71. *Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part II.*[1] *Cleavage of Arylmethylenemalononitriles by Water in 95% Ethanol.*

By Saul Patai and Zvi Rappoport.

The kinetics of the hydrolysis of various arylmethylenemalononitriles to aromatic aldehydes and malononitrile have been measured at various temperatures in 95% ethanol, alone and in the presence of added water, acids, bases, buffers, and salts. The reactions are of the first order in the compounds studied. The rates are enhanced by added base and by increasing the water content of the medium; acids in low concentrations retard and in higher concentrations inhibit the reaction. It is concluded that the rate-determining step is attack of a water molecule on the activated carbon–carbon double bond. The values of the Hammett reaction constants have been calculated for various reaction conditions and the mechanism of the reaction is discussed.

The catalysed hydrolysis of compounds containing activated carbon–carbon double bonds, to give the corresponding aldehydes and active methylene compounds according to the general scheme:

$$R^1R^2C{=}CR^3R^4 \xrightleftharpoons{H_2O} R^1R^2C{=}O + CH_2R^3R^4$$

was the subject of several kinetic investigations. Crowell and Francis [2] studied the base-catalysed hydrolysis of piperonylidenenitromethane at various acidities in water, and found evidence for the existence of a nitro-alcohol as intermediate. Stewart [3] studied the base-catalysed hydrolysis of vanillylidenenitromethane in water. Walker and Young [4] studied the base-catalysed decomposition of mononitrochalcones in 95% ethanol, and using Noyce and Pryor's results [5] with their own concluded that the ketol is not an intermediate in such reactions. Shemyakin and Shchukina [6] gave general qualitative rules about the influence of the substituent groups on the hydrolytic reactivity of ethylenic systems.

Our interest in this problem arose from the fact that cleavage of carbon–carbon double bonds is a reversal of a carbonyl–methylene condensation, the kinetics and mechanisms of which have been investigated in our laboratory.[7]

A simple system was wanted in which the reaction could be studied in the absence of catalysts. The compounds chosen were the substituted benzylidenemalononitriles:

$$\mathrm{Ar{\cdot}}\underset{\beta}{\mathrm{CH}}{=}\underset{\alpha}{\mathrm{C}}\mathrm{(CN)_2} \xrightarrow[\text{(EtOH)}]{H_2O} \mathrm{Ar{\cdot}CHO} + \mathrm{CH_2(CN)_2}$$

Results

The hydrolysis of substituted benzylidenemalononitriles at 30° and 40° in 95% ethanol was followed spectrophotometrically. The rate measurements (Table 1) show that each run is of first order in the substrate. The concentration of the compounds studied was limited by the slight solubility of a number of the compounds to ranges of 15- to 50-fold.

When the great sensitivity of the reaction to traces of both acids and bases (see Experimental section) is taken into account the reproducibility of the experiments was satisfactory. The behaviour of tricyanovinylbenzene was somewhat anomalous (see Discussion), but even in this case the difference between the rate coefficients of the various runs was not more than 20% in a 20-fold concentration range.

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[1] Part I, preceding paper.
[2] Crowell and Francis, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 591.
[3] Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 4531.
[4] Walker and Young, *J.*, 1957, 2045.
[5] Noyce and Pryor, *J. Amer. Chem. Soc.*, 1955, **77**, 1397.
[6] Shemyakin and Shchukina, *Quart. Rev.*, 1956, **10**, 261.
[7] (*a*) Patai and Israeli, *J.*, 1960, 2020, 2025; (*b*) Patai and Zabicky, *J.*, 1960, 2030; (*c*) Patai, Zabicky, and Israeli, *J.*, 1960, 2038.

TABLE 1.

Pseudo-first-order rate coefficients (k_1, in sec.$^{-1}$) of the hydrolysis of substituted benzylidenemalononitriles at 30° and 40° in 95% ethanol.[a]

