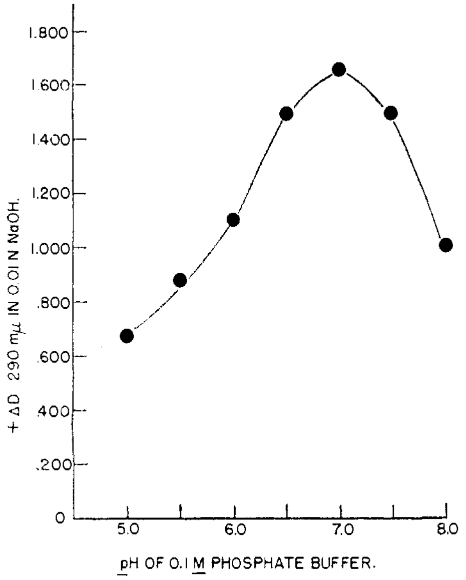

Fig. 3.—The *p*H-activity curve of yeast uridine nucleosidase in phosphate buffer.

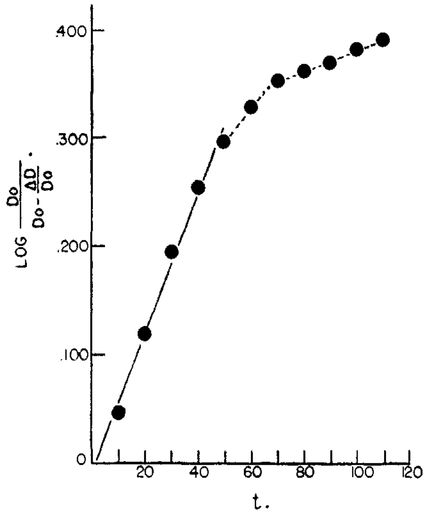

Fig. 4.—Kinetics of the enzymatic hydrolysis of uridine by yeast uridine nucleosidase. Data of curve A Fig. 2 plotted as log $D_0/(D_0 - \Delta D/D_0)$ *vs.* time.

lowed first order kinetics up to 83% hydrolysis of the substrate. The effect of products of the reaction on the rate of enzymatic hydrolysis of uridine was studied and it was found that the addition of 200 μg. of uracil to the reaction mixture produced a 27% inhibition of uridine nucleosidase activity whereas the addition of 2000 μg. of ribose produced only a 30% inhibition.

The purified yeast enzyme possesses only uridine nucleosidase activity; adenosine, inosine, guanosine, cytidine and thymidine are not degraded. As in the case of purine nucleosidase, the homologous nucleotide (uridylic acid) is not a substrate for yeast uridine nucleosidase. Uridylic acid does not act as an inhibitor of uridine nucleosidase.

Discussion

The finding of a hydrolytic pyrimidine nucleosidase in plasmolyzed yeast extracts suggests that a mechanism of synthesis and degradation of ribosides alternative to the previously described phosphorylitic nucleosidases exists in nature. The species distribution of the hydrolytic nucleosidases remains to be determined. We have been unable, however, to establish hydrolytic pyrimidine nucleosidase activity in mammalian tissues where all pyrimidine nucleosides have been found to be relatively resistant to enzymatic degradation.

The hydrolytic uridine nucleosidase of yeast may represent an instance of an isolated or anomalous pathway of riboside metabolism.

CLEVELAND 6, OHIO RECEIVED AUGUST 21, 1950

[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

Catalytic Reduction with Hydrazine

BY LESTER P. KUHN

The following reactions have been found to take place in the presence of a palladium or platinum catalyst: $2RONO_2 + 2N_2H_4 \rightarrow 2ROH + N_2O + 3H_2O + 2N_2$, $2RONO + N_2H_4 \rightarrow 2ROH + N_2O + H_2O + N_2$, $2R'NO_2 + 3N_2H_4 \rightarrow 2R'NH_2 + 3N_2 + 4H_2O$, where R is an alkyl group and R′ is aryl. When methylhydrazine is used instead of hydrazine methane and ethane are formed in addition to the products shown above.

