at 25°, $\Delta F = 288$ calories. Using the equation $\Delta F = \Delta H - T\Delta S$ and the best available data we find $\Delta F = 254$ calories. The calculation and the sources of the data used are summarized in Table IV. It is interesting to note that there are available two values for the heat of formation of ammonia one of which was obtained from thermal data and the other from equilibrium measurements. Stephenson and McMahon[9] have recently recalculated the available equilibrium data. From equilibrium data they find for the formation of ammonia at 25° $\Delta H = -10{,}930$ and from thermal data $\Delta H = -11{,}040$. If the latter datum is used we find for the reaction given above $\Delta F = 474$ calories.

The agreement of the free energy calculated from the best thermal data with that calculated from the equilibrium data of Lewis and Burrows[2] indicate that there is no randomness in the structure of urea which persists to extremely low temperatures.

The measurements were extended to 48° in hopes that we would obtain evidence of the second order transitions reported by Sokolov.[3] No anomalies in the specific heat curve were observed over the entire range with the exception of that previously discussed which we believe has been accounted for in a satisfactory manner.

Summary

The heat capacity of urea has been measured over the temperature range 19 to 320° K.

The molal entropy and free energy of formation at 298.16° K. have been calculated.

Excellent agreement between third law values and equilibrium values was demonstrated for a synthesis of urea.

BARTLESVILLE, OKLA. RECEIVED MAY 6, 1946

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[9] Stephenson and McMahon, THIS JOURNAL, **61**, 407 (1939).

[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

Catalytic Hydrogenolysis of Nitrate Esters

BY LESTER P. KUHN

The hydrolysis of nitrate esters to the corresponding alcohols is usually accompanied by undesirable oxidation reactions wherein the alcohols are converted to aldehydes and other products.[1] Hence denitration is usually effected by reducing agents such as tin and hydrochloric acid,[1] zinc and iron in acetic acid,[2] and ammonium polysulfide.[3] These methods leave much to be desired when dealing with certain sugar nitrates in that it is difficult to separate the free sugar from the inorganic salts in good yield. Also other groups may be attacked by the rather vigorous conditions employed.

The present work shows that nitrate groups may be smoothly reduced by catalytic hydrogenolysis, a method which has not been previously reported.

To determine the most effective catalyst a series of experiments was made using amyl nitrate and hydrogen at 1500 p.s.i. The results are given in Table I.

TABLE I

HYDROGENOLYSIS OF AMYL NITRATE

Catalyst	T, °C.	Time, hr.	Form of nitrogen in product	Pressure change in moles of gas/mole of nitrate
Copper–chromium	160–180	3	....	...
Raney nickel	60–70	1	Ammonia	3.5–4
Platinum	60–70	1	Ammonia	3.5–4
Palladium on calcium carbonate	25	0.25	N_2	2

Because of the high temperature required with the copper–chromium catalyst much decomposition ensues. The nickel and platinum catalysts are also unsatisfactory because they reduce the nitrogen to ammonia to which the unreacted nitrate groups are sensitive and side reactions occur. If the reaction is stopped when the pressure change is equivalent to two moles of gas per mole of nitrate, both ammonia and nitrate are present, indicating that it is impossible to halt the reaction at the elementary nitrogen stage. If acid is added to neutralize the ammonia that is formed, no reaction takes place.

In contrast to these catalysts, the palladium on calcium carbonate is highly satisfactory. The reaction appears to proceed according to the equation

$$2RONO + 5H_2 \longrightarrow 2ROH + N_2 + 4H_2O$$

Actually, two and one-half moles of hydrogen are consumed per mole of nitrate, but since one-half mole of nitrogen is formed the net pressure change is two moles of gas per nitrate. The equation is in harmony with the observed pressure change and the facts that the solution after hydrogenolysis is neutral and gives negative tests for nitrate, nitrite, and hydroxylamine.

Palladium on charcoal is a more active catalyst than palladium on calcium carbonate. In the presence of the former at 1,500 pounds pressure of hydrogen the nitrate is reduced to ammonia.

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[1] Sidgwick, "Organic Chemistry of Nitrogen," new edition revised by Taylor and Baker, Oxford University Press, 1942, p. 8.

[2] DeWar and Fort, *J. Chem. Soc.*, 495 (1944).

[3] Bock, Simmerl and Johnston, *J. prakt. Chem.*, **158**, 8–20 (1941).

However, the reaction can be stopped when the pressure change is equivalent to two moles of gas per nitrate group and the solution is found to be nitrate and ammonia free. At pressures of about 300 pounds the reduction of nitrogen to ammonia is not perceptible, whereas the rate of denitration is about the same as at 1,500 pounds. Thus, at pressures below 500 p.s.i. the palladium–charcoal catalyst gives the same results as the palladium–calcium carbonate catalyst. Unfortunately, we are not equipped to run these reactions at pressures slightly above atmospheric but it appears that they will proceed just as smoothly as at the higher pressures.

