malonic ester which had been prepared from 5 g. of malonic ester and 0.5 g. of sodium in 20 cc. of benzene. After being refluxed for four hours the mixture was hydrolyzed and the substituted malonic ester was heated with 40 cc. of 5% sodium hydroxide solution. From the aqueous solution the phenanthroyl-isoglutaric acid was obtained by acidification. The acid was decarboxylated by heating a suspension of the acid in water for three hours. The β-(3-phenanthroyl)-butyric acid which was formed was purified through its ammonium salt followed by recrystallization of the acid from acetic acid. β-(3-Phenanthroyl)-butyric acid crystallizes from acetic acid in colorless prisms; m. p. 144–146°; yield 1.5 g. (32%).

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 78.0; H, 5.6.

In a similar manner α-bromo-2-propionylphenanthrene was condensed with sodiomalonic ester. The substituted malonic acid which was obtained was heated at 180° for one hour in order to decarboxylate it to β-(2-phenanthroyl)-butyric acid. The latter acid was obtained as fine colorless crystals from acetic acid; m. p. 173–174°; yield 32%.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 78.0; H, 5.8.

Summary

2- and 3-Propionylphenanthrene have been isolated from the reaction between propionyl chloride, phenanthrene and aluminum chloride in nitrobenzene. The same ketones in addition to 9-propionylphenanthrene have been synthesized from the corresponding cyanophenanthrenes through the Grignard reaction.

β-(2-Phenanthroyl)-butyric acid and β-(3-phenanthroyl)-butyric acid have been synthesized.

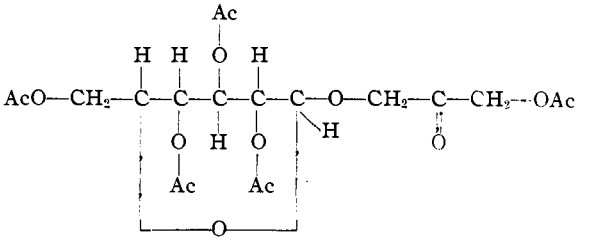
ANN ARBOR, MICHIGAN RECEIVED JUNE 30, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

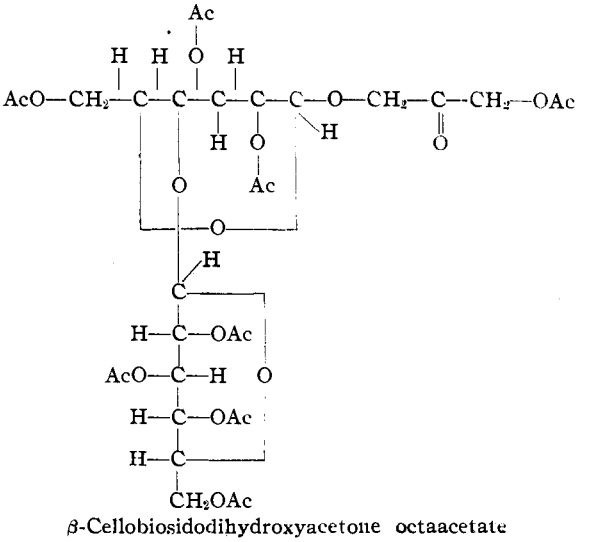
The Mechanism of Carbohydrate Oxidation. XX.[1] The Preparation of Oligosaccharide Acetates Containing Dihydroxyacetone Constituents

