413. *The Kinetics and Mechanisms of Carbonyl–Methylene Condensations. Part IX.* The Reaction of Cyanoacetamide with Aromatic Aldehydes in Ethanol and in Water.*

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The kinetics of the condensation of cyanoacetamide with aromatic aldehydes in ethanol and in water at different concentrations and temperatures have been measured. The reaction order is generally an intermediate one, varying from zeroth to first order in the aldehyde. The mechanism of the reaction is discussed, and some remarks are made on the reactivities of various active methylene compounds towards aromatic aldehydes.

The present paper describes the kinetic results obtained for the condensation of cyanoacetamide with aromatic aldehydes in ethanol at various temperatures and also in the presence of different acids, piperidine, water, and lithium nitrate (Table 1). Table 2 summarises the results for the same reaction in water at 40°.

Discussion

In previous papers of this series, we tried to show that, in the uncatalysed reaction between aromatic aldehydes and active methylene compounds, the two limiting mechanisms are unimolecular and bimolecular. The results of the present study show that the reaction of cyanoacetamide with aromatic aldehydes in ethanol approaches the bimolecular mechanism. For *p*-anisaldehyde the reaction follows second-order kinetics both in

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* Part VIII, preceding paper.

TABLE 1. *Initial rate coefficients of the condensation of cyanoacetamide* (CAM) *with anisaldehyde* (AA), *benzaldehyde* (BA), p-*chlorobenzaldehyde* (CA), *and* p-*nitrobenzaldehyde* (pNBA) *in 95% ethanol at different concentrations and temperatures.* (*Concentrations in mole l.*$^{-1}$; k_2 *in mole*$^{-1}$ *l. sec.*$^{-1}$.)

		k_2 at	
CAM	R·CHO	40°	50°
0·02	0·02 AA	8·4	—
0·02	0·04 ,,	8·8	15·0
0·02	0·06 ,,	8·3	15·8
0·02	0·01 ,,	8·8	14·9
0·03	0·06 ,,	8·3	15·6
0·04	0·06 ,,	8·3	—
0·02	0·01 BA	100	—
0·02	0·02 ,,	96	121
0·02	0·04 ,,	72·5	—
0·02	0·06 ,,	56	—
0·02	0·08 ,,	49	72·5
0·02	0·10 ,,	41	71
0·01	0·06 ,,	56	101
0·03	0·06 ,,	55	93
0·04	0·06 ,,	53	—

			k_2 at		
CAM	R·CHO	26°	40°	50°	65°
0·02	0·01 CA	—	227	317	—
0·02	0·02 ,,	—	217	342	535
0·02	0·04 ,,	—	150	310	490
0·02	0·06 ,,	—	128	310	490
0·02	0·10 ,,	—	83	—	470
0·02	0·20 ,,	—	42	—	—
0·01	0·05 ,,	—	120	320	—
0·04	0·06 ,,	—	117	285	—
0·06	0·06 ,,	—	128	—	—
0·01	0·01 pNBA	625	1930	2170	—
0·01	0·02 ,,	623	1630	2230	—
0·01	0·03 ,,	495	1380	2000	—
0·01	0·04 ,,	—	1220	1930	—
0·01	0·06 ,,	425	1150	1880	—
0·002	0·02 ,,	—	1920	—	—
0·005	0·02 ,,	—	1870	—	—
0·02	0·01 ,,	—	1250	—	—
0·03	0·01 ,,	—	1000	—	—

CAM	R·CHO	Added *	k_2 at 40°
0·02	0·02 AA	20% H_2O	18·5
,,	,, ,,	0·0002 Pip	38·4
,,	,, ,,	0·2 $LiNO_3$	15·1
,,	,, ,,	0·0002 $HClO_4$	0·0
,,	0·02 BA	20% H_2O	150
,,	,, ,,	0·0002 Pip	200
,,	,, ,,	0·2 $LiNO_3$	125
,,	,, ,,	0·0002 $HClO_4$	0
,,	,, ,,	0·0002 PhOH	85
,,	,, ,,	0·02 PhOH	0

CAM	R·CHO	Added	k_2 at 40°
0·02	0·02 BA	0·0002 AcOH	33
,,	,, ,,	0·02 *p*-$HO·C_6H_4·CHO$	0
,,	0·02 CA	20% H_2O	300
,,	,, ,,	0·2 $LiNO_3$	280
,,	,, ,,	0·0002 Pip	860
,,	,, ,,	0·0002 $HClO_4$	0
0·01	0·01 pNBA	20% H_2O	2250
,,	,, ,,	0·02 $LiNO_3$	2200
,,	,, ,,	0·0002 $LiNO_3$	2840

* Pip = Piperidine.

