263. *The Structure of Diketen : Potentiometric and Conductivity Measurements.*

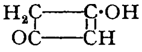
By Albert Wassermann.

It is shown that diketen dissolved in aqueous and in dry acetone is an acid. This observation appears to provide some evidence in favour of one of the two most probable formulæ for diketen.

Chick and Wilsmore (*J.*, 1908, **93**, 946) suggested structure (I) for diketen, whereas Staudinger and Beretza (*Ber.*, 1909, **42**, 4908) proposed (II), both formulæ being abandoned shortly afterwards in favour of (III) (Chick and Wilsmore, *J.*, 1910, **97**, 1978; Staudinger, " Die Ketene ", 1912, pp. 43, 46). Angus, Leckie, Le Fèvre, Le Fèvre, and Wassermann (*J.*, 1935, 1751) showed that (III) is not tenable and pointed out that (II) was compatible with all the experimental evidence then available. Hurd *et al.* (*J. Amer. Chem. Soc.*, 1936, **58**, 962, and subsequent papers) and Rice and Roberts (*ibid.*, 1943, **65**, 1674) suggested that (I), (III), or (IV) is more satisfactory than (II), but Boese (*Ind. Eng. Chem.*, 1940, **32**, 16) preferred (V). The various arguments were by no means convincing and, therefore, on the suggestion of the author,

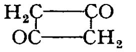
$CH_3{\cdot}CO{\cdot}CH{:}CO$

(I.)



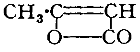
$\begin{array}{lcl}H_2C & \text{---} & C{\cdot}OH \\ | & & \| \\ OC & \text{---} & CH\end{array}$

(II.)



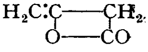
$\begin{array}{lcl}H_2C & \text{---} & CO \\ | & & | \\ OC & \text{---} & CH_2\end{array}$

(III.)



$\begin{array}{lcl}CH_3{\cdot}C & = & CH \\ | & & | \\ O & \text{---} & CO\end{array}$

(IV.)



$\begin{array}{lcl}H_2C{:}C & \text{---} & CH_2 \\ | & & | \\ O & \text{---} & CO\end{array}$

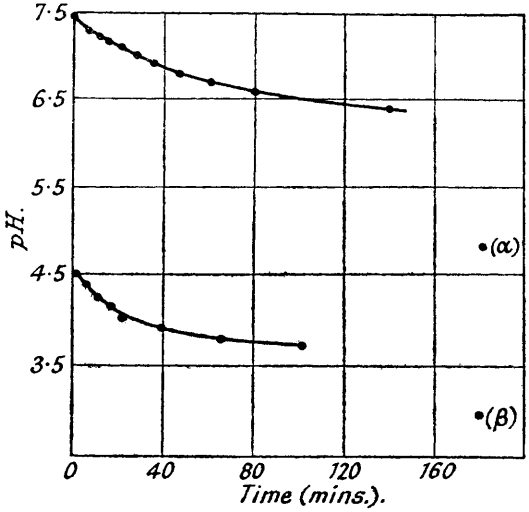
(V.)

Whiffen and Thompson (*J.*, 1946, 1005) determined the infra-red spectrum of diketen and compared it with the Raman spectrum which had already been measured by Angus *et al.* (*loc. cit.*) and subsequently by other authors (for references see Whiffen and Thompson).

The spectroscopic investigations confirmed that (III) is unsatisfactory, and (I) and (II) appeared also to be ruled out; formula (I) is moreover difficult to reconcile with the results of unpublished electron-diffraction measurements (Schomaker, Bauer, *et al.*, private communication). Structures (IV) and (V), on the other hand, are both compatible with the spectroscopic evidence, the latter being slightly more probable.

The Raman and infra-red spectra relate to liquid diketen and to solutions in carbon tetrachloride, carbon disulphide, or chloroform. It appeared of interest to find out whether some evidence in favour of either (IV) or (V) could be obtained by a study of the acid properties of diketen dissolved in aqueous or dry acetone and, therefore, the present experiments were carried out.

FIG. 1.



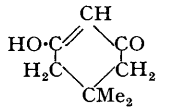
Dependence on time of pH of buffered and unbuffered diketen solutions.

