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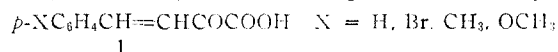
# Ionization Constants and Rates of Ester Hydrolysis in the Benzylidenepyruvic Acid Series

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RECEIVED MARCH 5, 1952

Ionization constants have been determined at 25° for benzylidenepyruvic acid and its *p*-bromo-, *p*-methyl- and *p*-methoxy derivatives. These are very strong acids ( $K'$  in water =  $1.1 \times 10^{-2}$ ) and show no significant variation of  $K'$  with substituent groups. Rates of hydrolysis have been determined at 25° for the corresponding methyl esters in 50% dioxane using hydrochloric acid as the catalyst. The rates are first order with respect to ester and hydrochloric acid concentrations ( $k' = 5.7-6.1 \times 10^{-3}$  hr.<sup>-1</sup>). Absorption spectra are reported for the methyl esters.

In the benzoic acid series, much is known about the variation of ionization constant with the introduction of substituent groups on the benzene ring.<sup>1</sup> The rates of acid-catalyzed hydrolysis of the corresponding methyl benzoates also show a small but definite variation with substitution.<sup>2</sup> In the cinnamic acid series, the variations of  $pK$  with substituent groups are smaller but in the same direction.<sup>1a</sup> Cinnamic esters hydrolyze much more rapidly than benzoic esters and substituent effects are larger.<sup>3</sup> In general these differences have been explained in terms of polarization of the molecule through inductive and resonance effects.<sup>1a,2</sup> It seemed of interest to obtain information concerning the effect of substituents on benzylidenepyruvic acid (I, X = H) and its methyl ester. This pro-



vides a system in which the benzene ring is not directly conjugated with the carboxyl group as it is in benzoic and cinnamic acids, but with the carbonyl group. Since it is this carbonyl group which makes pyruvic acid much stronger than acetic acid, one might expect detectable substituent effects.

The present study reports the measurement of the ionization constants of five benzylidenepyruvic acids, three of which are substituted in the para position and one in the meta position. In a second series of experiments, the methyl esters of the para substituted acids were hydrolyzed, using hydrochloric acid as the catalyst, and the rates of hydrolysis were measured.

## Experimental

**Preparation of Compounds.**—Table I lists the benzylidenepyruvic acids and esters prepared for this study together with their melting points. Determination of the equivalent weights of both acids and esters showed them to be 99.6–99.9% pure.

Benzaldehyde, anisaldehyde and pyruvic acid were Eastman Kodak Co. products. *p*-Tolualdehyde, b.p. 103–105° at 21 mm., was prepared according to a known method.<sup>4</sup> In the preparation of *p*-bromobenzaldehyde<sup>5</sup> only 60% of the suggested amount of chromium trioxide was used, and yields of 65–80% of the aldehyde diacetate were obtained.

For the preparation of the benzylidenepyruvic acids it was found necessary to observe certain precautions not described in the published methods.<sup>6</sup> A typical procedure

(1) (a) J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1937); (b) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 84 ff., p. 184 ff.

(2) E. W. Timm and C. N. Hinshelwood, *J. Chem. Soc.*, 862 (1938).

(3) K. Kindler, *Ann.*, **452**, 90 (1927).

(4) G. H. Coleman and D. Craig, "Organic Syntheses," Coll. Vol. 11, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 583.

(5) S. V. Liebermann and R. Conner, *ibid.*, p. 441.

(6) See Table I footnotes *c, d, e, f, g*.

TABLE I  
BENZYLIDENEPYRUVIC ACIDS<sup>a</sup>

| X   | M. p., °C.<br>(cor.) | Lit.<br>m. p., °C.   |
|---|----------------------|----------------------|
| H   | 61.5–62.5            | 61–62 <sup>b</sup>   |
| 4-OCH <sub>3</sub>                            | 130.5–131            | 131 <sup>c</sup>     |
| 3-OCH <sub>3</sub>                            | 117                  | 116–117 <sup>d</sup> |
| 4-CH <sub>3</sub>                             | 127–127.5            | 127 <sup>e</sup>     |
| 4-Br  | 141.5–142.5          | 143 <sup>f</sup>     |
| Benzylidenepyruvic methyl esters <sup>g</sup> |                      |                      |
| H   | 73.5–74.5            | 73–74 <sup>b</sup>   |
| 4-OCH <sub>3</sub>                            | 107–108              | 106 <sup>c</sup>     |
| 4-CH <sub>3</sub>                             | 81.5–82.5            | 81 <sup>e</sup>      |
| 4-Br  | 121.5–122.5          | 122 <sup>f</sup>     |

