## 27. *The Reactivity of O-Acylglycosyl Halides. Part VI.* Steric Effects of Neighbouring Groups.*

By G. L. Mattok and G. O. Phillips.

Reaction rates at varying temperatures were measured for the $S_N1$ solvolysis of a series of *O*-acylglycosyl halides, which proceed by way of an open carbonium-ion intermediate. The size and disposition of substituted groups markedly influence the reactivity of the halogen, and this may be accounted for almost entirely by the variation in $\Delta H^{\ddagger}$; $\Delta S^{\ddagger}$ is almost independent of these factors. An interpretation is proposed, by consideration of the conditions operating in the transition state of the reaction. In this way the completely different influence on reactivity at the lactol-carbon atom shown by similar structural changes in the hexose molecule may be explained.

The disposition and size of the substituted groups in a hexose molecule exert an important influence on the reactivity at the lactol-carbon atom.[1] In the previous paper of this series, participation of a 2-acetyl group in the solvolysis of 1 : 2-*trans*-*O*-acetylglycosyl halides was considered. The enhanced rate of solvolysis of these compounds compared with that of the corresponding 1 : 2-*cis*-compounds was accounted for on this basis. However, other factors, probably of steric origin, also influence the reactivity of these compounds, as shown by the marked differences in the reactivity of the two 1 : 2-*trans*-halides, tetra-*O*-acetyl-β-D-glucosyl and α-D-mannosyl halides. In this paper these factors are considered further.

Previously we attempted to rationalise the reactivity of *O*-acetylglycosyl halides on the basis of steric conditions near the halogen atom.[2] Consideration of the steric conditions operating in the transition state of reaction, however, would allow a clearer understanding of the main factors and this is the approach we adopt in this paper. Thus, a distinction must be drawn between the two courses which the solvolyses of *O*-acylglycosyl halides follow, since the steric requirements of forming the transition state from the initial state will be different in each case: in one case there is no participation by the 2-group and an " open-ion " intermediate is formed, and in the second a cyclic-ion intermediate is formed.[3]

The compounds studied in this paper are considered to belong to the former category. Lemieux and Brice [4] recently discussed the reactivity of sugar 1 : 2-*trans*-acetates, which proceed by way of a cyclic-ion intermediate. Here the 3-group exerts the dominant influence on reactivity and the rôle of the 5-group is relatively unimportant. This has been rationalised on the basis of steric inhibition to the formation of the resonance-stabilised, intermediate, 1 : 2-cyclic carbonium ion in the 2 : 3-*cis*-compounds. We shall show, however, that for the " open-ion " type of reaction the 5-group is dominant, a fact which may be understood on consideration of the conditions in the transition state. In this sense, therefore, the investigations are complementary.

### Results

*Reactions of* 1 : 2-trans-*Halides.*—Results for the uncatalysed solvolysis of 3 : 4 : 6-tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucosyl chloride (I) and the 3 : 4 : 6-triacetate 1-chloride (II) were given previously; [2] they are now supplemented with data for the catalysed reactions. The uncatalysed solvolysis was shown to proceed by the $S_N1$ mechanism.[2] In view of the close relation between this reaction and the solvolysis catalysed by mercuric chloride,[5] the catalysed

* Part V, *J.*, 1957, 268.

[1] Isbell and Frush, *J. Res. Nat. Bur. Stand.*, 1940, **24**, 125; Fletcher and Hudson, *J. Amer. Chem. Soc.*, 1948, **70**, 4052; Lemieux, *Canad. J. Chem.*, 1956, **34**, 1007.
[2] Newth and Phillips, *J.*, 1953, 2904.
[3] Mattok and Phillips, *J.*, 1957, 268.
[4] Lemieux and Brice, *Canad. J. Chem.*, 1956, **34**, 1006.
[5] Mattok and Phillips, *J.*, 1956, 1836.

reaction also probably proceeds by way of the intermediate carbonium ion. As confirmation the reaction order was determined for the methanolysis of 3 : 4 : 6-tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucosyl chloride catalysed by mercuric chloride. As in all other cases investigated, the kinetics are of the first power in both the sugar halide and the mercuric chloride. Table 1 shows the second-order constants. Further solvolysis results, including temperature effects and thermodynamic constants for this reaction and for the solvolysis of the 3 : 4 : 6-tri-O-acetyl-β-D-glucosyl chloride, are given in Tables 2 and 3.

