of 8 kcal. and a probability factor of 10^{-2}; a higher activation energy and lower probability for two more stable and more sterically hindered substituted benzyl radicals would not be surprising.

Experimental

Polymerizations were carried out with 2–10-g. samples of commercial styrene, vacuum-distilled to remove inhibitor purified by fractional freezing to constant melting point (30.6°) and then fractionated under reduced pressure. The samples were distilled on the high vacuum line into reaction tubes, degassed, and sealed at a vacuum of 10^{-4} mm. or better. The tubes were wrapped in tinfoil to exclude light and heated in a vapor-bath at 127.3 ± 0.1° for one-half to twenty-four hours. Yields were determined by weighing the polymer isolated by the method of Lewis and Mayo.[24] Results are given in Table I and are in good agreement with those of Schulz and Husemann[1d] as shown in Fig. 1.

Activity measurements were made by following the vapor pressure over polymerizing styrene. A sample of styrene (*a* in Table I) was polymerized in a tube on one side of a differential manometer, the other side of which was attached to a reservoir of bromobenzene, and the mercury levels in the manometer followed with a cathetometer. The manometer was thoroughly evacuated and degassed, and the purpose of the bromobenzene was merely to make it possible to follow a greater variation of pressure with a manometer which would still fit in the vapor-bath. Results are given in Table II. These results were checked by independently measuring the vapor-pressure of a 52 wt. % solution of polystyrene in styrene against styrene at 127.3°, each sample containing a few milligrams of chloranil as inhibitor. The difference in vapor pressure, 37.0 mm., corresponds to an activity of 0.914. From Fig. 2, the activity at 52% reaction is .922, a satisfactory check.

Summary

The rate of thermal polymerization of styrene at 127.3°, and the vapor pressure of the monomer in the polymerizing system have been measured over the range 0–95% reaction.

The rate has been found to be closely proportional to the square of the styrene activity over the entire range.

This result is discussed in terms of the Brønsted rate equation, and data are reviewed indicating that the shape of the rate curve cannot be due to chain termination being a diffusion controlled reaction.

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[24] Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, THE BARRETT DIVISION, ALLIED CHEMICAL AND DYE CORPORATION]

Equilibrium Studies on the Dehydrogenation of Primary and Secondary Alcohols. I. 2-Butanol, 2-Octanol, Cyclopentanol and Benzyl Alcohol

BY ADRIAN H. CUBBERLEY AND MAX B. MUELLER

Introduction

In connection with investigations being carried out in this Laboratory, the equilibrium constants for the dehydrogenation of a number of alcohols have been determined over the temperature range 150–300°. In view of the recent interest in this field[1] a portion of our results is being reported at this time.

Equilibrium studies have been reported on methanol,[2] ethanol,[3,4] isopropanol[1,3,5] and 2-butanol.[1] This paper reports the results of our studies on 2-butanol, 2-octanol, cyclopentanol and benzyl alcohol.

Experimental

Materials.—Commercial butanone was fractionated through a 30″ Vigreux column and the center cut boiling at 78–78.5° was used.

Commercial 2-butanol was fractionated through a 30″ Vigreux column and the center cut boiling at 98° was used.

Commercial 2-octanol (87.5% alcohol, 12.5% ketone) was used without purification.

2-Octanone was prepared by vapor phase dehydrogenation of 2-octanol over Cu-catalyst at 275°. The material, containing 95.5% ketone, was used without further purification.

Cyclopentanone was prepared by the "Organic Syntheses" method.[6] A center cut boiling at 128–130° was used.

Cyclopentanol was prepared by vapor phase hydrogenation of cyclopentanone over the Cu-catalyst at 155° and 1 atm. The crude material, containing 27.5% ketone, was distilled but not further purified.

Reagent grade benzaldehyde and benzyl alcohol were fractionated through a 24″ Vigreux column and center cuts were used.

A catalyst consisting of Cu and MgO precipitated on 6 to 8 mesh pumice was used throughout.

