is 0.0071 and in the bubble point temperature is 0.44 K.

Glossary

B_{ij}	second virial coefficient, cal/mol
C	number of components
D	deviation of pair of points c and d
h_0	height of the peak
K	constant defined by eq 1
m	weight, g
N	number of data points
P_i	vapor pressure of pure component, atm
P	total pressure, atm
Q	defined by eq 8
R	gas constant, 1.987 cal/(mol K)
T	temperature, K
V	molar vapor volume of the mixture mL/mol
V_i	molar vapor volume of component *i*, mL/mol
V_i^L	molar liquid volume of pure component *i*, mL/mol
x_i	mole fraction of component *i* in the liquid phase
y_i	mole fraction of component *i* in the vapor phase
Z	compressibility
Λ_{ij}	parameters in Wilson equation
γ_i	liquid-phase activity coefficient of component *i*
ϕ_i	vapor-phase fugacity coefficient of component *i*
ϕ_i°	vapor-phase fugacity coefficient of pure saturated component *i* at P_i° and system temperature
α_i, β_i, δ_i	constants in eq 5

Subscripts

b	boiling point
c, d	pair of data points
i	component *i*
j	component *j*
l	data point
s	base component

Registry No. MeOH, 67-56-1; EtOH, 64-17-5; *i*-PrOH, 67-63-0.

Literature Cited

(1) Gmehling, J.; Onken, U. "Vapor-Liquid Equilibrium Data Collection"; Dechema: Frankfurt, 1977; Chemistry Data Series Vol. 1, part 2a.
(2) Hala, E.; Pick, J.; Fried, V.; Vilim, O. "Vapor-Liquid Equilibrium"; Pergamon Press: London, 1958.
(3) Prausnitz, J. M. "Molecular Thermodynamics of Fluid-Phase Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1969.
(4) TRC Tables, "Selected Values of Properties of Chemical Compounds"; Thermodynamcis Research Center Data Project: Texas A & M University: College Station, TX, 1981.
(5) Ambrose, D.; Sparke, C. H. S.; *J. Chem. Thermodn.* **1970**, *2*, 631-45.
(6) Ellis, S. R. M.; Froome, B. A. *Chem. Ind.* (*London*) **1954**, 237-40.
(7) Medina, A. G. Ph.D. Thesis, University of Birmingham, Birmingham, U.K., 1976.
(8) Pirzada, I. M.; Hills, J. H. *Analyst* (*London*) **1983**, *108*, 1096-101.
(9) Weinberg, B. B. *J. Chromatogr.* **1964**, *16*, 40-6.
(10) Weissberger, A., Ed. "Technique of Organic Chemistry"; Elsevier: New York, 1965; Vol. VII.
(11) Delzenne, A. O. *Chem. Eng. Data Ser.* **1958**, *3*, 224-30.
(12) Tsonooulos, C. *AIChE J.* **1974**, *20*, 263-72.
(13) Boublik, T.; Fried, V.; Hala, E. "The Vapor Pressure of Pure Substances"; Elsevier: Amsterdam, 1973.
(14) Holmes, M. J.; Van Winkle, M. *Ind. Eng. Chem.* **1970**, *62*, 21-31.
(15) Prausnitz, J. M.; Anderson, J.; Grens, E.; Eckert, C.; Hsieh, R.; O'Connell, J. "Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria; Prentice-Hall: Englewood Cliffs, NJ, 1980.
(16) Ambrose, D.; Broderick, B. E.; Townsend, R. *J. Appl. Chem. Biotechnol.* **1974**, *24*, 359-72.
(17) Ballard, L. H.; Van Winkel, M. *Ind. Eng. Chem.* **1952**, *448* 2450-3.
(18) McDermott, C.; Ellis, S. R. M. *Chem. Eng. Sci.* **1965**, *20*, 293-6.
(19) Nagahama, K.; Suzuki, I.; Hirata, M. *J. Chem. Eng. Jpn.* **1971**, *4*, 1-5.

Received for review May 25, 1983. Revised manuscript received July 2, 1984. Accepted September 10, 1984.