TABLE 1. *Solvolysis of* 3 : 4 : 6-*tri*-O-*acetyl*-2-O-*trichloroacetyl*-β-D-*glucosyl chloride in methanol at* 25°, *catalysed by mercuric chloride.*

| | | | | |
|---|---|---|---|---|
| RCl ($10^2$M) | 4·9 | 5·15 | 5·7 | 3·85 |
| $HgCl_2$ ($10^2$M) | 5·5 | 4·1 | 4·1 | 5·05 |
| $10^4k_2$ (l. mole$^{-1}$ sec.$^{-1}$) | 5·0 | 5·12 | 5·12 | 5·49 |

TABLE 2. *Solvolysis of* 3 : 4 : 6-*tri*-O-*acetyl*-2-O-*trichloroacetyl*-β-D-*glucosyl chloride in* 100% *methanol, catalysed by mercuric chloride.*

| Temp. | 23·5° | 25·0° | 29·1° | 29·6° | 32·5° | 33·2° |
|---|---|---|---|---|---|---|
| $10^4k_2$ (l mole$^{-1}$ sec.$^{-1}$) | 4·91 | 5·42 | 7·52 | 7·75 | 9·52 | 9·75 |
| $E$ (kcal. mole$^{-1}$) | | | 16·6 | | | |
| $\Delta G^{\ddagger}$ (kcal. mole$^{-1}$) (at 25°) | | | 22·0 | | | |
| $\Delta H^{\ddagger}$ (kcal. mole$^{-1}$) (at 25°) | | | 16·0 | | | |
| $\Delta S^{\ddagger}$ (e.u.) (at 25°) | | | −20·1 | | | |

TABLE 3. *Solvolysis of* 3 : 4 : 6-*tri*-O-*acetyl*-β-D-*glucosyl chloride in* 100% *methanol catalysed by mercuric chloride.*

| Temp. | 22·5° | 25·4° | 31·0° |
|---|---|---|---|
| $10^2k_2$ (l mole$^{-1}$ sec.$^{-1}$) | 7·02 | 8·61 | 12·7 |
| $E$ (kcal. mole$^{-1}$) | | 12·5 | |
| $\Delta G^{\ddagger}$ (kcal. mole$^{-1}$) (at 25°) | | 19·0 | |
| $\Delta H^{\ddagger}$ (kcal. mole$^{-1}$) (at 25°) | | 11·9 | |
| $\Delta S^{\ddagger}$ (e.u.) (at 25°) | | −23·8 | |

*Reactions of* 1 : 2-cis-*Halides.*—The methanolysis of several 1 : 2-*cis*-acetylglycosyl halides was investigated, in the absence and presence of mercuric chloride. The halides chosen allowed consideration of (*a*) the effect of the 2-group and, in particular, the function of the oxygen atom, (*b*) the effect of the 6-group, and (*c*) the effect of increasing the size of the substituent groups throughout the glucose molecule. Throughout the rates were calculated by using the initial slope method as described in previous papers, to avoid complications due to subsequent mutarotation.

(a) *Variation of the* 2-*group.* The effect of temperature on the methanolysis of 2-acetamido-3 : 4 : 6-tri-*O*-acetyl-2-deoxy-α-D-glucosyl chloride (III) is shown in Table 4. For comparison with previous catalysed reactions studied, the rate of solvolysis of 3 : 4 : 6-tri-*O*-acetyl-2-*O*-toluene-*p*-sulphonyl-β-D-glucosyl chloride in methanol catalysed by mercuric chloride was measured, giving $k_2 = 1{\cdot}78 \times 10^{-5}$ l. mole$^{-1}$ sec.$^{-1}$ at 25°.

