[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, QUEENS COLLEGE]

Dissociation Constants of Acetylacetone, Ethyl Acetoacetate and Benzoylacetone

BY MAXWELL L. EIDINOFF

Widely different results have been reported in the literature for the dissociation constants of acetylacetone and ethyl acetoacetate in dilute aqueous solution. An approximate value has been estimated for benzoylacetone. The determination of the dissociation constants was undertaken, since the values were needed to interpret polarographic and titration data pertaining to these substances.

Tachi[1] estimated the K_a of benzoylacetone to be about 3.2×10^{-7} in dilute aqueous-alcoholic solution from polarographic measurements at 25°. Oslan[2] reported 4.4×10^{-8} for ethyl acetoacetate solutions from conductivity measurements. Goldschmidt and Oslan,[3] however, reported 2×10^{-11} for this compound over the concentration range 0.125–0.25 N from measurements of saponification velocity by weak bases. For acetylacetone, K_a values of 1.4×10^{-6},[4] 4.7×10^{-8},[5] and 1.5×10^{-6},[6] over the concentration range 0.06–0.001 M have been reported from conductivity data. These are all larger than the value 1.15×10^{-9} reported more recently from pH measurements by Schwarzenbach and Lutz.[7] The pH of aqueous solutions of these compounds, partially neutralized with sodium hydroxide, was measured at 25 ± 0.1°. In the case of benzoylacetone, the solutions contained 7.15 to 7.49% ethyl alcohol by weight. The classical dissociation constants were calculated following the method employed by Kumler[8] and using the equation

$$K_a = \frac{H^+ [(Na^+) + (H^+) - (K_W/(H^+))]}{M - [(Na^+) + (H^+) - (K_W/(H^+))]} \qquad (1)$$

where M is the total concentration of the tautomeric compound and $pH = -\log (H^+)$. The precision measure of the pK_a (average) reported in Table I $= \Sigma|d|/n\sqrt{n}$ where n represents the number of solutions taken for pH measurement. The results are listed in Table I.

The classical dissociation constants determined by these experiments for acetylacetone, ethyl acetoacetate and benzoylacetone are $1.17 \pm 0.02 \times 10^{-9}$, $2.09 \pm 0.02 \times 10^{-11}$ and $2.01 \pm 0.03 \times 10^{-9}$, respectively. Tachi's estimated value[1] for benzoylacetone is too high by a factor greater than 100. Inasmuch as the results of conductivity measurements cited above[2,4,5,6] are influenced by small quantities of electrolyte impurities, it is not surprising that the latter are considerably higher than the results of this research. The results of Goldschmidt and Oslan[3] for ethyl acetoacetate and of Schwarzenbach and Lutz[7] for acetylacetone are in satisfactory agreement with the results of this investigation.

TABLE I

ACID DISSOCIATION CONSTANTS

Acid	Approx. molarity $\times 10^3$	No. of solutions	Range of fraction neutralized	Average pK_a
Acetylacetone	3	7	0.2–0.8	$8.93_3 \pm 0.004$
Ethyl acetoacetate	9	7	0.2–0.8	$10.68_0 \pm 0.004$
Benzoylacetone[a]	1.5	6	0.33–0.66	$8.69_7 \pm 0.005$

[a] Percentage ethyl alcohol by weight varied from 7.15 to 7.49, average 7.3.

Experimental

Materials. Benzoylacetone.—An Eastman Kodak Co. C. P. sample was recrystallized four times from absolute ether and dried under vacuum to constant weight at 40°. The preparation melted between 58.5 to 59.0° during the three final crystallizations.

Acetylacetone.—A Paragon Co. C. P. product was fractionally distilled. The distillate boiling at 138.8 to 138.9° at 750 mm. pressure was distilled again at this temperature and pressure. Portions needed for pH studies were freshly distilled several hours before use.

Ethyl Acetoacetate.—An Eastman Kodak Co. sample was fractionally distilled under vacuum. The distillate boiling between 79.5 to 80.0° at 18 mm. pressure was redistilled at this temperature and pressure. Portions needed for pH studies were freshly distilled several hours prior to use.

