

scription is given of the preparation of lead, manganese, cobalt, nickel, iron and chromium abietates from pure abietic acid.

Acknowledgment is made to Messrs. Bright, Hickson and Scherrer of the Bureau staff for their assistance in the analysis of the metallic abietates.

WASHINGTON, D. C.

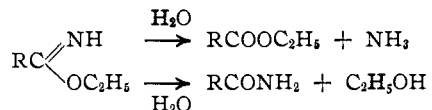
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SPONTANEOUS DECOMPOSITION OF IMIDO ESTERS

BY TREAT B. JOHNSON AND LAWRENCE W. BASS

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It is well known that imido esters are extremely susceptible to hydrolytic change with formation of the corresponding oxygen esters or acid amides respectively, and that they cannot be distilled at ordinary pressure



without undergoing dissociation into a nitrile and alcohol. This dissociation has also been observed to take place at ordinary temperature, and it



seems to be quite characteristic¹ also for the transformation to proceed beyond the nitrile stage and as a final result for the latter to undergo almost complete polymerization to its trimolecular form. In fact, Pinner² recommends as the best method of preparing cyaphenine ($\text{C}_6\text{H}_5\text{CN}$)₃ to allow crude undistilled benzimido-ethylether to undergo spontaneous decomposition at ordinary temperature. Wheeler, Walden and Metcalf³ state that pure benzimido-methylether can be kept for months without change.

A most interesting and striking fact in connection with these dissociations is the pronounced tendency for the nitriles to undergo polymerization. Ordinarily these compounds, when free from impurities, are not characterized by their instability, and where polymerization has been observed it has quite generally been induced by the action of a variety of polymerizing reagents such as sulfuric acid, metallic sodium, and aluminum chloride, or by heating at high temperatures.⁴

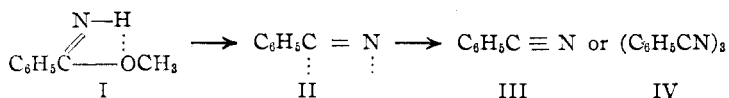
¹ Glock, *Ber.*, **21**, 2652 (1888).

² Pinner, *ibid.*, **22**, 1611 (1889).

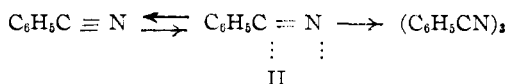
³ Wheeler, Walden and Metcalf, *Am. Chem. J.*, **20**, 68 (1898).

⁴ Pinner and Klein, *Ber.*, **11**, 764 (1878). Lottermoser, *J. prakt. Chem.*, [2] **54**, 1331 (1901). Frankland and Evans, *J. Chem. Soc.*, **37**, 563 (1880). Eitner and Krafft, *Ber.*, **25**, 2267 (1892). Scholl and Noir, *ibid.*, **33**, 1055 (1900). Meyer and Nabe, *J. prakt. Chem.*, [2] **82**, 536 (1910). Francis and Davis, *J. Chem. Soc.*, **85**, 259 (1904).

In imido ester decompositions we have only one dissociation product to influence the polymerization, namely, alcohol; therefore in such cases one might explain the tendency to polymerize as being due to the unsaturated condition of the nitrile at the moment of dissociation of the imido-ester molecule. This unsaturation may be expressed as follows.



In other words, polymerization to cyaphenine IV takes place before the free valences of the unsaturated cyanide group II have readjusted themselves into the stable condition of the nitrile molecule III. Both changes—formation of nitrile and polymerized nitrile—are therefore to be expected in imido ester decompositions at ordinary temperature. The rearrangement of ordinary benzonitrile into cyaphenine under the influence of polymerizing agents may also be interpreted as a case of disturbance of valence equilibrium in the nitrile by the catalyst, giving the unstable form II which then immediately polymerizes to a cyclic compound.



We are now able to record the results of a series of experiments which add further interest to this subject. In order to gain further data regarding the stability of imido ester combinations and the tendency for nitriles to polymerize to cyaphenines, Professor Henry L. Wheeler and T. B. Johnson in 1900 prepared fresh samples of benzonitrile and the following imido esters, namely, benzimido-methylester, benzimido-ethylester, benzimido-*isobutylester*, and *p*-tolylimido-methylester. They purified them very carefully by distillation under diminished pressure and then sealed them in glass containers and set them aside for future observation. These samples were examined by the writers in February, 1922, or after a period of storage covering 22 years. In every case, with the exception of the specimen of benzonitrile, we found heavy crystalline deposits of cyaphenine combinations and also unaltered nitrile. The pure benzonitrile showed no evidence of polymerization and the same behavior was also exhibited by *p*-tolynitrile which has been preserved in our cabinet for several years. In the case of benzimido-methylester this reagent had undergone practically complete decomposition and very little nitrile was present. The cyaphenine had deposited in beautiful prismatic crystals, some of which were over 2 cm. in length. They melted sharply without further purification at 229–230°.

The benzimido-*isobutylester* and the corresponding ethylester had not undergone complete dissociation. Benzonitrile and its polymer were

present in both cases, the latter having deposited in glistening prisms melting at 229–230°. From tolylimido-methylester we obtained almost a complete conversion into the polymerized tolylnitrile. This compound (cyantoline)⁵ which is recorded in the literature as crystallizing in needles, had deposited in the form of transparent tabular crystals which melted at the correct temperature, 277°, without further purification. Needles were also observed suspended in the remaining oil but the quantity was too small for ascertaining their melting point.

At what time the decomposition of these esters became apparent we have no reliable data, but it is evident from our observations that imido esters of the type examined are not organic combinations which can be preserved for long periods. It is also an extremely interesting fact that polymerization of the nitrile took place in the case of each imido ester, while the pure nitrile remained unchanged during this same period. These results are in accord with the assumption that dissociation of the imido ester leads to the formation of a labile nitrile containing free or residual valences, which rearranges to the stable nitrile and also polymerizes to cyclic derivatives.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE STRUCTURE OF ELASTIC GELS¹

BY ROBERT HERMAN BOGUE²

Introduction

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The structure of gels is a problem which has occupied the attention of physical chemists since the inception of colloid chemistry, and even before Graham had introduced the distinction between colloid and crystalloid.

Frankenheim³ in 1835 and von Nägeli⁴ in 1858 concluded that jellies were 2-phased and that the solid phase was crystalline. This view has been supported by von Weimarn⁵ and Levites,⁶ and is at present championed by Bradford.⁷

⁵ *Ber.*, **33**, 1055 (1900).

¹ Presented before the Pittsburgh Section of the American Chemical Society, March 18, 1922.

² Industrial Fellow of the Mellon Institute of Industrial Research of Pittsburgh, and Research Chemist for Armour and Company, of Chicago.

³ Frankenheim, "Die Lehre von der Kohäsion," Breslau, 1835.

⁴ von Nägeli, "Pflanzenphysiologischen Untersuchungen," Zürich, 1858.

⁵ von Weimarn, *Kolloid-Z.*, **2**, 76, 230, 275, 301, 326 (1908).

⁶ Levites, *ibid.*, **2**, 161, 208, 237 (1908).

⁷ Bradford, The "Physics and Chemistry of Colloids, and Their Bearing on Industrial Questions." Report of a General Discussion held jointly by the Faraday and Physical Societies of London, October 25, 1920. H. M. Stationery Office, London, 1921, p. 44.