# Temperature-jump Study of the Kinetics of Reactions of Arylethylmalonate Monoanions with Hydroxide Ion. The Effect of Ring Substituents

By **Takayuki Fueno**,\* **Okitsugu Kajimoto, Yoshikazu Nishigaki,** and **Toshiaki Yoshioka,** Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

The second-order rate constants $k_f$ of proton transfer reactions from ring-substituted arylethylmalonate monoanions toward hydroxide ions, $AH^- + OH^- \longrightarrow A^{2-} + H_2O$, in aqueous solution were measured by the temperature-jump relaxation method. The equilibrium constants $K$ for the reversible reactions were also determined by potentiometric titrations. Logarithms of both the rate and equilibrium constants obtained at 33 °C were found to be linearly correlated with Taft's substituent constants $\sigma^0$; $\log k_{f,X}/k_{f,H} = 0.38\sigma^0$ and $\log K_X/K_H = 0.93\sigma^0$. The results clearly indicate that the rates of both the forward and backward reactions are influenced by the electronic effects of substituents.

DISSOCIATION of organic Brönsted acids, e.g. phenol, in aqueous alkaline solution takes place by way of proton transfer from the acids to hydroxide ions.
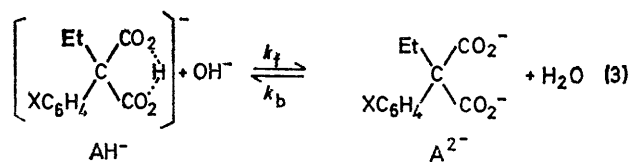
$$AH + OH^- \longrightarrow A^- + H_2O \qquad (1)$$
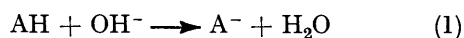
The reaction is essentially a diffusion-controlled process, the second-order rate constant being of the order of $10^{10} \, l \, mol^{-1} \, s^{-1}$.[1,2] However, in cases where the dissociating proton is intramolecularly hydrogen bonded, proton transfer is more or less retarded, thus reflecting structural effects on the reaction rate.[2,3]

Eyring and his co-workers [4] applied the temperature-jump relaxation technique to the studies of acid–base reactions of dialkyl substituted malonic acids. It was established that for pH $\geqslant 8.3$ the equilibrium perturbed is (2). The activation energy for the forward reaction

$$R^1R^2C(CO_2H)CO_2^- + OH^- \rightleftharpoons$$
$$R^1R^2C(CO_2^-)_2 + H_2O \quad (2)$$
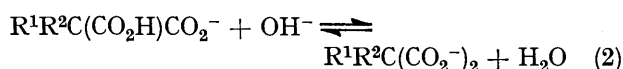
was about that expected for rupturing a hydrogen bond, and increased with the bulk of the substituents $R^1$ and $R^2$. They concluded that the principal effect of the substituents is steric in nature.

In the present work we examine the effect of ring substituents on the reaction rate of arylethylmalonate monoanions [reaction (3)]. The rate constants $k_f$ for



$$X = p-\text{MeO}, p-\text{Me}, m-\text{Me}, H, p-\text{Cl}, \text{and } m-\text{Cl}$$

the forward reactions, which are of the order of $10^8$ $l \, mol^{-1} \, s^{-1}$, conform to the Hammett-type relationship based on Taft's 'normal' substituent constants $\sigma^0$.[5]

The equilibrium constants $K = k_f/k_b$ were also correlated with $\sigma^0$. Clearly, both the forward and backward reactions are processes in which the electronic effect of substituents plays a dominant role in governing the relative rates of the series of reactions.