Apparatus.—The apparatus is illustrated diagrammatically in Fig. 1. It consisted essentially of a hydrogen preheater, vaporizer, reactor and condensing system cooled by Dry Ice in acetone, except in the case of benzyl alcohol, where ice was used.

Method of Operation.—Hydrogen at the rate of approximately one liter per minute was metered through the preheater coil and introduced into the bottom of the glass helix-filled vaporizer. The vaporizer, containing approximately 150 cc. of organic material (alcohol or ketone), was kept at a temperature such that the hydrogen entering the reactor contained 5–10 mole per cent. of organic material. The vaporizer oil-bath temperature was regulated by a bi-metallic thermoregulator. The mixed feed vapors passed through a glass preheating coil in the reactor bath and then into the U-shaped catalyst chamber containing 100 cc. of catalyst. The temperature of the reactor oil bath was controlled to within ±1° by means of a Brown potentiometer-controller. The catalyst temperature was measured by iron–constantan thermocouples in the glass thermocouple wells embedded in the catalyst. The or-

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[1] Kolb and Burwell, THIS JOURNAL, **67**, 1084 (1945).

[2] Newton and Dodge, THIS JOURNAL, **55**, 4747 (1933).

[3] Rideal, *Proc. Roy. Soc.* (London), **A99**, 153 (1921).

[4] Suin, Chin and Chu, *Ind. Eng. Chem.*, **34**, 674 (1942)

[5] Parks and Kelly, *J. Phys. Chem.*, **32**, 740 (1928).

[6] "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1932, Coll. Vol. I, p. 187.

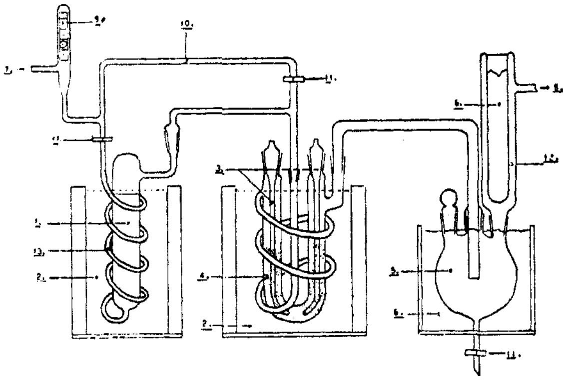

Fig. 1.—*Key*: 1, vaporizer-packed with glass helices; 2, oil-bath, electrically controlled; 3, thermocouple wells; 4, reactor (100 cc. catalyst); 5, receiver; 6, freezing mixture; 7, gas inlet; 8, gas exit to wet-test meter; 9, gas flow meter; 10, by-pass line; 11, stopcock; 12, condenser; 13, hydrogen preheater coil.

ganic vapors were condensed in the condensing system, and the exhaust hydrogen was metered. Samples were collected at half-hour intervals after a steady temperature state was established. Between runs, while the reactor oil-bath temperature was being changed, the vaporizer was by-passed and the catalyst was kept under an atmosphere of hydrogen.

Analytical Methods.—The ketone content of the sample was determined by a modified hydroxylamine titration.[7]

The alcohol content of the sample was determined by the well-known "hydroxyl number" procedure.

Experimental Results

The procedure outlined above was chosen because it is insensitive to minor changes in most of the variables. The equilibrium constant was calculated from the equation

$$K \text{ equ.} = \left(\frac{M_C}{M_A}\right)\left(\frac{M_H}{M_T}\right) P$$

where M_C = number of moles of carbonyl compound; M_A = number of moles of alcohol; M_H = number of moles of hydrogen; M_T = total number of moles; P = 1 atmosphere.

Since M_H (and therefore M_T) was large compared with M_C or M_A the effect of possible side reactions was ignored. We believe that the precision of the results reported is limited only by the precision of the determination of the alcohol–carbonyl ratio (M_C/M_A) and by the precision of the temperature measurement. The precision of the alcohol and carbonyl compound determination was conservatively estimated as ±0.5%. The precision of the temperature measurement was estimated as ±2°. Variations of such magnitude may be expected to cause an error of about ±200 cal. in ΔF.