Kinetics and Equilibrium Data of the Dehydration–Hydration Reaction between Diacetone Alcohol and Mesityl Oxide in Phosphoric Acid

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The velocities of dehydration of diacetone alcohol and hydration of mesityl oxide were studied in regions of 8.6–85.2% phosphoric acid. Because the reactions are acid-catalyzed, the reaction velocities in both directions were increased as the acid concentration increased. The reaction kinetics fit the reversible first-order model with respect to the concentration of reactants, including the activity of water. These results are consistent with the mechanisms proposed by a previous investigator in which the rate-determining step is addition or removal of protons. Equilibrium constants were derived from solution composition and specific rate constants which agreed with each other. The equilibrium constant did not change with acid concentration in the dilute range, but increased slightly at higher acid concentrations. The reaction velocities and the equilibrium constants increased with increasing temperature, and the activation energies were 18.8 and 12.7 kcal/mol for the dehydration and hydration reactions, respectively.

The condensation of acetone in strong acid produces mesityl oxide through the dehydration of diacetone alcohol (*1*–*3*). The dehydration kinetics have been investigated in the presence of catalysts such as ion-exchange resins (*4*), polymers (*5*, *6*), and dimethyl sulfoxide (*7*). The velocity of the reverse reaction, hydration, also has been investigated in different acids of modest concentration (*8*, *9*).

A recent study in this laboratory of the purification of wet-process phosphoric acid with acetone extraction (*10*) showed that small amounts of mesityl oxide were formed in removing the acetone from the purified acid by distillation at atmospheric pressure. The amount of mesityl oxide present was affected by the concentration of the acid and the temperature of the reaction.

During the analysis for mesityl oxide by gas chromatography, it also was found that the mesityl oxide was unstable in H_3PO_4 solution and gradually changed to another compound which had a different boiling point and gave a different peak in the gas chromatogram. This new peak position corresponds to that of diacetone alcohol, and the new compound was positively

Table I. Equilibrium Reactions of Diacetone Alcohol and Mesityl Oxide in Phosphoric Acid Media

				equilibrium soln[a]				
expt		initial soln		mo concn, % of total organic compd				
no.	series	H_3PO_4 concn, wt %	temp, °C	for A or B	av	$(mo)_e$:$(da)_e$	a_w	K_e[d]
1	A[b]	8.60	25	5.19	5.25	0.0553	0.981	0.0544
2	B[c]	8.60	25	5.30				
3	A	17.2	25	5.32	5.35	0.0565	0.956	0.0540
4	B	17.2	25	5.37				
5	A	25.8	25	5.52	5.51	0.0583	0.920	0.0536
6	B	25.8	25	5.49				
7	A	34.4	25	5.98	5.94	0.0632	0.869	0.0549
8	B	34.4	25	5.90				
9	A	51.6	25	7.10	7.12	0.0767	0.697	0.0535
10	B	51.6	25	7.14				
11	A	68.8	25	13.67	13.87	0.161	0.412	0.0663
12	B	68.8	25	14.07				
13	A	76.5	25	22.54	22.76	0.295	0.239	0.0705
14	B	76.5	25	22.97				
15	A	85.2	25	47.04	46.14	0.857	0.102	0.0874
16	B	85.2	25	45.23				
17	A	17.2	39.7	8.70	8.69	0.0956	0.956	0.0914
18	B	17.2	39.8	8.68				
19	A	17.2	55.1	13.15	13.06	0.1485	0.956	0.1420
20	B	17.2	54.8	12.97				
21	A	17.2	70.1	18.03	17.45	0.2114	0.956	0.2021
22	B	17.2	69.2	16.96				

[a] Reactions were started by adding 5 mL of either diacetone alcohol or mesityl oxide to 495 g of phosphoric acid solution. [b] Reaction starting with 0.93 wt % diacetone alcohol (da). [c] Reaction starting with 0.96 wt % mesityl oxide (mo). [d] $K_e = (mo)_e a_w/(da)_e$.

identified by its infrared absorption pattern. The object of this study was to determine the equilibrium kinetics of the hydration and dehydration reactions involving mesityl oxide and diacetone alcohol over a wide range of phosphoric acid concentration and at different temperatures. The effect of concentration of the organic reactant in the acid media at 25 °C also was determined.

Experimental Section

Reagent-grade diacetone alcohol and mesityl oxide were redistilled, and reagent-grade phosphoric acid was used without further purification. Acid of the desired concentration was preequilibrated in a water bath (±0.2 °C), and the specified amounts of diacetone alcohol or mesityl oxide were added to the acid while stirring. In each kinetic experiment 495 g of phosphoric acid solution and 5 mL of either diacetone alcohol (series A) or mesityl oxide (series B) were the starting solutions. The phosphoric acid concentration ranged from 8.6 to 85.2 wt % at 25 °C, while the concentration at 17.2% H_3PO_4 was used to study the temperature effect from 25 to 70.1 °C. A small portion of the reacting solution was removed after various times, and the reaction was quenched by dilution with water. The measurements were terminated and the system was considered at equilibrium when the ultraviolet absorption readings did not change for a period of 24 h.

