The average kinetic chain length is approximately three million in this temperature range, but polymer molecules are much smaller due to chain transfer.

3. The transfer constant for the methacrylate radical with hydroquinone is approximately 0.01.

PASSAIC, NEW JERSEY RECEIVED JANUARY 17, 1946

[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

The Kinetics of the Thermal Polymerization of Styrene

BY CHEVES WALLING, EMORENE R. BRIGGS AND FRANK R. MAYO

In the past eight years the uncatalyzed, purely thermal polymerization of styrene has been studied by several workers in different laboratories.[1] Since, with reasonable precautions, reproducible and consistent rates have been obtained, the existence of such an uncatalyzed reaction appears to have been demonstrated with a good deal of certainty. Nevertheless, although most workers favor a mechanism of bimolecular initiation, growth, and termination,[2] the rates of the separate steps are subjects of conjecture. Furthermore, a very important anomaly exists: while it has been amply demonstrated that the initial rate of thermal polymerization is second order in respect to styrene in a number of solvents,[1a,1c,1e] the rate in pure styrene in the range 0–90% reaction is approximately first order.[1d] This change in order leads to the rather striking result that *a 10% solution of styrene in polystyrene polymerizes approximately ten times as rapidly as in other solvents.*

Polymerization in Changing Medium.—Any attempt to interpret such a change in kinetic order leads at once into the important, but obscure, problem of the effect of changing medium upon reaction rates. Customarily, the problem is treated by the Brønsted rate equation[3] which states that in the reaction $A + B \rightarrow C$ the reaction rate is given by $k[A][B]\frac{f_a f_b}{f_{ab}}$, where f_a, f_b, and f_{ab} are activity coefficients for A, B, and the "activated complex" through which the reaction proceeds. Quantitative confirmation of such an expression has been possible only in ionic reactions in solvents of high dielectric constant where f_{ab} may be calculated by the Debye–Hückel law, but many attempts have been made to extend it, with varying success, to other reactions and media as well.[4]

Probably the simplest mechanism for thermal polymerization which is in keeping with the facts of organic chemistry is that of bimolecular initiation, growth, and termination with steps and rate expressions as follows, where M, M* and P are monomer, growing chain, and unreactive polymer, and the *f*'s the appropriate activity coefficients:

$$\text{Initiation: } 2M \longrightarrow 2M^* \qquad v_1 = k_1[M]^2\frac{f_m^2}{f_{2m}} \quad (1)$$

$$\text{Growth: } M^* + M \longrightarrow M^* \quad v_2 = k_2[M][M^*]\frac{f_m f_{m^*}}{f_{mm^*}} \quad (2)$$

$$\text{Termination: } 2M^* \longrightarrow 2P \quad v_3 = k_3[M^*]^2\frac{f_{m^*}^2}{f_{2m^*}} \quad (3)$$

Application of the steady state principle to these equations yields, for the over-all rate

$$-\frac{dM}{dt} = k_2\sqrt{\frac{k_1}{k_3}}[M]^2 f_m^2 [f_{2m^*}/f_{mm^*}^2 f_{2m}]^{1/2} \quad (4)$$

Equation (4) states that the rate of polymerization is second order in respect to monomer concentration in any given medium. How it will change with changing medium will depend upon variation in the various (immeasurable) activity coefficients, but three types of variation are experimentally distinguishable. (1) The ratio of all the activity coefficients remains sensibly constant, leading to a rate second order in respect to monomer *concentration.* In most discussions of polymerization kinetics this constancy is assumed, and it is further suggested by the statistical treatment of Flory.[5] (2) The ratio of activity coefficients of the activated complexes, $f_{2m^*}/f_{mm^*}^2 f_{2m}$, remains constant, but the activity coefficient of the monomer varies leading to a rate second order in respect to monomer *activity.* (3) Neither of the above ratios remains constant. Here, the polymerization rate would not be a simple function of any measurable quantity.