## EXPERIMENTAL

*Materials.*—Ethyl ethylphenylmalonate and its $p$-MeO, $p$-Me, $m$-Me, $p$-Cl, and $m$-Cl derivatives were synthesised by condensation of the corresponding derivative of ethyl phenylacetate with ethyl oxalate, followed by the ethylation of the $\alpha$-carbon with ethyl bromide. The esters were then hydrolysed in aqueous potassium hydroxide. All the acids thus prepared were recrystallised repeatedly from benzene–ether except for the $p$-MeO derivative for which toluene–ether was used. The acids were identified by i.r. and n.m.r. spectroscopy and by elemental analyses. Their m.p.s (°C, with decomposition) were as follows: $p$-MeO, 138; $p$-Me, 146; $m$-Me, 131; H, 152; $p$-Cl, 148; and $m$-Cl, 136.

*Acid Ionisation Constants.*—The ionisation constants of the ring-substituted malonic acids in 0·10M-KCl were determined by potentiometric titration at 25 and 33 °C. Sample solutions, $5.0 \times 10^{-3}$M with respect to the acid, were titrated with 0·01M carbonate-free NaOH under nitrogen. A Hitachi–Horiba F-5 type pH meter was used for pH measurements. The procedures for calculating the $pK_a$ values were those described by Ashton and Partington.[6] Since the $pK_a$ values for the first ionisation of the acids could not be estimated accurately and were less important in this study, the $pK_a$ values for the second ionisation only were calculated.

*Temperature-jump Experiment.*—The temperature-jump apparatus used for the present study was essentially the same as that described by Kresheck *et al.*[7] A 0·1 μF condenser, charged to *ca.* 25 kV, was discharged through a cell by means of a thyratron tube. The theoretical temperature rise, which is determined by the cell dimensions and the characteristic constants of the circuit, is calculated to be *ca.* 8° with a rise time of 6 μs.

The cell is the most important part of this apparatus. It was made of acrylic resin and equipped with pairs of

[1] M. Eigen and L. de Maeyer, in 'Technique of Organic Chemistry,' eds. S. L. Friess, E. S. Lewis, and A. Weissberger, Interscience, New York, 2nd edn., vol. 8, part II, 1963, pp. 895—1054.
[2] M. Eigen, W. Kruse, G. Maass, and L. de Maeyer, *Progr. Reaction Kinetics*, 1964, **2**, 285.
[3] M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1.
[4] M. H. Miles, E. M. Eyring, W. W. Epstein, and R. E. Ostrund, *J. Phys. Chem.*, 1965, **69**, 467.

[5] R. W. Taft, jun., and I. C. Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343; R. W. Taft, jun., S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, p. 5352.
[6] H. W. Ashton and J. R. Partington, *Trans. Faraday Soc.*, 1934, **30**, 598.
[7] G. C. Kresheck, E. Hamori, G. Davenport, and H. A. Scheraga, *J. Amer. Chem. Soc.*, 1966, **88**, 246.

platinised flat electrodes and quartz windows positioned orthogonal to each other. The cell dimension was *ca.* 1·5 ml, and the electrode surface area was *ca.* 1·1 cm². The temperature of the sample solution in the cell was controlled by circulating water from a thermostatted bath through the hollow arms of the electrodes. The electrodes were so constructed as to be easily detached for cleaning.

The light source was a Nikon 10 V–70 W tungsten lamp powered by a 10—12 V storage battery. The monochromatic light appropriate for relaxation monitoring was selected by a Toshiba KL57 interference filter. The light which was transmitted through the sample solution was collected on an EMI 9634Q photomultiplier operated at 600 V by means of a stabilised high voltage supply. The change in transmittance with time was recorded on an Iwatsu 5505 oscilloscope and photographed.

Sample solutions were 0·10M in KCl and 0·5—3·0mM in the acid. The pH was adjusted with an aqueous solution which was 0·010M in KOH and 0·10M in KCl. All solutions were prepared with doubly distilled water to reduce cavitation due to dissolved gases. Cresol Red (0·01mM) was used as an indicator.

The temperature-jump measurements were performed with 1·5 ml of each sample solution in the pH range 8·3—8·9 under nitrogen. Cresol Red has absorption maxima at 447 and 580 nm. However, because the maximal pH dependent change in absorption occurred at 565 nm, the monochromatic light of this wavelength was used for the measurements. Each relaxation profile was photographed several times and the relaxation time was evaluated from the slope of the semilog plots of absorbance *versus* time. Blank experiments involving only the indicator gave no observable relaxation in the time region of interest. Therefore, the relaxation observed for sample solution is definitely that of the reaction system involving the acid.

