TABLE II

ANALYTICAL DATA FOR POLYMERS

Polymer	Formula	Calcd.			Found			Infrared Maxima, cm.$^{-1}$
		C	H	N	C	H	N	
IIc	$(C_{18}H_{18})_n$	92.38	7.62	—	89.20	7.52	—	765, 725, 672[a]
IVa	$(C_{22}H_{28}O_2)_n$	81.95	8.07	—	82.09	8.33	—	1695, 905, 732[b]
IVb	$(C_{25}H_{32}O_2)_n$	82.63	8.86	—	81.01	8.81	—	1694, 903, 730[b]
IVc	$(C_{24}H_{22}O_2)_n$	84.20	6.48	—	83.80	6.55	—	1678, 916, 730[b]
Va	$(C_{30}H_{38}N_2O_4)_n$	73.44	7.81	5.71	—	—	5.76	1770, 1695, 722[c]
Vb	$(C_{33}H_{44}N_2O_4)_n$	74.40	8.33	5.50	73.40	8.44	5.95	1770, 1702, 724[c]
Vc	$(C_{32}H_{34}N_2O_4)_n$	75.27	6.12	5.48	74.84	6.44	5.02	1765, 1700, 724[c]

[a] Present in the spectrum of dicyclopentadiene. [b] The infrared spectrum of 1,4,4a,5,8,8a,9a,10a-octahydro-1,4,5,8-dimethano-9,10-anthraquinone,[11,12] shows maxima at 1693 (C=O str.), 912 and 729 cm.$^{-1}$ (=CH wag norbornene). [c] Compare to the infrared spectrum of *N,N'*-hexamethylenebis(3,6-endomethylene-Δ^4-tetrahydrophthalimide).

A 50:1 molar ratio of acetic anhydride solvent to *N,N'*-hexamethylenebismaleamic acid and a quantity of sodium acetate which corresponded to 10% of the molar amount of acetic anhydride, was employed in the conversion of *N,N'*-hexamethylenebismaleamic acid to *N,N'*-hexamethylenebismaleimide. From 25 g. (0.08 mole) of the maleamic acid was obtained 6.7 g. (30%) of the bismaleimide after two recrystallizations, m.p. 140–141°, reported[16] 139–140°.

N,N'-Hexamethylenebis(3,6-endomethylene-Δ^4-tetrahydrophthalimide). A solution of 1 g. (0.0036 mole) of *N,N'*-hexamethylenebismaleimide in 35 ml. of tetrahydrofuran was added to 0.52 g. (0.0079 mole) of freshly cracked cyclopentadiene. The mixture was allowed to remain at 25° for 24 hr., after which time the solvent was removed under reduced pressure leaving a solid residue. The residue was recrystallized twice from a methanol-water mixture to yield 0.50 g. (40%) of white needles, m.p. 133–134°.

Anal. Calcd. for $C_{24}H_{28}O_4N_2$: C, 70.57; H, 6.90; N, 6.85. Found: C, 70.07; 6.84; N, 6.79.

The infrared spectrum showed maxima at 3050 (=CH str.), 2940 and 2855 (—CH str.), 1765 and 1695 (imide C=O str.), 842 and 720 cm.$^{-1}$ (=CH wag).

Homopolymerization of Ia–c. In all homopolymerization reactions, *N*-phenyl-β-naphthylamine was added as a free radical inhibitor. Polymerizations in bulk carried out at temperatures from 10° to 140° afforded only insoluble rubbery to hard thermosetting polymers.

Solution polymerizations of Ia and Ib which were carried out in refluxing aromatic solvents gave only low molecular weight oils IIa, IIb (Table I) which were soluble in benzene, carbon tetrachloride and carbon disulfide. The infrared spectra of these polymers showed maxima at 724 cm.$^{-1}$.

Solution polymerizations of Ic carried out in benzene gave a solid polymer IIc (Table I) which was purified by reprecipitation from benzene by methanol. Exposure of the polymer to air for a few hours produced an insoluble polymer. Analytical data on IIc are shown in Table II.

