

## The Kinetics and Mechanisms of the Uncatalyzed and Acid-Catalyzed Decomposition Reactions of Meldrum's Acid and Its Methyl Derivatives

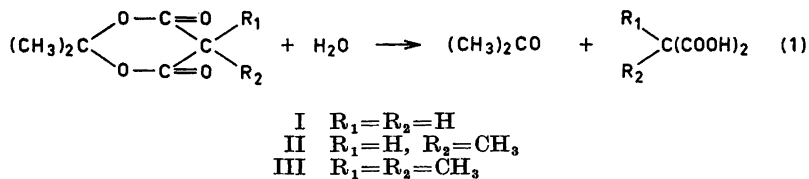
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Meldrum's acid (isopropylidene malonate or 2,2-dimethyl-1,3-dioxane-4,6-dione) and its methyl derivatives have been prepared from acetone and malonic acid and its methyl derivatives and the kinetics of their hydrolysis in water and dilute hydrochloric acid solutions have been studied. Two reactions, one uncatalyzed and the other catalyzed by hydrogen ion, were found to take place concurrently. The contribution of the catalyzed reaction in about 0.1 M hydrochloric acid is from 70 to 80 % of the total reaction. At an initially high enough hydrogen ion concentration, the over-all reaction is kinetically of the first order. In an initially neutral solution the reaction is autocatalytic as the formed malonic acid releases hydrogen ions.

From the values of the thermodynamic functions of activation and from the rates in H<sub>2</sub>O-D<sub>2</sub>O mixtures it is concluded that the acid-catalyzed reaction takes place by the A<sub>Ac</sub>2 mechanism. Also the mechanism of the uncatalyzed reaction is a bimolecular acyl-oxygen fission; the unimolecular alkyl-oxygen fission does not seem to play any significant role.

The neutral and acid-catalyzed hydrolysis reactions of 2,2-dimethyl- (I), 2,2,5-trimethyl- (II), and 2,2,5,5-tetramethyl-1,3-dioxane-4,6-dione (III) present interesting problems for kinetic study:



Like 1,3-dioxolone-4 and its derivatives,<sup>1</sup> these compounds are both acetals and esters (acylals) and may react simultaneously by different mechanisms. Also their structural similarity to 6-ring lactones makes them interesting objects for a study of structural effects.

### EXPERIMENTAL

2,2-Dimethyl-1,3-dioxane-4,6-dione (I) was prepared from acetone and malonic acid as described by Davidson and Bernard.<sup>2</sup> 52 g of powdered malonic acid was dispersed in 60 ml of acetic anhydride and 1.5 ml of concentrated sulfuric acid was slowly added to the suspension. When most of the malonic acid had dissolved, 40 ml of acetone was poured into the solution while the temperature was kept at 20–25°C by cooling. After the mixture had stood overnight in a refrigerator, it was filtered and the crystalline precipitate was washed three times with ice-cold water. Recrystallization was performed by dissolving 10 g of the crude product in 20 ml of acetone at room temperature. The resulting solution was filtered to remove undissolved impurities and 40 ml of water was added to the filtrate. The formed precipitate was collected by filtration, washed with cold water and carefully dried in a vacuum desiccator. After recrystallization, the yield of product melting at 92°C was 70 % of theory.

2,2,5-Trimethyl-1,3-dioxane-4,6-dione (II) was prepared by the same method from acetone and methylmalonic acid. After recrystallization, the yield of product melting at 115°C was about 58 % of theory.

2,2,5,5-Tetramethyl-1,3-dioxane-4,6-dione (III) was prepared by methylating Meldrum's acid (I). A solution containing 14.4 g of I in 50 ml of acetonitrile was added dropwise during 1 h to a stirred suspension which consisted of 26 g of silver oxide, 50 ml of acetonitrile, and 20 ml of methyl iodide, and the temperature of which was held at 10°C. The stirring was continued about 4 h and finally the mixture was left to stand for about 20 h. The remaining silver oxide and the formed silver iodide were filtered off and washed with acetonitrile. The solvent was removed from the filtrate by distillation at reduced pressure below 60°C. The remaining oil was separated from most of impurities by distillation at reduced pressure (b.p. 125–130°C/33 mm Hg); the distillate crystallized in the condenser. The crude product was washed many times with cold water, dissolved in the smallest possible amount of acetone and precipitated by adding water. The formed precipitate was isolated by filtration, washed with cold water and dried in a vacuum desiccator. The yield of product melting at 61°C was 75 % of theory.

