complicating factor. Those solutions in which aggregation can be assumed to be negligible on the basis of the homogeneity criterion almost invariably yield lengths in the range 500–700 A. This is far less than the value of about 1400 Å. which the protein could yield if it opened up fully to the extended (β-keratin) configuration. On the other hand the 500–700 range is in excellent agreement with the lengths observed in the case of heat denaturation under conditions yielding minimal aggregation, except in the case of denaturation in glycerol-rich media where somewhat shorter lengths were found.[3b]

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AMES, IOWA RECEIVED MAY 10, 1951

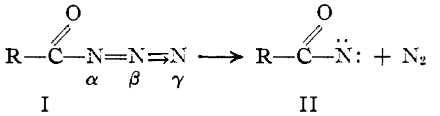
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

An N^{15} Tracer Study of Organic Azide Reactions. I. The Curtius Rearrangement of 3,5-Dinitrobenzazide-N^{15} [1]

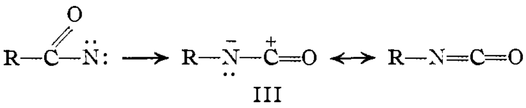
BY AKSEL A. BOTHNER-BY AND LEWIS FRIEDMAN

Nitric acid containing 31.4 atom % excess N^{15} has been converted to potassium nitrite which was used in the preparation of 3,5-dinitrobenzazide from 3,5-dinitrobenzhydrazide. Thermal decomposition of the azide gave nitrogen containing all the excess heavy nitrogen isotope, and dinitroaniline of normal isotopic composition. This confirms the currently accepted mechanism of rupture of the α-β N–N bond followed by the elimination of a molecule of nitrogen.

The currently accepted mechanism of the Curtius rearrangement of acyl azides is briefly outlined by equations (1) and (2).



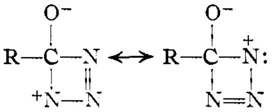
(1)



(2)

A similar mechanism serves to account for the gross behavior of molecules undergoing the closely parallel Hofmann, Lossen and Wolff rearrangements. These mechanisms have evolved from studies on: (a) the products obtained from the rearrangement of optically active compounds[2]; (b) kinetics of the rearrangements[3]; (c) tracer studies using isotopic carbon[4]; and (d) rearrangements in the presence of free radicals.[5] Such studies yield information concerning the general mechanism of the azide rearrangement, but leave the specific details of the role of the nitrogen atoms in the reaction essentially undetermined.

It has been assumed that the initial decomposition of the acyl azide (I) proceeds by rupture of the α-β N–N bond, yielding an unstable intermediate (II) and a molecule of nitrogen. It is possible that the activated azide undergoing decomposition might have a cyclic structure such as IV.



IV

The existence of such an intermediate would lead to an exchange of nitrogen atoms between the α- and γ-positions of the nitrogen chain. An alternative path for such an exchange is *via* the solvolysis of the acyl azide followed by an intermolecular exchange of azide ions.

An investigation of the products of thermal decomposition of a 3,5-dinitrobenzazide-N^{15} has been carried out. The azide was prepared by the treatment of 3,5-dinitrobenzhydrazide with nitrous acid enriched with N^{15}. It is probably correctly formulated as 3,5-dinitrobenzazide-γ-N^{15}; however, there is at present no evidence to exclude the possibility of nitrogen-isotope exchange between the β- and γ-positions. The nitrogen produced in the decomposition was analyzed with a Consolidated Nier Isotope Ratio mass spectrometer, scanning the individual peaks magnetically. The nitrogen contained approximately 0.1% $N^{15}N^{15}$, 31.1% $N^{15}N^{14}$, and the rest $N^{14}N^{14}$. The 3,5-dinitrophenyl isocyanate was hydrolyzed to 3,5-dinitroaniline, which was found to contain no excess N^{15} above the natural abundance of 0.4%.

