Table I shows the approximate constancy of the ratio $P^2_{HD}/(P_{H_2}P_{D_2})$ over a 25-fold variation of the initial P_{CH_2O}/P_{CD_2O} ratio. Kinetically this implies, assuming formation of the molecular hydrogen species by interaction of a radical with a formaldehyde molecule, that the radical concentration is directly proportional to the appropriate formaldehyde concentration. That is, if

$$\frac{dP_{HD}}{dt} = k[(D)(H_2CO) + (H)(D_2CO)],$$

$$\frac{dP_{H_2}}{dt} = k[(H)(H_2CO)] \text{ and } \frac{dP_{D_2}}{dt} = k[(D)(D_2CO)]$$

then

$$\frac{P_{HD}}{P_{H_2}P_{D_2}} = \frac{[(D)(H_2CO) + (H)(D_2CO)]^2}{[(D)(D_2CO)][(H)(H_2CO)]}$$

is a constant equal to 4 only if D and H are proportional to the first power of D_2CO and H_2CO, respectively. We have neglected the difference in rates due to isotope effects, although their inclusion would not alter the argument.

A scheme for the thermal decomposition of formaldehyde, consistent with the data and observations, is

$$CH_2O + CH_2O \xrightarrow{K_1 \text{ wall}} HCO + H + CH_2O \quad (I)$$

$$HCO \xrightarrow{k_2} H + CO \quad (II)$$

$$H + H_2CO \xrightarrow{k_3} H_2 + HCO \quad (III)$$

$$HCO \xrightarrow{K_4 \text{ wall}} \text{products} \quad (IV)$$

There is derived from the mechanism

$$\frac{dP_{H_2}}{dt} = \frac{dP_{CO}}{dt} = \frac{d\Delta P}{dt} = -\frac{dP_{CH_2O}}{dt} = \frac{K_1k_3}{K_4}P^2_{CH_2O}$$

Stoichiometrically, $CH_2O = CO + H_2$. P_{H_2} exceeds ΔP somewhat because of an unspecified condensation reaction. However, as shown in Table II, it is relatively small.

From the mechanism, and with the available data, it is possible to estimate k_3

$$P_H = \frac{K_1k_2}{k_3K_4}P_{CH_2O}$$

$$P_H = 4.6 \times 10^{-8} \text{ mm.}$$

$$\frac{1}{P_{H_2}} = \frac{1}{(P_{CH_2O})_0} + \frac{K_4}{(P_{CH_2O})_0K_1k_2t}$$

From the slope of the $1/P_{H_2}$ *versus* $1/t$ plot of Fig. 1

$$\frac{K_1k_2}{K_4} = 2 \times 10^{-5} (\text{mm.})^{-1} \text{ sec.}^{-1}$$

$$\frac{K_1k_2}{k_3K_4} = 3 \times 10^{-10}$$

Therefore

$$k_3 = 7 \times 10^4 (\text{mm.})^{-1} \text{ sec.}^{-1}$$

On the basis of collision theory, an upper limit for the activation energy of the $H + H_2CO \rightarrow H_2 + HCO$ reaction is calculated as 5.7 kcal. This agrees with the upper limit estimates of other investigators.[12]

[12] K. H. Geib, *Ergeb. Exakt. Naturwiss.*, **15**, 44 (1936).

PITTSBURGH, PA.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY]

Kinetics of the Hydrogen Fluoride Catalyzed Alkylation of Toluene by *t*-Butyl Chloride[1]

BY A. S. GOW, JR.,[2] AND J. H. SIMONS[3]

RECEIVED APRIL 4, 1955

Further measurements have been made on the reaction of *t*-butyl chloride and toluene as catalyzed by hydrogen fluoride. The reaction rate is greatly retarded by hydrogen chloride. The effect of five promoters was studied. It was found necessary to modify the equations and theory of Pearlson and Simons[5] to correlate the rate measurements in any one experiment. The mechanism postulated for the reaction explains all of the experimental facts. It is essentially a proton transfer mechanism.

Previous kinetic studies[4,5] of the alkylation reaction between toluene and *t*-butyl chloride as catalyzed by hydrogen fluoride present strong evidence against any ionic or free radical intermediates for this reaction. Two variations of a proton transfer mechanism in an amphoteric medium are presented.