Distilled water from which carbon dioxide had been removed by boiling was used in the kinetic experiments. The hydrochloric acid solutions were prepared by diluting reagent grade hydrochloric acid with water; their concentrations were determined by titration with standard diethylamine solution.

*Kinetic measurements.* Hydrolysis reactions were followed by a method described by Salomaa and Laiho.<sup>1</sup> Samples taken from the reaction mixture were added to ice-water mixtures and immediately titrated with an about 0.04 M diethylamine solution using a mixture of cresol red and thymol blue (for compound I) or phenolphthalein (for compounds II and III) as indicator. 8–20 samples were taken during the reaction and several samples after the reaction had proceeded to completion. The moment when the first sample was removed from the reaction mixture was taken as the zero time of the reaction. In the kinetic measurements of reactions in deuterium oxide, the reactions were followed by measuring the absorbance of the solution at 269 nm with a Beckman DU quartz spectrophotometer.

*Rate equations and calculations.* The hydrolysis reactions of the studied compounds were found to follow the same formal rate law as the hydrolysis of 1,3-dioxolone-4 and its derivatives:<sup>1</sup>

$$dx/dt = (k_0 + k_a[H^+])(a-x) \quad (2)$$

where  $a$  is the initial reactant concentration,  $x$  the number of moles per liter that have reacted by time  $t$ ,  $k_0$  the rate coefficient of the uncatalyzed reaction and  $k_a$  the rate coefficient of the acid-catalyzed reaction.

Table 1. Hydrolysis of 2,2,5,5-tetramethyl-4,6-diketo-1,3-dioxane in 0.2897 M hydrochloric acid solution at 45°C.

$t$ , min	0	10	18	25	32	40
$v_i - v_t$ , ml	10.70	8.55	6.95	6.07	5.21	4.32
$10^4(k_0 + k_a[\text{H}^+])$ , s <sup>-1</sup>	—	3.74	4.00	3.78	3.75	3.78
$t$ , min	48	57	66	75	87	i
$v_i - v_t$ , ml	3.60	2.90	2.34	2.02	1.49	0
$10^4(k_0 + k_a[\text{H}^+])$ , s <sup>-1</sup>	3.78	3.82	3.84	3.71	3.78	—

$$\text{Mean } k_i = k_0 + k_a[\text{H}^+] = (3.80 \pm 0.03) \times 10^{-4} \text{ s}^{-1}$$

When the reaction mixture initially contains a sufficiently high hydrochloric acid concentration, the formation of malonic acid or its methyl derivatives during the reaction does not change the hydrogen ion concentration to any significant extent. Hence the over-all first-order rate coefficient can be calculated from the equation:

$$k_i = \frac{2.303}{t} \log \frac{v_i - v_0}{v_i - v_t} = k_0 + k_a[\text{H}^+] \quad (3)$$

where  $v_0$  is the consumption of the titrant by the first sample,  $v_t$  the consumption at time  $t$ , and  $v_i$  the consumption when the reaction had proceeded to completion. A typical series of data for the determination of the over-all first-order rate coefficient is shown in Table 1.

When the reaction mixture was initially neutral, the relative magnitudes of  $k_0$  and  $k_a$  were such that the reaction became autocatalytic owing to the gradual increase in the concentration of hydrogen ions released by the formed malonic acid.