4-*Nitrobenzylidenemalononitrile*. (i) At 30°.							
Concn. (10^{-5} mole l.$^{-1}$)	5	19	38	76			
10^5k_1	87	81	84	88			Mean 85 ± 2
(ii) At 40°.							
Concn. (10^{-5} mole l.$^{-1}$)	2·98	4·22	5·97	8·95	52·2	104·4	
10^5k_1	125	129	136	130	125	139	Mean 131 ± 5
2-*Chlorobenzylidenemalononitrile*. (i) At 30°.							
Concn. (10^{-5} mole l.$^{-1}$)	4·24	7·28	7·84	8·48	39·2	78·4	
10^5k_1	12·6	12·4	12·0	11·1	12·2	12·2	Mean 12·1 ± 0·3
(ii) At 40°.							
Concn. (10^{-5} mole l.$^{-1}$)	2·36	4·73	9·46				
10^5k_1	28·0	29·2	29·6				Mean 28·9 ± 0·6
3-*Chlorobenzylidenemalononitrile*. At 30°.							
Concn. (10^{-5} mole l.$^{-1}$)	0·986	2·5	5·0	10·4	50		
10^5k_1	7·9	9·7	9·3	9·8	9·2		Mean 9·1 ± 0·5
4-*Chlorobenzylidenemalononitrile*. (i) At 30°.[b]							
Concn. (10^{-5} mole l.$^{-1}$)	1·08	2·71	4·68	6·15	45·0	54·0	
10^5k_1	5·1	5·6	5·4	6·0	5·4	5·1	Mean 5·4 ± 0·2
(ii) At 40°.							
Concn. (10^{-5} mole l.$^{-1}$)	1·53	3·07	6·13	37·4	74·8		
10^5k_1	11·3	10·6	11·3	11·8	11·4		Mean 11·3 ± 0·3
Benzylidenemalononitrile. (i) At 30°.							
Concn. (10^{-5} mole l.$^{-1}$)	1·6	3·2	7·9	79			
10^5k_1	1·25	1·06	1·14	1·19			Mean 1·16 ± 0·6
(ii) At 40°.							
Concn. (10^{-5} mole l.$^{-1}$)	2·18	4·33	8·65				
10^5k_1	3·16	3·79	3·43				Mean 3·46 ± 0·22
4-*Methoxybenzylidenemalononitrile*. (i) At 30°.[c]							
Concn. (10^{-5} mole l.$^{-1}$)	1·3	3·3	6·5	65			
10^5k_1	0·109	0·101	0·105	0·105			Mean 0·105 ± 0·005
(ii) At 40°.							
Concn. (10^{-5} mole l.$^{-1}$)	3·2	23·6	47·3				
10^5k_1	0·222	0·250	0·245				Mean 0·239 ± 0·011
Tricyanovinylbenzene. At 30°[d]							
Concn. (10^{-5} mole l.$^{-1}$)	5·6	11·3	11·9	119			
10^5k_1	12·3	12·4	11·6	10·2			Mean 11·6 ± 0·7

[a] Containing 1% of benzene (see Experimental). [b] Each run was repeated several times in ethanol kept in glass or in Polythene bottles. The rate coefficients given are average values of these runs. [c] As the reaction was very slow, nitrogen was bubbled through the solution each time the vessel was opened for sampling, to avoid oxidation. [d] The reproducibility of these runs was less satisfactory. Results given are the average values of several runs.

Effect of Added Acid on the Reaction Rate.—The effect of acid was investigated in order to prove that water molecules, and not hydroxyl ions, are the attacking species in the first step of the hydrolysis, and that in one of the intermediate stages of the reaction a hydrogen ion is formed.

Addition of small concentrations of perchloric acid strongly retarded the reaction, and higher concentrations stopped it completely (Table 2).

The following arguments may be brought in order to show that the inhibition by acid is not due to lowering of the concentration of hydroxyl ions in the ethanol–water mixture. The retardation ratio is not constant for the various reactions at identical acid concentrations, as it would be if the inhibition was due to removal of hydroxyl ions from the solution. Table 2 also shows the retarding effect of various concentrations of acid on different concentrations of 4-nitro- and 2-chloro-benzylidenemalononitrile. The relative retardation by identical acid concentrations is smaller with a high concentration of the substrate than with a low one. This shows that the inhibition is due to the substrate itself, or to one of the intermediates of the

TABLE 2.

Relative rate coefficients demonstrating the effect of various perchloric acid concentrations on the hydrolysis of different arylmethylenemalononitriles at 40° in 95% ethanol.

[HClO$_4$] (10^{-6} mole l.$^{-1}$) \ Aryl concn. (10^{-5} mole l.$^{-1}$)	p-NO$_2$·C$_6$H$_4$ 3·69	p-NO$_2$·C$_6$H$_4$ 7·2	p-NO$_2$·C$_6$H$_4$ 49·2	p-NO$_2$·C$_6$H$_4$ 61·9	o-Cl·C$_6$H$_4$ 8·21	o-Cl·C$_6$H$_4$ 77·7	p-Cl·C$_6$H$_4$ 5·16
0	1	1	1	1	1	1	1
2	1·02	0·94	—	—	—	—	—
4	0·57	0·73	—	—	—	—	—
6	0·49	0·74	—	—	—	—	—
6·7	0·16	0·67	0·93	0·97	1·03	—	—
13·4	—	—	0·74	0·99	0·58	—	—
19·8	—	0·65	0·38	0·79	0·34	—	—
26·8	—	0·20	0·25	0·73	0·13	—	—
33·4	—	0·10	0·16	—	—	—	0·24
47	—	0·06	—	—	—	—	—
67	—	—	—	0·42	—	0·83	—
134	—	—	—	0·15	—	—	—
165	—	—	—	—	—	0·47	—
10,000	0 [a]	0 [a]	0 [a]	0 [a]	0 [b]	0 [b]	0 [b]