## RESULTS

*Equilibrium.*—The equilibrium constant $K$ for reaction (3) in 0·10M-KCl, defined by equation (4), can be evaluated

$$K = [A^{2-}][H_2O]/[AH^-][OH^-] \qquad (4)$$

from the acid dissociation constant [equation (5)] measured

$$K_a = [A^{2-}][H^+]/[AH^-] \qquad (5)$$

for the monoanion in the same medium. The $K_a$ values obtained directly by the pH measurements are ' mixed constants '[4] which are based on the activity $a_H$ rather than the concentration [H⁺] of H⁺. Our $pK_a$ values are thus greater than the concentration-based $pK_a$ by a constant factor of $-\log \gamma_H = 0·08$, where $\gamma_H = 0·83$ is the activity coefficient of H⁺ in a KCl solution of ionic strength 0·10M. The equilibrium constant $K$, which has been defined on the concentration basis, is then related to this apparent $K_a$ by

$$K = \gamma_{OH} K_a [H_2O]/K_w \qquad (6)$$

equation (6) where $K_w = [H^+][OH^-]\gamma_H\gamma_{OH}$ is the ion product of water and where $\gamma_{OH}$ is the activity coefficient of OH⁻ in a solution of ionic strength 0·10M. For simplicity, we have assumed $\gamma_{OH}$ to be equal to $\gamma_H$.

The values of $K$ obtained for the various derivatives of ethylphenylmalonate monoanions at 25 and 33 °C are listed in Table 1, together with the apparent $pK_a$ values at these temperatures. As the temperature rises from 25 to 33 °C,

the $K_a$ values generally decrease by a factor of *ca.* $10^{-0·04}$. In the meantime, $K_w$ increases from $10^{-14·00}$ to $10^{-13·74}$.[8] The combined effect is that the $K$ values are decreased by a factor of approximately $10^{-0·30} = 0·5$, equilibrium (3) thus being shifted to the left with the rise in temperature.

TABLE 1

Equilibrium constants for AH⁻ in 0·10M-KCl [a]

| | $pK_a$ [b] | | $10^{-8}K$ [c] | | |
|---|---|---|---|---|---|
| X | 25° | 33° | 25° | 33° | $\sigma^0$ [d] |
| p-Me | 7·26 | 7·29 | 2·51 | 1·28 | −0·15 |
| p-MeO | 7·24 | 7·27 | 2·63 | 1·34 | −0·12 |
| m-Me | 7·21 | 7·24 | 2·82 | 1·44 | −0·07 |
| H | 7·12 | 7·16 | 3·46 | 1·66 | 0 |
| p-Cl | 6·86 | 6·90 | 6·31 | 3·16 | 0·27 |
| m-Cl | 6·79 | 6·83 | 7·38 | 3·72 | 0·37 |

[a] $AH^- = XC_6H_4(Et)C(CO_2H)CO_2^-$. [b] $K_a = a_H[A^{2-}]/[AH^-]$. [c] $K = [A^{2-}][H_2O]/[AH^-][OH^-] = 0·83[H_2O]K_a/K_w$. [d] From ref. 5.

It should be noted that at both 25 and 33 °C the equilibrium constants tend to increase with the increase in the electron-accepting ability of the ring substituents. This point will be discussed later on a more quantitative basis.

