deriving these values the most hazardous is the use of the equation: $\Lambda_x = \Lambda_0 - 3535C^{1/2} + 18{,}000C$; if the third term on the right-hand side of this equation is omitted the value $K = 0.008$ is obtained, but this must necessarily be too high.

If 73.5 is accepted as the mobility of the potassium ion,[5] that of the ferrocyanide ion now becomes 110.3. The use of this figure leads to the value 0.035 for the constant A of Falkenhagen and Vernon's theoretical viscosity equation, and greatly improves the agreement between this equation and the experimental results of Jones and Stauffer[6] for the viscosity of potassium ferrocyanide solutions at 25°.

(5) MacInnes, Shedlovsky and Longsworth, This Journal, **54**, 2758 (1932).

(6) Jones and Stauffer, *ibid.*, **58**, 2558 (1936).

BATTERSEA POLYTECHNIC
LONDON, ENGLAND
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The Preparation of Azomethane

BY FRANCIS P. JAHN

For some time azomethane has been prepared by workers in this and other laboratories by the oxidation of symmetrical dimethylhydrazine dihydrochloride by means of neutral potassium chromate in aqueous solution.[1] This method was first suggested by Thiele.[2] The method does not give good yields; moreover, according to the writer's experience the product is quite impure.

In an effort to find a more satisfactory method, a procedure based on the work of Diels and Koll was developed.[3] These workers found that oxidation of dimethylhydrazine dihydrochloride in aqueous sodium acetate solution by cupric chloride resulted in the precipitation of an addition compound of azomethane and cuprous chloride. This writer found that azomethane could be prepared satisfactorily by the heating of the dried precipitate.

The addition compound is prepared according to the directions given by Diels and Koll;[3] it may be recrystallized as they suggest but this is not necessary. Drying in a vacuum desiccator is very slow. The operation may be carried out more rapidly by placing the damp precipitate in a glass flask connected by means of a ground glass joint to a high vacuum system and pumping until the flask and contents have attained constant weight. The system includes a purification train arranged as described by Ramsperger,[1a] except that barium oxide is used in the drying tubes with soda lime and calcium chloride, and ordinary stopcocks are used in place of mercury cut-offs. During a drying period one of the traps was cooled with liquid air but no condensate formed; this indicates that the azomethane pressure above the compound at room temperature is negligible.

After completion of the drying the flask is heated from 125–140° by means of an oil-bath. One trap is cooled with solid carbon dioxide–toluene; one following is surrounded with liquid air. The heating is carried out with shaking until the precipitate has become entirely gray. It is found that the dry-ice trap contains practically all the liquid. The loss in weight of the flask during the heating is very close to the theoretical, assuming that the decomposition proceeds according to the equation

$$CH_3—N{=}N—CH_3 \cdot Cu_2Cl_2 \longrightarrow Cu_2Cl_2 + CH_3—N{=}N—CH_3$$

The yield of the addition compound from the dimethylhydrazine dihydrochloride is about 70%. Inasmuch as the preparation of the hydrazine derivative is a tedious process,[4] it would seem that the increased yield possible more than compensates for the additional operations as compared with the method of Thiele.

Explosion of Azomethane

Explosions of liquid azomethane have been attributed by other workers[1b] to the bubbling of the gas through mercury in manometers. On the other hand, explosions have not occurred in this Laboratory when azomethane was subjected repeatedly to these conditions by Burton and Davis and the writer. On the basis of his own experience the writer tends toward another explanation.

Some of a three-months old preparation of dimethylhydrazine dihydrochloride which had been preserved in a vacuum desiccator over calcium chloride was oxidized by the method described above. The recovery of addition product was only 29%. Upon heating, only a small amount of azomethane was condensed by liquid air. A large quantitity of a liquid of much lower vola-

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(1) (a) Ramsperger, This Journal, **49**, 912 (1927); (b) Allen and O. K. Rice, *ibid.*, **57**, 310 (1935); (c) Rice and Sickman, *J. Chem. Phys.*, **4**, 242 (1936); (d) Burton, Davis and H. A. Taylor, This Journal, **59**, 1038 (1937).