The previous work[4,5] had shown that the rate of this reaction is proportional to the first power of the concentrations of reactants, and a high power (6–7) of the catalyst pressure. In addition, it was found that the rate is greatly increased by the presence of extremely small amounts of organic oxygen-containing compounds. An extension of these measurements appeared highly desirable. In the present work the effect of catalyst pressure was studied at three temperatures. The effect of five promoters also was studied.

Experimental

Preparation of Materials.—The reactants and catalyst were prepared as previously described.[5]

Anhydrous hydrogen chloride was prepared by dropping degassed, concentrated sulfuric acid (m.p. 10.0–10.5°) onto sodium chloride (C.P.) in an evacuated system. The gas was dried by passage through anhydrous calcium chloride at −77°.

The promoters used were 2-fluoropyridine, trimethylacetic acid, trifluoroacetic acid, silver trifluoroacetate and water. 2-Fluoropyridine was prepared by the diazotization of 2-aminopyridine in hydrogen fluoride solution.[6] The product was distilled through an efficient fractionating column and a middle cut of constant index of refraction was stored over anhydrous potassium carbonate. Trimethylacetic acid (Eastman Kodak Co.) was distilled through an

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[1] Taken in part from the Ph.D. thesis of A. S. Gow, Jr., The Pennsylvania State University, 1954.

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[4] J. W. Spraner and J. H. Simons, THIS JOURNAL, **64**, 648 (1942).

[5] W. H. Pearlson and J. H. Simons, *ibid.*, **67**, 352 (1945).

[6] A. E. Chichibabin and M. D. Rjozancev, *J. Russ. Phys. Chem. Soc.*, **46**, 1571 (1951).

efficient fractionating column and further purified by fractional crystallization. The trifluoroacetic acid was a sample of that prepared in another investigation.[7] Silver trifluoroacetate was prepared by the addition of silver carbonate to the acid. The resulting solution was filtered and evaporated *in vacuo*. The salt was stored in the dark over phosphorus pentoxide.

Preparation of Samples.—The apparatus and techniques for preparing samples were the same as those used previously,[5] except that slight modifications were employed for those containing trifluoroacetic acid and its silver salt.

The Estimation of the Solubility of Hydrogen Fluoride in Toluene.—Crude values of the concentration of the catalyst in the liquid phase were determined over the extremes of temperature and pressure ranges to be encountered in the kinetic measurements. The method of determining these data was to introduce a known amount of hydrogen fluoride into a vessel almost completely filled with toluene in a thermostat and to measure the equilibrium pressure. From these data it was estimated that the concentration of catalyst varied from about 0.01 to 0.02 f.w./25 cc. of toluene.

The Rate Measuring Apparatus.—The rate measuring apparatus and the devices for introducing the reagents into the reaction system were, with minor modifications, essentially the same as those used previously.[5]

Results

Pressure–time plots of the data from each experiment were made, and values of dP/dt were determined at about ten points along the curve in the same manner as previously described.[5]

Attempts were then made to fit the kinetic data by the equation of the form

$$dP/dt = \frac{R(P_\infty - P)}{S - (P_\infty - P)} \qquad (1)$$

in which R and S are constants. These constants were calculated from the slope and intercept of the best straight line through the points, as determined by the method of least-squares. The constants were used in the integrated form of (1)

$$t = a + b(P_\infty - P) + c \log(P_\infty - P) \qquad (2)$$

The constant of integration was determined by fitting the experimental curve at a central point. In all cases there was a significant deviation of the integrated curve from the experimental points. The extent of this deviation for experiments 11 and 29 is seen in column 3 of Table I.

To obtain a closer fit equation 2 was fitted to the experimental curves by the method of least-squares. The equation was found to fit the data for most of the experiments satisfactorily, as seen in column 4 of Table I. This is also shown in Fig. 1 where the smooth curves for experiments 1, 14 and 16 were obtained from equation 2. For seven of the experiments the curve calculated from equation 2 was appreciably lower than the experimental points at the middle, and it was found that these experiments were correlated satisfactorily by the equation of the form

$$t = a + b \log(P_\infty - P) + c \log [d - (P_\infty - P)] \qquad (3)$$

in which the constants, a, b, c and d, were determined by the method of averages. The agreement with the experimental data is seen in Fig. 1 where the smooth curves for experiments 12 and 20 were obtained from equation 3. In Fig. 1 only one experimental point out of every six is indicated for the sake of clarity in the drawings.