TABLE 2. *Initial rate coefficients of the reaction of cyanoacetamide* (CAM) *with anisaldehyde* (AA), *benzaldehyde* (BA), p-*chlorobenzaldehyde* (CA), m-*nitrobenzaldehyde* (mNBA), *and* p-*nitrobenzaldehyde* (pNBA) *in water at 40°.* (*Concentrations in moles l.*$^{-1}$).

CAM	R·CHO	10^8k_1 (sec.$^{-1}$)	10^5k_2 (mole^{-1} l. sec.$^{-1}$)
0·0005	0·0005 AA	1·6	3·2
,,	0·002 ,,	6·6	3·3
0·001	0·0005 ,,	3·3	6·6
,,	0·001 ,,	4·8	4·8
,,	0·002 ,,	5·5	2·8
0·002	0·0005 ,,	2·7	5·3
,,	0·001 ,,	4·7	4·7
,,	0·002 ,,	5·5	2·8
0·0005	0·0005 BA	16	33
,,	0·001 ,,	15	15
,,	0·002 ,,	16	33
0·001	0·0005 ,,	14	28
,,	0·001 ,,	14	14
,,	0·002 ,,	16	8
0·002	0·001 ,,	15	15
,,	0·002 ,,	18	9
0·0005	0·001 CA	71·2	71·2
,,	0·002 ,,	65·0	32·5
0·001	0·001 ,,	67·1	67·1
,,	0·002 ,,	77·8	38·9
0·002	0·001 ,,	48·4	48·4

CAM	R·CHO	Added $HClO_4$	10^8k_1 (sec.$^{-1}$)	10^5k_2 (mole^{-1} l. sec.$^{-1}$)
0·002	0·002 CA	—	60·0	30·0
,,	,, ,,	0·00005	40·0	20·0
,,	,, ,,	0·0001	20·6	10·3
,,	,, ,,	0·0005	6·6	3·3
0·0005	0·0005 mNBA		196	392
,,	0·001 ,,		392	392
,,	0·002 ,,		696	348
0·001	0·0005 ,,		162	324
0·002	0·001 ,,		297	297
,,	0·002 ,,		690	345
,,	,, ,,	0·00005	441	220
,,	,, ,,	0·0001	300	150
,,	,, ,,	0·0005	0	0
0·0005	0·0005 pNBA		188	376
,,	0·001 ,,		429	429
0·001	0·0005 ,,		196	391
,,	0·001 ,,		437	437
0·002	0·0005 ,,		185	370
,,	0·001 ,,		335	335
0·001	0·001 ,,	0·0005	31	31

ethanol and in water. With the more reactive aldehydes deviations from the second-order rate law in ethanol are found at the lower temperatures, but they tend to disappear at higher temperatures. In water, the reaction follows first-order kinetics with benzaldehyde and with *p*-chlorobenzaldehyde, but very nearly second-order kinetics with the two nitrobenzaldehydes.

With cyanoacetamide, as with the other active methylene compounds investigated in this series, relatively small amounts of acid very strongly inhibit the condensation, again supporting our view that the first and necessary step in the reaction is the dissociation of the C–H bond of the active methylene compound:

$$\mathrm{CH_2(CN){\cdot}CO{\cdot}NH_2} \underset{v_{-1}}{\overset{v_1}{\rightleftharpoons}} \mathrm{H^+ + {}^-CH(CN){\cdot}CO{\cdot}NH_2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

This ionisation step may in some cases be rate-determining; but the actually measured kinetic order may depend on various other factors, as noted in the preceding papers.