<sup>a</sup> Recrystallized from benzene or benzene-petroleum ether and dried at 5 mm. <sup>b</sup> M. Reimer, *THIS JOURNAL*, **46**, 785 (1924); **48**, 2456 (1926); **53**, 3148 (1931). <sup>c</sup> M. Reimer, *ibid.*, **48**, 2458 (1926). <sup>d</sup> M. Reimer and H. Kammerling, *ibid.*, **55**, 4645 (1933). <sup>e</sup> M. Reimer and E. Chase, *ibid.*, **60**, 2470 (1938). <sup>f</sup> M. Reimer and E. Tobin, *ibid.*, **62**, 2518 (1940). <sup>g</sup> Recrystallized from benzene-petroleum ether and dried at 60° and 5 mm.

was as follows: To a 500-ml. wide-mouth bottle, fitted with an efficient stirrer, were added 17.2 g. (0.2 mole) of pyruvic acid (Eastman Kodak Co.), 21.2 g. (0.2 mole) of benzaldehyde and 10 ml. of methanol (reagent grade). To the cooled solution was added a solution of 16.8 g. (0.3 mole) of potassium hydroxide in 50 ml. of methanol, at such a rate as to maintain the temperature at 25°. After the addition of two-thirds of the alkali, the ice-bath was removed, and the rest of the alkali was run in rapidly to complete the condensation before precipitation of potassium pyruvate could occur. Immediately, the yellow color of the solution darkened to orange-red, the temperature rose to 35–40°, and a voluminous precipitate of yellow potassium benzylidenepyruvate appeared. The mixture was held at 30° for one hour, then at 10° overnight. The crystals were filtered, washed twice with methanol and once with ether and air-dried. A yield of 35–40 g. (82–92%) of potassium salt was obtained.

If a concentrated solution of potassium benzylidenepyruvate is acidified with hydrochloric acid, an acid-salt complex will precipitate instead of the free acid. To avoid this a saturated solution of the salt at 40° was poured into a rapidly stirred solution of an excess of 1.6 *N* hydrochloric acid. The benzylidenepyruvic acids precipitated from water solution as hydrates, which retained water on drying in air, and even on recrystallization from benzene. By distilling the benzene solution of a given acid with the aid of a Bidwell and Sterling trap until all the water was removed, an anhydrous product was obtained. After several recrystallizations from benzene-petroleum ether, the acids were dried for several hours at 35 or 60° and 5 mm. over phosphorus pentoxide. On exposure to air they rapidly absorb about 5% moisture.

The corresponding esters were prepared by treating the acids for a few minutes with boiling methanol, saturated with dry hydrogen chloride.

As a test of purity the equivalent weights of the acids were determined by dissolving them in methanol and titrating with

alkali using brom thymol blue as the indicator. It was found that the methyl benzylidenepyruvates were completely hydrolyzed by dilute sodium hydroxide in a few minutes, as are esters of other very strong acids. The equivalent weights of the esters were therefore easily determined by dissolving in purified methanol, adding a measured excess of standard sodium hydroxide solution, and titrating back with hydrochloric acid solution to the brom thymol blue end-point. Nitrogen was bubbled through the solution to exclude carbon dioxide.

**Absorption Spectra.**—Figure 1 shows the ultraviolet absorption spectra of the four benzylidenepyruvic esters dissolved in methanol (reagent grade, purified by distillation from potassium hydroxide pellets). A Cary Recording Quartz Spectrophotometer (Model 12) was used, with 1.00 cm. fused quartz absorption cells at room temperature. Since all the ester solutions were adjusted to the same concentration ( $8.0 \times 10^{-6}$  molar) both optical density and extinction coefficient may be read from the same plot. Table II summarizes the absorption data.

