furnishes hydrogen ions without hydrolysis and simultaneous formation of potassium hydroxide and more hydrochloric acid is therefore adsorbed.

## Summary

1. The data presented in this paper indicate that the view that hydrogen and hydroxyl ions are equally adsorbable by charcoal is based on erroneous experimental evidence.

2. It has been demonstrated that pure, activated sugar charcoal adsorbs more hydrochloric acid from mixtures of sodium chloride and hydrochloric acid than from hydrochloric acid alone.

3. It has been demonstrated that the addition of sodium chloride to sodium hydroxide and of potassium chloride to potassium hydroxide does not cause these hydroxides to be adsorbed. On the contrary, the addition of these salts results in an increase in concentration of alkali due to hydrolytic adsorption, whereby hydrochloric acid is adsorbed and an equivalent amount of base is set free.

4. Evidence has been presented which proves that the strong inorganic bases are "negatively adsorbed" by pure charcoal.

5. Adsorption from solutions of some salts is exclusively hydrolytic in nature, while from others it is partially hydrolytic and partially molecular.

6. It has been pointed out that the adsorption of electrolytes by activated sugar charcoal is in accord with the adsorption theorem of Gibbs, whereas the results obtained with blood charcoal under the same conditions are anomalous.

7. An explanation is offered for the effect of acids and bases on adsorption from salt solutions.

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# OPTICAL ROTATION AND ATOMIC DIMENSION. IV[1]

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The third article of this series[1] showed that the differences Cl-F, Br-Cl- and I-Br in specific rotations of monohalogen-triacetyl-*l*-arabinose are also approximately proportional to the differences in atomic diameters recorded by Bragg. The specific rotations for chloro- and bromo-tri-

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[1] This article is a continuation of "Fluoro-acetyl Derivatives of Sugars. III. Optical Rotation and Atomic Dimension" [THIS JOURNAL, **46,** 1484 (1924)]. The investigation of the fluoro-acetyl derivatives of sugars has not been concluded, as other fluoro-acetyl derivatives as, for example, of maltose, have been prepared. Fischer's bromination method yielded, however, a crystalline dibromo maltose derivative, instead of a monobromo derivative as reported by Fischer. Their preparation and general properties will be reported in a forthcoming paper in THIS JOURNAL.

acetyl-*l*-arabinose reported in the literature were found to be incorrect.[2] These results suggested the necessity of a revision of other values quoted. The values for the xylose and glucose derivatives have now been revised; those for the derivatives of cellose and other sugars are being revised. A comparison of the specific rotations of available halogen-acetyl derivatives is given in this article. All data were obtained from preparations purified with the same care and measured under similar conditions of concentration and identical conditions of temperature, solvent and light.

The results have been compiled in Table I. These corrected values show a markedly better agreement than did the set of values previously used by the writer[3] between the ratios of the differences of specific rotations and of atomic diameters (Bragg).

TABLE I

COMPARISON OF SPECIFIC ROTATIONS WITH ATOMIC DIAMETERS[a]

| | Derivatives of | | | | Respective Spec. rotat. diff. | | | | Resp. spec. rotat. diff. reduced | | | | Bragg's atomic diam. diff. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Glucose | Fructose | Xylose | *l*-Arabinose | | | | | | | | | |
| F | + 90.1 | − 90.4 | + 67.2 | +138.2 | | | | | | | | | |
| | | | | | 76.0 | 70.5 | 104.0 | 106.2 | 41.0 | 41.0 | 41.0 | 41.0 | 41 |
| Cl | +166.1 | −160.9 | +171.2 | +244.4 | | | | | | | | | |
| | | | | | 31.7 | 28.2 | 40.7 | 42.7 | 17.1 | 16.4 | 16.0 | 16.5 | 16 |
| Br | +197.8 | −189.1 | +211.9 | +287.1 | | | | | | | | | |
| | | | | | 39.6 | .. | .. | 52.0 | 21.4 | .. | .. | 20.0 | 24 |
| I | +237.4 | ..... | ..... | +339.1 | | | | | | | | | |

[a] See also Ref. 3.

Taking into consideration the fact that iodo-tetra-acetyl-glucose has undoubtedly been obtained in pure condition, the equal deviation (about one-fifth) of the reduced I-Br specific rotation value from the corresponding atomic dimension value, for the glucose derivatives as well as for the arabinose derivatives, suggests the following conclusions: (1) the prepared unstable iodo-triacetyl-*l*-arabinose has been measured in a fairly pure condition (the specific rotation found, +339, being about 4° too low);

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[2] Regarding Hudson's priority claim of detecting Chavanne's error [Hudson and Phelps, THIS JOURNAL, **46**, 2601, 2603 (1924)], I wish to state that I remeasured the rotation of Chavanne's compounds for *testing the atomic dimension relationship* in connection with the observed positive rotation of fluoro-tri-acetyl-arabinose and *not* for testing the application of the superposition principle nor for getting any credit for being first or second in establishing Chavanne's error. The application of the superposition principle gave Hudson the indication that Chavanne's determinations were not correct, for which of course all credit is due to Hudson.

