

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF ARTS AND SCIENCES, UNIVERSITY OF LOUISVILLE]

2-Pyrones. XI.<sup>1</sup> Behavior of 2-Pyrones in 100% Sulfuric Acid

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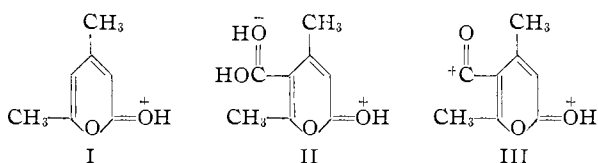
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Cryoscopic determination of the van't Hoff *i*-factors of 4,6-dimethyl-2-pyrone, isodehydroacetic acid, coumalic acid, 2-pyrone-6-carboxylic acid and  $\beta$ -methylglutaconic anhydride in 100% sulfuric acid has given values ranging from 1.83–2.16 for the first four and a value of  $3.3 \pm 0.07$  for the anhydride. These observations are consistent, for the first four, with simple conjugate acid formation by proton addition at the ring carboxyl coupled with a resultant increase in acidity of the carboxylic acid and, for the anhydride, with conjugate acid formation coupled with diprotonation or sulfate formation.

In a previous paper<sup>2</sup> it was reported that isodehydroacetic acid is not esterified and its ethyl ester not hydrolyzed when 100% sulfuric acid solutions are poured into alcohol or water, respectively. A comparison of this behavior with that of the sterically related 2,6-dimethylbenzoic acid or its ester would provide an additional understanding of the phenomenon. The van't Hoff *i*-factor for 2,6-dimethylbenzoic acid has been reported<sup>3</sup> as approximately 3.5, but the behavior of the sulfuric acid solutions of the acid, or its ester, on attempted esterification or hydrolysis, has apparently not been recorded. The present study was undertaken to provide data on the van't Hoff *i*-factors for isodehydroacetic acid, its ester, and some related 2-pyrones to provide a basis for comparison of the two sterically hindered, *ortho* disubstituted acids, the isodehydroacetic acid and 2,6-dimethylbenzoic acid.

Following techniques and procedures previously described<sup>3,4</sup> for the determination of molal freezing point depressions in 100% sulfuric acid, which in our hands gave reproducible results in good agreement with previously reported values for benzoic acid,<sup>3</sup> we have determined *i*-factors for isodehydroacetic acid, 4,6-dimethyl-2-pyrone,<sup>5</sup> coumalic acid, 2-pyrone-6-carboxylic acid and  $\beta$ -methylglutaconic anhydride. The results are recorded in Table I.

The *i*-factor of  $1.98 \pm 0.01$  for 4,6-dimethyl-2-pyrone is consistent with simple conjugate acid I formation. The carboxylic acid derivatives offer



the possibility for formation of doubly charged conjugate acids of the type II. Although it seems unlikely that such a doubly charged ion will form, there have been previous observations of the formation of multiply charged ions<sup>6</sup> with *i*-factors as high as 6.02 and, moreover, evidence of ideal behavior of such ions. This would indicate no

(1) For the previous paper in this series see R. H. Wiley, A. J. Hart, R. P. Davis and N. R. Smith, *THIS JOURNAL*, **76**, 4931 (1954).

(2) R. H. Wiley and N. R. Smith, *ibid.*, **73**, 3531 (1951).

(3) H. P. Treffers and L. P. Hammett, *ibid.*, **59**, 1708 (1937).

(4) M. S. Newman, H. G. Kuivila and A. B. Garrett, *ibid.*, **67**, 704 (1945).

(5) It is not clear whether it is this pyrone or the more common 2,6-dimethyl-4-pyrone for which previous studies have been recorded. L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 47.

(6) M. S. Newman and N. C. DeHo, *THIS JOURNAL*, **73**, 3644 (1951).