Copolymerization of Ia–c. The results of the copolymers of Ia–c with *p*-benzoquinone and *N,N'*-hexamethylenebismaleimide are shown in Table I. The analyses of these polymers are given in Table II. In each case 0.01 mole of *p*-benzoquinone or *N,N'*-hexamethylenebismaleimide was dissolved in 25 ml. of solvent. To this solution was added a solution of 0.01 mole of Ia, Ib, or Ic in 25 ml. of solvent. In the case of polymers Va–c, a small amount of *N*-phenyl-β-naphthylamine was added as a free radical inhibitor. The polymers were precipitated twice from benzene by methanol or pentane and subjected to freeze drying from a benzene solution.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Reaction Rates by Distillation. IX. The Condensation of Anilines with Benzaldehydes

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Received April 7, 1961

The acid-catalyzed condensation of aniline with benzaldehyde in benzene containing tributylamine as a "leveller" has been found to be first order with respect to each reactant and the catalyst. Electron-releasing *para* substituents decrease the rate when on the benzaldehyde and increase the rate when on the aniline; a satisfactory "rho-sigma" correlation is obtained in each case. The results are consistent with a mechanism closely analogous to those favored for related reactions.

The reaction of anilines with benzaldehydes has been studied by the distillation method[2] because of the significance of the reaction itself as well as the potential value of the results in elucidating the course of the related condensation of anilines with benzoins.[3]

$$p\text{-}RC_6H_4CHO + p\text{-}R'C_6H_4NH_2 \longrightarrow p\text{-}RC_6H_4CHOHNHC_6H_4R'\text{-}p \quad (1)$$

$$p\text{-}RC_6H_4CHOHNHC_6H_4R'\text{-}p \longrightarrow p\text{-}RC_6H_4CH{=}NC_6H_4R'\text{-}p + H_2O \quad (2)$$

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[1] From a portion of the Ph.D. thesis of M. J. Kamlet, March, 1954.

[2] For the preceding paper in this series see E. F. Pratt and H. J. E. Segrave, *J. Am. Chem. Soc.*, 81, 5369 (1959).

[3] E. F. Pratt and M. J. Kamlet, to be published.

In Table I are summarized the results obtained when the concentration of the catalyst, the aniline, and the benzaldehyde were independently varied. The tributylamine was added to the reaction mixture to minimize any changes in basicity as reaction progressed and to decrease its rate. The data tabulated for the first five experiments show that the reaction is first order with respect to the catalyst and the aniline.

TABLE I

REACTION OF BENZALDEHYDE WITH ANILINE

Standard conditions: 0.25 mole of benzaldehyde, 0.25 mole of aniline, 0.0005 mole of catalyst, and 0.25 mole of tributylamine with benzene to give 500 ml.

Variable	t 50%, Min.[a]	$k \times 10^3$, L./Mole^{-1}/Min.$^{-1}$
Standard conditions	530	4.18 ± 0.05
Half std. amt. PTS[b]	990	2.16 ± 0.03
Double std. amt. PTS[b]	296	7.96 ± 0.07
Double std. amt. $C_6H_5NH_2$	219	3.97 ± 0.04
Triple std. amt. $C_6H_5NH_2$	142	3.95 ± 0.01
Double std. amt. C_6H_5CHO	332	2.68 ± 0.09
0.250[c] mole C_6H_5CHO	305	15.2 ± 0.3
0.375[c] mole C_6H_5CHO	184	14.2 ± 0.1
0.500[c] mole C_6H_5CHO	135	13.5 ± 0.1

[a] This is the time required for a 50% yield of water to collect. [b] *p*-Toluenesulfonic acid. [c] These three experiments are based on the standard conditions given for Table II.

When the benzaldehyde concentration was doubled (sixth experiment) the rate constant decreased to a significant extent. If this decrease is the result of medium effects, it should be possible to minimize it by employing more dilute solutions. The results for the last three experiments, carried out at higher dilution, show only a small decrease in rate constant with increasing amounts of benzaldehyde and indicate the reaction is also first order with respect to this reactant. First order dependence on the benzaldehyde and the aniline is of course implicit in the fact that the rate constants, calculated on the assumption of such dependence, at successive stages of reaction showed no serious drift.