Other materials were of reagent grade. Dissolved gases were removed from the doubly distilled water used for preparing the solutions by boiling. Sodium hydroxide solutions were prepared carbonate-free and standardized against reagent grade potassium acid phthalate dried to constant weight. The results were periodically checked using constant boiling hydrochloric acid solutions as standards.

Measurements.—The pH of the partially neutralized solutions at 25.0 ± 0.1° was measured using a Beckman Model G pH meter, following the method used by Kumler.[8] The pH scale was standardized to ±0.01 pH unit using 0.05000 N potassium acid phthalate[9] and boric acid–sodium hydroxide–sodium chloride buffers. The pH of the latter was measured using a standard hydrogen electrode–saturated calomel electrode cell and a Leeds and Northrup Type K potentiometer. pH measurements were completed within ten and twenty minutes after preparation of the solution for acetylacetone and benzoylacetone, respectively. In the case of ethyl acetoacetate, pH measurements were made at minute intervals following preparation of the partially neutralized solution, and the pH was extrapolated to the mixing time. The uniform pH drift in these solutions results from the saponification reaction in alkaline medium.[10]

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[1] Tachi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **42**, Chem. Series, No. 22 (1938).

[2] Oslan, Diss. Heidelberg, 1901; "I. C. T.," Vol. VI, p. 275.

[3] Goldschmidt and Oslan, *Ber.*, **33**, 1140 (1900).

[4] Guinchant, *Compt. rend.*, **120**, 1220 (1895); "I. C. T.," Vol. VI, p. 269.

[5] Schilling and Vorländer, *Ann.*, **308**, 184 (1899).

[6] Guinchant, *Ann. chim.*, [9] **9**, 139 (1918).

[7] Schwarzenbach and Lutz, *Helv. Chim. Acta*, **23**, 1147 (1940).

[8] Kumler, THIS JOURNAL, **60**, 859 (1938).

[9] Dole, "Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 297.

[10] Grossman, *Z. physik. Chem.*, **109**, 305 (1924).

Summary

The classical dissociation constants of acetylacetone and ethyl acetoacetate at 25.0 ± 0.1° in dilute aqueous solution (3 and 9 $\times 10^{-3}$ M, respectively) are 1.17 ± 0.02 $\times 10^{-9}$ and 2.09 ± 0.02 $\times 10^{-11}$, respectively. The dissociation constant of benzoylacetone in dilute aqueous solution (1.5 $\times 10^{-3}$ M) containing 7.3% ethyl alcohol by weight is 2.01 ± 0.03 $\times 10^{-9}$. The constants were determined by measuring the pH of partially neutralized solutions of these compounds.

FLUSHING, NEW YORK RECEIVED AUGUST 17, 1945

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Tautomeric Equilibria in Partially Neutralized Solutions of Acetylacetone and Benzoylacetone

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The Kurt Meyer bromine addition reaction has been extensively applied to the study of tautomeric equilibria.[1] Equilibria in partially neutralized aqueous solutions of tautomeric compounds have received relatively minor consideration. Grossmann[2] modified the indirect bromine addition reaction and applied the latter to alkaline solutions of ethyl acetoacetate and acetylacetone. The experiments reported below were designed to correlate enol plus enolate content measured by the Kurt Meyer bromine reaction with the fraction of the tautomeric compound neutralized and the acid behavior of the enol form. Dilute solutions were studied in order to permit use of equilibrium constants involving concentration units without introducing significant errors. Acetylacetone and benzoylacetone were selected because the acid dissociation constants have been measured in dilute solution.[3]

An equation has been derived relating the enol plus enolate ion fraction (F) to the fraction of tautomeric compound neutralized (f), the pH and the keto–enol and acid dissociation equilibrium constants. Calculations based on this equation are compared with the experimentally determined (f) values.