The rate coefficient  $k_i$  calculated from the first-order rate eqn. (3) for the autocatalytic decomposition increased with time and the following method<sup>1</sup> was employed to evaluate the value of  $k_0$

$$dx/dt = (k_0 + k_a\sqrt{K}\sqrt{x})(a-x) \quad (4)$$

which in its partly integrated form is suitable for the present calculations:

$$\frac{1}{t} \ln \frac{a}{a-x} = k_0 + k_a\sqrt{K} \frac{1}{t} \int_0^t \sqrt{x} dt = k_i \quad (5)$$

Here  $x$  is the concentration of the formed malonic acid and  $K$  its dissociation constant. The value of the integral in eqn. (5) was evaluated from successive values of  $x$  at different times  $t$  by the trapezoidal rule:

$$\int_0^t \sqrt{x} dt = \frac{1}{2} \sum_{\nu=1}^i (\sqrt{x_\nu} + \sqrt{x_{\nu-1}})(t_\nu - t_{\nu-1}) \quad (6)$$

where the value of  $x_{\nu-1}$  when  $\nu=1$  is the value of  $x$  for the first sample taken from the reaction mixture. The value of  $k_a$  required in the calculation was estimated from the plot of the over-all rate coefficient against the hydrogen ion concentration. When the neutral

hydrolysis of the compounds I and II was studied, the correction due to the pseudo-acid character of these compounds was taken into account and eqn. (5) was used in the form:

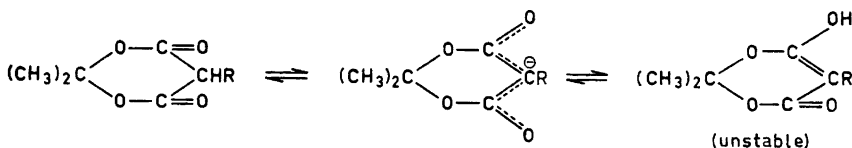
$$k_0^e = k_t - k_a (\sqrt{K} - \sqrt{K_2}) \frac{1}{t} \int_0^t \sqrt{x} dt \quad (7)$$

where  $k_0^e$  is a rate coefficient which includes an additional term  $k_a \sqrt{K_e c_0}$  to take into account the concentration of hydrogen ions released by the dissociation of the initial reactant (I or II). In other words,

$$k_0 = k_0^e - k_a \sqrt{K_e c_0} \quad (8)$$

where  $K_e$  is the dissociation constant and  $c_0$  the initial concentration of the reacting compound.

Meldrum's acid and its monomethyl derivative (I and II) have a pseudo-acid character and consequently the following equilibrium prevails in water:<sup>3,4</sup>



The values  $1.3 \times 10^{-5}$  and  $1.8 \times 10^{-5}$  were obtained for the dissociation constants of the pseudo acids I and II, respectively by pH measurements. The equilibrium will be discussed more closely in another paper.<sup>5</sup>

The values at 25°C were used for the first dissociation constants of malonic, methylmalonic, and dimethylmalonic acids at all temperatures and corrections for the second dissociation stages were neglected. The values used for the first dissociation constants were

Malonic acid <sup>6</sup>	$1.58 \times 10^{-3}$
Methylmalonic acid <sup>7</sup>	$8.47 \times 10^{-4}$
Dimethylmalonic acid <sup>8</sup>	$6.83 \times 10^{-4}$

Data from a typical experiment for the determination of the rate coefficient  $k_0$  of the uncatalyzed reaction are presented in Table 2.

## RESULTS AND DISCUSSION

The over-all first-order rate coefficients ( $k_t$ ) of the hydrolysis reactions of the studied compounds and the values of the rate coefficients of both the neutral ( $k_0$ ) and acid-catalyzed reactions ( $k_a$ ) under different conditions are shown in Table 3. The values of the rate coefficients of the uncatalyzed reaction were calculated directly from eqns. (6) and (7) as described above and the values of the rate coefficients of the acid-catalyzed reactions were obtained from the plot of the over-all rate coefficient *versus* hydrogen ion concentration (Fig. 1).

The values of the quantities in Table 4 for the catalyzed reactions are of the same order of magnitude as generally found for reactions proceeding by the  $A_{AC}2$  mechanism. The activation entropies have relatively high negative values which suggests a normal ester hydrolysis where an attack of water on the carbonyl group is involved.

