Table I

Index of Refraction of Nitromethane

Temp., °C.	Wave length, Å. 6678.1 (He_r)	6562.8 (H_C)	5892.6 (Na_D)	5460.7 (Hg_e)	5015.7 (He_v)	4861.3 (H_F)	4358.3 (Hg_g)
20	1.37900	1.37944	1.38197	1.38416	1.38705	1.38828	1.39354
25	1.37669	1.37713	1.37963	1.38179	1.38468	1.38588	1.39115
30	1.37442	1.37479	1.37730	1.37948	1.38232	1.38345	1.38874

were obtained at 20, 25 and 30° for seven different wave lengths of light. The temperatures were maintained by circulating water controlled to a maximum variation of ±0.005°. The ambient temperature was maintained to ±1° of the temperature of measurement to minimize heat loss or gain by the prisms. Accuracy of reported values is estimated to be ±0.00006.

Density.—Densities (Table II) were determined at 20, 25 and 30° with a Christian Becker chainomatic five-place specific gravity balance with a five-gram displacement plummet.[5] The accuracy of the measurements is estimated to be ±0.00005 g. ml.$^{-1}$. The equation $d_t = 1.16448 - 0.001351t$ expresses the density–temperature relationship over the range of 20 to 30°.

Table II

Properties of Nitromethane

Temp., °C.	Density, g./ml.	Abs. vis., cp.	Surface tension, dynes/cm.
20	1.13749	0.646	37.5
25	1.13064	.608	36.7
30	1.12398	.574	35.9

Viscosity.—Viscosities (Table II) were determined at 20, 25 and 30° using two Geist–Cannon viscometers designed for non-viscous fluids.[6] At least two consecutive efflux times agreeing to within 0.1 second were obtained on both viscometers controlled in a bath to ±0.005°.[5] The reported values are referred to a value of 1.002 centipoises for water at 20°,[7] the precision of the measurements is ±0.03% and the accuracy is estimated to be ±0.001 centipoise.

Surface Tension.—Surface tensions were measured at 20, 25 and 30° in capillarimeters of U-tube design as previously described.[5] Capillary rise was measured by means of a cathetometer on the sample controlled to ±0.005°. These values are referred to a value of 28.88 dynes cm.$^{-1}$ for benzene at 20°.[8] Accuracy of the reported values is estimated to be ±0.2 dyne cm.$^{-1}$.

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[6] J. M. Geist and M. R. Cannon, *Ind. Eng. Chem., Anal. Ed.*, **18**, 611 (1946).

[7] J. F. Swindells, J. R. Coe, Jr., and T. B. Godfrey, *J. Research Natl. Bur. Standards*, **48**, 1 (1952).

[8] "International Critical Tables," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1928, p. 54.

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[Contribution from the Department of Organic Chemistry of the Hebrew University]

The Kinetics of the Knoevenagel–Doebner Reaction

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The reaction of benzaldehyde with malonic acid in the presence of piperidine was studied in pyridine and in pyridine–cyclohexanone solutions. The condensation was shown to follow over-all second-order reaction kinetics. The decarboxylation curves of the condensation product in the original reaction mixture, after an induction period, seem to conform to a first-order kinetic equation, as does the decarboxylation of benzalmalonic acid itself in pyridine. It is shown that the general methods used for the description of the kinetics of consecutive reactions cannot be applied for the case considered. The role of the catalyst and that of the two solvents used is discussed.

The Knoevenagel–Doebner modification of the Perkin cinnamic acid synthesis[2] has been the subject of only very few quantitative kinetic studies,[3] although a number of papers deal with the mechanism of the reaction.[4–12] The previous investigations made no attempt to determine the exact rate of both the carbonyl–methylene condensation and the subsequent decarboxylation. In the present paper we followed the kinetics of the condensation by means of the Karl Fischer water-determination method,[13] and measured volumetrically the evolution of carbon dioxide from the reaction mixture. Analysis of the kinetic results has shown that the two reactions cannot be adequately described by the methods applicable for simple irreversible consecutive reactions[14,15] and, accordingly, the reaction must be a more complex one than generally accepted.

Experimental

Materials Used.—Pure commercial malonic acid (Eastman Kodak Co., white label, m.p. 134–135°) was used without purification. After drying to constant weight in a desiccator, it contained about 0.15% water. The benzaldehyde was twice distilled fractionally before use. It contained 0.2% water. The pyridine (B.D.H., redistilled)

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[1] To whom inquiries regarding this paper should be sent.

[2] For a review of the literature up to 1940, see J. R. Johnson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 210–265.