BY LEONARD C. KREIDER AND WM. LLOYD EVANS

When Evans and Hockett[2] advanced a mechanism to explain the action of potassium hydroxide on gentiobiose (6-glucosidoglucose) to produce lactic acid, they pointed out that 3-glucosidoglyceraldehyde was a theoretically possible intermediate in this degradation. In the alkaline environment of this reaction it is possible for this glyceraldehyde derivative to undergo the well-known Lobry de Bruyn and van Ekenstein rearrangement to give 3-glycosidodihydroxyacetone. In order to test the Evans and Hockett mechanism it was desirable to subject a 3-glucosidotriose, the postulated reaction intermediate, to the action of potassium hydroxide. At that time glucosidotrioses were unknown. We then succeeded in devising a general method for the synthesis of oligosaccharides that contain dihydroxyacetone as the reducing portion of the molecule. This synthesis has already been applied to the preparation of 3-glucosidodihydroxyacetone (described in a preliminary report[3]), β-*d*- and β-*l*-arabinosidodihydroxyacetone and β-*d*- and β-*l*-xylosidodihydroxyacetone, all as their acetates.[1] The present paper gives detailed directions for the preparation, in a pure crystalline form, of



β-*d*-Glucosidodihydroxyacetone pentaacetate

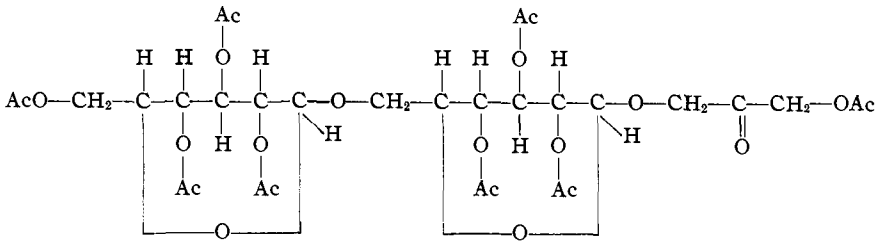


β-Cellobiosidodihydroxyacetone octaacetate

(1) Number XIX of this series: L. C. Kreider and W. L. Evans, THIS JOURNAL, **58**, 797 (1936).

(2) W. L. Evans and R. C. Hockett, *ibid.*, **53**, 4384 (1931).

(3) L. C. Kreider and W. L. Evans, *ibid.*, **57**, 229 (1935).



β-Gentiobiosidodihydroxyacetone octaacetate

Their crystalline *p*-nitrophenylhydrazones were also prepared and characterized.

The action of potassium hydroxide on the three oligosaccharides described here will be published later.

Experimental Part

Preparation of Starting Materials.—Dihydroxyacetone monoacetate was prepared according to the directions of Fischer, Baer and Feldmann.[4] Acetobromoglucose was made by the classical method of Fischer[5] except that the final crystallization was from absolute ether instead of amyl alcohol. Acetobromocellobiose was prepared from cellobiose octaacetate following the directions of Fischer and Zemplén,[6] and acetobromogentiobiose was prepared from gentiobiose octaacetate by the method of Brauns.[7] The final recrystallizations were made again from absolute ether. The acetobromo sugars were each left in a vacuum desiccator for a day over phosphorus pentoxide before being used. The benzene, Drierite and silver carbonate were prepared as before.[1]

All the following compounds reported here were obtained in crystalline condition and were recrystallized to constant melting point and rotation.

β-*d*-Glucosidodihydroxyacetone Pentaacetate.—The preparation of this compound was conducted in a 500-cc. three-necked round-bottomed flask which carried in the middle neck a high speed motor stirrer of efficient design running under a mercury seal. One side neck carried a drying tube charged with granular Drierite and the other a solid stopper. The stirring was then started and the following materials added: 14.1 g. (2.0 moles) of dihydroxyacetone monoacetate, 115 cc. (25 moles) of benzene, 14.5 g. (1.0 mole) of silver carbonate and 50 g. (7 moles) of finely powdered Drierite. That the reactants might be absolutely anhydrous the above mixture was stirred vigorously for twenty minutes and then 22.0 g. (1.0 mole) of β-acetobromo-*d*-glucose was added in ten equal portions at fifteen-minute intervals. Vigorous stirring was continued throughout this time and for at least three hours after the last addition of acetobromoglucose.