The concentrations of diacetone alcohol and mesityl oxide were determined by the ultraviolet absorbance of the diluted sample by using 1-mm depth in a variable path length cell of a Cary 17 spectrophotometer. Mesityl oxide has a strong absorption peak at 243 nm where $\epsilon = 1.14 \times 10^4$ (ϵ = molar extinction coefficient). This extinction coefficient is in good agreement with previous values (1.11×10^4) (*8*). Diacetone alcohol has a very weak peak at 249 nm, at which frequency $\epsilon = 72.4$. This extinction coefficient at 243 nm is reduced to 68.

Results and Discussion

The decomposition of diacetone alcohol to mesityl oxide can be expressed as a reversible reaction with the specific rate constants for dehydration and hydration being k_1 and k_{-1}, s^{-1}, respectively.

$$\underset{\text{diacetone alcohol}}{(CH_3)_2C(OH)CH_2COCH_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{mesityl oxide}}{(CH_3)_2C{=}CHCOCH_3} + \underset{\text{water}}{H_2O} \quad (1)$$

Neither mesityl oxide nor diacetone alcohol was converted to acetone under the experimental conditions of these tests, as had been reported under extreme conditions (*11*). Therefore, the compounds involved in this study are mesityl oxide, diacetone alcohol, phosphoric acid, and water. The activity of water influences the hydration rate and the equilibrium constant since water is a reactant in the hydration reaction and a product in the dehydration reaction. This effect can be significant at high acid concentrations where the activity of water changes significantly; this has been observed in the hydration rate of esters (*12*) and acid-catalyzed isomerization (*13*) in sulfuric acid.

The expression

$$K_e = (mo)a_w/(da) \quad (2)$$

was used to calculate the equilibrium constant, K_e, from the analysis of the equilibrated solutions, where it was assumed that the activity coefficients of mesityl oxide and diacetone alcohol are the same because of their similar structure. The concentrations of mesityl oxide (mo) and diacetone alcohol (da) were measured from the absorbance at 243 and 249 nm, respectively, by solving the two absorption equations for the two concentrations; the sum of the two concentrations was checked with the initial total input concentration of organic compounds in each experiment. The activity of water (a_w) was taken from Elmore et al. (*14*). The results (Table I) are in good agreement with respect to the percent of total organic material as mesityl oxide in the equilibrated solution, regardless of which material was the starting compound. The data indicate that the solutions had reached an equilibrium state (column 5, Table I); the equilibrium constant (K_e) was determined from the average of the equilibrium compositions for the A and B series where the starting compound was diacetone alcohol and mesityl oxide, respectively, and is shown in Table I (column 9) and Figure 1.

Table II. Kinetics of the Equilibrium Reaction of Diacetone Alcohol and Mesityl Oxide in Phosphoric Acid Media[a]

expt no.	H_3PO_4 concn, %	temp, °C	10^6k_1, s^{-1}	Δk_1, %	10^6k_{-1},[b] s^{-1}	Δk_{-1}, %	K_r[b]	ΔK_r, %
1, 2	8.6	25.0	1.951	0.59	35.13	0.36	0.0555	0.69
3, 4	17.2	25.0	4.710	0.54	84.90	0.40	0.0555	0.67
5, 6	25.8	25.0	9.146	0.50	164.5	0.37	0.0556	0.62
7, 8	34.4	25.0	16.77	0.36	299.2	0.30	0.0561	0.47
9, 10	51.6	25.0	47.95	0.90	855.7	0.30	0.0560	0.95
11, 12	68.8	25.0	130.3	0.56	2171	0.65	0.0600	0.86
13, 14	76.5	25.0	183.3	0.85	2835	0.93	0.0647	1.26
15, 16	85.2	25.0	263.5	0.90	3300	1.00	0.0799	1.35
17, 18	17.2	39.75	21.14	0.39	238.1	0.19	0.0888	0.43
19, 20	17.2	54.95	83.15	0.66	606.5	0.35	0.137	0.75
21, 22	17.2	69.70	295.9	0.86	1382	0.88	0.214	1.23

