Kinetic Isotope Effects and Aliphatic Diazo-compounds. Part VII.† The Decomposition of Diazomalonate Ions

By **W. John Albery,* Christopher W. Conway, and John A. Hall,** Physical Chemistry Laboratory, South Parks Rd., Oxford

Results are reported for the variation of the rate of decomposition of ethyl diazomalonate (EDM) and diazomalonate anions with pH and for the deuterium solvent isotope effect for EDM. The shape of the pH profile is explained by successive protonations of the anions. Ethyl diazoacetate is observed as an intermediate in the decomposition of EDM. The degree of proton transfer in the EDM transition state is deduced from the solvent isotope effect and the results together with those for other aliphatic diazo-compounds are discussed in terms of the Marcus theory.

KING and his co-workers [1,2] studied the decomposition in aqueous solution of the two diazomalonate ions EDM^- and DM^{2-}. Whereas aliphatic diazo-compounds normally decompose by acid catalysis, they found general *base* catalysis for the decomposition of DM^{2-}. This surprising feature and the complex variation of their reaction rates with pH have led to the authoritative [3]

---

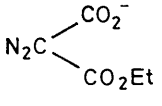
† Part VI, ref. 14.

[1] C. V. King, P. Kulka, and A. Mebane, *J. Amer. Chem. Soc.*, 1950, **72**, 1906.

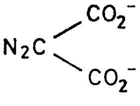
[2] C. V. King and P. Kulka, *J. Amer. Chem. Soc.*, 1952, **74**, 3128.

[3] R. P. Bell, ' The Proton in Chemistry,' Chapman and Hall, London, 1973, p. 171.

pronouncement that 'no satisfactory interpretation of the behaviour has yet been given'.



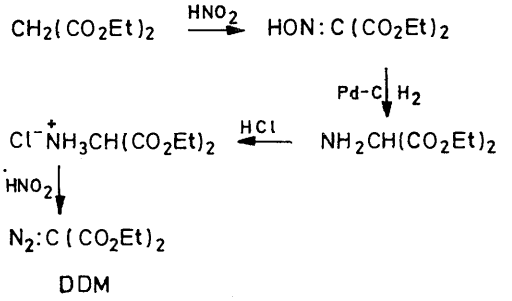
EDM^-



DM^{2-}

EXPERIMENTAL

The diazomalonate salts were prepared from hydrolysis of diethyl diazomalonate (DDM) which was itself prepared, using standard procedures,[4-6] according to Scheme 1. Salts containing EDM^- and DM^{2-} were not isolated but the ions were prepared for each kinetic run by hydrolysing DDM in 0.15M-NaOH at 25° for 14 min, and for at least 8 h respectively. The rate constant for hydrolysis of DDM to EDM^- is 14×10^3 l mol^{-1} s^{-1} and of EDM^- to DM^{2-} 0.25×10^3 l mol^{-1} s^{-1}.



SCHEME 1

To initiate a kinetic run 40 cm^3 of the hydrolysed solution was brought to the required pH using a Radiometer TTT 1C titrator for pH values >2 and by adding a calculated quantity of $HClO_4$ for pH values <2. The reaction was followed for a 2 cm^3 sample on a Cary 14 recording spectrophotometer at 250 nm. At certain pH values the reaction consumes H^+ and it can be followed on the Radiometer pH stat. Initial concentrations were *ca.* 10^{-6}M for the spectrophotometer and *ca.* 2×10^{-5}M for the pH stat method. The concentration of H^+ for each run was determined by titration for pH values <3 and otherwise by the observed pH value. The pH meter was calibrated with a standard solution of H^+ (10^{-3}M) of the same ionic strength as the reaction mixture. For many of the spectrophotometric runs a further classical technique was used;[7] after the run was over a small quantity of ethyl diazoacetate was added and the kinetics of its decomposition followed. All kinetic runs were carried out at 25.0°.