At this point the stirring was stopped and the solid materials removed from the benzene solution by suction filtration. The residue was washed twice with small amounts of benzene and the washings added to the filtrate. The combined benzene solutions were then placed in a separatory funnel and washed four times with about equal volumes of water to remove the excess dihydroxyacetone monoacetate. The resulting benzene solution was dried over calcium chloride and then evaporated under vacuum to a thick, light yellow sirup at a bath temperature below 45°. This sirup was dissolved in 100 cc. of warm ether to which was added about one-third of its volume of isoamyl alcohol. This was then placed in the ice box in a stoppered flask. Crystallization began after a few hours and was practically complete after four days.[8] The crystals were filtered from the mother liquor and washed with a little cold ether. The yield of crude product was 11.4 g. or 46% of the theoretical based on the amount of β-acetobromo-*d*-glucose used. For purification, the crystals were dissolved in chloroform, warmed and treated with Norite, filtered and then carefully evaporated to a sirup of moderate consistency. This was warmed to 40° and then ten times its volume of warm ether was added and mixed to homogeneous solution. Crystallization usually took place on cooling, but when it was not spontaneous it was induced by gentle rubbing with a glass rod. After the fourth recrystallization as above was completed both the melting point and the rotation were constant: m. p. 103° (corr.); $[\alpha]^{18}D$ −25.2° (*c*, 4.2; $CHCl_3$). This compound is very soluble in acetone and chloroform, fairly soluble in benzene, ether, and ethyl alcohol, sparingly soluble in butyl and amyl alcohols and insoluble in petroleum ether and water.

Anal. Calcd. for $C_9H_{11}O_8(COCH_3)_5$: acetyl, 10.82 cc. 0.1 *N* NaOH per 100 mg. Found: acetyl, 10.81 cc.

β-*d*-Glucosidodihydroxyacetone Pentaacetate *p*-Nitrophenylhydrazone.—This compound was most easily prepared by taking 1.0 g. (1.0 mole) of β-*d*-glucosidodihydroxyacetone pentaacetate and 0.39 g. (1.05 moles) of *p*-nitrophenylhydrazine and dissolving them in 25 cc. of absolute alcohol. Complete solution was effected by heating under slow reflux, which was continued for two hours. Often during this heating, and always after cooling in the ice box, feathery light yellow needles separated. It was recrystallized four times from ethanol. The yield was

(4) H. O. L. Fischer, E. Baer and L. Feldmann, *Ber.*, **63**, 1732 (1930).

(5) E. Fischer, *ibid.*, **49**, 584 (1916).

(6) E. Fischer and G. Zemplén, *ibid.*, **43**, 2536 (1910).

(7) D. H. Brauns, THIS JOURNAL, **49**, 3170 (1927).

(8) In case crystallization does not begin at the end of the first day it is because there has been some mistake made in following the directions as they are given here. Of all the Königs-Knorr reactions we have run, this is by far the most sensitive to changed conditions, and if the stipulated procedure is not carried out exactly as directed the yield may fall as low as half the amount this preparation records. When this happens the first crystallization of the product is often difficult, but we have found from experience that crystallization can nearly always be effected by the following simple device. Add another volume of isoamyl alcohol equal to the amount already in the flask, mix thoroughly and then leave the flask unstoppered in a warm place (25°) to allow the ether to evaporate spontaneously. Crystals often do not form for several days until the ether concentration is considerably diminished, and it may take as long as two weeks for crystallization to be complete, but if one is patient the method seldom fails. The last day before the crystals are removed the flask should be stoppered and placed in the ice box. From this point, proceed as in the regular directions.

nearly quantitative: m. p. 187° (corr.); $[\alpha]^{19}D$ −129.8° (*c*, 1.76; $CHCl_3$).

Anal. Calcd. for $C_{15}H_{16}O_9N_3(COCH_3)_5$: acetyl, 8.37 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 8.37 cc.