[a] Reactions were started by adding 5 mL of either diacetone alcohol or mesityl oxide to 495 g of phosphoric acid solution. Both starting materials were used at each acid concentration. [b] The units of k_{-1} are listed as s^{-1} because the bimolecular reaction becomes pseudo first order at constant water activity and the activity of water, a_w, in the reaction medium is referenced to pure water with an activity of unity. The second-order value of k_{-1} in $kg \cdot mol^{-1} \cdot s^{-1}$ can be obtained by dividing these values by 55.51 $mol \cdot kg^{-1}$. Similarly, the value of K_r in $mol \cdot kg^{-1}$ is obtained by multiplying the listed values by 55.51.

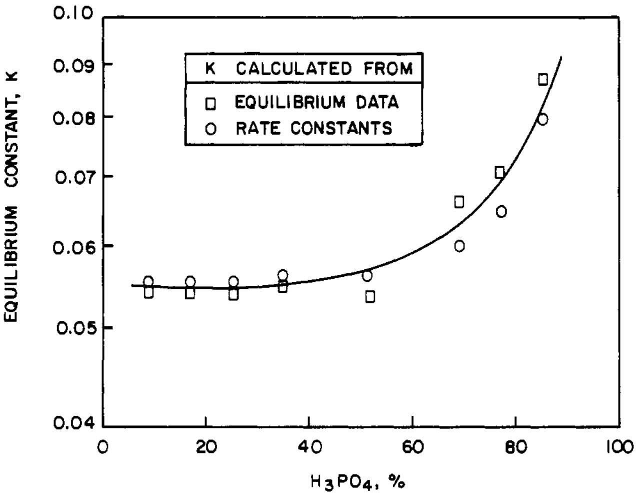

Figure 1. Effect of H_3PO_4 concentration on equilibrium constants in the system H_2O–H_3PO_4–mesityl oxide–diacetone alcohol at 25 °C (organic concentration <0.1 *m*).

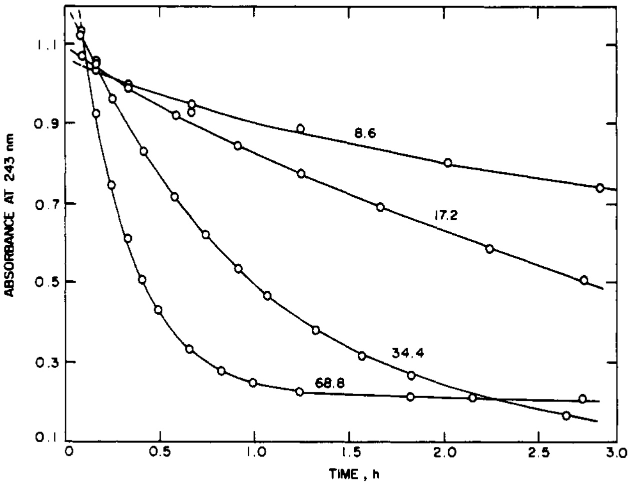

Figure 2. Effect of concentration of H_3PO_4 on reaction of mesityl oxide at 25 °C (numbers on curves denote H_3PO_4 concentration in percent).

The equilibrium constant also is defined as the ratio of the specific rate constants, $K_r = k_1/k_{-1}$. Starting with diacetone alcohol, the rate of production of mesityl oxide can be expressed as

$$d(mo)/dt = k_1(da) - k_{-1}(mo)a_w \tag{3}$$

The rate of production of diacetone alcohol when mesityl oxide is the starting material is

$$d(da)/dt = -k_1(da) + k_{-1}(mo)a_w \tag{4}$$

We let $\alpha = (mo)/(mo)_e$, e.g., the fraction of mesityl oxide formed at time *t* with respect to the equilibrium concentration when diacetone alcohol is the starting solution; and $\beta = (da)/(da)_e$, which similarly expresses the approach to equilibrium when mesityl oxide is the starting solution, where $(mo)_e$ and $(da)_e$ are the equilibrium concentrations of mesityl oxide and diacetone alcohol, respectively.

We also assume that the activity of water (a_w) is constant for a particular experiment since the concentration of organic matter was less than 0.1 *m* in the kinetic studies and other components are constant. The activity of water was calculated as the ratio of the partial pressure of water over the phosphoric acid solution to that of pure water at the same temperature (*14*). The activities of water in the system organic matter–H_3PO_4–H_2O were calculated from those of the system H_3PO_4–H_2O by using Raoult's law.

