mole), *tert*-butyl hydroperoxide (0.2 mole containing 90% of hydroperoxide), and cuprous chloride (0.1 g.) was heated at 92° for 8 hr. At the end of that time, a titration showed that 90% of the hydroperoxide had decomposed. The copper salt was collected on a filter. The volatile material was removed from the filtrate at a pressure of 12 mm. The residue, 12 g., was dissolved in hot benzene. Cooling produced a solid (3 g.) which was separated and collected on a filter. The solid material melted at 151–152° and did not depress the melting point of an authentic sample of adipic acid. The benzene was removed from the filtrate and the residue subjected to distillation. A fraction (4 g.) boiling at 52°/0.15 mm. was collected, leaving a residue I (5 g.). The distillate still contained a small amount of an acidic impurity. To remove it, the distillate was dissolved in benzene, and then washed with a water solution of sodium carbonate. The benzene was then removed at reduced pressure leaving an oil (n_D^{20} 1.4500) which was assumed to be compound G.

Preparation of compound H (N-methyl-N tert-butylperoxymethylaniline). A mixture containing dimethylaniline (0.19 mole), *tert*-butyl hydroperoxide (0.39 mole), cuprous chloride (0.0003 mole), and benzene (1.6 mole) was maintained at 35° for 12 hr. At the end of that time, iodometric titration indicated the loss of 50% of the active oxygen. Some neutral alumina was added, and filtered. The benzene and *tert*-butyl alcohol formed were distilled off *in vacuo.* The crude peroxide was purified by chromatographic separation through a short column of neutral alumina, using petroleum ether as the eluent. Small amounts of amine oxides were formed as by-products. The purified peroxide, b.p. 75°/0.1 mm., n_D^{20} 1.5160, was obtained in over 90% yield. It can be titrated iodometrically in acetic acid. It is soluble in dilute aqueous hydrochloric acid and its titer dropped only 5% after refluxing for 24 hr. in benzene.

Anal. Calcd. for $C_{12}H_{19}O_2N$: C, 68.86; H, 9.15; N, 6.70; mol. wt. 209. Found: C, 69.1; H, 8.9; N, 7.0; mol. wt. 212.

Comparison of its infrared spectrum to that of dimethylaniline indicated no additional substitution in the aromatic ring. After prolonged warming in aqueous hydrochloric acid, monomethylaniline was isolated.

Preparation of compound J (p-methylbenzyl tert-butyl peroxide). A mixture consisting of *p*-xylene (1.0 mole), *tert*-butyl hydroperoxide (0.26 mole), and cuprous chloride (0.1 gram) was heated to 50° and maintained at that temperature for 10 hr. At the end of that time, titration showed that 50% of the hydroperoxide had been consumed. The lower boiling materials were removed *in vacuo.* The crude peroxide was purified by a chromatographic separation, through a short column of neutral alumina, using petroleum ether as an eluent. The yield was 0.55 mole (85%) on the basis of the hydroperoxide that was decomposed. The byproduct was *p*-methylbenzaldehyde. The peroxide J is a pleasant smelling liquid, b.p. 65°/0.2 mm., n_D^{20} 1.4858.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; mol. wt. 194. Found: C, 74.40; H, 9.17; mol. wt. 186.

The infrared spectrum of the peroxide J had bands at 1360 cm.$^{-1}$ (strong) and 1385 cm.$^{-1}$ (medium), which indicated the presence of a *tert*-butyl group. The bands at 1190 cm.$^{-1}$ and 875 cm.$^{-1}$ are ascribed to the presence of the *tert*-butoxy group.

Preparation of compound K (tert-butylperoxydioxane 1,4). A mixture containing *tert*-butyl hydroperoxide (0.22 mole), dioxane 1,4 (1.00 mole), and cuprous chloride (0.05 g.) was heated to 70° and maintained at that temperature for 12 hr. At the end of that time, titration showed that 85% of the hydroperoxide had been consumed. The lower boiling materials were removed *in vacuo.* The infrared spectrum of the crude reaction product indicated strong keto and hydroxy bands. The peroxide was purified by chromatographic separation through a short neutral alumina column, using petroleum ether as an eluent. Yield of the peroxide K was 0.095 mole (50% on the basis of the hydroperoxide consumed).

The *tert*-butyl peroxy dioxane 1,4, b.p. 55°/0.25 mm., n_D^{20} 1.4325 is somewhat soluble in water. Its infrared spectrum contains bands at 1360 cm.$^{-1}$ (strong) and 1390 cm.$^{-1}$ (medium) indicating the presence of a *tert*-butyl group. The bands at 1185 cm.$^{-1}$ and 875 cm.$^{-1}$ are given to the presence of the *tert*-butoxy group.

Anal. Calcd. for $C_8H_{16}O_4$: C, 54.53; H, 9.15; mol. wt. 176. Found: C, 54.32; H, 8.93; mol. wt. 176.