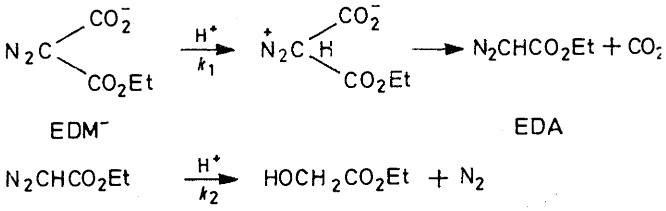
RESULTS AND DISCUSSION

When EDM^- is decomposed at pH values >3 the optical density, OD_t, passes through a maximum obeying a rate law of form (1) where $k_1 < k_2$. For the following

$$OD_t - OD_\infty = Ae^{-k_1t} - Be^{-k_2t} \qquad (1)$$

three reasons we believe that this behaviour is caused by the formation of an intermediate which is ethyl diazoacetate (EDA).

First, King *et al.*[1] found that CO_2 was released as well as N_2 and this can be explained by Scheme 2. Secondly, throughout the reaction the shape of the spectrum is characteristic of an aliphatic diazo-compound and furthermore the ratio of extinction coefficients found from equation (3) agrees with the ratio for known samples of EDA and EDM^-. Thirdly, when EDA is added to the same solution in which the EDM^- is decomposed the rate constant for its decomposition, k_{EDA}, is in reasonable agreement with k_2.



SCHEME 2

Because k_1 and k_2 differ only by a factor of two, in order to obtain reliable values of k_1 we have assumed that $k_2 = k_{EDA}$. Values of k_{EDA} are found by decomposing EDA in the same reactant solution. Then it can be shown that equation (2) applies giving the ratio (3)

$$y = \exp(k_{EDA}t)\,[OD_t - OD_\infty] = A\exp(k_{EDA} - k_1)t - B \qquad (2)$$

$$\varepsilon_I/\varepsilon_{EDM^-} = B(k_{EDA} - k_1)/[(OD_0 - OD_\infty)]k_1 \qquad (3)$$

where ε_I is the extinction coefficient of the intermediate. When plotted by the Swinbourne method[8] values of y give good straight lines. From the gradient we obtain values for $k_{EDA} - k_1$ and hence k_1. Where the straight line crosses $y = x$ we also obtain a value of B and hence the ratio of the extinction coefficients.

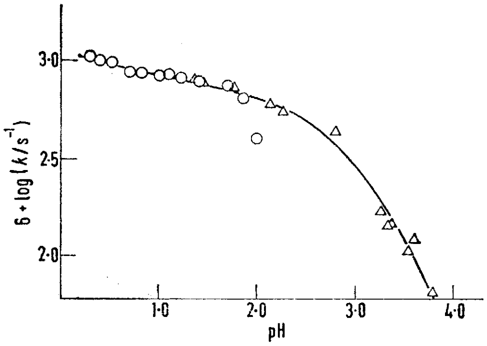


FIGURE 1 Variation of log k_1 for EDM^- with pH: ○, data from ref. 1; △, data from this work. The solid line is calculated from equation 4 and the values in Table 1

In all other solutions good first-order kinetics were observed. Figure 1 shows the variation of log k_1 with pH for EDM^-. Our and King's data (apart from one of his points) obey an equation of form (4) where α is *ca.*

$$k_1 = k_3 10^{\alpha[H^+]}/(K_1^{-1} + [H^+]^{-1}) \qquad (4)$$

---

[4] A. J. Zambito and E. E. Howe, *Org. Synth.*, 1960, **40**, 21.

[5] W. H. Hartung, J. H. A. Beauton, and G. Cocolas, *Org. Synth.*, 1960, **40**, 24.

[6] E. B. Womack and A. B. Nelson, *Org. Synth.*, 1944, **24**, 56.

[7] J. N. Brønsted and C. E. Teeter, *J. Phys. Chem.*, 1924, **28**, 579.

[8] P. Swinbourne, *J. Chem. Soc.*, 1960, 2731.

