Kinetic Measurements.—Measurements were carried out as described previously.[3] Thermostated solutions were mixed to give reaction solutions of the appropriate concentrations, and samples were withdrawn periodically and the

concentration of the unsaturated ketone determined spectrophotometrically.

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Carbonyl Reactions. VIII. The Kinetics of the Acid-catalyzed Condensation of Benzaldehyde and p-Nitrobenzaldehyde with Methyl Ethyl Ketone. Some Observations on ρ–σ Correlations[1]

BY DONALD S. NOYCE AND LLOYD R. SNYDER

The condensation of benzaldehyde and methyl ethyl ketone in acetic acid, catalyzed by sulfuric acid, proceeds via the intermediate β-hydroxy ketone, 4-phenyl-4-hydroxy-3-methyl-2-butanone (II); II undergoes competitive cleavage, esterification and dehydration in this medium. The condensation of p-nitrobenzaldehyde with methyl ethyl ketone proceeds similarly, but with no evidence of cleavage or esterification of the intermediate β-hydroxy ketone. The examination of the ρ–σ correlation gives further insight into situations where such correlations may fail.

Introduction

In continuing the study of the mechanism of acid-catalyzed reactions,[2-6] we have carried out kinetic studies of the condensation of benzaldehyde (I) and of p-nitrobenzaldehyde (IV) with methyl ethyl ketone, to supplement the study previously reported[4,5] of anisaldehyde and methyl ethyl ketone. The results obtained are generally similar to those reported earlier. There are, however, differences in degree which make necessary a fairly detailed kinetic analysis for each system. The similarities and divergencies provide additional insight into the reaction processes involved.

Gettler and Hammett[7] have studied the kinetics of the base-catalyzed condensation of benzaldehyde and methyl ethyl ketone. They have also carefully reviewed and corroborated the evidence showing that the formation of 4-phenyl-3-methyl-3-buten-2-one (III) takes place in acid to the essential exclusion of the isomer, 1-phenyl-1-penten-3-one, which is formed exclusively under basic conditions. Similarly the formation of 4-(p-nitrophenyl)-3-methyl-3-buten-2-one occurs under conditions of acid-catalyzed condensation.

From the results to be reported here, it is possible to detail the effect of substitution in the aromatic ring upon the relative rates of the various reactions processes which have been shown to be kinetically important.

Experimental

Preparation of Materials.—The materials used for the study are well-known, and have been carefully purified to give properties concordant with those in the literature. Spectral characterization was also used in purification of the required materials. 4-(p-Nitrophenyl)-3-methyl-3-buten-2-one was prepared from p-nitrobenzaldehyde and methyl ethyl ketone in 95% sulfuric acid, following the general procedure of Heller.[8] Better yields were obtained using sulfuric

acid in acetic acid as solvent. When 4-(p-nitrophenyl)-3-methyl-3-buten-2-one was prepared following the procedure of Burckhalter and Johnson[9] material identical to that obtained above (m.p. 94–95°) was obtained, in contrast to the reported value of 108° (Burkhalter and Johnson). Heller reports a value of 96°.

Kinetic Procedures.—Anhydrous acetic acid and sulfuric acid were prepared as described previously.[2] The kinetic procedures were those outlined previously.[2,4] Rate data were obtained by following the appearance of the characteristic absorption bands for the unsaturated ketone and the regenerated aldehyde as appropriate using a Beckman DU spectrophotometer.

Preparation of Intermediate β-Hydroxyketones.—From preliminary kinetic results the following conditions were chosen to isolate the intermediate β-hydroxyketone, 4-phenyl-4-hydroxy-3-methyl-2-butanone (II), from the condensation of benzaldehyde and methyl ethyl ketone. To 156 g. of methyl ethyl ketone was added 10 g. of sulfuric acid. The temperature was adjusted to 23° and 92 g. of benzaldehyde added. After maintaining the resulting solution at 25° for 12 minutes, the mixture was poured into ice, extracted with benzene, and the combined extracts washed with water. The excess solvent and methyl ethyl ketone and unreacted benzaldehyde were removed under reduced pressure below 60°. An oily brown residue (20 g.) resulted, which was approximately 75% ketol II. Crystallization of this oil from pentane at Dry Ice temperature yielded flocculent, colorless crystals, melting well below room temperature.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.12; H, 7.92. Found: C, 74.57; H, 8.21.