TABLE 4. *Solvolysis of* 2-*acetamido*-3 : 4 : 6-*tri*-O-*acetyl*-2-*deoxy*-α-D-*glucosyl chloride in* 100% *methanol.*

| Temp. | 56·8° | 30·2° | 25·8° |
|---|---|---|---|
| $10^4k_1$ (sec.$^{-1}$) | 14·9 | 1·79 | 1·14 |
| $E$ (kcal. mole$^{-1}$) | | 17·1 | |

TABLE 5. *Solvolysis of tri*-O-*acetyl*-α-D-*xylosyl chloride in* 100% *methanol in the absence and in the presence of mercuric chloride.*

| [$HgCl_2$] = nil. | | | [$HgCl_2$] = 0·05M. | | |
|---|---|---|---|---|---|
| Temp. | $10^5k_1$ (sec.$^{-1}$) | $E$ (kcal. mole$^{-1}$) | Temp. | $10^3k_2$ (mole$^{-1}$ sec.$^{-1}$) | $E$ (kcal. mole$^{-1}$) |
| 25·5° | 5·60 | | 21·6° | 3·05 | |
| 27·8 | 6·60 | | 25·0 | 3·89 | |
| 29·5 | 8·35 | 17·9 | 27·4 | 5·22 | 15·6 |
| 31·3 | 9·88 | | 29·2 | 6·04 | |
| 32·8 | 11·3 | | 31·4 | 7·13 | |

(b) *Variation of the* 6*-group.* The results for the catalysed and uncatalysed solvolysis of tri-*O*-acetyl-α-D-xylosyl chloride (IV) in methanol are given in Table 5.

(c) *Effect of increasing the size of the groups.* The catalysed solvolysis of tetra-*O*-toluene-*p*-sulphonyl-α-D-glucosyl chloride (V) in methanol is given in Table 6. The free energies and heats and entropies of activation for the 1 : 2-*cis*-halides investigated are shown in Table 7.

TABLE 6.

| | | | | | |
|---|---|---|---|---|---|
| Temp. | 100° | 81° | 79·5 | 67·5° | 56·5° |
| $10^5k_2$ (l. mole$^{-1}$ sec.$^{-1}$) | 98·1 | 25·7 | 23·6 | 6·22 | 2·75 |
| $E$ (kcal. mole$^{-1}$) | | | 20·0 | | |

TABLE 7. *Free energies and heats and entropies of activation of* 1 : 2-cis-*acetylglycosyl halides in* 100% *methanol at* 25°.

| Compound | III (uncat.) | IV | V | IV (uncat.) |
|---|---|---|---|---|
| $\Delta G^\ddagger$ (kcal. mole$^{-1}$) (at 25°) | 23·0 | 20·8 | 25·7 | 23·4 |
| $\Delta H^\ddagger$ (kcal. mole$^{-1}$) (at 25°) | 16·5 | 15·0 | 19·4 | 17·3 |
| $\Delta S^\ddagger$ (e.u.) (at 25°) | −21·8 | −19·5 | −21·2 | −20·5 |

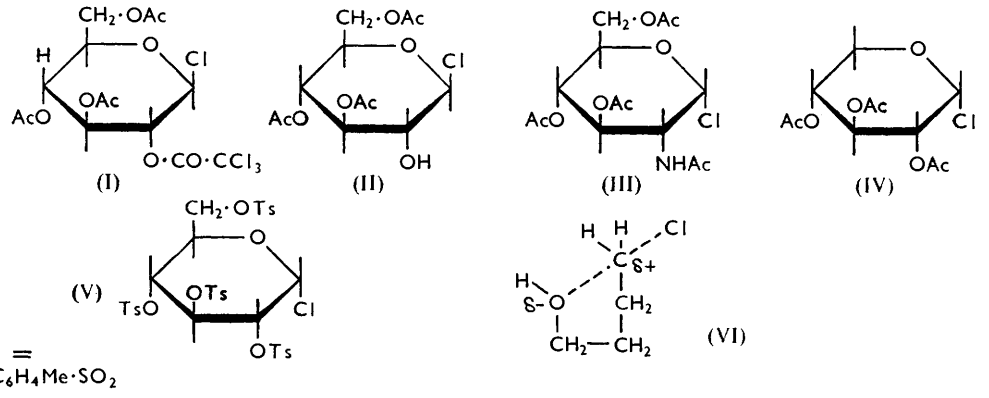
## DISCUSSION

The catalysed and uncatalysed solvolysis of the *O*-acetylglucosyl halides are well established as $S_N1$ type reactions.[5] In each case the intermediate is a carbonium ion and the reactions may be represented:

