

is not established. Despite this a value of  $\Delta H^\circ < 27$  kcal. is arrived at. Further, the reported activation energy of  $21.8 \pm 3$  kcal. leads to a value of  $A_3$  of  $10^{11.3}$  l./mole-sec. This is about 3 powers of 10 too high for a reaction of this type (step 3 refers to  $\text{BH}_3 + \text{B}_2\text{D}_6$ ).

No other  $A$  factor comparable to this has ever been obtained for such complex species. The lower limit of  $E$  of 18.3 kcal. would reduce this to  $10^{9.3}$  l./mole-sec. and be more reasonable. We conclude again that no value can be deduced for  $\Delta H^\circ$ .

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARLETON COLLEGE, NORTHFIELD, MINN.]

## The Thermodynamics of the Thermal Decomposition of Acetic Acid in the Vapor Phase<sup>1</sup>

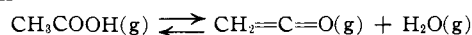
BY WILLIAM C. CHILD, JR., AND ARTHUR J. HAY

RECEIVED JULY 15, 1963

Acetic acid in the vapor phase has been found to decompose reversibly into ketene, water, and acetic anhydride at temperatures in the range 268–330°. Equilibrium constants for the two simultaneous equilibria implied have been measured over this temperature range, and  $\Delta H^\circ$  and  $\Delta S^\circ$  for the two reactions have been obtained. The calculated heats of reaction are in good agreement with calorimetric values. The product of the activity coefficients of water and acetic anhydride in acetic acid solution have also been calculated and found to agree with literature values. On the other hand, the entropy of acetic acid monomer which is derived differs from the spectroscopic value. For this reason, several changes in the statistical thermodynamic treatment are suggested to yield a set of thermodynamic functions for acetic acid monomer which are in fair agreement with all the experimentally determined thermodynamic properties of acetic acid.

More than 30 years ago Muhlhauser and Trautz<sup>2</sup> reported equilibrium constants for the thermal decomposition of acetic acid vapor, at 400–640°, into the assumed products acetic anhydride and water. The value which they obtained for  $\Delta H$  for the reaction, 41 kcal., seemed questionable at the time and can now be ruled out altogether when compared with the calorimetric value, 10 kcal.<sup>3</sup> Later, in a study of the kinetics of the thermal decomposition of acetic acid vapor at 500–900°, Bamford and Dewar<sup>4</sup> found that ketene and water are produced in one of several reactions which occur. It is therefore possible that Muhlhauser and Trautz, who did not confirm the identities of the products, were actually studying the latter reaction. In fact, a rough reworking of their data can be made, giving a  $\Delta H$  of approximately 35 kcal. for the ketene reaction, which is comparable to the calorimetric value of 31 kcal.<sup>3</sup> A further study of the equilibria occurring in acetic acid vapor at high temperature thus seems called for.

The possibility that the thermodynamics of the reaction



can be obtained offers a route to the thermodynamic properties of acetic acid monomer, because both ketene and water have been thoroughly studied. The most recent and complete study of acetic acid in the gaseous state is that of Weltner,<sup>5</sup> whose values for the monomer are based mainly on statistical thermodynamics. At the time of his publication, there were uncertainties regarding (1) the magnitude of the potential barrier hindering the internal rotation of the methyl group, (2) the frequency of the O–H out-of-plane bending motion and perhaps one or two of the other vibrational assignments, and (3) the energy difference between the *cis* and *trans* isomers for rotation of the O–H group about the C–O bond. During the intervening years the barrier to rotation of the methyl group has been determined by microwave spectroscopy,<sup>6</sup> but doubt remains on the other points. Therefore, it was felt that an independent determination of the entropy of acetic acid monomer would be desirable.

Finally, a comparison between the vapor phase decomposition and the liquid phase decomposition recently reported<sup>7</sup> should be of interest.

### Experimental

**Reagents.**—Analytical reagent grade acetic acid was purified and its purity checked as described previously.<sup>7</sup> The mole fraction of water in the acid was about  $7 \times 10^{-4}$ . (The acid used in the experiments at 300.6°, however, had a mole fraction of water of approx.  $1.3 \times 10^{-3}$ .) Reagent grade acetic anhydride was distilled at atmospheric pressure before use as a titrant in the water determinations.

**Apparatus for Thermal Decomposition.**—A static system was employed. A 2-l. reaction vessel, which was made from 110-mm. Pyrex tubing, was located in an electrically heated, crucible type furnace. Transfer of samples to and from the reaction vessel was accomplished by means of a conventional vacuum system.

At the beginning of an experiment, the reaction vessel was evacuated for 2 hr. at the temperature to be employed for the thermal decomposition. A sample of acetic acid was then admitted by connecting the vessel, through a three-way capillary stopcock and heated tubing, to a reservoir of liquid acetic acid, which was held at a temperature high enough to produce a vapor pressure somewhat greater than the pressure desired in the reaction vessel. The acetic acid vapor was equilibrated anywhere from several hours to several days. In some experiments, indicated in Table I, the initial temperature of the sample was at least 15° higher than the final temperature. This initial heating period was long enough to give an extent of reaction greater than that found ultimately at the final temperature. Equilibrium was thus approached from the product side of the reaction.

For removal of the sample, the three-way stopcock was turned to connect the vessel to a U-trap, filled with glass beads, at –78°, which in turn led to a small flask, at –196°, containing a weighed quantity (3 g.) of water. Unreacted acetic acid, acetic anhydride, and water were retained in the trap at –78°, while ketene passed through and was frozen in the flask at –196°. After a stopcock above this flask was closed, the latter was warmed to room temperature to allow the ketene to react with water to produce acetic acid, which later was determined spectrophotometrically, as described below. The contents of the U-trap were transferred to a small tube, which was sealed from the line and maintained at –78° until the time of analysis.