TABLE II

| ULTRAVIOLET ABSORPTION SPECTRA OF METHYL BENZYLIDENEPYRUVATES IN METHANOL <sup>a</sup> |   |                           |                        |                           |                           |
|--|---|---------------------------|------------------------|---------------------------|---------------------------|
| X  | $p\text{-XC}_6\text{H}_4\text{CH}=\text{CHCOCOOCH}_3$ |                           | Maxima                 |                           | $\epsilon \times 10^{-3}$ |
|  | $\lambda, \text{m}\mu$                                | $\epsilon \times 10^{-3}$ | $\lambda, \text{m}\mu$ | $\epsilon \times 10^{-3}$ |                           |
| H  | 227.5   | 6.25                      | 312                    | 17.7                      |                           |
| Br   | 232   | 7.12                      | 318.5                  | 20.8                      |                           |
| CH <sub>3</sub>  | 233.5   | 6.75                      | 324.5                  | 19.9                      |                           |
| OCH <sub>3</sub>   | 241   | 7.57                      | 347.5                  | 21.5                      |                           |

<sup>a</sup> Absorption maxima of the corresponding acids have been reported by E. P. Davey and E. B. Knott, U. S. Patent 2,443,157 (June 8, 1948).

**Solvents and Solutions.**—Lithium chloride (reagent grade) was dried at 110° for several hours. A solution of 0.2 M lithium chloride in 50% methanol was prepared by mixing, at 25°, equal volumes of purified methanol and of 0.4 M aqueous lithium chloride solution. Aqueous and methanolic sodium hydroxide were prepared by addition of a clear, saturated sodium hydroxide solution to the appropriate carbon dioxide-free solvents. These solutions were standardized against Bureau of Standards potassium acid phthalate using calibrated equipment.

**Ionization Constants.**—The classical ionization constants of the acids were determined by pH titration, both in water and in 50% by volume methanol-water containing lithium chloride. The latter solvent permitted the use of more concentrated solutions and provided a medium of relatively constant ionic strength. The  $pK'$  values were calculated from the relationship

$$pK' = pH - \log \frac{\text{BCOO}^-}{\text{BCOOH}} \quad (1)$$

in which  $K'$  is the classical ionization constant, and  $\text{BCOO}^-$  and  $\text{BCOOH}$  are the concentrations of the anion and undissociated acid. This does not include the activity correction which would be about 0.05  $pK$  unit in the aqueous solutions<sup>7</sup> and difficult to determine for the methanol solutions of the acids.

For the weak reference acids, benzoic and cinnamic acids,  $pK'$  was determined from the mid-point of the titration curve where  $pK' = pH$ . For the benzylidenepyruvic acids, which are strong acids,  $\text{BCOO}^-$  and  $\text{BCOOH}$  were calculated from the titration data and substituted in equation (1) to obtain the  $pK'$  values. In methanol all  $pK$  values have relative rather than absolute validity. For each titration, calculations were made at five points between 35 and 65% neutralization and the results were averaged.

**Titration.**—Titrations in 50% methanol solution were carried out as follows. A weighed sample (about 0.0012 mole) of acid was completely dissolved in 10 ml. of methanol in an open beaker kept in a water-bath at  $25 \pm 0.2^\circ$ . To this was added 150 ml. of 0.2 M lithium chloride in 50% methanol and finally 10 ml. of 0.4 M aqueous lithium chloride. This solution was titrated with 0.08188 N sodium

(7) Estimated by comparison with values for phosphoric acid solutions of comparable  $pK$  and ionic strength (R. G. Bates, *J. Research Natl. Bur. Standards*, **47**, 127 (1951)).