Although exact data are not available, it can be deduced from recorded data[1] that cyanoacetamide is a weaker acid than ethyl cyanoacetate and a much weaker one than malononitrile. If so, the results in Table 1 can be explained as follows: With a very unreactive aldehyde, such as *p*-anisaldehyde, the reaction follows pure second-order kinetics, for owing to the slowness of the condensation step (2), the equilibrium (1) will be established. In this case then, $v_1 \gg v_2$, and the rate-determining step will be (2). On the other hand, owing to the relatively lower acidity of the cyanoacetamide, the condition $v_1 \gg v_2$ will not be true with the more reactive aldehydes, and in these cases intermediate reaction orders will result, as the equilibrium (1) will not be established: the carbanions

$$\mathrm{{}^-CH(CN){\cdot}CO{\cdot}NH_2 + Ar{\cdot}CHO} \xrightarrow{v_2} \text{Products} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

will be used up by the aldehyde molecules at a rate which is of the same order of magnitude as the rate of the ionisation. The runs with *p*-chlorobenzaldehyde at 40° (Table 1) show that when the amide is in excess or when it is in equivalent concentration to the aldehyde, the second-order rate law is obeyed. With an excess of the aldehyde, however, the second-order rate coefficient falls strongly, and finally, doubling the aldehyde concentration exactly halves this coefficient, *i.e.*, in this region the first-order rate law is accurately obeyed. Hence, when the concentration of a reactive aldehyde is five times that of the cyanoacetamide, this is a " swamping " excess, giving kinetically zero-order dependence on this reactant.

At higher temperatures the reactions tend to conform much better to second-order kinetics. The results with *p*-chlorobenzaldehyde at 50° and 65°, and with *p*-nitrobenzaldehyde at 50°, illustrate this trend well, for they conform to the second-order rate law within the experimental error. We believe that at higher temperatures the rate of ionisation of the active methylene compound is much increased, thus making the establishment of the equilibrium (1) possible even with the most reactive aldehydes, and, on the other hand, the condensation has a rather low activation energy, and thus the overall reaction conforms to the second-order rate law.

Additional complications arise in the reaction in water. Here, the overall picture with differently substituted aldehydes is:

Substituent......	*p*-CH_3O	H	*p*-Cl	*m*-NO_2	*p*-NO_2
Rate	Slow ———	———	———	———→	Fast
Order	Intermediate ———	———→	1st ———	———→	2nd

As explained in the preceding paper, the second-order rate dependency found for the two nitrobenzaldehydes does not necessarily mean that the reaction takes place by a bimolecular mechanism, for it may be due either to complex formation or to the aldehydes' forming large molecular aggregates in solution.

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

As the preceding explanation of the kinetic results is mainly qualitative, we tried to apply to the results several of the more obvious rate expressions. Equations of the type $dx/dt = k[\text{CAM}]^n[\text{Aldehyde}]^m$ in which values of m and n were varied between 0 and 1 gave no consistent values for k. Equations of the type $dx/dt = k_1[\text{CAM}] + k_2[\text{CAM}][\text{Aldehyde}]$ can be eliminated, as the effect of acid, which even at relatively low concentrations stops the reaction completely, shows that the reaction must take place between the aldehyde and the carbanion formed from cyanoacetamide, and not the undissociated cyanoacetamide molecule.

A few examples taken from Table 1 illustrate the fact that any equation fitting all the rate data with a single reactant pair must indeed be an artificial and probably a meaningless one. In the reaction of 0·02M-cyanoacetamide with *p*-chlorobenzaldehyde at 40°, doubling of the initial aldehyde concentration has almost no effect on the second-order rate coefficient. Then the differences in the k_2 values grow, and finally doubling the concentration of the aldehyde from 0·1 to 0·2M exactly halves the value of k_2. Hence, any " general " rate equation would have to be practically identical with the second- or the first-order rate equation in the ranges of 0·01—0·02M-aldehyde, or 0·06—0·2M-aldehyde respectively.

p-Hydroxybenzaldehyde had to be excluded from the present kinetic study for it did not react in the absence of a basic catalyst. We attribute this to the acidity of the phenolic hydroxyl group, which, owing to the common hydrogen-ion effect of the protons supplied by its dissociation, depresses the ionisation of the methylene group of cyanoacetamide so strongly that no measurable reaction takes place. This effect was also noticed with malononitrile (see Part VII) but there the reaction still occurred (probably owing to the much higher acidity of malononitrile) although at an anomalously low rate.