Hydrazine is a strong reducing agent and reacts rapidly with many inorganic oxidizing agents such as ceric, ferric, cupric and iodate ions. In fact the determination of hydrazine is generally effected by titration with an oxidizing agent.[1] Toward organic oxidizing agents on the other hand the effectiveness of hydrazine as a reducing agent is variable depending upon the compound to be reduced. Certain quinones,[2] tetranitromethane,[3] halogenated polynitromethanes,[3] N-chloro and N-bromo compounds[3] are readily reduced by hydrazine at room temperature. The following compounds have also been reported to be reduced by hydrazine: nitrate esters at 150–200°,[4] *m*-dinitrobenzene to *m*-nitroaniline at room temperature,[5] nitrobenzene[6] slowly at room temperature and more rapidly at elevated temperature, and various substituted nitrobenzenes[5,7] at 80–140°. In the present work no perceptible reaction was observed between nitrobenzene or dinitrobenzene and hydrazine in alcohol solution at room temperature in 18 hours.

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(1) Penneman and Audrieth, *Anal. Chem.*, **20**, 1058 (1948).

(2) Dutt and Sen, *J. Chem. Soc.*, **123**, 3420 (1923); **127**, 297 (1925).

(3) Macbeth and co-workers, *ibid.*, **117**, 880 (1920); **119**, 1356 (1921); **121**, 904, 116, 2169 (1922).

(4) Walther, *J. prakt. Chem.*, **53**, 436 (1896).

(5) Bollenbach, *ibid.*, **76**, 233 (1907).

(6) Rothenburg, *Ber.*, **26**, 2060 (1883).

(7) Muller and Zimmerman, *J. prakt. Chem.*, **111**, 277 (1925).

It has now been found that the esters of nitric and nitrous acid and nitro compounds are rapidly and quantitatively reduced by hydrazine at room temperature in the presence of a palladium or platinum catalyst according to the equations

$$(1)\quad 2C_6H_{13}ONO_2 + 2N_2H_4 \longrightarrow 2C_6H_{13}OH + N_2O + 3H_2O + 2N_2$$

$$(2)\quad 2C_6H_{13}ONO + N_2H_4 \longrightarrow 2C_6H_{13}OH + N_2O + H_2O + N_2$$

$$(3)\quad 2C_6H_5NO_2 + 3N_2H_4 \longrightarrow 2C_6H_5NH_2 + 3N_2 + 4H_2O$$

It has been found experimentally that one mole of hydrazine reacts with one mole of hexyl nitrate to yield 1.5 moles of gas which contains 33% nitrous oxide. No ammonia, other oxides of nitrogen, hydrogen or oxygen are found in the products. Equations 2 and 3 are based on similar evidence. Excellent yields of hexyl alcohol were obtained in reactions 1 and 2 and of aniline in reaction 3. From *m*-chloronitrobenzene there was obtained a quantitative yield of *m*-chloroaniline and by the addition of 1.5 moles of hydrazine to 1 mole of *m*-dinitrobenzene there was obtained a 75% yield of *m*-nitroaniline. Previous workers[8] have shown that the palladium-catalyzed reduction of nitrobenzene with hydrazine results in the formation of azoxybenzene when the solvent is ethanolic KOH and azobenzene when the solvent is methanolic KOH. Neither of these was found in the work described here. The above reactions take place equally well in the presence of either a palladium or a platinum catalyst.

It appears from the above equations that nitrate and nitrite esters are reduced to nitrous oxide while the hydrazine is oxidized to elementary nitrogen since the amount of nitrogen in the nitrate or nitrite ester is equal to the amount of nitrogen in the nitrous oxide whereas the amount of nitrogen in the nitrogen gas is equal to that contained in the hydrazine. When nitrobenzene is the oxidizing agent no nitrous oxide is formed because the nitrogen is retained by the organic molecule and again the amount of nitrogen gas is equal to the amount of hydrazine used. Under the experimental conditions employed here there is no reaction between the oxidizing agent and the hydrazine in the absence of the catalyst.

To determine whether olefin or carbonyl containing compounds are reduced by hydrazine in the presence of a catalyst, experiments were performed using cyclohexene, formaldehyde and fluorenone, respectively, as the oxidizing agent. In no case did reduction take place. Thus catalytic reductions with hydrazine differ from similar reductions with hydrogen in that the latter readily reduces olefins and carbonyl containing compounds as well as those containing nitro and nitrate groups.