Results for 2-butanol, 2-octanol, cyclopentanol and benzyl alcohol are presented in Table I. The column headed "approach" signifies that (A) equilibrium was approached from the side of the carbonyl compound and (B) equilibrium was approached from the alcohol side.

TABLE I

EQUILIBRIUM CONSTANTS

Temp., °C.	Approach	Equil. const.	Temp., °C.	Approach	Equil. const.
		2-Butanol = Butanone + H_2			
172	B	0.544	248	A	3.64
174	B	.518	251	B	4.82
175	A	.572	251	A	4.90
193	B	.942	273	B	8.73
198	B	1.12	274	B	8.49
202	A	1.31	275	A	9.19
222	B	2.24	298	A	16.2
224	B	2.30	298	A	12.0
227	A	2.52	298	B	12.5
246	B	4.38	323	A	26.4
		2-Octanol = Methyl *n*-Hexyl Ketone + H_2			
135	B	0.230	225	B	3.28
176	B	0.681	247	A	6.02
182	A	1.37	249	B	5.10
200	B	1.68	260	B	9.25
216	B	2.86	272	B	12.8
219	A	3.25	276	B	17.8
			295	B	21.5
		Cyclopentanol = Cyclopentanone + H_2			
150	B	0.234	200	A	1.07
151	A	.246	200	B	1.25
155	A	.386	224	A	2.32
172	B	.428	225	B	2.00
174	A	.523	246	B	3.07
193	A	.776	250	A	3.96
			275	A	5.44
		Benzyl Alcohol = Benzaldehyde + H_2			
200	A	0.177	250	A	0.646
200	B	.130	270	B	1.06
225	A	.264	274	A	1.39
235	A	.468	275	A	1.04
243	B	.638	275	B	1.09
250	A	.558	275	A	1.09
250	A	.502	300	A	2.14

Discussion

In the absence of any reliable heat capacity data for the organic compounds used, heat capacity equations in the form

$$C_p = a + bT$$

TABLE II

CONSTANTS OF HEAT CAPACITY EQUATION

Compound	*a*	*b*
2-Butanol	6.94	0.0636
Butanone	7.05	.0549
2-Octanol	4.09	.1323
2-Octanone	4.41	.1207
Cyclopentanol	5.16	.0772
Cyclopentanone	6.04	.0666
Benzyl alcohol	4.59	.0801
Benzaldehyde	4.65	.0715
2-Propanol	7.06	.0482
Acetone	7.13	.0395
H_2	6.50	.0009

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(7) Eitel, *J. prakt. Chem.*, **159**, 292 (1942).

TABLE III

VALUES OF ΔH_0, A, B, I, ΔF_{298}, ΔH_{298} AND ΔS_{298}

Alcohol	ΔH_0	A	B	I	ΔF_{298}	ΔH_{298}	ΔS_{298}
2-Butanol	11,338	−15.22	0.0039	14.57 ± 0.18	4,810	12,960	27.4 ± 0.2
2-Octanol	11,264	−15.71	.0054	14.44 ± .32	4,470	12,660	27.5 ± .3
Cyclopentanol	10,498	−17.0	.0049	20.79 ± .31	4,600	12,260	25.7 ± .3
Benzyl Alcohol	11,272	−15.11	.0038	18.48 ± .27	5,980	12,890	23.2 ± .3
2-Propanol[a]	11,585	−15.13	.0039	14.28 ± .17	5,035	13,197	27.4 ± .2
2-Butanol[a]	11,338	−15.22	.0039	15.01 ± .15	4,940	12,960	26.9 ± .2

[a] Calculated using above values of C_P and ΔH but with the equilibrium data of ref. 1.

were estimated by a combination of the methods described by Dobratz[8] and Stull and Mayfield.[9]

The values of a and b used are listed in Table II. Free energy equations of the form

$$\Delta F = \Delta H_0 + AT \log T + BT^2 + IT$$

were obtained by integration of the ΔC_P equations. The values of ΔH_{355} reported by Kistiakowsky[10] were used to evaluate ΔH_0 in the cases of 2-butanol and cyclopentanol. For 2-octanol and benzyl alcohol the free energy equation was solved for I and ΔH_0 by the method of least squares. Values of the constants for the free energy equation as well as calculated values of ΔF_{298}, ΔH_{298} and ΔS_{298} are listed in Table III.