Temperatures were measured with an iron-constantan thermocouple, calibrated at the melting points of benzoic acid, tin, cadmium, and zinc. The thermocouple was located in a well along the axis of the cylindrical reaction vessel. Thermocouple e.m.f.'s were measured with a Leeds and Northrup potentiometer. The temperature was held constant to within  $\pm 1^\circ$  by means of a proportional controller, which supplied current to the main heater around the core of the furnace and to an auxiliary heater in the transite top above the reaction vessel. The temperature variation along the axis of the vessel was found to be no greater than 3° over the upper three-fourths of the vessel. Along the lower one-fourth there was a decrease toward the bottom of about 6°. Perpendicular to the axis of the vessel the variation was 3°. Since the thermocouple was in a position of nearly average temperature, the temperature is believed accurate to  $\pm 2^\circ$ .

(7) J. A. Knopp, W. S. Linnell, and W. C. Child, Jr., *J. Phys. Chem.*, **66**, 1513 (1962).

(1) Taken in part from the senior honors thesis (1961) of A. J. Hay.

(2) W. Muhlhauser and M. Trautz, *Z. physik. Chem. Bodenstein-Festband*, **319** (1931).

(3) See the Discussion section of this article.

(4) C. H. Bamford and M. J. S. Dewar, *J. Chem. Soc.*, 2877 (1949).

(5) W. Weltner, Jr., *J. Am. Chem. Soc.*, **77**, 3941 (1955). Erratum: *ibid.*, **83**, 5045 (1961).

(6) W. J. Tabor, *J. Chem. Phys.*, **27**, 974 (1957).

Pressures were measured with a "click" gage,<sup>8</sup> which was calibrated before and after each experiment, and a mercury manometer. The uncertainty in the pressure measurements is estimated as  $\pm 1$  mm.

The portion of the click gage which extended above the top of the furnace was heated with a separate Nichrome winding; the temperature of this part of the apparatus was within  $10^\circ$  of that of the reaction vessel. The combined volume of the click gage and the 6-cm. length of capillary tubing leading from the vessel to the three-way stopcock was less than 0.2% of the total volume.

**Identification of Products.**—In early experiments, acetic acid vapor at 300–500 mm. was maintained at a temperature in the range, 375–440°, for 2–3 hr. A portion of the sample was then led directly to an Aerograph, Model A-100, for analysis by gas chromatography. The number of peaks appearing in addition to the acetic acid and water peaks suggested that three or perhaps four reactions occur under these conditions. The study was therefore confined to temperatures below 350°, where only a few peaks were found.

In a second series of experiments at 260–310° and 150–500 mm., the sample, after 3 hr., was separated into fractions freezing at  $-78$  and  $-196^\circ$ . The  $-196^\circ$  fraction was transferred to the Aerograph, which contained a Ucon Polar column at  $25^\circ$ . One major peak appeared, which had a retention time identical with that of ketene prepared synthetically from the thermal decomposition of acetic anhydride. In one of these experiments, the exit gas from the Aerograph was passed through a trap at  $-196^\circ$  containing about 0.5 g. of methanol. The infrared absorption spectrum of the contents of the trap showed a peak at  $5.8 \mu$ , indicating the presence of methyl acetate. The spectra of methanol and 1% methyl acetate in methanol were also obtained for comparison.

The ultraviolet spectrum of the  $-78^\circ$  fraction exhibited a strong absorbance relative to pure acetic acid in the region, 250–280  $m\mu$ . The shape of the spectrum was identical with that of acetic anhydride in acetic acid.<sup>9</sup>

It was concluded, therefore, that under the experimental conditions noted above, the products of the thermal decomposition are water, ketene, and acetic anhydride.

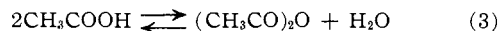
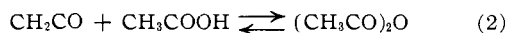
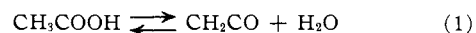
**Quantitative Analysis of Products.**—Ketene was determined as acetic acid in water solution by measuring absorbances at 210, 220, and 230  $m\mu$  with a Beckman DU spectrophotometer. Blank corrections were applied to account for small amounts of impurities picked up during the vacuum line operation. From the weight of solution and the concentration of acetic acid, the number of moles of ketene present at equilibrium could be calculated. The uncertainty in this value is believed to be  $\pm 5\%$ .

The fraction consisting of acetic acid, acetic anhydride, and water in the sealed tube was weighed, transferred in a drybox to a 1-cm. stoppered cell, and diluted with a measured amount of purified acetic acid if the liquid level was too low. The mole fractions of acetic anhydride and water were then determined as in the previous study.<sup>7</sup> The water present in the acetic acid which served as diluent was taken into account. The uncertainties in the mole fractions of acetic anhydride and water are estimated as  $\pm 2$  and  $\pm 5\%$ , respectively.

Since the extent of decomposition was never greater than 3.5 mole %, mole fractions were calculated by assuming that the total number of moles at equilibrium is equal to the weight of the acetic acid–anhydride–water fraction divided by the molecular weight of acetic acid.

## Results

In view of the product analyses, two simultaneous equilibria must occur in the temperature range 268–330°. These equilibria can be represented by any two of the equations



Only reaction 3 has been detected in the liquid phase.<sup>7</sup> The vapor phase equilibria will be discussed in terms of reactions 2 and 3. The expressions for  $K_p$  for these reactions are

$$K_2 = X_{\text{an}}/X_{\text{ket}}X_{\text{ac}}P \text{ and } K_3 = X_{\text{an}}X_{\text{w}}/(X_{\text{ac}})^2 \quad (4)$$

(8) D. F. Smith and N. W. Taylor, *J. Am. Chem. Soc.*, **46**, 1393 (1924).