$$R\text{–}Cl \longrightarrow R^+ + Cl^-$$

$$RCl + HgCl_2 \longrightarrow R^+ + HgCl_3^-$$

Thus for compounds where the uncatalysed solvolyses are slow, it is possible to obtain comparable data under catalysed conditions. This applies to sugar halides where an " open-ion " intermediate is formed and to halides where there is participation by the 2-group to give a cyclic-ion intermediate. In the present investigation, the sugar halides studied (I—V) are considered to be of the first type, although in two of the compounds the 2-group is *trans* with respect to the halogen (I and II). The structure of both 1 : 2-*trans*-halides investigated (I and II) makes it highly unlikely that there is participation from the 2-groups. The powerfully electron-attracting trichloromethyl group would drastically reduce the nucleophilic affinity of the carbonyl-oxygen atom in " anchimeric assistance."




Boschan and Winstein [6] reached a similar conclusion because the rate of acetolysis of *trans*-2-trichloroacetoxy*cyclo*hexyl toluene-*p*-sulphonate is almost three powers of ten slower than that of the corresponding *cis*-compound. The hydroxyl group also shows little tendency for participation,[7] except in rather special circumstances as in the solvolysis of 4-chlorobutan-1-ol. The solvolysis rate for this compound is about 1000 times as rapid

[6] Boschan and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 4921.

[7] Winstein and Grunwald, *ibid.*, 1948, **70**, 828; Lemieux and Huber, *Canad. J. Chem.*, 1953, **31**, 1040.

as that of 2-chloroethanol, and it yields tetrahydrofuran.[8] Here anchimeric assistance by the hydroxyl group probably occurs (cf. VI). Normally, however, the presence of the hydroxyl group decreases the rate.[9] Non-participation of the hydroxyl and the trichloromethyl group is further indicated by the nature of the products of solvolysis.[2]

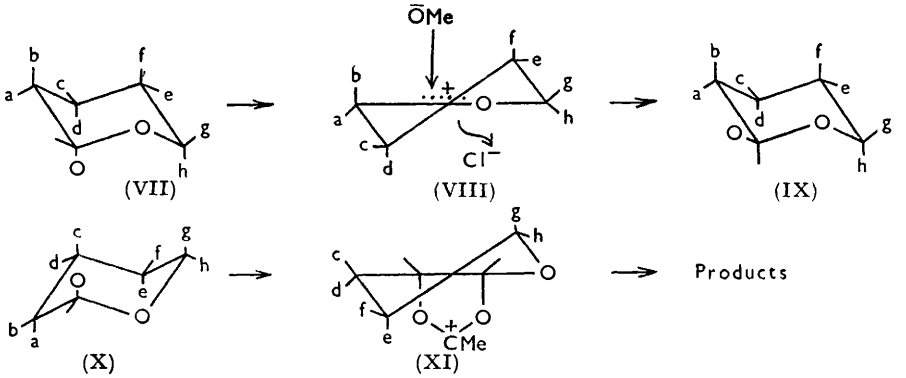
For the 1 : 2-*cis*-halides (III—V), participation by the 2-group can be discounted, and the open-ion intermediate is more likely. Comparative results for solvolysis of these compounds are shown in Table 8. It is clear that for the halides where no cyclic-ion

TABLE 8. *Solvolysis of O-acylglycosyl halides in methanol.*

| | $HgCl_2$ present | | | $HgCl_2$ absent | | |
|---|---|---|---|---|---|---|
| Glycosyl chloride | Rel. rate (at 25°) | *E* (kcal. mole$^{-1}$) | $\Delta S^{\ddagger}$ (e.u.) | Rel. rate (at 25°) | *E* (kcal. mole$^{-1}$) | $\Delta S^{\ddagger}$ (e.u.) |
| Tetra-*O*-toluene-*p*-sulphonyl-α-D-glucosyl ..... | 1 | 20·0 | −21·2 | — | — | — |
| 3 : 4 : 6-Tri-*O*-acetyl-2-*O*-toluene-*p*-sulphonyl-α-D-glucosyl ..... | 15·5 | — | — | — | — | — |
| 3 : 4 : 6-Tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucosyl ..... | 470 | 16·6 | −20·1 | — | — | — |
| Tri-*O*-acetyl-α-D-xylosyl ..... | 3380 | 15·6 | −19·5 | 1 | 17·9 | −20·5 |
| 2-Acetamido-3 : 4 : 6-tri-*O*-acetyl-2-deoxy-α-D-glucosyl ..... | — | — | — | 2 | 17·1 | −22·0 |
| 3 : 4 : 6-Tri-*O*-acetyl-β-D-glucosyl ..... | 72,000 | 12·5 | −23·8 | 2 | 16 | −20·8 |
| Tetra-*O*-acetyl-β-D-glucosyl ..... | — | — | — | 3 | 23 | 4·70 |

