saponifiable nitrile groups in stable aromatic systems.

Experimental

2,3,6,7-Tetramethylnaphthalene-1,4-dinitrile (II).—The author is indebted to Dr. P. E. Hoch for a sample of this material which he prepared by a standard Knoevenagel reaction of biacetyl with 3,4-dimethyl-*o*-phenylenediacetonitrile. This product, when decolorized with charcoal and recrystallized from cyclohexane, formed felted yellow needles which appear greenish in reflected light as a result of a blue fluorescence. It decomposed at about 240° without melting.

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.0; H, 5.98; N, 11.96. Found: C, 81.9; H, 5.88; N, 11.75.

2,3,6,7-Tetramethylnaphthalene-1,4-dicarboxamide (III).—A mixture of 250 mg. of the dinitrile II, 4.0 g. of potassium hydroxide, 40 ml. of ethylene glycol and 5 ml. of water was refluxed one hour. The solid II slowly dissolved to a clear yellow solution, which, when it was poured onto ice and filtered, gave 260 mg. (97% yield) of pale buff solid, m.p. above 320°.

2,3,6,7-Tetramethylnaphthalene (IV).—To a solution of 3.0 g. of phosphorus pentoxide in 7.0 g. of reagent 85% phosphoric acid was added 250 mg. of the diamide III. The mixture, contained in a small flask with reflux condenser, was heated at 200° for one hour with occasional shaking. White micro-platelets of product sublimed into the upper part of the flask and into the condenser. The mixture was cooled, diluted with water and extracted well with cyclohexane. The cyclohexane solution was dried and chromatographed on an 80 × 8 mm. column of alumina. The product, recovered from the effluent liquid by vacuum stripping, weighed 145 mg. (79% yield). One recrystallization from methanol gave shining, fluffy platelets, m.p. 191.2–191.8°.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.14; H, 8.80.

The **TNF derivative**, when recrystallized from benzene, gave scarlet microneedles, m.p. 176.0–176.6°.

Anal. Calcd. for $C_{27}H_{21}N_3O_7$: C, 65.0; H, 4.21; N, 8.42. Found: C, 65.5; H, 4.62; N, 8.32.

When 20 mg. of the dinitrile II and 2.0 g. of polyphosphoric acid were heated at 200° for a short time, white crystals sublimed into the upper part of the tube. The identity of these crystals with IV was confirmed by melting point and mixed melting point.

A comparison of the ultraviolet absorption spectrum and physical properties of this material with those of other tetramethylnaphthalenes has been made.[5]

---

[5] W. L. Mosby, This Journal, **75**, 3348 (1953).

Central Research Laboratory
General Aniline and Film Corporation
Easton, Pennsylvania

On the Starch–Iodine Complex

By Sôzaburo Ono, Shinpei Tsuchihashi and Takashi Kuge

Received February 4, 1953

This paper presents a quantitative study of the relationship between iodide concentration and wave length of maximum absorption of amylose–iodine complex. The authors attempt to explain the manner in which the iodide ion influences the starch–iodine complex formation.

Rundle and his co-workers[1] have found that the nature of the absorption spectra of the colored iodine in the starch–iodine complex is something quite different from that of iodine in any other medium. The structure of the amylose–iodine complex has been established as a helical amylose chain in which the iodine molecules are arranged in a linear array parallel to the helix axis, and resonance structures have been proposed for the polyiodine chains.[2] We may expect that this polyiodine chain has a structure similar to that of polyenes. The corresponding two p-electrons (those having the same symmetry) of each iodine atom may form a π-orbital along the polyiodine chain. The iodine chain may have two such π-orbitals, because each iodine atom possesses two pairs of such p-electrons, and these π-electrons may be responsible for the light absorption of the complex. We applied to our experimental results the relation which has been proposed by Kuhn[3] for polyenes. Kuhn's relation is expressed by

$$\lambda_{\max} = \left[\frac{V_0}{hc}\left(1 - \frac{1}{N}\right) + \frac{h}{8mc}\,\frac{N + 1}{L^2}\right]^{-1} \qquad (1)$$

where $\lambda_{\max}$ is the wave length of maximum absorption, L, the resonating chain length, N, the number of π-electrons, h, Planck's universal constant, m, the mass of the electron, c, the velocity of light, V_0, the perturbation parameter.