(9) There is a possibility that this anhydride is formed by a reaction between acetic acid and some ketene which might be caught in the trap at  $-78^\circ$ . However, a vapor pressure of about 240 mm. for ketene at  $-78^\circ$  makes this unlikely. The self-consistency of the final thermodynamic results should be regarded as additional evidence that the anhydride is present in the equilibrium system.

where  $X_{\text{an}}$ ,  $X_{\text{ket}}$ ,  $X_{\text{ac}}$ , and  $X_{\text{w}}$  are the mole fractions of anhydride, ketene, acid, and water, respectively, and  $P$  is the pressure.

The results are given in Table I. It was observed that reaction 2 reached equilibrium more rapidly than did reactions 3 or 1. Thus it was possible to use the values of  $K_2$  from several experiments in which the calculated values of  $K_3$  were significantly different from the equilibrium values. It should be noted that the results of five of the experiments in which equilibrium was approached from the product side are consistent with the other results. In the two remaining experiments of this type the equilibration time at the final temperature was not great enough to give an acceptable value for  $K_3$ . In each case  $K_3$  is too large.

The material balance is generally satisfactory. For many experiments the difference between  $X_{\text{w}}$  and  $X_{\text{ket}} + X_{\text{an}}$  is close to  $7 \times 10^{-4}$ , which is the approximate water content of the original acid. In other cases, the difference runs up to two or three times this value. The discrepancy can be attributed to the gain of a small amount of water from the Pyrex glass during equilibration and manipulation of the sample on the vacuum line, or, in a few instances, to the loss of some ketene during the removal of the sample.

**Equilibrium 3.**—At each temperature the values of  $K_3$  for the various pressures agree with one another within experimental error. The only exception occurs at the highest temperatures and lowest pressures, where  $K_3$  is significantly low. Perhaps this variation is caused by the appearance of side reactions. In any case, it is felt that departures from ideal gas behavior are slight. To support this judgment, the fugacity coefficients for the pure gases at the total pressures of the equilibrium mixtures were estimated at 300.6°. The fugacity coefficient for acetic acid was calculated from dimerization constants reported in the literature.<sup>10</sup> Extrapolation above experimental temperature ranges was necessary. Pitzer's method<sup>11</sup> of corresponding states was used to estimate the fugacity coefficient of acetic anhydride; the coefficient for water was obtained from the second virial coefficient.<sup>12</sup> It was found that the largest correction to be applied to  $K_3$  changed the value of  $K_3$  by only 1%. The experimental  $K_3$ 's are therefore regarded as thermodynamic quantities.

A plot of the logarithm of the average value of  $K_3$  at each temperature *vs.*  $1/T$  showed some curvature. However, the curvature could not be explained by any reasonable estimate of  $\Delta C_p$  for the reaction, and a straight line could be fitted to the points within experimental error. The equation for the line, determined by the method of least squares, is

$$\log K_3 = -2206.0/T - 0.202 \quad (5)$$

From the equation one obtains the thermodynamic quantities  $\Delta H_3^\circ = 10.1 \pm 0.8$  kcal. and  $\Delta S_3^\circ = -0.9 \pm 1.3$  e.u. at the average temperature, 572.3°K. The indicated errors represent the 90% confidence level as determined in the least squares treatment.

**Equilibrium 2.**—At the three highest temperatures a trend toward decreasing  $K_2$  with increasing pressure was observed. This is illustrated in Fig. 1 for the data at 313.6°. At 285.0° the scatter in the points obscures any possible trend, while at 268.4° only the high pressure region was covered because of the long times required to attain equilibrium.

(10) (a) M. D. Taylor, *J. Am. Chem. Soc.*, **73**, 315 (1951); (b) A. E. Potter, Jr., P. Bender, and H. L. Ritter, *J. Phys. Chem.*, **59**, 250 (1955); (c) E. W. Johnson and L. K. Nash, *J. Am. Chem. Soc.*, **72**, 547 (1950).

(11) K. S. Pitzer, D. Z. Lippmann, R. F. Curl, Jr., C. M. Huggins, and D. E. Petersen, *ibid.*, **77**, 3433 (1955).

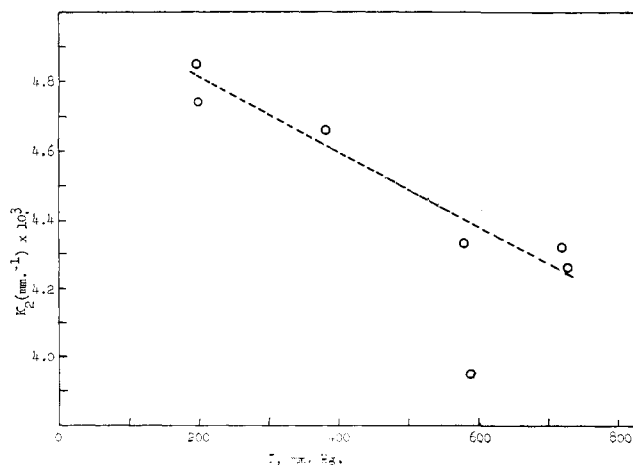
(12) J. S. Rowlinson, *Trans. Faraday Soc.*, **45**, 979 (1949).

