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George E. Knudson
Luther College

Jennifer Bickel
Luther College

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Computer Assisted Determination of the Ionization Constants of an Unusual Dibasic Acid

GEORGE E. KNUDSON and JENNIFER BICKEL¹

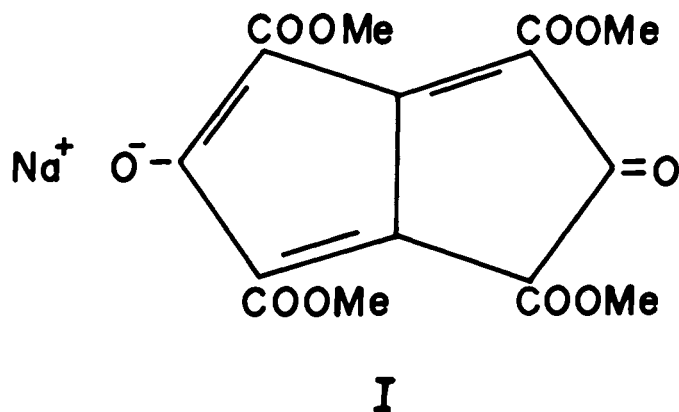
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The ionization constants for an unusual keto ester were determined by examination of the complex visible-UV absorption spectra of the monobasic salt. Interpretation of changes with pH of the spectra at four different wave

lengths required an estimate of 12 molar absorptancies and two ionization constants. A computer program permitted progressive selection of best values. The ratio of K_1 to K_2 for this acid is exceptionally high and exceeds that for any other acid for which we have found data.

INDEX DESCRIPTORS: Acid Ionization Constants, Spectroscopic Determination of Ionization Constants, Computer Program for Determination of Ionization Constants.

During the investigation of the chemistry of a deep red crystalline salt, tetramethyl bicyclo(3.3.0)octa-1,5-diene-3,7-dione-2,4,6,8-tetracarboxylate mono sodium salt, (I), prepared in this laboratory by Adrian Docken, it became obvious that the parent acid was much more acidic than the usual keto ester.



Of particular interest is the observation that a red aqueous solution of I becomes deep blue on addition of base, indicating that a second proton is fairly easily removed, giving a structure which may be regarded as related to pentalene. We became interested therefore in a determination of the ionization constants for this acid. Because of the observed color changes it seemed that these constants could be obtained from absorption spectra taken in the visible region. However it soon became apparent that the situation was complicated, with several overlapping peaks. Ignoring an isolated peak at 675 nm which appears only at high concentrations, it is necessary to select twelve values for molar absorptivities, plus two ionization constants, in order to account for the observed spectra. To assist in this attempt it seemed necessary to know concentrations for each species at any pH, given the two ionization constants. For a dibasic acid these may be calculated from the following equations, derived from the equilibrium expressions and the mass balance equation.

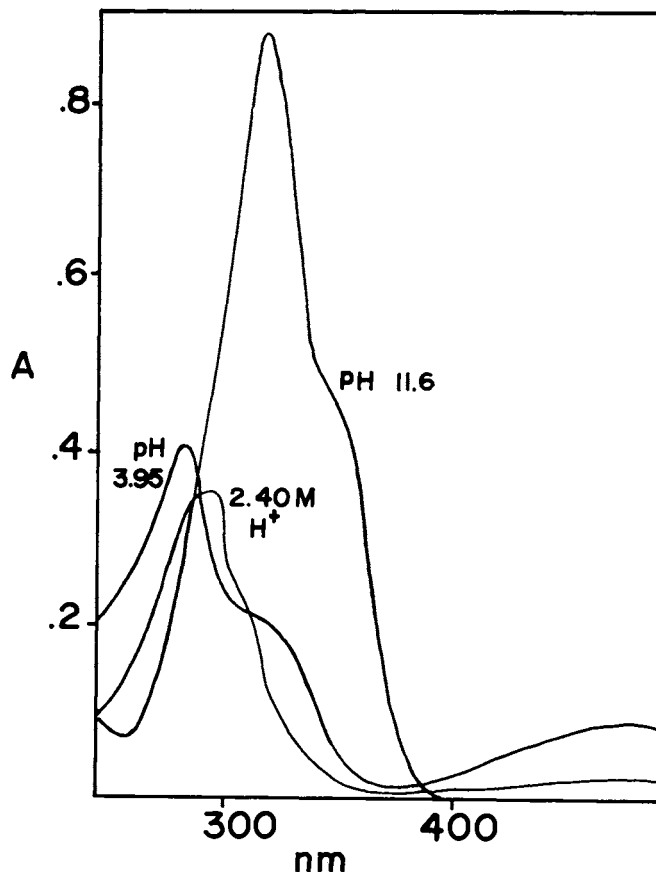
$$H_2A = C_s \frac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$

$$HA^- = C_s \frac{[H^+]K_1}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$

$$A^{2-} = C_s \frac{K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$

Where C_s is the original concentration of the salt.

A Beckman DB spectrophotometer was used to obtain spectra of $3.25 \times 10^{-5} M$ solutions of the salt at 25 different hydrogen ion



¹Department of Chemistry, Luther College, Decorah, Iowa 52101.

IONIZATION CONSTANTS OF A DIBASIC ACID

concentrations ranging from strongly acidic to strongly basic. Three of these curves are shown in the figure. To handle the large amount of data it was convenient to use a computer program to calculate and print out the concentration of each species as given by the above equations, multiply each concentration by an assigned molar absorptivity, and add the individual absorptions to give a total for each wavelength and pH which could be compared with the observed values. By examination of these printouts it was possible to progressively select values of the absorptivities and ionization constants until the calculated values were within the experimental error of the observed values.

The final values selected are shown in the table. The values for the ionization constants are $pK_1 = 1.4$ and $pK_2 = 8.4$. A deviation of more than .1 pK unit from these values gives calculated results

which differ from the actual data by more than the expected instrumental error. No correction was made for ionic strength, but this error is probably small since the total concentration was very low over much of the range. The ratio of pK_2 to pK_1 is 6.0, which is highly unusual since the ratio for most organic acids is usually about 2, with a value of 4 the highest we have found in an examination of available data.

To check the values for the ionization constants, the salt was titrated with standard acid and with standard base. Theoretical values of pH were calculated for 25 points on each titration curve using the above values for K_1 and K_2 and the exact equations for these titrations. The actual values checked within the limits of experimental error expected for the pH measurements.