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.

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 (mm. × 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).

gen and ethylene. In all runs three parts of hydrogen to one of ethylene were used, in order to cut the methane formation to a minimum.[2b]

It is to be noted that the observed temperature coefficient of the light hydrogen reaction agrees well with that found in the earlier research on this reaction. There is, however, a small discrepancy in the absolute values of the rate constants at a given temperature. This consistent discrepancy undoubtedly is due to temperature calibration errors, amounting to about four degrees. An error of two degrees in each research, working in opposite directions, is well within the realm of possibility.

Table I shows that over the temperature range investigated light hydrogen reacts with ethylene two and a half times as fast as the heavy isotope. Although this would apparently point to no difference in the activation energies of two reactions, a difference of one thousand calories might easily escape detection.

The evidence with regard to exchange reactions given by the viscometric measurements is as follows: (1) at 580° deuterium does not exchange with Pyrex glass previously exposed to the light isotope.
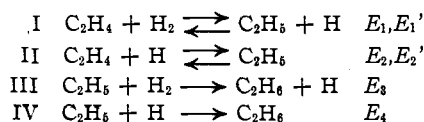
TABLE I

Run	H_2 or D_2	T, °C.	$k \times 10^7$ (mm. × sec.)$^{-1}$	$\alpha = \dfrac{k_{H_2}}{k_{D_2}}$	P^0_{Hyd}, mm.	$P^0_{C_2H_4}$, mm.
17	H_2	534	6.5	2.5	577.5	192.5
21	D_2	534	2.6		580.8	193.6
22	H_2	555	14.8	2.57	583.2	194.4
23	D_2	555	5.75		577.5	192.5
6	H_2	567	21.7	2.47	596.4	198.8
7	D_2	567	8.8		590.4	196.8
26	D_2	574	11.0		613	204.3

A sample of pure deuterium was allowed to remain for three hours in a Pyrex bulb maintained at 580°. The time of fall for the mercury pellet in the viscometer was 50.5 seconds for the sample, while for untreated deuterium it was 50.7 seconds, and for pure light hydrogen 36.4. It is to be noted that the ratio of viscosities η_{D_2}/η_{H_2} was consistently observed to be 1.395 ± 0.003. This is to be compared with the theoretical ratio of 1.41 obtained by Maass.[4] (2) Below 534° exchange reactions such as $D_2 + C_2H_4 \longrightarrow C_2H_3D + HD$ are absent or of negligible importance. The time of fall for the mercury pellet with pure D_2 filling the viscometer was 72.7 seconds, and with the D_2 residue from a run at 534° the time was 72.5. For pure light hydrogen the time was 52.0 seconds. (3) In the temperature region 570° exchange reactions may play roles of some importance. The time of fall for the mercury pellet with the deuterium residue from a run at 567° was 70.5 seconds, for pure D_2, 72.7 seconds, and for pure H_2, 52.0 seconds. For the deuterium residue from a 3 to 1 deuterium–ethylene mixture maintained at 567° for twenty-four hours, the time of fall was 66.5 seconds, indicating a maximum of about 20% light hydrogen.

Discussion of Homogeneous Reaction.—It has been shown[2b] that the reaction of ethylene with hydrogen in Pyrex bulbs is unambiguously homogeneous and second order. The actual mecha-

(4) Maass, *Can. J. Research*, **12**, 57–62 (1935).

nism of the reaction is, however, in dispute at the present time. Two mechanisms have been put forward: (1) that the reaction is a straightforward bimolecular association reaction[2b] and (2) that reaction proceeds through the following free-radical chain mechanism[5]

I	$C_2H_4 + H_2 \rightleftarrows C_2H_5 + H$	E_1, E_1'
II	$C_2H_4 + H \rightleftarrows C_2H_5$	E_2, E_2'
III	$C_2H_5 + H_2 \longrightarrow C_2H_6 + H$	E_3
IV	$C_2H_5 + H \longrightarrow C_2H_6$	E_4

