

and dried *in vacuo*. It was then extracted for 24 hr. with 500 ml. of anhydrous ether in a Soxhlet apparatus.<sup>24</sup> The ether-insoluble material in the thimble was then extracted for 48 hr. with 500 ml. of 95% ethanol. Pure 2,8-dimethylphenothiophosphinic acid crystallized from the alcoholic solution, and a second crop could be obtained by evaporating the mother liquor to incipient crystallization. The yield was 6.90 g. (25%), m.p. >300°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>PS: P, 11.21; S, 11.60; neut. equiv., 276.3. Found: P, 11.13; S, 11.80; neut. equiv. 279.1.

**2,8-Dimethyl-5,5-dioxophenothiophosphinic Acid.**—When a suspension of 1.05 g. of 2,8-dimethylphenothiophosphinic acid in 20 ml. of boiling glacial acetic acid was treated with 3.0 ml. of 30% hydrogen peroxide, virtually all the solid went into solution and soon a voluminous precipitate separated. The reaction

(24) This step served to remove an oily material which was not identified.

mixture was then allowed to sit on a steam bath for 2 hr. and finally cooled. The precipitate was removed by filtration and washed with copious quantities of water. The yield was 1.02 g. (87%), m.p. >300°. The infrared absorption spectrum in potassium bromide exhibited strong maxima at 1158 and 1315 cm.<sup>-1</sup>, which were assigned to the symmetric and asymmetric stretching modes of the SO<sub>2</sub> group.<sup>25</sup> These bands were absent in the parent sulfide.

*Anal.* Calcd. for C<sub>14</sub>H<sub>18</sub>O<sub>4</sub>PS: C, 54.54; H, 4.25. Found: C, 54.39; H, 4.29.

**Acknowledgment.**—The authors wish to acknowledge the invaluable technical assistance given by Mrs. Joyce Edmisten Carevic.

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## Kinetics of the Reaction of Aromatic Aldehydes with Ammonia

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The kinetics of the reaction of aromatic aldehydes with ammonia to form hydrobenzamides have been studied spectrophotometrically in methanol at 30°. The reaction is first order with respect to aldehyde and first order with ammonia. The effect of water, potassium hydroxide, and temperature on the rate has been studied. The application of Hammett's law to the rates gives a positive  $\rho$ -value for the reaction of aldehydes with electron-releasing substituents and a negative  $\rho$ -value with electron-withdrawing substituents. Induction periods were observed in the formation of hydrobenzamides with electron-withdrawing substituents. These results suggest a probable mechanism involving  $\alpha$ -aminobenzyl alcohol and benzylideneimine, etc.

The reaction of benzaldehydes with ammonia gives hydrobenzamides, ArCH=NCH(Ar)N=CHAR. Dobler has observed the rate of the reaction by means of acidimetry to be second order.<sup>1</sup> He observed no systematic substituent effect. The analogous condensation of aromatic aldehydes with *n*-butylamine,<sup>2</sup> semicarbazide,<sup>3,4</sup> or anilines<sup>5</sup> has been studied, Hammett's rule not being applicable for the benzylideneimine or semicarbazone formation. Some investigators have reported that the reaction of benzaldehyde with ammonia also produces benzylideneimine,<sup>6,7</sup> NH=CHPh;  $\alpha, \alpha'$ -dioxidibenzylamine,<sup>8</sup> NH(CH(OH)Ph)<sub>2</sub>; and 2,4,6-triphenyl-1,3,5-hexahydrotriazine,<sup>9</sup> (—NH—CH—Ph—)<sub>3</sub>. The present paper summarizes our data on the kinetic investigation of the reaction involving the effect of basicity of the solution, the effect of substituents, and a probable mechanism derived from the results. Since acidimetry gave no accurate rates of reaction, we employed spectrophotometry.

### Experimental

**Materials.**—Commercial benzaldehyde, b.p. 78.8° (26 mm.), and *p*-anisaldehyde, b.p. 159.0° (44 mm.), were purified by vacuum distillation under nitrogen. *p*-Chlorobenzaldehyde, m.p. 46.5–47.5°, and *p*-cyanobenzaldehyde, m.p. 101–102°, were prepared by the chromic acid oxidation of *p*-chlorotoluene and

*p*-tolunitrile,<sup>10</sup> respectively. Commercial methanol was purified by distillations and used as the solvent. Aqueous ammonia was of guaranteed reagent grade. Methanolic ammonia free of water was prepared by passing ammonia gas, dried with sodium hydroxide, into methanol dried by boiling with magnesium.