When methylhydrazine is used instead of hydrazine in the reduction of hexyl nitrate and nitrobenzene there are obtained, in addition to the products previously shown, methane and ethane. The same products are obtained whether the solvent is methanol, ethanol or aqueous dioxane. The fact that ethane is formed may indicate that in the course of the reaction methyl radicals are formed on the catalyst which subsequently either dimerize or react with hydrogen. In the reduction of hexyl nitrate with methylhydrazine, hexyl alcohol was found among the reaction products but no hexyl methyl ether. In the reduction of nitrobenzene aniline was obtained but no methylaniline. These reactions could not be represented by simple stoichiometric equations. During a given run the gas composition changes. In one experiment in which methylhydrazine was added slowly to nitrobenzene and catalyst in alcohol, the gas formed early in the reaction contained 22% ethane and 12% methane, somewhat later in the reaction it contained 19% ethane and 17% methane. The factors influencing the relative amount of methane and ethane were not further explored.

Experimental

The reactions were run in a 125-ml. erlenmeyer flask equipped with a dropping funnel and side arm which was connected to a calibrated gas buret. The gas was collected over mercury. A magnetic stirrer was used. One gram of 5% palladium–charcoal[9] was introduced into the flask and the system was flushed with nitrogen. The oxidant in 50 ml. of methanol was added through the dropping funnel. A 4 molar solution of hydrazine prepared by diluting 85% hydrazine hydrate with 3 parts of methanol was added slowly to the stirred solution of oxidant and catalyst from a buret. After each ml. of hydrazine was added the volume of gas given off was measured. The hydrazine was added in this manner until further addition produced no evolution of gas. The infrared spectrum of the gas from hexyl nitrite and nitrate showed that the only infrared active gas present was N_2O. The gas from the reduction of nitrobenzene was infrared inactive. The gases were analyzed chemically for oxygen and hydrogen and each was found to be absent, hence the infrared inactive gas was assumed to be nitrogen. The N_2O was determined quantitatively from the intensity of the infrared band at 7.7 microns. When the reaction was complete the catalyst was filtered off and the solvent removed by distillation at reduced pressure. The reduction products of hexyl nitrite and hexyl nitrate were obtained by distillation, b.p. 157°, and identified as hexanol by the identity of its infrared curve with that of pure hexanol. The reduction products of nitrobenzene and *m*-chloronitrobenzene were taken up in ether and precipitated as their hydrochlorides. Aniline hydrochloride, m.p. 196°, was identified from its infrared curve and the *m*-chloroaniline was converted to the substituted thiourea, m.p. 116°, by reaction with phenyl isothiocyanate, From *m*-dinitrobenzene, *m*-nitroaniline was obtained and identified as such, m.p. 114°, after recrystallization from dilute alcohol. The results of the various catalytic reductions with hydrazine are given in Table I. A platinum catalyst was prepared by reducing 0.2 g. of Adams oxide suspended in methanol under 2 atmospheres of hydrogen. Reduction of hexyl nitrite, hexyl nitrate and nitrobenzene was run as above with the palladium catalyst replaced by the platinum catalyst and the same products and yields were obtained.

When hydrazine was added to a solution of cyclohexene in alcohol and catalyst no gas was evolved and the cyclohexene was recovered unchanged. There was no organic amine formed. Similarly when formaldehyde and fluorenone were used as oxidants no gas was evolved. In the experiment with fluorenone the solution was refluxed but the product obtained was fluorenone azine, the same product which is obtained when no catalyst is used. Experiments were performed without a catalyst. The addition of hydrazine to hexyl nitrate, nitrobenzene and dinitrobenzene produced no evolution of gas and no reduction products were formed. To determine whether there is a reaction between the palladium catalyst and hydrazine, 5 ml. of the 4 molar hydrazine solution was added to 25 ml. of methanol. The titer of the resulting solution was determined by titration with standard acid and by oxidation with iodate according to the method of Audrieth.[1] One gram of catalyst was

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[8] Busch and Schulz, *Ber.*, **62B**, 1458 (1929).

[9] Purchased from the American Platinum Works, Newark, N. J.

TABLE I

Oxidant	Millimoles of oxid.	Moles of gas per mole of oxid.	Moles of gas per mole of hydrazine	N_2O in gas, %	Product	Yield, %
Hexyl nitrite	20	1	2	50	Hexanol	>90
Hexyl nitrate	13.6	1.5	1.5	38	Hexanol	>90
Nitrobenzene	20	1.5	1	0	Aniline	100
m-Chloronitrobenzene	20	1.5	1	0	*m*-Chloroaniline	100
m-Dinitrobenzene	20	1.4	0.9	0	*m*-Nitroaniline	75

added and the solution stirred in a nitrogen atmosphere for 30 min. No gas was evolved but the titer of the solution was reduced 10.5% as measured by titration with acid and 11% as measured by titration with iodate.