[a] No reaction detected after 6 hr. [b] No reaction detected after 12 hr.

hydrolysis, and not to a change in the amount of attacking species in the solution. It confirms the existence of an intermediate step involving the formation of a hydrogen ion.

Effect of Added Base on the Reaction Rate.—Addition of small quantities of base strongly enhanced the hydrolysis rates (Table 3). The rate in the presence of base was overall of the second order—first order in the substrate and in the base.

In order to find out whether the reaction is general base-catalysed or specific hydroxyl-ion-catalysed, the effects of triethylamine–triethylammonium chloride and of potassium hydrogen phthalate buffers were studied. A 50-fold increase in the concentration of the latter buffer did

TABLE 3.

Initial rate coefficients for the hydrolysis of various benzylidenemalononitriles in the presence of sodium hydroxide, triethylamine–triethylammonium chloride (TEA–TEA,HCl) buffer and potassium acid phthalate (PAP) buffer, in 95% ethanol.

	5 × 10^{-5}M-3-Chlorobenzylidenemalononitrile at 30°		5 × 10^{-5}M-Benzylidenemalononitrile at 40°	
[NaOH] (10^{-5} mole l.$^{-1}$)...	0	21·7	0	4·28
10^5k_1	9·1	16·2	3·46	109

4-Methoxybenzylidenemalononitrile at 30°				
Concn. (10^{-5} mole l.$^{-1}$)	6·5	3·77	5·3	6·28
[NaOH] (10^{-4} mole l.$^{-1}$)	0	0·937	1·68	0·937
10^4k_1	0·01 [a]	6·83	13·3	6·98
k_1/[NaOH]	—	7·30	7·90	7·45
5·97 × 10^{-5}M-4-Nitrobenzylidenemalononitrile at 40°				
PAP (10^{-4} mole l.$^{-1}$)	0	1	10	50
10^5k_1	131	115	119	119
TEA–TEA,HCl [b] (10^{-3} mole l.$^{-1}$)	0	1	2	5
5·97 × 10^{-5}M-4-Nitrobenzylidenemalononitrile at 40°				
10^5k_1	131	186	183	223
4·73 × 10^{-5}M-2-Chlorobenzylidenemalononitrile at 40°				
10^5k_1	28·9	42·1	48·8	63·5
6·13 × 10^{-5}M-4-Chlorobenzylidenemalononitrile at 40°				
10^5k_1	11·1	21·2	22·4	32·4
8·65 × 10^{-5}M-Benzylidenemalononitrile at 40°				
10^5k_1	3·46	7·46	8·08	13·1

[a] Constant of the uncatalysed reaction. [b] Each component of the buffer was added to the mixture in the concentrations stated.

not change the rate of hydrolysis of 4-nitrobenzylidenemalononitrile. However, when the former buffer was used, a 5-fold increase in its concentration increased the rates by 20—75%, with various substrates. This increase in the rates at high buffer concentrations could be understood by assuming a general base-catalysis by triethylamine or by the non-ideal behaviour of the buffer in ethanol. We believe that the second explanation is correct, as the increase in the rates is relatively slight and it is not proportional to the concentration of the buffer. The absence of general base-catalysis is evident in the case of the phthalate buffer, the behaviour of which seems to be ideal in ethanol as it is in water.

The ratio of the reaction rate in buffered solutions to that in 95% ethanol alone shows that specific base-catalysis is relatively weaker for substances with high than for those with low hydrolysis rates. (The reaction constants of the Hammett equation calculated by using Jaffe's values [8] are shown in Table 6.)

Effect of Added Salt on the Reaction Rate.—It was found that up to 0·6M-concentration of added lithium chloride the rate remained practically constant and decreased only very slightly in some cases with the addition of more salt up to M-lithium chloride. With 4-chlorobenzylidenemalononitrile, the rates were constant between 0 and 1M; with 4-nitrobenzylidenemalononitrile the rates were 1·25, 1·24, and 1·11 × 10^{-3} sec.$^{-1}$ with 0, 0·06M- and 1·0M-lithium chloride, respectively. Similarly, 0·1M-cetyltrimethylammonium bromide or M-sodium iodide had practically no effect on the rates.