**Products.**—Hydrobenzamides were prepared by the reaction of concentrated aqueous ammonia and aldehydes in methanol, the resulting precipitates being recrystallized from methanolic ammonia: hydrobenzamide, m.p. 100–101° (lit.<sup>11</sup> m.p. 102°); hydroanisamide, m.p. 128.5–130.5 (lit.<sup>12</sup> m.p. 130°); 4,4',4''-trichlorohydrobenzamide, m.p. 87–90°; 4,4',4''-tricyanohydrobenzamide, m.p. 130–132°. Infrared spectra<sup>13</sup> of these products showed the C=N band at 1632–1636 cm.<sup>-1</sup>, but no absorption corresponding to the C=O, =NH, or —OH band was observed. 4,4',4''-Trichlorohydrobenzamide and 4,4',4''-tricyanohydrobenzamide are new compounds.

*Anal.* Calcd. for C<sub>21</sub>H<sub>15</sub>Cl<sub>3</sub>N<sub>2</sub>: C, 62.78; H, 3.76; N, 6.97. Found: C, 62.73; H, 3.87; N, 6.87.

*Anal.* Calcd. for C<sub>24</sub>H<sub>15</sub>N<sub>5</sub>: C, 77.20; H, 4.05; N, 18.76. Found: C, 77.62; H, 4.10; N, 18.18.

**Rate Measurements.**—For the determination of the concentrations of benzaldehyde [B] and hydrobenzamide [H], two wave lengths of benzaldehyde at 245 (absorption max.) and 270 m $\mu$  (absorption min.) were selected. Their concentrations were determined by ultraviolet spectrophotometry for binary mixtures.<sup>14</sup> The values of the molar extinction coefficient were determined experimentally: for benzaldehyde,  $\epsilon_{\max}$  1.319  $\times$  10<sup>4</sup> (lit.<sup>15</sup>  $\epsilon_{240 \text{ m}\mu}$  1.32  $\times$  10<sup>4</sup>),  $\epsilon_{\min}$  1.098  $\times$  10<sup>3</sup>; for hydrobenzamide,  $\epsilon_{\max}$  2.800  $\times$  10<sup>4</sup>,  $\epsilon_{\min}$  1.016  $\times$  10<sup>4</sup>. The absorption of the product, hydrobenzamide, could be determined by converting the remaining benzaldehyde into acetal with a drop of sulfuric acid in methanol. The spectrum of hydrobenzamide ( $\lambda_{\max}$  251 m $\mu$ ) showed a bathochromic shift ( $\lambda_{\max}$  281 m $\mu$ ) by addition of sulfuric acid. A methanolic solution of hydrobenzamide was stable at room temperature. Since the decomposition of hydrobenzamide

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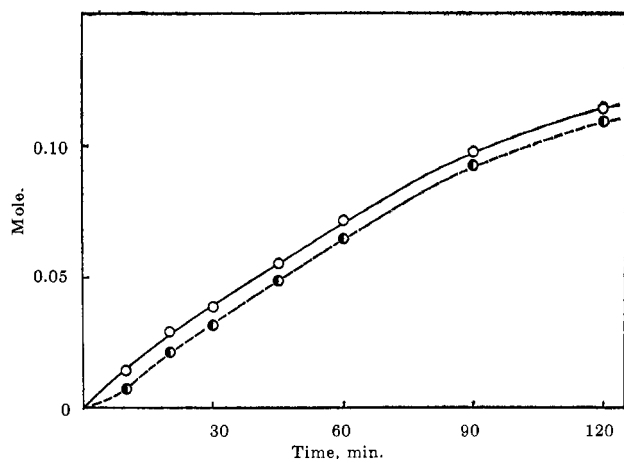


Fig. 1.—The comparison of the consumption of benzaldehyde and the formation of hydrobenzamide,  $[\text{NH}_3]_0 = 0.488 M$ ,  $[\text{PhCHO}]_0 = 0.255 M$ , at  $30^\circ$ : O, benzaldehyde consumed; ●, benzaldehyde converted to hydrobenzamide.