On integration, eq 3 and 4 become

$$\ln [Mk_1/(Mk_1 - C\alpha)] - Ct = 0 \tag{5}$$

$$\ln [Nk_{-1}/(Nk_{-1} - C\beta)] - Ct = 0 \tag{6}$$

where

$$C = k_1 + k_{-1}a_w$$

$$M = (da)_0/(mo)_e$$

$$N = \{(mo)_0/(da)_e\}a_w$$

Solving for α and β we obtain

$$\alpha = (Mk_1/C)(1 - e^{-Ct}) \tag{7}$$

$$\beta = (Nk_{-1}/C)(1 - e^{-Ct}) \tag{8}$$

Equations 5–8 were used to calculate the values of k_1 and k_{-1} by a nonlinear, least-squaring procedure using α,t or β,t measurements. Examples of kinetic data are presented in Figures 2 and 3 and complete experimental kinetic data are provided in the supplementary material (see paragraph at end of text regarding supplementary material). The four values of k_1 and k_{-1} from the four evaluation methods of eq 5–8 were averaged by weighting each value with the reciprocal of the square of its error to obtain the values shown in columns 4 and 6 of Table II. The errors associated with these averages were determined (*15*) and are shown in columns 5 and 7 of Table II. The values of the equilibrium constant, $K_r = k_1/k_{-1}$, and their errors are given in columns 8 and 9 of Table II, the errors being obtained by the law of propagation (*15*). The excellent agreement between the equilibrium values (K_e from Table I and K_r from Table II; Figure 1) at different temperatures and

Table III. Activation Parameters at 17.2% H_3PO_4[a]

reaction	ΔE^*, cal/mol	A, s^{-1}	ΔH^*,[b] cal/mol	ΔS^*,[b] eV
dehydration (k_1)	18755 ± 105	$(2.69 \pm 0.49) \times 10^8$	18174 ± 105	−16.37 ± 0.02
hydration (k_{-1})	12668 ± 81	$(1.66 \pm 0.22) \times 10^5$	12076 ± 81	−32.93 ± 0.30
equilibrium (K)	6048 ± 55	$(1.49 \pm 0.14) \times 10^3$	5546 ± 55	−44.32 ± 0.20

[a] Calculated by using least-squares method. [b] Enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) at 25 °C.

Table IV. Equilibrium in the System Mesityl Oxide–Diacetone Alcohol–Phosphoric Acid–Water at 25 °C

expt no.	initial soln: concn, wt %: H_3PO_4	initial soln: concn, wt %: da[a]	initial soln: concn, wt %: mo[b]	initial soln: concn, mol/L: da[a]	initial soln: concn, mol/L: mo[b]	final soln: mo concn, % of total organic compd	final soln: $(mo)_e$:$(da)_e$	a_w	K_e[c]
41	15.98	17.65	0	1.602	0	11.1	0.125	0.931	0.116
42	30.49	15.25	0	1.602	0	12.6	0.145	0.883	0.128
31	42.43	15.62	0	1.602	0	13.8	0.159	0.822	0.131
43	53.49	14.77	0	1.602	0	16.1	0.191	0.727	0.139
48	54.12	0	13.77	0	1.748	18.6	0.228	0.724	0.165
32	63.42	14.01	0	1.602	0	18.4	0.225	0.619	0.139
35	64.12	0	13.05	0	1.748	20.9	0.264	0.615	0.162
44	72.37	13.32	0	1.602	0	20.0	0.250	0.505	0.126
49	73.13	0	12.41	0	1.748	22.8	0.293	0.501	0.147
33	75.34	11.89	0	1.602	0	26.3	0.356	0.372	0.132
36	81.29	0	11.82	0	1.748	29.5	0.418	0.370	0.155
51	60.94	3.27	0	0.401	0	10.8	0.121	0.537	0.065
56	61.10	0	3.02	0	0.437	12.0	0.136	0.537	0.073
52	57.74	6.65	0	0.801	0	12.8	0.146	0.566	0.083
57	59.12	0	6.16	0	0.894	14.4	0.168	0.565	0.095
53	49.42	21.56	0	2.403	0	23.0	0.300	0.649	0.195
58	50.26	0	20.21	0	2.621	27.2	0.374	0.643	0.240
54	44.13	29.95	0	3.200	0	30.0	0.428	0.672	0.288
59	45.19	0	28.27	0	3.496	34.3	0.523	0.663	0.347
55	38.38	39.07	0	4.005	0	35.7	0.555	0.663	0.368
60	37.66	0	37.15	0	4.369	42.5	0.740	0.650	0.481

[a] Diacetone alcohol. [b] Mesityl oxide. [c] $K_e = (mo)_e a_w/(da)_e$.