TABLE I  
 RESULTS OF EQUILIBRIUM STUDIES

Temp., °C.	Pressure, mm.	Equil. time, hr.	$X_w$ $\times 10^3$	$X_{ket}$ $\times 10^3$	$X_{an}$ $\times 10^2$	$K_2$ (mm. <sup>-1</sup> ) $\times 10^3$	$K_3$ $\times 10^5$
268.4	715	22 <sup>a</sup>	8.00	0.54	6.87	18.1	5.50
	749	9.5 <sup>a</sup>	8.20	<sup>b</sup>	7.30		6.18 <sup>c</sup>
	781	39	7.83	0.48	6.55	17.7	5.13
	826	24	7.63	0.43	6.30	18.0	4.94
					Av. 17.9 ± 0.2	5.19 ± 0.21	
285.0	356	30 <sup>a</sup>	10.01	1.80	7.13	11.4	7.42
	362	7 <sup>a</sup>	9.99	1.78	7.63	12.1	7.92 <sup>c</sup>
	510	27	8.95	1.33	7.04	10.6	6.52
	550	40	9.49	1.19	7.68	12.0	7.56
	600	10.5 <sup>a</sup>	9.03	1.15	6.98	10.3	6.52
	639	39	9.83	0.82	7.18	13.9 <sup>d</sup>	7.32
	727	32	10.31	0.69	7.33	14.9 <sup>d</sup>	7.84
					Av. 11.0 <sup>e</sup> ± 0.7	7.2 ± 0.4	
300.6	331	43	12.88	3.19	6.80	6.59	9.18
	392	14 <sup>a</sup>	11.68	2.85	7.71	7.06	9.42
	429	32	11.87	2.65	7.26	6.53	9.01
	504	21.5	11.37	2.38	7.33	6.24	8.70
	705	20	11.79	1.86	7.54	5.87	9.28
	966	6.7	10.42	<sup>b</sup>	8.39		9.11
	977	6.4	11.38	1.34	7.86	6.13	9.34
					Av. 6.08 <sup>e</sup> ± 0.14	9.15 ± 0.18	
313.6	198	34	15.04	6.78	6.34	4.85	10.09 <sup>d</sup>
	200	5.3 <sup>a</sup>	15.84	7.45	6.86	4.74	11.55
	382	21	14.07	4.42	7.66	4.66	11.36
	580	9.3	12.62	3.41	8.35	4.33	11.06
	589	8.8	12.76	3.53	8.01	3.95	10.72
	720	3.2	10.94	2.26	6.89	4.32	7.85 <sup>c</sup>
	728	8.2	12.26	2.82	8.53	4.26	10.97
					Av. 4.22 <sup>e</sup> ± 0.13	11.13 ± 0.26	
329.9	180	16.9	18.64	10.75	6.34	3.40	12.72 <sup>f</sup>
	194	20	18.00	10.61	6.20	3.13	11.99 <sup>f</sup>
	201	11.3	16.50	10.11	5.77	2.93	10.16 <sup>c</sup>
	206	22	18.18	10.61	6.50	3.08	12.69 <sup>f</sup>
	409	11.5	16.26	7.28	7.93	2.75	13.73
	605	5.9	15.04	5.61	8.60	2.61	13.72
	730	5.8	14.60	4.80	9.10	2.67	14.09
					Av. 2.64 <sup>e</sup> ± 0.03	13.5 ± 0.5	

<sup>a</sup> Initial temperature of the sample was at least 15° above the stated temperature; time given refers to final temperature. <sup>b</sup> Ketene concentration was not measured. <sup>c</sup> This value was discarded because equilibrium had not been achieved. <sup>d</sup> Unacceptable result. <sup>e</sup> Average of values for pressures above 500 mm. <sup>f</sup> Since the pressures for these three experiments are nearly the same, the three values were averaged and the result included only once in the average value of  $K_3$ .

A first explanation for this trend was sought in possible departures from ideal gas behavior. In view of the above discussion, this seems unlikely for acetic


 Fig. 1.— $K_2$  vs. pressure at 313.6°.

acid and acetic anhydride. Ketene, having a relatively low critical temperature, should behave ideally at these temperatures. Therefore, such an explanation

seems tenable only if unusual interactions between unlike molecules are postulated.

Another possible cause for the trend is found in the fact that about 5 min. was required for the removal of a sample from the reaction vessel. During this time equilibrium 2 might shift to the left, giving values of  $K_2$  which are too small, mainly at the high pressures, in agreement with the observed behavior. However, an experiment in which the removal of the sample was interrupted for 5 min. after the pressure had decreased to half its original value failed to accentuate this behavior. On the other hand, unusually rapid removal of the sample did result in values of  $K_2$  which were as much as 20% larger than the others, but this change occurred at both high and low pressure. The authors are inclined to believe that in these instances some ketene was lost through reaction or adsorption during the quenching process. Finally, under the hypothesis of shifting equilibrium it is difficult to see why  $K_3$  is found to be independent of pressure, while  $K_2$  is not, unless both equilibria 2 and 3 shift during the removal of the sample. Yet the evidence indicates that reaction 3 is relatively slow.

In the absence of any satisfactory explanation, values of  $K_2$  at pressures above 500 mm. were averaged at each temperature, since these values are relatively constant. The temperature dependence of  $\log K_2$  is

given by the equation

$$\log K_2 (\text{atm.}^{-1}) = 4485.0/T - 7.134 \quad (6)$$

as determined by the method of least squares. The resulting thermodynamic quantities for reaction 2 are  $\Delta H_2^\circ = -20.5 \pm 1.3$  kcal. and  $\Delta S_2^\circ = -32.6 \pm 2.2$  e.u. at 572.3°K. Again, the uncertainties given are nine-tenths errors.

### Discussion

**Comparison of  $\Delta H_3^\circ$  with Calorimetric Value.**—An accurate value for  $\Delta H^\circ$  for reaction 3 in the liquid phase at 30° has been determined by Kistiakowsky and co-workers,<sup>13</sup> and this can be converted without difficulty into the corresponding value for the gas phase reaction at 572.3°K. The calculation is summarized in Table II. In the absence of heat capacity data for acetic anhydride vapor,  $\Delta C_p^\circ$  for reaction 3 in the gas phase was assumed to be zero, in accordance with the first approximation of Benson and Buss.<sup>14</sup> Therefore the calculated  $\Delta H_3^\circ$  is independent of temperature under this assumption. Agreement with the value obtained in this research is satisfactory.