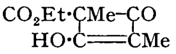
Upper graph : Initial concn. of diketen = 0·0624 *g.-mol./l.*
Initial concn. of KOH = 0·0312 *g.-mol./l.*
Lower graph : Initial concn. of diketen = 0·162 *g.-mol./l.*

(*The significance of the points designated by* α *and* β *is discussed below.*)

Results.—In estimating the electrolytic dissociation constant, *K*, of diketen in 50 vol. % acetone–water (77·0 mol. % water), potentiometric measurements were made at 18° and 0°, using glass electrodes and a Cambridge Instrument Company pH meter. The *K* values of

(VI.)





$$\begin{array}{l}\mathrm{CO_2Et{\cdot}\underset{|}{C}Me{-}\underset{|}{C}O}\\ \mathrm{HO{\cdot}C{=\!=}CMe}\end{array}$$

(VII.)

acetoacetic acid and an upper limit of *K* of methyl crotonate were determined under the same experimental conditions, and furthermore, some experiments with the enols (VI) and (VII) were made in order to test the experimental technique.

All the solutions were 0·100M with respect to potassium chloride, and in most runs buffers were prepared by partial neutralisation with sodium or potassium hydroxide. Some measurements with unbuffered solutions were also made and, therefore, the dissociation constants were calculated either from $K = [\mathrm{H}^+][\mathrm{B}^-]/([C] - [\mathrm{B}^-])$ or from $K = [\mathrm{H}^+]^2/[C]$ where $[\mathrm{H}^+]$ is the apparent hydrogen-ion concentration, as estimated from the dial readings of the previously standardised pH meter, $[C]$ is the concentration of the substance to be tested, and $[\mathrm{B}^-]$ is the concentration of the sodium or potassium salt as calculated from the amount of alkali added to the reaction mixture. No attempt has been made to find out whether the normal potential of the glass electrode changes on passing from water to 50% acetone–water nor has a correction been applied in order to eliminate diffusion potentials. The present K values should not be regarded as classical or thermodynamic dissociation constants in terms of concentration or activities, but they are useful for purposes of comparison (see Kumler, *J. Amer. Chem. Soc.*, 1938, **60**, 863). In the experiments with acetoacetic acid or with the enols (VI) and (VII) the initial hydrogen-ion concentration, measured 2 or 3 minutes after the preparation of the solution, remained constant for many hours, but in the case of diketen solutions a time dependence was observed as shown by the graphs in Fig. 1.

The hydrogen-ion concentration required for the calculation of K was estimated by extrapolating the pH–time curve to the time of mixing. Table I is a summary of the results of the potentiometric measurements.

TABLE I.

Results of potentiometric measurements in 50 vol. % acetone–water.

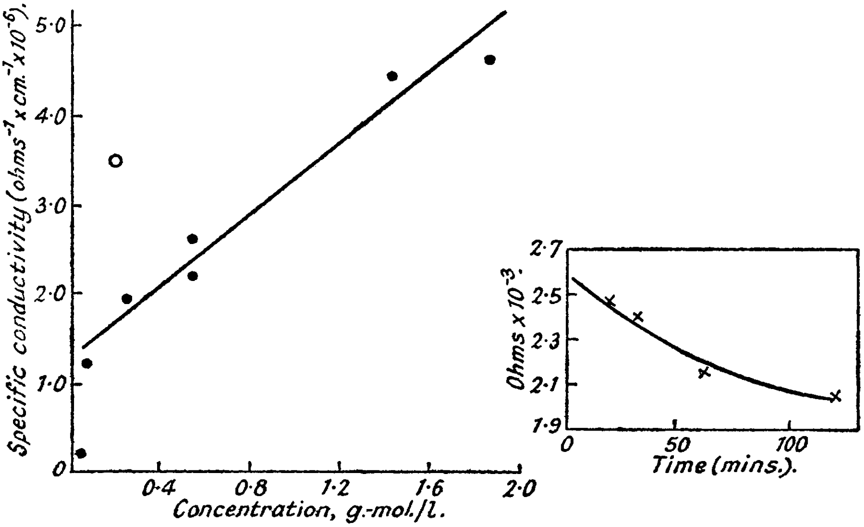
Substance.	Temp.	Solution.	Range of initial concns. (g.-mol./l.).	No. of runs.	Δ pH per 10 mins. (initial stage).	$-\log_{10} K$ (K in g.-mol./l.).
Diketen	18°	Buffered *	0·0641 —0·00119	15	0·1 —0·4	7·1 ± 0·4
	18	Unbuffered †	0·388 —0·0162	8	0·03—0·3	7·2 ± 0·2
	0·3	Buffered *	0·744 —0·0150	6	0·05—0·2	7·7 ± 0·3
	0·3	Unbuffered †	0·310 —0·0620	3	0·03—0·04	7·7 ± 0·1
Acetoacetic acid ‡	15	Buffered	0·138 —0·00488	10	—	4·7 ± 0·1
	0·3		0·00800—0·00100	4	—	4·3 ± 0·1
Enol (VI)	22		0·0384 —0·000984	5	—	6·40 ± 0·06
	0·3		0·0130 —0·00165	4	—	6·76 ± 0·04
Enol (VII)	19		0·00604—0·000155	5	—	6·40 ± 0·05
Methyl crotonate	19	Unbuffered	0·39	1	—	>12