Decomposition of tert-butyl hydroperoxide in iso-octane. A mixture containing *tert*-butyl hydroperoxide (0.1 mole), isooctane (0.4 mole), and cuprous chloride (1 g.) was heated to 67°. A violent reaction followed. Within 20 min., all of the hydroxyperoxide decomposed and oxygen gas (0.5 mole) had evolved. The reaction mixture did not react with dinitrophenyl hydrazine (no ketones), nor with concentrated HI (no peroxides).

CHICAGO, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

Kinetics and Mechanism of the Perkin Reaction

YOSHIRO OGATA AND MASARU TSUCHIDA

Received September 3, 1957

The condensation of benzaldehyde with acetic anhydride to yield cinnamic acid, using various basic catalysts such as triethyl-, tripropyl-, tributyl-, and triisobutylamine, has been studied kinetically at 125–155° in kerosine as solvent. The rate of the formation of cinnamic acid as well as that of the disappearance of benzaldehyde has been followed by ultraviolet spectrophotometry. The rate was found to be expressed as k(benzaldehyde) (acetic anhydride) in an excess of the catalyst, while as k(benzaldehyde) (catalyst) in an excess of acetic anhydride. The variation of the rates with changing catalysts was shown to be ascribed to the variation of both frequency factor and energy of activation. A precise fit to the Hammett equation was observed with substituted benzaldehydes, with a positive ρ value of 2.25 at 135°. A mechanism involving a rate-determining attack of a complex of acetic anhydride with trialkylamine [$Ac_2O.R_3N$] on the carbonyl carbon of benzaldehyde is presented and discussed.

Although the Perkin reaction has long been studied as a problem of organic chemistry,[1] only a few kinetic and mechanistic studies[2] have so far been reported. Buckles and Bremer[2b] followed the triethylamine-catalyzed reaction of benzaldehyde and phenylacetic acid by estimating a reactant (benz-

---

(1) For the review see, J. R. Johnson, *Org. Reactions,* I, 248 (1942).

aldehyde) and using an unsatisfactory rate equation.[3] Therefore, it seems of value to examine the reaction mechanism in detail.

It is now generally accepted that base-catalyzed condensations of carbonyl compounds with active-hydrogen compounds, *e.g.*, Claisen condensation, involve a preliminary equilibrium of proton elimination giving carbanion, followed by the condensation. It is expected that the Perkin reaction also occurs by this mechanism,[2b,c] but little is known regarding the rate-determining step and the attacking agent.

The purpose of the present investigation was to elucidate the mechanism of the reaction from the kinetic order with respect to acetic anhydride and base (trialkylamines) and from the effect of structural changes in the bases together with the effect of substituents in benzaldehyde on the rate.

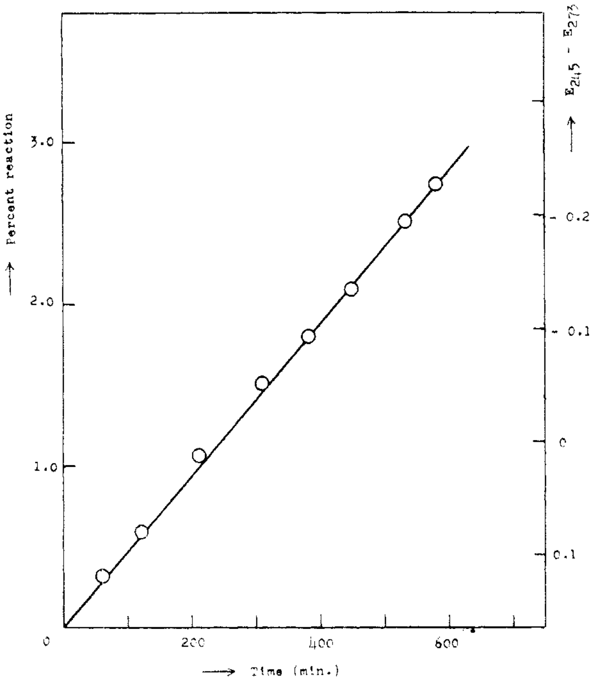


Fig. 1. A typical run for rate measurement. Initial concentrations: benzaldehyde 1.396*M*, acetic anhydride 1.136*M*, triethylamine 0.808*M*