Table 2. Hydrolysis of 2,2-dimethyl-4,6-diketo-1,3-dioxane in water at 25°C.  $10^6 k_a = 103$  mole<sup>-1</sup>s<sup>-1</sup>.  $K = 1.58 \times 10^{-3}$  mole/l and  $K_e = 1.3 \times 10^{-6}$  mole/l.

<i>t</i> min	<i>x</i> mole/l	$10^6 k_t$ s <sup>-1</sup>	$10^6 k_a (\sqrt{K} - \sqrt{K_e}) \frac{1}{t} \int_0^t \sqrt{x} dt$ s <sup>-1</sup>	$10^6 k_0^e$ s <sup>-1</sup>
0	0.0021	—	—	—
180	0.0047	4.40	0.21	4.19
1120	0.0261	4.49	0.40	4.09
1420	0.0319	4.49	0.44	4.05
1660	0.0364	4.52	0.47	4.05
1970	0.0416	4.54	0.52	4.02
2530	0.0502	4.57	0.58	3.99
2950	0.0564	4.67	0.62	4.05
3330	0.0620	4.82	0.66	4.16
4045	0.0699	4.92	0.71	4.21
4430	0.0736	4.99	0.74	4.25
4865	0.0774	5.06	0.76	4.30
5670	0.0820	5.00	0.81	4.19
i	0.1033	—	—	—

$$\text{Mean } 10^6 k_0^e = 4.13 \pm 0.04 \text{ s}^{-1}$$

$$10^6 k_0 = 4.02 \pm 0.04 \text{ s}^{-1}$$

If the acid-catalyzed reaction proceeded by the A-1 mechanism, a partial double bond between the positions 1 and 2 or 2 and 3 should be formed in the transition state which thus remains on a relatively high energy level owing to considerable angle strain. If the acid-catalyzed reaction proceeded by the A<sub>Ac</sub>2 mechanism, the angle strain in the transition state would be even less

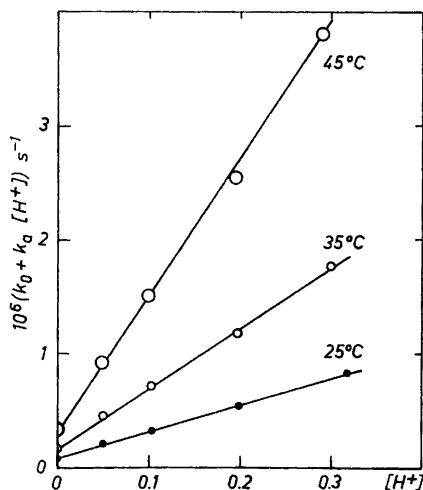


Fig. 1. The hydrolysis of 2,2,5,5-tetramethyl-1,3-dioxane-4,6-dione in water and in dilute hydrochloric acid solutions at 25, 35, and 45°C. The dependence of the over-all first-order rate coefficient on the acidity of the reaction medium.

Table 3. Hydrolysis of Meldrum's acid and its methyl derivatives at different temperatures in water and in dilute hydrochloric acid solutions. The over-all first-order rate coefficients and the rate coefficients of the neutral and acid-catalyzed reactions.