TABLE II

CALCULATION OF  $\Delta H_3^\circ$  AT 572.3°K. FROM CALORIMETRIC DATA

Process <sup>a</sup>	$\Delta H^\circ$ , cal.
2HOAc(l, 303.2°) → Ac <sub>2</sub> O(l, 303.2°) + H <sub>2</sub> O(l, 303.2°)	13,960 <sup>b</sup>
2HOAc(l, 358.5°) → 2HOAc(l, 303.2°)	-77°
Ac <sub>2</sub> O(l, 303.2°) → Ac <sub>2</sub> O(l, 358.5°)	
H <sub>2</sub> O(l, 303.2°) → H <sub>2</sub> O(l, 358.5°)	
2HOAc(g, <sup>d</sup> 358.5°) → 2HOAc(l, 358.5°)	-23,660 <sup>e</sup>
Ac <sub>2</sub> O(l, 358.5°) → Ac <sub>2</sub> O(g, 358.5°)	10,400 <sup>f</sup>
H <sub>2</sub> O(l, 358.5°) → H <sub>2</sub> O(g, 358.5°)	9,920 <sup>g</sup>
2HOAc(g, 572.3°) → 2HOAc(g, 358.5°)	0 <sup>h</sup>
Ac <sub>2</sub> O(g, 358.5°) → Ac <sub>2</sub> O(g, 572.3°)	
H <sub>2</sub> O(g, 358.5°) → H <sub>2</sub> O(g, 572.3°)	
2HOAc(g, 572.3°) → Ac <sub>2</sub> O(g, 572.3°) + H <sub>2</sub> O(g, 572.3°)	10,540
This research	10,100 ± 800

<sup>a</sup> All temperatures in °K. <sup>b</sup> Ref. 13. <sup>c</sup> A value of  $\Delta C_p^\circ = -1.4$  cal./°K. was employed. <sup>d</sup> This refers to the ideal gas, *i.e.*, acetic acid monomer. <sup>e</sup> J. W. Armitage and P. Gray, *Trans. Faraday Soc.*, **58**, 1746 (1962). <sup>f</sup> Taken from the nomogram of D. F. Othmer and D. Zudkevitch, *Ind. Eng. Chem.*, **51**, 791 (1959). <sup>g</sup> F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, Washington, D. C., 1952; and F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Press, Pittsburgh, Penna., 1953. <sup>h</sup>  $\Delta C_p^\circ = 0$  assumed.

**Comparison of  $\Delta H_1^\circ$  with Calorimetric Value.**—For a second comparison reaction 1 rather than 2 is chosen because of the lack of heat capacity data for acetic anhydride vapor.  $\Delta H_1^\circ$  of this research can readily be calculated as  $\Delta H_1^\circ = \Delta H_3^\circ - \Delta H_2^\circ = 30.6 \pm 1.0$  kcal. at 572.3°K. Calculation of the value based on calorimetric data is summarized in Table III. It can be seen that the agreement is again satisfactory.

**Reaction 3 in the Liquid and Gas Phases.**— $K_3$  for the gas phase reaction is related to  $K_3$  for the liquid phase through the equation

$$K_3(g) = K_3(l)[k_{an}k_w/(f_{ac}^\circ)^2]^{15} \quad (7)$$

where  $k_{an}$  and  $k_w$  are the Henry's law constants for acetic anhydride and water, respectively, in acetic acid, and  $f_{ac}^\circ$  is the fugacity of liquid acetic acid. It is

(13) J. B. Conn, G. B. Kistiakowsky, R. M. Roberts, and E. A. Smith, *J. Am. Chem. Soc.*, **64**, 1747 (1942).

(14) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

(15) F. T. Wall, "Chemical Thermodynamics," W. H. Freeman and Co., San Francisco, Calif., 1958, pp. 367-368.

TABLE III

CALCULATION OF  $\Delta H_1^\circ$  AT 572.3°K. FROM CALORIMETRIC DATA

Process <sup>a</sup>	$\Delta H^\circ$ , cal.
HOAc(l, 298.2°) → Ket(g, 298.2°) + H <sub>2</sub> O(g, 298.2°)	43,320 <sup>b</sup>
HOAc(l, 358.5°) → HOAc(l, 298.2°)	-1,845 <sup>c</sup>
HOAc(g, 358.5°) → HOAc(l, 358.5°)	-11,830 <sup>d</sup>
HOAc(g, 572.3°) → HOAc(g, 358.5°)	-4,779 <sup>e</sup>
H <sub>2</sub> O(g, 298.2°) → H <sub>2</sub> O(g, 572.3°)	2,276 <sup>f</sup>
Ket(g, 298.2°) → Ket(g, 572.3°)	3,996 <sup>g</sup>
HOAc(g, 572.3°) → Ket(g, 572.3°) + H <sub>2</sub> O(g, 572.3°)	31,140
This research	30,600 ± 1000

<sup>a</sup> All temperatures in °K. <sup>b</sup> From heats of formation: acetic acid: F. W. Evans and H. A. Skinner, *Trans. Faraday Soc.*, **55**, 260 (1959); ketene and water: National Bureau of Standards Circular 500. <sup>c</sup> Over this temperature range the average value of  $C_p$  for liquid acetic acid is 30.6 cal./°K. mole; see p. 1758 of ref. e, Table II. <sup>d</sup> Ref. e, Table II. <sup>e</sup> Obtained from the enthalpy functions of Table V. <sup>f</sup> Obtained from the enthalpy functions for H<sub>2</sub>O(g) given in "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Research Project 44. <sup>g</sup> Obtained from the enthalpy functions for CH<sub>2</sub>CO(g) given by A. P. Cox and A. S. Ebbitt, *J. Chem. Phys.*, **38**, 1636 (1963).

evident that the ratio on the right side of eq. 7 can be obtained by combining  $K_3(g)$  reported here with  $K_3(l)$  reported earlier.<sup>7</sup> This ratio can then be combined with vapor pressure data to give  $\gamma_{an}^* \gamma_w^*$ , the product of the activity coefficients (based on Raoult's law) of acetic anhydride and water at infinite dilution in acetic acid. Direct determinations of these activity coefficients have been reported in the literature.

