From these data the activity coefficients given in Table II were calculated.

The freezing point data have been used[4] to calculate the activity coefficient of potassium fluoride at 25°. A value of $\gamma = 0.848$ is computed at 0.1 *M*, which is considerably higher than that of other 1–1 electrolytes at this concentration (the value for lithium iodide is 0.811). Referring the freezing point data to $\gamma = 0.774$ at 0.1 *M* and 25°, however, values of 0.736, 0.676, 0.648 and 0.638 at 0.2, 0.5, 1.0 and 2.0 *M*, respectively, are obtained. Except at 2.0 *M*, the agreement with the isopiestic results is moderately good. The freezing point data for sodium fluoride cannot be corrected to 25°; a value of $\gamma = 0.752$ at 0.1 *M* is obtained[4] at 0°, compared with 0.764 at 25°. Referred to the latter value at 0.1 *M*, the freezing point data give $\gamma = 0.703$ and 0.625 at 0.2 and 0.5 *M*, respectively, again in moderate agreement with the isopiestic results.

The activity coefficient of potassium fluoride is very close to that of sodium chloride, while sodium fluoride has a much lower activity coefficient, close to that of rubidium iodide.

[4] Landolt–Börnstein, "Tabellen," Dritter Ergänsungsband, p. 2148.

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The Velocity of Rapid Chlorinations

BY HENRY C. THOMAS

Halford[1] has called attention to the possibility of studying rapid halogenations by measuring the distribution of radioactive halide between product and halide ion when the process is carried out in the presence of tagged halide ions. Long and Olson[2] have shown that the velocity of chlorination of acetanilide is slow compared to the velocity of interchange between chlorine and chloride ion in aqueous solution. Experiments have been carried out to investigate the possibility of measuring the rate of chlorination of an organic molecule with respect to the rate of exchange between chlorine and hydrochloric acid in benzene solution. Benzene was selected as the solvent in the hope that the low degree of dissociation of hydrochloric acid in this medium would bring about a moderately slow exchange reaction.

If it is assumed that the addition of chlorine is slow and that the exchange reaction

$$HCl^* + Cl_2 \leftrightarrows HCl + ClCl^*$$

and the chlorination

$$RH + Cl_2 \longrightarrow RCl + HCl$$

proceed at comparable rates, an expression for the distribution of radioactivity may be obtained as follows. If α is the fraction of Cl_2 exchanging before reacting with the organic molecule; a, the initial number of moles of Cl^- as HCl; θ_0, the initial fraction of Cl^- which is radioactive; and $\theta(x)$, the fraction of Cl^- which is radioactive after the addition of x moles of Cl_2, then

$$(a + x)\theta + \alpha \int_0^x \theta\, dx = a\,\theta_0 \qquad (1)$$

where $(a + x)\theta$ and $x\,\theta_p = \alpha \int_0^x \theta\, dx$ are the activities, respectively, of the final solution and of the chlorinated product. Equation (1) may be readily solved, and the ratio of the activity of the product to the initial activity of the solution is found to be

$$x\,\theta_p/a\,\theta_0 = 1 - [a/(a + x)]^{\alpha} \qquad (2)$$

Using the data of Long and Olson[2] one finds $\alpha = 1.04$. This result is unity within the experimental error, indicating, as the authors pointed out, complete exchange between Cl^- and Cl_2 before chlorination. (The experiment of Long and Olson was repeated using different ratios of Cl_2 to Cl^-. Calculated values of α were again unity within experimental error.)

In order to carry out experiments in benzene solution radioactive hydrogen chloride was introduced in the form of the dry gas, prepared directly from sodium chloride which had been bombarded by deuterons. The chlorinations were carried out on *p*-chlorophenol. Chlorine was introduced from a bulb of the gas attached to the flask of solution through a large-bore stopcock. The chlorinated product for radioactive analysis was recovered by distilling the benzene–hydrogen chloride solution through a fractionating column and dilution of the residue to an appropriate volume. The solutions, before and after chlorination, were analyzed for hydrochloric acid content by shaking with water and titration of the mixture. Two chlorinations of *p*-chlorophenol were carried out with the following results

Concn. *p*-ClC_6H_4OH, *m*	a	$a + x$	$x\,\theta_p/a\,\theta_0$
0.403	0.00960	0.01325	0.290
.409	.01045	.01330	.220

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[1] R. S. Halford, THIS JOURNAL, **62**, 3233 (1940).

[2] F. A. Long and A. R. Olson, *ibid.*, **58**, 2214 (1936).