TABLE I

RATE OF CONDENSATION OF BENZALDEHYDE WITH ACETIC ANHYDRIDE IN KEROSINE AT 135 ± 0.5° WITH TRIETHYLAMINE CATALYST

	Initial Concentration[a]			
	$Et_3N(m)$ M	$Ac_2O(a)$ M	BzH(*b*) M	Initial Rate, $v_0 \times 10^7$, Mole L.$^{-1}$ Sec.$^{-}$
(A)	0.808	1.986	1.396	9.97
	0.808	1.702	1.396	10.53
	0.808	1.419	1.396	10.39
	0.808	1.136	1.396	10.61
	0.606	1.419	1.396	7.63
	0.606	1.136	1.396	7.70
	0.606	0.851	1.396	7.54
(B)	0.808	1.419	1.703	12.91
	0.808	1.419	1.396	10.39
	0.808	1.419	1.118	7.98
	0.808	1.419	0.838	6.10
	0.808	1.419	0.698	5.14
	0.808	1.419	0.599	4.33
(C)	0.808	1.419	1.396	10.39
	0.606	1.419	1.396	7.62
	0.467	1.419	1.396	6.01
	0.404	1.419	1.396	4.74
	0.351	1.419	1.396	4.52
	0.301	1.419	1.396	3.68
(D)	1.010	1.136	1.396	9.54
	1.010	0.851	1.396	7.07
	1.010	0.712	1.396	5.95
	1.010	0.612	1.396	4.97
	1.010	0.566	1.396	4.63
	1.010	0.450	1.396	3.56
(E)	1.010	1.136	1.703	11.48
	1.010	1.136	1.396	9.54
	1.010	1.136	1.118	7.63
	1.010	1.136	0.838	5.69
	1.010	1.136	0.698	4.62
	1.010	1.136	0.599	3.83
(F)	1.212	0.851	1.396	6.55
	1.010	0.851	1.396	7.08
	0.808	0.851	1.396	6.60
	1.212	0.566	1.396	4.62
	1.010	0.566	1.396	4.63
	0.808	0.566	1.396	4.79

[a] $fa > m$ in the case of (A), (B) and (C), while $fa < m$ in the case of (D), (E), and (F).

Results. Table I summarizes data on the initial rates v_0 of the triethylamine-catalyzed condensation of benzaldehyde with acetic anhydride in kerosine with varying molar ratio of each reactant and catalyst. The v_0 value was obtained graphically.[4] A typical run is shown in Fig. 1.

It will be seen from the table that the initial rates are proportional to benzaldehyde and that they are also proportional to both acetic anhydride and triethylamine provided that their concentrations are not large, but the linearity departs and the rate becomes almost independent of the excess reagent.

Table II lists the initial rates of the condensation of benzaldehyde with acetic anhydride in kerosine using various catalysts, *i.e.*, triethylamine, tripropylamine, tributylamine, and triisobutylamine. The variation of the rates with temperature is also recorded in Table II together with the calculated energies of activation and frequency factors.

---

(2) (a) D. S. Breslow and C. R. Hauser, *J. Am. Chem. Soc.*, **61**, 786 (1939); (b) R. E. Buckles and K. G. Bremer, *J. Am. Chem. Soc.*, **75**, 1487 (1953); (c) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, N. Y., 1940, p. 345.

(3) Their equation should read

$$v = k\,[C_6H_5CHO]\,[C_6H_5CH_2COOH]\,[CH_3COO^-]/[CH_3COOH]^2$$

although their equation is valid provided that $[C_6H_5CH_2COOH]$ in the equation means the stoichiometric concentration of phenylacetic acid.

(4) R. Livingston, *Investigation of Rates and Mechanism of Reactions*, (*Technique of Organic Chemistry*, Vol. VIII), S. L. Friess and A. Weissberger, ed., Interscience, New York, N. Y., 1953, p. 182.

Table III shows the effect of para substituents in benzaldehyde on the rate with triethylamine catalyst. It is apparent that the effect of the substituents on the rate constant satisfies the Hammett equation (Fig. 2), giving a ρ value of $+2.25$.

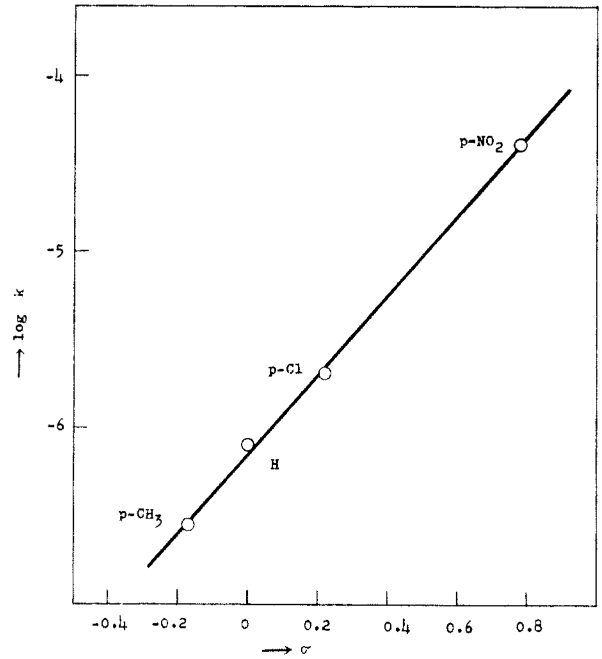
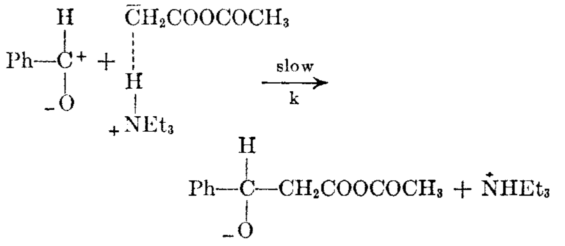