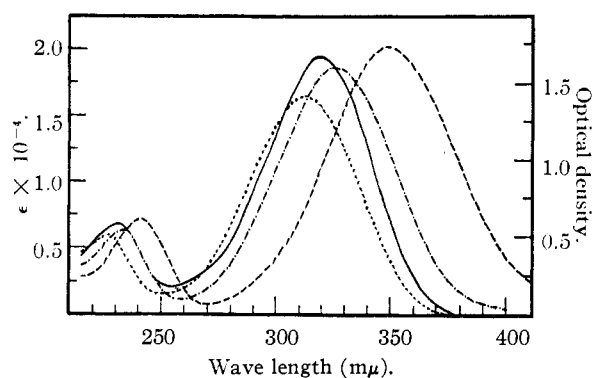


Fig. 1.—Ultraviolet absorption spectra in methanol of  $p\text{-XC}_6\text{H}_4\text{CH}=\text{CHCOCOOCH}_3$ : ····, X = H; —, X = Br; —·—, X = CH<sub>3</sub>; — — —, X = OCH<sub>3</sub>.

hydroxide in 50% methanol. The pH measurements were made with a Beckman pH meter, model G, using an outside glass electrode. Nitrogen was bubbled through the solution which was stirred mechanically. The pH meter was checked before and after each titration by means of a standard potassium acid phthalate buffer (0.0500 M, pH 4.005 at 25°),<sup>8</sup> and a standard buffer of pH 2.075.<sup>9</sup> In no case did the values of the standard buffers shift more than 0.02 pH unit during the time required for the titration. A blank value was obtained by titrating the same volume of solvent to a brom thymol blue end-point.

Due to the limited solubility of the benzylidenepyruvic acids in water, titrations were made on very nearly saturated solutions. These were prepared by shaking the finely ground solid with water for one-half hour at 23°. The solutions were filtered and 200–300 ml. aliquots containing  $8\text{--}16 \times 10^{-4}$  mole were then titrated as above at 25° with 0.07392 N sodium hydroxide solution. The total amount of acid present was determined from the end-point of the titration curve. Values given are based on duplicate titrations on each of two different solutions. A large inaccuracy in the method is in reading the pH meter ( $\pm 0.01$  pH unit). Calculation shows that for the strong acids an error of 0.02 pH unit corresponds to a difference of 0.1  $pK$  unit in the final answer or 10% in the ionization constant. For a typical titration in water solution, Table III lists the points which were used in the calculation of  $pK'$  values.

TABLE III

SAMPLE DATA AND CALCULATIONS FOR  $p$ -METHYLBENZYLIDENEPYRUVIC ACID IN WATER SOLUTION<sup>a</sup>

| Ml. NaOH<br>0.07392 N | pH   | Moles <sup>b</sup><br>H <sup>+</sup><br>$\times 10^4$ | Moles <sup>c</sup><br>BCOO <sup>-</sup><br>$\times 10^4$ | Moles <sup>d</sup><br>BCOOH<br>$\times 10^4$ | $pK'$ <sup>e</sup> |
|-----------------------|------|---|--|--|--------------------|
| 6.97                  | 2.61 | 5.08  | 10.23  | 2.16   | 1.94               |
| 7.47                  | 2.63 | 4.87  | 10.39  | 2.00   | 1.91               |
| 7.97                  | 2.66 | 4.55  | 10.44  | 1.95   | 1.93               |
| 8.97                  | 2.72 | 3.98  | 10.61  | 1.78   | 1.94               |
| 9.97                  | 2.78 | 3.48  | 10.86  | 1.53   | 1.93               |

<sup>a</sup> Titration end-point 16.76 ml., original volume of solution 200 ml. <sup>b</sup> H<sup>+</sup>,  $\text{BCOO}^-$  and  $\text{BCOOH}$  refer to moles of hydrogen ion, benzylidenepyruvate ion and undissociated acid present in the titration vessel. H<sup>+</sup> is derived from the observed pH and the total volume of the solution. <sup>c</sup>  $\text{BCOO}^-$  = moles of sodium hydroxide added, plus moles of H<sup>+</sup>. <sup>d</sup>  $\text{BCOOH}$  = moles of acid used ( $12.39 \times 10^{-4}$ ) minus  $\text{BCOO}^-$ . <sup>e</sup> From equation (1).