β-Cellobiosidodihydroxyacetone Octaacetate.—The following materials were used: 4.0 g. (2.0 moles) of dihydroxyacetone monoacetate, 65 cc. (50 moles) of benzene, 4.2 g. (1.0 mole) of silver carbonate, 14 g. (7.0 moles) of Drierite and 10.5 g. (1.0 mole) of acetobromocellobiose. The procedure for the synthesis and subsequent purification of this compound was exactly like that for β-*d*-glucosidodihydroxyacetone pentaacetate through the point where the benzene solution had been evaporated to a thick sirup. Here the product was dissolved in warm, absolute ethanol, treated with Norite, filtered and concentrated to about 40 cc. by boiling. Crystallization occurred by allowing this solution to cool to room temperature and was completed after the solution had been left in the ice box for an additional three hours. The yield of well crystallized product was 5.92 g. or 52.5% of the theoretical based on the amount of acetobromocellobiose used. It was recrystallized for analysis alternately from chloroform–ether and from acetone–ether, using each thrice, after which its melting point and rotation did not change further: m. p. 169° (corr.); $[\alpha]^{20}D$ −27.1° (*c*, 3.78; $CHCl_3$). This compound is very soluble in acetone and chloroform, moderately soluble in hot ethyl alcohol, sparingly soluble in warm ether and benzene and practically insoluble in cold petroleum ether and water.

Anal. Calcd. for $C_{16}H_{18}O_{13}(COCH_3)_8$: acetyl, 10.67 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 10.59 cc.

β-Cellobiosidodihydroxyacetone Octaacetate *p*-Nitrophenylhydrazone.—The preparation of this compound was similar to that of β-*d*-glucosidodihydroxyacetone pentaacetate *p*-nitrophenylhydrazone as described above. A nearly quantitative yield of fine, light yellow needles resulted. This was recrystallized from ethanol twice and then from benzene once, after which it had a constant melting point and rotation: m. p. 176° (corr.); $[\alpha]^{20}D$ −72.9° (*c*, 1.4; $CHCl_3$).

Anal. Calcd. for $C_{21}H_{23}O_{14}N_3(COCH_3)_5$: acetyl, 9.04 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 8.98 cc.

β-Gentiobiosidodihydroxyacetone Octaacetate.—The procedure for the preparation of this compound is exactly like that of β-cellobiosidodihydroxyacetone octaacetate. The following materials were used in a typical experiment: 3.6 g. (2.0 moles) of dihydroxyacetone monoacetate, 60 cc. (50 moles) of benzene, 3.75 g. (1.0 mole) of silver carbonate, 13.0 g. (7 moles) of finely powdered Drierite, and 9.5 g. (1.0 mole) of acetobromogentiobiose.

The yield of well crystallized product was 6.0 g. or 59% of the theoretical based on the acetobromogentiobiose used. Its solubility behavior is very nearly the same as that of its cellobiosido analog; m. p. 172° (corr.); $[\alpha]^{23}D$ −25.9° (*c*, 3.3; $CHCl_3$).

Anal. Calcd. for $C_{15}H_{18}O_{13}(COCH_3)_8$: acetyl, 10.67 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 10.55 cc.

β-Gentiobiosidodihydroxyacetone Octaacetate Methyl Alcoholate.—When β-gentiobiosidodihydroxyacetone octaacetate is recrystallized from methyl alcohol, a crystalline alcoholate appears to be formed. When this substance is heated slowly it melts at 110–112°, but on heating further it crystallizes again, melting the second time more sharply at 171–172°. The methyl alcohol may also be removed from the complex by heating it in a vacuum oven at 50° at 20 mm. of mercury pressure. A micro-rotation of this alcoholate was made and gave $[\alpha]^{20}D$ −25.0° (*c*, 2.1; $CHCl_3$). If the alcoholate would readily dissociate in chloroform solution we might expect this ratio to hold:

$$\frac{\text{mol. wt. alcoholate}}{\text{mol. wt. gentiobiosido-}} = \frac{\text{rotation gentiobiosido-}}{\text{rotation alcoholate}}$$

$$782/750 = -25.9/X$$

X may be calculated to be $[\alpha]D$ −24.9°, which is in good agreement with the observed $[\alpha]^{20}D$ −25.0°. Hence, it is probable that this compound is β-gentiobiosidodihydroxyacetone octaacetate methyl alcoholate, in which one molecule of the methyl alcohol is loosely bound.