The spectral characteristics of the isolated material indicated that it was contaminated with 2% of benzaldehyde and 2% of the unsaturated ketone III.

In a similar fashion following conditions dictated by preliminary kinetic results, an impure sample of 4-(p-nitrophenyl)-4-hydroxy-3-methyl-2-butanone (IV) was prepared.

Results

Benzaldehyde and Methyl Ethyl Ketone.—The reaction of benzaldehyde with an excess of methyl ethyl ketone in solutions of sulfuric acid in acetic acid proceeds to the extent of 90%. It is possible to analyze for the appearance of the condensation product as a function of time, and there is observed, as previously with anisaldehyde and methyl ethyl ketone, an apparent initial induction period in the formation of the condensation product. The failure of the reaction to proceed to 100% completion under these conditions precludes the simple analysis of the limiting slope obtained.

(1) Supported in part by the Office of Ordnance Research, Contract No. DA-04-200-ORD-171.

(2) D. S. Noyce and W. A. Pryor, THIS JOURNAL, 77, 1397 (1955).

(3) D. S. Noyce, W. A. Pryor and A. T. Bottini, *ibid.*, 77, 1402 (1955).

(4) D. S. Noyce and L. R. Snyder, *ibid.*, 80, 4033 (1958).

(5) D. S. Noyce and L. R. Snyder, *ibid.*, 80, 4324 (1958).

(6) D. S. Noyce and W. L. Reed, *ibid.*, 80, 5539 (1958).

(7) J. D. Gettler and L. P. Hammett, *ibid.*, 65, 1824 (1943).

(8) G. Heller, H. Lauth and A. Buchwaldt, *Ber.*, 55, 483 (1922).

(9) J. H. Burckhalter and S. H. Johnson, THIS JOURNAL, 73, 4835 (1951); M. Stiles has reported a similar observation (private communication).
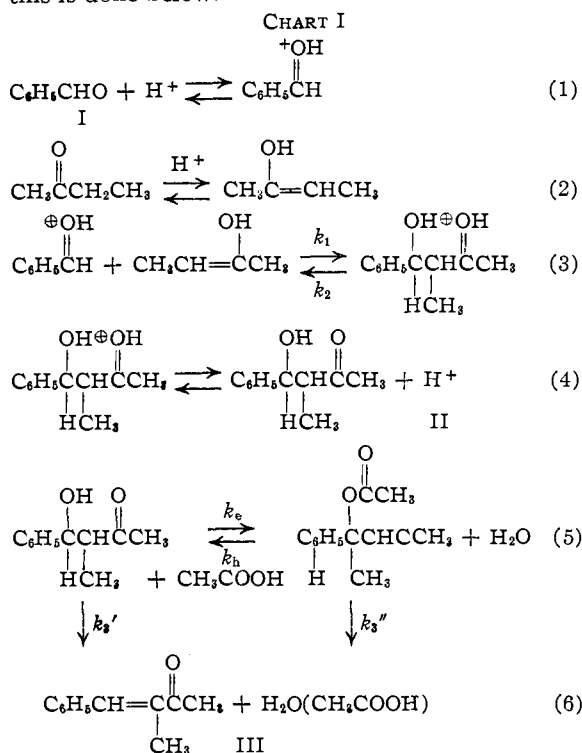
However, it is possible to measure directly the rate of disappearance of benzaldehyde during the initial portion of the kinetic run, and from such data, the tabulated rate constants which are presented in Table I for the condensation step k_1 have been obtained.

