experimental error for the heats of solution for each of the three glucose sugars. When the heats of solution were measured for samples prepared by mixing solid alpha and beta *d*-glucose in measured proportions approximating the composition of the equilibrium mixture at 20–25°, the experimental results check the calculated heats of solution in a very satisfactory manner.

A comparison of the heat of solution of hydrated glucose with that of *d*-glucose suggests that a small percentage of the hydrate in a sample of *d*-glucose would account for the discrepancy just noted. Preliminary experimental studies made in this Laboratory seem to support this explanation, that commercial dextrose, commonly considered as *d*-glucose, is not strictly anhydrous.

Summary

1. The heats of solution to a dilution of 0.00035 ± mole of solute per mole of water are here reported for the first time as: −21.4 for *d*-galactose, −3.13 for α-methyl-*d*-glucoside, and −11.0 calories per gram of sugar for α-methyl-*d*-mannoside.

2. Redeterminations of heats of solution to the same dilution are presented for *d*-glucose, −14.5; β-*d*-glucose, −5.65, and *d*-glucose hydrate, −25.2 calories per gram of sugar.

3. Heats of mutarotation are shown to be zero for *d*-galactose and *d*-glucose.

4. Heats of mutarotation are proposed as positive for β-*d*-mannose and α-*d*-fructose, and a procedure is suggested for their experimental determination.

5. The inconsistent heat of solution for samples of *d*-glucose is considered and the inconsistency attributed to traces of hydrated glucose in the samples used.

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NOTE

The Reaction of Nitrous Oxide with Hydrogen Atoms

BY J. K. DIXON[1]

The reaction of nitrous oxide with hydrogen atoms has been studied at low pressures. The hydrogen atoms were produced in a discharge at low pressures and the concentration of the atoms measured by means of a calorimetric method. The type of apparatus and the procedure used has been described in detail,[2] so that only certain modifications of the same need be mentioned. Since water was added to the hydrogen which was admitted to the discharge, it was necessary to make blank runs without adding nitrous oxide. Water was expected to form as a result of reaction. The difference between the water collected in the blank experiments and the amount found in experiments with added nitrous oxide, under identical conditions, gave the quantity of water formed in the reaction. The water was collected in a trap by cooling with dry ice and in some cases with liquid air. At the end of an experiment dry air was admitted to the apparatus slowly, the cooling mixture surrounding the trap removed and the water which had been collected was blown through a tared tube containing phosphorus pentoxide. Experiments showed that the air and nitrous oxide were free from water.

Careful tests for oxygen and hydrogen peroxide showed that these substances were not formed to any measurable extent. Table I gives the results of a few typical experiments in which the amount of water formed by reaction was determined. The temperature of the reaction tube was in each case 25°. Owing to the difficulty of obtaining results in the blank experiments reproducible to better than about 2 mg., it is difficult to draw any conclusions with regard to the effects of the hydrogen atom concentration, the nitrous oxide pressure and the amount of water added to the hydrogen upon the amount of water formed. The addition of nitrous oxide always gave a small increase in the amount of water above that in the blank experiment. The maximum increase observed was 5 mg. in thirty minutes. Table I shows that when the water was collected by cooling with liquid air the increase was about the same. There was no appreciable change when the temperature of the reaction tube was changed from 2 to 45°. For example, in certain experiments the quantities of water formed were 2.8, 3.5 and 0.3 mg. at 2, 24.5 and 45°, respectively. Table I

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[2] Dixon, THIS JOURNAL, **54**, 4262 (1932).

shows that the amount of water added to the hydrogen was without effect on the quantity of water resulting from reaction.

There are several factors which may have affected the amount of water collected. The presence of nitrous oxide and the increase in total pressure due to it may have increased the quantity of water condensing in the trap. The experiments with liquid air indicate that the presence of nitrous oxide had no such effect. As stated above, the measurements were not accurate enough to show whether the amount of water collected varied with the nitrous oxide pressure and hence total pressure. Changes in the pressure may have changed the rate of decomposition of water in the discharge and hence the amount of water leaving. The increase in the water collected upon adding nitrous oxide can be attributed in part to the sum of all the above disturbing factors without altering the general conclusions presented below.

TABLE I

THE FORMATION OF WATER IN THE REACTION OF HYDROGEN ATOMS WITH NITROUS OXIDE AT 25°

p_{H_2}, mm.	p_H, mm.	p_{N_2O}, mm.	Total flow rate cc./min. (25°, 760 mm.)	Milliamperes in discharge	H_2O collected in 30 min.
0.220	0.040	0.178	60.1	230	12.2
.220	.040	0	53.6	230	11.7
.202	.061	0	50.6	230	19.0
.202	.061	.323	63.2	230	23.1
.202	.061	0	49.6	230	18.7
.202	.061	.164	55.7	230	19.4
.097	.029	0	28.8	215	14.8[a]
.097	.029	.010	28.3	215	17.9[a]

[a] Water collected by cooling with liquid air.

The reaction expressed by the equation $H + N_2O \longrightarrow N_2 + OH$ must possess considerable activation energy even though it is exothermic and obeys the spin rule. The hydroxyl formed should yield water as a final product. If the data of Table I are used and the upper limit for the increase in water collected upon adding nitrous oxide is assumed to be 4 mg. in thirty minutes, then the approximate lower limit for the activation energy is 10 kg. cal. Since the reaction shown above is a slow one, then the relatively fast mercury-photosensitized reaction of hydrogen and nitrous oxide[3] must be attributed to some other primary reaction than the one given above. Manning and Noyes[4] have shown that nitrous oxide possesses an abnormally large cross-sectional area for quenching excited mercury. It thus seems most probable that in a system of hydrogen and nitrous oxide the excited mercury transfers most of its energy, which is given up in collision, to the nitrous oxide.

(3) Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

(4) Manning and Noyes, THIS JOURNAL, **54**, 3907 (1932).

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The Vapor-phase Oxidation of Hydrocarbons. I. The Amount and Rate of Oxidation of *n*-Heptane as a Function of Temperature[1]

BY HAROLD A. BEATTY AND GRAHAM EDGAR

Introduction

This series of three papers presents briefly certain data which appear to be of general interest, selected from studies on hydrocarbon oxidation carried on during the past two years in this Laboratory. No attempt has been made to give the material theoretical analysis or to correlate it with the results of other investigators, since the authors feel that the subject as a whole is so complex and the available data are so limited that such procedure is of little utility at the present time.

The present paper reports the effect of temperature on the extent and rate of oxidation of pure *n*-heptane in air, under the same experimental conditions as were used in previous work on the octanes.[2] Our knowledge of the effect of temperature on reactions of this type is decidedly meager. In general, it seems to have been taken for granted that both the amount and rate of oxidation increase with temperature.[3] Different hydrocarbons are spoken of as having a low or high "temperature coefficient of reaction," the criteria for these statements being simply the temperature of initial attack or of initial rapid reaction, or the

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(1) Presented in part at the Spring meeting of the American Chemical Society at Washington, D. C., April, 1933.

(2) Pope, Dykstra and Edgar, THIS JOURNAL, **51**, 1875, 2203 (1929).

(3) Mondain-Monval and Quanquin, *Ann. chim.*, [10] **15**, 309 (1931); Prettre, *Bull. soc. chim.*, **51**, 1132 (1932).