To test whether the inhibition of the reaction is indeed caused by the acidity of the phenolic group, or by some other property of *p*-hydroxybenzaldehyde, an experiment was made in which 0·02M each of the benzaldehyde, phenol, and cyanoacetamide were mixed in ethanol (Table 1). No measurable reaction occurred, showing again that there is no mechanism operating in which the aldehyde could react with an undissociated active methylene group, and that even a weak acid such as phenol is able to inhibit completely the dissociation of the active methylene group. The inhibitory effect of different acids is dependent on their acid strength; the rate coefficient of the reaction of 0·02M-benzaldehyde with 0·02M-cyanoacetamide in the presence of 0·0002M-acids is 0, $3{\cdot}3 \times 10^{-5}$ and $8{\cdot}5 \times 10^{-5}$ mole^{-1} l. sec.$^{-1}$ with perchloric acid, acetic acid, and phenol respectively, *i.e.*, inhibition increases with acid strength. Incidentally, in 0·02M-cyanoacetamide, 0·02M-benzaldehyde, and 0·02M-*p*-hydroxybenzaldehyde no reaction could be detected at all with either of the aldehydes present, the effect of the *p*-hydroxybenzaldehyde being similar to that of phenol.

In the presence of 0·0002M-piperidine, 0·2M-*p*-hydroxybenzaldehyde reacted with 0·02M-cyanoacetamide in ethanol at a rate ($1{\cdot}2 \times 10^{-6}$ mole^{-1} l. sec.$^{-1}$) which was only about 3% of the similarly catalysed rate for anisaldehyde. The added base probably buffers the acidity of the phenolic group sufficiently to permit the reaction to proceed, even though only very slowly.

From the values of k_2 for runs with 0·02M of each of the reactants (0·01M with *p*-nitrobenzaldehyde) the value of the reaction constant, ρ, of the Hammett equation $\log (k/k_0) = \sigma\rho$ was calculated from the σ^+ values given by Brown and Okamoto.[2] The value of ρ in 95% ethanol was found to be 1·52, *i.e.*, very near to those found for the reaction of malononitrile (1·45) and of ethyl cyanoacetate (1·65) with various aromatic aldehydes.[3] The runs with the same reactant concentrations in the presence of lithium nitrate gave $\rho = 1{\cdot}44$, *i.e.*, within the experimental error. In the presence of 20% of water and of 0·0002M-piperidine ρ fell to 1·3 and 1·1, respectively. It is noteworthy that the fall in the ρ values is due to the fact that the catalysts (added water or piperidine) influence relatively

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

[3] Parts VII and VIII, preceding papers.

more strongly the rates with the " slow " aldehydes than with the " fast " aldehydes. The lowering of ρ in the presence of catalysts may show a tendency for a change to the direction of a mechanism in which the importance of the aldehyde in the rate-determining step is smaller. The value of ρ calculated from runs in which the concentration of each of the reactants was 0·001M in water was 1·2.

Reactivity of Active Methylene Compounds in Condensation Reactions.—The data in the literature for the rates of ionisation (k_1) and for the acid dissociation constants (K_a) of various methylene compounds were summarised by Pearson and Dillon.[1] Although a rough correlation exists in most cases between k_1 and K_a, there are cases where the deviations are considerable. For the active methylene compounds used by us, the following data (in water, at 25°) are given: malononitrile, $k_1 = 9 \times 10^{-1}$ min.$^{-1}$, $K_a = 6{\cdot}5 \times 10^{-12}$; ethyl cyanoacetate, $k_1 = 7 \times 10^{-2}$ min.$^{-1}$, $K_a = 10^{-9}$; diethyl malonate, $k_1 = 1{\cdot}5 \times 10^{-3}$ min.$^{-1}$, $K_a = 5 \times 10^{-4}$. No data are available for cyanoacetamide.

TABLE 3. *Rate coefficients of the reactions of various aromatic aldehydes* $X{\cdot}C_6H_4{\cdot}CHO$ *with different active methylene compounds.*

	10^8k_1 (sec.$^{-1}$) in water				
	$CH_2(CN)_2$		$CH_2(CN){\cdot}CO_2Et$		$CH_2(CN){\cdot}CO{\cdot}NH_2$
X	32°	40°	32°	40°	40°
p-MeO	6000	9000	300	500	5
H	14,000	18,000	1000	2500	15
p-Cl	24,000		2000	—	65
p-NO_2	50,000	52,000	50,000	—	300

	10^5k_2 (mole^{-1} l. sec.$^{-1}$) in ethanol				
	$CH_2(CN)_2$		$CH_2(CN){\cdot}CO_2Et$		$CH_2(CN){\cdot}CO{\cdot}NH_2$
X	30°	40°	30°	40°	40°
p-MeO	220	330	7	14	1
H	2300	3300	—	50	7
p-Cl	5700	8000	—	—	15
p-NO_2	46,000	60,000	4500	6000	150

In general, one would expect that the rates should be proportional to the proton-transfer rates (k_1) in the unimolecular cases and to the K_a values in the bimolecular cases. However, many quantitatively unknown factors are involved in a fairly complex chemical reaction such as the present, so one cannot expect more than a qualitative agreement between the data quoted and the experimentally determined rates.