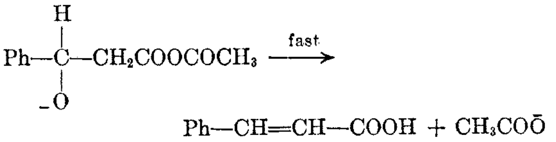
Fig. 2. The Hammett's relationship for the triethylamine-catalyzed condensation of benzaldehydes with acetic anhydride in kerosine at 135° ($\rho = +2.25$)

Discussion. The above facts seem to imply the presence of a complex[5] consisting of triethylamine and acetic anhydride as an attacking agent instead of a simple conjugate base of acetic anhydride as suggested in the Claisen condensation.[2c,6] Thus an excess reagent will take little part in the rate-determining step. The observed rate dependence upon benzaldehyde in Table I together with a high positive ρ value ($+2.25$) suggests that the rate-determining attack of the above complex occurs on the positive carbonyl carbon of benzaldehyde

$$Ac_2O + NEt_3 \underset{K}{\overset{\text{fast}}{\rightleftarrows}} CH_3COOCO\bar{C}H_2 \cdots\cdots H\text{—}\overset{+}{N}Et_3 \quad (1)$$



$$Ph\text{—}\underset{\underset{-O}{|}}{\overset{\overset{H}{|}}{C^+}} + \begin{matrix}\bar{C}H_2COOCOCH_3\\ \vdots\\ H\\ |\\ {}^+NEt_3\end{matrix} \xrightarrow[k]{\text{slow}} Ph\text{—}\underset{\underset{-O}{|}}{\overset{\overset{H}{|}}{C}}\text{—}CH_2COOCOCH_3 + \overset{+}{N}HEt_3 \quad (2)$$



$$Ph\text{—}\underset{\underset{-O}{|}}{\overset{\overset{H}{|}}{C}}\text{—}CH_2COOCOCH_3 \xrightarrow{\text{fast}} Ph\text{—}CH{=}CH\text{—}COOH + CH_3CO\bar{O} \quad (3)$$

where K and k denote equilibrium constant and rate constant of the steps 1 and 2, respectively.

Provided that the rate of reaction 2 is negligible in calculating the concentration of complex p, the initial stoichiometric concentrations of acetic anhydride and triethylamine m are related by

$$K = \frac{p}{(fa - p)(m - p)} \quad (4)$$

where f is a correction factor for the concentration of acetic anhydride, the meaning of which, however, is still obscure. If the initial concentration of acetic anhydride is much larger than that of tri ethylamine, *i.e.*, $fa >> m$, it follows that $(fa - p)$ approximates to fa, since p cannot exceed m; thus Equation 4 is simplified to

$$K = \frac{p}{fa(m - p)} \quad (5)$$

or

$$p = \frac{fKam}{fKa + 1} \quad (6)$$

Thence the initial rate v_0 is expressed approximately as follows:

$$v_0 = kpb = \frac{kfKamb}{fKa + 1} \quad (7)$$

where b denotes the initial concentration of benzaldehyde. If fKa is sufficiently large than unity, the rate may be expressed as follows.

$$v_0 = k\,m\,b \quad (8)$$

Analogously, when $fa << m$, the rate becomes, if mK is larger than unity

$$v_0 = k\,f\,a\,b \quad (9)$$

The results shown in Table I satisfy these relations; *i.e.*, if acetic anhydride is in excess over the amine, the rate varies linearly with concentrations of both benzaldehyde and triethylamine but is independent of acetic anhydride (Eq. 8), and if triethylamine is in excess over the anhydride, linear dependence on both benzaldehyde and acetic anhydride and independence of triethylamine are observed (Eq. 9). These relationships are also shown in Fig. 3. The value of f was calculated from Equations 8 and 9 to be 1/1.395.

With regard to the complex formation, the fact that the very low solubility of acetic anhydride in kerosine is much increased by addition of triethylamine suggests the intimate interaction between both components. Ultraviolet and infrared absorption spectra (Fig. 4) also suggest the complex formation.

It seems of interest to note that the present reaction is somewhat different from the analogous pi-

---

(5) It is probable, however, that the fact is due to a solvent effect, *i.e.*, this nonpolar solvent may be unable to effect dissociation into $CH_2\bar{C}OOCOCH_3$ and $\overset{+}{N}HEt_3$, which might be conceivable in polar solvents.

(6) A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, John Wiley & Sons, Inc., New York, N. Y., 1953, p. 208.