Compound	°C	[H <sup>+</sup> ], mole/l	10 <sup>3</sup> k <sub>t</sub> s <sup>-1</sup>	10 <sup>3</sup> k <sub>0</sub> <sup>e</sup> s <sup>-1</sup>	10 <sup>3</sup> k <sub>0</sub> s <sup>-1</sup>	10 <sup>3</sup> k <sub>a</sub> l mole <sup>-1</sup> s <sup>-1</sup>
I	25	—	4.13			
I	25	0.0999	14.8	4.13	4.02	103
I	25	0.1998	25.2			
I	25	0.3176	36.1			
I	25	0.4165	45.8			
I	35	—	9.60			
I	35	0.1026	38.3	9.60	9.31	269
I	35	0.1972	63.9			
I	35	0.2978	88.9			
I	35	0.4153	116			
I	45	—	23.2			
I	45	0.1022	88.9	23.2	22.6	621
I	45	0.1964	146			
I	45	0.2966	206			
I	45	0.4137	272			
II	25	—	3.25			
II	25	0.0499	8.70	3.25	3.15	112
II	25	0.0999	14.4			
II	25	0.1998	25.4			
II	25	0.3176	39.8			
II	35	—	6.43			
II	35	0.0498	20.0	6.43	6.19	275
II	35	0.1026	34.9			
II	35	0.1972	61.2			
II	35	0.3167	92.1			
II	45	—	13.0			
II	45	0.0496	49.5	13.0	12.4	650
II	45	0.0992	77.5			
II	45	0.1964	133			
II	45	0.2897	188			
III	25	—	7.84			
III	25	0.04995	20.8	7.84	7.84	241
III	25	0.1029	32.0			
III	25	0.1978	53.9			
III	25	0.3177	82.9			
III	35	—	16.6			
III	35	0.0498	45.5	16.6	16.6	540
III	35	0.1026	71.3			
III	35	0.1972	117			
III	35	0.2978	177			
III	45	—	34.0			
III	45	0.0496	91.8	34.0	34.0	1168
III	45	0.0992	151			
III	45	0.1944	254			
III	45	0.2897	380			

Table 4. Values of the parameters of the Arrhenius equation, entropies and free energies of activation, and rate coefficients at 25°C of the neutral and acid-catalyzed hydrolysis reactions of 2,2-dimethyl- (I), 2,2,5-trimethyl- (II), and 2,2,5,5-tetramethyl-4,6-diketo-1,3-dioxane (III).

	<i>E</i> kcal/mole	log <i>A</i>	$\Delta S^\ddagger$ E.U.	$\Delta G^\ddagger$ kcal/mole	
Acid-catalyzed hydrolysis					$10^4 k_a$ l mole <sup>-1</sup> s <sup>-1</sup>
I	16.9	8.44	-21.9	22.89	1.045
II	16.6	8.20	-23.0	22.85	1.12
III	14.9	7.29	-27.2	22.39	2.41
Neutral hydrolysis					$10^6 k_0$ s <sup>-1</sup>
I	16.3	6.52	-30.7	24.84	3.97
II	12.9	3.96	-42.4	24.97	3.13
III	13.8	5.03	-37.5	24.42	7.85

than in the initial reactant. Hence the transition state of the A<sub>Ac</sub>2 mechanism would be much more favored and the hydrolysis obviously occurs by this mechanism.

*Deuterium solvent isotope effects.* Eqn. (9) presented by Salomaa, Schaleger and Long<sup>9</sup> can be used under certain circumstances to make a distinction between different accessible transition state structures. This equation is very satisfactory for the compounds studied in this work.

$$\frac{k_n}{k_H} = \frac{(1-n+n\phi)^i}{(1-n+nl)^3} \quad (9)$$

By assuming that there is only one exchangeable hydrogen atom in the transition state, as is the case with the A-1 mechanism, eqn. (10) represents the kinetic behavior in H<sub>2</sub>O-D<sub>2</sub>O mixtures. In this equation  $k_H$ ,  $k_n$ , and  $k_D$  are the rate coefficients in light water, mixed water and heavy water, respectively, and  $l$  is the isotopic fractionation factor for hydronium ion which has the value 0.706 at 45°C (0.67 at 25°C).

$$k_n/k_H = \frac{(1-nl^3k_D/k_H)}{(1-n+nl)^3} \quad (10)$$

If one assumes that a water molecule is also involved in the formation of the transition state, there are three exchangeable hydrogens, which gives

$$k_n/k_H = \frac{(1-n+nl(k_D/k_H)^{1/3})^3}{(1-n+nl)^3} \quad (11)$$

In deriving eqn. (11) it has been assumed that the isotopic fractionation factor is the same for every exchangeable hydrogen. When the measured value, 0.94

Table 5. Hydrolysis of 2,2,5,5-tetramethyl-1,3-dioxane-4,6-dione (isopropylidene dimethylmalonate) in  $L_2O$  at 45°C.