β-Gentiobiosidodihydroxyacetone Octaacetate *p*-Nitrophenylhydrazone.—The method of its preparation and purification was very similar to that used for β-cellobiosidodihydroxyacetone octaacetate *p*-nitrophenylhydrazone. Again a nearly quantitative yield of fine light yellow needles was obtained, which after recrystallization twice from ethanol and once from benzene gave a constant melting point and rotation; m. p. 155° (corr.); $[\alpha]^{20}D$ −77.2° (*c*, 1.5; $CHCl_3$).

Anal. Calcd. for $C_{21}H_{23}O_{14}N_3(COCH_3)_8$: acetyl, 9.04 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 9.00 cc.

Deacetylation of the Oligosaccharide Acetates.—It is known that great care must always be exercised in the deacetylation of any carbohydrate if it contains either a free aldehyde or a free ketone group. Ketone sugars are especially sensitive in this respect.[9] As all the new oligosaccharide acetates contained the alkali-sensitive ketone group, only the mildest deacetylation agents were employed. The acetyl groups were easy to remove, but we invariably encountered the difficulty of the deacetylating agent attacking the sensitive free ketone group and causing deep-seated changes in the free oligosaccharide that had been liberated. This yielded a complex mixture of substances from which it was impossible to separate a pure crystalline product.

For this work we chose what appeared to be the three mildest deacetylating agents in the literature: the barium methylate–methyl alcohol method of Isbell[10] where the barium methylate is eventually decomposed by an exact titration with sulfuric acid; Levene and Tipson's modification[11] of Isbell's method where the excess reagent is decomposed with carbon dioxide; and finally the slightly more vigorous ammonia–methyl alcohol method where the directions of Fischer and Taube[12] were followed. All three methods caused the formation of small amounts of yellow to brown decomposition products that seemed similar in character, but much smaller in amount, to the prod-

(9) C. S. Hudson and D. H. Brauns, THIS JOURNAL, **37**, 1283 (1915).

(10) H. S. Isbell, *Bur. Standards J. Research*, **5**, 1185 (1930).

(11) P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **93**, 637 (1931).

(12) H. O. L. Fischer and C. Taube, *Ber.*, **60**, 1704 (1927).

ucts formed by sugars through alkaline degradation according to methods of Evans and co-workers.[18]

Discussion

It should be pointed out that the use of finely powdered Drierite as an internal desiccant in Königs–Knorr reactions is a very worthwhile practice. In the past when this reaction was used to prepare oligosaccharides (without the use of internal desiccants), yields ranging from a low of 0.25%[14] to a maximum of about 25%[15] were recorded. Yields of from 10 to 20% were the most common,[16] This is in sharp contrast to the 46, 52 and 59% yields recorded in this paper for the preparation of the same type of compounds.

The use of the new oligosaccharide acetates reported here in further elucidating the mechanism of the alkaline degradation of the more complex carbohydrates will be discussed in detail in a later paper.

The assignment of the β-configuration follows from the fact that the values of Hudson's *A* for the new oligosaccharide acetates are in each case positive, as was explained in a previous paper.[1]

β-*d*-glucosidodihydroxyacetone pentaacetate
$A = +32{,}200$

β-cellobiosidodihydroxyacetone octaacetate
$A = +29{,}300$

β-gentiobiosidodihydroxyacetone octaacetate
$A = +35{,}400$

The configuration of the *p*-nitrophenylhydrazones and of the methyl alcoholate follows from the configuration proved for the parent oligosaccharide acetates from which they were prepared.