**Hydrolysis Rates.**—The four methyl benzylidenepyruvates were hydrolyzed in 50% by volume dioxane-water, using hydrochloric acid as the catalyst. Calculation shows that under these conditions the equilibrium point corresponds to 99.97% hydrolysis. The reaction is therefore essentially irreversible and the unimolecular rate constant

(8) D. A. MacInnes, D. Belcher and T. Shedlovsky, *THIS JOURNAL*, **60**, 1099 (1938).

(9) 0.01 N HCl + 0.09 N KCl, pH 2.075 at 25° [D. I. Hitchcock and A. C. Taylor, *ibid.*, **60**, 2712 (1938)].

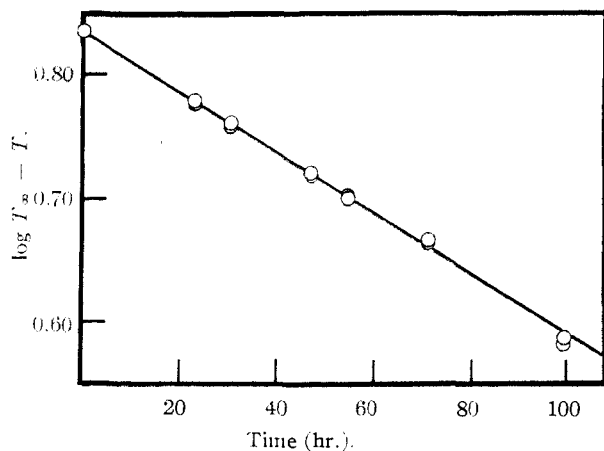


Fig. 2. Hydrolysis of methyl *p*-methoxybenzylidenepyruvate in 50% dioxane solution at 25°.

may be calculated from the familiar integrated form of the first-order rate equation

$$k't = 2.303 \log \frac{T_{\infty} - T_0}{T_{\infty} - T} \quad (2)$$

in which  $k'$  is the rate constant, and includes terms for the concentration of water and of hydrochloric acid,  $t$  is the time in hours,  $T_{\infty}$  is the alkali titer calculated for complete hydrolysis of the ester, and  $T_0$  and  $T$  are the titration values at the beginning and at time,  $t$ . By plotting  $\log T_{\infty} - T$  against time, a straight line of slope  $-k'/2.303$  was obtained, from which  $k'$  could be calculated. In practice a least squares calculation was used to obtain this slope.

Separate experiments demonstrated that benzylidenepyruvic esters hydrolyze completely in a few minutes in the presence of sodium hydroxide, but much more slowly in an ammonia solution. Therefore the acid hydrolysis mixtures were titrated with ammonium hydroxide using the mixed indicator, methyl red-brom cresol green. This gave sharp, stable end-points. A pH titration in the presence of indicator showed that the color change coincided well with the end-point of the titration.

**Rate Determinations.**—In a typical run, a weighed sample of about 0.002 mole of ester was transferred to a 250-ml. volumetric flask using 125 ml. of purified dioxane.<sup>10</sup> One hundred milliliters of 0.1050 *N* hydrochloric acid was added and the solution was made up to volume with water at 25°, and sealed by greasing the ground glass stopper. The volumetric flask was supported by the neck in a thermostat held at 25.0 ± 0.2°. Aliquots of 25 ml. were titrated at intervals of 5–12 hours. Because of the high viscosity of the 50% dioxane solutions a standard long drainage period was adopted for pipetting. A blank was run in parallel containing all the reagents except the ester. The titer of the blank was used as the value corresponding to zero time. Daily titration of the blank for a period of one week gave checking values, showing that there was no evaporation.

Table IV lists data and calculations for a typical hydrolysis of one of the esters. Figure 2 is a plot of the data in Table IV together with that from a duplicate hydrolysis. It shows the straight line relationship between  $t$  and  $\log T_{\infty} - T$ , the slope of which is  $-k'/2.303$ .