[3] These values included some from the literature [THIS JOURNAL, **45**, 2384 (1923)]. In the present article the differences of specific rotations are reduced on the basis of Bragg's atomic dimension values. This procedure seems more logical than the reverse procedure, which has been followed in the preceding articles in reducing the Bragg values on the individual differences of specific rotations of each sugar. Recalculated on the basis of this comparison, the old values for glucose become 41.0, 17.5, 18.4, and those for xylose, 41.0, 19.7. The ratio derived from the remeasured values for glucose and xylose in Table I, therefore, shows a marked improvement.

and (2) taking into consideration the fact that the atomic dimension values or even their differences here considered are not finally established values, it is possible that such a comparison of specific rotations of derivatives of this kind is a valuable method for measuring atomic dimension values, as these values may be more constant for organic compounds than for inorganic salts.

TABLE II

COMPARISON OF MOLECULAR ROTATIONS WITH ATOMIC DIAMETERS

| | Derivatives of | | | | Respective Mol. rotat. diff. | | | | Bragg's atomic diam. diff. |
|---|---|---|---|---|---|---|---|---|---|
| | Glucose | Fructose | Xylose | *l*-Arabinose | | | | | |
| F | +315 | −316 | +187 | +384 | | | | | |
| | | | | | 294 | 274 | 317 | 336 | 41 |
| Cl | +609 | −590 | +504 | +720 | | | | | |
| | | | | | 204 | 187 | 214 | 253 | 16 |
| Br | +813 | −777 | +718 | +973 | | | | | |
| | | | | | 274 | ... | ... | 336 | 24 |
| I | +1087 | ... | ... | +1309 | | | | | |

With reference to the disagreement on the values for atomic diameters,[4] Fajans,[5] in collaboration with others, defends the view that the outer electronic orbits in different *inorganic* chemical combinations are susceptible to deformation (the anions more than the cations) and for this reason the atomic diameter is not a constant quantity for these compounds. This deformation may be judged by optical and other measurements of series of salts (molecular refraction, color, atomic dimensions, volatility, solubility, etc.).

It is further derived that this deformability increases from fluorine over chlorine to bromine and iodine. This would make the iodine salts the most susceptible for deformation and consequently they would give the most varying results. A new series of atomic dimension values just published[6] makes it possible to derive for the differences Cl-F, Br-Cl and I-Br, 0.50, 0.15 and 0.20. These yield an agreement in ratio of the last two differences, with the ratio of the respective specific rotation differences. However, Dr. Wherry states (in a private communication) that the data for fluorine are less certain than those for chlorine, bromine and iodine.

## Experimental Part

The values for chloro-, bromo- and iodo-tetra-acetyl-glucose and chloro- and bromo-triacetyl-xylose were revised.

**Chloro-tetra-acetyl-glucose.**—This derivative was prepared according to the method of von Arlt,[7] modified by Skraup and Kremann.[8] It was recrystallized from

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[4] See note in THIS JOURNAL, **45,** 2383 (1923).

[5] Fajans, Die Naturwissenschaften, **11,** 165 (1923).

[6] Wherry, *Am. Mineralogist,* **9,** 165 (1924).

[7] von Arlt, *Monatsh.,* **22,** 144 (1901).

[8] Skraup and Kremann, *ibid.,* **22,** 376 (1901).

boiling ligroin according to the method of Fischer and Armstrong;[9] m. p., 75–76° (von Arlt, 72–74°; Fischer and Armstrong, 73–74°). For measuring the rotation, approximately the same concentration was used as in the case of the other compounds investigated. After the third recrystallization, 0.6033 g. in U. S. P. chloroform in a volume of 24.9767 cc. produced a rotation in a 4dm. tube of 16.046 circular degrees to the right; hence, $[\alpha]_D^{20} = +166.07°$; 0.6061 g. dissolved in purified chloroform[10] gave a rotation of 16.126 circular degrees under identical conditions; hence, $[\alpha]_D^{20} = +166.13°$. After a fourth recrystallization from petroleum ether, 0.6056 g. produced a rotation of 16.115 circular degrees to the right with U. S. P. chloroform under identical conditions; hence, $[\alpha]_D^{20} = +166.15°$, which is taken as the specific rotation of the pure substance (von Arlt gives $[\alpha]_D^{20} = +165.76$).

**Bromo-tetra-acetyl-glucose.**—The preparation of this compound has received attention from many investigators.[11] The method of Moll van Charante was followed. After the fourth crystallization from ether, 0.6061 g. dissolved to a volume of 24.9767 cc. with purified chloroform produced a rotation in a 4dm. tube at 20° of 19.200 circular degrees to the right; hence, $[\alpha]_D^{20} = +197.80°$. After a fifth crystallization from ether, 0.6157 g. gave a rotation of 19.498 circular degrees to the right under identical conditions; hence, $[\alpha]_D^{20} = +197.74$. After a sixth recrystallization from petroleum ether, 0.6038 g. produced a rotation of 19.131 circular degrees to the right under identical conditions; hence, $[\alpha]_D^{20} = +197.84$, which is taken as the specific rotation of the pure substance (Koenigs and Knorr, $[\alpha]_D^{19} = +198.16$; Fischer, $[\alpha]_D^{17} = +200.3$ and $[\alpha]_D^{17} = +198.0$).