The effects on the rate of varying the *para* substituent in each reactant independently are summarized in Table II. It is pertinent to note that all the reactions of Tables I and II proceeded smoothly and completely since the mean yield of water was 99.4 ± 1.1%. The four representative benzalanilines isolated were obtained in 81 to 85% yields. As the electron releasing ability of the substituent on the aniline was decreased a ten-fold over-all decrease in rate occurred while a similar change on the benzaldehyde produced a six-fold increase in rate. These results gave a quantitative "rho-sigma" correlation as shown in Fig. 1. The value of rho for the reaction of substituted anilines with benzaldehyde is −2.004 while for the reaction of substituted benzaldehydes with aniline its value is 1.539.

TABLE II

EFFECT OF CHANGING THE *para* SUBSTITUENTS

Standard conditions: 0.25 mole of the aldehyde, 0.25 mole of the aniline, 0.004 mole of catalyst, 0.50 mole of tributylamine with benzene to give 1 l.

Substituent	t 50%, Min.	$k \times 10^3$, L./Mole^{-1}/Min.$^{-1}$
Benzaldehyde and *para*-substituted anilines		
CH_3O	85	55.2 ± 0.6
CH_3	148	31.9 ± 0.4
H	305	15.2 ± 0.3
Cl	860	5.44 ± 0.08
Aniline and *para*-substituted benzaldehydes		
CH_3O	750	6.45 ± 0.08
$(CH_3)_2CH$	464	10.3 ± 0.1
H	305	15.2 ± 0.3
Cl	119	39.1 ± 0.3

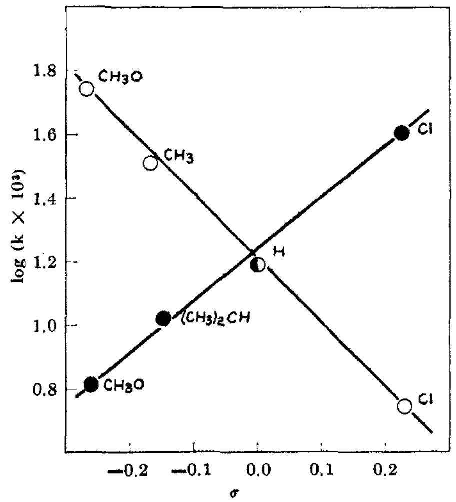
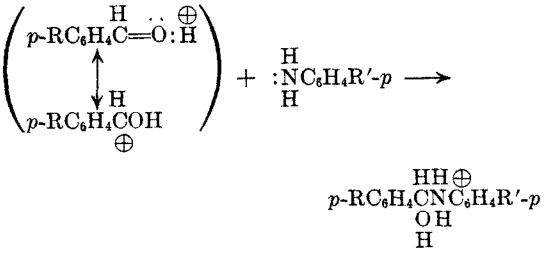


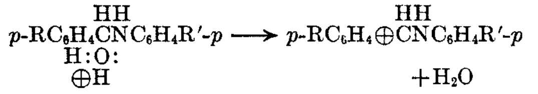
Fig. 1. Plots of log ($k \times 10^3$) for the reaction of benzaldehydes with *para*-substituted anilines, ○, and of aniline with *para*-substituted benzaldehydes, ●, versus Hammett's *sigma* constants