The results obtained indicate that the $\lambda_{\max}$ shifts toward the shorter wave lengths and the resonating chain length becomes shorter with the increasing iodide concentrations. Our data are also in good agreement with those obtained by Rundle and co-workers[4] and Swanson,[5] concerning the relationship between starch chain length and $\lambda_{\max}$. Potentiometric[6] and spectrophotometric titrations[4] suggested that iodide enters the helix with iodine. Our suggested explanation for the shift of $\lambda_{\max}$ with the change of iodide concentration is that iodide ions enter into the polyiodine chains and break the resonating chains into shorter lengths.

Experimental

Amylose used was obtained from potato starch by hot water extraction (at 60°), and it had the following characteristics: intrinsic viscosity was $[\eta] = 0.80$. Using this value, the degree of polymerization was calculated to be D.P. = 480 glucose units.[7]

Absorption spectra were measured with a G. E. Recording Spectrophotometer at room temperature, using a cuvette 10 mm. thick. Amylose concentration used in this investigation was 0.01%. Iodide concentrations were varied from zero to 0.5 M at constant iodine concentration (13% of theoretical maximum complex formation). A parallel investigation was conducted using ethanol instead of iodide.

Results and Discussion

In our study, N is equal to twice the number of iodine atoms, n, and L is equal to $6.2(n/2 - 1)$ Å., based on the average I–I distance of 3.1 Å. in the polyiodine chain.[8] It was postulated that in the complex free of iodide, 80 iodine molecules form one polyiodine chain, since D.P. of the amylose used was 480 glucose units and 6 glucose units take up one iodine molecule.[4,9] At zero iodide concentration, all terms in equation (1) are known except V_0. V_0 is then calculated to be 3.09×10^{-12} erg (1.9 e.v.).

---

[1] R. E. Rundle, J. F. Foster and R. R. Baldwin, This Journal, **66**, 2116 (1944).

[2] R. S. Stein and R. E. Rundle, *J. Chem. Phys.*, **16**, 195 (1948).

[3] H. Kuhn, *ibid.*, **17**, 1198 (1949).

[4] R. R. Baldwin, R. S. Bear and R. E. Rundle, This Journal, **66**, 111 (1944).

[5] M. A. Swanson, *J. Biol. Chem.*, **172**, 825 (1948).

[6] F. L. Bate, D. French and R. E. Rundle, This Journal, **65**, 142 (1943).

[7] A. L. Potter and W. Z. Hassid, *ibid.*, **73**, 593 (1951).

[8] C. D. West, *J. Chem. Phys.*, **15**, 689 (1947).

[9] R. E. Rundle and D. French, This Journal, **65**, 1707 (1943).

Hach and Rundle[10] stated that it had not been determined experimentally whether polyiodine consists of chains with two different I–I distances, or whether all distances have become equal to 3.1 Å. From the V_0 value determined above, 1.9 e.v., it seems likely that polyiodine consists of chains with two I–I distances, due to unequal contributions of two limiting forms A and B.

$$\cdots\mathrm{I{-}I}\cdots\cdots\mathrm{I{-}I}\cdots\cdots\mathrm{I{-}I}\cdots \qquad \text{(A)}$$

$$-\mathrm{I}\cdots\cdots\mathrm{I{-}I}\cdots\cdots\mathrm{I{-}I}\cdots\cdots\mathrm{I}- \qquad \text{(B)}$$

TABLE I

No.	Concn. of KI, *M*	Concn. of EtOH, *M*	$\lambda_{\max}$	*n* (chain length)
1	....	....	628	160
2	1.2×10^{-4}	....	625	134
3	6.1×10^{-4}	....	621	108
4	5.0×10^{-3}	....	613	77
5	3.0×10^{-2}	....	600	52
6	2.1×10^{-1}	....	572	30
7	5.0×10^{-1}	....	557	22
8	....	8.2×10^{-1}	594	45
9	....	1.6	588	40

Table I shows the values of $\lambda_{\max}$ observed and the corresponding chain lengths (n) which have been calculated with equation (1) and the V_0 value. Both the $\lambda_{\max}$ and the estimated chain length change in a regular fashion with the iodide concentration. Also, it appears that ethanol causes an effect similar to that of iodide.

Our data may not describe exactly the quantitative relation between the chain length and the $\lambda_{\max}$, because the length of the polyiodine chain at zero iodide concentration is estimated. Nevertheless, our results indicated that Kuhn's theory is applicable to the polyiodine chain. They also account for the behavior of iodine in shifting the absorption spectrum of the complex.