was negligible within a minute after the addition of sulfuric acid, the absorbances were measured at just 1 min. after the addition. Then the rate of the formation of hydrobenzamide was measurable. The rate constants by both methods were identical within experimental error with unsubstituted benzaldehyde. The rates with other substituted benzaldehydes were estimated by the latter method. Absorption maxima of substituted hydrobenzamides were as follows: *p*-MeO, 320; *p*-Cl, 295; and *p*-CN, 270  $m\mu$ . The rate constants,  $k_2$ , with *p*-chloro- and *p*-cyano-benzaldehyde were calculated by eliminating their induction periods, which were obtained by the extrapolation of plots of the concentration of formed hydrobenzamides *vs.* time to zero concentration.

The typical experiment for the rate measurements was as follows: 0.450 *M* benzaldehyde (25 ml.) in methanol and 0.976 *M* methanolic ammonia (25 ml.) which had previously attained thermal equilibrium were mixed in a 100-ml. thermostated flask kept at  $30.0 \pm 0.1^\circ$ . Aliquots were periodically withdrawn and diluted with methanol by a factor of  $1.6 \times 10^3$ . Then their absorbances at 245 and 270  $m\mu$  were determined by Shimadzu automatic spectrophotometer SV 50 A at room temperature. Infrared spectra were measured by Shimadzu spectrophotometer IR-27 B.

## Results and Discussion

**Rate Law.**—The reaction was found to be second order and satisfied the rate equation that follows.

$$v = \frac{dx}{dt} = k_2(a - \frac{2}{3}x)(b - x) \quad (1)$$

or

$$k_2 = \frac{1}{t} \frac{2.303}{\left(a - \frac{2}{3}b\right)} \left( \log \frac{a - \frac{2}{3}x}{b - x} - \log \frac{a}{b} \right) \quad (2)$$

Here,  $a$  and  $b$  are the initial concentrations of ammonia and benzaldehyde, respectively,  $x$  the concentration of consumed benzaldehyde at time  $t$ , and  $k_2$  the apparent second-order rate constant. Typical rate data are shown in Table I. The rate constant tended to decrease very slightly with increasing initial molar ratio of ammonia *vs.* benzaldehyde (Table II). As the reaction proceeds, the molar ratio with an excess of ammonia increases and hence the rate constants decrease very slightly at the end of the reaction. If the reactants are converted completely to the product,  $x$  moles of consumed benzaldehyde should yield  $x/3$  moles of hydrobenzamide according to the following stoichiometric equation.

TABLE I  
TYPICAL RATE DATA FOR THE REACTION OF BENZALDEHYDE AND AMMONIA AT  $30^\circ$ <sup>a</sup>

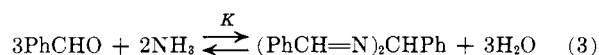
Time, sec.	[PhCHO] <i>M</i>	Conversion, %	$k_2 \times 10^4$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
0	0.225	0	
610	0.211	6.2	2.16
1225	0.196	12.8	2.34
1810	0.187	17.0	2.15
2710	0.170	24.4	2.19
3610	0.154	31.6	2.29
5400	0.128	43.1	2.31
7200	0.112	50.3	2.19

Av.  $2.23 \pm 0.02$

<sup>a</sup> Initial concentration: ammonia, 0.488 *M*; benzaldehyde, 0.225 *M*.

TABLE II  
THE EFFECT OF THE INITIAL MOLAR RATIO OF AMMONIA *vs.* BENZALDEHYDE ON THE SECOND-ORDER RATE CONSTANT AT  $30^\circ$

Initial concn. of benzaldehyde, [PhCHO] <sub>0</sub> , <i>M</i>	Initial concn. of ammonia, [NH <sub>3</sub> ] <sub>0</sub> , <i>M</i>	$\frac{[\text{NH}_3]_0}{[\text{PhCHO}]_0}$	$k_2 \times 10^4$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
0.0480	0.489	10.2	1.42
0.0968	0.744	7.7	1.68
0.0956	0.489	5.1	1.65
0.0927	0.360	3.9	1.89
0.143	0.489	3.4	1.86
0.0913	0.247	2.7	2.06
0.0887	0.196	2.2	2.06
0.225	0.488	2.2	2.23
0.142	0.251	1.8	2.46
0.105	0.148	1.4	2.54
0.179	0.239	1.3	2.24
0.252	0.251	1.0	2.37
0.292	0.201	0.7	2.84