To test for decomposition of the ester in the acid medium, solutions of methyl benzylidenepyruvate ( $8.00 \times 10^{-3}$  *M* in ester and 0.1037 *M* in hydrochloric acid) were stored in sealed ampules at 25° for periods up to six weeks. Aliquots were titrated at intervals for total acid and ester by the method used for equivalent weights. Decomposition was not detectable after one week, 5% after three weeks, and 50% after six weeks. To avoid decomposition and to minimize loss by evaporation, determinations were usually continued for four to five days, corresponding to 41–45% hydrolysis. In two instances they were continued for seven days (60% hydrolysis) without change in rate constant.

Ethyl acetate was hydrolyzed under the same conditions

TABLE IV

SAMPLE HYDROLYSIS OF METHYL *p*-METHOXYBENZYLIDENE-PYRUVATE IN 50% DIOXANE AT 25.2°

$8.00 \times 10^{-3}$  *M* ester; 0.0415 *M* HCl;  $k' = 5.69 \times 10^{-3}$  hr.<sup>-1</sup>

| Time, hr. | Ml. NH <sub>4</sub> OH<br>0.02921 <i>N</i> | $\log T_{\infty} - T$ |
|-----------|--|-----------------------|
| 0.0       | 35.48                                      | 0.8357                |
| 23.1      | 36.34                                      | .7774                 |
| 30.4      | 36.59                                      | .7589                 |
| 46.9      | 37.09                                      | .7193                 |
| 54.6      | 37.29                                      | .7024                 |
| 71.0      | 37.70                                      | .6656                 |
| 99.1      | 38.51                                      | .5821                 |
|           | 42.33 <sup>b</sup>                         |                       |

<sup>a</sup> From two to four runs were made on each ester. The data from all runs for each ester were used in a single least squares determination from which  $k'$  was calculated. <sup>b</sup>  $T_{\infty}$  = alkali titer calculated for the complete hydrolysis of ester in each 25-ml. aliquot (0.2000 mmole).

for comparison. A weighed sample of purified<sup>11</sup> ester was introduced into the volumetric flask from a weighed dropping bottle. Aliquots were titrated with standard sodium hydroxide solution, using phenolphthalein as indicator.

**Results and Discussion.**—The classical  $pK'$  values obtained for the series of benzylidenepyruvic acids and for two reference acids are summarized in Table V. It will be noted that the benzylidenepyruvic acids are about 200 times as strong as benzoic or cinnamic acid. This high degree of ionization is attributable to the pyruvic acid structure ( $K'$  for pyruvic acid =  $5.6 \times 10^{-3}$ <sup>(12)</sup>,  $3.2 \times 10^{-3}$ <sup>(13)</sup>). Also, within the unavoidable, large experimental error of ±10% of the  $K'$  value for strong acids, the benzylidenepyruvic acids are all of the same strength ( $K'$  in water = 1.0 to 1.1 ± 0.1 × 10<sup>-2</sup>; in 50% methanol-0.2 *M* LiCl,  $K' = 2.7$  to 3.3 ± 0.3 × 10<sup>-3</sup>). There may well be small group effects less than 10% in magnitude, which we have not detected, as are found with phenylacetic acid.<sup>2</sup> In *p*-methoxybenzylidenepyruvic acid one would expect a resonance form of the

$$\begin{array}{c} \text{O}^- \\ | \\ \text{CH}_2\text{O}=\text{C}_6\text{H}_4=\text{CHCH}=\text{C}=\text{C}=\text{C}=\text{O} \end{array}$$

type  $\text{CH}_2\text{O}=\text{C}_6\text{H}_4=\text{CHCH}=\text{C}=\text{C}=\text{O}$  to place a partial negative charge in the neighborhood of the carboxyl group, thus retarding ionization. Clair and Wiesner<sup>13</sup> report the following ionization constants for other substituted pyruvic acids: phenylpyruvic acid  $2.09 \times 10^{-3}$ , 3,4-dimethoxyphenylpyruvic acid  $7.94 \times 10^{-4}$ . Here the two electron-repellant methoxyl groups reduce the ionization considerably even though they are conjugated with the carbonyl rather than the carboxyl group. We expected larger substituent effects in our acids but before proposing a theory we plan to investigate the problem further by studying other derivatives, as well as the series *p*-XC<sub>6</sub>H<sub>4</sub>COCOOH.

