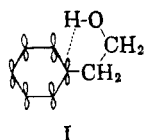the aromatic nucleus in those molecules having the conformation shown:

I

This interesting possibility was confirmed by examining the spectra of p-methoxyphenethyl alcohol (IV) and p-nitrophenethyl alcohol (V): IV showed the expected doublet; V showed only a singlet.[6] Since compounds I to V all showed only one peak in the 1.417 to 1.424 μ region when the spectra were run in *benzene* solution, the peak at longer wave length for each doublet is assigned to the first overtone of the fundamental stretching vibration of the bonded hydroxyl group. The expected doublets were also observed in the spectra of 1,2-diphenyl ethanol (VI) and 1-phenyl-2-propanol (VII). All spectra are recorded in Table I.

TABLE I

ABSORPTION BANDS IN THE 1.4 μ REGION[7]

	0.5% CCl₄ Soln.	Δ[8]	0.5% Benzene Soln.
Phenethyl alcohol (I)	1.4084, 1.4209	0.0125	1.4235
Benzyl alcohol (II)	1.4155		1.4193
3-Phenyl-1-propanol (III)	1.4067		1.4170
p-Methoxyphenethyl alcohol (IV)	1.4085, 1.4223	0.0138	1.4220
p-Nitrophenethyl alcohol (V)	1.4088[9]		1.4220
1,2-Diphenyl ethanol (VI)	1.4161, 1.425[10]		
1-Phenyl-2-Propanol (VII)	1.4129, 1.4229		

That the above spectral data are compatible with the postulated intramolecular hydrogen bonding at the 1-position rather than at the 2,6-positions is shown by comparison of the Δ values above. The order $\Delta_{IV} > \Delta_I$ would be expected on the basis of Hammett's σ constants[11] for interaction at the 1-position. If, on the other hand, the interaction were at the 2,6-positions the reverse order $\Delta_I > \Delta_{IV}$ should have been observed.

(6) The absence of a second peak at longer wave length in the spectrum of V is attributed to the powerful electron-withdrawing ability of the p-nitro group.

(7) Spectra were measured on a Cary recording spectrophotometer, Model 14. Wave lengths, in microns, are accurate to ±0.0003 micron.

(8) Δ = distance in microns between the peaks for I and IV.

(9) 0.15% solution.

(10) Shoulder.

(11) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 188.

Using the value of 70 cm⁻¹ for each kcal/mole of bond energy[12] the strengths of the hydrogen bonds in compounds I and IV are determined to be 0.88 and 0.98 kcal/mole, respectively.

EXPERIMENTAL

The phenethyl alcohol (Dow Chem. Co.) was purified by fractional distillation, n_D^{20} 1.5325 (lit.[13] n_D^{20} 1.5310–1.5330). p-Methoxyphenylacetic acid (Aldrich Chem. Co.), m.p. 86–88° (lit.[14] m.p. 85–87°), was reduced with lithium aluminum hydride to give IV, semicrystalline at 25° (lit.[15] m.p. 24°). Nitration of I according to the published procedure[16] yielded V, m.p. 61.5–62.5° (lit.[16] m.p. 62°). A commercial sample of 1,2-diphenyl ethanol (VI), m.p. 66–67° (Eastman), was used without further purification. 1-Phenyl-2-propanone (Eastman) was reduced with lithium aluminum hydride to give VII, n_D^{20} 1.5217 (lit.[17] $n_D^{14.5}$ 1.5243).

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Carbonyl Reactions. III. The Formation of Aromatic Semicarbazones. A Nonlinear Rho-Sigma Correlation[1]

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The formation of semicarbazones represents one of the important examples of general acid catalysis.[2-4] The effect of structure upon reactivity has been studied by Price and Hammett[3] who point out that the relative entropy of activation fluctuates in a series of aliphatic compounds. Cross and Fugassi[5] have reported a satisfactory Hammett-type correlation for a limited number of p-substituted acetophenones. On the other hand, the report of

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(2) J. B. Conant and P. D. Bartlett, *J. Am. Chem. Soc.*, **54**, 2881 (1932); F. H. Westheimer, *J. Am. Chem. Soc.*, **56**, 1962 (1934).

(3) F. B. Price, Jr., and L. P. Hammett, *J. Am. Chem. Soc.*, **63**, 2387 (1941).

(4) G. H. Stempel and G. S. Schaffel, *J. Am. Chem. Soc.*, **66**, 1158 (1944).

(5) R. P. Cross and P. Fugassi, *J. Am. Chem. Soc.*, **71**, 223 (1949).

Vavon and Montheard[6] indicates that simple rho-sigma correlation may not obtain with aromatic aldehydes in the formation of phenylhydrazones and oximes.

Since the formation of semicarbazones, phenylhydrazones, and oximes almost certainly proceeds by the same general mechanism, and since the details of semicarbazone formation have been the most thoroughly investigated, we have carried out a study of the rate of reaction of a representative series of aromatic aldehydes with semicarbazide.