Effect of Solvent Composition on Reaction Rates.—No measurable reaction took place in the absence of water. For a control experiment, the most reactive compound (4-nitrobenzylidenemalononitrile) was heated for six hours in dry methanol at 40° without measurable decomposition.

Addition of water to alcohol (from 1% to 50% by volume) raised the rate of the reaction with all the compounds studied. The increase was approximately linear in the lower concentrations, and the influence of added water was somewhat less than proportional at higher concentrations (Table 4). Higher concentrations of water (>50%) were not studied because of the slight solubilities of the compounds in such mixtures.

TABLE 4.

Effect of solvent composition on the initial rate coefficients ($10^5 k_1$ in sec.$^{-1}$) of the hydrolysis of ~5·6 × 10^{-5}M-solutions of 4-substituted benzylidenemalononitriles at 40° in ethanol.

H_2O (%, v/v)	(0) *	1	2	4	6	8	10	20	32	40	50
Subst.											
4-NO_2	6·29	20·7	33·4	71·5	131	151	175	355	416	445	469
4-Cl	—	1·06	2·23	5·71	8·87	14·6	20·0	40·2	67·9	70·6	81·0
H	0·209	0·604	0·86	1·69	3·30	4·44	7·76	15·0	25·4	—	37·9
4-Me	0·191	0·232	0·35	0·73	1·39	1·68	2·22	6·87	10·2	—	15·2

* Ethanol dried by sodium formate method.[9]

No linear correlation was observed with Grunwald and Winstein's *Y*-function.[10] Hammett's reaction constants ρ, calculated from data in Table 4 by using σ values (given by Jaffe [8]), are summarised in Table 6.

Effect of Various Alcohols on the Reaction Rate.—The effect of 20% (v/v) of water in seven alcohols on the 4-chlorobenzylidenemalononitrile hydrolysis was studied. 20% solutions were chosen to eliminate small differences in the degree of dryness of the pure alcohols. 4-Chlorobenzylidenemalononitrile was chosen because of its convenient rate of hydrolysis in these solvent mixtures.

No correlation was found between the observed rate coefficients (see Table 5) in the various alcohols and any of their possibly relevant physical properties such as acidity or dielectric constant.

Activation Energies.—The following values were calculated from the mean values of the

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[8] Jaffe, *Chem. Rev.*, 1953, **53**, 191.

[9] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p. 168.

[10] Grunwald and Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

TABLE 5.

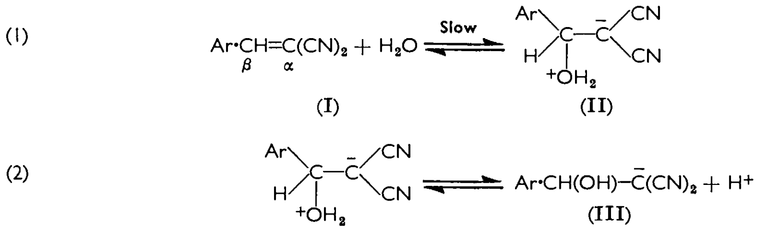
Effect of various alcohols on the hydrolysis rate of $4{\cdot}75 \times 10^{-5}$M-4-chlorobenzylidenemalononitrile, in 20% water–alcohol mixtures (v/v) at 40°.

Alcohol	MeOH	EtOH	Pr^nOH	Pr^iOH	Bu^tOH	Bu^iOH	$HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$
10^4k_1	1·15	4·24	0·93	3·54	2·04	1·93	3·18

hydrolysis rates as given in Table 1, for the substituted benzylidenemalononitriles: 4-NO_2 7·3; 4-Cl 13·8; 2-Cl 16·2; H 20·3; 4-MeO 15·5 kcal./mole.

DISCUSSION

We believe that the following mechanism is in accordance with the experimental results:



$$(3)\qquad Ar{\cdot}CH(OH){-}\bar{C}(CN)_2 + H^+ \rightleftharpoons \underset{(IV)}{Ar{\cdot}CH(OH){-}CH(CN)_2} \rightleftharpoons \underset{(V)}{Ar{\cdot}CH(O^-){-}CH(CN)_2} + H^+$$

$$(4)\qquad Ar{\cdot}CH(O^-){-}CH(CN)_2 \rightleftharpoons Ar{\cdot}CH{=}O + {}^-CH(CN)_2$$