TABLE 1

Equilibrium and rate constants

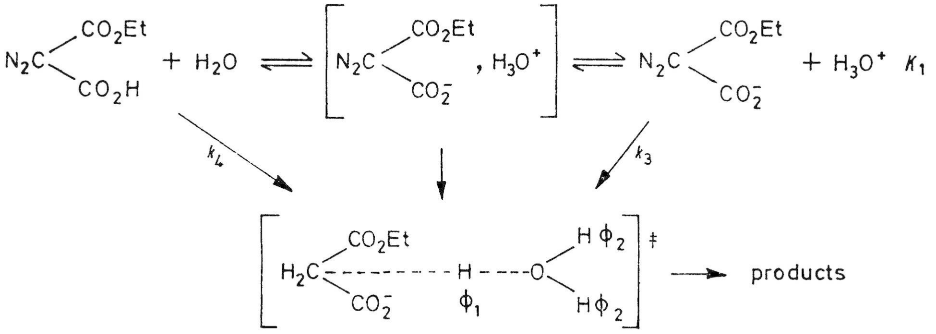
Dissociation constants		pK_n	Rate constants		$3 + \log(k_n/\text{l mol}^{-1}\,\text{s}^{-1})$
HEDM	K_1	2.80	$H^+ + EDM^-$	k_3	2.68
H_2DM	K_2	0.96	$H^+ + HDM^-$	k_5	1.34
HDM^-	K_3	6.4 [a]	$H^+ + DM^{2-}$	k_6	5.8
	K_3	6.0 [b]			
					$6 + \log(k_n/\text{s}^{-1})$
	K_3	6.0 [c]	$H_2O + HEDM$	$k_4 = k_3K_1$	2.88
			$H_2O + H_2DM$	k_5K_2	3.37
			$H_2O + HDM^-$	k_6K_3	2.37

[a] From kinetic measurements in Figure 4 and equation (7). [b] From pH stat titration curve. [c] From kinetic measurements in acetic acid buffers [1] and equation (9).

0.2 and describes a salt effect for King's results at ionic strengths greater than 0.2M. The values of the other constants (at our ionic strength of 0.15M-NaClO_4) are given in Table 1. The form of equation (4) can be explained by Scheme 3. In this Scheme k_4 and k_3 are the observed rate constant at low and high pH respectively. Providing that the two processes go through the same transition state, then equation (5) applies. The

$$k_4 = k_3K_1 \qquad (5)$$

reversible protonation of EDM^- in Scheme 3 is confirmed by the observation that the u.v. spectrum of a solution of EDM^- taken to pH 2 shows a more pronounced maximum which is similar to that of uncharged DDM; on adding base the spectrum of EDM^- is recovered.



SCHEME 3

We have further investigated the transition state in Scheme 3 by studying the solvent isotope effect at pH *ca.* 2. After correcting for the small H^+ term we obtain the results given in Table 2. The reactant fractionation for

TABLE 2

Isotopic results for LEDM and L_2O

$k_1/k_0 = 0.170 \pm 0.003$ $\qquad k_{\frac{1}{2}}/k_0 = 0.51 \pm 0.01$

$\phi_1 = 0.27 \pm 0.02$ $\qquad \phi_2 = 0.79 \pm 0.04$

the k_4 process can be assumed to have fractionation factors of unity since the reactants are L_2O and RCO_2L.[9] Thus for this system we can calculate the curvature parameter γ[10] from equation (6). In equation (6) and Table 2 the subscripts refer to the atom fractions of D in

$$\gamma = \frac{4\ln(k^2_{\frac{1}{2}}/k_0k_1)}{[\ln(k_1/k_0)]^2} = 0.54 \pm 0.06 \qquad (6)$$

the solvent. One advantage of reaching the transition state from L_2O and EDML is that one does not need to know l, the fractionation factors for L_3O^+, in order to calculate γ. Figure 2 shows a plot of γ[10] to find the different possible transition states. We can argue first that a transition state with only a single proton in flight (A) or transition states with three or more protons simultaneously in flight are ruled out, secondly that a transition state [intersection (C)] with one proton in flight and a medium effect of *ca.* 0.6 would fit the data but such a large medium effect is unlikely, thirdly that a transition state [intersection (C)] with two protons simultaneously in flight (ϕ *ca.* 0.4) is possible but for other diazo-compounds [11] such transition states have not been found and therefore finally that the transition state of Scheme 3 [intersection (D)] is the most likely. The