In the case of the initial thermal polymerization of styrene in hydrocarbons, (1) at first appears the correct alternative since smooth, consistent second order rates are obtained. However, monomer activity and concentration are nearly enough identical in the system studied to make it impossible to rule out alternative (2). In the thermal polymerization of styrene to high extents of reaction, on the other hand, a choice is possible, since a wide variation between monomer concentration and activity takes place. Accord-

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[1] (a) Suess, Pilch and Rudorfer, *Z. physik. Chem.*, **179A**, 361 (1937); (b) Dostal and Jorde, *ibid.*, **179A**, 23 (1937); (c) Suess and Springer, *ibid.*, **181A**, 81 (1937); (d) Schulz and Husemann, *ibid.*, **36B**, 184 (1937); (e) Schulz, Dinglinger and Husemann, *ibid.*, **43B**, 47, 385 (1939); also unpublished work carried out in this Laboratory by R. A. Gregg and F. M. Lewis.

[2] Flory, THIS JOURNAL, **59**, 241 (1937).

[3] Brønsted, *Z. physik. Chem.*, **102**, 109 (1922).

[4] For a detailed discussion with many references, Ch. VIII, Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

[5] Flory, *J. Chem. Phys.*, **12**, 425 (1944).

ingly, we have measured the rate of polymerization and monomer activity in pure styrene at 127.3° over the range of 0–95% reaction. Results of rate experiments are listed in Table I.

TABLE I

THERMAL POLYMERIZATION OF STYRENE AT 127.3°

Reaction time, hr.	Polymer yield, %	Reaction time, hr.	Polymer yield, %
0.5	7.04	6.0	70.0
0.5	5.74	6.0	63.6
1.0	13.8	8.0	79.5
1.0	16.3	10.0	85.4
2.0	25.9	10.33	85.9
2.0	22.6	13.0	90.5[a]
4.0	46.1	15.5	92.0
4.0	46.1	15.75	90.8
4.33	54.4	24.0	95.9

[a] Experiment carried out in differential manometer for activity measurements.

Monomer activity was determined by polymerizing styrene in a system attached to a manometer and determining the vapor pressure of the system. Results are given in Table II, with pure styrene being chosen as the standard state. The data of Tables I and II are plotted in Fig. 1, together with the experiments of Schulz and Husemann at 132° corrected to 127.3° with their temperature coefficient.[1d] By comparing the curves of Fig. 1, and by graphical differentiation, plots of polymerization rate and activity *vs.* extent of reaction may be constructed as shown in Fig. 2. The activity plot has the form predicted by Huggins for solvent–polymer systems,[6] the dashed line being the activity function calculated by his equation with $\mu_1 = 0.33$. From Fig. 2, Fig. 3 may be obtained. The straight line is that calculated for a rate proportional to the square of the monomer activity, in quite reasonable agreement with experiment considering that there is considerable latitude in drawing the smooth curves of Fig. 1, and that several graphical operations are involved.

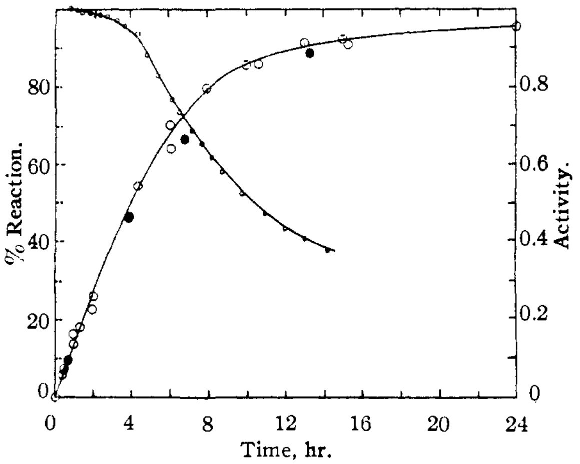

Fig. 1.—Styrene activity (small circles) and % reaction (large circles) *vs.* time in the thermal polymerization of styrene at 127.3°. Black circles are Schulz' results at 132.0°, corrected to 127.3°, using his temperature coefficient.

TABLE II

VAPOR PRESSURE OF POLYMERIZING STYRENE AT 127.3°

Time, hr.	Vapor pressure styrene,[a] mm.	Activity	Corrected time, hr.[b]
0.00	(431)	1.00	0.000
0.50	(423)	(0.982)	.547
0.67	(426)	(0.988)	.734
0.83	431	1.00	.902
1.16	429	0.996	1.28
1.42	428	.993	1.55
1.83	426	.988	2.00
2.25	424	.984	2.46
2.67	420	.975	2.92
3.00	417	.968	3.28
3.50	411	.954	3.83
4.08	403	.935	4.56
4.50	378	.877	4.92
5.00	355	.824	5.47
5.58	330	.766	6.10
6.00	314	.729	6.56
6.67	290	.673	7.30
7.00	279	.649	7.66
7.30	264	.613	8.20
8.00	249	.578	8.75
9.00	224	.520	9.85
10.00	204	.473	10.9
11.00	185	.429	12.0
12.00	175	.406	13.1
13.00	161	.374	14.2