After the publication of the liquid phase study, it was found that the stated purity of the acetic anhydride, used to obtain the Beer's law absorptivity for anhydride in acid, was in error. The revised equation for  $K_3(l)$  is

$$\log K_3(l) = -3318.3/T + 1.340 \quad (8)$$

The change is small enough so that the thermodynamic functions reported earlier for acetic anhydride are not affected.

Since the  $\Delta H_3^\circ$  based on calorimetric data and given in Table II is believed more accurate than that derived in this research, we prefer an equation for  $\log K_3(g)$  which is slightly different from eq. 5. The revised equation is particularly needed for extrapolation outside the temperature range of the experiments. Combining the calorimetric  $\Delta H_3^\circ$  with the experimental value of  $K_3(g)$  at 313.6°, we obtain

$$\log K_3(g) = -2303.5/T - 0.030 \quad (9)$$

Equations 7, 8, and 9 can now be combined to give

$$\log [k_{an}k_w/(f_{ac}^\circ)^2] = 1014.8/T - 1.370 \quad (10)$$

For comparison with the literature, the ratio on the left side of eq. 10 can be multiplied by  $(f_{ac}^\circ)^2$  and divided by  $P_{an}^\circ P_w^\circ$  to give

$$k_{an}k_w/P_{an}^\circ P_w^\circ = \gamma_{an}^* \gamma_w^* \quad (11)$$

an equation which is valid provided that  $P_{an}^\circ$  and  $P_w^\circ$ , the vapor pressures of acetic anhydride and water, are equal to the respective fugacities. The fugacity of liquid acetic acid is equal to the partial pressure of monomer in the vapor in equilibrium with the liquid. Thus, dimerization and trimerization constants from the literature must be included along with the other data.

The results at two temperatures, 25 and 99°, are given in Table IV. To confirm that the fugacity of water does not differ significantly from its vapor pressure, the fugacity coefficient of the saturated vapor at 99° was calculated from an equation given by Broch.<sup>16</sup>

(16) J. Broch, *Chem. Abstr.*, **47**, 10931a (1953).

The value is 0.964. It seems unlikely that the deviation for acetic anhydride is any greater.

TABLE IV

PRODUCT OF ACTIVITY COEFFICIENTS OF ACETIC ANHYDRIDE AND WATER IN ACETIC ACID

$t, ^\circ\text{C.}$	$k_{an}k_w / (f_{ac}^\circ)^2$	$P_{an}^\circ, \text{mm.}$	$P_w^\circ, \text{mm.}$	$f_{ac}^\circ, \text{mm.}$	$\gamma_{an}^* \gamma_w^*$	$\gamma_{an}^* \gamma_w^*$
25.0	108	5.0 <sup>a</sup>	23.8	2.73 <sup>b</sup>	6.8	6.9 <sup>e</sup>
99.0	22.8	197 <sup>a</sup>	733	167 <sup>c</sup>	4.4	4.2 <sup>f</sup>
99.0	22.8	197 <sup>a</sup>	733	151 <sup>d</sup>	3.6	4.2 <sup>f</sup>

<sup>a</sup> T. E. Jordan, "Vapor Pressure of Organic Compounds," Interscience Publishers, Inc., New York, N. Y., 1954. <sup>b</sup> J. O. Halford, ref. 17. <sup>c</sup> Calculated from the dimerization and trimerization constants of Ritter and Simons, ref. 22, as revised by Potter, *et al.*, ref. 10b, and the vapor pressure given by A. E. Potter, Jr., and H. L. Ritter, *J. Phys. Chem.*, **58**, 1040 (1954). <sup>d</sup> Calculated from the same vapor pressure and the dimerization constant of Taylor, ref. 10a. <sup>e</sup> References 20, 21, and 7. <sup>f</sup> Reference 21. <sup>g</sup> This research. <sup>h</sup> Literature.

The fugacity of acetic acid at 25° calculated by Halford<sup>17</sup> is based on vapor density data of MacDougall<sup>18</sup> and Fenton and Garner.<sup>19</sup> To correct for the effect of the vapor phase association of acetic acid on their values of  $\gamma_w$  at 25°, Hansen, *et al.*,<sup>20</sup> also used the results of MacDougall. The corresponding correction for  $\gamma_{an}^*$ <sup>7,21</sup> is based on data of Ritter and Simons.<sup>22</sup> Hence, in a comparison of the last two columns of Table IV at 25°, the vapor phase association of acetic acid tends to cancel out, and the comparison shows principally that  $K_3(g)/K_3(l)$  of this research is in accord with the liquid-vapor phase diagrams of Hansen, *et al.*, and Marek.<sup>21</sup> Similarly, at 99°, the values in the second row of Table IV are based on the vapor density data of Ritter and Simons,<sup>10b,22</sup> and the agreement between final values is again satisfactory. The agreement at the end of the third row of the table, however, is not quite so good. In this case the fugacity of liquid acetic acid at 99° has been obtained from the results of Taylor,<sup>10a</sup> who measured the vapor density of acetic acid at low pressure. Taylor assumed the existence of dimer but no higher polymer, while the other authors<sup>10b,c</sup> have postulated a trimer in addition. Undoubtedly the poor agreement in the second comparison at 99° is caused in part by the use of vapor density data from two sources rather than one. Nevertheless, this result does suggest that at temperatures above 99° the saturated vapor may contain trimers.<sup>23</sup>

While eq. 10 should be most valid in the temperature range of the experiments, 200–300°, unfortunately no additional comparisons are possible, because the needed fugacities and Henry's law constants are not available.