All the results are consistent with the suggestion that the rate-controlling step is that part of reaction (1) symbolized in (3). The literature contains many closely related mechanisms for additions to carbonyl groups. Electron release by R would be expected to decrease the rate and electron release by R′ would be expected to increase the rate as was found. It is reasonable to consider that the catalyst protonates the benzaldehyde[4] in a rapidly attained equilibrium and electron release by R does not increase the equilibrium concentration of the protonated aldehyde sufficiently to overcome the effect of its decreased reactivity. It seems clear that reaction



$$\left(\begin{array}{c} p\text{-RC}_6\text{H}_4\overset{\text{H}}{\text{C}}{=}\overset{..}{\text{O}}{:}\overset{\oplus}{\text{H}} \\ \updownarrow \\ p\text{-RC}_6\text{H}_4\overset{\text{H}}{\underset{\oplus}{\text{C}}}\text{OH} \end{array}\right) + {:}\overset{\text{H}}{\underset{\text{H}}{\text{N}}}\text{C}_6\text{H}_4\text{R}'\text{-}p \longrightarrow p\text{-RC}_6\text{H}_4\overset{\text{H}}{\underset{\underset{\text{H}}{\text{O}}}{\text{C}}}\overset{\text{H}\oplus}{\underset{\text{H}}{\text{N}}}\text{C}_6\text{H}_4\text{R}'\text{-}p \qquad (3)$$

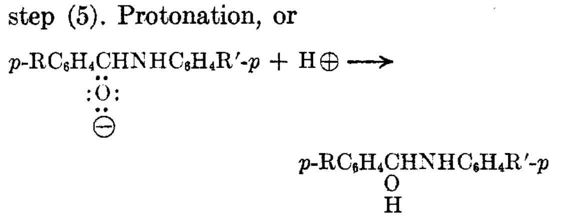
(2) proceeds too fast to influence the overall rate since, by analogy with numerous related processes, its rate-controlling step would be (4) and electron release by R would, in



$$p\text{-}\mathrm{RC_6H_4}\underset{\substack{\mathrm{H{:}O{:}}\\ \oplus\mathrm{H}}}{\overset{\mathrm{HH}}{\mathrm{CN}}}\mathrm{C_6H_4R'}\text{-}p \longrightarrow p\text{-}\mathrm{RC_6H_4}\oplus\overset{\mathrm{HH}}{\mathrm{CN}}\mathrm{C_6H_4R'}\text{-}p + \mathrm{H_2O} \qquad (4)$$

contrast to the experimental findings, increase the over-all rate.

In an alternative route, not excluded by the results, the benzaldehyde and aniline would interact rapidly, and reversibly to give the complex which then must react with acid in the rate controlling[5] step (5). Protonation, or



$$p\text{-}\mathrm{RC_6H_4}\underset{\substack{:\ddot{\mathrm{O}}:\\ \ominus}}{\mathrm{CH}}\mathrm{NHC_6H_4R'}\text{-}p + \mathrm{H}\oplus \longrightarrow p\text{-}\mathrm{RC_6H_4}\underset{\substack{\mathrm{O}\\ \mathrm{H}}}{\mathrm{CH}}\mathrm{NHC_6H_4R'}\text{-}p \qquad (5)$$

interaction with un-ionized acid,[4] however, would seem to be an improbable rate-controlling process even at low concentrations of the complex.

In the most closely related work of which we are aware[6] the condensation of butylamine with benzaldehydes in methanol was studied. For the uncatalyzed reaction a maximum was found in the "rho-sigma" type plot near the point corresponding to benzaldehyde. It is of interest to note the not unexpected similarity of results of a study of the condensation of anilines with nitrosobenzenes in acetate-buffered 94% ethanol[7] with those reported here for the condensation of anilines with benzaldehydes.

EXPERIMENTAL

Starting materials. The *p*-toluenesulfonic acid monohydrate used as the catalyst was Eastman's white label grade and was used as obtained, as it had been found to have close to the calculated neutralization equivalent. All other constituents of the reaction mixtures were purified by standard methods until their melting points or refractive indices agreed closely with the literature values.

