410. *The Kinetics and Mechanisms of Carbonyl–Methylene Condensations. Part VI.*[1] *The Reaction of Malononitrile with Aromatic Aldehydes in Water.*

By Saul Patai and Yigal Israeli.

The kinetics of the reaction of malononitrile with four aromatic aldehydes have been measured at different temperatures in aqueous solution, alone and with added acids, salts, and ethanol. The reactions are of first order in malononitrile and zero order in aldehyde and show the diagnostic features of a unimolecular process. It is concluded that the rate-determining step is ionisation of the carbon–hydrogen bond of the active methylene group, although the aldehyde has some influence on the overall rate of the reaction. The mechanism is discussed.

Introduction to a Series of Papers.—In investigations[1] we proposed a mechanism for various carbonyl–methylene condensations whereby one of the controlling factors is dissociation of the C–H bond of the methylene group. In this series of papers we show that, according to the nature of the reactants and the solvents, the kinetic order may be strictly first or strictly second, or it may appear as any intermediate order between these two. We believe that, independently of the actual overall kinetic order, the reaction is always of first order in the active methylene component and that the ionic dissociation of the C–H bond is the first and necessary step in the mechanism:

$$R^1R^2CH_2 \xrightarrow[k_1]{} R^1R^2CH^- + H^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$R^1R^2CH^- + R^3R^4CO \xrightarrow[k_2]{} {}^-O{\cdot}CR^3R^4{\cdot}CHR^1R^2 \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

$${}^-O{\cdot}CR^3R^4{\cdot}CHR^1R^2 \xrightarrow[\text{(several steps)}]{k_3} R^3R^4C{=}CR^1R^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

If in this sequence the dissociation rate k_1 is very slow compared with all other rates, the result will be overall of the first order, *i.e.*, of the first order in $R^1R^2CH_2$ and of zero order in the other reactants. In other cases, k_1 may be fast compared with k_2 and the overall order will be second, but the reaction will still show characteristic properties of a dissociation reaction, *e.g.*, it will be retarded or even completely inhibited by added protonic acids and will be strongly accelerated by more polar media or by added salts.

---

[1] Parts I—V, *J. Amer. Chem. Soc.*, 1954, **76**, 3446; *Bull. Res. Council Israel*, 1958, **7**, *A*, 59; *Chem. and Ind.*, 1957, 1671; *Bull. Res. Council Israel*, 1958, **7**, *A*, 186; *ibid.*, p. 100.

RESULTS

The reaction of the aldehydes with malononitrile in water at 32° was followed spectrophotometrically. The rate measurements (see Table 1) show that each run is of first order in the malononitrile and of zero order in the aldehyde. With benzaldehyde the reproducibility of the rate data was less satisfactory and the first-order rate coefficient rose somewhat with higher concentrations of reagents, owing partly to experimental difficulties and partly to a medium effect caused by the larger concentrations of the reagents themselves. Even so, the difference between the smallest and the largest concentrations studied is 13-fold in each of the reactants, while the first-order rate coefficient changes only by a factor of 1·67 (compare the runs marked *).

With benzaldehyde and *p*-anisaldehyde precipitation of the product generally started before equilibrium was reached. With *p*-chloro- and with *p*-nitro-benzaldehyde, owing to their low solubility in water, the concentration range at which runs could be carried out was rather narrow. At concentrations below 0·001M, equilibrium was reached too quickly for reliable kinetic measurements. With 0·002M-*p*-nitrobenzaldehyde and 0·002M-malononitrile the reaction came to equilibrium when about 0·0003M of the starting materials had reacted.

TABLE 1. *First-order initial rate coefficients of the reaction between malononitrile* (MN) *and anisaldehyde* (AA), *benzaldehyde* (BA), p-*chlorobenzaldehyde* (CA), *and* p-*nitrobenzaldehyde* (NBA) *at* 32° *in water.*

p-*Anisaldehyde.*

MN (mole l.$^{-1}$)	0·004	0·004	0·005	0·008	0·010	0·012	0·015
AA (mole l.$^{-1}$)	0·00412	0·0149	0·0066	0·00825	0·0099	0·0124	0·015
10^5k_1 (sec.$^{-1}$)	5·90	6·10	6·25	5·85	6·10	5·75	6·20

Benzaldehyde.