**The Entropy of Acetic Acid Monomer.**—The thermodynamic functions for acetic acid monomer have been calculated by Weltner<sup>5</sup> on the basis of an assignment of the vibrational frequencies. A potential barrier of 2500 cal./mole for the hindered rotation of the methyl group was used in these calculations. Recently, a barrier of 483 cal./mole<sup>6</sup> has been found by microwave spectroscopy. A revision of Weltner's values to incorporate this change yields the standard entropies, 68.6 e.u. at 298.15°K., and 81.4 e.u. at 572.3°K., the average temperature of this research. In addition to these statistical thermodynamic values, there are presently available two values based on the third

law entropy of liquid acetic acid.<sup>24</sup> Halford's calculation<sup>17</sup> gives  $69.4 \pm 1.0$  e.u. at 298.15°K., while Weltner's calculation<sup>5</sup> yields 66.9 e.u. (uncertainty not estimated) at 298.15°K.

The entropy of acetic acid monomer can also be obtained from  $\Delta S_1^\circ$  of this research, which is calculated from the relationship,  $\Delta S_1^\circ = \Delta S_3^\circ - \Delta S_2^\circ$ . For  $\Delta S_3^\circ$ , a value of  $-0.1$  e.u., obtained from eq. 9, is used, because eq. 9 is believed to be more accurate than eq. 5. The resulting value of  $\Delta S_1^\circ$  is 32.5 e.u. at 572.3°K. This in turn is combined with the entropies<sup>25</sup> of water and ketene to give for the entropy of acetic acid monomer,  $85.0 \pm 2.2$  e.u. at 572.3°K., 3.6 e.u. greater than Weltner's value.

Starting with the entropy of liquid acetic anhydride at 298.15°K. obtained in the liquid phase study,<sup>7</sup> a calculation of the entropy of acetic acid monomer at 298.15°K. can be made. First, by use of the heat of vaporization<sup>26</sup> and the vapor pressure<sup>27</sup> of acetic anhydride at 298.15°K., the standard entropy of acetic anhydride in the gas phase at 298.15°K. is found to be 93.5 e.u. This value is then combined with  $\Delta S_3^\circ$  and the standard entropy of water vapor to give 69.4 e.u. as the entropy of acetic acid monomer at 298.15°K. The good agreement with Halford's value is not surprising in view of the agreement between values of  $\gamma_{an}^* \gamma_w^*$  (Table IV) and the fact that both calculations are based on the third law entropy of liquid acetic acid at 298.15°K.

It is evident that although the entropy at 298.15°K. calculated from statistical thermodynamics lies between the two experimental values at 298.15°K., the calculated and experimental values differ significantly at 572.3°K. Because of the discrepancy at the higher temperature, two changes have been made in the statistical treatment. First, the C–O bending frequency, which Weltner regards as the most doubtful assignment, is arbitrarily lowered from 536 to 300  $\text{cm.}^{-1}$ . Second, the O–H out-of-plane bending motion, assigned at 650  $\text{cm.}^{-1}$ , is now treated as a hindered rotation rather than as a simple vibration, and the contribution from the 650  $\text{cm.}^{-1}$  frequency is omitted. This change can be important at high temperatures where the harmonic oscillator approximation is questionable.

In a study of the infrared spectra of formic acid monomer, Miyazawa and Pitzer<sup>28</sup> found that the potential barrier hindering the internal rotation of the O–H group is 10.9 kcal./mole above the *cis* configuration and 8.9 kcal./mole above the *trans* configuration. After several trials, it was found that the best agreement with experimental entropies can be achieved if for acetic acid monomer the barriers to rotation of the O–H group are chosen as 5 and 3 kcal./mole for the *cis* and *trans* isomers, respectively. These lower barriers are in qualitative agreement with the conclusion, based on bond lengths, that the bond between the carboxyl carbon and the oxygen of the O–H group has less double bond character in acetic acid than in formic acid.<sup>29</sup> The potential function employed for the internal rotation is

$$V = 2.5(1 - \cos 2\theta) \text{ kcal./mole} \quad (-90^\circ < \theta < 90^\circ)$$

$$V = 2.0 + 1.5(1 - \cos 2\theta) \text{ kcal./mole} \quad (90^\circ < \theta < 270^\circ) \quad (12)$$

(24) G. S. Parks, K. K. Kelley, and H. M. Huffman, *J. Am. Chem. Soc.*, **51**, 1969 (1929).

(25) See ref. *f* and *g* of Table 111.

(26) Reference *f*, Table II.

(27) Reference *a*, Table IV.

(28) T. Miyazawa and K. S. Pitzer, *J. Chem. Phys.*, **30**, 1076 (1959).

(29) F. E. Morris and W. J. Orville-Thomas, *J. Mol. Spectry.*, **6**, 572 (1961). It should be noted, however, that the bond lengths for acetic acid come from an electron diffraction study in 1944 and hence are of unknown accuracy.

(17) J. O. Halford, *J. Chem. Phys.*, **9**, 859 (1941).

(18) F. H. MacDougall, *J. Am. Chem. Soc.*, **58**, 2585 (1936).

(19) T. M. Fenton and W. E. Garner, *J. Chem. Soc.*, 694 (1930).

(20) R. S. Hansen, F. A. Miller, and S. D. Christian, *J. Phys. Chem.*, **59**, 391 (1955).

(21) J. Marek, *Collection Czech. Chem. Commun.*, **21**, 269 (1956).

(22) H. L. Ritter and J. H. Simons, *J. Am. Chem. Soc.*, **67**, 757 (1945).

(23) For other discussion on this point, see ref. 5.