TABLE I

COMPARISON OF THE METHODS OF FITTING THE KINETIC DATA FOR RUNS 11 AND 29

Pressure, mm.	Time obsd., min. elapsed	$\Delta_t(1)^a$	$\Delta t(2)^a$
	Run 11		
495.6	3.8	...	+1.0
505.6	9.8	+0.5	+0.4
531.7	29.6	+0.9	−0.1
559.7	60.5	+0.9	−0.8
589.3	109.9	0.0	−1.6
613.5	170.5	−0.9	−1.2
634.4	250.3	−2.3	0.0
648.5	330.7	−2.8	+2.7
657.8	410.7	−6.8	+2.0
664.4	490.0	−11.2	+2.2
669.1	570.3	−19.1	−3.1
	Run 29		
443.8	4.5	...	0.0
448.0	10.0	+1.3	−0.1
465.8	35.2	+1.4	+0.3
485.5	70.0	+0.8	+0.1
510.1	125.1	0.0	0.0
533.9	194.8	−0.8	+0.1
554.8	275.1	−1.5	+0.4
568.9	345.0	−3.5	−0.7
581.6	419.9	−3.5	+0.2
591.2	490.1	−5.4	−0.8
600.6	570.1	−5.3	+0.4

[a] Δt is the time as calculated by the particular equation minus the experimental time at the pressure indicated.

Anomalous initial kinetic effects were observed in six of the experiments. At the start of experiments 14, 16 and 17, in which the initial pressure of hydrogen chloride was high, the pressure rapidly decreased below that observed prior to the addition of *t*-butyl chloride. Also, the initial points determined in experiments 14 and 16 formed a very slightly S-shaped curve. These effects are probably due to the solution of hydrogen chloride and catalyst in the increased quantity of liquid and are shown in Fig. 1. In experiments 7, 8 and 35 at 35° there was an initial rapid decrease in the rate as the reaction proceeded. This kinetic effect was similar to that previously observed at low hydrogen fluoride pressure.[4] No expression could be found which

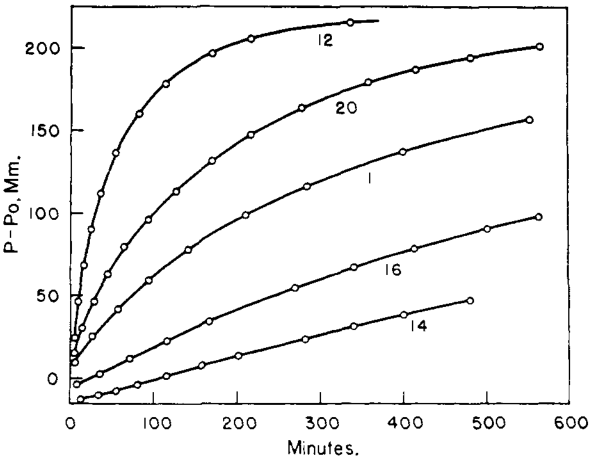

Fig. 1.—Typical rate curves.

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[7] J. H. Simons and K. E. Lorentzen, THIS JOURNAL, **74**, 4746 (1952).

Table II

Summary of Rate Data for the Alkylation of Toluene with t-Butyl Chloride as Catalyzed by Hydrogen Fluoride and Promoted by Various Bases

W, refers to water; P, to fluoropyridine; T, trimethylacetic acid; S, silver trifluoroacetate; F, trifluoroacetic acid.