[a] At 127.3° the vapor pressure of styrene is 431 mm., of bromobenzene, 331 mm. [b] As this polymerization gave 90.5% polymer in thirteen hours, while the curve of Fig. 1 indicates that 14.2 hr. should be required, all observed times are multiplied by 14.2/13.0.

This result, that the rate of thermal polymerization of styrene is second order in respect to monomer activity, is presumptive evidence for alternative (2), namely, that the ratio $(f_{2m*}/f^2_{mm*}\cdot f_{2m})^{1/2}$ is sensibly constant during the entire course of a polymerization. If so, it is possible to reconcile results at high extents of reaction in pure styrene with those obtained at low extents of reaction in the presence of solvent. How reasonable it is to expect such a constancy of the ratio of activity coefficients is hard to say, particularly as it is impossible to state to what extent an active center partakes of the nature of an isolated radical and to what extent it resembles the polymer molecule of which it is part. However, extensive copolymerization experiments in this laboratory show that monomer reactivity ratios in copolymerization (which depend upon similar ratios) are not detectably dependent upon medium and extent of reaction.[7]

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(6) Huggins, THIS JOURNAL, **64**, 1712 (1942).

(7) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944), also unpublished work.

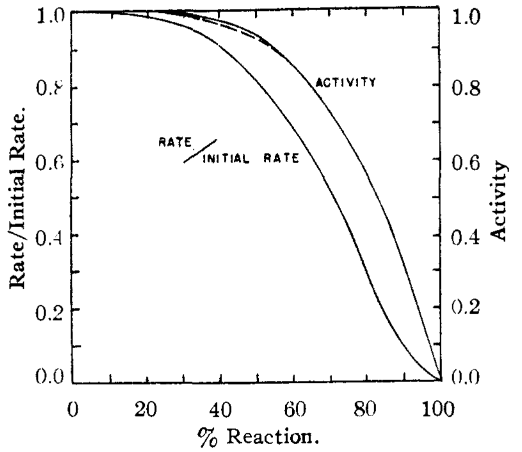

Fig. 2.—Rate and monomer activity as functions of % reaction in the thermal polymerization of styrene at 127.3°.

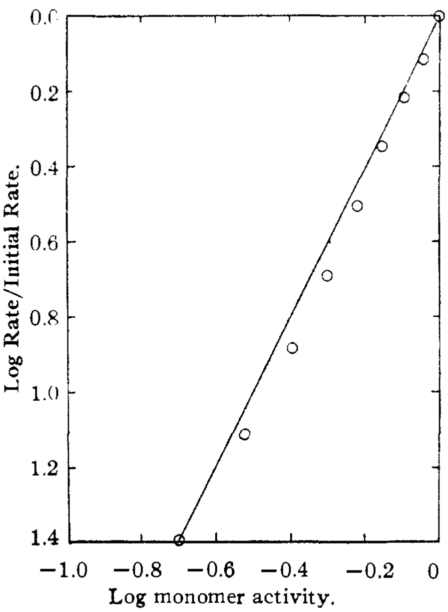

Fig. 3.—Log Rate/Initial Rate *vs.* Log Monomer Activity in the thermal polymerization of styrene at 127.3°.

Such a constancy may, of course, arise in two ways: either through the constancy of the individual activity coefficients of the complexes, or through their compensatory variation. The former is suggested by the fact that here we are dealing with uncharged, essentially non-polar activated complexes of which the energy of formation might be quite insensitive to changes of the medium. Furthermore, the high instability and reactivity of all these activated complexes suggests that their behavior might depend more on potential energy considerations than on the statistical considerations which govern the activity of polymer and monomer molecules.[8] On the other hand, the alternative of compensating variation cannot be excluded.

Regardless of the reasonableness of the results obtained on treating polymerization by the Brønsted rate equation, and the fruitfulness with which the equation has been applied to other systems, an alternative treatment cannot be ruled out: namely, to abandon the Brønsted treatment entirely and to ascribe variations in rate with changing medium to variations in the rate constants themselves. This course would definitely be necessary in the case that the thermal polymerization of styrene were a diffusion-controlled reaction, and the possibility and consequences of diffusion controlling the rate of chain termination are considered in detail in the next section.