(2) J. Thiele, *Ber.*, **42**, 2579 (1909).

(3) Diels and Koll, *Ann.*, **443**, 262 (1925).

(4) Hatt, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Vol. XVI, 1936, p. 18.

tility was condensed in the dry-ice trap. The remainder of this preparation was oxidized by the method of Thiele. The product consisted entirely of a high-boiling liquid; apparently no azomethane was formed. During a distillation of this liquid to another trap an explosion occurred which demolished the purification train. The cause of this explosion is not known; at the time the system was completely closed off from mercury manometers and the diffusion pump. It seems highly improbable that azomethane should be explosive in these circumstances.[1b] On the basis of these facts it is suggested that azomethane is not responsible for this and other explosions; rather it is the high boiling liquid which is explosive. This latter seems to arise upon oxidation of dimethylhydrazine dihydrochloride which has been kept in a vacuum desiccator over calcium chloride for long periods of time. The 29% yield quoted above lends credence to the conclusion that the hydrazine derivative is perhaps oxidized in the desiccator. The identity of the liquid product has not been determined conclusively, but it is suggested that it may be methyl nitrate. It must be pointed out that Burton and Davis using an equally old preparation of dimethylhydrazine dihydrochloride which had been stored over sulfuric acid found that little high boiling liquid was formed upon oxidation by Thiele's method.

The product resulting by oxidation with cupric chloride has a molecular weight ranging from 57.5 for the first fraction to about 59 for the end fraction, as determined by means of a gas density balance. The writer contemplates preparation of pure azomethane by the use of an all-glass low temperature fractionating column of the Podbielniak type.

The writer acknowledges with appreciation a suggestion by Dr. T. W. Davis which led to the development of this method.

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Improved Methods of Conditioning Surfaces for Adsorption

BY IRVING LANGMUIR AND VINCENT J. SCHAEFER

In a previous communication[1] a method was described for conditioning the surface of a built-up barium stearate film so that visible adsorbed monolayers of organic and inorganic substances could be taken up from solution.

We now find that thorium nitrate can be used as well as aluminum chloride and that a barium stearate Y-multilayer can be conditioned by immersion into a 1×10^{-3} molar aqueous solution of either salt. The fact that a B-layer can be conditioned in this manner is evidence of the overturning of barium stearate molecules. Such a surface when conditioned is hydrophilic but when dried becomes hydrophobic.

When sodium silicate is added to a hydrous multilayer conditioned with thorium and then washed and dried, an increment of 10 Å. is observed. This surface after drying is hydrophilic and oleophilic. Successive layers of thorium and silicate may be added, five alternate layers of each giving a thickness of about 52 Å.

A film of pure stearic acid covered by five such layers retains 60% of its thickness after soaking in benzene for ten minutes although it instantly dissolves in its normal state. This coating also provides complete protection from water injury.

When a barium stearate film is conditioned with aluminum, its thickness increases 3.2 Å. If some sodium silicate is placed on the wet surface it causes the water to peel back suddenly and removes not only the aluminum but also 8 Å. of the underlying film. This loss is the equivalent of one-third of the molecules in a monolayer and possibly measures those which turned around. When the aluminum conditioning is followed by thorium conditioning, the peeling back does not occur upon the addition of the silicate, although the increment is removed with no injury to the underlying film.

Better adsorption of protein from solution is found when thorium is used instead of aluminum. Using a 1% solution of egg albumin in water the thickness on thorium was 48 Å., on aluminum 33 Å., and on thorium silicate 35 Å.

The use of a small 60-cycle solenoid vibrator replaces manual stirring and greatly facilitates uniform monolayer adsorption.

A monolayer of desoxycholate may be applied by bringing sodium desoxycholate in contact with a hydrous thorium conditioned surface. When washed the increase due to desoxycholate is 17 Å. The resulting dehydrated surface is hydrophobic and highly oleophilic.

When vapors of decane and tetradecane were

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[1] I. Langmuir and V. J. Schaefer, THIS JOURNAL, **59**, 1406(1937).