TABLE I

RATE OF CONDENSATION OF BENZALDEHYDE AND METHYL ETHYL KETONE[a]

(MEK)	(C$_6$H$_5$-CHO)[b] × 10^3	H$_2$SO$_4$	k_1' × 10^5, sec.$^{-1}$	$k_1'/$MEK × 10^5, l. mole^{-1} sec.$^{-1}$	H_0	X^{*c}	log k_1^0 + $H_0{}^d$
0.250	9.65	1.00	17.83	71.3	−2.98	0.814	−6.04
.250	9.65	1.00	17.78	71.1	−2.98	.814	−6.04
.1005	4.90	1.00	6.44	64.1	−2.98	.814	−6.08
.1005	4.90	1.00	6.97	69.4	−2.98	.814	−6.05
.0505	2.45	1.00	3.42	67.7	−2.98	.814	−6.06
.0505	2.45	1.00	3.44	68.2	−2.98	.814	−6.06
.251	9.89	0.626	8.83	35.2	−2.67	.794	−6.02
		.400				.780	
.196	7.80	.351	2.72	13 8	−2.30	.777	−6.05
.196	7.80	.351	2.64	13.5	−2.30	.777	−6.06
.196	7.80	.200	1.28	8.52	−1.94	766	−6.01
.196	7.80	.200	1.18	7.82	−1.94	.766	−6.05

[a] Solvent acetic acid, water content 0.02%; temperature 25.00°. [b] Initial concentration. [c] $X^* = (k' + k'_3)/k_2 + k' + k'_3$). [d] Average value log $k_1^0 + H_0 = −6.05 ± 0.015$.

The kinetic picture is far more complex in solutions containing appreciable amounts of water, and hence almost all data have been obtained in virtually anhydrous solution. The additional complexity is due to the moderate rate for the esterification of the intermediate hydroxy ketone. However, it is possible to carry through a complete analysis of the data under such circumstances, and this is done below.

CHART I

$$C_6H_5CHO + H^+ \rightleftharpoons C_6H_5\overset{\overset{+OH}{\|}}{C}H \quad (1)$$
I

$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3 \overset{H^+}{\rightleftharpoons} CH_3\overset{OH}{\overset{|}{C}}=CHCH_3 \quad (2)$$

$$C_6H_5\overset{\oplus OH}{\overset{\|}{C}}H + CH_3CH=\overset{OH}{\overset{|}{C}}CH_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_5\overset{OH}{\overset{|}{C}}CH\overset{\oplus OH}{\overset{\|}{C}}CH_3 \quad (3)$$
$$\overset{|}{H}\overset{|}{C}H_3$$

$$C_6H_5\overset{OH}{\overset{|}{C}}CH\overset{\oplus OH}{\overset{\|}{C}}CH_3 \rightleftharpoons C_6H_5\overset{OH}{\overset{|}{C}}CH\overset{O}{\overset{\|}{C}}CH_3 + H^+ \quad (4)$$
$$\overset{|}{H}\overset{|}{C}H_3 \qquad \overset{|}{H}\overset{|}{C}H_3 \quad II$$

$$C_6H_5\overset{OH}{\overset{|}{C}}CH\overset{O}{\overset{\|}{C}}CH_3 \underset{k_h}{\overset{k_e}{\rightleftharpoons}} C_6H_5\overset{O\overset{O}{\overset{\|}{C}}CH_3}{\overset{|}{C}}CH\overset{O}{\overset{\|}{C}}CH_3 + H_2O \quad (5)$$
$$\overset{|}{H}\overset{|}{C}H_3 + CH_3COOH \qquad \overset{|}{H}\overset{|}{C}H_3$$
$$\downarrow k_3' \qquad\qquad \downarrow k_3''$$

$$C_6H_5CH=\overset{O}{\overset{\|}{C}}CH_3 + H_2O(CH_3COOH) \quad (6)$$
$$\overset{|}{C}H_3 \quad III$$

It is to be noted that the rate of the condensation step shows satisfactory correlation (Table I)

with the acidity function as measured in acetic acid, and as in the case of the condensation of methyl ethyl ketone with anisaldehyde, it is concluded that the condensation step proper takes place between the protonated salt of the aldehyde and the enol of methyl ethyl ketone (Chart I, equations 1–3).

