convection. These fractions were found to have gaussian mobility distributions, which, when properly normalized and added together, yield a mobility distribution in agreement with that possessed by γ-globulin itself.

This investigation demonstrates the applicability of electrophoresis-convection to the subfractionation of the plasma fractions obtained by ethanol precipitation.

PASADENA, CALIF. RECEIVED FEBRUARY 7, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN]

The Kinetics of the Decomposition of Malonic Acid in Aqueous Solution

BY GEORGE A. HALL, JR.

Recent studies of the thermal decomposition of trichloroacetic and trinitrobenzoic acids, as well as of salts of these acids, in water and in mixed solvents,[1] have led to a reasonable understanding of the factors which affect the rate of decarboxylation for those acids studied. In order to see how the theory proposed as a result of these investigations might apply to other acids, particularly dicarboxylic acids, it seemed desirable to study the similar reaction of malonic acid. Kinetic studies on the decarboxylation of dilute aqueous solutions of malonic acid were first carried out by Bernoulli and Wege[2] who reported that the reaction was of first order for temperatures around 100° and for concentrations in the neighborhood of 0.2 *N*. Fairclough[3] reported studies on the two sodium salts and found that, while disodium malonate was thermally stable up to 125° sodium acid malonate decomposed by a first order reaction. He suggested that, since the rate constants for the acid malonate ion were less than those reported for the acid by Bernoulli and Wege, the mechanism of the decomposition of malonic acid differed from that of the monocarboxylic acids where it had been shown[1] that the rate determining step is the decomposition of the unassociated acid anion.

The rate of decomposition of dibromomalonic acid as a function of *p*H was studied by Muus[4] who found that the rate was proportional to the concentration of the acid dibromomalonic ion.

This paper reports a study of the effect of changing concentration and of changing *p*H on the rate of decomposition of malonic acid and the results obtained confirm Fairclough's suggestion that the mechanism is not the same as in the case of the monocarboxylic acids previously studied.

Experimental

Materials.—Malonic acid obtained from the Eastman Kodak Company was dissolved in a minimum amount of methyl alcohol and recrystallized in a Dry Ice–acetone-bath. The product gave a neutral equivalent of 52.1 (52.02 calcd.). The water used as a solvent was doubly distilled and was of conductivity grade. Solutions of *p*H outside the range obtainable with pure malonic acid were prepared by using as solvents either standard hydrochloric acid solutions or standard sodium hydroxide solutions of appropriate strengths.

Procedure.—The reaction was followed by the previously described procedure[1c] of preparing a series of identical samples of the desired concentration and removing them from the constant-temperature bath at appropriate times. Each sample was analyzed by bubbling air through it for several minutes to remove the carbon dioxide and then titrating with standard sodium hydroxide solution. Since during the course of the reaction the dibasic malonic acid is changed to the monobasic acetic acid the amount of malonic acid present at any time is proportional to the quantity $(v_t - {}^1/_2 v_0)$ where v_t is the volume of standard base used at time *t* and v_0 is the volume used at zero time. For those solutions containing hydrochloric acid a correction for the amount of additional acid was applied and the solutions containing sodium hydroxide were corrected for the amount of sodium acid malonate present. The *p*H measurements were made on samples of the solutions used for the reaction velocity measurements using a Beckman glass electrode *p*H meter at 25°.

Results

The rate of decomposition of malonic acid was investigated at temperatures of 80 and 90° for a series of concentrations of malonic acid ranging from 0.005 to 0.05 *M*. The results obtained are given in Table I. In addition to the range of *p*H available from the dissociation of the acid a series of measurements were carried out in which hydrochloric acid or sodium hydroxide was added to the solution giving a total *p*H range of 0.4 to 4.89. Table II gives the data for the decomposition of malonic acid in the presence of hydrochloric acid and sodium hydroxide.

It was found that while each experiment gave a good first order rate constant, the values of these constants increase regularly with an increase in malonic acid concentration. With a decrease in *p*H beyond the range available in pure malonic

---

[1] (a) Verhoek, THIS JOURNAL, **56**, 571 (1934); (b) Verhoek, *ibid.*, **61**, 186 (1939); (c) Trivich and Verhoek, *ibid.*, **65**, 1919 (1943); (d) Verhoek, *ibid.*, **67**, 1062 (1945); (e) Hall and Verhoek, *ibid.*, **69**, 613 (1947); (f) Cochran and Verhoek, *ibid.*, **69**, 2897 (1947).

[2] Bernoulli and Wege, *Helv. Chim. Acta*, **2**, 511 (1919).