[3] (a) E. F. Pratt and E. Werble, This Journal, **72**, 4638 (1950); (b) E. J. Corey, *ibid.*, **74**, 5897 (1952).

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[15] S. W. Benson, *J. Chem. Phys.*, **20**, 1605 (1952).

was dried by azeotropic distillation with benzene and then fractionally distilled. It contained 0.2–0.3% water. The piperidine (B.D.H.) after fractional distillation contained 0.4% water. The cyclohexanone (B.D.H., technical) after fractionation contained 0.4% water.

Water determinations were carried out by the "Dead stop" back titration method.[13] The accuracy of the method in our hands was 0.3–0.4 mg. on samples containing 15–30 mg. of water.

Standard Experimental Procedures. (a) **Condensation.**—Malonic acid, benzaldehyde, solvent (pyridine or cyclohexanone) and piperidine were mixed in a small flask until a homogeneous solution resulted and from this solution six portions of 1 ml. each were placed in six tubes, each connected by means of a ground-glass joint and a capillary tube to a U-shaped bubbling tube. A measured amount of pyridine (0.2–0.3 ml.) was previously placed into the bubbling tube and served to trap any escaping moisture. A drying tube filled with Drierite was connected to the outlet of the bubbling tube and then the reaction tube proper was placed into a holder in the pre-heated and automatically controlled oil-bath, but the bubbling tube was cooled in an ice-bath. The preparation of the reaction mixture, the filling and assembly of the six reaction tubes took about 3–5 minutes; during this time no measurable reaction occurred at room temperature. The contents of the tubes reached the reaction temperature in 1–2 minutes; this time lag was insignificant under the conditions of our experiments. The initial water content calculated on basis of the previously determined water content of each of the components of the mixture was taken as nil in the subsequent calculations. The reaction tubes were removed from the oil-bath after predetermined times and 0.5 ml. of the reaction mixture containing the bulk of the water formed, were transferred into an erlenmeyer flask, diluted with "dry" pyridine and titrated. (Weighing the amount of the reaction mixture taken for the titration, instead of measuring it in a pipet did not improve the results.) The pyridine in the outlet tube (containing the water which escaped the reaction tube proper during the heating) was flushed into a second erlenmeyer flask with a measured amount of pyridine and again titrated.[16] At least two or three series of measurements were made for each kinetic curve. The bath temperature was kept constant in all experiments within ±0.1°.

(b) **Decarboxylation.**—The evolution of carbon dioxide was measured volumetrically in a 500-ml. gas measuring buret with a leveling device, using a saturated solution of sodium chloride in dilute (0.25 *N*) hydrochloric acid, saturated by carbon dioxide, as the confining fluid. This buret was connected to the upper end of a small condenser, which was joined to a 25-ml. flask with an up-turned side arm carrying a 10-ml. dropping-funnel. When the flask reached the temperature of the oil-bath, the reaction mixture was added from the dropping funnel. In the course of 2–3 minutes the mixture reached the temperature of the bath. Readings were taken frequently at the beginning and every 10–15 minutes after the first hour. Reproducibility of these experiments was generally better than ±1%. Two experiments were made at each temperature. Experiments made using pyridine saturated with carbon dioxide at the different reaction temperatures, gave results identical within the normal experimental errors to the results of the standard decarboxylation procedure. It seems that the solubility of carbon dioxide in pyridine, in the presence of the various acid components, is small and does not affect appreciably the experimental results for the decarboxylation.

Reaction of Standard Mixtures.—The standard mixtures consisted of 0.01 mole (1.04 g.) of malonic acid, 0.01 mole (1.06 g.) of benzaldehyde, 5.0 ml. of pyridine and 0.01 ml. of piperidine. Both the condensation and the decarboxylation were measured at the following temperatures: 75.8°, (Fig. 1), 58.75° (Fig. 2) and 48.2° (Fig. 3).

The total volume of the reaction mixture at 48.2 and 75.8° was 6.9 and 7.1 ml., respectively. These volumes diminished during the reaction owing to the evolution of carbon dioxide and some evaporation, by 0.1–0.15 ml. Nevertheless, during the course of the whole reaction, 7 ml. was taken as the volume of the mixture, as the error caused by

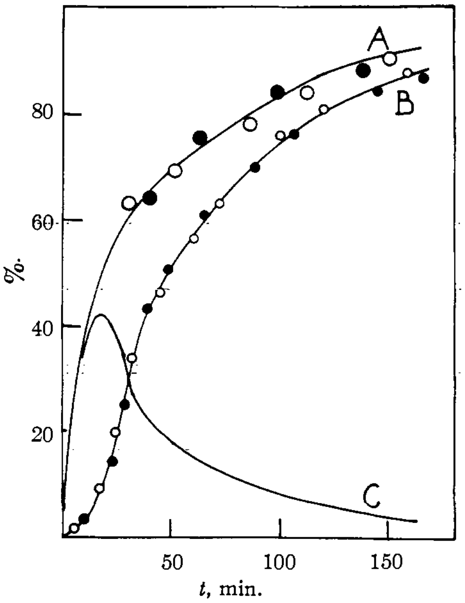

Fig. 1.—Reaction of 0.01 mole of benzaldehyde with 0.01 mole of malonic acid in the presence of 0.1 ml. of piperidine and 5 ml. of pyridine at 75.8°: A, water elimination; B, decarboxylation; C, concentration of condensed products (A-B).