Behavior of 4-Phenyl-4-hydroxy-3-methyl-2-butanone (II) in Acetic Acid.—The intermediate hydroxy ketone II undergoes competitive reactions when placed in acetic acid–sulfuric acid. Analysis of the spectrum as a function of time makes it possible to determine the rate of formation of regenerated benzaldehyde and of the ultimate condensation product, 4-phenyl-3-methyl-3-butene-2-one (equations 3–6).

Data for a typical kinetic experiment are presented in Table II. Figure 1 represents a typical kinetic experiment in 1.00 molar sulfuric acid.
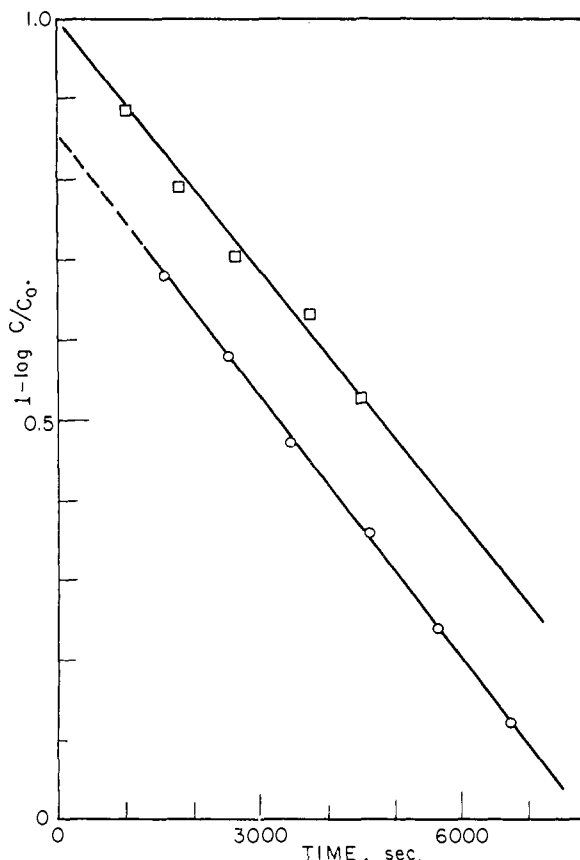

Fig. 1.—Rate of reaction of 4-phenyl-4-hydroxy-2-butanone; solvent, acetic acid, 0.02 M, H$_2$O; 1.00 M sulfuric acid; temperature 25.00°: O—O, 0.00369 M II; □—□, 0.00180 M acetate of II.

Two features of the above data are noteworthy: (1) while the concentration of the condensation product III continues to increase with time, the concentration of benzaldehyde reaches a maximum value after 9400 seconds; (2) at the same time the plot of log (II)/(II)$_0$ has become linear. The mechanism outlined in Chart I would appear to be the only one consistent with the facts (equations 3–6). Thus, at 9400 seconds, the intermediate alcohol has been converted completely to benzal-

TABLE II
TYPICAL RATE DATA FOR THE DECOMPOSITION OF 4-PHENYL-4-HYDROXY-3-METHYL-2-BUTANONE[a]

Time, sec. $\times 10^{-3}$	III/(II$_0$)	I/(II)$_0$	(II)/(II)$_0$[b]
0.27	0.041	0.038	0.921
2.88	.235	.182	.583
6.30	.315	.226	.459
9.43	.363	.238	.389
13.68	.415	.238	.347
17.64	.460	.235	.308
22.5	.505	.247	.257
26.9	.540	.229	.222

[a] Solvent acetic acid; water concentration 0.02%, sulfuric acid 0.200 molar; $T = 25.00°$. [b] Apparent relative concentration of II, by difference.