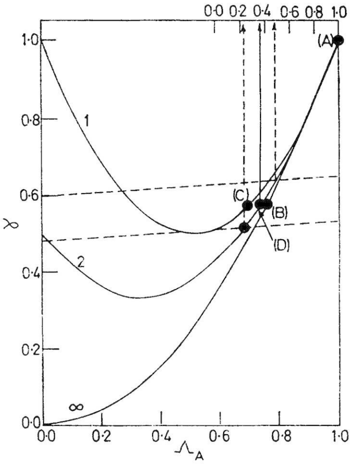


FIGURE 2 Plot of γ for EDM^- transition state with fractionation of the form $(1 - x + \phi_A x)\ (1 - x + \phi_B x)$,[b] where $\Lambda_A = \ln\phi_A/\ln(k_1/k_0)$. Each parabola is labelled with the value of b, and each intersection is a possible transition state. The zero on the $\alpha_{L_3O^+}$ scale is calculated for $b = 2$ and $\phi_B = \phi_A = 0.69$

---

[9] W. J. Albery, 'Proton-transfer Reactions,' Chapman and Hall, London, 1975, p. 285.

[10] Ref. 9, p. 273.

[11] Ref. 9, p. 289.

point where the curvature parameter γ crosses the parabola corresponding to the 1 : 2 transition state is determined by the relative magnitudes of the effects of the L in flight and the two Ls left behind. In Table 2 we report values of the fractionation factors for this transition state; the values confirm the interpretation. For this type of transition state the degree of proton transfer $\alpha_{L_3O^+}$ can be calculated from [12] $\phi_2 = l^{1-\alpha_{L_3O^+}}$. By calculating the maximum secondary solvent isotope effect ($\phi_2 = l = 0.69$) we can set up a scale in Figure 2 to read off directly $\alpha_{L_3O^+}$.

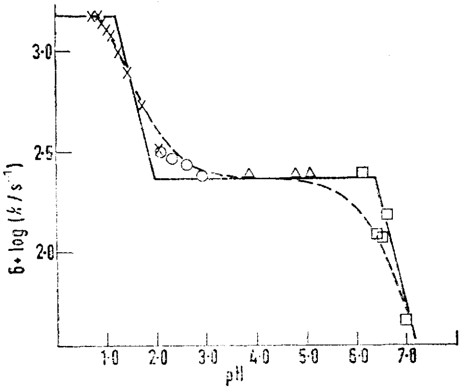


FIGURE 3 Variation of log k for DM^{2-} with pH: ×, data from ref. 1; △, data extrapolated to zero buffer concentration from ref. 2; ○, spectrophotometric data from this work; □, pH stat data from this work. The broken line is calculated from equation 7 and the values in Table 1

Hence the solvent isotope effect data support Scheme 3 and suggest that a transition state of the type shown is the most probable. The reason for the pH profile in Figure 1 is that the protonation of EDM^- on the carboxylate group stabilises the compound; the CO_2H and CO_2Et groups are better able to conjugate with the adjacent diazo-group than CO_2^-. However the protonated EDM^- carries with it the seed of its own destruction; water molecules transfer the proton from the CO_2H onto the adjacent carbon atom.