* pH of reaction mixture = 6—8; in some of these runs the ratio $[C]/[B^-]$ was varied from 1·4 to 5·7.

† pH of reaction mixture = 4.

‡ In these runs the reaction mixture contained also some ethyl alcohol (see p. 1327).

FIG. 2.



Specific conductivities at 0°. ● = *Diketen.* ○ = *Enol (VI).*

The graph in the right-hand corner indicates the time-dependence of the resistance of a 0·611M-*diketen solution.*

The specific electrical conductivities, κ, of solutions of diketen in dry acetone were also determined. The resistance of the freshly prepared diketen solution decreased slowly with time, and, therefore, initial resistance values were calculated, by using a back extrapolation method similar to that mentioned above. The concentration dependence of the initial κ values, calculated from the extrapolated resistance, in shown in Fig. 2, which indicates also the specific conductivity of an acetone solution of (VI); in the latter test the resistance did not change with time.

The pH values corresponding to the points α and β in Fig. 1 are theoretical values which should be reached if, after infinite time, the diketen were quantitatively converted into acetoacetic acid, but the flat portions of the graphs correspond to far higher pH values, and similar discrepancies were observed within the whole concentration range, in experiments done at 0° and room temperature and with unbuffered or buffered solutions. Control tests showed that carbon dioxide is not given off and it is probable, therefore, that under the conditions of these measurements diketen is converted not only into acetoacetic acid but also into a non-acidic substances. A reaction of a different kind appears to proceed in the absence of water and this must be responsible for the time-dependence of the electrical conductivity.

The K values listed in the first four lines of Table I indicate that it should be possible to titrate diketen with alkali. If freshly dissolved diketen is titrated, fairly accurate results are obtained as shown by the figures in Table II. If, on the other hand, a diketen solution is kept for several days at room temperature, the titration results are too low, which is understandable in view of the consecutive reaction referred to above.

TABLE II.

Titration experiments with freshly prepared diketen solutions.

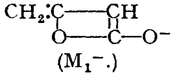
Temp. during titration.	Vol. % of acetone in reaction mixture at end-point of titration.	Concn. of alkali (g.-mol./l.) at end-point of titration.	No. of tests.	Mols. of alkali used per mol. of diketen.*
20—25°	8—33	0·02—0·07	12	0·99 ± 0·04
10	25	0·07	1	1·02
4	25	0·07	2	1·05 ± 0·04

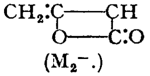
* The indicator was phenolphthalein and the titration was done in a stream of nitrogen; the end-point was taken to be reached when the pink coloration remained visible for 30 secs.

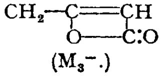
Unsuccessful attempts were made to prepare salts of diketen which are soluble in organic solvents and to determine the number of double bonds by Meyer's bromine titration. The use of a more refined technique does not appear promising in view of the work of Chick and Wilsmore and of Boese (*locc. cit.*) who showed that even under mild conditions the addition of halogens to diketen leads to open-chain compounds.

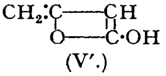
If solutions of ferric chloride and acetoacetic acid are mixed, a colour is produced but no coloration of this kind could be observed in control experiments with freshly dissolved diketen.