These data correspond to values of α of 1.06 and 1.03, again indicating that exchange is complete before chlorination takes place.

While these experiments are of a preliminary nature they do indicate that in the present favorable case there is no indication but that the velocity of the exchange reaction is far greater than that of the chlorination. As an investigation of chlorination reactions the method seems to hold little promise. It is, of course, not impossible that the Br_2–Br^- or the I_2–I^- exchanges might be sufficiently slow so that significant measures of rates of halogenation could be obtained in these cases.

The author wishes to express his indebtedness to Prof. Ernest C. Pollard of the Sloane Physics Laboratory in Yale University through whose kindness the radioactive samples were made available.

STERLING CHEMISTRY LABORATORY
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Crystal Form of Sucrose Octaacetate

BY C. D. WEST

When an acetone solution of sucrose octaacetate[1] is allowed to stand at room temperature for several weeks, well-formed prisms of m. p. 84.5°, density 1.335, develop which are suitable for goniometric measurement. The expectation that this optically active molecule would crystallize in one of the enantiomorphous symmetry classes is confirmed by the finding of orthorhombic bisphenoidal symmetry (point group V), as shown by the accompanying orthogonal projection.

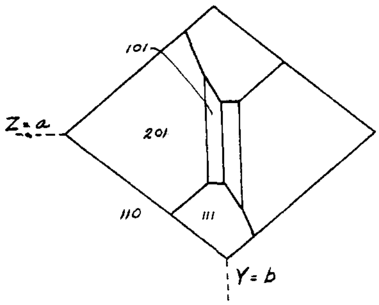

Fig. 1.—End faces and optical orientation.

The elements as calculated for a single crystal, the best of several measured, are set out in the table.

TABLE I

TWO CIRCLE ANGLES OF SUCROSE OCTAACETATE

$a:b:c = 1.2156:1:0.4605$; $p_0:q_0:r_0 = 0.3789:0.4605:1$

hkl	Faces	Measured	Mean	Calculated	
		φ	ρ	φ	ρ
110	4	39°27′	90°0′	39°26½′	90°0′
101	2	90 0	20 16	90 0	20 45
201	2	90 0	37 10	90 0	37 9
111	2	39 26	30 48	39 26½	30 48½

Cleavage planes are absent, and doubly terminated prisms were not noted. Crystals from ethanol solution have the same melting point and show the same faces. Optically the crystals are biaxial negative with the orientation $\alpha//c$, $\beta//b$, $\gamma//a$; the refractive indices are identical with Brandt's published values, namely, $\alpha = 1.470$, $\beta = 1.488$, $\gamma = 1.500$, all ±0.002 (2). Dispersion of the optic axes was not observed. The present crystals are thus identified with the stable, unsolvated form of sucrose octaacetate of m. p. 89° in the pure state.[2]

For the glassy form of this material the reported constants $n^{20}_D = 1.4660$, $d. = 1.28$[3] yield the specific refraction $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} = 0.2164$. The same constant for the crystals, as calculated from the average refractive index 1.486, is 0.2150.

The writer is indebted to Dr. Harry Berman for the opportunity to make the foregoing angle measurements at the Harvard Mineralogical Laboratories.

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(1) From Niacet Chemicals Corporation, Niagara Falls, N. Y.

(2) In Linstead, Rutenberg, Dauben and Evans, THIS JOURNAL, **62**, 3260 (1940).

(3) Cox, Ferguson and Dodds, *Ind. Eng. Chem.*, **25**, 968 (1933).

CAMBRIDGE, MASSACHUSETTS
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NEW COMPOUNDS

Derivatives of Piperazine. XIX. Reactions with Aryl Sulfonyl Chlorides and Aryl Sulfonic Acids

N,N′-Bis-(arylsulfonyl)-piperazines.[1]—The benzene, *p*-toluene, *p*-bromobenzene, and 2-nitrotoluene sulfonyl derivatives were prepared by adding with stirring a hot ethanolic solution of 0.1 mole of the appropriate sulfonyl chloride to an ethanolic solution of 0.05 mole (9.7 g.) of piperazine hexahydrate which contained a suspension of 6 g. of anhydrous sodium carbonate. The *o*-toluenesulfonyl derivative was prepared by gently refluxing 34 g. of *o*-toluenesulfonamide, 65 g. of ethylene bromide, and 30

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[1] The melting points of N,N′-bis-(benzenesulfonyl)-piperazine[1] and N,N′-bis-(*p*-toluenesulfonyl)-piperazine[2] have been reported in the literature as being 282–283 and 286°, respectively, values which are lower than those which we have found for these compounds.