TABLE III
RATE OF REACTION OF 4-PHENYL-4-HYDROXY-3-METHYL-2-BUTANONE[a]

H_2SO_4, M	0.200	0.400	1.00	1.00
II$_0$, M	.00905	.00715	0.00524	0.00180[b]
k_2[c]	11.9 ± 0.5	31.4 ± 2		
k_e[c]	23.1 ± 1	80.5 ± 5		
k_3'[c]	15.7 ± 1	29.2 ± 1		
k_3''[c]	3.49 ± 0.1[a]	8.33 ± 0.1[d]	24.8 ± 1	23.3 ± 1
k_e/Z[e]	0.49 ± 0.05	0.61 ± 0.03		
X/X_0[f]	0.545 ± 0.02	0.62 ± 0.02	0.71 ± 0.01	

[a] Solvent acetic acid; 0.02% water, $T = 25.00°$. [b] Acetate of II as starting material. [c] Rate constants $\times 10^5$ sec.$^{-1}$. [d] Initial concentration of II 0.00340 M. [e] Calculated from k_2, k_e, k'_3 and k''_3. [f] From limiting slope extrapolated to zero time.

dehyde, intermediate acetate and condensation product. The only further reaction is then the simple first-order elimination of the intermediate acetate. The conclusion that the limiting rate of reaction (past 9400 seconds in Table II) represents the reaction of the intermediate acetate is strengthened by the following observation. An impure sample of the intermediate acetate was isolated and subjected to similar experimental conditions. A reaction cleanly first order over the entire interval studied was observed (Fig. 1).

Utilizing initial rate data for the reaction of II, one may calculate the sum of k_2, k_e and k_3'. The quantity of benzaldehyde formed by reversal of the condensation gives a measure of the ratio of k_2 to k_e and k_3'. Since, however, k_1 and k_3'' are of the same order of magnitude, steady state approximations are not immediately applicable. The complete solution for the different equations for the reactions of the intermediate ketol II, which may be schematically represented by

$$\begin{array}{ccc} B & \xrightarrow{k_e} & C \\ k_2 \downarrow & \underset{k_3'}{\searrow} & \downarrow k_3'' \\ A & & D \end{array}$$
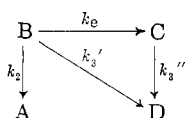
may be set in the following form after integration

$$\frac{(X)}{B_0} = 1 - \frac{A}{B_0} - \frac{C}{B_0} = [(k_2 + k_3')/Q - k_e/QZ]e^{-Qt} + k_e/Ze^{-k_3''t}$$

where $Q = (k_2 + k_e + k_3')$, $Z = (k_2 + k_e + k_3' - k_3'')$ and X refers to the apparent remaining concentration of II as calculated by difference. Since k_3'' is a good deal smaller than Q, a limiting rate is quickly reached as e^{-Qt} becomes negligible with respect to $(k_e/Z)e^{-k_3''t}$. At longer time values

$$\ln (X)/(X_0) = \ln(k_e/Z) - k_3''t$$

which is the expression for the limiting straight line of Fig. 1. Extrapolation of this latter line to zero time gives a value of $\ln (k_e/Z)$, and provides a further verification of the relationship of the constants k_2, k_e, k_3' and k_3''. The values of the rate constants which have been determined by these methods are summarized in Table III.

A coherent representation of the reactions of the intermediate β-hydroxyketone is thus obtained.

The acidity dependence of the various reactions presents a generally consistent picture, though the data are severely limited by the inaccessibility

in the higher acidity ranges of limiting initial rate data. As demanded by the total reaction sequence, the reversal of the condensation step proper parallels the acidity function with linear slope.

The True Rate of Condensation.—Examination of the rate of disappearance of benzaldehyde in solutions containing low concentrations of methyl ethyl ketone should reveal no induction period. This expectation is fulfilled experimentally. The pseudo first-order rate constant thus obtained, k_1', is a function not only of the methyl ethyl ketone concentration, but also of the ratio $(k_e + k_3')/(k_2 + k_e + k_3')$ in any one medium of constant acidity. This correction term (X^*) has been applied to the rate data given in Table I. The true rate of condensation is thus larger than the apparent pseudo first-order rate. The necessity for such a correction does not arise in the case of the condensation of anisaldehyde with methyl ethyl ketone, since evidence was presented previously[4] that the esterification process is very fast relative to any other reactions of the initially formed 4-(p-methoxyphenyl)-4-hydroxy-3-methyl-2-butanone.