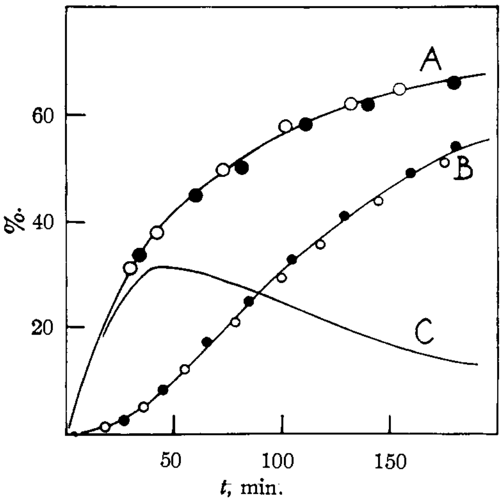

Fig. 2.—Reaction of 0.01 mole of benzaldehyde with 0.01 mole of malonic acid in the presence of 0.1 ml. of piperidine and 5 ml. of pyridine at 58.75°: A, water elimination; B, decarboxylation; C, concentration of condensed products (A-B).

TABLE I

REACTION OF 0.01 MOLE OF BENZALDEHYDE WITH 0.01 MOLE OF MALONIC ACID IN THE PRESENCE OF 0.1 ML. OF PIPERIDINE IN DIFFERENT SOLVENTS, AT 58.75°

No.	Pyridine, ml.	Cyclohexanone, ml.	Condensation, %			Decarboxylation, %			Ratio, decarboxylation/condensation		
			1h	2h	3h	1h	2h	3h	1h	2h	3h
1[a]	5	Nil	45	60	67	15	27	53	0.33	0.45	0.79
2	2	3	26	40	50	14	34	46	.54	.85	.92
3	0.5	4.5	22	32	36	8	21	30	.36	.65	.83
4	Nil	5	21	30	34	2	2.5	3	.09	.08	.09

[a] Standard experiment, see Fig. 2.

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(16) The water content of the "dry" pyridine used in the different manipulations had to be determined at least once every day, as relatively large amounts of it were used (5-15 ml. per ml. of reaction mixture) and could cause large errors. For the other components, the storage bottles of which had to be opened only once or twice a day, weekly controls were sufficient.

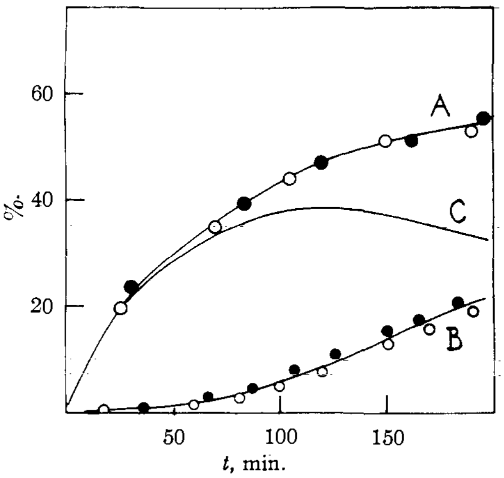

Fig. 3.—Reaction of 0.01 mole of benzaldehyde with 0.01 mole of malonic acid in the presence of 0.1 ml. of piperidine and 5 ml. of pyridine at 48.2°: A, water elimination; B, decarboxylation; C, concentration of condensed products (A-B).

this in the calculations (not more than 2% and generally less than 1%) was much smaller than the experimental errors of the sampling and the water determination itself.

An experiment was made at 58.75° with double the stoichiometric amount of benzaldehyde, with a correspondingly smaller amount of pyridine, so that the volume of the reaction mixture remained 7 ml. (Fig. 4).