intermediate is formed the variations in solvolysis rate may be attributed almost entirely to variations in *E*; $\Delta S^{\ddagger}$ is relatively constant throughout. This may be compared with the dominating influence of $\Delta S^{\ddagger}$ on solvolysis of tetra-*O*-acetyl-β-D-glucosyl chloride, where a cyclic-ion intermediate is formed and the enhanced solvolysis rate depends entirely on the more favourable entropy of activation; the activation energy is slightly less favourable. The variation in reactivity for the halides studies (I—V) is thus consistent with steric factors' being mainly responsible. Previously we have considered steric factors only in their relation to the amount of " bunching " of groups in the vicinity of the halogen.[2]

The dominance of *E* in controlling reactivity of the 1 : 2-*cis*- and 1 : 2-*trans*-sugar halides studied suggests consideration of the steric conditions operating in the transition state of the reaction. From the results it is unlikely that the compounds differ in the ring conformation of the initial state. The comparable entropy values indicate comparable




(VII) (VIII) (IX) (X) (XI)

probabilities of achieving the transition state from the initial state. Thus the solvolyses of the *O*-acetylglycosyl halides which proceed by way of an open ion may be represented as in (VII—IX), showing the change in conformation necessary to form the products with inversion. The Cl-conformation (VII) is preferred to the 1C conformation (X) because, in the latter, substituents are in the unfavourable axial-positions.

[8] Heine, Miller, Barton, and Greiner, *J. Amer. Chem. Soc.*, 1953, **75**, 4778.
[9] Lemieux, *Adv. Carbohydrate Chem.*, 1954, **9**, 6.

Entry of the substituting group is predominantly on the side leading to inversion. This could be due to obstruction to the entering group by the departing group on the side leading to retention of configuration, or alternatively to an ion-pair intermediate postulated by Lemieux and Huber.[10] Shielding by substituent groups may also be a contributing factor.

Consideration of the transition state shows that large substituent groups at certain positions would inhibit resonance and achievement of the planar ion. A large 2-group would cause greater interaction between 2- and 3-substituents (a and c), which would account for the relative unreactivity of 3 : 4 : 6-tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glycosyl chloride. This effect would probably outweigh the polar influence of the trichloromethyl group which would be weakened by transmission through the saturated carbon atom.

The presence of the larger toluene-*p*-sulphonyl groups would considerably increase the interaction between the 2- and the 3-substituent (a and c) and also between the 4-group and the 6-group (e and g). Similarly, removal of the $-CH_2OAc$ as in (IV) would lead to a release of the latter interaction and a higher reactivity. The reactivity of 2-acetamido-3 : 4 : 6-tri-*O*-acetyl-2-deoxy-α-D-glucosyl compared with that of 3 : 4 : 6-tri-*O*-acetyl-β-D-glucosyl chloride is slightly anomalous if steric factors alone are considered, and suggests that there is a contribution from polar factors. Indeed Lemieux *et al.*[10] found a deactivating influence on progressive replacement of the hydrogen atoms of the acetyl group by chlorine. Some measure of the relative importance of the interaction between 2- and 3-, and between 4- and 6-groups, is given by the relative reactivities of tri-*O*-acetyl-α-D-xylosyl and 3 : 4 : 6-tri-*O*-acetyl-β-D-glucosyl chloride: the former interaction is the more effective but only to a small extent.