EXPERIMENTAL

Reagents. The aromatic aldehydes were crystallized or distilled under nitrogen as appropriate. The physical constants were concordant with those in the literature. Other reagents were of reagent grade.

The kinetic runs were carried out in 75% ethanol by volume. Solutions of semicarbazide hydrochloride were made up in 60% ethanol and of 1:1 sodium acetate–acetic acid ($0.04M$) in 75% ethanol. Solutions of the aldehydes were made up in 95% ethanol. The pH of the sodium acetate–acetic acid buffer is calculated to be 6.5 from the data of Grunwald and Berkowitz.[7]

Procedure. One hundred milliliters of the sodium acetate–acetic acid buffer solution was pipetted into a 250-ml. glass stoppered flask, and to this was added 20 ml. of $0.05M$ aldehyde solution. At the start of the reaction 20 ml. of $0.05M$ semicarbazide hydrochloride solution was added, and the mixture made up to volume. The rate of reaction was followed by iodimetric titration, essentially as described by Bartlett.[8] Reactions were followed to better than 50% completion.

RESULTS AND DISCUSSION

The kinetic results are summarized in Table I. It is apparent that, under the conditions of our experiments, a simple linear rho-sigma relationship is not obtained. Such failure has been observed in other situations. The reactions of benzyl nitrate with bromide ion,[9] benzyl fluoride with sodium ethoxide,[10] benzyl chloride with trimethylamine,[11] and the copolymerization of methyl methacrylate with substituted styrenes[12] are examples in which the rho-sigma plots are generally concave upward. In the case of the formation of Schiff's bases from substituted benzaldehydes and butylamine[13] Santerre, Hansrote, and Crowell have observed results

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(11) C. G. Swain and W. P. Langsdorf, Jr., *J. Am. Chem. Soc.,* 73, 2813 (1951).

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(13) G. M. Santerre, C. J. Hansrote, Jr., and T. I. Crowell, *J. Am. Chem. Soc.,* 80, 1254 (1958). We are indebted to Dr. Crowell for informing us of his results prior to publication.

in which the rho-sigma plot is concave downward. Jaffé[14] and Branch and Calvin[15] have also commented on the possible reasons for failure to obtain simple rho-sigma correlations.

TABLE I

RATE OF FORMATION OF SEMICARBAZONES OF SUBSTITUTED BENZALDEHYDES

Substituent	σ^a	k_2 (Liter Mole^{-1} Sec.$^{-1}$) $\times 10^{2b}$
p-(C$_2$H$_5$)$_2$N	−0.600	0.21^c
p-CH$_3$O	−0.268	1.93, 2.10, 1.93^d
p-CH$_3$	−0.170	4.58, 4.57
m-CH$_3$	−0.069	5.76
H	0.000	6.18, 6.02, 6.30, 5.80^d
m-CH$_3$O	0.115	5.23
p-Cl	0.227	5.40, 5.42
m-Cl	0.373	5.00
m-NO$_2$	0.710	3.42, 3.42, 3.25^d
p-NO$_2$	0.778	4.45, 4.32

^{a} Ref. 14, p. 222. ^{b} ± 4% unless otherwise noted. ^{c} ± 8%. ^{d} Followed spectrophotometrically under pseudo first order conditions with semicarbazide in 50-fold excess. Initial aldehyde concentration, $3 \times 10^{-4}M$.

Our view at the present time is that the most likely cause of failure to obtain a linear rho-sigma correlation with substituted benzaldehydes is that the addition and dehydration steps in the reaction sequence[16] have rate constants such that addition and dehydration are comparable.[17] Willi and Robertson[18] have considered the hydrolysis of Schiff bases from this point of view. On this basis it is also explicable that a more straightforward correlation is obtained with ketones; the rate of addition will be slower, and the rate of dehydration appreciably faster, and the rate controlling step is more simply the rate of addition to the carbonyl group.

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(15) G. E. K. Branch and M. Calvin, *The Theory of Organic Chemistry,* Prentice-Hall, Inc., New York, N. Y. (1941), p. 419.

(16) For suggested reaction sequences see L. P. Hammett, *Physical Organic Chemistry,* McGraw-Hill Co., New York, N. Y. (1940), pp. 333–336; and Ref. 4.

(17) By using the steady state approximation it can be shown for the general case

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \overset{k_3}{\longrightarrow} C$$
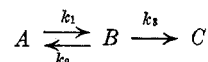
that the observed rate $k_r = k_1 k_3/(k_2 + k_3)$ and that the equation for the relative observed rate is of the form

$$\log (k_r/k_0) = (\rho_1 + \rho_3 - \rho_2)\sigma - \log \left[\frac{1 + \frac{k_3^0}{k_2^0} 10^{(\rho_3 - \rho_2)\sigma}}{1 + \frac{k_3^0}{k_2^0}} \right]$$

This function is not linear in σ, and may be shown to pass through a maximum by successive differentiation.

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