The Condensation of p-Nitrobenzaldehyde with Methyl Ethyl Ketone.—Preliminary examination of the reactions of the intermediate β-hydroxyketone revealed that no reversal of the condensation step occurred under the conditions of the kinetic experiments. There is thus no correction term to be applied to measured rates of condensation, such as was necessary in the case of benzaldehyde and methyl ethyl ketone. At high concentrations of methyl ethyl ketone, an induction period in the formation of the ultimate condensation product 4-(p-nitrophenyl)-3-methyl-3-buten-2-one is observed, again indicating that a significant concentration of an intermediate is being formed. The rate data are all consistent with the reaction sequence (Chart II) and the relevant rate data are presented in Table IV.
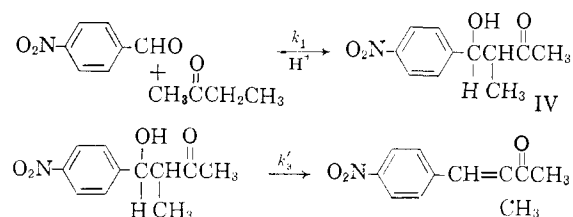
CHART II
FORMATION OF 4-(p-NITROPHENYL)-3-METHYL-3-BUTEN-2-ONE

<div align="center">TABLE IV</div>

<div align="center">RATE OF CONDENSATION OF p-NITROBENZALDEHYDE AND METHYL ETHYL KETONE[a]</div>

H_2SO_4, M	MEK, M	p-Nitro-benzaldehyde $\times 10^3$, M	IV $\times 10^3$, M	$k_1 \times 10^5$, sec.$^{-1}$	$k_1^0 \times 10^5$, l. mole^{-1} sec.$^{-1}$	log k_1^0 + H_0	$k_3' \times 10^5$, sec.$^{-1}$	log k_3 + H_0
1.00	0.496	10.1		14.1 ± 0.1	28.4	−6.53		
1.00	.199	4.04		6.1 ± .1	30.6	−6.49		
1.00	.1015	2.06		2.79 ± .05	27.5	−6.54		
1.00	.0512	1.01		1.46 ± .02	28.5	−6.53		
1.00			3.00				44.4 ± 0.8	−6.33
0.870			2.82				40.3	−6.27
.627			3.74				31.2	−6.19
.625	0.496	10.1		6.45 ± .1	13.0	−6.56		
.401			2.30				16.9	−6.16
.378	.501	9.94		4.00	7.98	−6.45		
.302			4.13				13.3	−6.08
.250	.502	9.94		2.55 ± .1	5.09	−6.37		
.200			3.91				8.0	−6.04

^a Solvent acetic acid, 0.02% H_2O; $T = 25.00°$.

The acidity dependence of the two steps in the condensation of p-nitrobenzaldehyde with methyl ethyl ketone does not correlate as satisfactorily with the acidity function in the previous cases for anisaldehyde and for benzaldehyde. We feel that for the condensation step the correlation reflects a failure of p-nitrobenzaldehyde to give a satisfactory activity coefficient term, which leads to a failure to obtain a linear, unit slope correlation.

For the final dehydration step, it is significant that failure to obtain good unit slope correlation is the result observed in precisely those situations where Noyce and Reed[6] obtained evidence that final dehydration in water is taking place via an acid-catalyzed enolization process.

Correlation of the Rates of the Various Processes with Change in Substituent.—In Table V derived rate constants for the various processes determined to be important for the condensation of the three aldehydes with methyl ethyl ketone are collected.

<div align="center">TABLE V</div>

<div align="center">COMPARISON OF RATES OF VARIOUS PROCESSES</div>

	CH₃O-	H-	NO₂-
$k_1' \times 10^5$ l. mole^{-1} sec.$^{-1}$	13.2[a]	7.22	4.31
$k_1^0 \times 10^5$ l. mole^{-1} sec.$^{-1}$[a]	13.2	9.53	4.31
$k_2 \times 10^5$ sec.$^{-1}$	Large	11.9	Very small
$k_e \times 10^5$ sec.$^{-1}$	Large	23.1	Very small
$k_3' \times 10^5$ sec.$^{-1}$	...	15.7	8.0
$k_3'' \times 10^5$ sec.$^{-1}$	7.8	3.49	..