The steric effects of the substituent groups described above apply only to the mechanism now under consideration. For another mechanism, it is possible that the same structural changes could lead to different changes in reactivity. This may be demonstrated by reference to reactions at a lactol-carbon atom, which proceed by way of a cyclic-ion intermediate or the open-ion mechanism.

Lemieux and Brice [4] have correlated reactivity and configuration for the reactions of 1 : 2-*trans*-sugar acetates by considering the transition state of the reactions. For these compounds there is participation by the neighbouring 2-acetyl group to form a cyclic-ion intermediate, and here it is the 3-group which exerts the overriding influence on reactivity. For compounds containing 2 : 3-*trans*-groups the sugar acetate is 25 times more reactive than for compounds having a 2 : 3-*cis*-relation, as shown by the relative reactivity of corresponding altrose and mannose derivatives. We have observed this important influence of position 3 for sugar halides whose reaction proceeds by way of a cyclic-ion intermediate. Of the two 1 : 2-*trans*-acetylglycosyl halides, tetra-*O*-acetyl-α-D-mannosyl and -β-D-glucosyl chloride, the latter undergoes solvolysis 380 times faster than the D-mannose derivative. The much higher $\Delta H^{\ddagger}$ for the latter (*ca.* 8 kcal. mole$^{-1}$) is consistent with deactivation resulting from steric inhibition to achievement and resonance-stabilisation of the ion when the 3-acetoxy-group is *cis* to the 2-substituent.

Further, Lemieux and Brice [4] show that, for 1 : 2-*trans*-acetates, there is little difference in reactivity as a result of varying the configuration of the 4-group, while introduction of the acetoxymethyl group for hydrogen at position 5 of a pentose causes a four-fold decrease in reactivity when in *trans*-relation to the 1-group. These results may be rationalised by reference to the transition state scheme (X) ⟶ (XI), etc.

These results may be compared with the changes in reactivity accompanying similar configurational changes in reactions where no cyclic-ion intermediate is formed. For solvolysis of 1 : 2-*cis*-acetylglycosyl bromides, changing the configuration of the 4-group (glucose–galactose) produces a 4·5-fold change in rate, and introduction of a 5-acetoxymethyl group (glucose–xylose) produces a 50-fold decrease in the reactivity of the halogen.[2] For 1 : 2-*cis*-acetylglycosyl chlorides introduction of the acetoxymethyl group results in a

[10] Lemieux and Huber, *Canad. J. Chem.*, 1955, **33**, 128.

40-fold decrease. The differences arise directly from the difference in the transition state. Reactivity should therefore be related to a particular mechanism.

## Experimental

Methanol and acetone were purified as described in earlier papers. The compositions of the solvent mixtures are given according to the convention used throughout this series.

Tri-*O*-acetyl-α-D-xylosyl chloride was prepared by boiling xylose and acetyl chloride in the presence of a trace of zinc chloride; the m. p. was 105° and $[\alpha]_D$ 171° (*c* 2 in $CHCl_3$).

3 : 4 : 6-Triacetyl-2-*O*-trichloroacetyl-β-D-glucosyl chloride was prepared by treating penta-*O*-acetyl-β-D-glucose with phosphorus pentachloride and had m. p. 139° and $[\alpha]_D$ +9° (*c* 2·1 in $CHCl_3$).

3 : 4 : 6-Triacetyl-β-D-glucosyl chloride was prepared by deacetylation of the preceding compound with dry ethereal ammonia; the m. p. was 154—155° and $[\alpha]_D$ +45° (*c* 1·8 in $CHCl_3$).

Tetra-*O*-toluene-*p*-sulphonyl-α-D-glucosyl chloride was prepared by treating a solution of toluene-*p*-sulphonyl chloride in chloroform with glucose in pyridine. The m. p. was 81° and $[\alpha]_D$ 61° (*c* 2 in acetone).

3 : 4 : 6-Tri-*O*-acetyl-2-*O*-toluene-*p*-sulphonyl-α-D-glucosyl chloride was prepared by treating a suspension of tri-*O*-acetyl-β-D-glucosyl chloride in chloroform with toluene-*p*-sulphonyl chloride in pyridine–chloroform. The m. p. was 121° and $[\alpha]_D$ 149° (*c* 1 in acetone).