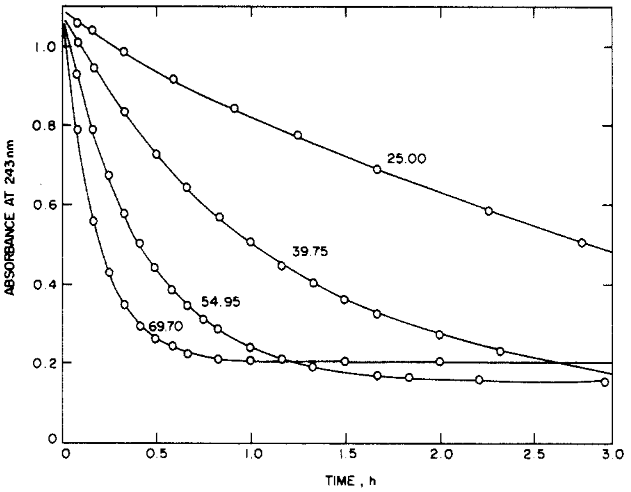

Figure 3. Effect of temperature on reaction of mesityl oxide in 17.25% H_3PO_4 (numbers on curves denote temperature in degrees Celsius).

phosphoric acid concentrations indicates the validity of the data and its interpretation.

The equilibrium constants at low concentrations of organic matter remained essentially constant as the concentration of phosphoric acid was increased up to 50%, but the values gradually increased at the higher acid concentrations (Figure 1). The values of k_1 and k_{-1} increased as the acid concentration increased, and the increases are parallel to each other to 50% phosphoric acid. The increase of the reaction rates with increasing acid concentration indicates that the acid acts as a promoter of the reaction in both directions. However, k_{-1} appeared to approach a plateau faster than did k_1 at very high concentrations of phosphoric acid (Figure 4).

The effect of temperature on k_1, k_{-1}, K_r, and K_e in 17.2% H_3PO_4 was studied in the range 25–70 °C (Tables I and II).

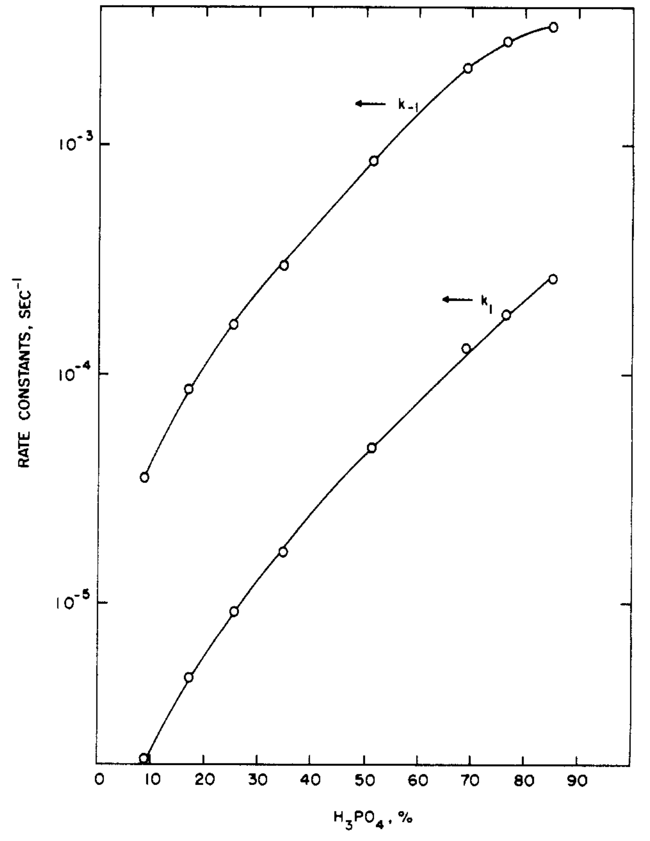

Figure 4. Effect of H_3PO_4 concentration on rate constants and in the system H_2O–H_3PO_4–mesityl oxide–diacetone alcohol at 25 °C (organic concentration <0.1 *m*).