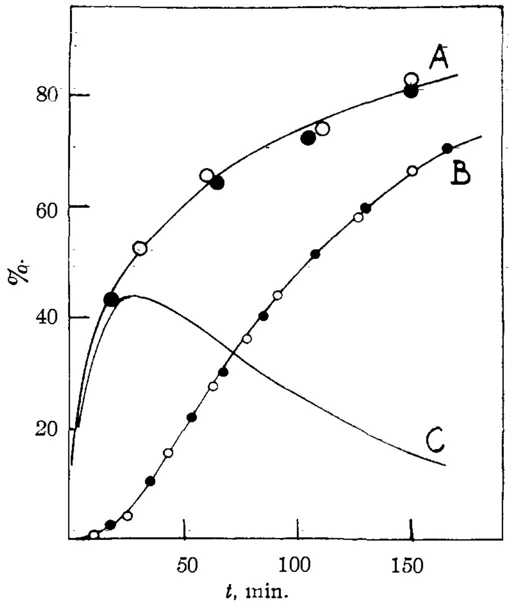

Fig. 4.—Reaction of 0.02 mole of benzaldehyde with 0.01 mole of malonic acid in the presence of 0.1 ml. of piperidine and 4 ml. of pyridine at 58.75°: A, water elimination; B, decarboxylation; C, concentration of condensed products (A-B).

Experiments with Cyclohexanone.—Table I shows the effect of substituting a part or all of the pyridine with cyclohexanone as solvent. No other solvent could be found in which the reaction could be carried out homogeneously and which did not interfere with the water determination (see also under Control Experiments).

Experiments with Different Amounts of Piperidine.—Table II shows the results of experiments made at 58.75° with different amounts of piperidine. In experiments no. 3 after 30 minutes, and in no. 4 immediately, a precipitate formed which was identified as the piperidine salt of benzalmalonic acid (m.p. 164–165°, no depression in mixed m.p. with an authentic sample[6]). In experiment no. 4 no water determination was made as the whole reaction mixture solidified immediately on cooling, making transference to the titration vessel impracticable. In experiment no. 5 no precipitate was formed, but after evaporation of the solvent at reduced pressure the residue was found to consist again of the piperidine salt of benzalmalonic acid.

TABLE II

REACTION OF 0.01 MOLE OF BENZALDEHYDE WITH 0.01 MOLE OF MALONIC ACID IN PYRIDINE AT 58.75° IN THE PRESENCE OF DIFFERENT AMOUNTS OF PIPERIDINE

No.	Pyridine, ml.	Piperidine, ml.	Condensation, % 1 h.	2 h.	3 h.	Decarboxylation, % 1 h.	2 h.	3 h.
1	5.1	0.0	9	15	19	3	9	15
2	5.0	0.1	45	60	67	15	27	53
3	4.8	0.3	52	60	70	20	34	44
4	4.5	0.6		?		2	12	22
5	3.0	2.1	78	87	92	0	0	0

Decarboxylation of Benzalmalonic Acid.—Figure 5 shows the rate of decarboxylation of 0.01 mole of benzalmalonic acid in 5 ml. of pyridine, measured at 75.8, 58.75 and 48.2°. In the presence of 0.1 mole of piperidine at 58.75° some piperidine salt of the acid precipitated, but the decarboxylation rates up to 50% were substantially the same as without piperidine. After 50% the rate of decarboxylation in the presence of piperidine fell below that without piperidine.

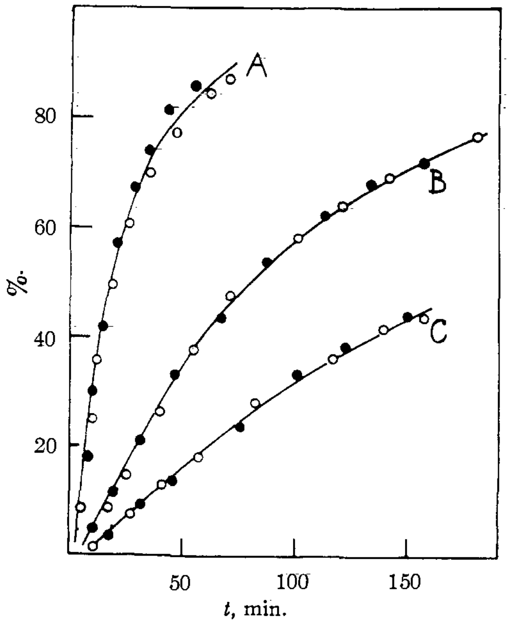

Fig. 5.—Decarboxylation rates of 0.01 mole of benzalmalonic acid in 5 ml. of pyridine at different temperatures: A, 75.8°; B, 58.75°; C, 48.2°.