Relation between (F) and (f).—(E), (K), (E⁻), (Na⁺) and (C) signify the concentrations of enol, keto, enolate ion, added base and total concentration of tautomeric compound, respectively.

$$(\mathrm{f}) = (\mathrm{Na}^+)/(\mathrm{C}) \text{ and } (\mathrm{F}) = [(\mathrm{E}) + (\mathrm{E}^-)]/(\mathrm{C})$$

The equilibrium constants K_E, K_a and K_G refer to the keto-enol equilibrium constant, the dissociation constant of the enol form and the gross dissociation constant, respectively, and are defined by the following

$$K_E = (\mathrm{E})/(\mathrm{K});\quad K_a = (\mathrm{E}^-)(\mathrm{H}^+)/(\mathrm{E});\quad K_G = \frac{(\mathrm{E}^-)(\mathrm{H}^+)}{(\mathrm{E}) + (\mathrm{K})}$$

From the latter definitions, it follows that $K_G = K_E K_a/(1 + K_E)$. Equating charges, the relationship $(\mathrm{H}^+) + (\mathrm{Na}^+) = (\mathrm{OH}^-) + (\mathrm{E}^-)$ is obtained. Dividing the latter equation by (C) and using the readily derived relation

$$(\mathrm{E})/(\mathrm{C}) = \left[1 + \frac{1}{K_E} + \frac{K_a}{(\mathrm{H}^+)}\right]^{-1}$$

the following general expression is obtained

$$(\mathrm{F}) = (\mathrm{f}) + \left[1 + \frac{1}{K_E} + \frac{K_a}{(\mathrm{H}^+)}\right]^{-1} - (\mathrm{OH}^-)/(\mathrm{C}) + (\mathrm{H}^+)/(\mathrm{C}) \qquad (1)$$

(H⁺) and (OH⁻) may be obtained by measuring the pH of the solution or more generally by using the experimentally determined value for K_G and solving the quadratic equation for (H⁺)

$$K_G = \frac{(\mathrm{H}^+)[(\mathrm{f}) + (\mathrm{H}^+)/(\mathrm{C}) - (\mathrm{OH}^-)/(\mathrm{C})]}{1 - (\mathrm{f}) - (\mathrm{H}^+)/(\mathrm{C}) + (\mathrm{OH}^-)/(\mathrm{C})} \qquad (2)$$

For solutions in which (H⁺)/(C) and (OH⁻)/(C) are small relative to (f) and [1 − (f)], equation (2) may be replaced by the more familiar approximate equation: $K_G = (\mathrm{H}^+)\,(\mathrm{f})/[1 - (\mathrm{f})]$. For the range of conditions in which the latter equation is obeyed closely, equation (1) may be replaced by the simple linear equation

$$(\mathrm{F}) = (\mathrm{f})/(1 + K_E) + K_E/(1 + K_E) \qquad (3)$$

or the equivalent equation

$$(\mathrm{F}) = (\mathrm{f})(\mathrm{K}^*)/(\mathrm{C}) + (\mathrm{E}^*)/(\mathrm{C}) \qquad (4)$$

where (K*)/(C) and (E*)/(C) are the fractions of tautomeric compound in the keto and enol form, respectively, in solutions containing a negligible amount of enolate ion.

Under the experimental conditions reported below, equation (4) agrees with equation (1) to within 0.5% over the (f) interval 0 to 0.6 and 0.7 for acetylacetone and benzoylacetone, respectively. At (f) = 0.95, equation (4) yields values that are larger than those calculated from equation (1) by 2.7 and 2.4%, respectively.

Experimental

Materials.—The purification of the benzoylacetone and acetylacetone and the sodium hydroxide standardization have been described elsewhere.[3] Sodium thiosulfate solutions were standardized using purified reagent grade potassium iodate. The results were periodically checked using iodine solutions standardized against arsenious oxide.

Measurement of Enol plus Enolate Fractions.—Following the modification tested by Grossmann,[2] the bromine

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[1] Meyer (a) *Ann.*, 380, 212 (1911); (b) *Ber.*, 44, 2720 (1911); (c) 45, 2852 (1912); (d) 47, 837 (1914); (e) 53, 1410 (1920); (f) 54, 579 (1921).

[2] Grossmann, *Z. physik. Chem.*, 109, 305 (1929).

[3] Eidinoff, THIS JOURNAL, 67, 2072 (1945).