The activity of water in the acid was assumed to be independent of the temperature. The activation energy, E^*, cal/

mol, and the frequency factors, A, s^{-1}, were evaluated from the linear relationship of the Arrhenius plots (Figure 5); and other activation parameters were derived from the activation energy, frequency factor, and calculated k values (*16*) and are listed in Table III.

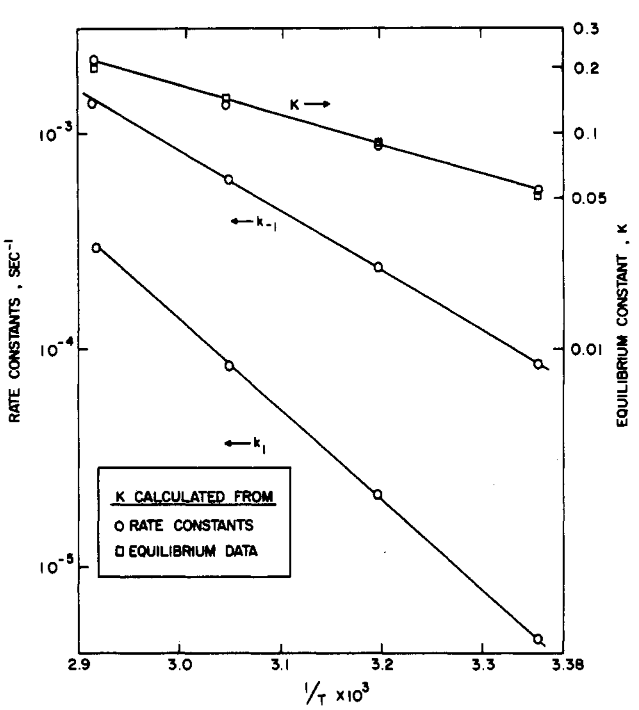

Figure 5. Effect of temperature on rate and equilibrium constants in 17.2% H_3PO_4 (organic concentration <0.1 *m*).

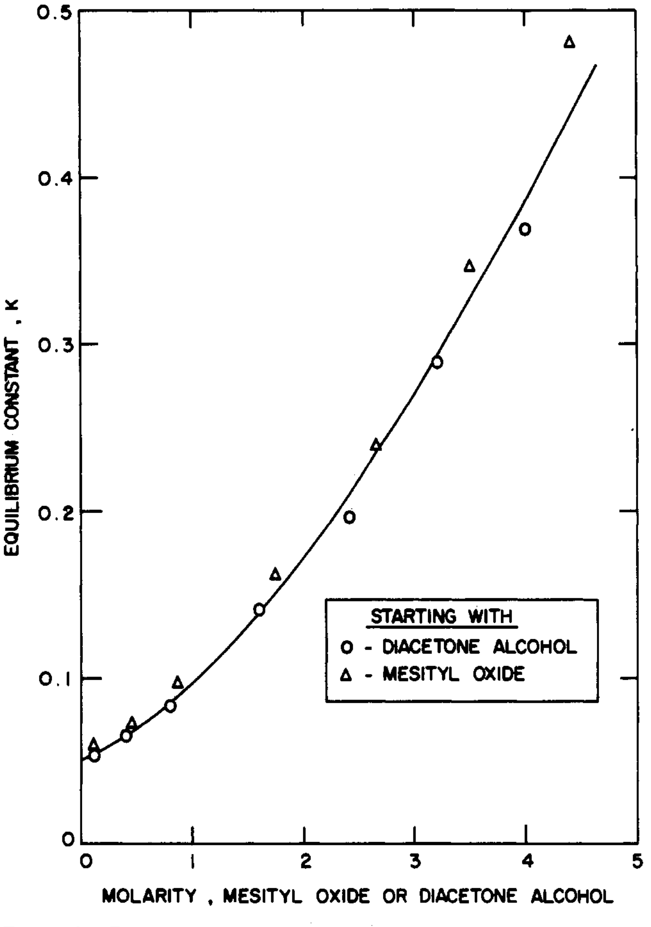

Figure 6. Effect of initial concentration of organic compounds on equilibrium constants at 25 °C.