If changes in kinetics with changing medium are ascribed to changes in rate constants rather than in activity coefficients, the observation of Schulz and Husemann[1d] that the intrinsic viscosity, and by inference the molecular weight, of the polymer formed in the thermal polymerization of styrene remains constant throughout the reaction, leads to the interesting conclusion that $k_2/(k_1k_3)^{1/2}$ is constant, providing that chain transfer with the monomer can be neglected.[9] Further, the observed over-all kinetics are approximately first order in respect to monomer concentration, whence $k_2(k_1/k_3)^{1/2}$ is approximately proportional to $1/[M]$. Accordingly, it is easily shown that k_1 is roughly proportional to $1/[M]$, and, if k_2 is assumed constant, $k_1 \backsim 1/k_3$. *I. e.*, as the reaction progresses the rate constant for initiation increases while that for chain termination decreases.[9a] On the other hand, if the Brønsted treatment is retained, the constancy of molecular weight during reaction, still assuming no chain transfer, requires that $f_{2m}f_{2m^*}/f^2_{mm^*}$ be constant. This requirement, taken with the constancy of $f_{2m^*}/f^2_{mm^*}f_{2m}$ noted above, leads to the result that f_{2m} is constant and that the other activity coefficients either remain constant or vary so that $f_{2m^*} \backsim f^2_{mm^*}$.

Polymerization as a Diffusion-Controlled Reaction.—In most considerations of the mechanism of radical polymerizations, the termination reaction by interaction of two radicals is considered to have an activation energy of 0–8 kcal.[2,10] Although this value is low enough to put it within the range of diffusion controlled reactions, the possibility of diffusion playing a role in polymerization rates has only rarely received attention.[11,12] According to Rabinowitsch,[13] the correct rate

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[8] This suggestion was made by Dr. Huggins in conversation with one of the authors.

[9] Unpublished work by Dr. R. A. Gregg in this Laboratory has shown chain transfer of a styrene type radical with styrene at 60°.

[9a] The authors are indebted to Dr. P. J. Flory for pointing out this interesting relationship.

[10] (a) Schulz and Husemann, *Z. physik. Chem.*, **39B**, 246 (1938); (b) Cohen, THIS JOURNAL, **67**, 17 (1945); (c) Burnett and Melville, *Nature*, **156**, 661 (1945).

[11] Dostal and Mark, *Oesterr. Chem. Ztg.*, **1**, 25 (1937).

[12] Norrish and Smith, *Nature*, **150**, 336 (1942).

[13] Rabinowitsch, *Trans. Faraday Soc.*, **33**, 1225 (1937).

equation for a bimolecular reaction in solution is

$$v = \frac{n\,\nu\,e^{-E/RT}}{1 + \frac{a^2\,\nu}{D_1 + D_2}\,e^{-E/RT}} \qquad (5)$$

where n is the coördination number (12 for close-packed spheres), ν the frequency of oscillation ($\backsim 10^{12}$ sec.$^{-1}$), a the lattice constant ($\backsim$ 10 Å., allowing for some motion of the active center independent of the rest of the polymer molecule), D_1 and D_2 the diffusion constants for the two reacting species, and E the activation energy for the reaction. In cases where E is very large, (5) reduces to the ordinary Arrhenius equation. On the other hand, if E is small, or the rates of diffusion slow enough, (5) reduces to

$$v = n(D_1 + D_2)/a^2 \qquad (6)$$

and the reaction is diffusion-controlled. Calculation shows that for reactions between small molecules which, in ordinary solvents, have diffusion constants of $\backsim 10^{-5}$ cm.^{2}/sec. (or between one large and one small molecule) diffusion becomes important for reactions with activation energies of less than about 4 kcal.[14] In the case of the termination reaction, which involves the diffusion together of two polymer molecules with diffusion constants of the order of 10^{-7} cm.^{2}/sec. in dilute solution, the critical activation energy is about 8 kcal. In polymerizations carried out to low extents of reaction, the fact that chain termination was a diffusion-controlled reaction would lead to no change in reaction order, but any attempt to measure the activation energy for the termination reaction would give, instead, the activation energy for polymer diffusion. On the other hand, in a polymerization carried to a high extent of reaction, an enormous increase in the viscosity of the medium takes place. Although quantitative data are not available, it is qualitatively evident that as reaction progresses the rate of diffusion together of growing chains will drop tremendously, a given active center will produce more polymer, and an over-all rate of polymerization of lower apparent kinetic order will result. Conceivably, such an effect could account for the apparent first order rate in the thermal polymerization of pure styrene—in fact, a much greater effect might be anticipated with an actual increase in rate with extent of reaction.[15]