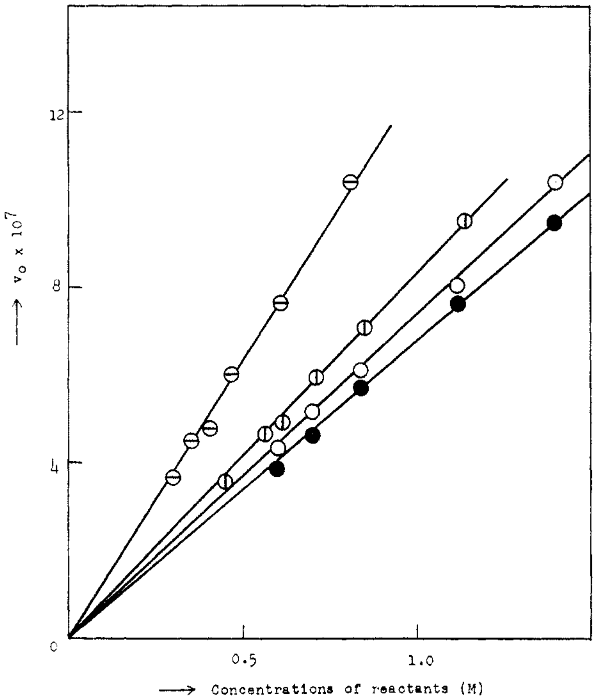


Fig. 3. Plots of initial rates (v_0) against initial concentrations of the reactants (Equation 8 and 9). Data of (B)○, (C)⊖, (D)⦶, and E ● in Table I

peridine-catalyzed condensation of benzaldehyde with diethyl malonate.[7] The addition of a small amount of organic acid greatly increases the rate of the latter reaction, while it has little effect on the present condensation. Moreover, although both electron-releasing and attracting para substituents retard the condensation of benzaldehyde and diethyl malonate, a precise fit to Hammett equation and a high ρ value (+2.25) are observed in the present reaction. Mechanistic difference between the two condensations is thus apparent; it is probable that in the piperidine-catalyzed condensation of benzaldehyde with diethyl malonate a complex consisting of benzaldehyde and piperidine reacts with diethyl malonate, while in the triethylamine-catalyzed condensation of benzaldehyde with acetic anhydride a complex composed of triethylamine and acetic anhydride attacks the positive carbonyl carbon of benzaldehyde.

The effect of catalyst. In spite of the fact that energy of activation is comparable to those of the related reactions, this condensation is considerably slow, owing to the low frequency factors (Table II). The bulkiness of the attacking agent as well as the complex formation, as shown in Equation 1, may explain the low frequency factors. This complex will be favored particularly in nonpolar solvents, and such a polar structure will make the frequency factor especially small in this solvent.[8]

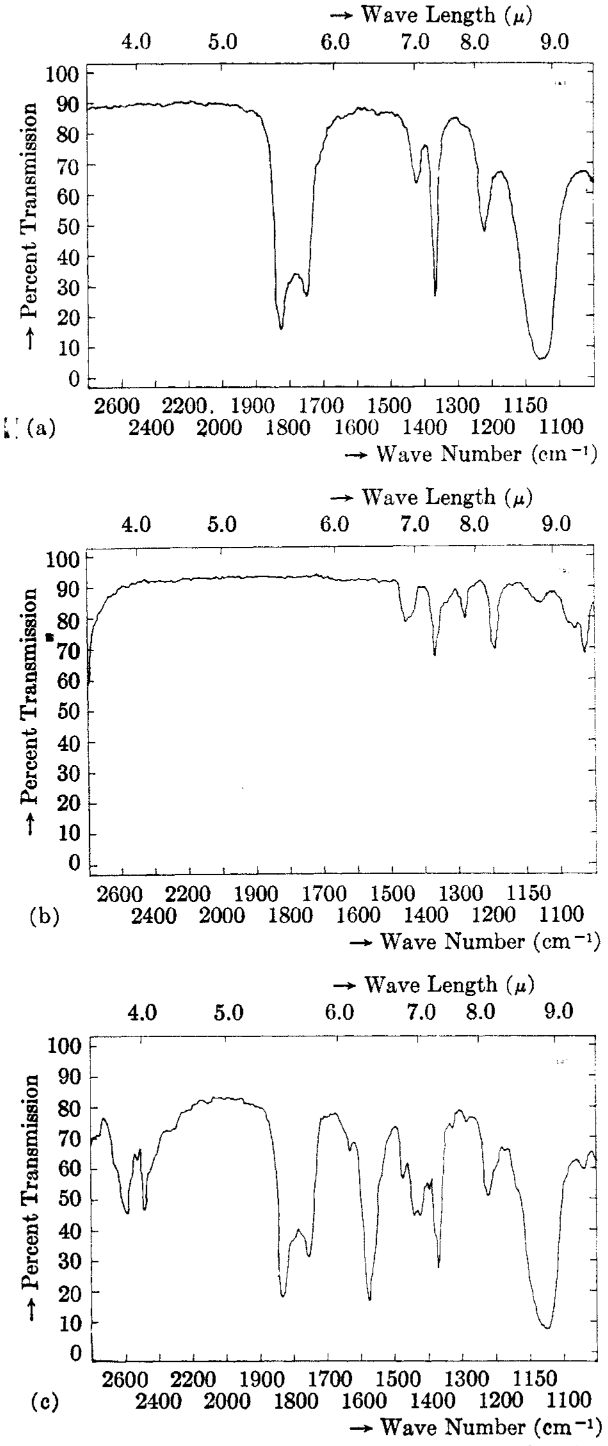


Fig. 4. Infrared absorption spectra of acetic anhydride (a), triethylamine (b), and an equimolar mixture of them (c)