$n$	$n_H$	$[L^+]$ mole/l	$10^4 k_i$ $s^{-1}$	$10^3 k_a$ $\text{mole}^{-1} s^{-1}$	$10^6 k_0$ $s^{-1}$
0	1	—	—	1.168	34.0
0.500	0.500	0.345	4.30	1.150	33.2 <sup>a</sup>
0.978	0.022	0.338	4.03	1.104	30.0
0.978	0.022	0.168	2.155	1.104	30.0
1.000	0	—	—	1.102 <sup>b</sup>	—

$k_D/k_H = 1.102/1.168 = 0.94$  (catalyzed reaction)  
 $k_D/k_H = 30.0/34.0 = 0.88$  (uncatalyzed reaction)

<sup>a</sup> Calculated from eqn. (9), when  $i=2$ .

<sup>b</sup> Extrapolated value.

The value 0.94 for  $k_D/k_H$  at 25°C was obtained later.<sup>13</sup>

(Table 5), of  $k_D/k_H$  is substituted in eqns. (10) and (11) and the value of  $k_n/k_H$  when  $n=0.500$  is calculated, eqn. (10) gives the value 1.07 and eqn. (11) the value 0.98 for this quantity. The transition state hence includes at least three exchangeable hydrogens since the experimentally obtained value for  $k_{0.5}/k_H$  was also 0.98.

The gross deuterium solvent isotope effect ( $k_D/k_H=0.94$ ) is smaller than usually obtained for esters (1.68<sup>9,10</sup>), but Butler and Gold,<sup>11</sup> reasoning that the solvent isotope effect is smaller in the hydrolysis of this type of compound when it occurs by acyl-oxygen cleavage, reported the value 0.86 for  $\beta$ -propiolactone at 25°C.

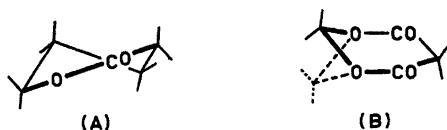
Salomaa<sup>12</sup> has calculated the value 1.19 for the deuterium solvent isotope effect in the hydrolysis of 2,2,5,5-tetramethyl-1,3-dioxane-4,6-dione at 25°C for a normal  $A_{Ac}2$  mechanism. However, the experimentally determined value at this temperature was 0.94.<sup>13</sup> The difference between this value and the values for the hydrolysis of open-chain esters may be largely due to the fact that the hydrolysis reaction proceeds relatively far before the transition state is reached and hence the experimental value of  $k_D/k_H$  is slightly smaller than the calculated value.

The large negative values of the activation entropy for the neutral hydrolysis reactions (Table 5) suggest that the reactions proceed by the  $B_{Ac}2$  mechanism. A bimolecular mechanism of neutral hydrolysis similar in principle to the mechanism of normal alkaline hydrolysis (in neutral hydrolysis a water molecule and not a hydroxyl ion attacks the carbonyl group) is supported also by the observation that 2,2,5,5-tetramethyl-1,3-dioxane-4,6-dione decomposes almost instantaneously in alkaline media.<sup>1,14</sup> Meldrum's acid (I) and its monomethyl derivative (II) are stable in alkaline media since they form salts owing to their pseudo-acid character.