MN (mole l.$^{-1}$)	0·002	0·002	0·004	0·006	0·01	0·02	0·026
BA (mole l.$^{-1}$)	0·00205	0·00615	0·004	0·00615	0·0102	0·0205	0·0263
10^5k_1 (sec.$^{-1}$)	12·4 *	14·7	13·3	14·3	15·2	18·0	20·7 *

p-*Chlorobenzaldehyde.*

MN (mole l.$^{-1}$)	0·002	0·002	0·003	0·004
CA (mole l.$^{-1}$)	0·002	0·004	0·003	0·004
10^5k_1 (sec.$^{-1}$)	19·5	24·3	25·4	25·5

p-*Nitrobenzaldehyde.*

MN (mole l.$^{-1}$)	0·002	0·002	0·003	0·004
NBA (mole l.$^{-1}$)	0·002	0·004	0·003	0·004
10^5k_1 (sec.$^{-1}$)	47·0	47·5	52·5	55·8

Table 1 shows that the reaction is essentially of zero order in the aldehyde. Nevertheless, the aldehyde influences the overall rate of the reaction; the values for *p*-nitrobenzaldehyde, *p*-chlorobenzaldehyde, benzaldehyde, and *p*-anisaldehyde being in the ratio 4 : 2 : 1 : 0·3—0·5.

Effect of Added Acid on the Reaction Rates.—To test the assumption that the reaction is governed by a dissociation step, we studied the effect of added acid. Addition of hydrochloric acid strongly retarded the reaction and, at higher concentrations, stopped it completely (see Table 2).

TABLE 2. *Effect of added hydrochloric acid on the initial rate coefficients* (k_1 *in sec.*$^{-1}$) *of the reaction between aromatic aldehydes and malononitrile in water at* 32°.

0·00412M-*Anisaldehyde with* 0·004M-*malononitrile.*

[HCl] (M)	None	0·00004	0·0001	0·0004	0·0006	0·001
10^5k_1	5·9	4·0	1·9	0·4	0·19	0·14

0·004M-*Benaldehyde with* 0·004M-*malononitrile.*

[HCl] (M)	None	0·0001	0·001
10^5k_1	13·3	3·8	0·53

0·002M-p-*Nitrobenzaldehyde with* 0·002M-*malononitrile.*

[HCl] (M)	None	0·0004
10^5k_1 (sec.$^{-1}$)	47·0	2·02

Effect of Added Salt on the Reaction Rates.—Addition of lithium enhanced the reaction rates (see Table 3).

TABLE 3. *Effect of added lithium chloride on the initial rate coefficients* (k_1 *in sec.*$^{-1}$) *on the reaction between* 0·00412M-*anisaldehyde and* 0·004M-*malononitrile in water at* 32°.

0·004M-*Malononitrile in water at* 32°.

[LiCl] (M)	None	0·2	0·4	0·6	0·8	1·0
10^5k_1	5·9	6·85	8·0	9·0	12·5	16·0

Effect of Solvent Composition on Reaction Rates.—Addition of up to about 30% (v/v) of ethanol to the water raised the reaction rates, but larger amounts depressed them (see Table 4).