Gilbert and Marriott[11] suggested that the amylose complex is composed mostly of groups of the type ($3\mathrm{I_2}\cdot 2\mathrm{I^-}$), each probably a linear resonating group which develops the pure blue color in the complex. According to our model, it may be that iodide is chain terminating, even if it is in the resonating chain.

It is well known that the color of the complex disappears at higher temperature. The authors intend to investigate this phenomenon spectrophotometrically.

We are indebted to Mr. Tamotsu Fukuda of the Osaka Industrial Research Institute for the measurement of absorption spectra.

---

(10) R. J. Hach and R. E. Rundle, THIS JOURNAL, **73**, 4321 (1951).

(11) G. A. Gilbert and J. V. Marriott, *Trans. Faraday Soc.*, **44**, 84 (1948).

LABORATORY OF BIO-PHYSICAL CHEMISTRY
FACULTY OF AGRICULTURE
NANIWA UNIVERSITY
SAKAI CITY, JAPAN

Removal of Halogen from Aromatic Nitrohalo Compounds

BY WALTER T. SMITH, JR., AND LOUIS CAMPANARO

RECEIVED FEBRUARY 20, 1953

Earlier work has shown that the replacement of chlorine by hydrogen in aromatic compounds having a nitro group ortho to the chlorine can be accomplished by heating the compound with copper and benzoic acid.[1]

We wish to report a study of the application of this reaction to nitro compounds containing fluorine, bromine or iodine, and also the use of the reaction for the preparation of 3,5-dinitrotoluene.

In the earlier work it was found that a chlorine meta or para to a nitro group was not removed by the treatment with copper and benzoic acid. It has now been shown that a chlorine or bromine ortho to a nitro group can be removed without removal of a chlorine or bromine located meta to the same nitro group. Thus, the dehalogenation of 2,5-dichloro- and 2,5-dibromonitrobenzene leads to *m*-chloro- and *m*-bromonitrobenzene. The yields in these cases are 37–38%.

The monofluoronitrobenzenes did not dehalogenate under the conditions used. The *o*-, *m*- and *p*-isomers were all recovered without any formation of nitrobenzene.

The results observed with the monobromonitrobenzenes were comparable to those obtained with the chloronitrobenzenes. Only in the case of *o*-bromonitrobenzene did dehalogenation take place. While it might be expected that *p*-bromonitrobenzene might be sufficiently more reactive than the corresponding chlorine compound to permit dehalogenation, such was not the case. *p*-Bromonitrobenzene was recovered in 78% yield and there was no evidence that any nitrobenzene was formed.

The results with the iodonitrobenzenes are quite different than those obtained with the other halonitrobenzenes. As would be expected, the ortho isomer dehalogenated readily to give a 53% yield of nitrobenzene. It was not surprising to find that the presence of a nitro group para to the iodine was sufficient to activate the iodine, so that it was easily replaced by hydrogen upon treatment with copper and benzoic acid. The experiment with *m*-iodonitrobenzene indicates, however, that the location of the nitro group, and probably even its presence, is not an important factor in determining if iodine is replaced. The yield of nitrobenzene was 32% when *m*-iodonitrobenzene was used.

The dehalogenation of 2-chloro-3,5-dinitrotoluene provides a new synthesis of 3,5-dinitrotoluene. The presence of nitro groups located both ortho and para to the chlorine appears to enhance the ease of dehalogenation and 3,5-dinitrotoluene is obtained in 83% yield. This method of synthesis suffers from the low yield obtained in the preparation of the 2-chloro-3,5-dinitrotoluene. The usual "mixed acid" nitration of *o*-chlorotoluene was not successful, even at elevated temperatures. The use of concentrated sulfuric acid and sodium nitrate was also unsuccessful. By using a mixture of nitric, sulfuric and fuming nitric acids, *o*-chlorotoluene may be dinitrated to give a 9% yield of 2-chloro-3,5-dinitrotoluene.

Experimental

Dehalogenations.—The dehalogenations and attempted dehalogenations were carried out as illustrated below for *o*-fluoronitrobenzene. The results are summarized in Table I.

---

(1) W. T. Smith, Jr., THIS JOURNAL, **71**, 2855 (1949).