Control Experiments. Decarboxylation of Malonic Acid.—Malonic acid alone at 90–95° gave no measurable gas evolution in the course of one hour. The decarboxylation of malonic acid (in the absence of benzaldehyde) in all the variations of pyridine, cyclohexanone and piperidine used, was negligible (1–4% in three hours at 58–76°). Benzaldehyde (0.01 mole) and cyclohexanone (3 ml.) in the presence of pyridine (2 ml.) and piperidine (0.1 ml.) gave practically no condensation at 58° (0.6 mg. of water formed after three hours, *i.e.*, not more than 0.33% condensation). Benzaldehyde (0.01 mole) and piperidine (2.1 ml.) in pyridine (3 ml.) after three hours heating at 59° gave 42% condensation. On cooling, a crystalline precipitate formed and was identified as benzaldipiperidine by melting point

(80°) and mixed melting point with an authentic sample.[17] From a mixture of benzaldehyde (0.01 mole), piperidine (2.1 ml.) and acetic acid (0.6 g., 0.01 mole) in 3 ml. of pyridine after three hours of heating at 59°, there was obtained 1.1 g. (45%) of benzaldipiperidine, which was also formed and precipitated immediately upon mixing 0.01 mole each of benzaldehyde and malonic acid with 5 ml. of piperidine at room temperature (25°). Benzaldipiperidine (0.01 mole) after three hours heating at 58° with malonic acid (0.01 mole) in 5 ml. of pyridine, gave an almost quantitative yield of the piperidine salt of benzalmalonic acid. The same reaction occurred slowly also at room temperature.

Discussion

Kinetics of the Reaction. (a) Condensation.—The curves marked with A in Figs. 1–4 conform in the range of the measurements (up to 50–80%) satisfactorily to the second-order kinetic equation

$$dx/dt = k(a - x)^2 \qquad (1)$$

where a is the initial (equivalent) concentration of the reactants and x the concentration, at time t, of the condensed product. This latter was taken as equivalent to the concentration of the water formed in the course of the reaction, and was probably a mixture of several different molecular species (see below). Figure 6 shows the values of kt obtained from the integrated form of equation 1 plotted against the corresponding values of t at the three experimental reaction temperatures. Table III shows the values of k calculated from the slopes of the lines in Fig. 6 together with the value of k calculated for curve A in Fig. 4 from the equation

$$dx/dt = k(a - x)(b - x) \qquad (2)$$

where a is the initial concentration of benzaldehyde and b that of malonic acid. In view of the complexity of the condensation reaction, of which the values of k are the *over-all* rate constants, the difference between the two values obtained at 58.75° with different concentrations does not seem to be too significant.[18] The critical increment of the Arrhenius equation was calculated from the values of log k plotted against $1/T$°K. and was found to be 15 ± 1 kcal.

TABLE III

VALUES OF SECOND-ORDER KINETIC CONSTANTS FOR THE CONDENSATION

T, °C.	Aldehyde, mole/l.	Malonic acid, mole/l.	$k \times 10^6$, l. mole^{-1} sec.$^{-1}$
75.8	1.43	1.43	545
58.75	1.43	1.43	159
58.75	2.36	1.43	190
48.2	1.43	1.43	84

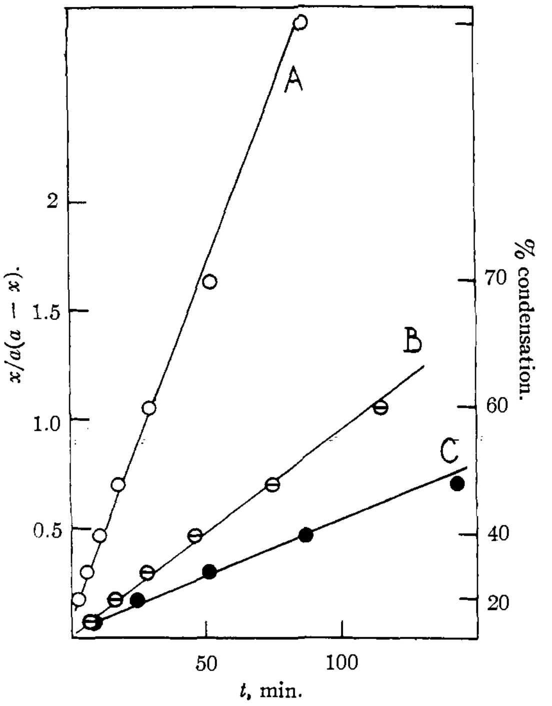

Fig. 6.—Values of kt calculated from $dx/dt = k(a - x)^2$ (equation 1) for the water elimination at different temperatures: A, 75.8°; B, 58.75°; C, 48.2°.

