order rate constant, N the normality of acid) against $1/T$, the reciprocal of the absolute temperature, gave two virtually parallel curves, Fig. 1. We therefore prepared more chlorophyll *a*, the more abundant and more easily purified component, and repeated measurements at three intermediate temperatures. In view of the number of measurements at different time intervals, for the various acid concentrations, we are confident that the averages for k/N, Table I, are substantially correct.

TABLE I

EFFECT OF TEMPERATURE ON RATE CONSTANT

T, °K.	N	k	k/N	Av.
		Chlorophyll *a*		
273	0.01	0.410	41	
	.002	.098	49	45
280	.01	.522	46	
	.005	.222	52	49
295	.002	.221	110.5	
	.001	.108	108	109
301.5	.01	1.39	139	
	.007	0.907	129	
	.004	.539	135	
	.002	.211	105.5	127
310	.002	.676	338	
	.001	.373	373	356
324	.001	1.725	1725	1725
		Chlorophyll *b*		
273	0.05	0.23	4.6	
	.02	.04	2.00	3.3
301.5	.10	1.69	16.9	
	.05	0.804	16.1	
	.02	.328	16.4	
	.01	.148	14.8	16.1
324	.01	1.47	147	147

Explanations for the deviations of ln k at the higher temperatures (Fig. 1) from the expected straight line relationship include the possibility that secondary reactions occur without being detected. As pointed out by Zscheile and Comar,[2] a considerable proportion of the chlorophyll could be allomerized without affecting the phase test. Variation in the effect of solvent with chlorophyll may also be involved. Regardless, however, of the true explanation, there is no significant difference in the energies of activation for the two chlorophylls whatever basis we select for our calculations.

If we ignore the values for the higher temperatures, and take the slopes of the lines of best fit, we find from the expression

$$d \ln k = -(E/R)d\,(1/T)$$

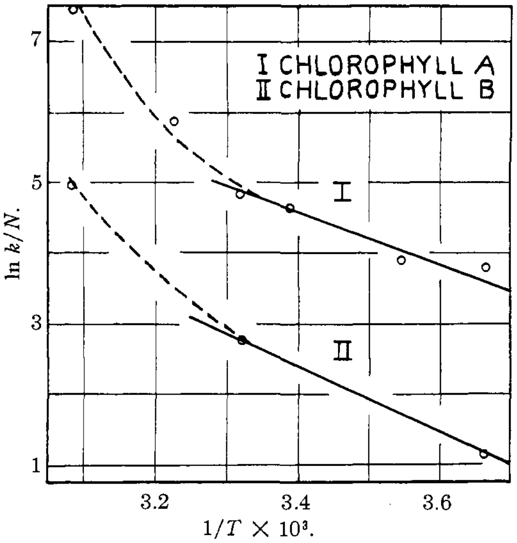

Fig. 1.—First order rate constants as a function of temperature: I, chlorophyll *a*; II, chlorophyll *b*.

energies of 7500 and 9000 cal. for chlorophylls *a* and *b*, respectively. If the values at 0 and 51° be selected, in the two cases, we obtain values of 12,500 and 13,000 cal., respectively. The similarity of these results indicates that the higher rate constant for chlorophyll *a* cannot be explained on the basis of a greater reactivity, and the most plausible explanation is the possibility of steric hindrance in the case of chlorophyll *b*. Phytol also, for example,[3] is less readily split off the chlorophyll *b*.

It is of interest that the stability of the magnesium is markedly affected by the state of oxidation of the isocyclic ring. Preliminary experiments indicate that the effect of a few drops of hydrogen peroxide is to cause a rapid increase in the reaction rate. We hope to report later on the effect of various oxidizing and reducing agents on the stability of magnesium, as this may provide clues to the remarkable ease with which chlorophyll disappears in many biological systems, under conditions as yet ill-defined.

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(2) Zscheile and Comar, *Bot. Gaz.*, **102**, 463 (1941).

(3) Weast and Mackinney, *J. Biol. Chem.*, **133**, 551 (1940).