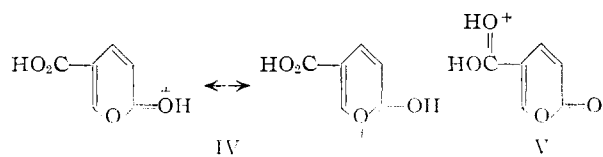
TABLE I  
CRYOSCOPIC BEHAVIOR OF 2-PYRONES IN SULFURIC ACID<sup>a</sup>

<i>i</i> <sup>b</sup>	<i>m</i> <sup>c</sup>	$\Delta\theta$ <sup>d</sup>	$\mu$ <sup>e</sup>	<i>i</i> <sup>f</sup>
Isodehydroacetic acid				
10.14	0.0393	0.471	0.09	1.95
10.14	.0641	.776	.11	1.98
4,6-Dimethyl-2-pyrone				
10.20	0.0837	1.010	0.13	1.97
10.16	.0792	0.966	.14	1.99
Coumalic acid				
10.10	0.0556	0.735	0.13	2.16
10.10	.0575	.713	.12	2.02
10.14	.0664	.878	.14	2.16
2-Pyrone-6-carboxylic acid				
10.26	0.0413	0.469	0.08	1.84
10.23	.0459	.514	.09	1.83
$\beta$ -Methylglutaconic anhydride				
10.18	0.0367	0.727	0.09	3.23
10.21	.0355	.734	.09	3.37
Benzoic acid				
10.24	0.0358	0.387	0.08	1.76
10.24	.0316	.373	.11	1.93

<sup>a</sup> Duplicate values are for independent determinations, not for successive determinations following addition of more solute. <sup>b</sup> Freezing temperature. <sup>c</sup> Molality of solution. <sup>d</sup> Depression of freezing point. <sup>e</sup> Ionic strength. <sup>f</sup> From the relation  $\Delta\theta/m = 6.154i(1 - 0.0047\theta)$ .

*a priori* reason for the non-existence of such ions as II or for further conversion of these to acyloxonium ions such as III where proper steric and resonance conditions, as in the *o,o'*-dimethyl structure of isodehydroacetic acid, indicate such to be a conceivable structural possibility.

The *i*-factors for isodehydroacetic, coumalic and 2-pyrone-6-carboxylic acids vary from 1.83 ( $\mu$  0.9) for 6-pyrone-2-carboxylic acid to 2.16 ( $\mu$  0.14) for coumalic acid and are, thus, well within the range of values reported for compounds whose structure is uncomplicated—such as benzoic acid and benzophenone—as previously reported provided, of course, that comparisons are made at similar ionic strengths. These values indicate simple conjugate acid formation from all three acids. There are at least two possible structures for such a conjugate acid, IV and V. A preference



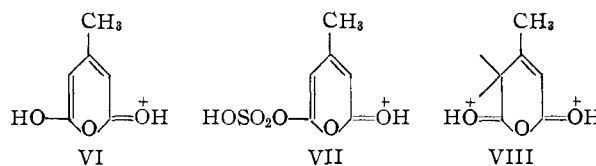
for IV can be based on the reasoning that the more basic ester carboxyl combines first with the proton giving a structure IV in which the acidity of the carboxylic acid is increased by the electron-attracting oxonium ion to the point where the acid is no longer sufficiently basic to accept a proton from sulfuric acid. Observations of the acidic dissociation constants, recorded here for the first time, indicate that the 2-pyronecarboxylic acids are sufficiently strong ( $pK$  2.4–3.37) that little additional structural variation would increase their acidity to the point ( $pK$  ca. 1.0) where they would no longer be sufficiently basic to ionize in sulfuric acid. The  $pK$  value for coumalic acid is 3.37 and for isodehydroacetic acid is 2.42. These values are comparable to the value of 2.86 for chloroacetic acid which, however, is completely ionized ( $k$  2.0) in 100% sulfuric. Since dichloroacetic acid ( $pK$  1.3) is incompletely ionized and trichloroacetic acid ( $pK$  0.89) is not ionized ( $i$  1.0), conversion to the oxonium salt must have an effect at least equivalent to the introduction of two  $\alpha$ -chloro atoms in increasing the acidity of the carboxylic group. This interpretation provides, moreover, an explanation for our observation that the behavior of the isodehydroacetic acid type of  $o,o'$ -dimethylcarboxylic acid and its ester is different from that of other structurally similar carboxylic acids and esters. The isodehydroacetic types fail to undergo hydrolysis or esterification from concentrated sulfuric acid solution apparently because the acyloxonium ion necessary for these reactions is never formed.