A reduced moment of inertia for the O-H group equal to  $1.31 \times 10^{-40}$  g. cm.<sup>2</sup> was used in the calculations.<sup>17</sup> With the help of standard tables,<sup>30</sup> the revised entropies of each isomer were calculated. The mole fractions of the two isomers were calculated from  $\Delta E_0^\circ = 2.0$  kcal./mole, the partition functions for the isomers being assumed equal for this calculation. Finally, an entropy of mixing was calculated and included with the contributions from each isomer. The resulting molar entropies for acetic acid monomer are: 69.7 e.u. at 298.15°K. and 83.4 e.u. at 572.3°K. These are to be compared with the experimental values,  $69.4 \pm 1.0$  and  $66.9$  e.u. at 298.15°K. and  $85.0 \pm 2.2$  e.u. at 572.3°K.

The proposed alterations in the vibrational assignment for acetic acid monomer are clearly speculative and are intended only to indicate the type of change which is needed to remove discrepancies. The new treatment does at least yield entropies which represent a compromise between values presently available. A complete set of thermodynamic functions based on this revision is given in Table V. In obtaining each function, the contributions from the *cis* and *trans* isomers have been combined. Entropies (and free energies) of mixing have been included,  $\Delta E_0^\circ$  has been added to  $H^\circ - E_0^\circ$  (and  $F^\circ - E_0^\circ$ ) for the *trans* isomer to take account of the different energy zeros, and  $C_p^\circ$  includes the contribution from the change in the mole fractions of isomers with temperature.<sup>31</sup> In addition to these functions, the heat of formation of acetic acid monomer is needed for practical calculations. This value can be calculated from data given in Table III and the references to that table along with  $(H^\circ - E_0^\circ)/T$  from Table

(30) G. N. Lewis and M. Randall, revised by K. S. Pitzer and L. Brewer, "Thermodynamics," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(31) J. G. Aston and J. J. Fritz, "Thermodynamics and Statistical Thermodynamics," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 394-398.

V. The resulting heat of formation is  $-103.1$  kcal./mole at 298.15°K., which becomes  $-100.1$  kcal./mole at 0°K.

TABLE V  
THERMODYNAMIC FUNCTIONS FOR ACETIC ACID MONOMER (CAL./°K. MOLE)

T, °K.	S°	(H° - E <sub>0</sub> °)/T	-(F° - E <sub>0</sub> °)/T	C <sub>p</sub> °
298.15	69.7	12.0	57.7	16.8
300	69.8	12.0	57.8	16.9
400	75.2	13.7	61.5	20.4
500	80.1	15.4	64.7	23.5
600	84.6	16.9	67.7	25.9
700	88.8	18.3	70.5	27.9

$$\Delta H_f^\circ = -100.1 \text{ kcal./mole at } 0^\circ\text{K.}$$

A comparison of  $C_p^\circ$  from Table V with the experimental heat capacity<sup>5</sup> can now be made to test further the plausibility of the revised thermodynamic functions. The most stringent comparison which can be made is at the highest temperature of the heat capacity measurements, 540.0°K., where the contribution from the monomer is greatest and the contribution from the  $\Delta H$  of the monomer-dimer reaction is smallest. When the value of  $C_p^\circ$  (24.4 cal./°K. mole) at 540.0°K., interpolated from Table V, is used with Taylor's results<sup>5,10a</sup> for the monomer-dimer equilibrium, the calculated value is 26.2 cal./°K. mole, compared with the experimental value of 25.7 cal./°K. mole. Thus the thermodynamic functions of Table V are in fair agreement with all the experimentally determined thermodynamic properties of acetic acid which are presently available.

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### The Mechanism of the Anionic Polymerization of Methyl Methacrylate. III. Effects of Solvents upon Stereoregularity and Rates in Fluorenyllithium-Initiated Polymerizations<sup>1</sup>

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Rates of fluorenyllithium-initiated polymerizations of methyl methacrylate have been measured at  $-60^\circ$  in toluene-tetrahydrofuran mixtures containing from 0.1 to 15% tetrahydrofuran by volume and in toluene-diethyl ether mixtures containing from 2 to 20% diethyl ether by volume. The rate of disappearance of monomer under all conditions was kinetically first order, though the slope of plots of  $-\ln M/M_0$  vs. time depended upon monomer concentration in some cases. In all cases, the first-order plots had a finite intercept at zero time, indicating essentially instantaneous formation of the pseudo-terminated low molecular weight polymer first described in paper II of this series.<sup>4</sup> Polymers prepared in toluene-diethyl ether mixtures were highly isotactic, while in toluene-tetrahydrofuran mixtures the polymers were isotactic at low tetrahydrofuran concentrations and syndiotactic at the higher concentrations. In the intermediate range of tetrahydrofuran concentrations, stereoblock polymers were obtained. A kinetic scheme is presented which serves to rationalize the dependence of the rate of polymerization upon initiator concentration and solvent composition. It is assumed that the steady-state concentration of active chains and the configurations of the polymer are a reflection of equilibria between monomer and solvent in the complex about the lithium at the chain end. On the other hand, the molecular weight distribution is assumed to be kinetically determined. Data on the dependence of gel melting point upon molecular weight of low molecular weight fractions indicate that a change in conformation of the polymer chains occurs when the chain length reaches 8-10 monomer units. This conformational change is believed to be responsible for the decrease in probability for pseudo-termination which must occur at this point.

#### Introduction

The great importance of association, dissociation, and exchange equilibria of the organometallic species which are responsible for both initiation and propagation in homogeneous anionic polymerization is uni-

versally recognized. The exact features of the reactions differ appreciably in the polymerizations of different monomers and are strongly affected by solvent composition. In the polymerization of styrene by *n*-butyllithium in hydrocarbon solvents, the initiator exists as hexameric aggregates and the rate of initiation is slow with respect to that of propagation; thus, over a considerable range of the polymerization, there is

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