The double arrows in reactions I and II indicate that the reactions are reversible, not that equilibrium is maintained. E_1 is the activation energy for reaction I in the forward direction; E_1' the activation energy for the reverse reaction, etc. It has been shown[5] that the above mechanism gives a second order rate of formation of ethane, with approximately the correct temperature coefficient. The actual expression is

$$-\frac{d\,C_2H_4}{dt} = \sqrt{\frac{k_1 k_2}{k_1' + k_4}}\,(C_2H_4)(H_2)$$

Here the k's and k''s are the rate constants for the corresponding forward and reverse reactions. It was hoped that the difference in the rates of hydrogenation and deuterization of ethylene might enable one to decide whether the reaction is a straightforward association or a chain reaction. Unfortunately no clear-cut decision may be made. However, the following evidence may be brought forward. Since in the chain mechanism $k_2/(k_1' + k_4)$ involves in each k only the reaction of a hydrogen or a deuterium *atom* (no zero point considerations for reactants) it is reasonable to suppose that this ratio is the same for both the hydrogen and deuterium reactions. This being so, according to the chain mechanism the ratio of rates of the hydrogenation and deuterization processes must depend solely on the ratio of $\sqrt{k_1}$ for the two processes. In terms of a collision theory this means that

$$2.5 = \left[1.4\,e^{-\frac{\Delta E_0}{RT}}\right]^{1/2}$$

where ΔE_0 is the difference in zero-point energy for H_2 and D_2 as they enter into reaction I of the chain mechanism. In order for the above equation to be fulfilled, ΔE_0 must equal 2400 calories. It is well known,[6] however, that the *maximum* zero-point energy difference for reaction involving H_2 or D_2 is 1800 calories. It would appear, then, that the chain mechanism given above is

(5) F. O. Rice and K. F. Herzfeld, THIS JOURNAL, **56**, 284 (1934).
(6) Eyring and Sherman, *J. Chem. Phys.*, **1**, 6 (1933).

in questionable agreement with the experiments. In addition it may be cited that packing the reaction vessel[2b] in no way affects the rate of formation of ethane, and that in the present investigation the addition of one-half an atmosphere of nitrogen to a deuterium–ethylene mixture had no marked effect on the observed rate. Recent experiments on the reverse reaction[7] (*i. e.*, the decomposition of ethane) indicate that free radicals are absent during the initial stages of reaction. In view of the total lack of evidence for a chain reaction, it seems more likely that the hydrogenation of ethylene proceeds by a straightforward association mechanism.[8]

If, then, the hydrogenation of ethylene proceeds through a bimolecular association, the observed ratio of 2.5 for the hydrogen and deuterium reactions is easily accounted for. In terms of collision theory

$$k_{H_2}/k_{D_2} = 2.5 = 1.4\ e^{+\Delta E_0/kT}$$

where ΔE_0 is the effective difference in zero-point energy of H_2 and D_2, as they enter into this reaction. At 550°, ΔE_0 must be 950 cal. in order to satisfy the above equation.

According to an activated complex picture

$$\frac{k_{H_2}}{k_{D_2}} = \left(\frac{m_{H_2}^*}{m_{D_2}^*}\right)^{3/2}\left(\frac{I_{H_2}^*}{I_{D_2}^*}\right)^{1/2}\left(\frac{V_{H_2}^*}{V_{D_2}^*}\right)\left(\frac{m_{D_2}}{m_{H_2}}\right)^{3/2}\left(\frac{I_{D_2}}{I_{H_2}}\right)e^{+\frac{\Delta E_0}{kT}}$$

