

## Solvatochromic Shifts for Some 4-Nitroaniline and 4-Nitrophenol Derivatives as Measures of Relative Solvent Proton Affinities

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Enhanced red shifts ( $-\Delta\Delta\nu_{\max}$ ) of the [ ${}^+R_2N=C_1\rightarrow C_4=NO_2^-$ ] band in the ultraviolet spectrum for 4-nitroaniline relative to *N,N*-diethyl-4-nitroaniline on going from cyclohexane to oxygen-base solvents are attributable primarily to the bathochromic influence of hydrogen bonding by 4-nitroaniline to these solvents and are considered to be measures of relative solvent-proton affinity. Such  $\Delta\Delta\nu_{\max}$  values show good correlation with  $\sigma^*$  values of R in a series of ROH solvents which includes water. Good correlations between  $-\Delta\Delta\nu_{\max}$  and  $\sigma^*$  values are also obtained from the following pairs: *N*-ethyl-4-nitroaniline/*N,N*-diethyl-4-nitroaniline and 4-nitrophenol/4-nitroanisole. These probes of relative solvent-proton affinity do not, however, show ethers to be better hydrogen-bond acceptors than alcohols, probably because of steric factors.

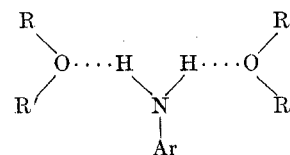
In terms of inductive effects, one would expect ethers to be better proton acceptors than alcohols which, in turn, should show stronger proton affinities than water. However, most indicator and titration studies represent water as being more basic than alcohols and ethers,<sup>1</sup> and among the simple alcohols the basicity order is often reported as antiinductive.<sup>1,2</sup> Indeed, Arnett has argued convincingly that any attempt to establish a single ordering for the oxygen bases toward differing classes of acidic species is likely to be doomed from the start;<sup>1</sup> it is difficult to disagree with this appraisal.

The complications arise from three factors which are liable to outweigh simple proton affinity effects: (a) significant solvent reorganization under the influence of the titrant or indicator; (b) differential solvation of conjugate anions or anionic ends of undissociated acid dipoles; and (c) steric effects. We wish now to report a reasonably sensitive method for the estimation of proton affinities of solvents wherein type a and b effects appear to be minimal.

This new method derives from the following observations, certain of which have been reported earlier.<sup>3,4</sup> The [ ${}^+R_2N=C_1\rightarrow C_4=NO_2^-$ ] bands in the ultraviolet spectra of 4-nitroaniline and its *N*-alkyl and *N,N*-dialkyl derivatives<sup>5</sup> show significant red shifts ( $-\Delta\nu_{\max}$ ) in going from cyclohexane to more polar solvents. Where the more polar solvents are incapable of accepting a hydrogen bond, these spectral displacements are of closely comparable magnitudes for the primary, secondary, and tertiary nitroaromatic amines (*e.g.*,  $-\Delta\nu_{\max} = 0.72 \pm 0.03$  kK on going from cyclohexane to carbon tetrachloride,  $-\Delta\nu_{\max} = 2.57 \pm 0.10$  kK on going to 1,2-dichloroethane for the parent compound and a large variety of *N*-mono and *N,N*-dialkyl derivatives).

This suggests that the bathochromic influences of increased solvent polarity or polarizability are quite similar for the three classes of compounds. It is reasonable, then, that appreciably enhanced red shifts ( $-\Delta\Delta\nu_{\max}$ ) for 4-nitroaniline relative to an *N,N*-dialkyl-4-nitroaniline on going from cyclohexane to oxygen-base solvents should be a consequence pri-

marily of the bathochromic influence<sup>6</sup> of hydrogen bonding by 4-nitroaniline to the solvent, *e.g.*,



which is excluded in the case of the *N,N*-dialkyl derivatives.<sup>7</sup>

A logical next step is that the enhanced red shift in a given solvent should be greater, the greater the strength of the hydrogen bonds by 4-nitroaniline to that solvent. Hence, the magnitudes of  $-\Delta\Delta\nu_{\max}$  values in a variety of solvents provide the basis for our estimating relative solvent proton affinities.

Positions of maximal absorption for the [ ${}^+R_2N=C_1\rightarrow C_4=NO_2^-$ ] bands of 4-nitroaniline and *N,N*-diethyl-4-nitroaniline in cyclohexane, nine alcohols, and water are listed in Table I. Also tabulated are values of the red shifts from cyclohexane to each solvent ( $-\Delta\nu_{\max}$ ), the enhanced bathochromic shifts for the primary relative to the tertiary amine ( $-\Delta\Delta\nu_{\max}$ ), and the Taft  $\sigma^*$  values<sup>8</sup> of R- in ROH. It is seen that the  $-\Delta\Delta\nu_{\max}$  values for the alcohols follow the inductive order, the greater the electron density on oxygen the higher being the  $-\Delta\Delta\nu_{\max}$  value. Very significantly, also, the  $-\Delta\Delta\nu_{\max}$  value for water is near that which would be expected on the basis of the  $\sigma^*$  for R = H.