1 Expt. T = 25° except as noted below	2 Initial HCl pressure, mm.	3 t-BuCl, g.	4 HF pressure, mm.	5 P_0, mm.	6 $P_\infty - P_0$, mm.	7 $t_{1/2}$, (min.)	8 a	9 b	10 $-c$	11 d
15	201.4	0.9788	509.7	742.7	212.6	82.3	816.8	0.3071	377.6	
14	400.4	0.9659	400.4	832.3	210.4[a]	1206[a]	9150.6	1.476	4028	
16	201.3	1.0114	401.4	634.4	220.7	660[a]	6568.5	2.370	3015	
17	101.0	0.9839	401.4	534.5	216.5	476.3	4983.9	2.161	2331	
18	50.7	1.0216	401.8	483.8	224.1	375.9	4263.6	2.048	2009	
19	20.8	0.9643	402.5	455.4	212.1	317.2	3859.7	2.306	1870	
1		0.9670	401.6	434.0	210.4	234.4	2830.8	1.599	1367	
2		1.0078	401.2	433.4	220.2	277.6	3384.9	1.804	1619	
3		0.9627	401.8	434.3	211.1	259.9	3669.2	2.192	1651	
24		0.9350	401.2	432.1	194.7	242.0	2937.3	1.954	1451	
25		1.0001	401.4	433.5	217.2	285.8	3493.2	1.966	1680	
34		1.0016	401.0	433.0	218.0	245.9	3118.7	1.824	1507	
4 (15)		1.0282	300.3	320.3	205.7	297.1	3852.7	2.642	1902	
10 (15)		1.0263	300.5	320.5	209.1	291.0	3893.0	2.709	1924	
5 (15)		1.0069	321.3	341.4	199.1	149.8	3101.7	−902.6	560.7	353.2
6 (15)		1.0378	351.8	372.1	206.6	78.3	1840.9	−502.9	314.8	343.9
7 (35)		0.9933	452.6	503.1	236.2	1098[a]	10711.9	2.572	4804	
8 (35)		1.0141	505.6	556.1	242.2	405.1	4784.3	1.942	2215	
35 (35)		0.8294	503.7	553.5	194.3	345.3	4028.3	2.303	1965	
9 (35)		0.8883	552.8	602.8	209.3	158.0	1937.6	1.095	938.1	
13	Promoter concn., mole/25 cc. $\times 10^4$	0.9954	415.6	447.5	220.6	202.2	2601.4	1.526	1257	
11		0.9344	450.2	482.1	201.6	97.4	1329.0	1.027	667.2	
12		0.9944	510.8	542.7	219.5	34.1	5297.6	−236.1	1452.7	2064.7
26	1.5P	1.0084	400.8	432.3	222.3	185.0	2195.9	1.055	1040	
27	2.9P	1.0006	400.9	432.6	220.8	153.4	1866.3	0.9439	889.6	
20	5.9P	0.9954	400.3	432.0	221.1	119.4	1975.9	−641.7	233.0	329.4
21	11.8P	1.0125	400.3	432.2	224.1	78.5	1251.7	−454.6	109.5	266.5
22	17.7P	0.9946	399.7	431.3	222.0	59.3	943.8	−349.9	77.59	253.1
23	24.5P	1.0074	401.0	432.9	223.1	53.9	1505.9	−333.9	299.4	477.8
28	1.5T	1.0108	401.8	434.0	222.7	236.0	2926.0	1.585	1400	
29	2.9T	1.0054	400.4	432.6	221.9	228.6	2869.2	1.590	1377	
30	5.8T	0.9989	399.9	431.9	222.4	202.3	2525.6	1.393	1211	
31	11.6T	0.9919	401.1	433.4	217.7	156.3	1890.0	0.9814	903.5	
32	17.4T	1.0227	400.3	432.1	225.5	143.0	1740.0	0.8816	826.4	
33	6.6W	0.9883	400.8	432.8	215.7	171.8	1982.4	0.9524	941.1	
36	0.5S	1.0086	401.1	431.2	219.5	240.7	3039.6	1.799	1469	
37	6.6W + 0.5S	1.0203	402.8	434.8	224.6	176.0	2078.0	0.9663	980.2	
38	32.4F	1.0004	402.0	436.2	219.8	102.0	1593.6	−530.8	175.7	317.4

[a] Estimated.

would satisfactorily correlate these initial points. For these six experiments the initial data were not used in determining the constants in equation 2. The initial portions of the smooth curves for these experiments in Fig. 1 were drawn through the experimental points, while the remainder were obtained from equation 2.