Here the m^*, I^*, V^* are respectively the masses, products of moments of inertia, and vibrational partition functions, for the activated complexes. A quantity referring to a complex formed by the union of H_2 with C_2H_4 is denoted by the subscript H_2, and has an asterisk after it; similarly for D_2. m_{D_2} and I_{D_2} are the mass and moment of inertia of the normal deuterium molecule; and similarly for the subscript H_2. If we denote the zero-point energy of a species by E_0, ΔE_0 is defined by $E_0 = E_{0D_2}^* - E_{0H_2}^* + E_{0H_2} - E_{0D_2}$. We know all quantities in the above except for the I^*'s, V^*'s and ΔE_0. Substituting numerical values we find

$$\frac{k_{H_2}}{k_{D_2}} = 2.5 = 5.14\left(\frac{I_{H_2}^*}{I_{D_2}^*}\right)^{1/2}\left(\frac{V_{H_2}^*}{V_{D_2}^*}\right)e^{\Delta E_0/kT}$$

For the normal ethane molecule in the region 850°K., V, the vibrational partition function, is only about eight,[9] and some, if not most, of the low frequencies contributing to this are associated with motions of the carbon atoms. A reasonable value for $V_{H_2}^*/V_{D_2}^*$ is 0.9. A reason-

able value for $(I_{H_2}^*/I_{D_2}^*)^{1/2}$ is $1/2$. This is equivalent to assuming that each of the three moments of inertia of the activated complex is 60% larger for the deuterium complex than in the light hydrogen complex. This may seem like a large percentage, but it must be remembered that the distended hydrogen atoms are contributing heavily to the moments of inertia, and hence the effect of the heavier deuterium atoms will be considerable.

Putting these values in our expression we get

$$\frac{k_{H_2}}{k_{D_2}} = 2.32\ e^{\frac{\Delta E_0}{kT}} = 2.5\ \text{(observed)}$$

From this it follows that ΔE_0 must be a very small quantity, about 120 calories. Indeed, this is what one would expect. Since the activated complex has seventeen modes of vibration, many of them with high frequencies, it is reasonable to suppose that zero-point energy differences for H_2 and D_2 would almost cancel, and it would not even be surprising if ΔE_0 were negative. In the case of $H_2 + I_2 \longrightarrow 2HI$, and $D_2 + I_2 \longrightarrow 2DI$, calculations by one of us[10] show that zero-point energy differences cancel, even though the activated complex has only five modes of vibration.

II. The Catalytic Reaction.—Reaction was carried out at two temperatures, 0 and 20°, on an active copper catalyst. The results are shown in Table II. In the earlier work[2a] on the light hydrogen reaction, it was shown that the reaction rate is unimolecular with respect to hydrogen and is inhibited by ethylene. It was found in the present experiments that this is also true for deuterium.

TABLE II

Run	Temp., °C.	H_2 or D_2	$k \times 10^{+3}$ (min.$^{-1}$)	$\alpha = \dfrac{k_{H_2}}{k_{D_2}}$	$P_{Hyd.}^0$ mm.	$P_{C_2H_4}^0$ mm.
30	0	H_2	5.2		372	372
31	0	D_2	2.5	2.08	352	352
32	0	H_2	4.45	1.78	353	353
33	0	D_2	2.18	2.07	345	345
35	20	D_2	9.9		380	380
36	20	H_2	20.9	2.1	378	378
37	0	D_2	2.2		366	366
38	0	H_2	4.0	1.83	366	366

The rate constants in Table II are first order constants, calculated with respect to hydrogen. Pressures are in mm. and times in minutes. Otherwise the quantities in Table II have the same significance as in Table I. The activity of the freshly prepared catalyst was falling consid-

(7) Sachsse, *Z. physik. Chem.*, **31B**, 79 (1935).

(8) See also Rice and Gershinowitz, *J. Chem. Phys.*, **2**, 857 (1934).

(9) Teller and Topley, *J. Chem. Soc.*, 878 (1935).