TABLE 4. *Effect of solvent composition on the initial rate coefficients (k_1 in sec.$^{-1}$) of the reaction between malononitrile and benzaldehyde,* p-*anisaldehyde, and* p-*nitrobenzaldehyde.*

EtOH (%, v/v) ...	0	9·4	18·4	28·4	37·9	47·4	56·9	66·4	75·9	85·3	90·2	95·0
0·00412M-*Anisaldehyde and* 0·004M-*malononitrile at* 32°.												
10^5k_1	5·9	9·0	10·7	14·0	11·3	10·3	7·5	7·17	4·85	2·85	2·09	0·9
0·004M-*Benzaldehyde and* 0·004M-*malononitrile at* 32°.												
10^4k_1	1·33	—	1·92	2·33	2·20	—	1·9	—	1·67	1·44	—	1·0

0·01M-*Anisaldehyde and* 0·01M-*malononitrile at* 40°.

EtOH (%, v/v) ...	0	10	20	28·4	38	58	80·7	95
10^5k_1	9·0	11·5	13·3	16·0	13	9·0	6·6	4·3

0·02M-p-*Nitrobenzaldehyde and malononitrile at* 32°.

EtOH (%, v/v) ...	0	28·4
10^5k_1	47·0	55·0

It is noteworthy that the highest rate was found always in mixtures of about 70% of water and 30% of ethanol (v/v). The plots of rate coefficients against solvent compositions were straight lines on both sides of the maximum, but the slope of these lines varied with the reaction investigated and with the temperature. Deviation from linearity was found at the highest ethanol concentrations; unfortunately, no experiments could be carried out in absolute ethanol owing to the formation of the acetals of the aromatic aldehydes in this solvent. In all cases the slopes leading from the maximum to the pure water side are steeper than those leading to the ethanol side of the graph.

Dependence of the Reaction on Temperature.—To determine the activation energies, rate measurements were made at several temperatures. The results are in Table 5. The critical increment of the Arrhenius equation calculated from these data was 9600 ± 300 cal. mole^{-1} for the reaction of malononitrile with anisaldehyde, 7200 ± 200 for that with benzaldehyde, and 2400 ± 300 for that with *p*-nitrobenzaldehyde.

TABLE 5. *First-order initial rate coefficients (k_1 in sec.$^{-1}$) of the reaction of malononitrile* (MN) *with anisaldehyde* (AA), *benzaldehyde* (BA), *and* p-*nitrobenzaldehyde* (NBA) *at different temperatures.*

MN (M)	Aldehyde (M)	Temp.	10^5k_1	MN (M)	Aldehyde (M)	Temp.	10^5k_1
0·004—0·0015	0·004—0·0015 AA	32°	6·0	0·004	0·004 BA	32°	13·3
0·006	0·0066 ,,	36	6·9	,,	,, ,,	36	16·0
0·004	0·00412 ,,	40	8·75	,,	,, ,,	40	18·5
0·006	0·0066 ,,	40	8·90	0·002	0·002 NBA	32	47·0
0·004	0·00412 ,,	49	13·5	,,	,, ,,	40	52·0
0·006	0·0066 ,,	49	13·5				

DISCUSSION

The experiments described above show that the reaction between malononitrile and aromatic aldehydes in water is governed by a rate-determining unimolecular ionisation of the malononitrile molecule (1) (where $R^1 = R^2 = CN$). This ionisation is facilitated by the high solvating power and basicity of the solvent water. It is, in fact, a slow proton-transfer involving the breaking of a C–H bond in the active methylene compound. The other steps of the reaction, *i.e.*, (2) and (3) (where R = Ar, R = H) are, according to our scheme, faster than step (1), although the subsequent steps too have some influence on the overall rates. This is shown by the alteration of the rates with different aldehydes.

The results with different concentrations of reagents (Table 1) in themselves give rather convincing evidence for the validity of the mechanism proposed. The retardation of the rates by added hydrochloric acid (Table 2) must therefore be explained as a common-ion effect, in which the added hydrogen ions depress the ionisation of the C–H bond of the active methylene group, in analogy to the observed common-ion effects in S_N1 reactions.

Similarly, the faster rates observed in the presence of added lithium chloride (see Table 3) conform to the expected effect of the higher ionic strength of the solvent on the reaction rates of a reaction dependent on a unimolecular rate-determining ionisation.