*Kinetics.*—In the pH region 8·3—8·9, each sample solution gave a simple temperature-jump relaxation curve due to the indicator absorption. As established by Eyring *et al.*,[4] this relaxation is ascribable to the reversible process (7).

$$AH^- + OH^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} A^{2-} + H_2O \qquad (7)$$
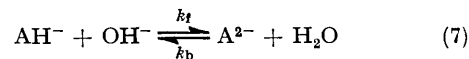
$$K = k_f/k_b$$

The relaxation time $\tau$ is given by relation (8) where

$$1/\tau = k_f\{[AH^-] + [OH^-] + [H_2O]/K\} \qquad (8)$$

[AH⁻] and [OH⁻] are the equilibrium concentrations of the monoanions and hydroxide ions, respectively, after the temperature jump. The rate constant $k_f$ can be obtained from equation (8) by use of the observed relaxation time. Under our experimental conditions, the term involving $K$ was negligibly small when compared with [AH⁻] and [OH⁻]. Thus, the reciprocal of $\tau$ observed at varying total acid concentrations and pH should be proportional to the sum of [AH⁻] and [OH⁻]. This was confirmed for all the acid monoanions studied at 33 °C. An example is shown for the case of the *p*-Me derivative in Figure 1. The proportionality leads to $k_f = (1·04 \pm 0·05) \times 10^8$ l mol⁻¹ s⁻¹ for this particular example. The uncertainty indicates the probable error. The rate constant for the backward reaction was calculated to be $k_b = k_f/K = 0·81 \pm 0·04$ l mol⁻¹ s⁻¹.

The values of $k_f$ and $k_b$ obtained as above for the reactions of the various arylethylmalonate monoanions in 0·10M-KCl at 33 °C are summarised in Table 2. It can be seen that $k_f$ increases with increasing electron-accepting ability of substituents. On the contrary, $k_f$ tends to decrease as the electron-accepting ability of substituents increases.

## DISCUSSION

Figure 2 shows that the logarithms of the $K$ values for the series of arylethylmalonate monoanions are linearly

[8] H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, 1940, 36, 973.

correlated with Taft's ' normal ' substituent constants $\sigma^0$.[5] At 33 °C, the reaction constant was found to be

$$\log K_X/K_H = \rho\sigma^0 \qquad (9)$$

$\rho = 0.92_9$ with correlation coefficient $r = 0.998$ and standard deviation $s = 0.028$.

Our $K$ values correlate better with $\sigma^0$ than with Hammett's $\sigma$. This is reasonable because the $\sigma^0$ constants were defined on the basis of the ionisation equilibria of substituted phenylacetic acids.[5] The acids under study are structurally analogous to phenylacetic acids in that the substituents on the phenyl ring do not conjugate with the reaction centre because of the intervention of an $sp^3$ carbon atom.

Figure 3 shows plots of log $k_f$ against $\sigma^0$ at 33 °C. Even though the range of error of log $k_f$ is relatively large
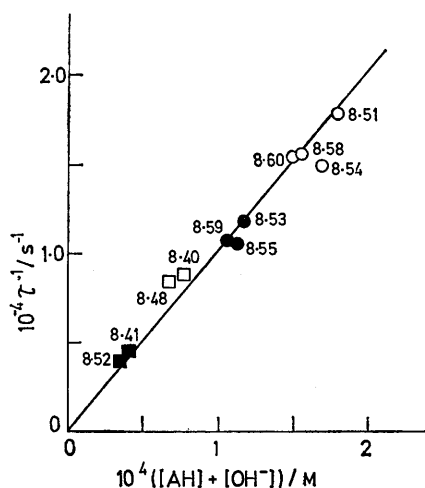


FIGURE 1    Plots of $\tau^{-1}$ vs. ([AH⁻] + [OH⁻]) for $p$-MeC₆H₄(Et)C-(CO₂H)CO₂⁻ in 0·10M-KCl at 33 °C; [Cresol Red] = 10⁻⁵M. The figures appended to the plots indicate the pH at which measurements were conducted. 10³[AH₂]ₜ: ○, 3·0M; ●, 2·0M; □, 1·0M; ■, 0·5M. Slope: $k_f = 1·04 \times 10^8$ l mol⁻¹ s⁻¹. pH = 8·40—8·60

