

small amount of ash was removed by addition of ethyl ether and filtration. The remainder of the glycosidic sirup (5.7 g.) was distilled at 0.04 mm. and 120–142° (bath temperature). The product, a water-white viscous sirup, weighed 5.6 g.; the methoxyl content was 51.9%.

Fractionation of the Distilled Glycosides.—The distilled mixture of glycosides (4.44 g.) was placed in a 25-ml. pear-shaped flask containing glass wool and attached to a high-vacuum fractionating apparatus similar to that described by Hibbert.⁴ The mixture was slowly fractionated during twelve hours under a vacuum of 0.006 mm. and a bath temperature range of 110–160°. The last fraction was not distilled through the column because of its high boiling point and extremely viscous nature. The data for the various fractions are presented in Table I.

TABLE I

DATA CONCERNING THE METHYLATED GLYCOSIDE FRACTIONS OF METHYLATED GUAR POLYSACCHARIDE

Fraction	Weight obtained, g.	Methoxyl, %	Yield, %	Molar ratio	$[\alpha]_{25}^D$	$n_{20}^{D^a}$
1	1.2873	60.8	39.1	1.7	37.6	1.4493
2	0.4155	60.1				
3	0.9486	52.1	21.9	1.0	20.7	1.4599
4	1.6890	43.5	38.9	1.9		
Total	4.3314					1.4738

^a Refractive index of mixed glycosides 1.4597.

Preparation of the Anilide of Fraction One.—Fraction one (0.28 g.) was hydrolyzed under reflux at 85° in 10 ml. of *N* sulfuric acid for fifteen hours and then converted to the anilide by the method described by White.⁵ The product, after five recrystallizations from absolute ethanol, melted at 193–194°. Calcd. for 2,3,4,6-tetramethylgalactose anilide, m. p. 193.5°, C₁₈H₂₅O₅N: C, 61.7; H, 8.1; N, 4.5; OCH₃, 39.8. Found: C, 61.7; H, 8.2; N, 4.4; OCH₃, 39.8. A 90% yield of the galactose was obtained in the form of this crystalline anilide.

A sample of the mixed glycosides was also hydrolyzed and similarly converted to the anilides. Only one crystalline anilide was recovered in 85% yield; this was identical with that obtained from fraction one.

- (4) I. Levi, W. L. Hawkins and H. Hibbert, *ibid.*, **64**, 1957 (1942).
 (5) E. V. White, *ibid.*, **63**, 2871 (1941).

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Mechanism of the Copper and Halogen-Ion Catalysis of Dissolution of Copper

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The rate of solution of Cu in acid, in the presence of oxygen at saturation, is known to increase with the concentration of H⁺ and Cl⁻ ions, and to increase linearly with the concentration of the Cu⁺⁺ ions produced, except at high [Cu⁺⁺] where it lags behind the first-order rate with respect to [Cu⁺⁺]. The observed independence of the rate of stirring indicates that the rate of dissolution is not controlled by diffusion to and from the metal surface. These facts can be accounted for by the three-step mechanism

- (1) $\text{Cu} = \text{Cu}^{++} + \ominus$
- (2) $\text{Cu}^{++} + \text{Cu} = 2\text{Cu}^+$
- (3) $\text{Cu}^+ + \oplus = \text{Cu}^{++}$

where (1) includes reactions between Cu and O₂ or OH, and (3) is representative, in particular, of the reaction (3') $2\text{Cu}^+ + 2\text{H}^+ + 1/2\text{O}_2 = 2\text{Cu}^{++} + \text{H}_2\text{O}$.

Since the activity of Cu⁺ in the solution is low at all times, and these ions are steadily removed through (3'), the oxidation-reduction potential Cu⁺/Cu⁺⁺ is very much higher than Cu/Cu⁺, and reaction (2) proceeds from left to right. Absence of an effect of the rate of stirring indicates that (2) is a fast reaction. Consequently, the rate determining step is (3), specifically (3'). The activity of Cu⁺ is still further lowered, and (2) still further shifted to the right, by formation of complex ions [CuCl_n(ⁿ⁻¹)⁻]. This accounts for the accelerating effect of Cl⁻ ions.

From (3'), the rate of solution of the metal is

$$-d[\text{Cu}^+]/dt = k'[\text{Cu}^+]^2[\text{O}][\text{H}^+]^2$$

or, if Cu⁺ is mainly present as complex ion

$$-\frac{d[\text{CuCl}_n^{(n-1)-}]}{dt} = k''[\text{CuCl}_n^{(n-1)-}]^2[\text{O}][\text{H}^+]^2$$

With the equilibrium constants $[\text{Cu}^+]/[\text{Cu}^{++}] = K_1$

$$\frac{[\text{Cu}^+][\text{Cl}^-]^n}{[\text{CuCl}_n^{(n-1)-}]^2} = K_2, \text{ and}$$

$$\frac{\sum_1 [\text{Cu}^{++}][\text{Cl}^-]^{2n}}{[\text{CuCl}_n^{(n-1)-}]^2} = K_2^2$$

and noting $k'K_1 = k_1$, and $k''K_1 = k_2$, these equations become, respectively

$$-d[\text{Cu}^+]/dt = k_1[\text{Cu}^{++}][\text{H}^+]^2[\text{O}] \quad (A)$$

and

$$-\frac{d[\text{Cu}^+]}{dt} = k_2[\text{Cu}^{++}][\text{H}^+]^2[\text{O}] \frac{[\text{Cl}^-]^{2n}}{K_2^2} \quad (B)$$

Either A or B accounts for the first-order rate law in [Cu⁺⁺]. With regard to the effect of Cl⁻ ions, if one assumes $n = 3$ and $[\text{Cl}^-] = 10^{-2}$, the ratio $[\text{Cl}^-]^6/K_2^2$ becomes ~ 1 .¹ The concentration $[\text{Cl}^-] \approx 10^{-2}$ actually divides the ranges of applicability of equations A and B, the former being valid at $[\text{Cl}^-] < 10^{-2}$, the latter at $[\text{Cl}^-] > 10^{-2}$. There are not enough data to test the second order with respect to [H⁺]; in an experiment of Glauner,² the ratio of the amounts of Cu dissolved in 0.27 *N* and in 0.135 *N* acid was 32:5, that is higher than proportional to [H⁺].²

The corrosion is predominantly brought about by (2), the role of (1) being primarily to initiate the autocatalytic process, whereas the rate is determined by (3').

By analogous considerations, autocatalysis can be expected in the dissolution of iron but not in the case of lead. This is in agreement with observations.

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(1) St. v. Náráy-Szabó and Szabó, *Z. physik. Chem.*, **A166**, 228 (1933).

(2) R. Glauner, *ibid.*, **A142**, 67 (1929).