The fact that all of the excess N^{15} in the azide appeared in the nitrogen in the reaction products indicates that the initial dissociation does take place by rupture of the α-β N–N bond. It shows that no exchange takes place between the α- and γ-positions, and consequently eliminates from consideration both the cyclic structure IV, and the possibility of intermolecular exchange of azide ion. Furthermore, this coupled with the small amount of $N^{15}N^{15}$ implies that the β-γ N–N bond remains intact throughout the reaction. Nitrogen atoms produced by this bond rupture would in recombination lead to an equilibrium distribution of

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(1) Work performed under the auspices of the Atomic Energy Commission.

(2) E. S. Wallis and S. C. Nagel, THIS JOURNAL, **53**, 2787 (1931); L. W. Jones and E. S. Wallis, *ibid.*, **48**, 169 (1926); E. S. Wallis and W. W. Moyer, *ibid.*, **55**, 2598 (1933); R. P. Bell, *J. Chem. Soc.*, 835 (1934).

(3) E. W. Barrett and C. W. Porter, THIS JOURNAL, **63**, 3434 (1941); L. W. Jones and E. S. Wallis, *ibid.*, **48**, 169 (1926); C. W. Porter and L. Young, *ibid.*, **60**, 1497 (1938).

(4) C. Huggett, R. T. Arnold and T. I. Taylor, *ibid.*, **64**, 3043 (1942).

(5) G. Powell, *ibid.*, **51**, 2436 (1929); E. S. Wallis, *ibid.*, **51**, 2982 (1929).

isotopic N_2 molecules and in this case produce 9.86% $N^{15}N^{15}$.

Experimental

Potassium Nitrite-N^{15}.[6]—10.0 ml. of 1.67 *N* nitric acid containing 31.4 atom per cent. excess N^{15} was titrated to *p*H 7 with 2 *N* potassium hydroxide using a glass electrode. Evaporation of the solution on the steam-bath gave a quantitative yield of potassium nitrate-N^{15}. Of this, 0.950 g. was finely powdered and intimately mixed with 1.950 g. of pure powdered lead in the bottom of an eight-inch Pyrex test-tube. The temperature of the lower end of the tube was slowly raised to 350° in a small wire-wound furnace. The tube was cooled and the contents were rinsed into a centrifuge tube with two 5-ml. portions of distilled water. The lead oxide was centrifuged down and the clear supernatant liquid transferred to an evaporating dish. Evaporation gave a 0.682-g. residue, which contained 94% potassium nitrite as determined on a small sample by addition of standard acid permanganate and back-titration.[7] The yield was therefore 80.2%.

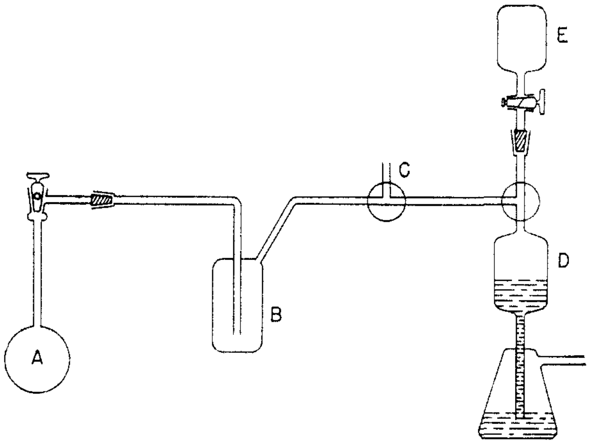

Fig. 1.

3,5-Dinitrobenzazide.—The procedure used was that of Sah and Ma.[8] By the use of 0.171 g. of the potassium nitrite-N^{15}, 0.412 g. or 89.7% yield of the dinitrobenzazide was obtained.

Thermal Decomposition of 3,5-Dinitrobenzazide.—A suspension of 0.150 g. of 3,5-dinitrobenzazide-N^{15} in 10 ml. of water was placed in bulb A of the apparatus (Fig. 1). The suspension was frozen by cooling the bulb with a Dry Ice–acetone-bath, and the entire system was then evacuated by pumping at C. The stopcock on vessel A was closed, and the contents of A were gradually warmed to 100° by an external water-bath. Heating was continued for half an hour, and the contents were then allowed to cool. A liquid nitrogen-bath was placed around trap B, and A was connected by means of the various stopcocks to the reservoir of the Toepler pump D. The gaseous products were slowly toeplerred into a gas storage bulb E, avoiding sudden rushes through the trap B. Mass spectrometric analysis of the gas showed it to be nitrogen of 99.5$^+$% purity, and to contain 31.1 atom per cent. $N^{14}N^{15}$ and 0.1% $N^{15}N^{15}$.