$$(5)\qquad {}^-CH(CN)_2 + H^+ \rightleftharpoons CH_2(CN)_2$$

The first and rate-determining step is the attack of a water molecule on the electrophilic (β-)carbon atom of the carbon–carbon double bond. It could be claimed that attack by a much more nucleophilic species also present in the mixture, *i.e.*, hydroxyl ion, would be a more plausible first step even though it is present in a very much smaller concentration. In our opinion the following arguments show that this claim is not tenable: As in that case the hydroxyl ion concentration must enter the rate equation, the rate of attack on any substrate by hydroxyl ions should be depressed proportionally to the acid concentration, and the rate depression by acids should be independent of the concentration of the substrate. The results in Table 2 show that this is not the case. Further, it can be shown that if hydroxyl ions attack the substrate at all (*i.e.*, if there are two parallel reactions, one with water molecules and one with hydroxyl ions, leading to the same product) the importance of this attack is kinetically negligible with all but the most inert substances. The concentration of hydroxyl ions in 95% ethanol must be less than 10^{-7} mole $l.^{-1}$, and therefore a concentration of $2{\cdot}17 \times 10^{-4}$ mole $l.^{-1}$ of sodium hydroxide should give at least a 2000-fold acceleration of a reaction pathway depending on hydroxyl ions. The experiments in Table 3 with 3-chlorobenzylidenemalononitrile show that the rate enhancement by this concentration of base is less than 80%. Accordingly, the reaction going through hydroxyl ions in 95% ethanol must be less than $0{\cdot}8/2000 = 0{\cdot}04\%$. The same argument still holds for the rather unreactive benzylidenemalononitrile, where according to the same calculation not more than 7% of the reaction can go by hydroxyl ions. These calculated values (0·04% and 7%) may well be too high by a whole power of ten, or even more, as the ionisation of water in ethanol must be lower than that of pure water. On the other hand, with 4-methoxybenzylidenemalononitrile which is a very inert substrate, the same arguments do not hold, and in this case it is possible that a considerable part of the reaction involves hydroxyl attack. An additional argument pointing to attack by neutral molecules (the fact that acids do not affect the *cis–trans*-isomerisation rates of a similarly built compound, ethyl α-cyano-β-*o*-methoxyphenylacrylate) will be discussed in detail in Part IV of this series.

Addition of hydroxyl ions increases the rate by introducing the step (1′) instead of (1) and (2),

$$(1') \qquad \mathrm{Ar{\cdot}CH{=}C(CN)_2 \xrightleftharpoons{OH^-} Ar{\cdot}CH(OH){-}\bar{C}(CN)_2} \quad \text{(III)}$$

which produces ion (III) directly. Thus, the catalytic effect of hydroxyl ions is due to the greater nucleophilicity of hydroxyl ions (relative to water) towards the positively polarised carbon atom. As the hydroxyl ion concentration increases, so reaction (1′) becomes the main step instead of (1).

The general rate expression for simultaneous reactions with both water molecules and hydroxyl ions will be:

$$-\mathrm{d}[\mathrm{S}]/\mathrm{d}t = k[\mathrm{S}][\mathrm{H_2O}] + k'[\mathrm{S}][\mathrm{OH^-}]$$

where [S] is the concentration of the substrate. As shown above for 95% ethanol, the second term can be generally neglected for our experiments. Its relative importance may be calculated by assuming that in the presence of $2{\cdot}17 \times 10^{-4}$M-sodium hydroxide the first term remains unchanged, and the rate enhancement is due to the second term. Hence, as [S] is the same in both experiments, the ratio of the efficiencies of hydroxyl ions and water attacking 3-chlorobenzylidenemalononitrile will be given by the ratio of $k' : k$ which is given by $[(16{\cdot}2 - 9{\cdot}1) \times 2{\cdot}7]/[9{\cdot}1 \times 2{\cdot}17 \times 10^{-4}] \approx 10^4$. (Here 9·1 is the rate coefficient of the hydrolysis of the compound in 95% ethanol; 16·2 is the corresponding value in the presence of $2{\cdot}17 \times 10^{-4}$M-sodium hydroxide; 2·7 is the molarity of water in 95% ethanol.) This ratio depends on the nature and reactivity of the substrate attacked. With benzylidenemalononitrile a similar calculation gives the $k' : k$ ratio as $\sim 2 \times 10^6$.

The absence of general base-catalysis in the hydrolysis can be explained as follows: General bases such as triethylamine can attack the double bond giving intermediates such as $\mathrm{Et_3N^+{\cdot}CHAr{\cdot}C^-(CN)_2}$, but this reverts rapidly to compound (I) as there is no path to the completion of the hydrolysis. However, such an intermediate may allow *cis–trans*-isomerisation in cases when $R^3 \neq R^4$, as will be seen in Part IV of this series.