Discussion.—The decrease of the pH values of diketen solutions in aqueous acetone is most probably due to the gradual formation of acetoacetic acid (cf. Chick and Wilsmore; Boese, *locc. cit.*); it could be suggested that, immediately after the dissolution of diketen, the rate of this reaction is relatively large and that the acidity, as estimated with the help of the back extrapolation method, is due to hydrogen ions dissociated from the carboxyl group of the acetoacetic acid. If this were the case one would have to postulate that the alkali hydroxide added to the reaction mixture is converted into the alkali salt of acetoacetic acid, and this in turn implies that the equilibrium diketen + water $\rightleftarrows$ acetoacetic acid is markedly dependent on the pH of the solution. It can easily be shown, however, with the help of the K values listed in the fifth and sixth lines of Table I, that this supposition cannot be reconciled with the observed initial pH values and with the approximate agreement of the dissociation constants of diketen, calculated from the results of measurements done in unbuffered and buffered solution. It should also be noted that no coloration is produced if ferric chloride is added to freshly dissolved diketen, and that the dissociation constant of diketen, like that of the enol (VI), increases slightly with increasing temperature, while the K values of acetoacetic acid decrease with increasing temperature. The electrical conductivity of diketen dissolved in dry acetone shows, moreover, that a marked ionisation occurs also if the formation of acetoacetic acid is excluded, and for all of these reasons it is believed that the initial acidity of diketen solutions is mainly due to hydrogen ions dissociated from the diketen itself.


(M_1^-.)

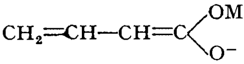

(M_2^-.)


(M_3^-.)


(V′.)

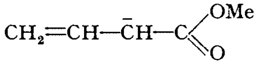
If diketen is represented by formula (IV) or (V), one has to assume that the dissociation will lead to a mesomeric anion, M^-, of a charge distribution intermediate between (M_1^-), M_2^-), and

(M_3^-), rather than to an anion with two endocyclic angular double bonds. M^- is now compared with the anion of methyl crotonate (m^-), the charge distribution of which is probably intermediate between, (m_1^-), (m_2^-), and (m_3^-). If structure (IV) were correct one would have to assume that



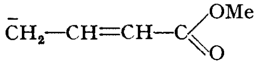
$CH_2{=}CH{-}CH{=}C(OMe){-}O^-$

(m_1^-.)



$CH_2{=}CH{-}\bar{C}H{-}C(OMe){=}O$

(m_2^-.)



$\bar{C}H_2{-}CH{=}CH{-}C(OMe){=}O$

(m_3^-.)

the observed electrolytic dissociation of diketen is due to the reaction (IV) $= M^- + H^+$ in which the hydrogen ion is abstracted from a methyl group. Such a dissociation is of the same type as the process methyl crotonate $= m^- + H^+$, which also involves the rupture of a methyl group followed by a resonance stabilisation, the entropy changes of these two reactions being probably similar. It is recognised that an endocyclic oxygen atom facilitates the electrolytic dissociation; this effect can be very large if the dissociable hydrogen of the open-chain compound is kept in position by the formation of a hydrogen bond, while in the cyclic compound the chelation is prevented by the requirements of ring strain. Apart from such cases, however, the increase of dissociation constants, due to endocyclic oxygen atoms, is only moderately large; tetronic acid, for instance, has no measurable second acid dissociation constant (Kumler, *loc. cit.*), and the K values of ethylene oxide-dicarboxylic acid are respectively about 10 and 100 times larger than those of fumaric and succinic acid (Wassermann, *Helv. Chim. Acta*, 1930, **12**, 207). The acid dissociation constant of diketen on the other hand is at least 10^5 times larger than that of methyl crotonate, and this is difficult to reconcile with the assumption that the observed acidity of the former substance is due to the abstraction of a hydrogen ion from the methyl group. These experiments indicate, therefore, that formula (IV) for diketen is less satisfactory than the alternative structure (V).

It is relevant to consider not only the dissociation of electroneutral species, but also consecutive associations, involving the anion M^- and hydrogen ions, which could lead to three isomers, (IV), (V), and (V′) in amounts depending on the relative rates of the various processes. In view of the above considerations it appears improbable that the reaction (IV) $= M^- + H^+$ proceeds to any appreciable extent; if, therefore, in the presence of the solvents here considered, (IV) is gradually formed, a decrease of the acid titre of diketen solutions should take place. This has actually been observed, but the over-all effects referred to on p. 1326 will also involve other reactions, *e.g.*, a slow polymerisation of diketen.