The same pattern is found for DM^{2-}. Figure 3 shows the pH profile for this compound. Now there are two CO_2^- groups and so the pattern found for EDM^- is repeated twice over. The reactions to which the rate constants and equilibrium constants refer and their values (in 0.15M-$NaClO_4$) are given in Table 1.

$$k = \frac{k_5[H^+] + k_6K_3}{K_2^{-1}[H^+] + 1 + K_3[H^+]^{-1}}$$

$$\simeq \frac{k_5}{K_2^{-1} + [H^+]^{-1}} + \frac{k_6}{K_3^{-1} + [H^+]^{-1}} \quad (7)$$

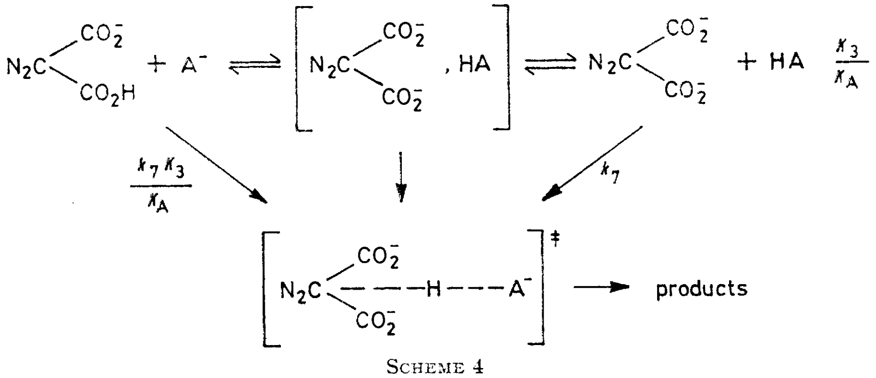
If the Radiometer titrator is used to titrate DM^{2-} with acid a titration curve corresponding to that of a weak acid with a pK of *ca.* 6.0 is found; this is in reasonable agreement with K_3. We can now understand the base catalysis found by King.[2] Ignoring small terms from the k_5 process we write equation (8) for an acid HA, which has a dissociation constant K_A. The k_7 term corresponds

$$k = \frac{k_6 + k_7K_A^{-1}[A^-]}{K_3^{-1} + [H^+]^{-1}} = \frac{k_6 + k_7[HA]}{K_3^{-1}[H^+] + 1} \quad (8)$$

to a transition state formed from either HA and DM^{2-} or from A^- and HDM^- as shown in Scheme 4. When $[H^+] \gg K_3 = 10^{-6}$ then k will increase linearly with $[A^-]$; this explains the base catalysis found by King.[2] Some of his data [1] for acetic acid do not satisfy this condition and rearranging equation (8) we obtain (9).

$$\frac{k_6 + k_7K_A^{-1}[A^-]}{k} = \frac{1}{K_3}\left(1 + \frac{K_3[A^-]}{K_A[HA]}\right) \quad (9)$$

For experiments at constant $[A^-]$, the ratio of the gradient to the intercept of a plot of k^{-1} against $[HA]^{-1}$ gives the third value of K_3 in Table 1. This determination is in reasonable agreement with the other values thus confirming the interpretation.



SCHEME 4

Dissociation constants for diazocarboxylic acids cannot usually be measured since their salts decompose before they protonate. For our compounds the diazo-group has no dramatic acid strengthening or weakening effect. However, the dibasic diazomalonic acid shows an unusually large ΔpK of 5 units compared for instance with malonic acid (ΔpK 3); this is probably caused by the extensive delocalisation of the π electrons, the consequent planarity, and a rather stable hydrogen bond in HDM^-.

The rate constants for the H_2O reactions depend upon

---

[12] A. J. Kresge, *Pure Appl. Chem.*, 1964, **8**, 243.

two features, the stability of the diazo-compound and the acidity of the relevant CO_2H group. Also unlike the rate constants for the H_3O^+ reaction they cannot be compared with rate constants for other diazo-compounds. Similarly the general base catalysis [2] of HDM^- with β 0.27 [1] should rather be considered as general acid catalysis of DM^{2-} (k_7) with a Bronsted coefficient α_B of 0.73.