Table VI summarizes the hydrolysis rate constants for all of the esters studied. The rates of hydrolysis of the four methyl benzylidenepyruvates in 50% dioxane using hydrochloric acid as the cat-

(11) L. F. Fieser, ref. 10, p. 364. To avoid the formation of purple gelatinous by-products, drying with phosphorus pentoxide was reduced to five minutes.

(12) A. Hantzsch and A. Miolati, *Z. physik. Chem.*, [A] **10**, 8 (1892).

(13) M. H. Boeseken, L. W. Hansen and S. H. Bertram, *Rec. trav. chim.*, **35**, 313 (1906); E. G. Clair and K. Wiesner, *Nature*, **165**, 202 (1950).

(10) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, 1911, p. 399.

TABLE V

$pK'$  VALUES IN WATER AND IN 50% METHANOL AT 25°  
BENZYLIDENEPYRUVIC ACIDS,<sup>a</sup> XC<sub>6</sub>H<sub>4</sub>CH=CHCOCO<sub>2</sub>H

| X                              | Water                      |       | 50% aqueous methanol-0.2 M LiCl |                               |
|--------------------------------|----------------------------|-------|---------------------------------|-------------------------------|
|                                | Moles/l. × 10 <sup>2</sup> | $pK'$ | Moles/l. × 10 <sup>2</sup>      | $pK'$ <sup>c</sup> (relative) |
| H                              | 3.54                       | 1.97  | 6.71-8.87                       | 2.49                          |
| 3-OCH <sub>3</sub>             | 3.60-6.54                  | 1.97  |                                 |                               |
| 4-OCH <sub>3</sub>             | 2.68-3.89                  | 1.96  | 6.53-6.75                       | 2.57                          |
| 4-Br                           | 1.81-2.30                  | 1.99  | 6.60-6.75                       | 2.48                          |
| 4-CH <sub>3</sub>              | 3.33-6.20                  | 1.96  | 5.24-6.78                       | 2.52                          |
| Reference acids <sup>a,b</sup> |                            |       |                                 |                               |
| Benzoic                        | 5.30-11.60                 | 4.15  | 7.18                            | 5.03                          |
| Cinnamic                       | 1.49-3.23                  | 4.47  | 7.30                            | 5.10                          |

<sup>a</sup> Average deviation of  $pK'$  values in  $pK'$  units: benzylidenepyruvic acids in water, 0.05; in 50% methanol, 0.02; reference acids in water, 0.02; in 50% methanol, 0.01.

<sup>b</sup> J. F. J. Dippy, ref. 1a, p. 206, lists the following values at 25°: benzoic acid in water,  $K' = 6.27-6.527 \times 10^{-5}$  ( $pK' 4.185-4.20$ ); *trans*-cinnamic acid in water,  $K' = 3.65 \times 10^{-5}$  ( $pK' 4.43$ ). Dippy's values were determined by conductivity measurements and include activity corrections of about +0.02  $pK$  unit. <sup>c</sup> The  $pK'$  values in methanol were obtained by substituting  $pH$  values as given by the glass electrode, and have only relative validity.

alyst were found to have the expected first-order kinetics with respect to the concentration of ester and of hydrochloric acid. The activation energy for the hydrolysis of benzylidenepyruvic acid calculated from rates at 25° and at 45° was found to be about 15 kcal./mole. Timm and Hinshelwood<sup>4</sup> report a value of 18.24 kcal./mole for the activation energy of methyl benzoate in 60% methanol and 16.20 kcal./mole for ethyl acetate in 60% ethanol.