Whiffen and Thompson (*loc. cit.*) showed that the infra-red spectrum of diketen does not contain the characteristic OH band; this, however, does not necessarily exclude the formation of (V′) under conditions conducive to electrolytic dissociation because in the solvents used for the spectroscopic measurements or in pure liquid diketen the equilibrium (V) $\rightleftarrows$ (V′) could be far on the left-hand side, while in the presence of water or acetone a shift to the right-hand side could occur.* In other keto–enol systems the equilibrium proportion of the enol decreases on increasing the polarity of the solvent (see, *e.g.*, Branch and Calvin, " The Theory of Organic Chemistry ", 1944, p. 297), but there is no theoretical reason why a similar solvent effect should also operate in the case of diketen.

EXPERIMENTAL.

Keten was made according to Williams and Hurd (*J. Org. Chem.*, 1940, **5**, 122); it was condensed at $-80°$, small portions being polymerised by gradually raising the temperature to $+20°$. The polymers were fractionally distilled until the m. p. was above $-50°$; solid diketen was then partially melted, the liquid fraction was separated, and the remaining portion was repeatedly distilled at 1 mm. pressure until the m. p. was between $-8°$ and $-7°$. Spectroscopic tests showed that this diketen did not contain a detectable quantity of acetic anhydride, and further purification did not alter the acidity or the electrical conductivity. The purified diketen was stored in sealed glass vessels at $-80°$, if it was not immediately used. Ethyl acetoacetate and methyl crotonate were redistilled at 3 mm. pressure and the first ester was hydrolysed at room temperature with a slight excess of potassium hydroxide. The reaction mixture thus obtained was used for the determination of the K values of acetoacetic acid, after addition of the required quantity of hydrochloric acid and acetone. The enol (VI) was a commercial sample and was repeatedly recrystallised fron acetone. The substance (VII) was prepared according to Schroeter (*Ber.*, 1916, **49**, 2711) and recrystallised from dilute ethyl alcohol. The water used for the potentiometric measurements was doubly redistilled and freed from carbon dioxide. The acetone was purified by a method similar to that described by Walden, Ulich, and Busch (*Z. physikal. Chem.*, 1926, **23**, 429), its specific conductivity at 0° being less than $0{\cdot}5 \times 10^{-6}$ ohm^{-1} $\times$ cm.$^{-1}$.

The standardisation of the pH meter was done with the help of phthalate buffers (see Dole, " The Glass Electrode ", New York; 1941, p. 297) or with acetate buffers the pH of which can also be deduced for 0° (cf. Harned and Owen, *Chem. Reviews*, 1939, **25**, 46). The glass electrode was fitted into a vessel

---

* A shift of the equilibrium proportion of the various species referred to above could also be brought about by temperature change.

similar to that described by Coates (*J.*, 1945, 489). The conductivity measurements were done in an all-glass cell with platinised platinum electrodes. The zero instrument was an amperemeter connected with a two-stage radio valve amplifier and rectifier.

In studying the bromine consumption of diketen, 2—5 c.c. of a 0·05 M-solution in acetone or in 50% acetone-water were cooled to − 10° and then mixed with 10—15 c.c. of ethyl alcohol also cooled to − 10°; a N/10-alcoholic bromine solution was then slowly added, while the temperature of the reaction mixture was kept at − 10°; no sharp end-point could be observed, but 2—3 g.-equivs. of bromine were used per g.-mol. of diketen before the colour of bromine persisted for 10 secs. In a different set of experiments, 2—5 c.c. of 0·05M-diketen in acetone were added at 0° to 10 c.c. of 0·05N-bromine in water; the bromine was immediately decolorised in all these tests.

Diketen dissolved in acetone and aqueous copper acetate do not form a complex which is markedly soluble in chloroform, benzene, or carbon disulphide. When diketen in acetone was shaken with dry lithium carbonate no detectable quantity dissolved. The tests with ferric chloride referred to on p. 1326 were done with 0·01M-solutions.

I am grateful to Mr. R. P. Bell and Mr. A. Maccoll for many helpful discussions, and to Mr. C. H. Greenstreet for having placed the conductivity apparatus at my disposal.

THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

[*Received, October* 20*th*, 1947.]