2-Acetamido-3 : 4 : 6-tri-*O*-acetyl-2-deoxy-α-D-glucosyl chloride, prepared as described by Baker *et al.*,[11] had m. p. 126°.

Rate measurements were carried out in a polarimeter tube (2·2 dm.) kept at constant temperature. For α-D-glucose tetratoluenesulphonate 1-chloride the sealed-ampoule technique, described in Part IV,[12] was used.

The rate constants were calculated from the initial rates of the reaction.

Tables 9—12 show typical runs, only a part of the experimental observations being given. In general the calculated values of the activation energy are accurate to ±0·5 kcal. mole$^{-1}$.

Table 9. *Solvolysis of tri-O-acetyl-α-D-xylosyl chloride in* 100% *methanol at* 29·5°. [RCl] = 0·05M.

| Time (min.) | 3 | 7 | 9 | 11 | 15 | 19 | 25 | 31 | 35 | 45 | 55 | ∞ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| α | 5·25° | 5·15° | 5·03° | 5·97° | 4·86° | 4·74° | 4·55° | 4·39° | 4·28° | 4·01° | 3·75° | −1·20° |

$(d\alpha/dt)_{t=0}$ = 3·2 × 10$^{-2}$ degree min.$^{-1}$. $k$ = 8·35 × 10$^{-5}$ sec.$^{-1}$.

Table 10. *Solvolysis of 2-acetamido-3 : 4 : 6-tri-O-acetyl-2-deoxy-α-D-glucosyl chloride in* 100% *methanol at* 25·8°. [RCl] = 0·19M.

| Time (min.) | 4 | 15 | 22 | 29 | 36 | 50 | 68 | 82 | 97 | 117 | 151 | ∞ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| α | 1·89° | 1·76° | 1·69° | 1·61° | 1·54° | 1·41° | 1·24° | 1·13° | 1·02° | 0·90° | 0·72° | 0·05° |

$(d\alpha/dt)_{t=0}$ = 1105 × 10$^{-2}$ degree min.$^{-1}$. $k_1$ = 1·14 × 10$^{-4}$ sec.$^{-1}$.

Table 11. *Solvolysis* 3 : 4 : 6-*tri*-O-*acetyl*-2-O-*trichloroacetyl*-β-D-*glucosyl chloride in* 100% *methanol at* 29·6°, *in presence of mercuric chloride.* [RCl] = 0·05M. [$HgCl_2$] = 0·049M.

| Time (min.) | 5 | 17 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | 150 | 240 | ∞ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| α | 0·53° | 0·67° | 0·83° | 0·93° | 1·02° | 1·13° | 1·23° | 1·32° | 1·41° | 1·51° | 1·96° | 2·66° | 5·24° |

$(d\alpha/dt)_{t=0}$ = 1·1 × 10$^{-2}$ degree min.$^{-1}$. $k_2$ = 7·75 × 10$^{-4}$ l. mole$^{-1}$ sec.$^{-1}$.

Table 12. *Solvolysis of* 3 : 4 : 6-*triacetyl*-2-O-*toluene*-p-*sulphonyl*-α-D-*glucosyl chloride in* 100% *methanol at* 25°, *in presence of mercuric chloride.* [RCl] = 0·018M. [$HgCl_2$] = 0·018M.

| Time (days) | 0 | 7 | 15 | 19 | 22 | 24 | 26 | 29 | 31 | 37 | ∞ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| α | 2·80° | 2·45° | 2·04° | 1·88° | 1·65° | 1·50° | 1·33° | 1·08° | 0·94° | 0·60° | −0·05° |

$(d\alpha/dt)_{t=0}$ = 4·44 × 10$^{-5}$ degree min.$^{-1}$. $k_2$ = 1·78 × 10$^{-5}$ l. mole$^{-1}$ sec.$^{-1}$.

The authors thank Professor A. G. Evans for his continued interest and advice. A maintenance grant by the Department of Scientific and Industrial Research (to G. L. M.) is gratefully acknowledged.

University College, Cathays Park, Cardiff. [*Received, June 3rd,* 1957.]

[11] Baker, Joseph, Shand, and Williams, *J. Org. Chem.*, 1954, **19**, 1786.
[12] Mattok and Phillips, *J.*, 1956, 1836.