[3] Fairclough, *J. Chem. Soc.*, 1186 (1938).

[4] Muus, *J. Phys. Chem.*, **39**, 343 (1935).

TABLE I

THE EFFECT OF CHANGING CONCENTRATION ON THE DECOMPOSITION OF MALONIC ACID

Initial concn., m./l.	*p*H	k_{80} sec.$^{-1}$ × 10^6	k_{90} sec.$^{-1}$ × 10^6	E_{80-90} kcal.
0.0497	2.09	1.85	6.12	30.4
.0446	2.11	1.82	6.15	31.0
.0370	2.18	1.79	6.02	30.9
.0253	2.27	1.77	5.70	29.7
.0151	2.40	1.63	5.33	30.2
.0101	2.51	1.50	5.05	30.7
.0051	2.72	1.30	4.38	30.9

TABLE II

THE EFFECT OF CHANGING *p*H ON THE DECOMPOSITION OF MALONIC ACID

Concn. of added substance, m./l.	*p*H	k_{80} sec.$^{-1}$ × 10^6	k_{90} sec.$^{-1}$ × 10^6	E_{80-90} kcal.
A. Malonic Acid Initial Concentration 0.0365 *M* with Added HCl				
0.00667	1.98	1.90	6.27	30.4
B. Malonic Acid Initial Concentration 0.0480 *M* with Added HCl				
.0639	1.18	2.08	6.95	30.7
.3810	0.42	2.12	7.17	31.0
C. Malonic Acid Initial Concentration 0.0049 *M* with Added NaOH				
.00327	3.28	0.719	2.40	30.7
.00423	3.68	.468	1.55	30.4
.00460	4.02	.407	1.38	31.1
.00577	4.89	.293	0.979	30.7

acid solutions the rate constant increases and then levels off at a maximum value. With increasing *p*H the rate constants fall off sharply and then approach a minimum value. Figure 1 shows the values of the rate constant obtained as a function of *p*H. It was further found that the activation energy of the reaction is essentially constant over the range studied.

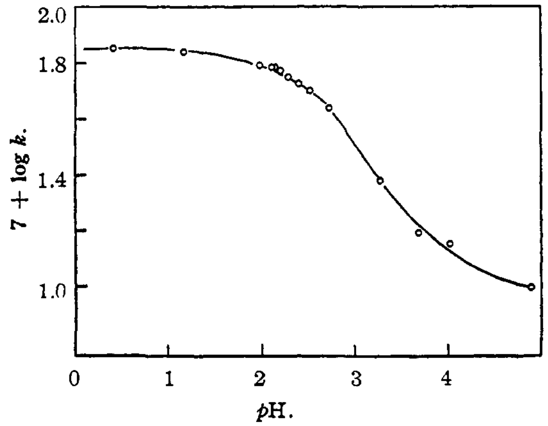

FIG. 1.—Rate constant for the decomposition of malonic acid as a function of *p*H at 90°.

Discussion

Attempts to explain the observed change in rate constant on the basis of simple salt effect failed to produce any clear picture of the present reaction. The appearance of Fig. 1 suggests that the effect of concentration change and of change in *p*H are not independent and that the concentration effect observed is the result of the changing dissociation of the acid and the subsequent change in *p*H. It becomes apparent that the simple mechanism of the decomposition of the unassociated anions proposed by Verhoek[1a] and substantiated by other researches[1] does not apply to the case in hand. The present data show, at least in the range of concentrations investigated, that the decomposition is not a case of simple acid catalysis as has been long considered for malonic acid and malonic esters. If the increase in rate constant with increasing hydrogen concentration were simple acid catalysis the rate constant should increase indefinitely with increasing hydrogen ion concentration in place of leveling off at a maximum value as shown in Fig. 1. The appearance of this curve suggests that the change in the dissociation of malonic acid by changing the hydrogen ion concentration, which will result in essentially only malonic acid being present at low *p*H and only the acid malonate ion being present at high *p*H, is the factor producing the observed change in rate constant.