A summary of the essential data from thirty-eight of the experiments is given in Table II. Column 1 gives the number of the experiments. Column 2 gives the initial pressure of hydrogen chloride or the concentration of the promoter. Column 3 gives the amount of t-butyl chloride introduced into the reaction vessel. In column 4 is recorded the initial pressure of hydrogen fluoride. Where no promoter was in solution this is the recorded increase in pressure on addition of hydrogen fluoride. Where a promoter was used, a correction equal to the initial pressure of the promoter in the vessel was added to the recorded increase in pressure, as hydrogen fluoride would combine with the promoter and reduce its pressure to a negligible amount. This was obtained from the observed vapor pressure of a sample of dry toluene prepared in the same sampling operation with those containing various amounts of a given promoter. Column 5 gives the pressure observed prior to the addition of t-butyl chloride. In column 6 is recorded the observed total rise in pressure ($P_\infty - P_0$). That for experiment 14 was estimated from the total rise in pressure per gram of t-butyl chloride as determined from the other experiments and the amount of t-butyl chloride introduced. In column 7 is recorded the reaction half-time, which is the observed elapsed time when the pressure rise was one-half of the total. For experiments 14–19 the half-time was determined from the final equilibrium pressure and a corrected initial pressure as calculated from equation 2. The half-times for experiments 7, 14 and 16 were calculated from equation 2. In column 8–11 are recorded the constants for equations 2 and 3. Although experiment 12 could also be correlated by equation 2, a better fit near the initial portion of the experimental curve was obtained using equation 3.

Discussion of Results

It was found that slopes calculated from equations 2 or 3 were significantly different in magnitude from those observed at the same points along the initial portion of the experimental curve for most of the experiments. This was particularly true of experiments in which the rate was greatly accelerated. This can be seen from the data of experiment 11 in Table I. Therefore reaction half-times, instead of calculated initial rates, were used in comparing the rates of reaction.

A comparison of experiments 1, 2, 3, 24, 25 and 34 indicates the precision of the measurements. The results are in good agreement with those obtained earlier.[5] Experiments 4–13 confirm the previously observed high order dependency of the rate upon the hydrogen fluoride pressure.[4,5]

The strong retardation of the rate by hydrogen chloride in experiments 14–19 indicates that the mechanism involves a reaction of hydrogen chloride.

The initial rapid decrease in the rate and the large half-times observed in experiments 7, 8 and 35 indicate a rapid decrease in the concentration of the catalyst by reaction with *t*-butyl chloride in the early stages of the reaction in these experiments, as the reaction under study has a high order rate dependency upon the hydrogen fluoride pressure, and it is known that organic fluorides alkylate very slowly in the absence of hydrogen fluoride.[8]

The rate of reaction, as seen in Table II, increases with the increasing concentration of promoter. It can be seen that the three oxygen-containing promoters have approximately the same effect at the same molar concentration, and this effect is essentially equal to that found by Pearlson and Simons[5] for the promoters they studied. A comparison of experiment 27 with 31 indicates that the promotional effect of 2-fluoropyridine is approximately four times as great as that observed for the other promoters, probably indicating a greater basicity. Experiments 33, 36 and 37 indicate that the promotional effect of silver trifluoroacetate is negligible at low concentrations.

Mechanism

The preferred mechanism for the reaction under study which explains all of the experimental facts is essentially the same as that proposed by Pearlson and Simons,[5] with a few modifications. It involves the mutual action of an acid molecule (hydrogen fluoride) and a basic one (the promoter) on an assemblage of molecules containing the reactants. A hydrogen transfer throughout this assemblage results in the formation of the products.

In the mechanism herein proposed most of the *t*-butyl chloride reacts in a reversible reaction forming *t*-butyl fluoride and hydrogen chloride, while the remainder reacts in a one-step alkylation reaction to form the products. Assuming a mechanism of this type the reactions are

$$n\mathrm{HF} + m\mathrm{BH} + \mathrm{TH} + \mathrm{BuCl} \xrightarrow{k_1} n\mathrm{HF} + m\mathrm{BH} + \mathrm{BuT} + \mathrm{HCl} \quad (4)$$

$$\mathrm{BuCl} + (n+1)\mathrm{HF} + m\mathrm{BH} \underset{k_3}{\overset{k_2}{\rightleftarrows}} \mathrm{BuF} + \mathrm{HCl} + n\mathrm{HF} + m\mathrm{BH} \quad (5)$$

$$n\mathrm{HF} + m\mathrm{BH} + \mathrm{TH} + \mathrm{BuF} \xrightarrow{k_4} (n+1)\mathrm{HF} + m\mathrm{BH} + \mathrm{BuT} \quad (6)$$