The effect of the concentration of initial diacetone alcohol or mesityl oxide on the equilibrium constant at 25 °C was studied over a range of acid concentrations. The experimental conditions and results are summarized in Table IV and Figure 6. In evaluating the equilibrium constant at different acid concentrations, we used the water activity data of Elmore et al. (*14*) for the system $H_2O-H_3PO_4$; and this was modified further by Raoult's law for the mole fraction of the organic material. The increase of the equilibrium constant with increasing concentration of organic material may indicate that the activity coefficients of mesityl oxide and diacetone alcohol at equilibrium in phosphoric acid solution are not constant under the conditions studied. Another possibility is the formation of a complex compound between mesityl oxide and phosphoric acid. This assumption is partly verified by our tests that show the complete extraction of mesityl oxide by CCl_4 from dilute phosphoric acid solution and the incomplete extraction from concentrated phosphoric acid or from higher mesityl oxide solution where K is larger than 0.055. This result may be due to different distribution coefficients of the postulated complex compound and of mesityl oxide between the phosphoric acid and CCl_4 phase.

In conclusion, the kinetic and equilibrium data of the acid-catalyzed dehydration and hydration reactions between diacetone alcohol and mesityl oxide in wide ranges of phosphoric acid concentration were obtained. The data suggest that the reaction mechanism is first order relative to the organic reactants and is consistent with several mechanistic interpretations proposed by earlier workers (*9*, *13*, *17*, *18*). However, the reversible hydration mechanism suggested by Jensen et al. (*17*) may be the most plausible one where the rate-determining step is the proton removal or addition step because our results fit very well with the model if the activity of water in the medium is considered.

Registry No. Mesityl oxide, 141-79-7; diacetone alcohol, 123-42-2.

Literature Cited

(1) Guidry, C. L.; Walker, M. A. F. *Polymer* **1970**, *11*, 548–52.
(2) Nagakura, S.; Minegishi, A.; Stanfield, K. *J. Am. Chem. Soc.* **1957**, *79*, 1033–7.
(3) Noller, C. R. "Chemistry of Organic Compounds", 2nd ed.; W. B. Saunders: Philadelphia, PA, 1957; p 208.
(4) Lemcoff, N. O.; Cunningham, R. E. *J. Catal.* **1971**, *23*, 81–92.
(5) Kazanskaya, A. S.; Ryabtseva, N. V.; Panidi, I. S.; Paushkin, Ya. M.; Sladkov, A. M.; Kudryavtsev, Yu. P. *Dokl. Akad. Nauk SSSR* **1971**, *198*, 629–30.
(6) Paushkin, Ya. M.; Panidi, I. S.; Ryabtseva, N. V.; Kazanskaya, A. S.; Sladkov, A. M.; Mescheryakov, S. V.; Yatsko, O. I.; Lunin, A. F. *Kinet. Katal.* **1970**, *11*, 1354–6.
(7) Traynelis, V. J.; Hergenrother, W. L.; Hanson, H. T.; Valicenti, J. A. *J. Org. Chem.* **1964**, *29*, 123–9.
(8) Bell, R. P.; Preston, J.; Whitney, R. B. *J. Chem. Soc.* **1962**, 1166–70.
(9) Scott, J. J.; Brower, K. R. *J. Am. Chem. Soc.* **1967**, *89*, 2682.
(10) Walters, H. K., Jr.; Kim, Y. K.; Hatfield, J. D. U.S. Patent 4 152 402, May 1, 1979.
(11) Smith, G. G.; Yates, B. L. *J. Org. Chem.* **1965**, *30*, 2067–8.
(12) Yates, K.; McClelland, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 2686–92.
(13) Noyce, D. S.; Jorgenson, M. J. *J. Am. Chem. Soc.* **1963**, *85*, 2420–6.
(14) Elmore, K. L.; Mason, C. M.; Christensen, J. H. *J. Am. Chem. Soc.* **1946**, *68*, 2528–32.
(15) Meyer, S. L. "Data Analysis for Scientists and Engineers"; Wiley: New York, 1975; p 43.
(16) Jensen, J. L.; Corré, D. J. *J. Org. Chem.* **1971**, *36*, 3180–3.
(17) Jensen, J. L.; Corré, D. J. *J. Org. Chem.* **1974**, *39*, 2103–7.
(18) Noyce, D. S.; Reed, W. L. *J. Am. Chem. Soc.* **1958**, *80*, 5539–42.

Received for review December 14, 1982. Revised manuscript received July 30, 1964. Accepted September 5, 1984.

Supplementary Material Available: Kinetic data (12 pages). Ordering information is given on any current masthead page.