However, consumed benzaldehyde was not quantitatively converted to hydrobenzamide, as shown in Fig. 1, which suggested that a very small but constant amount of benzaldehyde existed as some intermediates during the reaction. The difference in the curves of Fig. 1 is more than the experimental error on the basis of several experiments. The difference is more obvious at a very early stage of the reaction. This effect was so small with benzaldehyde that the rate constant obtained by the estimation of the product ( $1.91 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>) and that of the reactant ( $1.83 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>) agreed. However, an induction period was observed with benzaldehydes having electron-withdrawing substituents, as will be stated later.

**The Effect of Addition of Water or Alkali.**—The addition of water retarded the apparent rate and the rate equation deviates from eq. 1. Conversions at 120 min. were as follows (added water in vol. % and conversion in %): 5, 47.5; 10, 43.6; 15, 37.8; 20, 35.2. These facts may be due to the predomination of the decomposition of the product or the reverse reaction of eq. 3. Observed equilibrium constants  $K$  in the presence of various amounts of water held constancy (Table III).

$$K = \frac{[(\text{PhCH=N})_2\text{CHPh}][\text{H}_2\text{O}]^3}{[\text{PhCHO}]^3[\text{NH}_3]^2} \quad (4)$$

In the presence of 20 vol. % of water, hydrobenzamide corresponding to 54% of consumed benzaldehyde was precipitated, hence the observed equilibrium constant

TABLE III  
EFFECTS OF WATER ADDED AT 30°

Initial concn.		[H <sub>2</sub> O], vol. %	Rate constants, $k_2 \times 10^4$ l. mole <sup>-1</sup> sec. <sup>-1</sup>	Equilibrium constants, $K \times 10^{-6}$ l. mole <sup>-1</sup>
[NH <sub>3</sub> ] <sub>0</sub> , M	[PhCHO] <sub>0</sub> , M			
0.494	0.215	5	2.11	1.37
0.494	0.219	10		1.37
0.490	0.224	15		1.24
0.490	0.227	20		2.62 <sup>a</sup>

(1.21)<sup>b</sup>  
Av. 1.30

<sup>a</sup> Hydrobenzamide was precipitated. <sup>b</sup> The value of the calculated equilibrium constant by eliminating the amount of precipitate.

became higher, while the equilibrium constant calculated by eliminating the amount of precipitate of hydrobenzamide agreed with other values.

It is well known that Schiff's base formation is subject to acid catalysis. The data in Table IV show that

TABLE IV  
EFFECT OF POTASSIUM HYDROXIDE AT 30°

Initial concn.			$k_2 \times 10^4$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>	Time, min.	Conversion, %
[NH <sub>3</sub> ] <sub>0</sub> , M	[PhCHO] <sub>0</sub> , M	[KOH] <sub>0</sub> , M			
0.251	0.142	0	2.46	240	60
0.250	0.149	0.152	1.52	240	33
0.252	0.139	0.247	0.94	240	26.7
0.232	0.123	0.280		240	23.2

an increase of concentration of alkali results in retardation of the formation of hydrobenzamide, hence increase in the concentration of intermediates (amino alcohols) and deviation from the above kinetic equation; *i.e.*, the order of the reaction became more than 2. These results may be caused by the suppression of acid catalysis for the dehydration of amino alcohols with added alkali.

**Energy and Entropy of Activation.**—The apparent energy and entropy of activation were calculated to be 9.73 kcal. mole<sup>-1</sup> and -40.3 e.u., respectively, by means of the Arrhenius equation from the rate data:  $k_2 \times 10^4$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, 0.690 at 10°, 2.23 at 30°, 5.13 at 50°. These values can be expected in the analogous reaction, *i.e.*, the reaction of *p*-dimethylamino-benzaldehyde with ammonia (10.9 kcal. mole<sup>-1</sup> -43.7 e.u.)<sup>6</sup>, *p*-chlorobenzaldehyde with *n*-butylamine (7.0 kcal. mole<sup>-1</sup>, -41.3 e.u.)<sup>2</sup> or *p*-nitrobenzaldehyde with *n*-butylamine (8.0 kcal. mole<sup>-1</sup>, -33.7 e.u.)<sup>2</sup> These resemblances in energies and entropies of activation suggest that the analogous imine formation and transition state are involved. If the rate-determining step is the addition of ammonia to aldehyde, such a large negative value for entropy of activation is conceivable, since reactions in which the total number of molecules decreases<sup>16</sup> or the reactions involving a strongly polar transition state<sup>17</sup> produced from neutral molecules may be remarkably negative.