In this connection, it is significant that previous studies<sup>7</sup> with ethyl isodehydroacetate have demonstrated another anomalous characteristic. There is a very marked contrast in the ease with which pyridones are formed from methyl coumalate or methyl 2-pyrone-6-carboxylate, and the impossibility of this reaction with ethyl isodehydroacetate. This can probably best be explained in terms of hyperconjugation possibilities, present only in the isodehydroacetate, which lower the electron density in the ring with resultant increased resistance to nucleophilic attack at the ring carboxyl carbon. The data reported in this paper indicate that such effects are inoperative in acid media where the characteristics of the ring are altered by oxonium ion formation.

The observed  $i$ -factor for  $\beta$ -methylglutaconic anhydride is  $3.30 \pm 0.07$  ( $\mu$  0.09). This value indicates some ionic process in addition to simple conjugate acid formation VI observed with the above 2-pyrones. These may involve partial formation of the protonated acid–enol sulfate VII, diacyl sulfate or diprotonated anhydride VIII.<sup>8</sup>

(7) R. H. Wiley, P. Beasley and L. H. Knabeschuh, *ibid.*, **76**, 311 (1954).

(8) R. J. Gillespie and J. A. Leisten, *Quart. Rev. (London)*, **8**, 40 (1954).



The possibility that sulfonation reactions might invalidate these conclusions has been eliminated by recovery of unchanged solute on dilution of the 100% sulfuric acid solutions. 4,6-Dimethyl-2-pyrone, coumalic acid and isodehydroacetic acid were recovered unchanged.  $\beta$ -Methylglutaconic anhydride was recovered as  $\beta$ -methylglutaconic acid.

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### Experimental

No substantial deviations were made from the previously described techniques<sup>3–5,7</sup> used for determining  $i$ -factors. Temperature readings were made with a Beckmann thermometer, uniform stirring was achieved with a windshield wiper motor, and seeding was made uniformly reproducible by using a spring device to hold a piece of Dry Ice against the outer wall. The cooling bath was held at 1.9° below the freezing point (determined by a preliminary approximation) of the solution to provide a uniform rate of cooling. Data obtained on repetitive determinations with new solutions (of each compound) and on redeterminations with the same solution of isodehydroacetic acid after 24 and 36 hours standing gave freezing point depressions which check within the limits of accuracy in reading the Beckmann thermometer. The ester and dimethyl-2-pyrone probably also gave values which do not change with time since their structures are similar to that of the acid. No data are available from our studies for the possibility of change in the value for  $\beta$ -methylglutaconic anhydride with time. Values recorded in Table I are for separate determinations; not for redeterminations following addition of more solute (except for the values recorded for benzoic acid).

The materials used were prepared and purified by methods described in previous papers in this series. The 4,6-dimethyl-2-pyrone was vacuum distilled and a middle fraction separated for use. The isodehydroacetic acid, coumalic acid, 2-pyrone-6-carboxylic acid and  $\beta$ -methylglutaconic anhydride were recrystallized before use. The samples were pelleted and dried thoroughly over phosphorus pentoxide.

The acidic dissociation constants were determined from the  $pH$  values of solutions of half-neutralized acid.<sup>9</sup> This method was preferred because it requires a shorter exposure of the alkali-sensitive pyrones to more dilute alkali than is required by the spectrophotometric method. The  $pH$  values were determined with a Beckmann  $pH$  meter standardized with potassium acid phthalate. A solution of 0.195 g. of coumalic acid in 120 ml. of distilled water to which was added 7.20 ml. of 0.0968  $N$  potassium hydroxide had a  $pH$  of 3.22 and ten minutes later a  $pH$  of 3.30. A solution of 0.244 g. of isodehydroacetic acid in 120 ml. of distilled water, with 7.50 ml. of 0.968  $N$  potassium hydroxide, had a  $pH$  of 2.42 and ten minutes later a  $pH$  of 2.42. The  $pH$  values were taken as equivalent to the  $pK$  values, assuming activity coefficients to be unity.

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(9) J. M. Vandenberg, C. Henrich and S. G. Vandenberg, *Anal. Chem.*, **25**, 776 (1954).