DIVISION OF FRUIT PRODUCTS
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

RECEIVED MAY 19, 1941

The Preparation of Hydrosols by Freezing

BY THOMAS J. SHEA, WILLIAM E. DOOLEY AND CLAUDE SCHWOB

In a previous investigation in this Laboratory[1] hydrosols of active charcoal were prepared by a

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(1) Schwob, THIS JOURNAL, **58**, 1115 (1936).

modification of von Weimarn's procedure. These sols are contaminated with considerable amounts of sodium chloride or other "diluent" used in the grinding. Subsequent work showed a need for a substantially electrolyte-free charcoal hydrosol. One of us (T. J. S.) suggested that freezing the water in the capillaries of wet charcoal should cause enough expansion to give the required subdivision. This was found to be the case. Several other substances, such as Patrick's silica gel, which are easily wet by water were found to produce hydrosols when an aqueous paste was rapidly frozen and treated with water. This Laboratory not being equipped for precise colloidal work, it has been decided to forego any attempt to study the nature of the systems so obtained. A description of the general methods used by us is given here.

The charcoal or other solid is covered with water and wet by boiling or evacuation or both. Excess water is then decanted, and the resulting paste frozen in a beaker or flask immersed in a freezing mixture. The usual dry-ice–acetone mixture is very satisfactory for this purpose. The mass is thawed and frozen several times and then mixed with a large volume of distilled water. Alternately, after each freezing, about 200 cc. of water per g. of charcoal may be added to the frozen mass and the resulting sol decanted.

Many varieties of commercial carbons and sugar charcoals were found to give fairly stable sols of low concentration. Often better results were obtained if the water was made slightly acid or basic. The usual protective colloids seem to have very little effect.

DEPARTMENT OF CHEMISTRY
ST. PETER'S COLLEGE
JERSEY CITY, N. J.

RECEIVED JUNE 16, 1941

Preparation of 3,4-Dimethylaniline

BY W. A. WISANSKY AND S. ANSBACHER

In the synthesis of riboflavin, the preparation of 3,4-dimethylaniline is an important step. This xylidine is usually obtained by the method of Karrer, *et al.*,[1] comprising nitration of *o*-xylene, isolation by repeated fractionation of the 4-nitro-*o*-xylene and subsequent catalytic hydrogenation of the latter compound. In our hands, Karrer's procedure proved to be tedious and gave relatively low yields; in fact, we confirmed Karrer's 15% yield of xylidine. James, *et al.*,[2] likewise made use of a nitration and reduction method; they obtained a 27% yield of 4-nitro-*o*-xylene by conducting the nitration at a higher temperature. These workers adopted Karrer's laborious fractionation procedure for their subsequent steps of the process.

We have found that 4-bromo-*o*-xylene, obtained from *o*-xylene by bromination and subsequent vacuum distillation in 85% yield, according to Ghigi,[3] may be transformed to 3,4-dimethylaniline, when subjected to high pressure ammonolysis by the procedure of Groggins and Stirton[4] for the conversion of aromatic halides to the corresponding amines. Using pure *o*-xylene as the basic material, 4-bromo-*o*-xylene is obtained free from isomers. Hence, the finally resulting 1,2-dimethyl-4-aminobenzene will likewise be practically free of isomers.

In a bomb of a high-pressure hydrogenator, 200 g. of 4-bromo-*o*-xylene, 14 g. of copper wire and 600 ml. of 28–29% ammonia containing 12 g. of cuprous chloride were placed and treated at 195° and 900–1000 lb. pressure for fourteen hours under agitation by tilting back and forth. The bomb was emptied after cooling, the two layers were separated and 40 ml. of 40% alkali was added to the organic layer. The product was steam distilled and the crude xylidine, which crystallized on cooling, was further purified by dissolving it in 500 ml. of 8% hydrochloric acid and extracting the acid solution twice with 100-ml. portions of ether. The acid solution was made alkaline with 160 ml. of 40% alkali and steam distilled. The distillate was cooled and filtered and the dry product thus obtained was further purified by vacuum distillation at 116–118° and 22–25 mm.

The yield was 103 g. of 3,4-dimethylaniline (79%). A mechanically stirred autoclave may be more suitable than the apparatus employed, since more uniform mixing appears to result in a better yield. It is not known whether a large excess of ammonia is necessary for the reaction.

RESEARCH LABORATORY OF THE
INTERNATIONAL VITAMIN CORPORATION
NEW YORK, N. Y.

RECEIVED JUNE 21, 1941

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[1] Karrer, Becker, Benz, Frei, Salomon and Schöpp, *Helv. Chim. Acta*, **18**, 1435 (1935).

[2] James, Snell and Weissberger, THIS JOURNAL, **60**, 2084 (1938).

[3] Ghigi, *Ber.*, **71**, 684 (1938).

[4] Groggins and Stirton, *Ind. Eng. Chem.*, **28**, 1051 (1936).