in which HF is hydrogen fluoride; BH, any basic species; TH, toluene; BuCl, *t*-butyl chloride; BuF, *t*-butyl fluoride; BuT, *p*-*t*-butyltoluene; and n and m, coefficients. In the mechanisms previously proposed for this reaction,[4,5] it was assumed that reaction (4) was the primary reaction, while reaction (5) occurred to only a small extent. In addition, it was postulated that some of the *t*-butyl fluoride formed could react with *t*-butyl chloride to form polymers which would alkylate to form *t*-butyltoluene. Strong doubt is cast upon some of these assumptions, however, by the following facts: (1) the concentration of tertiary halide is low, (2) *t*-butyl chloride and hydrogen fluoride react to form a mixture of products which would alkylate the aromatic ring forming other products in addition to the *t*-butyl compound,[9] (3) *t*-butyltoluene was the only alkylate found by Spraner and Simons,[4] and (4) fluorides alkylate approximately ten times as fast as chlorides of the same carbon structure under conditions similar to those of the present work.[8]

Assuming that reactions (4), (5) and (6) are the principal reactions involved in the mechanism, the rate equations are

$$\mathrm{d(HCl)}/\mathrm{d}t = K_1(\mathrm{BuCl})(\mathrm{HF})^n + K_2(\mathrm{BuCl})(\mathrm{HF})^{(n+1)} - K_3(\mathrm{BuF})(\mathrm{HCl})(\mathrm{HF})^n \quad (7)$$

$$\mathrm{d(BuF)}/\mathrm{d}t = K_2(\mathrm{BuCl})(\mathrm{HF})^{(n+1)} - K_3(\mathrm{BuF})(\mathrm{HCl})(\mathrm{HF})^n - K_4(\mathrm{BuF})(\mathrm{HF})^n \quad (8)$$

In these equations the contributions of the basic species and toluene have been omitted, as these can be considered constant for any one experiment. The contribution of hydrogen chloride to the acidic species has been neglected, as Simons and Hart[10] have shown it to be effective as an alkylating agent but only significant at higher temperatures and pressures.

To obtain an approximate correlation of the data it is assumed that $\mathrm{d(BuF)}/\mathrm{d}t$ is negligibly small and that the acidic species remains constant. As these assumptions are invalid at the start of the reaction, the derived expressions are, therefore, unsatisfactory for use in calculating the initial rates. In addition, it is assumed, as justified previously,[4] that (BuCl) is proportional to $(P_\infty - P)$ and (HCl) to $[(P_\infty - P_0) + (P_\infty - P)]$. The rate equations become

$$\mathrm{d}P/\mathrm{d}t = K_1(P_\infty - P) + K_2(P_\infty - P) - K_3(\mathrm{BuF})[(P_\infty - P_0) - (P_\infty - P)] \quad (9)$$

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(8) J. H. Simons and G. C. Bassler, THIS JOURNAL, **63**, 880 (1941).

(9) J. H. Simons, G. H. Fleming, F. C. Whitmore and W. E. Bissinger, *ibid.*, **62**, 451 (1940).

(10) J. H. Simons and H. Hart, *ibid.*, **66**, 1309 (1944).

$$K_2(P_\infty - P) - K_3(\mathrm{BuF})[(P_\infty - P_0) - (P_\infty - P)] - K_4(\mathrm{BuF}) = 0 \quad (10)$$

When the expression for (BuF) obtained from equation 10 is substituted in (9), the rate equation in terms of the experimental variables is

$$\mathrm{d}P/\mathrm{d}t = K_1(P_\infty - P) + \frac{K_2K_4(P_\infty - P)}{K_3[(P_\infty - P_0) - (P_\infty - P)] + K_4} \quad (11)$$

Upon integration of equation 11 and rearrangement of terms, equation 3 is obtained. If it is assumed that the contribution of reaction (4) to the total rate of reaction is negligibly small, equation 2 is obtained upon integration of equation 11 and rearrangement of terms. This would indicate that reactions (5) and (6) are the principal reactions in the mechanism, while reaction (4) becomes more important as the reaction is greatly accelerated, as, for example, in experiments 5, 6, 20–23 and 38. Since P_0 and the "steady state" concentration of catalyst are not accurately known, values of the rate constants in equation 11 cannot be calculated from the present data.

