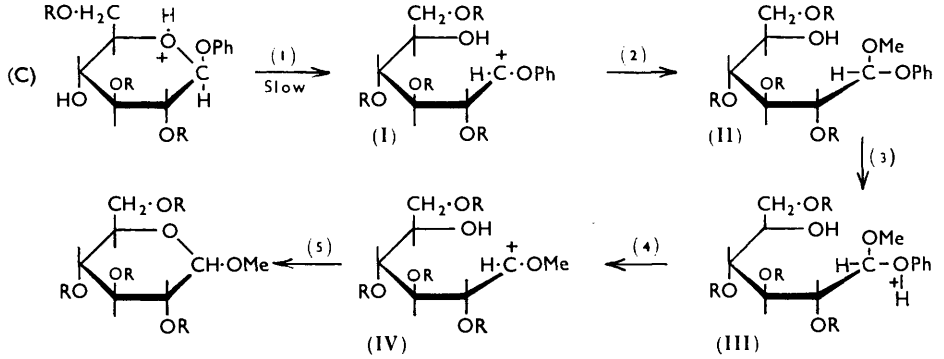
A final complication remains, however, in that these stereochemical results may be partially determined by the high concentrations of methanesulphonate ions necessarily present. To test this possibility the effects of added methanesulphonic acid and of added lithium methanesulphonate on the methanolysis of 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranosyl chloride were studied. This reaction is known [2] to proceed by a carbonium ion process and to give, largely (94%), the product of inverted configuration. It was found (Table 1) that the rate of methanolysis is increased by high concentrations of methanesulphonic acid. This arises, however, from a salt effect and not from the emergence of an acid-catalysed process since lithium methanesulphonate, chloride, acetate, and perchlorate give similar increases in rate. Nevertheless, the methanesulphonate ion has an effect apart



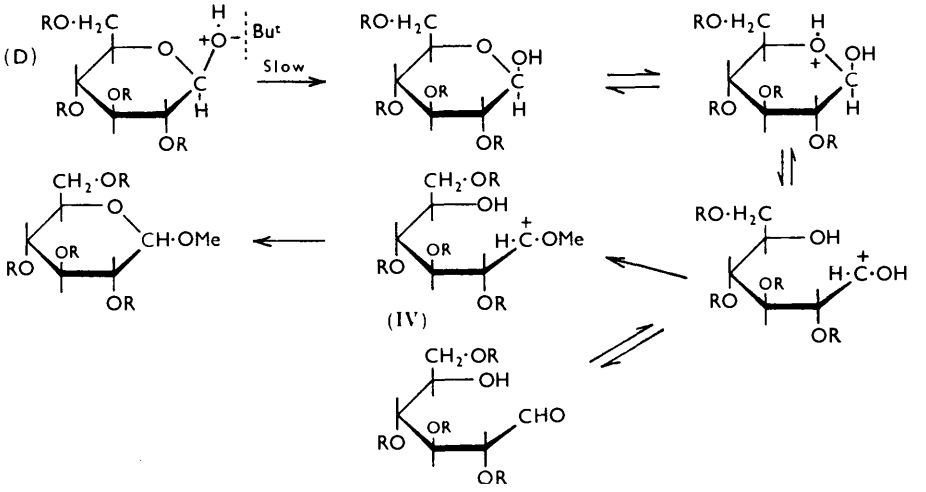
from simply increasing the polar character of the medium since the presence of either the acid or the lithium salt reduces the amount of product of inverted configuration. The same effect is observed with chloride ions, but not with acetate or perchlorate. A possible explanation, previously applied to the effect of chloride ions and discussed in greater detail elsewhere,[2] is provided by the annexed scheme, in which ionisation of the substrate produces an intermediate (ion-pair) without loss of α-configuration (α-Ion). This intermediate either passes directly into products by reaction with methanol or is captured by a methanesulphonate ion to produce a new ion-pair having the β-configuration (β-Ion). Solvolysis of the β-ion leads to a product with the same configuration as the starting material. Hence, the intervention of the methanesulphonate ion reduces the observed overall proportion of product with inverted configuration. However, irrespective of the detailed mechanism of this process, it is clear that any effect on the composition of the products of the acid-catalysed methanolysis of phenyl D-glucopyranosides, specifically due to the presence of the methanesulphonate ion, will be in the direction of reducing the observed proportion of inversion. Hence, the conclusion that these reactions proceed largely with inversion at position 1 is in no way invalidated.

