the zinc oxide caused a selective activation toward one or the other of the two reactions, but the effect seems to be specific for the particular substance and does not depend on its acidic or basic character.

MADISON, WISCONSIN

THE MECHANISM OF THE AZIDE REARRANGEMENT

BY GARFIELD POWELL

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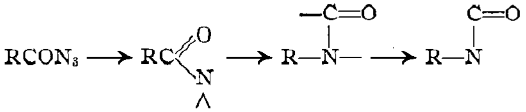
The Beckmann rearrangement and other rearrangements involving the migration of a radical from carbon to nitrogen, including the azide rearrangement to isocyanate, involve a problem of mechanism which is still not solved, though the plausible univalent nitrogen explanation of Stieglitz[1] can be employed as a formulation of the rearrangement in many cases. In the case of the azides the rearrangement involves the univalent nitrogen, thus



Experimental support for the postulate by the examination of the products of decomposition of a di-azide compound has been adduced by Schroeter,[2] and the results are indeed a support of the hypothesis in that they are most simply and directly explained or, rather, represented theoretically, in such a way. There are, however, many possible theories of such mechanisms and the desirable test is one in which the phases postulated in the reaction are shown to exist. In the case of the univalent nitrogen hypothesis the question arises, indeed, as to the possibility of determining the truth of the hypothesis by ordinary chemical means at all. Thus the alkaline reduction of the azides leads to diacyl hydrazines, a reaction well formulated by the univalent nitrogen hypothesis, but not impossible to formulate otherwise. The acid reduction of azides to acid amides is of the same kind. Experiments by the author on the decomposition of azides in a neutral solvent in the presence of triphenylmethyl in the hope of isolating addition compounds of the formula $RCONM_2$ would, if successful, give more valuable support to the hypothesis because of the greater limitation of variables. Benzoyl azide decomposes in benzene solution to give nitrogen and phenyl isocyanate and if the univalent nitrogen phase formed an amide $RCONM_2$ by simple addition in the same solution with a body MM known to be stable in the same solution and not to react with phenyl isocyanate, the number of alternative formulations of the mechanism

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[1] Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); THIS JOURNAL, **25**, 289 (1903); etc.

[2] Schroeter, *Ber.*, **42**, 2336, 3356 (1909).

would be thereby limited and the postulate gain in plausibility. The highly unsaturated univalent phase would not, in general, be expected to react by addition to other molecules while it is so smoothly capable of saturation by rearrangement but there seems, at first glance, some chance of reaction with bodies such as triphenylmethyl, which has, as conventionally represented, a primary valence capable of direct saturation. However, no reaction takes place and benzoyl azide decomposes in the presence of triphenylmethyl as easily and smoothly as when alone. This, from another point of view, is not unexpected, for whatever intermediary is postulated in the azide rearrangement, it is known to be, in the sense of practice, a saturated one; that is, addenda are not known and it has not been shown to be unusually reactive toward other molecules. Further, it is even stable to the very reactive triphenylmethyl and thus we have a representation of a highly unsaturated substance with one free valence (the unsaturation of triphenylmethyl has been used as an argument in favor of the free radical hypothesis) and its very opposite, in practice, represented with two free valences. There seems to be danger of forming wrong concepts from the simple representation $RCON<$ and it appears to the author that such phases might better be represented in parentheses thus $(RCON<)$, whereby the fact of non-reactivity toward external molecules is evidenced in the formulation. As to the most desirable test, success in the isolation of a simple addition compound would still not be conclusive, for the addition could still be formulated otherwise and the question as to how the compound $RCON_3$ became the compound $RCONM_2$ is one that has, possibly, no relation at all to the question as to how $RCON_3$ became RNCO. It seems that the phase of univalent nitrogen is really a representation of the unobservable dynamic of all reactions and the isolation of any resultants from any reactants leaves the problem still unsolved and still represented in the same way. The next most desirable test, in which the possible alternative formulations are increasingly limited by the chosen conditions of experiment, must therefore be devised, in the present case leading to failure. In the course of the work some new azides and a quinoline hydroximic acid were prepared. Their properties are described below.

Experimental

The decomposition of benzoyl azide into isocyanate and nitrogen was found to be complete in two hours of refluxing in benzene, the isocyanate being recovered as diphenylurea by the addition of aniline and the nitrogen collected and measured by using a current of carbon dioxide into potassium hydroxide to remove the gas. The experiment was repeated, the reaction flask now containing triphenylmethyl, and at the end, after cooling and precipitation of any isocyanate as urea, air was led in to decompose the unchanged triphenylmethyl. The conditions were varied as far as possible and in all cases about 50% of the triphenylmethyl was recovered as peroxide (the usual quantity), nearly all of the isocyanate as urea and no new compounds were recovered. The experiments were persisted in for a long time without success and no evidence of reaction could be obtained by examination of the residues.