Mechanisms involving isobutylene, carbonium ions or free radicals as intermediates in reaction (5) cannot explain the initial kinetic effects in experiments 7, 8 and 35. In addition, mechanisms involving ions or free radicals involve too high an energy of activation, as shown by Pearlson and Simons.[5]

The results of the present work indicate that a simple step by step mechanism cannot explain the experimental facts, but that a hydrogen or proton transfer is involved. This, despite the fact that the reaction under study is probably one of the very simplest of the organic chemical reactions of the condensation type, points out the necessity for a more critical examination of other reactions for which mechanisms have been proposed.

Acknowledgments.—We express our appreciation to the Allied Chemical and Dye Corporation for financial aid during part of the time this research was in progress. Thanks are due Dr. R. W. Taft, Jr., for his helpful suggestions concerning the interpretation of the data.

UNIVERSITY PARK, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XXVI. Some Heat Capacity, Entropy and Free Energy Data for Seven Compounds Containing Oxygen

BY GEORGE S. PARKS, WILLIAM D. KENNEDY, ROBERT R. GATES, JOHN R. MOSLEY, GEORGE E. MOORE AND MELVIN L. RENQUIST

RECEIVED JULY 26, 1955

Heat capacity measurements between 80 and 300°K. have been made upon the following seven compounds: *n*-heptyl alcohol, cetyl alcohol, furfuryl alcohol, cyclopentanol, *n*-butyraldehyde, *n*-heptaldehyde and methyl ethyl ketone. From these calorimetric data the corresponding molal entropies at 298.16°K. have been derived and in turn, with the aid of suitable enthalpy values, the free energies of formation have been computed for all the compounds, save the heptaldehyde.

The present measurements were made during the decade starting with 1940 and available facilities did not provide temperatures below the boiling point of liquid nitrogen. However, extrapolation of entropies below 80°K. introduces uncertainties of the order of one unit, or less, in the molal entropy of any of these compounds, corresponding to a maximum of about 300 cal. in the resulting free energy value. This latter figure is equivalent to an uncertainty of merely 0.012% in the heat of combustion of cetyl alcohol and about 0.049% in that of furfuryl alcohol. Thus the accuracy of the enthalpy data is generally the limiting factor in evaluating the molal free energies of such organic compounds.

Materials.—Our samples of these compounds were the best obtainable at the time of the measurements. The observed melting points and the mole % purity, as estimated from relative equilibrium melting temperatures in the course of fusion determinations, are given in Table I. In the case of the six substances which are liquids at room temperature the main impurities were undoubtedly the air (or nitrogen in the case of furfuryl alcohol) dissolved at 1 atm. pressure and small amounts of water. The values for the probable "weight % purity" given in the last column were accordingly computed on the assumption that these were the only significant contaminants.

TABLE I

OBSERVED MELTING POINTS AND ESTIMATED PURITY

Compound	Formula	M.p., °K.	Purity Mole %	Purity Wt. %
n-Heptyl alcohol	$C_7H_{16}O$	240.0	98.2	99.7
Cetyl alcohol	$C_{16}H_{34}O$	321.8	99.7	..
Furfuryl alcohol	$C_5H_6O_2$	258.5	99.2	99.8
Cyclopentanol	$C_5H_{10}O$	256.9	99.8	99.9
n-Butyraldehyde	C_4H_8O	176.2	97.7	99.4
n-Heptaldehyde	$C_7H_{14}O$	229.3	96.9	99.5
Methyl ethyl ketone	C_4H_8O	186.0	99.7	99.9

The *n*-heptyl alcohol, *n*-butyraldehyde and *n*-heptaldehyde were Eastman Kodak Co. materials, which were dried, respectively, with calcium oxide, calcium chloride and anhydrous sodium sulfate, and then fractionally distilled. The cetyl alcohol, also an Eastman Kodak Co. product, was used without further purification. The cyclopentanol and methyl ethyl ketone were special preparations which had been made for us by the Phillips Petroleum Co. and the Shell Development Co., respectively. The furfuryl alcohol was a similar preparation from the Quaker Oats Co., which we subsequently purified further in a fractional distillation over sodium carbonate in an atmosphere of nitrogen.

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure