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 *p*H of partially neutralized solutions of these compounds.

FLUSHING, NEW YORK RECEIVED AUGUST 17, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, QUEENS COLLEGE]

Tautomeric Equilibria in Partially Neutralized Solutions of Acetylacetone and Benzoylacetone

BY MAXWELL L. EIDINOFF

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 *p*H 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.

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

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

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

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

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

the following general expression is obtained

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

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

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

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: $K_G = (H^+)\,(f)/[1 - (f)]$. For the range of conditions in which the latter equation is obeyed closely, equation (1) may be replaced by the simple linear equation

$$(F) = (f)/(1 + K_E) + K_E/(1 + K_E) \quad (3)$$

or the equivalent equation

$$(F) = (f)(K^*)/(C) + (E^*)/(C) \quad (4)$$

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 b 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).

solutions contained excess hydrochloric acid. The solutions were 0.047 molar with respect to bromine and 0.14 molar with respect to hydrochloric acid. One per cent. by weight aniline hydrochloride and 0.2 molar potassium iodide solutions (iodate-free) were used.

The acetylacetone solution was maintained at 25 ± 0.1° for fifteen minutes after partial neutralization. Forty ml. of chilled bromine solution (containing excess ice) were added rapidly and with vigorous shaking to the partially neutralized solution containing approximately 3.8×10^{-4} mole of acetylacetone. After three seconds, 25 ml. of aniline hydrochloride solution was added to remove excess bromine. Twenty ml. of 0.2 *M* potassium iodide solution was then added. The resulting solution was maintained at a temperature of 35° for approximately one and a half hours. The iodine liberated was titrated with approximately 0.01 *N* sodium thiosulfate solution.

In the corresponding titration of the benzoylacetone solutions (containing 1.9×10^{-4} mole of this compound) the volumes of bromine solution, aniline hydrochloride and potassium iodide solutions were 20, 10 and 10 ml., respectively.

Results and Discussion

The enol plus enolate ion fraction at 25 ± 0.1° as a function of fraction neutralized is plotted in Fig. 1, curves 1 and 2 for benzoylacetone and acetylacetone, respectively. The experimental results are compared with calculated values based on equations (1) and (2) in Table I. The molarity of the acetylacetone solutions varied from 3.0 to 3.8×10^{-3}. The benzoylacetone solutions varied in molarity from 1.6 to 1.9×10^{-3} and contained from 7 to 8% ethyl alcohol by weight. When (f) = 0, equation (1) yields (F) equal to 0.170 and 0.341, namely, the experimentally determined fractions for acetylacetone and benzoylacetone, respectively.

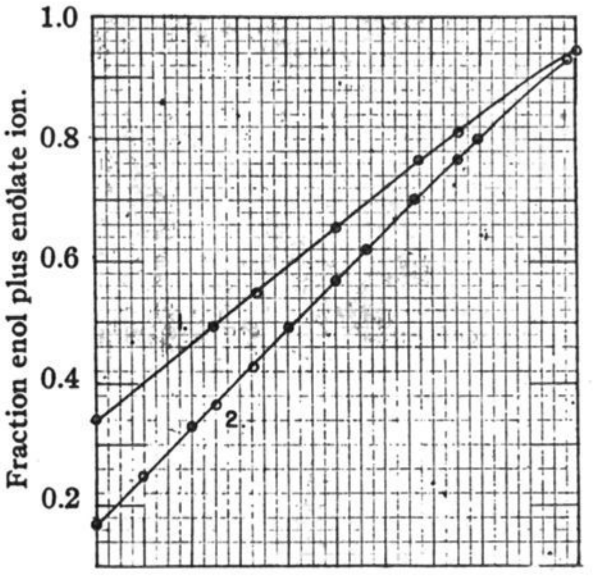

Fig. 1.—Enol plus enolate ion fraction as a function of fraction neutralized: curve 1, benzoylacetone; curve 2, acetylacetone.

TABLE I

COMPARISON OF EXPERIMENTAL RESULTS FOR FRACTION ENOL PLUS ENOLATE ION WITH EQUATION (1)

Fraction neutralized	(F) Experimental[b]	(F) Equation (1)
A. Acetylacetone[a]		
0.0500	0.206	0.211[c]
.1000	.248	.253
.3000	.404	.418
.5000	.568	.583
.7000	.724	.746
.9000	.870	.901
.9800	.930	.950
B. Benzoylacetone[d]		
0.0500	0.371	0.374[e]
.1000	.402	.407
.3000	.528	.538
.5000	.655	.669
.7000	.780	.798
.9000	.894	.920
1.0000	.944	.961

[a] *p*H calculated from equation (2) and the following: $K_G = 1.17 \times 10^{-9}$; (C) = 3.30×10^{-3} molar; $K_W = 1.01 \times 10^{-14}$; *p*H = −log (H⁺). [b] Experimental values from Fig. 1. [c] For acetylacetone, $K_E = 0.205$; $K_a = 6.88 \times 10^{-9}$. [d] *p*H calculated from equation (2) and the following: $K_G = 2.01 \times 10^{-9}$; (C) = 1.7×10^{-3} molar; $K_W = 1.01 \times 10^{-14}$. [e] For benzoylacetone, $K_E = 0.517$; $K_a = 5.89 \times 10^{-9}$.