(b) The Decarboxylation.—The curves marked with B in Figs. 1–3 show the amount of carbon dioxide evolved from the reaction mixture. In each decarboxylation measurement the volume of carbon dioxide corresponding to 100% decarboxylation was taken as 224 ml. NTP, and the percentage of decarboxylation from the volumetric measurements was calculated accordingly. (In decarboxylation experiments made at 75.8 and at 97° the value of 224 ml. NTP was obtained within ±2%, remaining unchanged thereafter, thus proving, incidentally, that no decarboxylation of cinnamic acid occurs in the conditions of our experiments).

Evidently, these are not true kinetic curves, as the amount of the intermediate undergoing decarboxylation in the mixture first rises, reaches a maximum value and only then begins to fall (curves marked C in Figs. 1–3). Nevertheless, the form of the curves B, after the apparent induction period, could be represented by the first-order rate expression[14]

$$dx/dt = k_1(a - x) \qquad (3)$$

where a, the "initial amount" was taken as = 100, and x read directly from curves B, as the per cent. of carbon dioxide formed. Figure 7 shows the values of ln $[a/(a - x)]$ from the decarboxylation curves B in Figs. 1–3, plotted against t, and also the corresponding values of k_2 obtained from the decarboxylation of benzalmalonic acid in pyridine at the same temperatures (see Fig. 5).

The values of the pseudo constants k_1, calculated from curves A, B and C, as well as the values of k_2 calculated from the curves D, E and F in Fig. 7 are given in Table IV. Surprisingly, both sets of constants gave, within the experimental error, the same value for the critical increment of the Arrhenius equation: 18.5 ± 1 kcal. (from the values of k_1) and 19 ± 1 kcal. (from the values of k_2).

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(17) W. Laun, *Ber.*, **17**, 678 (1884).

(18) The values of x in the two concentration terms of equation 2 is not strictly identical, owing to the presence of benzaldipiperidine in the reaction mixture: The value of x was measured by the amount of the water formed and $(a - x)$ is the real amount of unchanged benzaldehyde in the reaction mixture, as benzaldehyde takes part in *all* the reactions leading to the formation of water, including the reaction which gives benzaldipiperidine, while the value of x in $(b - x)$ is too great, as malonic acid does *not* participate in all the reactions leading to water elimination. The amount of piperidine used (0.1 ml. or 0.001 mole) could, theoretically, form 0.0005 mole of water by reacting with benzaldehyde, thus making possible a *maximum* deviation of 5% between the values of x in $(a - x)$ and $(b - x)$, but the actual deviation is probably much less. The same applies for the use of equation 1 in which $(a - x)$ is taken to be identical to $(b - x)$. Nevertheless, both equations give a satisfactory approximation, as can be seen from Fig. 6.

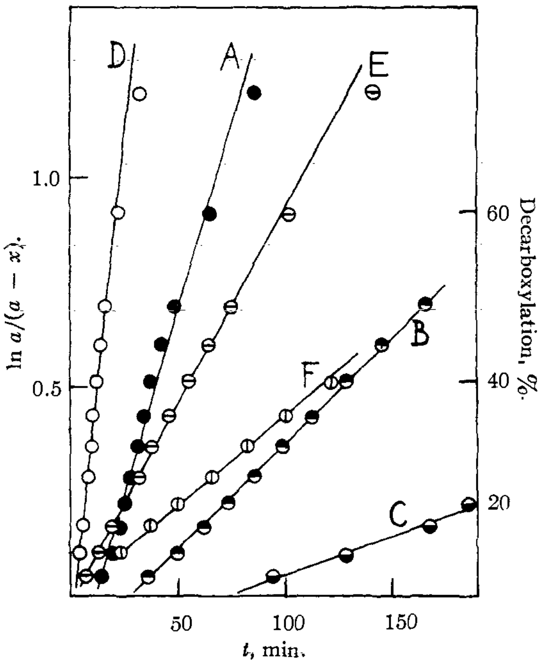

Fig. 7.—Values of kt calculated from $dx/dt = k(a - x)$ (equation 3) for the decarboxylation at different temperatures: curves A, B and C correspond to the curves B in Figs. 1–3; curves D, E, F correspond to curves A, B and C in Fig. 5.

Table IV

First-order Decarboxylation Constants

T, °C.	$k_1 \times 10^6$, sec.$^{-1a}$	$k_2 \times 10^6$, sec.$^{-1b}$
75.8	288	770
58.75	83	157
48.2	31	72

[a] From curves A, B, C, in Fig. 7 (reaction curves B in Fig. 1–3). [b] From curves D, E, F, in Fig. 7 (reaction curves in Fig. 5).

