1.5569). The alkylated aminoquinoline was very susceptible to air-oxidation, and it was necessary to preserve it under nitrogen in the cold.

Anal. Calcd. for $C_{23}H_{37}N_3O$: C, 74.34; H, 10.04. Found: C, 74.50; H, 10.14.

Attempts to prepare the dihydrochloride were unsuccessful, but it was found that the **dihydrobromide** could be prepared easily. To 10 g. of the free amine was added a solution of 10 ml. of 40% hydrobromic acid (sp. g. 1.38) in 100 ml. of absolute ethanol and 100 ml. of absolute ether. The salt separated as a fine, yellow powder, m. p. 192.5–193.5°, when the solution was cooled. The analytical sample was crystallized from hot absolute ethanol.

Anal. Calcd. for $C_{23}H_{39}Br_2N_3O$: C, 51.79; H, 7.34; Br, 29.97. Found: C, 51.71; H, 7.11; Br, 29.97.

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CHARLES C. PRICE
HARRY F. HERBRANDSON

RECEIVED FEBRUARY 4, 1946

COMMUNICATIONS TO THE EDITOR

FRACTIONATION OF CELLULOSE

Sir:

In the course of our work on the fractionation of cellulose by a refined procedure using cuprammonium solvent at low temperatures (below 0°), we have observed phenomena similar to those recently reported by Morey and Tamblyn[1] for cellulose acetate and cellulose acetate butyrate which demonstrate the importance of the choice of solvent and precipitant in fractionation work.

With cellulose the choice of solvent is limited, but with cuprammonium, which is recognized as the best solvent, we have found the choice of precipitant to be important.

For example, when a 5% aqueous solution of sodium potassium tartrate (Rochelle salt) was used as the precipitant, precipitation of fractions took place on a weight basis, but the respective fractions did not show a significant amount of resolution on a molecular weight basis. However, by selecting other precipitants, varying degrees of resolution on a molecular weight basis became possible, as illustrated in Table I.

TABLE I

FRACTIONATION OF CELLULOSE

Experimental rayon tire yarn; 100% wood pulp base; av. basic D. P. = 490.

	Sodium potassium tartrate soln.		Acetone		*n*-Propyl alcohol	
Fraction	% Recov.	Basic D. P.	% Recov.	Basic D. P.	% Recov.	Basic D. P.
1	19.7	480	46.6	535	18.8	615
2	19.3	478	13.2	392	20.2	465
3	18.3	473	8.5	314	20.8	316
4	17.5	470	18.4	250	16.6	272
5	13.4	470	8.1	142	9.7	247
6	13.7	478	..	...	6.1	132

The average molecular chain length values of the fractions are expressed as Basic D. P.'s.[2]

The same general phenomena have been observed for the fractionation of viscose rayons, and viscose rayon pulps, respectively, from cuprammonium solvent.

Further work is in progress in which additional precipitants possessing wide variations in molecular structure are being used with the hope that resolving power can be correlated with molecular structure.

CHEMICAL RESEARCH DEPARTMENT
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WAYNE A. SISSON

RECEIVED APRIL 20, 1946

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[1] D. R. Morey and J. W. Tamblyn, *J. Phys. Chem.*, **50**, 12–22 (1946).

[2] O. A. Battista, *Ind. Eng. Chem., Anal. Ed.*, **16**, 351–354 (1944).

A REACTION VELOCITY WITH LARGE NEGATIVE TEMPERATURE COEFFICIENT

Sir:

Iodine shows very large departures from Raoult's law in a number of solvents, and it occurred to me to use iodine solutions to decide between activity and concentration as the determinant for reaction velocity. I chose the reaction between iodine and chlorine to form ICl, in CCl_4 to begin with, as one likely to meet the specifications. As so often happens in scientific research, it is not answering the original question, but has yielded results of such interest as to seem worth this brief preliminary report. They are as follows:

(1) The reaction is accelerated by light, but this is neither surprising nor disturbing, since one can let it proceed in the dark.

(2) It is enormously sensitive to minute traces of water. Although the solubility of water in CCl_4 is extremely small, the reaction runs to completion in minutes if the solutions are not carefully dried, whereas hours are required if the solutions are mixed after being kept sealed for a day in contact with P_2O_5.

(3) The "wet" reaction appears to be bimolecular, but the "dry" reaction is monomolecular with respect to chlorine through a wide range of iodine concentrations.

(4) And this is the truly astonishing feature, the wet reaction not only proceeds several times

as fast as 20° as at 25°, but upon addition of chloroform to prevent freezing and cooling with solid carbon dioxide it appeared to be instantaneous.

The only hypothesis that seems to accord with all of these results is the one suggested by Liebhafsky,[1] that the reactive halogen is in the form of hydrate. If these hydrates contain a number of molecules of water, like the solid $Cl_2 \cdot 6H_2O$, they could involve the large heat of formation required to explain the large negative temperature coefficient of the reaction. There is, of course, ample evidence that the number of "icebergs" in water falls off rapidly from 0° to room temperature.