Enol Acid Dissociation Constants.—The gross classical dissociation constants have been measured at 25° in concentration ranges equivalent to those studied in this investigation.[3] K_G is $1.17 \pm 0.02 \times 10^{-9}$ and $2.01 \pm 0.03 \times 10^{-9}$ for acetylacetone and benzoylacetone, respectively. The enol fraction in aqueous solution is 0.170 and 0.341, respectively. K_a, the dissociation constant of the enol form is related to K_G by the relation: $K_a = K_G(1 + K_E)/K_E$. The percentage average deviations from the mean of the enol fractions (three determinations) are 0.4 and 0.2 for acetylacetone and benzoylacetone, respectively. Estimating the enol fractions to be accurate within 1% for this calculation, the classical enol acid dissociation constant for acetylacetone at 25° is $6.88 \pm 0.15 \times 10^{-9}$ in aqueous solution. For benzoylacetone in aqueous solution containing 7.5% ethyl alcohol by weight, the dissociation constant is $5.89 \pm 0.11 \times 10^{-9}$.

Comparison of Results Predicted by Equation (1) with Experiment.—The deviations between the (F) values (calculated minus experimental) have been computed at 0.10 intervals of (f). The deviations are all positive for both acetylacetone and benzoylacetone. For acetylacetone, the average difference between the (F) values over the (f) range, 0.0 to 1.0 is 0.017, corresponding to an average percentage difference of 2.7%. For benzoylacetone, the average deviation is 0.015 corresponding to an average percentage difference of 2.0.

Several factors may contribute to the deviations noted above. The chemical procedure is based on (a) the very rapid reaction with bromine of the enol and enolate form relative to the keto form and (b) the complete freezing of the keto–enol–enolate equilibrium during the bromine addition period. The calculations have assumed the invariance of the classical keto–enol and acid dissociation constants over the entire neutralization range. Thus, within the 2.7 and 2.0% differences noted above for acetylacetone and benzoylacetone, a satisfactory correlation has been demonstrated between the enol plus enolate ion fraction determined by the Kurt Meyer procedure and that calculated from the acid enol properties. Taking the latter as a basis, it may be concluded that the Kurt Meyer bromine addition procedure described above for partially neutralized solutions furnishes results that are reliable to within the 2.7 and 2.0% deviations observed.

Summary

1. At 25°, the fraction of acetylacetone present in the enol form in dilute aqueous solution (3.3×10^{-3} *M*) is 0.170. The corresponding value for benzoylacetone in 1.7×10^{-3} *M* aqueous solution containing 7.5% ethyl alcohol by weight is 0.341. The classical acid dissociation constants of the enol forms of the above compounds at $25.0 \pm 0.1°$ are $6.88 \pm 0.15 \times 10^{-9}$ and $5.89 \pm 0.11 \times 10^{-9}$, respectively.

2. The fraction of the above compounds present in the enol plus enolate ion form at 25° has been measured as a function of the fraction neutralized in dilute aqueous solution by the Kurt Meyer bromine addition reaction. An equation expressing this relationship has been derived that is based on the dissociation constant and the keto–enol equilibrium. Values predicted by this equation are larger than the measured values for acetylacetone and benzoylacetone by 2.7 and 2.0%, respectively.

FLUSHING, NEW YORK RECEIVED AUGUST 28, 1945

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

The Heat Capacity, Heat of Fusion and Entropy of 11-*n*-Decylheneicosane

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This is the beginning of a series of investigations at The Pennsylvania State College, dealing with hydrocarbons of high molecular weight. A similar series of investigations has been in progress at Stanford University since 1937. The object of both series is the establishment of a relationship between structure and various thermodynamic functions. Thus it should be possible to estimate the entropy of a high-molecular weight hydrocarbon from previous systematic calorimetric data on other compounds.

This paper furnishes a comparison of data on the same compound obtained independently in the laboratories of Stanford University and The Pennsylvania State College.

Preparation and Purification of Sample.—The sample was one of the first compounds prepared by API Project 42. It was synthesized by treating decylmagnesium bromide with ethyl carbonate. The alcohol, after careful fractionation, was dehydrated to the olefin which was catalytically hydrogenated. The saturated hydrocarbon was fractionated through a 10-plate low pressure fractionation column (0.1 mm.) and passed several times through silica gel.

The Heat Capacity Measurements.—In the measurements at The Pennsylvania State College the sample was accurately weighed into calorimeter D, which was designed for the measurement of thermal data of solids and liquids. After freeing the sample from the last traces of air by repeated freezings and evacuations to 10^{-6} mm. of mercury, the calorimeter space above the compound was filled with approximately one-half atmosphere of helium.

The detailed description of this adiabatic solids calorimeter will be published shortly along with a discussion of the accuracy.[3] It is estimated that all thermal data obtained with it, above 40°K., have an accuracy of 0.2%. It is possible to reproduce the heat capacity data on the solid with a precision of better than 0.1% above 80°K.

The measurements at Stanford University were carried out as described previously.[4] In view of the accuracy of the various factors involved, the absolute error in the experimental values of the heat capacities and heat of fusion is probably less than 0.7%, except insofar as impurities in the sample of this hydrocarbon may cause premelting or otherwise influence the results. The fortuitous errors were ordinarily under 0.25%.

The *defined calorie*, taken equal to 4.1833 international joules, has been used throughout the studies in both laboratories. Temperature measurements have been on the basis: 0°C. = 273.16° K. The value 436.822 has been adopted as the molecular weight of 11-*n*-decylheneicosane. The sample of this material used in the calorimeter at The Pennsylvania State College was 0.15216 mole; that used at Stanford was 0.06905 mole.

The heat capacities measured at The Pennsylvania State College on the solid compound, uncorrected for premelting, are listed in Table IA. Here the temperature rise can be estimated from the intervals between points of a series. The results of the heat capacity measurements ob-

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(1) At The Pennsylvania State College.

(2) At Stanford University.

(3) Aston and Ziemer, to be published.

(4) Parks, THIS JOURNAL, 47, 338 (1925).