The order of the basicity of trialkylamines ($Et_3N < Pr_3N < Bu_3N < i\text{-}Bu_3N$)[9] is in the reverse order of the catalytic ability of these amines ($Et_3N > Bu_3N > Pr_3N >> i\text{-}Bu_3N$). The fact implies an importance of steric requirements in this reaction. If the conjugate base of acetic anhydride was an at-

---

[7] Unpublished work.

[8] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 347.

[9] H. Landolt-R. Boernstein, *Physikalischen Chemische Tabellen*, 5 Auflage, Julius Springer, Berlin, 1936.

TABLE II

EFFECT OF CATALYSTS ON RATE, ENERGY OF ACTIVATION, AND FREQUENCY FACTOR OF THE CONDENSATION OF BENZALDEHYDE WITH ACETIC ANHYDRIDE IN KEROSINE AT VARIOUS TEMPERATURES[a]

Amine	Temp., °C.	$v_0 \times 10^7$ (Mole L.$^{-1}$ Sec.$^{-1}$)	Ea ($k_{\text{cal.}}$mole^{-2})	Log PZ
$\mathrm{Et_3N}$	117.5	6.77	10.8	−0.27
	132.5	9.99		
	135	12.25		
	140	13.77		
$\mathrm{Pr_3N}$	135	3.96	11.4	−0.22
	145	5.63		
	155	7.66		
$\mathrm{Bu_3N}$	135	4.61	12.0	+0.14
	145	6.87		
	155	9.25		
i-$\mathrm{Bu_3N}$	135	0.44[b]	9.8[b]	−1.62[b]
	155	1.14		

[a] Initial concentrations: trialkylamine, 1.10*M;* acetic anhydride, 1.419*M;* benzaldehyde, 1.396*M*. [b] The rate was too slow for accurate measurements.

TABLE III

EFFECT OF PARA SUBSTITUENTS ON RATE OF TRIALKYLAMINE-CATALYZED CONDENSATION OF BENZALDEHYDE WITH ACETIC ANHYDRIDE IN KEROSINE AT 135 ± 0.5°[a]

p-Substituent	v_0 (Mole L.$^{-1}$ Sec.$^{-1}$)
$\mathrm{CH_3}$	3.94×10^{-7}
H	1.23×10^{-6}
Cl	2.88×10^{-6}
$\mathrm{NO_2}$	5.73×10^{-5}
	$\rho = +2.25$

[a] Initial concentrations: triethylamine, 1.010*M;* acetic anhydride, 1.419*M;* benzaldehydes, 1.396*M*.

tacking agent, the rate order would be identical to the basicity order. It has been found, however, that the yields of the metallic acetate–catalyzed Perkin reactions of o-chlorobenzaldehyde and acetic anhydride at 180° for 8 hr. depend on the metals of the acetate as follows: Li, 58%; Na, 71%; K, 78%; Rb, 82%.[10] The order is consistent with the order of the basicity of the acetate and strongly suggests the importance of the acetate ion concentration in this polar medium.

The effect of substituents. The polar effect of substituents in benzaldehyde (or the Hammett's ρ value) is especially large ($\rho = +2.25$). This will also be an indication of rate-determining combination of strongly polarized reactants as indicated in Equation 2.

EXPERIMENTAL

Materials. Acetic anhydride was purified by double distillation, b.p. 139° (lit.[11] b.p. 139.5°). The triethyl- and tributylamines used were of best grade and purified by careful distillations, b.p. 89° (lit.[12] b.p. 89°) and 215° (lit.[13] b.p. 216.5°), respectively. Propyl and isobutyl bromides were prepared by the reaction of the corresponding alcohols, potassium bromide, and sulfuric acid, which was then heated with ammonia in aqueous methanol. The resulting tripropylamine and triisobutylamine were repeatedly rectified, b.p. 156° (lit.[14] b.p. 156.5°) and 185° (lit.[15] b.p. 185°), respectively.