For the purposes of this discussion we use first-order rate coefficients in the experiments made in water and second-order ones in those made in ethanol. The values given in Table 3 are average and rounded-off values; where the experimental results fitted neither the first- nor the second-order rate equation, the coefficients given in Table 3 indicate only the order of magnitude, but even these values are useful for comparison. In addition to the values in Table 3, extrapolation of the data given in Part IV of this series[4] shows that the second-order coefficient of the uncatalysed condensation of diethyl malonate with benzaldehyde in ethanol at 40° must be of the order of 1—2 × 10^{-6} mole^{-1} l. sec.$^{-1}$. The order of reactivities of the various methylene compounds towards aromatic aldehydes in ethanol is accordingly:

$$CH_2(CN)_2 > CH_2(CN){\cdot}CO_2Et > CH_2(CN){\cdot}CO{\cdot}NH_2 > CH_2(CO_2Et)_2$$

This order does not fit Pearson and Dillon's estimated value of 10^{-9} for K_a of ethyl cyanoacetate[1] which, as judged from our data, should be rather smaller than the value for malononitrile.

In water, the order of reactivity found by us is again the same for the first three compounds and here our data are consistent with the values given for the ionisation rates.

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[4] Patai, Saltiel, and Zabicky, *Bull. Res. Council Israel*, 1958, **7**, *A*, 186.

The data in Table 3 show some quantitative regularities. Thus, in water the first-order rate coefficients of malononitrile with *p*-anisaldehyde, benzaldehyde, and *p*-chlorobenzaldehyde are some 10—20 times higher than those with ethyl cyanoacetate and about 1000—2000 times higher than those with cyanoacetamide, but the differences in the rates of *p*-nitrobenzaldehyde with the same active methylene compounds are smaller. The second-order rate coefficients of malononitrile with *p*-anisaldehyde, benzaldehyde, and *p*-chloro- and *p*-nitro-benzaldehyde are all between 300 and 400 times higher than the corresponding rates with cyanoacetamide. The ratios of the rates with malononitrile and ethyl cyanoacetate are 10 with *p*-nitrobenzaldehyde, 20—30 with *p*-anisaldehyde, and 55 with benzaldehyde, *i.e.*, although the differences are considerable, the rate ratios are still of the same order of magnitude. Very roughly, the relative reactivities of the different active methylene compounds towards aromatic aldehydes according to our results are:

$CH_2(CN)_2$	$CH_2(CN)\cdot CO_2Et$	$CH_2(CN)\cdot CO\cdot NH_2$	$CH_2(CO_2Et)_2$
10,000	1000	10	1

EXPERIMENTAL

The aromatic aldehydes and the solvents were purified as described in the previous papers.[3] Cyanoacetamide was prepared from ethyl cyanoacetate.[5]

Preparation of Substituted Benzylidenecyanoacetamides.—To cyanoacetamide (0·01 mole) and the aromatic aldehyde (0·01 mole) in 95% ethanol (100 ml.) there was added 0·1 ml. of 2N-aqueous sodium hydroxide. The mixture was refluxed for 3 hr., then cooled, the product being precipitated. Water had to be added to the mixture to precipitate the product from benzaldehyde. The products were obtained in 75—85% yield and were recrystallised from ethanol. (Omission of the alkali led to smaller yields.) Benzylidenecyanoacetamide [6] (m. p. 123°) and *p*-anisylidenecyanoacetamide [7] (m. p. 210°) are described in the literature. *p*-Hydroxybenzylidenecyanoacetamide (m. p. 258—259°) (lit.,[7] m. p. 191°), was obtained as light yellow plates and columns (Found: C, 64·0; H, 4·1. Calc. for $C_{10}H_8O_2N_2$: C, 63·7; H, 4·3%). p-*Chlorobenzylidenecyanoacetamide*, m. p. 207°, crystallised in colourless needles (Found: C, 58·7; H, 3·5; N, 13·4. $C_{10}H_7ON_2Cl$ requires C, 58·1; H, 3·4; N, 13·6%). p-*Nitrobenzylidenecyanoacetamide*, m. p. 240°, formed light yellow plates (Found: C, 55·3; H, 3·5; N, 19·4. $C_{10}H_7O_3N_3$ requires C, 55·3; H, 3·25; N, 19·35%). m-*Nitrobenzylidenecyanoacetamide* was prepared by leaving overnight at room temperature 0·06 mole each of cyanoacetamide and *m*-nitrobenzaldehyde with 15% aqueous potassium hydroxide (1 ml.) in ethanol (50 ml.). The product (0·045 mole) had m. p. 163° (from ethanol) (Found: C, 55·2; H, 3·7; N, 19·6.