Measured values of the per cent. conversion of alcohol to carbonyl compound have been recalculated to a common basis (the conversion in the presence of an infinite amount of hydrogen) by use of the law of mass action. In Figs. 2 and 3 these values (squares and circles) are compared with the values calculated from the free energy equation.

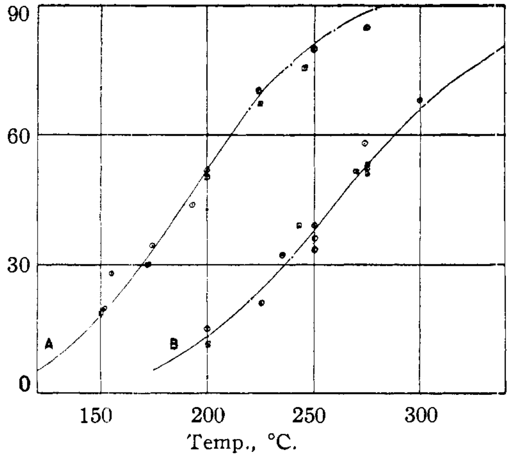

Fig. 2.—Per cent. conversion of alcohol to carbonyl compound in the presence of an infinite amount of hydrogen: (A) cyclopentanol, (B) benzyl alcohol: ⊡ dehydrogenation of alcohol (experimental values); ⊙ hydrogenation of carbonyl compound (experimental values); —·— calculated from free energy equation.

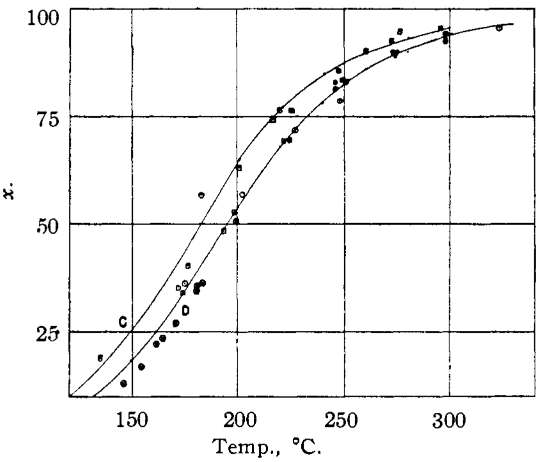

Fig. 3.—Per cent. conversion of alcohol to carbonyl compound in the presence of an infinite amount of hydrogen: (C) 2-octanol, (D) 2-butanol: ⊡, dehydrogenation of alcohol (experimental value); ⊙, hydrogenation of ketone (experimental value); ⊗, average experimental values for 2-butanol (ref. 1); —·— calculated from free energy equation.

The distribution of squares (approach from the ketone side) and circles (approach from the alcohol side) about the calculated values indicates that true equilibrium was approached.

It is interesting to note that while the entropy change associated with the dehydrogenation of the three straight chain secondary alcohols is practically constant, changes associated with the dehydrogenation of the cyclic compound and the primary alcohol are sensibly different. It is intended to study this effect of structure in more detail.

Summary

1. A simple technique for determination of the equilibrium in the dehydrogenation of alcohols has been developed.

2. Free energy equations for the dehydrogenation of 2-butanol, 2-octanol, cyclopentanol and benzyl alcohol have been derived.

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[8] Dobratz, *Ind. Eng. Chem.*, **33**, 759 (1941).

[9] Stull and Mayfield, *ibid.*, **35**, 639 (1943).

[10] Kistiakowsky, *et al.*, THIS JOURNAL, **61**, 1868 (1939); **60**, 440 (1938).