(10) Wheeler, Topley and Eyring, *J. Chem. Phys.*, **4**, 178 (1936).

erably, and for this reason the quantity α goes through periodic variations. That is, α for two runs in which the deuterium run followed the hydrogen run is larger than for the inverted case, as one would expect if the catalyst is losing activity. The average value for α at $0°$ is 1.94. The data at $20°$ are insufficient to be conclusive, but the 2.1 value of α at $20°$ must be compared with 2.07 at $0°$. Within the experimental error, then, the temperature coefficients (in the range $0-20°$) for the hydrogen and deuterium reactions are the same. However, it is to be noted that a difference sufficient to take account of all the difference between the rates of the two reactions in terms of unequal activation energies would have escaped detection.

The observed ratio of two between the rates of the hydrogen and deuterium reactions might be due to any of a number of causes. Collision rates of hydrogen and deuterium with the surface would introduce a factor of 1.4; rates of adsorp-

tion may differ by as much as $3.3;$[11] different rates of surface reaction may result in rates differing by a factor of 4.4, if the difference in zero-point energies of the Cu–H and Cu–D complexes be taken as 800 cal.[6] It is fairly obvious that we are dealing with something more than a collision frequency. However, extended discussion seems hardly profitable at this time.

Analysis showed no exchange between deuterium and ethylene on the copper catalyst at $0°$.

Summary

It has been found that the rate of reaction of hydrogen with ethylene is greater than that of deuterium by a factor of 2.5 in the homogeneous reaction at $\sim 500°$; and by a factor of 2 in the catalytic reaction over copper at $0°$. Exchange reactions are unimportant.

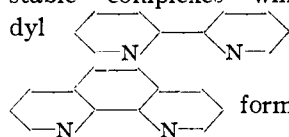(11) Soller, Goldwasser and Beebe, THIS JOURNAL, **58**, 1703 (1936).

The Structure and Properties of Mononuclear and Polynuclear Phenanthroline-Ferric Complexes[1]

BY ALLISON GAINES, JR., LOUIS P. HAMMETT AND GEORGE H. WALDEN, JR.

The beautifully complete papers in which Blau[2] reported the discovery of the unusually stable complexes which the bases dipyridyl and o-phenanthroline

 form with metallic ions propounded, nevertheless, a puzzling problem for valence theory in the existence of two different ferric complexes. One of these, blue in color, is obtained only by oxidation of the ferrous complex. Analysis of the chloroplatinate showed that its formula is $[Fe(C_{12}H_8N_2)_3]^{+++}$ and it would indeed be difficult to reconcile any other composition with the fact that it forms a mobile oxidant–reductant system with the ferrous complex, whose formulation as $[Fe(C_{12}H_8N_2)_3]^{++}$ is well established. By contrast direct reaction of phenanthroline and ferric salts leads to the formation of brown solutions from which Blau isolated no solid com-

pounds. He noted, however, color reactions which suggested the existence of a brown complex with the same ratio, $3:1$, of phenanthroline to ferric ion as that which obtains in the blue complex.

We have, however, obtained from these brown solutions a crystalline salt of definite composition whose properties correspond to the formula

$$\left[(C_{12}H_8N_2)_2Fe \underset{\underset{H}{O}}{\overset{\overset{H}{O}}{\diagdown\diagup}} Fe(C_{12}H_8N_2)_2 \right] Cl_4 \qquad (A)$$
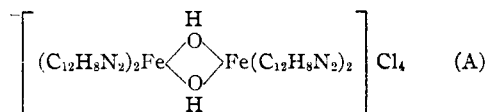
of a tetraphenanthroline-diol-diferric chloride. The polynuclear complex ion contained in this salt appears to be the major constituent of the brown solutions. In spite of the fact that the phenanthroline–iron ratio in this complex is $2:1$, there is no contradiction between our result and Blau's, which we have indeed confirmed, because in the formation of the bridge hydroxyl or "ol" groups, one hydrogen ion is set free from a water molecule for each ferric ion reacting. The combination of this hydrogen ion with phenanthroline raises to a value considerably above two

(1) Dissertation submitted by Allison Gaines, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the faculty of Pure Science, Columbia University.

(2) Blau, *Monatsh.*, **19**, 647 (1898).