Commercial benzaldehyde was washed with an aqueous solution of sodium carbonate and then water, dried, and distilled with addition of a small amount of hydroquinone, b.p. 178° (lit.[16] b.p. 178°). p-Tolualdehyde was prepared from p-xylene by the chromyl chloride oxidation in chloroform[17] and purified by duplicate distillations, b.p. 205° (lit.[17] b.p. 204°). p-Chlorobenzaldehyde was prepared from p-chlorotoluene *via* p-chlorobenzal bromide[18] and purified by recrystallization from aqueous methanol, m.p. 47° (lit.[19] m.p. 47°). p-Nitrobenzaldehyde was obtained by the oxidation of p-nitrotoluene with chromium trioxide in a mixture of glacial acetic acid and acetic anhydride[20]; yellow needles, m.p. 106° (lit.[20] m.p. 106°).

Cinnamic acid, p-nitro-, p-chloro-, and p-methylcinnamic acids were prepared by the Perkin condensation of the corresponding aldehydes with acetic anhydride, using potassium acetate as a catalyst, and purified by recrystallization from aqueous acetic acid, m.p. 137° (lit.[21] m.p. 137° , 285° (lit.[22] m.p. 286°), 251° (lit.[23] m.p. 250°), and 197° (lit.[24] m.p. 197°), respectively.

Commercial kerosine was treated several times with fuming sulfuric acid, washed with water, and rectified. A fraction boiling between 240 and 280° was collected, which showed no appreciable absorption at 240–290 mμ in a methanolic solution of the experimental concentration.

A typical procedure for the rate measurements. As an example, the rate measurements of triethylamine-catalyzed condensation of benzaldehyde and acetic anhydride is described below. A mixture of definite amounts of benzaldehyde, acetic anhydride, triethylamine, and kerosine (20 ml.) was placed in a 100-ml. three-necked flask fitted with a thermometer, a reflux condenser, and an outlet tube, and immersed in an oil bath thermostated at 138° ± 0.5°. The reaction mixture was shaken vigorously. In general, 3 min. were necessary to establish the temperature equilibrium; hence all kinetic runs were commenced after that interval. At appropriate time intervals aliquots (0.5 ml.) were taken out, being poured into a 25-ml. volumetric flask containing an insufficient amount of methanol, and diluted accurately to 25 ml. The solution (0.2 ml.) was then diluted to 10 ml. with acidic methanol (5 ml. of concentrated sulfuric acid in 1 l. of methanol), the optical density of the resulting solution being measured at appropriate wave lengths, as indicated in Table IV, by a Beckmann spectrophotometer model DU. The per cent compositions of these solutions were determined in the same manner as previously described.[25] These spectrophotometric data are summarized in Table IV.

The optical density of acetic anhydride was negligible at the concentrations of these measurements. The absorption

---

(10) F. Böck, G. Lock, and K. Schmidt, *Monatsh.*, **64,** 401 (1934).

(11) D. C. Jones and H. F. Betts, *J. Chem. Soc.*, 1181 (1928).

(12) J. Timmermans, *Chem. Zentr.*, **85,** 619 (1914).

(13) A. Lieben and A. Rossi, *Ann.*, **158,** 172 (1871).

(14) A. Zander, *Ann.*, **214,** 171 (1882).

(15) R. Sachtleben, *Ber.*, **11,** 734 (1878).

(16) F. W. Perkin, *J. Chem. Soc.*, **69,** 1247 (1875).

(17) H. D. Law and F. M. Perkin, *J. Chem. Soc.*, 259 (1907).

(18) *Cf.*, G. H. Coleman and G. E. Honeywell, *Org. Syntheses*, Coll. Vol. II, 89 (1948).

(19) W. L. McEwen, *Org. Syntheses*, Coll. Vol. II, 133 (1948).

(20) S. V. Lieberman and R. Connor, *Org. Syntheses*, Coll. Vol. II, 441 (1948).

(21) J. Kendall, *J. Am. Chem. Soc.*, **36,** 1726 (1914).

(22) P. Pfeiffer and G. Haefelin, *Ber.*, **55,** 1771 (1922).

(23) J. van der Lee, *Rec. trav. chim.*, **45,** 680 (1926).

(24) T. Posner and G. Schreiber, *Ber.*, **57,** 1131 (1924)

(25) Y. Ogata, M. Tsuchida, and Y. Takagi, *J. Am. Chem. Soc.*, **79,** 3397 (1957).

TABLE IV

SPECTROPHOTOMETRIC DATA FOR RATE MEASUREMENTS. OPTICAL DENSITY OF BENZALDEHYDES AND CINNAMIC ACIDS IN ACIDIC METHANOL (5 ML. OF CONCD. SULFURIC ACID IN 1 L. OF METHANOL)[a]