Correlation of the Kinetics of Condensation and Decarboxylation.—Using the methods of the present investigation there was no possibility to identify the structure of the "condensed product" the concentration of which was taken as being equivalent to the amount of the water formed. The condensation product (CP) is very probably a mixture of several different molecules, such as benzaldipiperidine,[4] benzalmalonic acid and also dissociated and undissociated salts of the latter acid with piperidine and pyridine. It can be seen directly from Figs. 1–3, that no simple relationship exists between the CP and the rate of the decarboxylation. If any relation of the kind $dCO_2/dt = k(CP_t)^n$ would exist, then the time at which CP reaches its maximum value, should coincide with the time corresponding to the inflection point on the curves B, where the value of dCO_2/dt is at maximum.

The time lag between those two maxima shows clearly that a part of the CP does *not* undergo decarboxylation. This part could consist either of benzaldipiperidine or the piperidinium benzalmalonate or both. The total amount of these two products cannot be more than 10% of the original amount of the two reactants, corresponding to the 0.001 mole of piperidine present in the reaction mixture. Calculations have shown that neither could there be found a correct equation of the form $dCO_2/dt = k(CP_t - SI)^n$ in which the concentration of the stable intermediate (SI) has a constant value, not greater than 10%. Accordingly, the methods developed for the kinetic analysis of simple irreversible consecutive reactions[14,15] cannot be applied for our case. Moreover, these results seem to indicate that most of the proposals regarding the mechanism of the reaction[3–12] are oversimplified.

The mechanism proposed by Corey,[3b] according to which in some cases the water elimination and the decarboxylation should occur practically simultaneously, does not seem to be the main mechanism operating in our case, as the results shown in Figs. 1–4 clearly indicate that the major part of the water elimination occurs prior to the decarboxylation.[19] Benzaldipiperidine alone cannot account for the amount of water formed. Although we cannot decide, on basis of the present experiments, the route of the reaction up to the water elimination it is certain that benzalmalonic acid or the corresponding anion is formed and can be accumulated in the reaction mixture up to 30–40% of the initial amount of the reactants.

The Influence of the Catalyst and the Solvent. (a) The Role of the Piperidine.—Although piperidine exerts a catalyzing influence on the condensation, its presence is by no means indispensable (see Table II). On the other hand, excess of piperidine lowers the rate of decarboxylation and is even able to block it absolutely. When working in pure piperidine as the solvent, only benzaldipiperidine is formed and remains unaffected by the presence of malonic acid, while in the presence of both malonic acid and pyridine it is converted into the piperidine salt of the benzalmalonic acid, which again does not undergo decarboxylation even when heated in pyridine (see control experiments). Benzaldipiperidine may be the primary condensation product, as already postulated by Knoevenagel,[4] and both its rate of transformation first into benzalmalonic acid (or benzalmalonate ions) and then to cinnamic acid (of cinnamate ions) seems to be dependent on the piperidine/pyridine ratio and probably also on the amount of malonic acid still present in the solution.[20]

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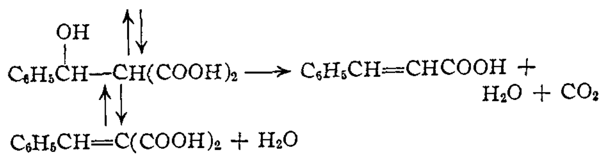
(19) We are indebted to one of the referees for bringing to our attention the following reaction scheme, according to which the decarboxylation and the water elimination could proceed simultaneously



$$C_6H_5CHO + H_2C(COOH)_2 \rightleftarrows C_6H_5CH(OH)-CH(COOH)_2 \longrightarrow C_6H_5CH{=}CHCOOH + H_2O + CO_2$$
$$C_6H_5CH(OH)-CH(COOH)_2 \rightleftarrows C_6H_5CH{=}C(COOH)_2 + H_2O$$

This reaction scheme would not be excluded by our data, but the results of the decarboxylation experiments (Fig. 5) show that there exists a fairly quick and probably direct route from benzalmalonic to cinnamic acid, notwithstanding the fact that in this case the amount of water (which, in the above reaction scheme, would be needed for the hydration of benzalmalonic acid prior to a simultaneous elimination of carbon dioxide and water), in the whole reaction mixture was only 10–15 mg.

(20) Competition between malonic and benzalmalonic acid in the formation of their piperidine salts must influence the amount of the (non-decarboxylating) piperidine–benzalmalonate molecules. When the amount of piperidine present is greater than the total amount of all acidic species present in the solution, not even a trace of carbon dioxide is formed (see Table II, no. 5).