TABLE 2

Rate constants for the reaction AH⁻ + OH⁻ $\underset{k_b}{\overset{k_f}{\rightleftharpoons}}$ A²⁻ + H₂O in 0·10M-KCl at 33 °C [a]

| X | $10^{-8}k_f$/l mol⁻¹ s⁻¹ | $k_b$/l mol⁻¹ s⁻¹ |
|---|---|---|
| $p$-Me | 1·04 ± 0·05 | 0·81 ± 0·04 |
| $p$-MeO | 1·06 ± 0·09 | 0·79 ± 0·06 |
| $m$-Me | 1·15 ± 0·10 | 0·80 ± 0·07 |
| H | 1·21 ± 0·06 | 0·73 ± 0·04 |
| $p$-Cl | 1·52 ± 0·14 | 0·48 ± 0·04 |
| $m$-Cl | 1·63 ± 0·10 | 0·44 ± 0·03 |

[a] AH⁻ = XC₆H₄(Et)C(CO₂H)CO₂⁻.

for each monoanion, it does appear that a straight line fits the points. Least-squares treatment of the plots led to the regression line represented by equation (10) with $\rho_f = 0.38$. Because of the errors in the individual

$$\log k_{f,X}/k_{f,H} = \rho_f\sigma^0 \qquad (10)$$

values of $k_f$, the reaction constant $\rho_f$ here obtained can only be accurate to within ±0·08. Nonetheless, it

shows convincingly enough that the relative rates of reaction for the series of AH⁻ are governed by the electronic effect of the ring substituents.
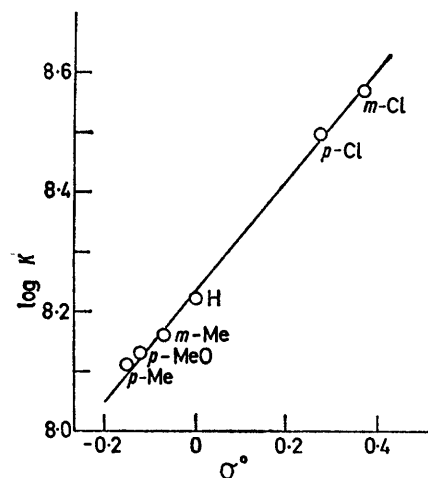


FIGURE 2    Linear correlation of log $K$ with $\sigma^0$ for AH⁻ + OH⁻ $\rightleftharpoons$ A²⁻ + H₂O in 0·10M-KCl at 33 °C; AH⁻ = XC₆H₄(Et)C(CO₂H)CO₂⁻. $\rho_t = 0.93$

Eyring et al.[4] noted that the rate of the forward reaction of (2) tends to decrease with increasing bulk of the alkyl groups R¹ and R². They interpreted this as a reflection of the steric repulsion between the groups strengthening the hydrogen bond. However, because the steric effect of alkyl groups generally parallels their inductive electron-releasing ability, the possibility that the electronic effect is even a more important factor in controlling the rate cannot entirely be ruled out.

No matter what the precise nature of the substituent effects may be, there is no doubt that intramolecular
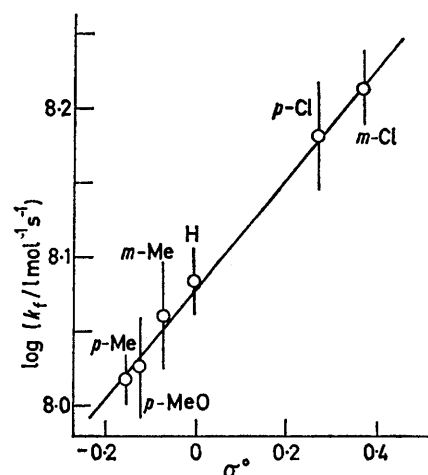


FIGURE 3    Linear correlation of log $k_f$ with $\sigma^0$ for AH⁻ + OH⁻ $\longrightarrow$ A²⁻ + H₂O in 0·1M-KCl at 33 °C; AH⁻ = XC₆H₄(Et)C(CO₂H)CO₂⁻. The vertical lines indicate the range of the probable errors. $\rho_t = 0.38$

hydrogen bonding hinders proton transfer, which would otherwise be a diffusion-controlled process. Mechanistic details of this hindrance, however, still remain to be

settled. In interpreting the effect of the relative rigidity of the hydrogen bond upon $k_f$, Eyring et al.[4] assumed the proton transfer to take place by a single-step mechanism involving the activated complex (A).