Materials	Concentration, (M) × 10^5	Optical Density at Various Wave Lengths		
		(245 mμ)	(251 mμ)	(273 mμ)
C_6H_5CHO	384	0.802	0.805	0.080
$C_6H_5CH{:}CH$ CO_2H	3.84	0.112	0.175	0.410
		(240 mμ)	(245 mμ)	(278 mμ)
p-$Cl.C_6H_4CHO$	213	1.074	0.972	0.058
p-$Cl.C_6H_4CH{:}$ $CHCO_2H$	7.10	0.101	0.162	0.876
		(250 mμ)	(265 mμ)	(297.5 mμ)
p-$O_2N.C_6H_4CHO$	19.2	0.608	0.872	0.210
p-$O_2N.C_6H_4CH{:}$ $CHCO_2H$	9.60	0.144	0.271	0.746
		(255 mμ)	(260 mμ)	(285 mμ)
p-$H_3C.C_6H_4CHO$	250	1.100	1.053	0.140
p-$H_3C.C_6H_4CH{:}$ $CHCO_2H$	8.33	0.349	0.481	1.002

[a] It was shown that Beer's law was obeyed in these solutions, and that these optical densities were unaltered with the modest variation of the acidity of the solvent.

of trialkylamines used was conveniently eliminated by the addition of a small amount of sulfuric acid as noted previously. Moreover, the addition of sulfuric acid is advantageous, because the absorption of benzaldehydes is markedly reduced, while that of cinnamic acids is almost unchanged; thus it is possible to estimate accurately a small change in the composition of any reaction mixture.

Complementary experiments. Since most of the kinetic runs were followed only up to 2% conversion, some complementary tests seemed necessary in order to ensure the reaction path. It was confirmed in preliminary tests that the reaction followed spectrophotometrically was truly the Perkin reaction and no appreciable side reaction occurred and also that the sulfuric acid in methanol did not cause any oxidation of benzaldehydes. A typical run carried out with the same reaction mixture as in the kinetic experiments up to 30% conversion at 160° shows a satisfactory agreement of the observed reaction course with the calculated one (Fig. 5).

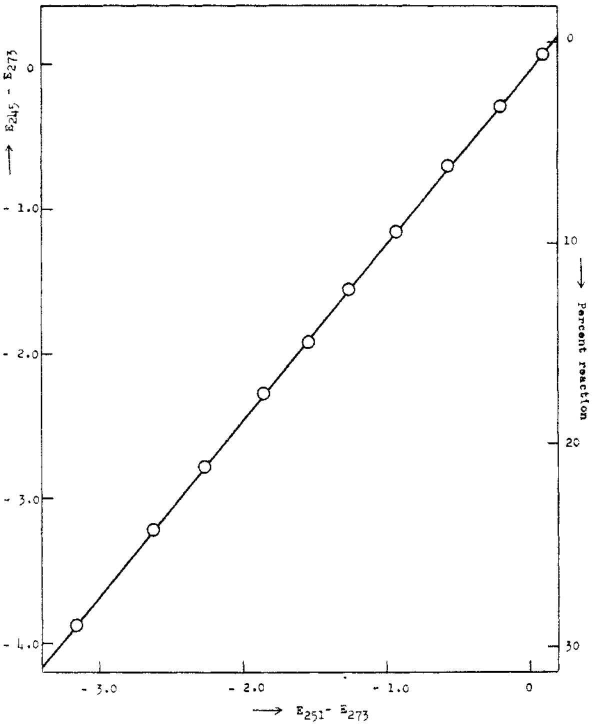


Fig. 5. Agreement of the observed reaction course (circles) with the calculated one (a line). E's are optical densities at the subscripted wave lengths

It was confirmed that no appreciable quantity of acetic acid was produced from the acetic anhydride used, since no kinetic deviation was observed with the same typical runs carried out after three weeks. It is sure also that acetic and cinnamic acids produced during the reaction will have little catalytic effect, since an addition of benzoic acid to the reaction mixture did not change the rate, especially with p-nitrobenzaldehyde, where no effect was observed until separation of the solution into two layers occurred (*ca.* 20% conversion). A report[26] that the effect of the added acid was very small in the base-catalyzed Knoevenagel condensation of cyanoacetic acid with aldehydes at high temperature is consistent with the above observation.

YOSHIDA, KYOTO, JAPAN

---

[26] M. J. Astle and W. C. Gergel, *J. Org. Chem.*, **21**, 493 (1956).

[CONTRIBUTION NO. 75 FROM E. I. DU PONT DE NEMOURS & COMPANY, INC., ELASTOMER CHEMICALS DEPARTMENT]

Chemistry of Aryl Isocyanates: Rate and Equilibrium Constants for the Formation of Ethyl α,γ-Diarylallophanate

I. C. KOGON

Received March 20, 1958

By means of the near infrared spectrum the equilibrium and rate constants for the formation of ethyl α,γ-diarylallophanates from aryl isocyanates and ethyl substituted carbanilates at elevated temperatures have been measured.

In the near infrared region between 14,000 and 4,000 cm.$^{-1}$ are found the absorption bands arising from N—H, C—H and O—H stretching vibrations. In particular, the first overtone of the NH stretching vibration is found near 6750 cm.$^{-1}$ Recently, we have shown that the NH group of ethyl, ethyl-p-methyl and ethyl o-methylcarbanilate exhibit absorption in the region of 6750 cm.$^{-1}$ However, the