Spectra of Benzylidenecyanoacetamides.—The following data were determined for the various *p*-substituted products: H, $\lambda_{max.}$ 301 mμ [ε 17,200 (for the kinetic runs the absorption at 320 mμ, ε 10,000, was used, as benzaldehyde interfered with the measurements at 301 mμ]; *p*-MeO, $\lambda_{max.}$ 337 mμ (ε 27,600); *p*-OH, $\lambda_{max.}$ 345 mμ (ε 21,500); *p*-Cl, $\lambda_{max.}$ 308 mμ (ε 22,500); *p*-NO_2, $\lambda_{max.}$ 304 mμ (ε 18,000) (in the kinetic runs, the absorption of *p*-nitrobenzaldehyde at this wavelength, ε 1900, had to be taken into consideration). *m*-Nitrobenzylidenecyanoacetamide [$\lambda_{max.}$ 266 mμ (ε 22,000)] was measured at 308 mμ (ε 7600). At this wavelength *m*-nitrobenzaldehyde had ε 800.

Kinetic Measurements.—Standard solutions of the reagents were prepared and used the same day. A sample of the aldehyde solution (and of the acid when needed) was placed in a 50 ml. measuring flask, and solvent was added, leaving room only for the necessary volume of the cyanoacetamide solution, which was added when the desired temperature was reached. Measurements of the rate of reaction in the case of anisaldehyde and benzaldehyde were made by transferring samples from time to time into an absorption cell and measuring the optical density of the solution. With *p*-chloro-, *m*-nitro-, and *p*-nitro-benzaldehyde, a sample of the mixture was rapidly transferred to a ground-stoppered silica absorption cell placed in the cell compartment of a Beckman DU spectrophotometer which was heated to the desired temperature with a Beckman dual thermospacer set. The operation from time zero (taken as the

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[5] Corson, Scott, and Vose, *Org. Synth.*, Coll. Vol. I, 2nd edn., 1941, p. 179.

[6] Day and Thorpe, *J.*, 1920, **117**, 1465.

[7] Curtis and Day, *J.*, 1923, **123**, 3131.

delivery of half-volume of the cyanoacetamide solution) until the closure of the cell compartment took 30 sec. or less.

With *p*-hydroxybenzaldehyde and cyanoacetamide in ethanol no measurable reaction occurred at various concentrations up to 0·2M-cyanoacetamide and 0·5M-aldehyde.

Calculations.—Rate coefficients were calculated either from the integrated form of the equation $dx/dt = k_2(a - x)(b - x)$ or graphically from the optical density–time plots, as described previously. Both methods gave practically identical values for k (see typical run, Table 4).

TABLE 4. *Reaction of* 0·02M-*cyanoacetamide with* 0·02M-*benzaldehyde in* 95% *ethanol at* 40°. *Optical density measured at* 320 mμ; *samples diluted* 20-*fold.*

Time (sec.)	1080	1980	3350	4550	5820	7150	8750	10,000
Optical density	0·052	0·075	0·100	0·120	0·143	0·170	0·195	0·228
Product (%)	0·18	0·40	0·70	0·85	1·125	1·35	1·60	1·825
10^5k_2 (mole^{-1} l. sec.$^{-1}$)	8·9	10·1	9·19	9·35	8·85	9·60	9·25	9·24

Average of k_2 values, 9·45 × 10^{-5} mole^{-1} l. sec.$^{-1}$; k_2 calc., from slope of the optical density–time plot, 9·60 × 10^{-5} mole^{-1} l. sec.$^{-1}$.

Analysis of Products.—The products (apart from the unsubstituted benzylidenecyanoacetamide) usually separated from the reaction mixture in work with higher concentrations. They were identical with the authentic samples prepared.

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