The absence of pronounced salt effect seems to show either that there is no large difference between the charge separation in the initial and the intermediate stage of the rate-determining step, or (as these experiments were carried out in the presence of 5%, *i.e.*, 2·7M-water) that the salt effect, superimposed on the effect of a comparatively large concentration of water in the solvent, is negligible. Varying the concentration of water in the solvent between 5% and 50% (Table 4) enhances the rates by an average of one power of ten. Such effects are common in S_N2 hydrolyses in ethanol–water.[11] In the present case, the rate of step (1) cannot be influenced by entrance into the rate equation of the water concentration which in all runs was in at least 10^4-fold excess, and by isolating step (1) (*i.e.*, in the *cis–trans*-isomerisation discussed in Part IV) no such effect was observed. Hence, water probably affects either step (2) or step (3), which are ionisation and protonation steps.

The intermediate carbanion (III) can lose a hydroxyl ion and revert to compound (I), or it can accept a proton from the medium to form compound (IV), which in turn by loss of the proton of the hydroxyl group gives ion (V).

No hydroxy-compound (IV) could be detected in the reaction mixture. Attempts to isolate such a compound in various conditions, especially at low temperatures, failed. Moreover, in three typical cases it was found that the rate of appearance of the aldehyde and of disappearance of the substrate were identical, within experimental error. Thus, the hydroxy-compound can exist in the mixture only in very small concentrations if at all.

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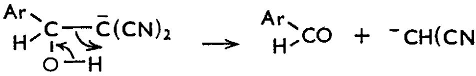
[11] (*a*) Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, 1953, pp. 346—348; (*b*) Clement and Rice, *J. Amer. Chem. Soc.*, 1959, **81**, 326.

It is possible that the transition of one intermediate into another takes place by intramolecular proton transfer, *e.g.*, intermediate (III) may give (V) directly, or intermediate (II) may give (IV) directly. Further, these proton transfers may take place with solvent participation, involving cyclic transition states, as in the mechanism proposed by Walker and Young[4] for the hydrolysis of nitrochalcones and by Laidler and Landskroener[12] for the base-catalysed ester hydrolysis.

Cleavage of ion (V) gives the aldehyde and the malononitrile carbanion. Protonation of the latter is very rapid; its value is given by Pearson and Dillon[13] as $1\cdot4 \times 10^{11}$ l. mole^{-1} min.$^{-1}$, in water at 25°.

A possible alternative mechanism would be the direct cleavage of ion (III) to give (by a four-centre mechanism) the aldehyde and the malononitrile carbanion:



This mechanism is in conflict with the principle of microscopic reversibility, as the mechanism which we believe to be correct for the carbonyl–methylene condensation[7a] includes ion (V) as the first intermediate in the condensation step. Accordingly, it must also appear as one of the intermediates in the hydrolysis sequence.

The inhibition by acids is interpreted as follows: The presence of hydrogen ions causes protonation of ion (III) to give compound (IV) and prevents the dissociation (IV) ⟶ (V) and at the same time catalyses the dehydration (IV) ⟶ (I).

The Effect of Substituents.—The results in Table 1 show that electron-attracting substituents on the aryl group bound to the β-carbon atom increase the hydrolysis rate while electron-donating substituents decrease it. The rate decreases 800-fold from the 4-nitro- to the 4-methoxy-compound. The positive sign of Hammett's reaction constant (Table 6) is in accordance with the proposed mechanism of nucleophilic attack. The effect of the ring-substituents on the β-carbon atom is mainly inductive,* both with electron-withdrawing and electron-donating substituents. 2-Chlorobenzylidenemalononitrile is hydrolysed more rapidly than the 3- and the 4-isomer, showing the greater inductive effect of the chlorine atom in the *ortho*-position.

TABLE 6.

ρ Values of the hydrolysis.

Temperature	30°	40°							
ρ in 95% ethanol	2·36	2·04							
% of Water in ethanol	1	2	4	6	8	10	20	32	50
ρ at 40°	2·12	2·14	2·10	2·00	2·02	1·92	1·80	1·58	1·56
[TEA–TEA,HCl] (10^{-3} mole l.$^{-1}$)	0	1	2	5					
ρ at 40°	2·04	1·80	1·72	1·55					

In view of the resonance effect of the α-substituents, structures can be drawn in which the β-carbon atom is positive, *e.g.*, $^{+}CHAr{\cdot}C(CN){:}C{:}N^{-}$. These structures contribute largely towards the reactivity of the β-carbon atom.