(A)
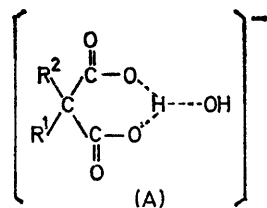
It was deduced that the activation process should involve a serious weakening of the intramolecular hydrogen bond, which primarily determines the activation energy.

Alternatively, the proton transfer may well be conceived to proceed through a two-step mechanism as originally broached by Eigen.[3] It is implicit in this mechanism that, in the hydrogen-bridged monoanions, approach of $OH^-$ to the proton in question is completely blocked and that only the monoanion having the



(11)



(12)
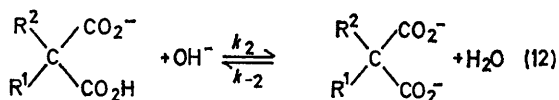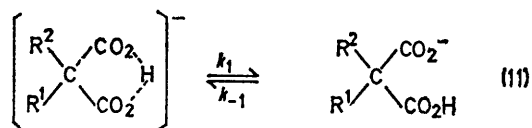
hydrogen bond broken can enter into proton transfer (12) through transient formation of an intermolecular hydrogen bond with $OH^-$.

Provided the unimolecular 'rearrangement' of the monoanion (11) is a rapid pre-equilibrium, the concentration of the unbridged, and hence reactive, monoanion $AH^-(r)$ is given by equation (13) where $K_1 =$

$$[AH^-(r)] = \{K_1/(1 + K_1)\}[AH^-] \qquad (13)$$

$k_1/k_{-1}$ is the equilibrium constant of the first step (11)

and where $[AH^-]$ is the total concentration of the monoanion, both bridged and unbridged. The overall rate constant for the forward reaction should then be expressed by equation (14). The rate constant $k_f$ will

$$k_f = \{K_1/(1 + K_1)\}k_2 \qquad (14)$$

become equal to $k_2$ in the limit $K_1 \longrightarrow \infty$, a case in which all monoanions are present as the unbridged structure. The reaction must then be diffusion-controlled as in the case of ordinary Brönsted acids. On the contrary, if $K_1 \ll 1$, i.e. if the bridged form is of considerable stability as compared with the unbridged, $k_f$ will become smaller than $k_2$ by a factor approximately equal to $K_1$. Because proton transfer from $AH^-(r)$ to $OH^-$ should essentially be a diffusion-controlled process and hence involve virtually no structural effect, the substituent effects on the reaction rate are considered to show up primarily by influencing the magnitude of $K_1$.

Investigation of the kinetics under our experimental conditions cannot discriminate between the two possible mechanisms mentioned above. Nevertheless, we feel that the two-step mechanism is more probable, particularly because the formation of hydrogen bonds is generally a rapid equilibration. For the malonate monoanions investigated here $K_1$ should be of the order of $10^{-2}$. The observed value of $\rho_f = 0.38 \pm 0.08$ would be a factor characteristic of the electronic effects of substituents affecting the equilibrium (11).

Finally, we comment briefly on the backward reaction. The rate constant $k_b$ of the backward reaction is identical with the $k_{-2}$ defined for the reversible bimolecular process (12). Its relative magnitude is also governed by the effects of substituents. Combining equation (9) with equation (10), one can write equation (15) where $\rho_b = \rho_f - \rho = -0.55 \pm 0.08$. It is interest-

$$\log k_{b,X}/k_{b,H} = \rho_b\sigma^0 \qquad (15)$$

ing to note that the linear free-energy correlation of the Hammett type holds for a series of reactions in which water acts as a proton donor.