Thus, our results show the most characteristic diagnostic features of a unimolecular mechanism, *i.e.*, common-ion retardation, independence of the concentration of the attacking reagent, and positive (non-common ion) salt effect. On the other hand, the rates are not independent of the nature of the attacking reagent, *i.e.*, the aldehyde. Similar cases of unimolecular substitutions in which the rates are dependent on the nature of the substituting agent, although in a much smaller degree than would be expected in a bimolecular process, are well known and have been discussed in detail.[2] The reaction has a necessarily unimolecular first step (1), but the overall order and the molecularity of the rate-determining step will be a result of the relative rate ratios of steps 1—3. The kinetic complications due to the rates of step (2) and/or step (3) cannot be completely disregarded. This is shown by both the dependence of the overall rates on the nature of the aldehyde and, to a much smaller extent, also on its concentration. Nevertheless, both influences are much smaller than would be expected for a bimolecular reaction.

The dependence of the reaction rates on the carbonyl constituent is also reflected in the differences of the activation energies.

In a pure unimolecular reaction, the activation energies, like the reaction rates, should be independent of the nature of the aldehyde. Nevertheless, it seems that the energy barrier between the reagents and the products is much lower with the reactive *p*-nitrobenzaldehyde than with the less reactive *p*-anisaldehyde. Owing to the kinetic complications encountered, the activation energy values reported are only approximate.

Influence of the Solvent Constitution on the Reaction Rates.—Table 4 shows that a small amount of ethanol in water acts as a catalyst for the reaction and, conversely, addition of water to ethanol also enhances the reaction rates. The two effects together result in a maximum in the rates at about 70% water and 30% ethanol (v/v). These facts are further discussed in Part VIII of this series.

The Hammett Reaction Constant.—The reaction constant, ρ, of the Hammett equation $\log (k/k_0) = \sigma\rho$ has been calculated from the values given in Table 4. With Brown's σ values[3] a straight line was obtained for the four aldehydes studied. From the slope of this line, the ρ value of the Hammett equation was found to be 0·55 for the reaction in water. In the above solvent giving the fastest rates in all the water–ethanol mixtures, the ρ value was even smaller, namely, 0·35. It seems that, given a faster reaction, the composition of the solvent has a relatively smaller influence; hence the rate coefficients tend to converge in the " fastest " solvent. At this composition, obviously, the Hammett ρ values are at a minimum; in ethanol, where the mechanism changed (see following paper) the ρ value is nearly normal for a bimolecular reaction.

EXPERIMENTAL

Materials.—The aldehydes and the malononitrile were freshly distilled or recrystallised every day immediately before the runs. Aldehyde solutions prepared more than 12 hr. after the purification gave erroneous results, probably owing to oxidation to the corresponding acid and the great sensitivity of the reaction towards acid. Malononotrile solutions were used within 6—7 hr. of their preparation. Distilled water was redistilled before use and boiled for about an hour so as to expel dissolved carbon dioxide; it then had pH 7. Ethanol was distilled from 1% (v/v) of concentrated sulphuric acid, the appropriate fraction was refluxed for 6 hr. with 100 g. of zinc and 100 g. of potassium hydroxide per 5 l. of ethanol, distilled, and passed through an Amberlite IR-120 (H) resin (Fisher Scientific Co.), redistilled, and adjusted to 5% water content.

---

[2] Bird, Hughes, and Ingold, *J.*, 1954, 634; Bruton, Greenstreet, Hughes, and Ingold, *ibid.*, p. 647; Gelles, Hughes, and Ingold, *ibid.*, p. 2918.

[3] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4980.

Spectral Data.—Those for the aldehydes and products are given in the following paper. The spectra of the products were identical in water and in ethanol.