^a Interpolated from ref. 4 and the data in this paper, for 0.220 molar sulfuric acid ($H_0 = -2.00$) in anhydrous acetic acid at 25.00°. ^b For 0.200 molar sulfuric acid in anhydrous acetic acid, 25.00°.

Though direct numerical data have not been obtained for the rate of reversal of the condensation step for all three systems studied, the nature of the various rate processes clearly indicate that this step (k_2) shows a very high sensitivity to structure. The cleavage reaction increases in speed with electron-donating substituents in the ring. The esterification step which is observed in acetic acid medium shows a surprisingly strong sensitivity to the nature of the aromatic substituent, and it is attractive to suggest that it may be a solvolytic esterification of the alcohol. The elimination steps

show little dependence upon structure, as was observed by Noyce and Reed,[6] and it would appear plausible to suggest that in the situations examined in the present paper, enolization processes are also playing an important role in the final dehydration stages of the reaction sequence.

Examination of the rate of the initial condensation step reveals that there is a rather small dependence upon the nature of the aromatic substituent.[10] Much more significant is the observation that it would have been very easy to observe an apparent non-linear ρ–σ correlation in the present instance. If the present condensation reaction had been studied in anhydrous solutions with the concentration of methyl ethyl ketone less than 0.1 molar, simple bimolecular kinetics (apart from acidity dependence) would have been observed, the rate constants calculated. In the case of anisaldehyde and p-nitrobenzaldehyde, these rate constants would have been equal to k_1^0. However, in the case of benzaldehyde the rate constant would have been equal to $k_1^0 X^*$. An attempted correlation of these rates for an apparently simple reaction would then have been observed to deviate markedly from a linear ρ–σ correlation as illustrated by the dotted line in Fig. 2. The true
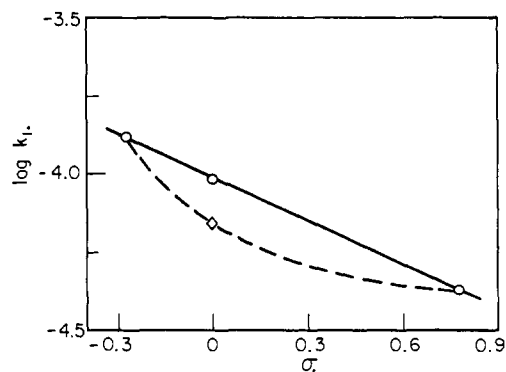

Fig. 2.—Correlation of rates with sigma: − − ◊ − −, uncorrected rates; O——O, corrected rates.

rate constants are presented in this figure and show excellent correlation. This situation represents a type of failure of Hammett's equation which is

(10) D. S. Noyce and W. A. Pryor, THIS JOURNAL, **81**, 618 (1959).

somewhat more subtle than a simple change in mechanism.[11]

Position of Reaction in the Condensation of Aromatic Aldehydes with Methyl Ethyl Ketone.— It has been pointed out that the kinetic results observed are inconsistent with the formation of any

(11) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

appreciable amounts of the linear β-hydroxyketone. These results strongly suggest that in acid solution, selectivity enters into the condensation step. The situation in alkaline medium is discussed in the following paper.

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Carbonyl Reactions. IX. The Rate and Mechanism of the Base-catalyzed Condensation of Benzaldehyde and Acetone. Factors Influencing the Structural Course of Condensation of Unsymmetrical Ketones