*Structural factors.* Abramovitch *et al.*<sup>15</sup> reported that Meldrum's acid (I) and its methyl derivatives (II and III) are chair forms. They found only one



signal for methyl protons in isopropylidene dimethylmalonate (III) and deduced that this is due to a rapid chair-chair interconversion of the six-membered ring. However, several authors<sup>16</sup> have found that  $\delta$ -lactones assume the half-chair conformation and Sheppard and Turner<sup>16</sup> have shown that this half-chair is slightly flattened (A):



On the basis of structural similarity with  $\delta$ -lactones it is likely that the rings in Meldrum's acid and its methyl derivatives may be nearly planar (B) except for the carbon 2 which fluctuates so that the methyl groups at position 5 in isopropylidene dimethylmalonate (III) are identical when the NMR spectrum is recorded. Isopropylidene malonate (I) and isopropylidene methylmalonate (II) are nearly equally stable since the "axial" methyl group at position 2 in the latter compound remains on the same side as the hydrogen at position 5 in order to avoid the great interaction between methyl groups at positions 2 and 5. However, in 2,2,5,5-tetramethyl-1,3-dioxane-4,6-dione (III) there is always this interaction on one or the other side of the ring and hence this compound is on an energy level that is about 1 kcal/mole higher than the energy levels of the other two compounds.

One of the carbonyl groups has vanished in the transition states of the hydrolysis reactions of the studied compounds and the angular strain has decreased greatly. This decrease is somewhat greater for isopropylidene dimethylmalonate and this greater decrease together with the higher energy level of the ground state is more than enough to compensate for the steric hindrance of the *gem*-methyl groups at position 5 in this compound to the attack of water on the carbonyl group. Hence this compound should hydrolyze about 2–3 times faster than the other two compounds (I and II).

The higher rate of hydrolysis of the dimethyl derivative is readily understood when the keto-enolate equilibrium is considered.<sup>5</sup> 2,2,5,5-Tetramethyl-1,3-dioxane-4,6-dione is a pure ester, whereas 2,2-dimethyl- and 2,2,5-trimethyl-1,3-dioxane-4,6-dione are also pseudoacids. They are, true enough, practically in the diketo form in acidic media but their tendency to form an enolate anion may slightly reduce the rate of hydrolysis. The attack of water on the "pure" carbonyl group in the dimethyl derivative (III) is also in this respect slightly easier than the attack of water on the carbonyl groups of compounds (I and II) which have a tendency to assume the enolate form. This conclusion is supported by the fact that the neutral hydrolysis of 2,2-dimethyl-1,3-dioxane-4,6-dione is slightly faster than that of the monomethyl derivative and that the *pK* value of the former is greater than that of the latter; this means that 2,2-dimethyl-1,3-dioxane-4,6-dione has a slightly weaker tendency to form the enolate anion than 2,2,5-trimethyl-1,3-dioxane-4,6-dione.

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## REFERENCES

1. Salomaa, P. and Laiho, S. *Acta Chem. Scand.* **17** (1963) 103.
2. Davidson, D. and Bernhard, S. A. *J. Am. Chem. Soc.* **70** (1948) 3426.
3. Eistert, B. and Geiss, F. *Tetrahedron* **7** (1959) 1.
4. Eistert, B. and Geiss, F. *Chem. Ber.* **94** (1961) 929; Eigen, M., Ilgenfritz, G. and Krase, W. *Chem. Ber.* **98** (1965) 1623.
5. Pihlaja, K. *Unpublished results.*
6. Adell, B. *Z. physik. Chem. Abt. A* **186** (1940) 39.
7. Jeffery, G. H. and Vogel, A. I. *J. Chem. Soc.* **1936** 1756.
8. Gane, R. and Ingold, C. K. *J. Chem. Soc.* **1931** 2153.
9. Salomaa, P., Schaleger, L. L. and Long, F. A. *J. Am. Chem. Soc.* **86** (1964) 1.
10. Salomaa, P. *Acta Chem. Scand.* **20** (1966) 1263.
11. Butler, A. R. and Gold, V. *Chem. Ind. (London)* **1960** 1218.
12. Salomaa, P. *Personal communication.*
13. Pihlaja, K. and Launosalo, T. *Unpublished results.*
14. Euranto, E. *Ann. Univ. Turku. Ser. A I* (1959) No. 31.
15. Abramovitch, R. A., Rajan, J. B. and Walker, C. E. *J. Chem. Eng. Data* **12** (1967) 594.
16. *For references, see Sheppard, R. C. and Turner, S. Chem. Commun.* **1968** 77.

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