**Effect of Substituents in Aldehydes on the Rate.**—A simple Hammett's rule was not applicable to the reaction as shown in Fig. 2. The Hammett's plot

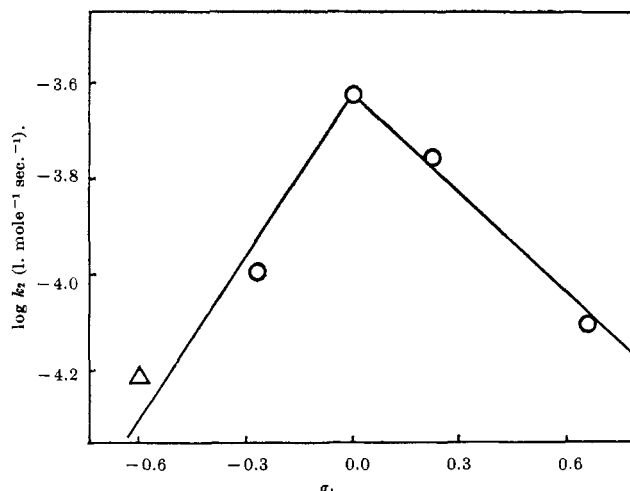


Fig. 2.—Hammett's plot for the reaction of aromatic aldehydes with ammonia:  $\Delta$ , the value was calculated from the data of McLeod and Crowell.<sup>6</sup>

gave a positive  $\rho$ -value (+1.1) for the reaction of aldehydes with electron-releasing groups and a negative  $\rho$ -value (-0.65) with electron-withdrawing groups. Analogous relationships have been observed previously for the reaction of aromatic aldehydes with semicarbazide in 75% ethanol<sup>3</sup> and with *n*-butylamine in methanol.<sup>2</sup> The reaction was followed by the estimation of the rate of the formation of the products. No induction period was observed with an electron-releasing group (OCH<sub>3</sub>), whereas an induction period was observed with electron-withdrawing groups (CN, Cl) as has been reported in the formation of oximes and semicarbazones<sup>18</sup> of aromatic aldehydes.

A 0.8 M *p*-chlorobenzaldehyde solution and a 0.8 M methanolic ammonia solution were mixed at 30°, and the absorption corresponding to carbonyl group (250-260 m $\mu$ ) was measured. The absorption of the aldehyde at 255 m $\mu$  decreased at the start of reaction, and after an interval the absorption of hydrobenzamide at 259 m $\mu$  increased, until it became stronger than that at the start. The same phenomenon was also confirmed by means of infrared spectrum. The carbonyl absorption of *p*-cyanobenzaldehyde at 1702 cm.<sup>-1</sup> decreased at room temperature to 91% of the initial absorbance after 5 min., 86% after 14 min., 80% after 20 min., and 61% after 94 min. The absorption at 1635 cm.<sup>-1</sup> corresponding to C=N did not appear within 20 min., whereas the absorption was appreciable after 94 min. On the contrary, the absorption of unsubstituted hydrobenzamide at 1634 cm.<sup>-1</sup> increased with decreasing absorption at 1697 cm.<sup>-1</sup> in the reaction of benzaldehyde which had no induction period. The second-order rate constant ( $1.90 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>) of the consumption of *p*-cyanobenzaldehyde calculated from the absorption at 1702 cm.<sup>-1</sup> was ca. twice as large as that of benzaldehyde ( $0.83 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>) from 1697 cm.<sup>-1</sup> within 20% conversion under the same conditions. As shown in Fig. 2, the rate constant for the formation of hydrobenzamide was higher than that of 4,4',4''-tricyano-hydrobenzamide. These facts show that electron-withdrawing groups accelerate the rate of the consumption of aldehyde but retard the rate of the formation of

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