In connection with the deacetylation of the oligosaccharide acetates it is very interesting to note that C. L. Bernier[17] found that the Kunz method[18] of acetyl determination was inapplicable to dihydroxyacetone monoacetate, as the results were invariably high. We also observed that the Kunz method failed for oligosaccharide acetates that contained dihydroxyacetone as a reducing constituent, for here too the results were about ten per cent. high. (In a typical analysis, 0.2132 g. of β-*d*-glucosidodihydroxyacetone pentaacetate required 25.42 cc. of 0.1 *N* NaOH; calcd. is 23.07 cc.) The acetyl analyses recorded in this paper were all made by the Freudenberg absolute method[19] and in no case was there any difficulty in either duplicating results or getting values that checked closely with theory. These facts indicate an unusual susceptibility of dihydroxyacetone to degradation by alkali.

Attention should also be called to the fact that the preparation of β-*d*-glucosidodihydroxyacetone pentaacetate and of β-gentiobiosidodihydroxyacetone octaacetate now make possible the study of a fairly complete sugar series where each higher member differs from the preceding one by the addition of three carbohydrate carbons to the carbohydrate chain as it lengthens:

	M. p., °C.	$[\alpha]_D$ in $CHCl_3$
Dihydroxyacetone diacetate[20]	42–45	...
β-*d*-Glucose pentaacetate[21]	132	+3.8°
β - *d* - Glucosidodihydroxyacetone pentaacetate	103	−25.2°
β-Gentiobiose octaacetate[22]	192–193	−5.3°
β - Gentiobiosidodihydroxyacetone octaacetate	172	−25.9°
6 - β - Gentiobiosido - β - *d* - glucose hendecaacetate	221	−8.0°

These may be thought of as constituting an "homologous series" among the carbohydrates, as it is analogous to the various homologous series among the hydrocarbons. A detailed study of the physical and chemical properties of the members of this series should prove interesting and profitable. The periodic rise and fall both of the melting points and the magnitude of the optical rotations are apparent from the data presented above.

Summary

1. The following new compounds were prepared in pure crystalline form and their characteristic properties determined: β-*d*-glucosidodihydroxyacetone pentaacetate, β-*d*-glucosidodihydroxyacetone pentaacetate *p*-nitrophenylhydrazone, β-cellobiosidodihydroxyacetone octaacetate, β - cellobiosidodihydroxyacetone octaacetate *p* - nitrophenylhydrazone, β-gentiobiosidodihydroxyacetone octaacetate, β-gentiobiosidodihydroxyacetone octaacetate methyl alcoholate and β-gentiobiosidodihydroxyacetone octaacetate *p*-nitrophenylhydrazone.

2. The first trisaccharide to contain a triose

(13) G. F. Nadeau, M. R. Newlin and W. L. Evans, THIS JOURNAL, **55**, 4957 (1933); W. L. Evans and C. C. Clark, *ibid.*, **54**, 698 (1932).

(14) B. Helferich and H. Bredereck, *Ann.*, **465**, 166 (1928).

(15) B. Helferich and W. Schafer, *ibid.*, **450**, 229 (1926).

(16) H. O. L. Fischer and L. Feldmann, *Ber.*, **62**, 854 (1929); B. Helferich and H. Rauch, *ibid.*, **59**, 2655 (1926); *Ann.*, **455**, 168 (1927).

(17) C. L. Bernier, unpublished work.

(18) A. Kunz and C. S. Hudson, THIS JOURNAL, **48**, 1978 (1926).

(19) K. Freudenberg and M. Harder, *Ann.*, **443**, 230 (1923).

(20) H. O. L. Fischer and H. Mildbrand, *Ber.*, **57**, 707 (1924).

(21) C. S. Hudson and J. K. Dale, THIS JOURNAL, **37**, 1264 (1915).

(22) C. S. Hudson and J. M. Johnson, *ibid.*, **39**, 1272 (1917).

constituent has been synthesized as its acetate.

3. A postulated intermediate in alkaline degradation of gentiobiose has been synthesized in a pure form as its acetate.

4. Attention is directed to the importance of using Drierite as an internal desiccant when the Königs–Knorr reaction is used to prepare oligosaccharides.

5. The susceptibility of dihydroxyacetone to degradation by alkali is pointed out.

6. With the synthesis of β-*d*-glucosidodihydroxyacetone pentaacetate and β-gentiobiosidodihydroxyacetone octaacetate the first six members of a homologous series among the carbohydrates are now available for study.