Deamination of 3,5-Dinitroaniline.—The aqueous suspension from the decomposition reaction was extracted with two 10-ml. portions of ethyl acetate. The ethyl acetate was removed in a current of air, and the residue refluxed with 3 ml. of concentrated hydrochloric acid for three hours, during which time the solution was gradually concentrated to approximately 1 ml. The whole was taken up in 10 ml. of 50% sulfuric acid and transferred back to reaction vessel A. The solution was chilled to −10°, and 1 ml. of 5 *M* sodium nitrite solution added. The liquid in the bulb was frozen and pumped out as before, then the stopcock was closed and the contents gradually warmed to 100°, at which temperature it was held for 15 minutes. The liquid was then refrozen, and the gaseous products toeplerred through a liquid nitrogen-cooled trap into a storage bulb, as before. Mass spectrometric analysis showed no difference in isotopic composition from tank nitrogen.

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(6) A new method for the preparation of sodium nitrite-N^{15}, giving better yields has been described by K. Clusius and M. Hoch, *Helv. Chim. Acta*, **33**, 2122 (1950).

(7) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1945.

(8) Sah and Ma, *J. Chinese Chem. Soc.*, **2**, 159 (1934).

UPTON, L. I., N. Y. RECEIVED MAY 21, 1951

[CONTRIBUTION FROM THE ROSS CHEMICAL LABORATORY, ALABAMA POLYTECHNIC INSTITUTE]

Comparison of Hydrogen Bonding Abilities of Some Organic Compounds of Phosphorus

BY GENNADY M. KOSOLAPOFF AND JOHN F. MCCULLOUGH

The maximum heats of mixing of chloroform with fifteen organophosphorus compounds were determined. Representative members of the families of types: $R_2P(O)OR$, $RP(O)(OR)_2$, $(RO)_3PO$, $(RO)_2P(O)Cl$, $ROP(O)Cl_2$, $(RO)_3P$ and $(RO)_2POH$ display differences in their hydrogen bonding ability, as reflected by the heat of mixing. These differences are qualitatively predictable from the structures of the compounds, showing enhanced activity with increased electron density at the central group.

Some time ago the heat of mixing of chloroform with phosphorus oxychloride[1] and with triethyl phosphate[1,2] was used as a method for estimation of the ability of the latter substances to form hydrogen bonds. It was of interest to extend such a study to the several rather readily available families of organophosphorus compounds in order to secure direct comparison of the hydrogen bonding tendencies in substances with various structures.

Accordingly, representative specimens of dialkyl phosphites, trialkyl phosphates, dialkyl chlorophosphates, alkyl dichlorophosphates, dialkyl alkanephosphonates and alkyl dialkylphosphinates were examined using the technique of the previous investigators.[1,2]

The results, which are summarized in Table I, readily show that the changes of structure bring about variations of the hydrogen bonding ability that can be qualitatively expected from considerations of the structural theory. Replacement of alkoxy groups (OR) by radicals (R) that are directly bonded to the central atom raises the hydrogen bonding ability. Replacement of chlorine atoms by alkoxy radicals causes a similar shift. The series: phosphorus oxychloride, alkyl dichlorophosphate, dialkyl chlorophosphate, trialkyl phosphate, shows the progressive manifestation of this effect very well. The relatively small change which takes place upon substitution of the first alkoxy group is rather unexpected, but the results are qualitatively in line with the grossly observable chemical behavior of the alkyl dichlorophosphates.

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(1) Audrieth and Steinman, THIS JOURNAL, **63**, 2115 (1941).

(2) Marvel, Copley and Ginsberg, *ibid.*, **62**, 3109 (1940).