(b) **The Role of the Solvent.**—The experiments shown in Table I indicate that pyridine as solvent has a catalytic influence on the condensation too, and not only on the decarboxylation.[8,9] Substitution of pyridine by cyclohexanone as the solvent almost exactly halves the rates of condensation. It is interesting to note that the relative rates of decarboxylation *versus* condensation are practically the same with pyridine alone (Table I, no. 1) and with a mixture of 10% pyridine and 90% cyclohexanone (no. 3). Substitution of the last 10% of pyridine by cyclohexanone (no. 4) lowers the condensation rate only slightly, while practically stopping the decarboxylation, thus showing the essential role of pyridine in the decarboxylation, while experiment no. 2 shows that a mixture of 40% pyridine with 60% cyclohexanone gives much higher relative decarboxylation rates than pyridine alone.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Relative Sensitivity of Triphenylmethyl Chloride to Electrophiles and Nucleophiles in Benzene Solution

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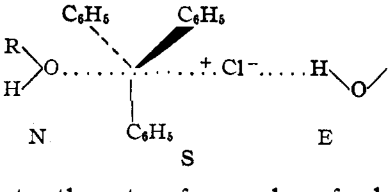
The benzolysis of triphenylmethyl chloride in the presence of trimethylamine in benzene solution has been investigated employing five benzyl alcohols (p-CH_3O–, p-CH_3–, p-H–, p-Cl– and p-NO_2– substituted). Kinetic studies revealed the reactions to be first order in the chloride and second order in the alcohols through at least the first 50% of the reaction. Addition of phenol to the reaction medium enhanced the over-all rate of substitution through the addition of a new *competing* reaction (also leading to the benzyl ether) that appeared to be first order in both chloride and alcohol. The effects of the *para*-substituents of the benzyl alcohols on the rate of the above two independently occurring reactions indicate that the sensitivity of triphenylmethyl chloride to the electrophilic component of these termolecular reactions is significantly greater than to the nucleophilic component. The reaction of equimolar phenol, triphenylmethyl chloride and triethylamine in benzene was found to be second order over-all, a fact which suggests that phenol and triethylamine are completely complexed in benzene solution.

The investigations of Swain[3] on the mechanism of the substitution reactions of triphenylmethyl (trityl) chloride in benzene solution stimulated the present study. As had been demonstrated earlier in other, but similar, systems,[4] solvolyses involving a termolecular mechanism were demonstrated to occur. For instance in the methanolysis of trityl chloride in benzene solution, the reaction was demonstrated to be first order in trityl chloride and second order in methanol, whereas in the presence of added phenol, the reaction rate was enhanced and found to be first order in trityl chloride and in methanol. Swain interpreted these observations in terms of a transition state (I) involving both a displacing nucleophile and an anion-solvating electrophile. More recently these concepts were put on a more quantitative basis through the agency of the linear free-energy relationship (equation 1) which correlates the rates of a number of substitution reactions in terms of four parameters. Thus *n* measures the nucleophilic reactivity of N, *e* the electrophilic reactivity of E, and *s* and *s'* the sensitivity of the substrate (S) to different N and E reagents, respectively, while *k* represents the rate constant of the reaction



I

$$\log (k/k^\circ) = sn + s'e \qquad (1)$$

being compared to the rate constant (k°) of the reaction of the same substrate under the same conditions but with water as both N and E.

The present investigation reports a kinetic study of the benzolysis of trityl chloride in the presence of trimethylamine in benzene solution in which five benzyl alcohols (p-CH_3O–, p-CH_3–, p-H–, p-Cl– and p-NO_2–substituted) have played the role of both N and E. The results of a second series of kinetic experiments are also recorded which deal with the same reactions carried out in the presence of added phenol, which for the most part assumed the role of E in the mechanism. The objective of these studies was to evaluate as quantitatively as possible the relative sensitivity in this medium of trityl chloride to the N and E components of these termolecular processes.

Results

The first set of kinetic experiments was conducted at 30° in a benzene solution saturated with triethylamine hydrochloride, with triethylamine present in concentrations about equal to that of the trityl chloride. The reaction was followed acidimetrically essentially by a method previously reported.[4b] Under these conditions, third-order kinetics of the form of equation 2 were observed in all

$$-\frac{d[(C_6H_5)_3CCl]}{dt} = k_3[ROH]^2[(C_6H_5)_3CCl] \qquad (2)$$

cases, the constants being calculated for each point by the integrated equation of Swain.[3a] The third-order rate constants (k_3) were reproducible to within

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[3] (a) C. G. Swain, THIS JOURNAL, **70**, 1121 (1948); (b) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

[4] (a) N. T. Farinacci and L. P. Hammett, *ibid.*, **59**, 2542 (1937); (b) P. D. Bartlett and R. W. Nebel, *ibid.*, **62**, 1345 (1940).