Nitrous acid behaves like the nitrate esters in the palladium catalyzed reaction. However, a solution of either sodium nitrite, nitric acid or sodium nitrate does not react. The lack of reactivity of the nitrate ion as compared with the nitrate ester probably is due to the greater resonance stabilization of the former. This parallels the behavior of the carboxylic esters, which are susceptible to hydrogenolysis whereas the carboxylate ions do not react. If the nitrate ester is contaminated with nitrate ions it will still yield a positive nitrate test after denitration. Treatment of a dioxane and/or alcohol solution of the ester with barium carbonate effectively removes the nitrate ions before denitration.

To determine the general usefulness of this method of denitration alpha methyl glucoside tetranitrate, beta methyl glucoside tetranitrate, levoglucosan trinitrate, and sucrose octanitrate were subjected to catalytic hydrogenolysis with palladium characoal catalyst at pressures below 500 p.s.i. The yields of the pure denitrated sugars were practically quantitative.

Using the palladium on calcium carbonate catalyst, the alpha- and beta-methyl glucoside etranitrate again yielded alpha- and beta-methyl glucose, respectively, but the levoglucosan trinitrate and sucrose octanitrate yielded products whose melting points and specific rotations were not those of levoglucosan and sucrose. Elementary analyses showed that these products contained calcium. They appear to be addition compounds of the free sugar and calcium carbonate.

Experimental

Palladium on charcoal catalyst was prepared according to the method of Hartung.[4] Palladium on calcium carbonate was prepared by suspending in water 25 g. of C. P. calcium carbonate, which had been washed with boiling distilled water, and adding with good stirring 0.5 g. of palladium chloride. The mixture was heated to boiling, filtered and washed with distilled water. The palladium hydroxide on calcium carbonate thus formed was reduced by shaking with hydrogen at 1,000 pounds pressure for ten minutes. It was then filtered and washed with alcohol and stored in a brown bottle. Both catalysts have retained their activity after repeated use over several months.

Nitrate Esters.—The sugar nitrates were prepared in about eighty per cent. yield by the method of Brissaud.[5] They were purified by recrystallization from alcohol followed by solution in hot benzene and precipitation by the addition of petroleum ether. Thus there were prepared alpha-methyl glucoside tetranitrate m. p. 46–47°, $[\alpha]^{20}\mathrm{D}$ +146° (chloroform); β-methyl glucoside tetranitrate m. p. 117–118°, $[\alpha]^{20}\mathrm{D}$ +11.5° (chloroform); levoglucosan trinitrate m. p. 100°, $[\alpha]^{20}\mathrm{D}$ −61.0° (ethanol); and sucrose octanitrate m. p. 85–86°, $[\alpha]^{20}\mathrm{D}$ +55.9° (methanol). Amyl nitrate was prepared by the method of Michael and Carlson,[6] b. p. (240 mm.) 118–120°, $d^{26}{}_4$ 1.010.

Hydrogenolysis

The reactions were run in a 110-ml. bomb with a Pyrex liner sold by the American Instrument Company. Two grams of sugar nitrate was dissolved in 8 ml. of dioxane and diluted to 20 ml. with 95% ethanol. The solution was introduced into the bomb with 10 g. of palladium calcium carbonate catalyst and 1,500 pounds of hydrogen. After shaking for fifteen minutes the pressure was constant. The catalyst was filtered off and washed with hot methanol. The filtrate, which was neutral and gave a negative test for nitrate with diphenylamine, and the washings were evaporated on a steam-bath until crystallization set in. After the addition of ether to complete the precipitation the product was filtered off and dried. It was identified by rotation, melting point and mixed melting point with an authentic specimen. The yield of methyl glucoside was 0.95 g. or 92%. The nitrates of levoglucosan and sucrose yielded products which did not melt below 200. They were soluble in alcohol but very difficultly soluble in water. Each gave a positive test for calcium. They were not investigated further.

Using 2 g. of the palladium–charcoal catalyst and less than 500 pounds pressure of hydrogen, the nitrates of the methyl glucosides, levoglucosan, and sucrose yielded the corresponding denitrated sugars in yields ranging from 92 to 98%.

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Summary

An investigation of the catalytic hydrogenolysis of amyl nitrate showed that the reduction of the nitrate groups to ammonia caused undesirable side reactions. These side reactions were avoided with palladium on calcium carbonate catalyst because at room temperature and with 1500 pounds of hydrogen, reduction ceased at molecular nitrogen. The same result was obtained at 300 pounds with palladium on charcoal but at 1,500 pounds this hydrogenation had to be interrupted at the proper point. Nearly quantitative yields of sucrose, levoglucosan, and methyl glucoside were obtained from the fully nitrated derivatives.

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(4) Hartung, THIS JOURNAL, **50**, 3373 (1928).

(5) Brissaud, *Mem. Ser. chim. l'État.*, **30**, 120 (1943).

(6) Michael and Carlson, THIS JOURNAL, **57**, 1268 (1935).