Experiments of Table I. A 500-ml. volumetric flask was filled to the mark with benzene and a volume withdrawn equal in milliliters to the total number of grams of reactants and tributylamine. The 0.250 mole of tributylamine and the desired amount of aniline were placed in a 1-l. three necked round bottomed flask; one neck held a thermometer well containing a recalibrated thermometer, one held a glass stopper, and the third a Dean-Stark water collector (5-ml. capacity and calibrated to 0.1 ml.) surmounted by a West condenser. About 0.3 ml. of water was placed in the water collector, the remainder of which was filled with benzene. All joints were ground glass. After adding the bulk of the benzene, the air was replaced by nitrogen by repeatedly reducing the pressure and restoring it to normal by admitting nitrogen; a very slight nitrogen pressure was maintained throughout the reaction. Heat was applied with a hemispherical mantle and the 0.0005 mole of catalyst added at about 50°. The reaction mixture was heated under reflux about 15 min. until the trace of water in the catalyst had collected in the trap and the benzaldehyde, freshly distilled under nitrogen, was then added. The benzaldehyde was distilled and the reactions were carried out in a nitrogen atmosphere to minimize oxidation of the aldehyde to benzoic acid; when the benzaldehyde was not freshly distilled, considerably increased reaction rates were obtained. Heating was continued at a rate just insufficient to flood the condenser until there was no further evolution of water over a 2-hr. period. Frequent readings of the water volume and temperature were taken.

The temperature tended to increase 0.2 to 0.4° over the 10 to 60% portion of the reaction for which rate constants were calculated. Proceeding downward in Table I, the median temperatures were 85.3, 85.4, 84.9, 87.1, 88.0, 87.8, 83.5, 84.0, and 84.5°. It is apparent that increasing the amount of aniline or benzaldehyde tended to increase the temperature and that doubling the volume of reaction mixture for the last three experiments slightly decreased the temperature. The average total yield of water was 99.6%.

When an experiment with no tributylamine, but otherwise identical with the first one tabulated, was carried out, an 80% yield of water collected in less than 10 min.

Experiments of Table II. The modifications of the standard procedure just given for the experiments of Table I in order to give the standard conditions described at the top of Table II are readily apparent. The volume of benzene was doubled in order to decrease the medium effects of the benzaldehyde as noted in the discussion above. As it was felt advisable to maintain the same concentration of the tributylamine "leveller," the amount of catalyst was increased in order to restore a convenient rate.

In the experiments of Table II the temperature tended to rise about 0.2° over the 10 to 60% portion of the reaction. The median temperatures proceeding downward in the table were 83.6, 83.6, 83.5, 83.6, 83.5, 83.7, 83.5, and 83.8°. The average yield of water was 99.0%.

The rate constants for both Tables were calculated on the assumption the reactions were first order with respect to the aniline and the benzaldehyde. Allowance was made for the fact that 500- and 1000-ml. volumes of the benzene solution at room temperature expand to 531 and 1062 ml. at the reflux temperature. In a given experiment successive rate constants were calculated from the time and water volume data at 10 and 20% reaction then from the data at 10 and 30% reaction, and so on, to and including the data at 10 and 60% reaction. Beyond 60% reaction the calculated values showed significant drifts. The tabulated rate constants are the arithmetic mean of the five separate values plus or minus the average deviation of a single value from this mean.

Isolation of products. The products from the first, third, fifth and eighth experiments of Table II were selected as representative and isolated so as to minimize hydrolysis. The well cooled reaction mixture was rapidly washed six times with 100-ml. portions of cold 30% acetic acid and then three times with 100-ml. portions of water. Removal of the solvent by distillation, using reduced pressure for the final stages, gave a viscous liquid which was dissolved in 50 ml. of 80% ethanol. All of the products crystallized in 81 to 85% yields when the solution was allowed to stand in the refrigerator. The tan to yellow platelets melted within 3° of the literature values.

COLLEGE PARK, MD.

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(4) In these benzene solutions hydrogen bonding with un-ionized *p*-toluenesulfonic acid may occur in place of simple protonation.

(5) An entirely analogous mechanism for semicarbazone formation has been suggested by Hine, *Physical Organic Chemistry*, McGraw-Hill, New York, 1956, p. 246.

(6) G. M. Santerre, C. J. Hansrote, Jr., and T. I. Crowell, *J. Am. Chem. Soc.*, **80**, 1254 (1958).

(7) Y. Ogata and Y. Takagi, *J. Am. Chem. Soc.*, **80**, 3591 (1958).