COLUMBUS, OHIO RECEIVED JULY 6, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Relative Rates of Combination of Hydrogen and Deuterium with Ethylene

BY A. WHEELER AND R. N. PEASE

In the present investigation the relative rates of combination of hydrogen and deuterium with ethylene have been measured, both for the homogeneous reaction and on a copper catalyst at 0°. Preliminary results with deuterium of unknown purity have already been published.[1] The present data are in good agreement with the earlier experiments, indicating that the heavy hydrogen used in the first experiments contained about 20% of the light isotope. This considerable contamination in the earlier experiments was due to the fact that, for the removal of oxygen, the heavy isotope was passed through a supported nickel catalyst often exposed to the light isotope for the same purpose. (The contamination of light hydrogen by deuterium probably did not occur, since the catalyst was always subjected to copious sweeping out before a sample of the light isotope was taken.) As is obvious, the earlier experiments were performed before the importance of exchange reactions between hydrogen and deuterium was realized.

Experimental Procedure

The apparatus and experimental procedure have been described by one of us elsewhere.[2] Both light and heavy hydrogen were prepared by electrolysis from caustic solution. The light hydrogen was passed subsequently through a calcium chloride tube, over a supported nickel catalyst at 500°, and finally through a trap at −80°. The deuterium was led over a hot platinum wire spiral and through a trap at −80°. Analysis (mass spectrographic and gas balance) showed the purity of the deuterium to be >99%. Compressed ethylene of high purity was subjected to fractional distillation before use. For the catalytic experiments, Kahlbaum copper oxide granules, "zur analyse," were reduced in light hydrogen at 200°, and the resulting product deactivated by heating *in vacuo* for one hour at 500°.

Since preliminary experiments indicated that exchange reactions of the type $D_2 + C_2H_4 \longrightarrow C_2H_3D + HD$ were to be looked for in the runs with deuterium, provision was made for the analysis of the light hydrogen content in the residual gas at the end of a run. The analysis was effected by freezing out ethylene and ethane with liquid air, and measuring the viscosity of the residual hydrogen gas in a Rankine-type viscometer.[3] By comparing the viscosity of the residual gas with that of pure deuterium, the approximate light hydrogen content of the sample could be found. The reproducibility of the viscometric readings was better than 1%, but the presence of methane (vapor pressure about 93 mm. at liquid air temperature) in the high temperature homogeneous runs, together with the possibly incomplete freezing out of the ethylene and ethane, make the viscometric results somewhat uncertain. However, they should set an upper limit for the light hydrogen content in the residual gas at the end of any given run.

I. **The Homogeneous Reaction.**—Reaction was carried out at four temperatures, namely, 534, 555, 567 and 574°. In agreement with the earlier work[2b] on the reaction of light hydrogen with ethylene, it was observed that one does not obtain good second order rate constants by extrapolating the pressure measurements to zero time and computing the rate constants from this point. Instead the procedure adopted, as before,[2b] was to use the fifth minute as zero time, the partial pressure of hydrogen and ethylene at this point being calculated from the extrapolated value for the initial pressure. In this way good rate constants were obtained, leading to the same value for the relative rates of the hydrogen and deuterium reaction which one calculates by comparing directly the times necessary for corresponding pressure drops. In Table I the rate constants are in the units $(\text{mm.} \times \text{sec.})^{-1}$. The second column indicates whether light hydrogen or deuterium was used in a given run, while the fifth column gives the ratio of the rate of the light hydrogen reaction to the rate of the deuterium reaction. The sixth and seventh columns contain the extrapolated initial partial pressures of hydro-

(1) R. N. Pease and A. Wheeler, THIS JOURNAL, **54**, 1144 (1935).

(2) R. N. Pease (a) *ibid.*, **45**, 1196 (1923); (b) *ibid.*, **54**, 1876 (1932).

(3) A. O. Rankine, *J. Sci. Instruments*, **1**, 4 (1934).