Actually, other data exist which make it possible to show that chain termination in the polymerization of styrene probably is not a diffusion-controlled reaction. In the first place, polymerization to high extents of reaction should lead to polymer chains of higher and higher molecular weight, as with increasing solution viscosity, diffusion together of growing chains becomes more difficult.[16] However, as noted earlier, it has been shown by Schulz and Husemann[1d] that the intrinsic viscosity of the polymer formed is the same at low and high extents of reaction. Secondly, diffusion rates are undoubtedly functions of polymer molecule size, so that chains which have grown very long will diffuse more slowly, and thus have a lower probability of terminating than short chains. Qualitatively, the result of such a change in the ratio of rates of growth and termination with degree of polymerization will be a broadening of molecular weight distribution over that usually calculated which leads to a weight average molecular weight twice the number average.[17] In contrast to this expectation, fractionation experiments by Schulz and co-workers[1e] have shown that the molecular weight distribution in polystyrene is close to that calculated. Further, numerous recent determinations in this laboratory of light scattering (weight) and osmotic (number) average molecular weights of polystyrene samples prepared at small extents of reactions in no case have shown ratios appreciably greater than 2:1.[18] Finally, with long chains terminating less easily than short ones, addition of a solvent[2,19] which prevents the formation of large molecules, should lead to a drop in the over-all rate of polymerization. Actually the data of Schulz, Dinglinger and Husemann[1e] and Suess and co-workers[1a,1c] show that the rate of polymerization in solvents is independent of the effectiveness of the solvent as a transfer agent[19] except when transfer leads to a relatively inactive radical,[20] and their observations have been extended and confirmed in this laboratory.[24] In turn, if termination is not a diffusion-controlled reaction, it must have an activation energy of at least 8 kcal.[22] or else a very low probability. In this regard, it should be noted that Rice and Herzfeld[23] consider the recombination of two ethyl radicals to have an activation energy

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[14] Using the values of the constants listed under Equation (5). Actually Rabinowitsch's treatment assumes a "probability factor" of unity in the rate expression. Reactions with small probability factors would not be diffusion-controlled even though they had activation energies lower than 4 kcal.

[15] This discussion considers only the termination reaction to be diffusion-controlled. If chain growth is as well, the direction of the effect cannot be predicted. However, estimates for the activation energy for the growth reaction of 8–14 kcal., indicate that diffusion is not critical. In the case that growth and termination are both *equally* influenced by diffusion rate, the over-all polymerization rate should *drop* with increasing viscosity.

[16] Assuming, of course, that chains do not end by transfer; *cf.* ref. 9.

[17] A simple calculation shows that, if diffusion rate decreases with increasing chain length, the probability of a chain terminating decreases toward an asymptotic value for very long chains. Assuming a suitable mathematical expression in this form and calculating the resulting molecular weight distribution gives a broadened distribution as stated above.

[18] Unpublished work by R. H. Ewart, and C. P. Roe, and M. Wales.

[19] (a) Mayo, This Journal, **65**, 2324 (1943); (b) Hulburt, Harman, Tobolsky and Eyring, *Ann. N. Y. Acad. Sci.*, **44**, 371 (1943); (c) Medvedev, Koritskaya and Aleksieva, *J. Phys. Chem.*, U. S. S. R., **17**, 391 (1943).

[20] (a) Walling, This Journal, **66**, 1602 (1944); (b) Bartlett and Altschul, *ibid.*, **67**, 816 (1945).

[21] Unpublished work by Dr. R. A. Gregg.

[22] Assuming a diffusion constant of 10^{-7} cm.^{2}/sec. However, in concentrated polymer solutions the diffusion constant for polymer, while unmeasured, is probably several magnitudes smaller still.

[23] Rice and Herzfeld, *ibid.*, **56** 284 (1934).

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.