separation between absorption and emission, and ready photodecomposition is found for the naphthacene carbonium ions.

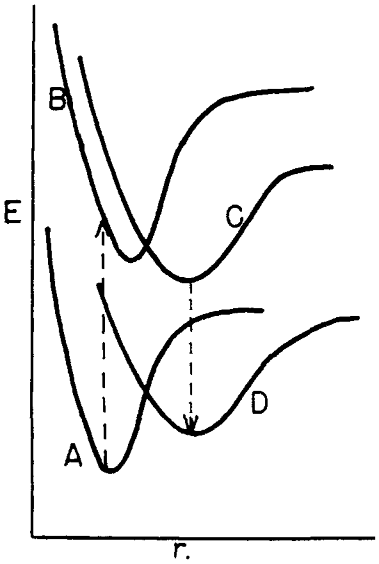

Fig. 10.—Possible potential curves for pyrene carbonium ion system: A, initial carbonium ion; B, excited state of same; C, curve onto which system moves in upper-state tautomerism; D, ground state of photoproduct.

(4) Some ambiguity is present in the case of hexaethylbenzene. The BF_3–hydrocarbon complex and the carbonium ion may in this case be expected to absorb in approximately the same region of the spectrum. The observed absorption peak is very sharp, and so is the corresponding emission. The bands are certainly different in appearance from the usual "carbonium ion" bands, and it is tentatively suggested that they are in fact charge-transfer bands. If this is so, the non-appearance of the "carbonium" band must be attributed to a greater stability of the charge-transfer complex, which perhaps is itself not a good enough donor to form a carbonium ion. This different behavior may be due to the steric effect of the bulky ethyl groups which probably result in some buckling of the aromatic ring.

(5) Finally it is noteworthy that of all the hydrocarbon carbonium ions examined, only that of anthracene showed a long-lived (presumably triplet) phosphorescence spectrum. Although perhaps coincidental, it is remarkable that anthracene is the one hydrocarbon which itself shows so little phosphorescence that the position of its lowest triplet level is in debate.[9]

If it is granted as reasonable that the triplet levels like the singlets will shift to the red in the carbonium ion, the position of the carbonium ion triplet (5,800 Å.) is evidence in favor of the assignment of the anthracene triplet[8] at 5,200 Å. rather than at 6,900 Å.

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(9) C. Reid, *J. Chem. Phys.*, **20**, 1214 (1952).

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The Effect of Water on the Vapor Phase Dissociation of Acetic Acid

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A study of the effect of added water on the vapor phase dissociation of acetic acid shows that dissociation to anhydride and water offers at most a small contribution to the over-all equilibrium at temperatures around 100°. The *PVT* data in the temperature range 90–120° suggest a reversible interaction of water and acid vapor.

The 1 : 1 compound of water and acetic anhydride has long been known to dissociate in the vapor phase.[1] The density of the "compound" falls with increasing temperature or with decreasing pressure from approximately the sum of the densities of water and acetic anhydride to half this value. It is usual to attribute the variable density to an equilibrium between monomer and dimer, *viz.*

$$(CH_3COOH)_2 \rightleftarrows 2CH_3COOH \qquad (I)$$

The data are equally consistent with an equilibrium between water, acetic anhydride and acetic acid dimer, *viz.*

$$(CH_3COOH)_2 \rightleftarrows (CH_3CO)_2O + H_2O \qquad (II)$$

A similar ambiguity concerning the nature of the dissociation products, Ricci has pointed out,[2] applies to any monohydroxy acid, for example HNO_3, HClO, or the like. A resolution of the ambiguity can be achieved in the case of acetic acid by determination of the way added water affects the density of acetic acid vapor. We have made such determinations.

Experimental

We have used a tensiometer of the type described by Sanderson.[3] The acetic acid (C.P.) was recrystallized eleven times according to the method of Ritter and Simons.[4] The acid, however, showed premelting to an extent correspond-

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[1] W. Ramsay and S. Young, *J. Chem. Soc.*, **49**, 790 (1886).

[2] J. E. Ricci, "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand Co., Inc., New York, N. Y., 1951, p. 121.

[3] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 83.

[4] O. H. Ritter and J. H. Simons, THIS JOURNAL, **67**, 757 (1945).

ing to the presence of 0.5 mg. of water per gram of acid. This content of water was assumed in the computation of the equilibrium constants and the expected molecular weights in the presence of added water as shown in Table I.

Both the recrystallized acid and the added water were handled in a vacuum system. A known weight of acetic acid was transferred to the tensiometer and the pressure measured at constant volume (1.1314 l.) over a series of temperatures. Keeping the same charge of acid, a known weight of water was introduced into the tensiometer and the pressure of the acid–water mixture was measured over the same temperature range.

Ideally, water would have no effect on equilibrium I but through "mass action" would affect equilibrium II. Proper choice of the proportions of acid and water maximizes the difference between the average molecular weights to be expected on the basis of the two different equilibria. The difference is at most about six molecular weight units and in our experiments averaged about 5.9 units.