It has been difficult to secure sufficient reproducibility to give satisfactory quantitative data, and since this may take some time, it seems appropriate to publish the above preliminary results.

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(1) H. A. Liebhafsky, *Chem. Rev.*, **17**, 89 (1935).

DEPARTMENT OF CHEMISTRY
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RECEIVED APRIL 15, 1946

THE ISOLATION OF LEVOGLUCOSAN FROM THE ENZYMIC HYDROLYSATES OF WAXY CORN STARCH

Sir:

Waxy corn starch[1,2,3] has been subjected to the consecutive action of β-amylase, α-amylase, β-amylase, and an amylase prepared from *Aspergillus oryzae* in order to obtain information on its structure.

The starch, pasted at 80°, was first treated with β-wheat amylase[4] free from α-amylase and maltase. Dextrin A[5] and maltose, the end-products of this hydrolysis, were isolated in yields of 49 and 48%, respectively.

Dextrin A was then subjected to the action of α-malt-amylase,[6] free from β-amylase and maltase, until no further increase in the reducing power of the hydrolysate occurred. From this hydrolysate, dextrin B-1 was separated by the addition of ethanol to a concentration of 85% by volume; after two reprecipitations the new dextrin was dialyzed continuously against distilled water for nine hours. The liquor remaining after dialysis was concentrated and the dextrin B-1a was recovered by precipitation with ethanol; yield, 44% of the weight of dextrin A; $[\alpha]^{25}\text{D}$ +160.2° in water; reducing power 3.8 and 8.0% of that of glucose by Shaffer–Hartmann and Gore–Steele methods, respectively.

Dextrin B-1a was next submitted to the action of β-amylase until the rotation and reducing power were constant. The products of this hydrolysis were dextrin B-1a$_1$ and maltose, the yields being 62 and 30% of the weight of dextrin B-1a, respectively. Dextrin B-1a$_1$ rotated +146.0° in water and had a reducing power by the Gore–Steele method equivalent to 12% of that of glucose. On treatment with the amylase of *Aspergillus oryzae*, the reducing power of dextrin B-1a$_1$ increased about sixfold and the rotation decreased to +38°. This hydrolysate after fermentation with yeast did not reduce Fehling solution and was levorotatory. After removal of the yeast and concentration of the solution, a solid was obtained by addition of ethanol; $[\alpha]^{25}\text{D}$ −32° in water; yield, 4.2% of the weight of dextrin A. This solid was acetylated and from the resulting product levoglucosan triacetate was isolated; yield, 0.6% of that calculated for levoglucosan on the basis of waxy corn starch; $[\alpha]^{25}\text{D}$ −65.5° in $CHCl_3$ (c, 1); m. p. 110–111°,[7] (mixed m. p. unchanged). On deacetylation, levoglucosan was obtained in pure crystalline form and characterized. Levoglucosan was also obtained from the hydrolysate resulting from the action of the amylase from *Aspergillus oryzae* on dextrin B-1a without prior fermentation. Isolation was effected both by distillation and by fractional crystallization after acetylation. Further work will have to be carried out to determine whether the 1,6-anhydro linkage is formed during enzymic fission of the substrate or actually occurs in waxy starch.

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(1) Hixon and Sprague, *Ind. Eng. Chem.*, **34**, 959 (1942).

(2) MacMasters and Hilbert, *ibid.*, **36**, 958 (1944).

(3) Schopmeyer, Felton and Ford, *ibid.*, **35**, 1168 (1943).

(4) Hanes, *Biochem. J.*, **30**, 174 (1936).

(5) *Cf.* Haworth, Kitchen and Peat, *J. Chem. Soc.*, 619–625 (1943).

(6) Hanes, *Can. J. Research*, **13B**, 185–208 (1935).

(7) Zemplén, Gerecs and Valatin, *Ber.*, **73**, 576 (1940).

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RECEIVED MARCH 4, 1946

6-CHLOROVANILLIN FROM THE CHLORITE OXIDATION OF LIGNIN

Sir:

In a fundamental study of the reaction of lignin with sodium chlorite in acid solution, the original filtrate from the preparation of holocellulose from black spruce (*Picea mariana*) by means of sodium chlorite in dilute acetic acid according to Wise and co-workers[1,2] was investigated. The filtrate was further acidified with sulfuric acid and fractionated. The steam non-volatile aldehyde fraction was identified as 6-chlorovanillin, colorless plates from ethanol melting at 167–168°. (*Anal.* Calcd. for $C_8H_7O_3Cl$: C, 51.49; H, 3.78; Cl, 19.00; CH_3O, 16.63. Found: C, 51.34; H, 3.76; Cl, 19.19; CH_3O, 16.70.) The oxime, prepared by heating with a solution of hydroxylamine hy-

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(1) Wise, *Ind. Eng. Chem., Anal. Ed.*, **17**, 63–64 (1945).

(2) Wise, Murphy and D'Addieco, *Paper Trade J.*, **122**, No. 2, 35 (1946).