Analysis of Products.—The solubility of the products in water was rather small (~10^{-4}M). The crystals which separated were collected and identified by m. p. and mixed m. p. with authentic samples (benzylidenemalononitrile,[4] m. p. 84°; anisylidenemalononitrile,[4] m. p. 115°; *p*-nitrobenzylidenemalononitrile,[5] m. p. 161°). p-*Chlorobenzylidenemalononitrile* had m. p. 163° (from ethanol) (Found: C, 63·3; H, 3·1; N, 14·5. $C_{10}H_5ClN_2$ requires C, 63·7; H, 2·7; N, 14·8%).

Kinetic Runs.—Stock solutions of the reactants in the appropriate solvents (water or ethanol–water) were prepared at the temperature at which the runs were made. Owing to the low solubility of the reactants and especially of the products in water, runs could be made only at rather low concentrations. Reaction was generally interrupted as soon as the product started to separate. The rate data, therefore, are only initial ones, but were calculated on the basis of at least 8—10 experimental points. Owing to precipitation of the products, the position of the equilibrium for the reaction could not be determined.

One ml. samples were taken every minute and quenched in a measured amount (25—100 ml.) of 0·02M-hydrochloric acid. This procedure stopped the reaction immediately and completely. The acid influenced slightly the absorption spectra of the aldehydes, but had no effect on those of the products, which were used for the measurements. When the absorption data were plotted against time, the experimental points fell on a straight line. First-order rate coefficients were calculated from the equation

$$k_1 = f(D_2 - D_1)/(t_2 - t_1)\varepsilon c$$

where D_1 and D_2 are the measured optical densities at times t_1 and t_2 respectively, at the wavelength of the maximum absorption of the product; the " dilution factor " (f) is the final volume to which 1 ml. of the sample is diluted before measurement of its absorption, ε is the molar absorption of the product, and c is the concentration of the active methylene compound. Data for a sample run are given below.

0·012M-*Malononitrile* (MN) *with* 0·0124M-p-*anisaldehyde in water at* 32°. *Dilution factor* = 50; ε = 30,300.

Time (sec.)	120	180	240	300	360	420	480	540	600	660	720	780
D	0·049	0·070	0·102	0·130	0·160	0·195	0·205	0·228	0·245	0·270	0·285	0·315
MN reacted (%)	0·68	0·97	1·42	1·80	2·22	2·70	2·84	3·17	3·40	3·75	3·96	4·38
10^5k_1	5·70	5·42	5·98	6·15	6·18	6·50	6·06	5·90	5·81	5·75	5·65	5·73

Average $k_1 = 5{\cdot}88 \times 10^{-5}$ sec.$^{-1}$. Calc. from graph of D against t, $k_1 = 5{\cdot}75 \times 10^{-5}$ sec.$^{-1}$.

Control Experiment.—In order to prove that no hold-up of any intermediate product occurred in the reaction mixture, a run was made with *p*-anisaldehyde and malononitrile in which both the disappearance of the carbonyl absorption at 281 mμ and the appearance of the absorption of the product (at 351 mμ) were measured concurrently. From the measured values, reaction percentages were calculated both for the amount of aldehyde which reacted and for the amount of product formed. These points, when plotted against time, conformed to the same curve, although the points for formation of product were much nearer to the curve than those for carbonyl-absorption data. The deviation from smoothed-out curves with the carbonyl-absorption data was up to 0·5—0·6%, whereas with the measurements of the absorption of the product the deviations were generally less than 0·2%. We believe this to be due to two experimental difficulties: (*a*) the carbonyl absorption is influenced by added acids; therefore, the samples were not quenched in acid but only in water and the reaction was not stopped completely; and (*b*) the aldehydes are very sensitive to oxidation and possibly gave some reaction during the dilution with atmospheric or dissolved oxygen. Neither of these factors influenced the measurements of the product.

Department of Organic Chemistry,
The Hebrew University, Jerusalem, Israel.

[*Received, July* 14*th*, 1959.]

---

[4] Corson and Staughton, *J. Amer. Chem. Soc.*, 1928, **50**, 2825.

[5] Hertel and Hoffman, *Z. phys. Chem.*, 1941, *B*, **50**, 382.