Methanolysis of phenyl D-glucopyranosides proceeding with predominant inversion cannot easily be accommodated by mechanism (B). The scheme (C) shows the steps

which would be involved (R = Me, H). Unless steps 2—5 were very rapid, high proportions of inverted product could not arise and, for a given glucoside, the α- and β-isomers should give the same product mixture since the original configurational information contained at the $C_{(1)}$ centre would be lost on passage through the intermediates (I)—(IV). Intermediate (IV) must, in fact, be formed during the methanolysis of t-butyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside which may be assumed, by analogy with the known



result for hydrolysis, to proceed by alkyl–oxygen bond fission.[10] The scheme (D) shows the steps involved.



Consistently, it was found that the product ratio is quite different from that observed with the corresponding phenyl compound, the isomers being formed in roughly equal amounts (α : β = 42 : 58). Mechanism (B) also fails to account for the relative inertness of *S*-phenyl 2,3,4,6-tetra-*O*-methyl-β-D-thioglucopyranoside to methanolysis. With this compound, even if step 3 were unfavourable, reversal of step 1 should lead, contrary to what was found, to relatively ready anomerisation.

Mechanism (A), on the other hand, is consistent with the observed facts since (*a*) a ring-closed carbonium ion derived from a D-glucopyranose structure would be expected [2,3] to lead to products with a large degree of inversion at position 1 and (*b*) replacement of the glucosidic oxygen atom by sulphur should, since the latter is the less basic, reduce the overall rate of reaction. We conclude, therefore, that methanolysis of phenyl D-glucopyranosides, at least under the specified experimental conditions, proceeds by mechanism (A).

[10] Armour, Bunton, Patai, Selman, and Vernon, *J.*, 1961, 412.

This conclusion cannot be immediately applied to hydrolytic reactions since, for these, the stereochemical criterion detailed above is inapplicable. However, isotopic analysis of the methanol produced over the first 7% of the hydrolysis of methyl α-D-glucopyranoside showed that the reaction is associated with an appreciable oxygen isotope effect. This can be accommodated by mechanism (A) but not by mechanism (B).

The maximum isotope effect to be expected for the hypothetical process, C–O ⟶ C + O, may be calculated, if complete loss of bonding in the transition state, is assumed, from a simplified version of the equation given by Bigeleisen and Goeppert-Mayer,[11] namely:

$$k_1/k_2 = (m_2^{\ddagger}/m_1^{\ddagger})^{\frac{1}{2}}[1 + G(u)\Delta u]$$

where $u = h c\omega/kT$, Δu is the difference in the value of u for the two isotopic species, and $G(u)$ is a function for which numerical values are available from tables.[11] Taking ω as 1100 cm.$^{-1}$ (*i.e.*, an average for the stretching frequency observed with aliphatic ethers of the type C·O·CH_2 [12]) and calculating $(m_2^{\ddagger}/m_1^{\ddagger})^{\frac{1}{2}}$ from the reduced masses of the fragments obtained by rupture of the hexose–oxygen bond in the conjugate acid of methyl α-D-glucopyranoside,[13] k_1/k_2 is found to be 1·064. The observed value *ca.* 1·03 is, therefore, reasonable for mechanism (A). Mechanism (B) might give rise to a small secondary isotope effect, but the observed effect is too large for this.

The evidence from studies of both methanolysis and hydrolysis of some simple glucopyranosides points, therefore, to the generalisation that acid-catalysed solvolyses of these compounds all proceed by mechanism (A). A possible inconsistency is that, since the acid-catalysed formation of methyl α-D-glucopyranoside from glucose and methanol appears to involve methyl α-D-glucofuranoside as an intermediate, the reverse reaction, *i.e.*, the hydrolysis of methyl α-D-glucopyranoside, must, since it must follow the same path, involve ring-opening. This inconsistency may be removed by assuming that the reaction between glucose and methanol occurs as in the annexed scheme.

If k_1 and k_{-1} are much greater than k_2 and k_{-2} and if the formation of the pyranoside is thermodynamically preferred, then the occurrence of the furanoside as an apparent intermediate in the reaction of glucose and methanol is explained. In the above scheme ring-opening need be assumed only for glucose itself.

One of us (C. A. V.) thanks Cornell University (Ithaca, N.Y.) for their hospitality while part of this work was carried out. We also thank the Nuffield Foundation and the Department of Scientific and Industrial Research for grants (to B. E. C. B. and A. J. R.-T., respectively). Useful discussion with Professor W. H. Saunders (University of Rochester) is also acknowledged.

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[*Received, February 7th*, 1961.]

[11] Bigeleisen and Goeppert-Mayer, *J. Chem. Phys.*, 1947, **15**, 261.
[12] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1957, p. 115.
[13] Bigeleisen and Wolfsberg, " Theoretical and Experimental Aspects of Isotope Effects in Chemical Kinetics," in " Advances in Chemical Physics," Interscience Publ. Inc., New York, 1958, p. 28.