**Iodo-tetra-acetyl-glucose.**—This compound was prepared by the method of E. Fischer and H. Fischer;[12] m. p., 108–109° (E. Fischer and H. Fischer, 109–110°). The pure preparation kept in a vacuum desiccator over sodium hydroxide in the ice box showed no signs of decomposition after six months. After the first recrystallization from petroleum ether, 0.6202 g. dissolved to a volume of 24.9767 cc. with purified chloroform produced a rotation in a 4dm. tube at 20° of 23.584 circular degrees to the right; hence, $[\alpha]_D^{20} = +237.44°$. After a second recrystallization from petroleum ether, 0.6172 g. gave a rotation of 23.463 circular degrees to the right under identical conditions; hence, $[\alpha]_D^{20} = +237.37°$. After a third recrystallization from petroleum ether, 0.6195 g. produced a rotation of 23.560 circular degrees to the right under identical conditions; hence, $[\alpha]_D^{20} = +237.46°$. This record shows that the pure compound can be obtained even after the first recrystallization. From these three determinations, we derive $[\alpha]_D^{20} = +237.43 \pm 0.03$ (mean error) for the pure compound. For the specific rotation of the pure compound in acetylene-tetrachloride E. Fischer and H. Fischer found values ranging from +232.2° to +228.5°.

*Anal.* Subs., 0.1198: AgI, 0.0611. Calcd. for $C_{14}H_{19}O_9I$: I, 27.71. Found: 27.57.

**Chloro-triacetyl-xylose.**—The method of preparation described by Hudson and Johnson[13] was followed. The crude product was recrystallized by evaporating a filtered ether solution in the air. After the second recrystallization, 0.6027 g. dissolved to a volume of 24.9767 cc. with chloroform produced a rotation in a 4dm. tube at 20° of

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[9] Fischer and Armstrong, *Ber.*, **34,** 2890 (1901).

[10] THIS JOURNAL, **46,** 1486 (1924).

[11] Koenigs and Knorr, *Ber.*, **34,** 957 (1901). Fischer and Armstrong, *Ber.*, **34,** 2892 (1901); **35,** 833 (1902). Moll van Charante, *Rec. trav. chim.*, **21,** 42 (1902). Fischer, *Ber.*, **44,** 1903 (1911). Dale, THIS JOURNAL, **38,** 2187 (1916).

[12] E. Fischer and H. Fischer, *Ber.*, **43,** 2535 (1910).

[13] Hudson and Johnson, THIS JOURNAL, **37,** 2751 (1915).

16.497 circular degrees to the right; hence, $[\alpha]^{20}_{D} = +170.91°$. After a third recrystallization from ether, 0.6079 g. gave a rotation of 16.670 circular degrees to the right under identical conditions; hence, $[\alpha]^{20}_{D} = +171.23°$, which is taken as the specific rotation of the pure substance (Hudson and Johnson, $[\alpha]^{20}_{D} = +165°$, for a 12% solution); m. p., 105° (Hudson and Johnson, 95–97°; Ryan and Ebrill, 101°).[14]

*Anal.* Subs., 0.2003: AgCl, 0.0959. Calcd. for $C_{11}H_{15}O_7Cl$: Cl, 12.04. Found: 11.84.

**Bromo-triacetyl-xylose.**—This substance was prepared according to the method of Hudson and Johnson (l. c.) and recrystallized from ether until the specific rotation became constant. After the second recrystallization, 0.6120 g. dissolved to a volume of 24.9767 cc. with purified chloroform produced a rotation in a 4dm. tube at 20° of 20.770 circular degrees to the right; hence, $[\alpha]^{20}_{D} = +211.91°$, which is taken as the specific rotation of the pure substance, as it was not changed on a subsequent crystallization (Hudson and Johnson, +210.8°; Dale,[15] $[\alpha]^{20}_{D} = +212.1°$); m. p., 101–102° (Hudson and Johnson, 100–101°; Dale, 102°).

*Anal.* Subs., 0.1995: AgBr, 0.1082. Calcd. for $C_{11}H_{15}O_7Br$: Br, 23.57. Found: 23.10.

## Summary

A revision of the specific rotation values reported in the literature has been made for chloro-, bromo- and iodo-tetra-acetyl-glucose and for chloro- and bromo-triacetyl-xylose. The corrected values, as contrasted with the values given in the literature, show a markedly better agreement between the ratio of the difference in specific rotation, Cl-F, Br-Cl and I-Br and the ratio of the differences of atomic diameters recorded by Bragg.

It may be inferred from the relation stated above that the rotation of the pure iodo-triacetyl-*l*-arabinose is about 4° higher than the measured rotation (+339) of this unstable compound.

The determination of specific rotations of sets of derivatives the same as or similar to those investigated may furnish a new method for ascertaining atomic dimension values.

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[14] Ryan and Ebrill, *Proc. Roy. Dublin Soc.*, **11**, 249 (1905–8).

[15] Dale, THIS JOURNAL, **37**, 2746 (1915).