The cyano-substituted benzylidenemalononitrile, tricyanovinylbenzene, was found to be about ten times more reactive than benzylidenemalononitrile. This is in contrast to Shemyakin and Shchukina's assumption[6] that the reactivity of symmetrically substituted ethylenes should be lower in cleavage reactions. We believe that, while the

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* Except for the methoxy-group, which has a conjugative electron-releasing effect. We are indebted to a Referee for calling our attention to structures of the form $MeO^{+}{:}C_6H_4{:}CH{\cdot}C(CN){:}C{:}N^{-}$ which may be responsible for the reduction of the positive charge on the β-carbon atom and hence for the slow rates with these compounds.

[12] Laidler and Landskroener, *Trans. Faraday Soc.*, 1956, **52**, 200.

[13] Pearson and Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

resonance effect of the β-cyano-group reduces the electron density at the α-carbon atom, its inductive effect explains the greater reactivity of tricyanovinylbenzene than of benzylidenemalononitrile.

It is of interest that the decrease with time of the ultraviolet absorption of tricyanovinylbenzene in ethanol was postulated as due to complex-formation with the solvent. In our opinion the decrease in absorption is a result of cleavage, giving benzoyl cyanide and malononitrile as the primary products (see Experimental, product analysis, section *c*). The results of our experiments with this compound were somewhat erratic. We attribute this to side reactions such as substitution of the labile β-cyano-group by OH^-, OEt^-, etc. Also, in this case, addition of acid raised the rate of disappearance of the compound, possibly owing to cyclisation [14] and other side-reactions.

The Hammett Reaction Constant.—The reaction constant ρ of the Hammett equation $\log (k/k_0) = \sigma\rho$ has been calculated in all the cases in which sufficient data were available by using σ values given by Jaffe.[8] Except for the 4-methoxy-compound all points fell on a straight line.

Table 6 shows that the sensitivity of the reaction to substituents is large ($\rho > 2$) but decreases if the reaction is rendered faster by raising the temperature or by the adding of more water or more buffer. (The rate enhancement by the buffer is due to its non-ideal behaviour in ethanol as explained above.) In other words, the effects of temperature, catalyst, and more aqueous solvent are greater for the compounds having low than for those having high hydrolysis rates. The same phenomena for temperature, solvent effect, and base-catalysis were observed previously for the reverse reaction.[7a,b]

EXPERIMENTAL

Materials.—4-Methoxy- [15] (m. p. 115°), 4-nitro- [7a] (m. p. 161°), 4-chloro- [7a] (m. p. 163·5—164°), 2-chloro- [15] (m. p. 95·5°), 4-methyl- [16] (m. p. 131°), and unsubstituted benzylidenemalononitrile [15] (m. p. 84°) were synthesised by condensing the appropriate aldehyde with malononitrile in 95% ethanol, with one drop of 0·1N-aqueous sodium hydroxide as the catalyst. The compounds were crystallised from propan-1-ol to constant m. p. and to constant spectra. Tricyanovinylbenzene (m. p. 97°) was prepared according to directions of Sausen, Engelhardt, and Middleton [14] from benzoyl cyanide and malononitrile.

Ethanol.—This was distilled from 1% (v/v) of concentrated sulphuric acid. Distilled ethanol (5 l.) was refluxed for 6 hr. with 100 g. each of zinc and potassium hydroxide, and passed through an Amberlite IR-120(H) resin (Fisher Scientific Co.), then redistilled and the fraction boiling at 76·6°/720 mm. was collected and stored in Polythene bottles. In view of the great sensitivity of the reaction to traces of acids or bases, the same batch of ethanol was used for all the experiments. The solvent was boiled for 0·5 hr. immediately before use to expel any dissolved carbon dioxide.

The various other alcohols were purified carefully.

Distilled water was redistilled from potassium permanganate, distilled again, and boiled for ½ hr. to expel any dissolved carbon dioxide.

Analytical-grade perchloric acid (Baker's analysed) and salts were used.

Spectral Data.—Those were determined with a Beckman DU spectrophotometer with a photomultiplier. The values obtained were in good agreement with those found in the literature.[7a,b]

The following new data were obtained: 2-, $\lambda_{max.}$ 305 mμ (ε 14,700) and 3-chlorobenzylidenemalononitrile $\lambda_{max.}$ 303 mμ (ε 19,400).

The spectra were determined in a 0·02M-solution of perchloric acid in ethanol. The acid did not change the spectral values but prevented errors due to hydrolysis. The extinction coefficient of tricyanovinylbenzene could not be measured in this way, because of its rapid reaction in acid medium. By extrapolation to zero time of optical density–time curves, we

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[14] Sausen, Englhardt, and Middleton, *J. Amer. Chem. Soc.*, 1958, **80**, 2815.