The effect of substituent groups on the rate of acid-catalyzed hydrolysis of methyl benzylidenepyruvate is slight ( $k' = 5.6$  to  $6.1 \times 10^{-3}$  hr.<sup>-1</sup>) and is of the order of magnitude of these effects in the benzoic acid series. The actual rate of hy-

TABLE VI

HYDROLYSIS RATE CONSTANTS IN 50% DIOXANE  
BENZYLIDENEPYRUVIC ESTERS XC<sub>6</sub>H<sub>4</sub>CH=CHCOCO<sub>2</sub>CH<sub>3</sub>

| X                              | Temp., <sup>a</sup> °C. | HCl, <sup>b</sup> moles/l. × 10 <sup>2</sup> | Ester, moles/l. × 10 <sup>3</sup> | $k' \times 10^3$ hr. <sup>-1c</sup> |
|--------------------------------|-------------------------|--|-----------------------------------|-------------------------------------|
|                                |                         |  |                                   |                                     |
| H                              | 25.0                    | 4.28   | 8.00                              | 6.0                                 |
| H                              | 44.9                    | 4.28   | 8.00                              | 29.6 <sup>d</sup>                   |
| 4-OCH <sub>3</sub>             | 25.2                    | 4.28   | 8.00                              | 5.9                                 |
| 4-Br                           | 25.2                    | 4.28   | 6.40                              | 6.1                                 |
| 4-CH <sub>3</sub>              | 25.0                    | 4.28   | 8.00                              | 5.6                                 |
| Reference ester: ethyl acetate |                         |  |                                   |                                     |
|                                | 25.2                    | 4.28   | 22.76-24.44                       | 12.6                                |

<sup>a</sup> ±0.2°. <sup>b</sup> Determined by titration at zero time. <sup>c</sup> Calculated probable error ± 1%. <sup>d</sup> The activation energy  $E$  for methyl benzylidenepyruvate calculated from  $d \ln k/dt = E/RT^2$ , is about 15 kcal./mole.

drolysis of the methyl benzylidenepyruvates, however, is about 90 times as fast as that of the methyl benzoates. In the benzoates, steric hindrance by the phenyl group inhibits the addition of water to the carbon atom of the carboxyl group as postulated in the Ingold mechanism.<sup>14</sup> Ethyl acetate was hydrolyzed as a reference substance with a rate at 25° of  $12.6 \times 10^{-3}$  hr.<sup>-1</sup>, or twice as fast as the methyl benzylidenepyruvates. Methyl pyruvate in water solution hydrolyzes 1.2 times as fast as methyl acetate<sup>15</sup> and ethyl cinnamate has a rate 0.22 times that of ethyl acetate.<sup>4</sup> In ethyl cinnamate and methyl benzylidenepyruvate the phenyl group is farther away from the carboxyl group so that it exerts little steric effect, and as a result the rates are higher than that of methyl benzoate.

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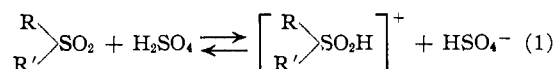
## The Cryoscopic Behavior of Organic Compounds in Sulfuric Acid. III. Diaryl Sulfones

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RECEIVED JANUARY 14, 1952

Additional cryoscopic data of substituted diaryl sulfones in sulfuric acid are reported. The effect of the substituents on the basicity of the sulfone group is interpreted in terms of changes in the electronic structure of the latter.

In a recent publication<sup>1</sup> from this Laboratory it was shown that sulfones are weak bases in sulfuric acid, and that substituents present on the two aryl groups affect equilibrium (1) so that the observed "i" factor can vary between the values of 1 and 2. In view of the fact that di-(*p*-nitro-



phenyl) sulfone gave an "i" factor of 2 while di-(*p*-nitrobenzyl) sulfone gave an "i" factor of 1, it was concluded that the site of the protonation is the sulfone (rather than nitro) group. Since the

cryoscopic study of the sulfones in sulfuric acid seemed to offer an opportunity to compare the basicity of the sulfone group as a function of the electronic effects caused by the substituents R and R', we have extended this work so that a total of eleven diaryl sulfones has now been investigated.

### Experimental

Di-(*p*-chlorophenyl) sulfone, di-(*p*-aminophenyl) sulfone, and bis-(3-nitro-4-chlorophenyl) sulfone were obtained from the Monsanto Chemical Co. and were carefully purified and dried before use. Di-(*m*-nitrophenyl) sulfone<sup>2</sup> was prepared by the nitration of phenyl sulfone, while 2,4-dinitrophenyl phenyl sulfone<sup>3</sup> and 2,4-dinitrophenyl 4-chlorophenyl sul-

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