BY DONALD S. NOYCE AND WILMER L. REED

The rate of condensation of benzaldehyde and acetone has been studied in aqueous sodium hydroxide solution. It is concluded that the reaction is first order in each component and also shows first-order dependence upon the hydroxide ion concentration. The rates of reaction of the intermediate ketol, 4-phenyl-4-hydroxy-2-butanone (I), in alkaline media have been examined; I undergoes two competitive reactions; dehydration to form benzalacetone II, and cleavage to form benzaldehyde and acetone. The base-catalyzed reactions of 4-(p-methoxyphenyl)-4-hydroxy-2-butanone (III) and 4-(p-methoxyphenyl)-4-hydroxy-3-methyl-2-butanone (V) have also been examined; III likewise undergoes competitive dehydration and cleavage; V is rapidly and completely cleaved by base to give anisaldehyde and methyl ethyl ketone. Consideration of the results supports the conclusion that the structurally definitive process in the acid-catalyzed reaction is the condensation step, but that dehydration of the intermediate ketol is the structurally determining process in the base-catalyzed reaction involving methyl ethyl ketone.

Introduction

In recent papers[1-5] we have pointed out the important kinetic role of β-hydroxyketones in the acid-catalyzed aldol condensation. It is the purpose of the present report to examine the base-catalyzed condensation reaction and the behavior of β-hydroxyketones in basic solution.

The base-catalyzed condensation of benzaldehyde and acetone has been studied by Nikitin[6] and by Gettler and Hammett[7] utilizing different methods of measuring the rate. Nikitin found the reaction to be second order with respect to benzaldehyde in the presence of excess acetone and first order with respect to acetone in excess benzaldehyde. The order in base was not determined. The description of the method leads one to consider that the colorimetric determination was involved with the benzopyrylium salts of the type studied by Wizinger.[8]

Gettler and Hammett found the reaction to be first order in benzaldehyde and acetone with an apparent half-order dependence on the sodium hydroxide concentration in the 70% aqueous dioxane solvent system employed.

We have shown[5] that the ketol 4-phenyl-4-hydroxy-2-butanone (I) is an intermediate in the base-catalyzed condensation reaction. In aqueous sulfuric acid solution I dehydrates to yield 4-

phenyl-3-buten-2-one (II) (benzalacetone). However, in aqueous sodium hydroxide solution we have found that I undergoes competitive reactions, one leading to the formation of II and the second resulting in cleavage to form benzaldehyde and acetone. The product II is unstable in aqueous sodium hydroxide and cleaves slowly to benzaldehyde and acetone. We are thus dealing with an equilibrium process analogous to the acetone–diacetone alcohol–mesityl oxide equilibrium studied by Koelichen,[9] La Mer and Miller,[10] and Brewer.[11]

Experimental

Preparation of Materials.—The preparation of 4-phenyl-4-hydroxy-2-butanone (I), 4-phenyl-3-buten-2-one (II), 4-(p-methoxyphenyl)-4-hydroxy-2-butanone (III) and 4-(p-methoxyphenyl)-3-buten-2-one (IV), has been described previously.[5] 4-(p-Methoxyphenyl)-3-methyl-3-buten-2-one (VI) was prepared by the method of Woodruff and Conger,[12] m.p. 28°. Benzaldehyde was purified by the method of Noyce and Pryor.[1]

Preparation of 4-(p-Methoxyphenyl)-4-hydroxy-3-methyl-2-butanone.—A mixture of 11.2 g. of freshly distilled anisaldehyde and 200 ml. of methyl ethyl ketone was cooled to 0° and 10 ml. of 1 M NaOH was added. The reaction mixture was maintained between 0 and −5° for three hours with stirring and then neutralized with dilute H_2SO_4. The organic material was extracted with ether, the extract concentrated and dried by addition of benzene and distillation of the water azeotrope. The excess anisaldehyde was removed by distillation at reduced pressure. The material remaining was indicated to be mainly ketol by the infrared spectrum. Attempts to achieve crystallization failed.[13]

(1) D. S. Noyce and W. A. Pryor, THIS JOURNAL, **77**, 1397 (1955).

(2) D. S. Noyce, W. A. Pryor and A. T. Bottini, *ibid.*, **77**, 1402 (1955).

(3) D. S. Noyce and L. R. Snyder, *ibid.*, **80**, 4033 (1958).

(4) D. S. Noyce and L. R. Snyder, *ibid.*, **80**, 4324 (1958).

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