TABLE 3

Data for $N_2CR^1R^2$

No.	R^1	R^2	log (k/l mol^{-1} s^{-1}) [a]	ϕ_1	$\alpha_{L_3O^+}$	α_B
1	H [b]	CO_2^-	4.8	0.24	0.30	0.51
2	CO_2^-	CO_2^-	2.8			0.73
3	Me [c]	CO_2Et	1.3	0.22	0.29	0.59
4	Me [c]	COMe	−0.1	0.22	0.27	0.61
5	CO_2Et	CO_2^-	−1.7	0.27	0.36	

[a] Rate constant for H_3O^+ catalysed reaction. [b] M. M. Kreevoy and D. E. Konasewich, *J. Phys. Chem.*, 1970, **74**, 4464. [c] Ref. 13.

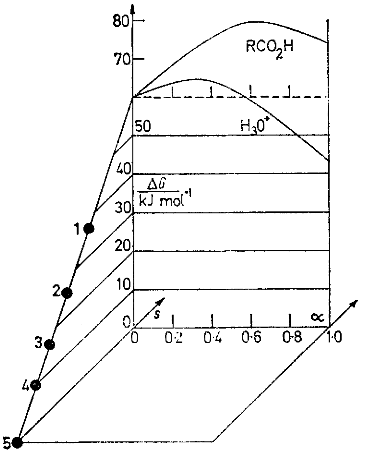
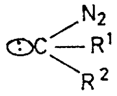


FIGURE 4 Free energy broken down into that from the proton transfer (α) and that from the ' solvation ' change (s) for the different diazo-compounds numbered in Table 3 and for H_3O^+ and a carboxylic acid catalyst. The free energies on the left-hand side are the desolvated encounter complex [HA, S]; the actual proton transfers obey the Marcus theory. In calculating [14] this simplified picture the following values have been assumed: $w_{R.O}$/kJ mol^{-1} = 10 for RCO_2H and 18 for H_3O^+, λ/kJ mol^{-1} = 48, $\alpha_{L_3O^+}$ = 0.33, and α_B = 0.65

The results for the diazomalonates are compared with results for other diazo-compounds in Table 3. The new data agree with earlier conclusions [12] in that first ϕ_1, the primary fractionation factor describing the proton in flight, is similar in size for the different diazo-compounds, and secondly the degree of proton transfer when the catalyst is L_3O^+ ($\alpha_{L_3O^+}$) is smaller than when the catalyst is RCO_2H (α_B). This difference is in the direction predicted by the Marcus theory.[13] For these compounds the change of acid catalyst from H_3O^+ to acetic acid reduces the rate by *ca.* 10^{-2} and increases α from 0.3 to 0.6. On the other hand for the same catalyst, H_3O^+, the change from diazoacetate anion to ethyl diazomalonate anion reduces the rate by over six orders of magnitude but hardly affects α_I. This asymetry of behaviour can be explained [14] by the type of free energy surface shown in Figure 4. The s co-ordinate describes the effect of solvation and bond changes on the basicity of the diazo-compound. At the front of the diagram it starts as a very weak base. If it travelled all the way to the back of the diagram it would be a strong base with structure (A). It can be shown from the Marcus theory that proton transfers will be most rapid between bases of equal strength. Thus the more stable the diazo-compound the more it has to travel uphill until the thermodynamics for the proton transfer are roughly in balance. There is then a relatively small barrier to proton transfer (5—20 kJ mol^{-1}) and the different diazo-compounds exhibit similar characteristics (ϕ_1, $\alpha_{L_3O^+}$, and α_B) as they move along the proton transfer co-ordinate across the diagram. This separation into the movement along two different co-ordinates is an oversimplification but it emphasises the main feature of proton transfer to these aliphatic diazo-compounds; the change of catalysing acid affects the profile on the proton transfer co-ordinate, whereas the change of diazo-compound affects the position on the solvation co-ordinate.



(A)

[5/1519 *Received*, 31*st July*, 1975]

---

[13] R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891.

[14] W. J. Albery, A. N. Campbell-Crawford, and J. S. Curran, *J.C.S. Perkin II*, 1972, 2206.