The experimental results appear in Table I. Observed molecular weights (mol. wt. obsd.) are computed on the basis of the ideal gas relations. Molecular weights expected on the basis of equil. I are weighted averages of the experimental molecular weights of acetic acid as determined in this study and corrected molecular weights of water vapor.[5] To some extent the non-ideality of the separate components is allowed for also in the molecular weights expected on the basis of equil. II (mol. wt. II) through the use of the empirically found equilibrium constants, and corrected molecular weights for the added water.

TABLE I

VAPOR DATA FOR ACETIC ACID–WATER SYSTEMS

Pure acid			Pure acid plus added water				
					Apparent molecular weights		
t, °C.	P, mm.	K_p,[a] mm.	t, °C.	P, mm.	(mol. wt. obsd.)	(mol. wt. I)	(mol. wt. II)
Series I							
Acid = 1.4209 g.			Water = 0.0712 g.				
93.0	296.0	63.6	93.7	373.4	80.82	79.90	86.32
104.7	323.7	140.8	102.1	395.8	78.00	77.41	82.94
110.8	338.5	190.7	103.7	399.2	77.66	76.94	82.53
116.8	354.2	257.8	113.4	427.3	74.42	74.03	79.25
119.9	362.8	301.7	118.7	443.5	72.69	72.41	77.56
Series II							
Acid = 1.0031 g.			Water = 0.1477 g.				
84.8	204.5	50.2	91.0	370.2	62.41	61.06	66.75
87.5	208.0	56.6	98.0	386.2	60.98	59.95	65.82
94.6	219.7	85.2	107.8	409.7	59.00	58.36	64.12
100.7	230.4	119.1	111.2	418.0	58.34	57.77	63.73
104.5	236.1	138.4	112.7	421.6	58.07	57.48	63.40
107.1	243.0	171.9					
110.8	247.8	190.5					
117.2	260.4	262.4					
Series III							
Acid = 2.0502 g.			Water = 0.1476 g.				
104.5	445.2	121.2	106.4	603.0	76.27	73.90	80.41
108.2	457.3	148.6	112.5	628.5	74.35	72.36	78.42
113.6	475.5	196.9	115.4	641.7	73.37	71.63	77.70
118.2	492.5	259.4	117.8	649.8	72.90	71.05	76.98
123.4	511.3	324.2	122.0	667.8	71.70	69.99	75.88
Series IV							
Acid = 1.3763 g.			Water = 0.1460 g.				
99.3	299.9	94.6	97.5	455.8	68.26	67.42	73.63
105.7	315.9	143.8	102.4	469.0	67.21	66.42	72.59
111.0	329.0	188.2	108.1	485.6	65.90	65.17	71.38
117.2	344.2	255.4	113.5	502.4	64.59	64.01	70.18
120.9	354.7	312.2	118.1	516.5	63.58	62.98	69.17

[a] Computed for monomer–dimer equilibrium.

Discussion

In all four series of experiments, as recorded in Table I, (mol. wt. obsd.) was always slightly higher than (mol. wt. I) but was considerably lower than (mol. wt. II). In three of the four series, the differences (mol. wt. obsd.) − (mol. wt. I) and (mol. wt. II) − (mol. wt. obsd.) averaged 0.71 and 5.15 molecular weight units, respectively. In the other series where the pressure range was considerably higher, the differences averaged 1.93 and 4.16 units, respectively. It is estimated that the experimental error is about 0.2 molecular weight unit. The differences noted suggest that the principal equilibrium in the vapor phase around 100° is I.

It was noticed in all four series of measurements that agreement between mol. wt. I and mol. wt. obsd. was better at higher temperatures than at lower. The deviations may be caused by nonideality of the "mixture," that is, specific interaction of water with any one of the possible acetic acid species. Unfortunately this non-ideality cannot be predicted quantitatively. Rough values of a dissociation constant for a 1:1 hydrate of the acid monomer may be computed in an attempt to explain the difference between mol. wt. obsd. and mol. wt. I. For series I, II and IV, values of about 7 (liters per mole) at 113° and 20 at 90° were obtained. In series III, where the pressure was considerably higher, the constant was 24 at 113°. These numbers do not establish the reality of the equilibrium and series III suggests that some other process or processes must be operating.[6]

A plot of ln K_p for pure acid against $1/T$ leads to a heat of dissociation equal to 14.4 kcal./mole which is close to the average of previous estimates.[7] Heats of combustion of acetic acid and of acetic anhydride indicate a value of 42.5 kcal./mole for the heat of hydration of acetic anhydride vapor.[8] Since this figure represents the difference between much larger experimental figures, it may be in considerable error. The disparity between 14.4 and 42.5 kcal./mole is large enough, however, to lend weight to the conclusion that equilibrium II is of little importance in the temperature range 90–120°.

Acknowledgment.—The authors were helped by discussions with Drs. Morris Ziff and John E. Ricci.

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(5) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1923, pp. 1323–1324.

(6) G. Allen and E. F. Caldin, *Quart. Rev.* (*London*), **7**, 255 (1953).

(7) For references see M. D. Taylor, THIS JOURNAL, **73**, 315 (1951).

(8) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, Vol. III, pp. 138, 165, 166.