The reduction of hexyl nitrate and nitrobenzene in the presence of palladium with methylhydrazine was performed in the same manner as the reductions with hydrazine. Both methane and ethane were formed and identified from the infrared spectra of the gases. No ethylene was present. In the reduction of nitrobenzene successive samples taken during one run showed that the ethane band at 6.8 microns became weaker and the methane band at 7.6 microns became stronger as the reaction progressed.

ABERDEEN PROVING GROUND MD.

RECEIVED JUNE 21, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Two Stage Polymerizations. I. Preparation and Polymerization of Substituted Allyl Phenyl Ethers[1,2]

BY GEORGE B. BUTLER AND FRANCIS L. INGLEY

Eight new substituted allyl ethers of allyl substituted phenols have been prepared and characterized. These compounds were polymerized under the influence of boron trifluoride to produce thermoplastic polymers containing residual unsaturation indicating that the allyl side chains attached to the ring were not involved in the polymerization. It has been shown that the unsaturated polymers may be copolymerized with drying oils at elevated temperatures.

The industrial importance of two stage polymerizations has been demonstrated in the vulcanization of rubber, and in the thermosetting of phenol-formaldehyde, urea-formaldehyde and alkyd type polymers. More recently Mark[3] has shown that when vinyl *n*-propyl ketone is copolymerized with 10% of vinyl allyl ketone, linear chain-molecules are formed primarily through the more readily polymerized groups only, leaving the less reactive allyl groups intact. More vigorous treatment then results in a cross-linking of the primary chains through the less readily polymerized allyl groups.

The purpose of this investigation was to locate and study other systems which lend themselves to two stage polymerizations.

A review of the literature revealed that little work had been done in connection with the polymerization of allyl phenyl ethers. Related compounds, 2-allylphenol and 2-allylanisole, were converted to polysulfones by Ryden, Glavis and Marvel.[4] These products were prepared by treating the compounds with sulfur dioxide in a pressure bottle, using ascaridole as catalyst. Staudinger and Dreher[5] found that allylbenzene, 4-methoxy- and 4-ethoxyallylbenzene did not undergo polymerization under the influence of boron trifluoride as did the isomeric propenylbenzenes.

Preliminary experiments showed that allyl and 2-methylallyl phenyl ethers would undergo polymerization under the influence of the boron trifluoride-diethyl ether complex. This information in conjunction with Staudinger's experiments with allylbenzenes led us to believe that it would be possible to selectively polymerize allyl ethers of allyl substituted phenols to produce thermoplastic polymers containing residual unsaturated groups. The possibility of further polymerization of polymers of this type under different conditions to produce cross-linked polymers adds to their potential usefulness.

This paper deals with the preparation of several allyl ethers of allyl substituted phenols and polymerization of the compounds with boron trifluoride. The resulting polymers are thermoplastic, indicating that the allyl ether groups undergo polymerization while the allyl side chains of the ring are unaffected.

Attempts to catalyze polymerization of these compounds with benzoyl peroxide, *t*-butyl hydroperoxide and di-*t*-butyl peroxide were unsuccessful. Attempts to copolymerize these compounds with styrene and diallyl maleate, using the above catalysts, were also unsuccessful.

The fact that these compounds, even those containing as many as three unsaturated groups per molecule, do not undergo bulk polymerization as a result of peroxide catalysis is perhaps understandable in the light of the recent work of Erickson.[6] Phenols, which are potential by-products by Claisen rearrangement when allyl phenyl ethers are heated, are known to be polymerization inhibitors.

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(1) Abstracted from a thesis presented by Francis L. Ingley to The Graduate School of the University of Florida in partial fulfillment of the requirements for the M.S. degree, February, 1949.

(2) Presented before the Division of Organic Chemistry at the Atlantic City, N. J., Meeting of the American Chemical Society, Sept., 1949.

(3) Ritchie, "A Chemistry of Plastics and High Polymers," Cleaver-Hume Press, London, 1949, pp. 58-59.

(4) Ryden, Glavis and Marvel, THIS JOURNAL, **59**, 1014 (1937).

(5) Staudinger and Dreher, *Ann.*, **517**, 73 (1939).

(6) Erickson, U. S. Patent 2,455,745.