It is possible to interpret the present data on the basis of the assumption that the malonic acid is actually decomposing by two mechanisms

$$\text{(1)}\quad HOOCCH_2COOH \longrightarrow CO_2 + CH_3COOH \text{ (slow)}$$

and

$$\text{(2)}\quad HOOCCH_2COO^- \longrightarrow CO_2 + HOOCCH_2^- \text{ (slow)}$$

Reaction (2) is then followed by one or more rapid reactions in which the $HOOCH_2^-$ ion reacts with the solvent to form the acetate ion. The over-all rate of reaction obtained will then be the sum of the rates of the two slow steps. If reaction (1) is slightly more rapid than reaction (2) as was indicated by previous work,[2,3] then an increase in hydrogen ion concentration which will increase the concentration of malonic acid would produce an increase in reaction rate. In solutions of sufficiently low *p*H the concentration of the acid malonate ion would be reduced to such a small amount that within the accuracy of the experiment all the malonic acid present would be undissociated and reaction (1) would be the only one occurring. At higher values of *p*H nearly all the malonic acid present would be dissociated and reaction (2) would be the only one occurring. At very high values of *p*H (beyond the range studied) the unreactive malonate ion would be present and a further decrease in rate constant should be observed.

The over-all rate of the reaction is then given by

$$\text{rate} = ka = k_1(a - x) + k_2x$$

where k is the observed rate constant at stochiometric malonic acid concentration a, k_1 and k_2 are the rate constants for reactions (1) and (2) and x is the concentration of the acid malonate ion. This expression may be rearranged to give

$$k = k_1 + (k_2 - k_1)\ x/a$$

The quantity x/a may be obtained from the known value of a, the measured value of the pH and the first dissociation constant of malonic acid. Within the accuracy of the experiments the second dissociation of malonic acid may be neglected. Figure 2 gives a plot of the observed rate constant against the quantity x/a (using the value of the dissociation constant of 1.40×10^{-3} given by Jeffery and Vogel[5]) for which the above equation predicts a linear relationship. It can be seen that the experimental data fit the proposed mechanism reasonably well. Deviations in the linearity of Fig. 2 may be attributed to the use of pH measurements and the value for the dissociation constant at 25° in place of those at the experimental temperatures and to the fact that the limit of precision of the original data is being approached.

It is possible to determine the value of k_1 from the intercept and of k_2 from the slope of the line in Fig. 2 and its counterpart at 80°. The values so obtained together with the activation energies for the separate reactions are given in Table III. The value of the activation energy obtained for the acid malonate ion agrees well with the value reported by Fairclough[3] (28.1 kcal.).

TABLE III

RATE CONSTANTS FOR THE DECOMPOSITION OF MALONIC ACID AND THE ACID MALONATE ION

	$k_{80} \times 10^6$ sec.$^{-1}$	$k_{90} \times 10^6$ sec.$^{-1}$	E_{80-90} kcal.
Malonic acid (k_1)	2.12	7.11	30.8
Acid malonate ion (k_2)	0.24	0.71	28.5

It is of interest to compare the behavior of malonic acid with that of dibromomalonic acid. Muus[4] found that since dibromomalonic acid is such a strong acid it is impossible even in solutions of a pH of zero to obtain any appreciable amount of the undissociated acid. Hence the rate of dibromomalonic acid decomposition remains constant over a range of low pH and then decreases as the amount of the doubly charged ion increases. A similar situation should occur for malonic acid in solutions of pH greater than 5.

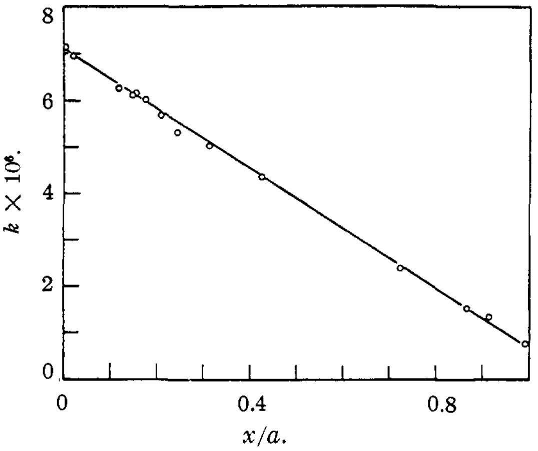

Fig. 2.—Rate constants for the decomposition of malonic acid *vs.* the quantity x/a at 90°.

Summary

1. The rate constant for the decomposition of malonic acid was found to increase with increasing acid concentration and with decreasing pH.

2. The activation energy of the reaction was found to be essentially independent of acid concentration and pH.

3. The observed changes in the rate constant have been shown to be consistent with a mechanism in which the undissociated acid and the acid malonate ion are undergoing independent reactions at different rates.

4. The rate constants for the two independent reactions have been calculated.

MADISON, WISCONSIN RECEIVED JANUARY 28, 1949

---

[5] Jeffery and Vogel, *J. Chem. Soc.*, 21 (1935).