Dibenzylacetazide.—In the preparation of acid azides by the interaction of the acid chloride and potassium azide, the employment of a water–acetone mixture was found convenient. Thus the addition of benzoyl azide in acetone to a concentrated solution of potassium azide in water gave, on separation and extraction, an almost theoretical yield of benzoyl azide in a state of purity. Similarly 2,4-dinitrochlorobenzene gave 2,4-dinitro-azidobenzene in purity and good yield, the reaction mixture being kept below 20° and poured into water after shaking. The solid thrown out was collected and recrystallized by dilution of acetone, or otherwise. The melting point is high (67–68°) and the product is colorless, giving on heating on the water-bath dinitrosonitrobenzene as yellow needles melting at 70°. Dibenzylacetazide was prepared in the same way. The reaction mixture was kept below 15° and, after good shaking, thrown into a large excess of water and again shaken until the globules solidified. The solid was collected and washed well with water, dissolved in acetone and water added till cloudy. The crystals were collected, washed with methyl alcohol, and dried in a vacuum desiccator; yield 90%; colorless solid, unstable. When isolated and dried in the desiccator for one hour a melting point (slow) was observed at 51–53°. On standing for one day it becomes completely liquid, gas bubbles arising. The same decomposition into isocyanate takes place on warming or melting.

Dibenzylmethylisocyanate.—A thick liquid, not solidifying in a freezing mixture, it resembles triphenylmethylisocyanate in being only slowly rearranged on heating with water. It is only slightly soluble in alcohol. On refluxing with alcohol in excess for one hour, collecting the solid thrown out when water is added, crystallizing from dilute alcohol and washing with ether, dibenzylmethylethylurethan is obtained, a colorless substance melting at 106–107° (uncorr.). On warming the isocyanate in benzene solution with aniline for a few minutes, and recrystallizing the product from benzene, dibenzylmethylphenylurea is obtained as fine silky needles melting at 153–154° (uncorr.). A specimen of the isocyanate was refluxed with water for six hours, the solid formed being occasionally broken up with a rod. Crystallized from benzene, recrystallized from alcohol, *sym.*-di-dibenzylmethylurea was obtained melting at 160–161° as described by Hurd.[3]

2-Phenyl-4-quinolylformhydroximic Acid (Atophane Hydroximic Acid).—The insolubility of the chloride of atophane prevents the formation of the hydroximic acid from the acid chloride and free hydroxylamine. The methyl ester was therefore prepared and the hydroximic acid prepared. Six grams of the methyl ester was dissolved, together with hydroxylamine hydrochloride (1.2 moles) in 50 cc. of methyl alcohol and to the solution was added sodium methylate (2 moles) in methyl alcohol. The mixture was kept just below the boiling point for seven hours and then brought down to small bulk by reduction of pressure, the salt filtered off and an excess of water added. A little of the unchanged ester is thrown out and filtered off. On acidifying, the hydroximic acid is thrown out as a white precipitate; yield, about 80%. It is washed well with water, then with alcohol and benzene successively in small quantities and again with methyl alcohol. Taken up in dilute soda and reprecipitated as before, washed as before, dried at 70° and then *in vacuo*, it analyzes for nitrogen as 10.35%, the calculated

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[3] Hurd, This Journal, **43**, 2242 (1921).

being 10.50% (a gas rush is hard to prevent in the analysis, even after careful grinding of the specimen with fine copper oxide). The compound is very slightly soluble in benzene, more so in ether, most in methyl alcohol and even in this case cannot be said to be more than somewhat soluble in the hot solvent, hydrolysis taking place. It is colorless, melting with gas evolution at 155–156° (uncorr.). It forms a copper salt, drying emerald green and not decomposing under 240°. The silver salt darkens after separation. The benzoyl derivative forms from the sodium salt in water on shaking with an ether solution of benzoyl chloride; it is soluble in methyl alcohol, insoluble in water and melts at 150–151°. It seems to suffer the ordinary decomposition with sodium hydroxide with the formation of an oily and very stable isocyanate.

Summary

A discussion of the azide rearrangement and the possibilities of test of the univalent nitrogen hypothesis is presented. An attempt to arrange an experiment limiting the alternative formulations of the rearrangement is given and the preparation of some azides and a quinoline hydroximic acid is described.

NEW YORK CITY

[CONTRIBUTION NO. 3 FROM THE CHEMICAL RESEARCH LABORATORY OF THE UNITED FRUIT COMPANY]

QUANTITATIVE CHANGES IN THE CHLOROPLAST PIGMENTS IN THE PEEL OF BANANAS DURING RIPENING[1]

BY HARRY VON LOESECKE

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Introduction

The purpose of this investigation was to gain some knowledge of the changes which the pigments in banana peel undergo during the process of ripening of the fruit, and the cause of the yellow color. It is a well-known fact that during maturation the fruit changes in color from green to yellow, but no quantitative data seem ever to have been collected indicating the relation of these pigments in the peel of the banana to one another during ripening.

The three pigments estimated were chlorophyll (a + b), xanthophylls and carotin. These are not the only pigments present, as during the process of separation there were indications of flavones and anthocyanins. These latter pigments are present in the cell sap, while chlorophyll, xanthophylls and carotin are present only in the specialized portions of the protoplasm known as plastids.

Method of Investigation

Each determination (Table I) represents the peel from three fingers and these fingers were taken from three separate hands on a specially

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[1] This is one of a series of investigations carried out by the Research Department of the United Fruit Company, to be published in scientific journals.