[15] Corson and Stoughton, *J. Amer. Chem. Soc.*, 1928, **50**, 2825.

[16] Gal, Fund, and Greenberg, *Cancer Res.*, 1952, **12**, 565.

obtained $\lambda_{max.}$ 335 mμ (ε 14,300), consistently with the values reported by Sausen *et al.* for chloroform solutions,[14] but differing widely from their value for ethanol solutions (ε = 5950).

Product Analysis.—(*a*) After equilibrium had been reached the final spectra of the solutions were measured. The sum of the concentrations of the arylmethylenemalononitrile and the appropriate aldehyde as calculated from the spectra gave a total of 100%.

(*b*) Each compound (200 mg.) was boiled for 1 hr. in 95% ethanol, then acidified, and the aldehydes were identified by m. p. and mixed m. p. of their 2,4-dinitrophenylhydrazones.

(*c*) Tricyanovinylbenzene (300 mg.) and *p*-methoxybenzaldehyde (600 mg.) in ethanol (20 ml.) were kept at 40° for 20 hr. From the mixture, 4-methoxybenzylidenemalononitrile (220 mg., 72%) was obtained and characterised by m. p. and mixed m. p. The mother liquor gave a positive test for cyanide ions.

Kinetic Runs.—Owing to the slow and low solubility of the reactants in alcohol–water mixtures, and to the relatively rapid hydrolysis the following procedure was used: Concentrated stock solutions of the various compounds in benzene were prepared and kept at the reaction temperature. Appropriate amounts of this stock solution were added to measured amounts of the solvent at the same temperature, so that the benzene in the mixture did not exceed 1% by volume. Control experiments showed that the presence of 1—2% of benzene had no effect on the rates.

Two kinetic procedures were used: With concentrated solutions of the substrate, samples (1 ml.) were taken at appropriate time intervals and quenched in 0·01M-perchloric acid in ethanol (25 ml.). This procedure stopped the reaction immediately, while the acid had no effect on the spectra. With more dilute solutions the reaction mixture was placed in a ground-glass-stoppered silica absorption cell in a spectrophotometer chamber (thermostat) (Beckman Dual Thermospacer), and the changes in the absorbance were measured *in situ*.

Treatment of Data.—The optical densities were plotted against time and first-order rate coefficients were calculated for each point. Two examples of typical runs are given in the annexed Table.

Hydrolysis of 7·84 × 10^{-5}M-2-*chlorobenzylidenemalononitrile in* 95% *ethanol at* 30°.

t (min.)	0	4	6	10	14·5	18	22·5	31	40	50	75	104
D	1·100	1·064	1·045	1·013	0·990	0·964	0·935	0·880	0·825	0·770	0·660	0·550
Reaction (%)	0	3	5	8	10	12·5	15	20	25	30	40	50
10^5k_1	—	12·3	12·2	12·2	12·1	12·3	12·0	12·0	12·1	11·8	11·4	11·2

Hydrolysis of 3·92 × 10^{-4}M-2-*chlorobenzylidenemalononitrile in* 95% *ethanol at* 30°.

t (min.)	0	4	7	11	16	20	23	31	40	49	75	114
D	0·656	0·636	0·623	0·603	0·590	0·574	0·557	0·524	0·491	0·459	0·393	0·328
Reaction (%)	0	3	5	8	10	12·5	15	20	25	30	40	50
10^5k_1	—	12·3	11·9	11·2	11·1	11·1	11·6	12·0	12·0	12·0	11·4	10·1

Although approach to equilibrium causes a decrease in the rate coefficients, these are reasonably constant up to 30—40% reaction. The coefficients in Table 1 are calculated average values. Initial rate coefficients given in the other Tables were calculated from the first 10—20% of the reaction, where all the experimental points fall on a straight line, by means of the equation $k_1 = (D_0 - D_t)/D_0t$, where D_0 and D_t are the measured optical densities at the beginning and at the time t of the reaction, respectively. The two methods gave good agreement.

Control Experiment.—In order to prove that no hold-up of any intermediate occurred in the reaction mixture, runs were made with various substituted benzylidenemalononitriles. The disappearance of the arylmethylenemalononitrile and the appearance of the aldehyde were measured concurrently. Cleavage of the substrate and appearance of the aldehyde occurred at the same rate in the whole measured range of the reaction. In previous work the same result was obtained for the reverse reaction, namely, condensation of *p*-methoxybenzaldehyde with malononitrile.[7a]

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