A plot of  $-\Delta\Delta\nu_{\max}$  vs.  $\sigma^*$  is given in Figure 1. The data show good linear regression and fit the equation

$$-\Delta\Delta\nu_{\max} \text{ (in kK)} = 2.03 - 2.69 \sigma^* \quad (1)$$

with the correlation coefficient,  $r = 0.98$ , and the standard deviation,  $s = 0.14$  kK. By Jaffé's criteria for  $\rho$ - $\sigma$  type relationships, these represent good correlation.<sup>9</sup>

We consider that the almost unique success of this method in arranging the alcohols and water in the

(6) Such hydrogen bonding serves toward charge concentration on the amine nitrogen in the ground state and a strengthened hydrogen bond in the electronic excited state and hence tends toward lowered electronic transition energy; see ref 3, 4, and J. H. P. Utley, *J. Chem. Soc.*, 3252 (1963).

(7) In our previously used classification of solvation types,<sup>3,4</sup> this is referred to as type-B hydrogen bonding. Type-A hydrogen bonding involves the proton of the solvent and the nitrogen of the amine. For a discussion of spectral effects of type-A hydrogen bonding, see M. J. Kamlet, R. R. Minesinger, E. G. Kayser, M. H. Aldridge, and J. W. Eastes, *J. Org. Chem.*, in press.

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TABLE I  
SPECTRAL DISPLACEMENTS ( $-\Delta\nu_{\max}$  RELATIVE TO SPECTRA IN CYCLOHEXANE) FOR 4-NITROANILINE AND *N,N*-DIETHYL-4-NITROANILINE IN SOME WEAKLY BASIC SOLVENTS<sup>a</sup>

Solvent, ROH, R =	$\sigma^*$ of R	4-Nitroaniline			<i>N,N</i> -Diethyl-4-nitroaniline			$-\Delta\Delta\nu_{\max},$ kK <sup>c</sup>
		$\lambda_{\max}, \text{nm}$	$\nu_{\max}, \text{kK}$	$-\Delta\nu_{\max}, \text{kK}^b$	$\lambda_{\max}, \text{nm}$	$\nu_{\max}, \text{kK}$	$-\Delta\nu_{\max}, \text{kK}^b$	
(CH <sub>3</sub> ) <sub>3</sub> C-	-0.30	377.5	26.49	4.52	390.5	25.61	1.79	2.73
(CH <sub>3</sub> ) <sub>2</sub> CH-	-0.19	378	26.46	4.55	392	25.51	1.89	2.66
<i>n</i> -C <sub>4</sub> H <sub>9</sub> -	-0.13	375	26.67	4.34	392	25.51	1.89	2.45
C <sub>2</sub> H <sub>5</sub> -	-0.10	372.5	26.85	4.16	392.5	25.48	1.92	2.24
CH <sub>3</sub> -	0.00	371	26.95	4.06	397.5	25.16	2.24	1.82
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> -	+0.08	375	26.67	4.34	401	24.94	2.46	1.88
HO-CH <sub>2</sub> CH <sub>2</sub> -	+0.20	382.5	26.14	4.87	415	24.10	3.30	1.57
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -	+0.22	381	26.25	4.76	411	24.33	3.07	1.69
Cl-CH <sub>2</sub> CH <sub>2</sub> -	+0.38	373.5	26.77	4.24	414	24.15	3.25	0.99
H-	+0.49	380.5	26.28	4.73	430.5	23.23	4.17	0.56
Cyclohexane		322.5	31.01		365	27.40		

<sup>a</sup> Precision in  $\lambda_{\max}$  ca.  $\pm 0.5$  nm. <sup>b</sup> Red shift relative to spectrum in cyclohexane solvent. <sup>c</sup> Enhanced red shift for 4-nitroaniline as compared with its *N,N*-diethyl derivative; attributable to hydrogen bonding by 4-nitroaniline to weakly basic solvent.

"theoretical" order may arise from the following. Solute concentrations required for the spectrophotometric determinations are low, and 4-nitroaniline is about as weak an acid as can be used to test solvent proton affinities. Hence, solvent reorganization effects (factor a above) should be relatively minor. Factor b should also introduce only minimal complications because differential solvation effects at the anionic ends of the indicator dipoles (*i.e.*, solvation at the nitro group) should be relatively little influenced by *N,N*-dialkylation and should cancel out in the nitroaniline *vs.* dialkylnitroaniline comparisons.

We are on less firm ground as concerns factor c, steric effects on hydrogen bond strengths. The good fit of the *tert*-butyl alcohol result to the correlation equation suggests that steric effects are relatively unimportant in the ROH series. They may play a more significant part, however, in weakening hydrogen bonds by 4-nitroaniline to other ROR' compounds. Proton affinities by this method do not arrange a series of ethers in the inductive order, nor do the ethers prove to be better hydrogen bond acceptors than the alcohols discussed above. Values of  $-\Delta\Delta\nu_{\max}$ , determined as before, are for tetrahydrofuran, 1.67 kK; diethyl ether, 1.66 kK; 1,2-dimethoxyethane, 1.85 kK; dioxane, 1.13 kK. Sterically weakened hydrogen bonds by 4-nitroaniline to ROR' compounds might result from ortho repulsions, which would be expected to be significantly greater where R' is alkyl than where R' is hydrogen.

An exercise similar to the above has also been carried out in obtaining  $-\Delta\Delta\nu_{\max}$  values for *N*-ethyl-4-nitroaniline relative to the *N,N*-diethyl derivative in the same series of solvents; the data are assembled in Table II. The trend of  $-\Delta\Delta\nu_{\max}$  again follows the in-

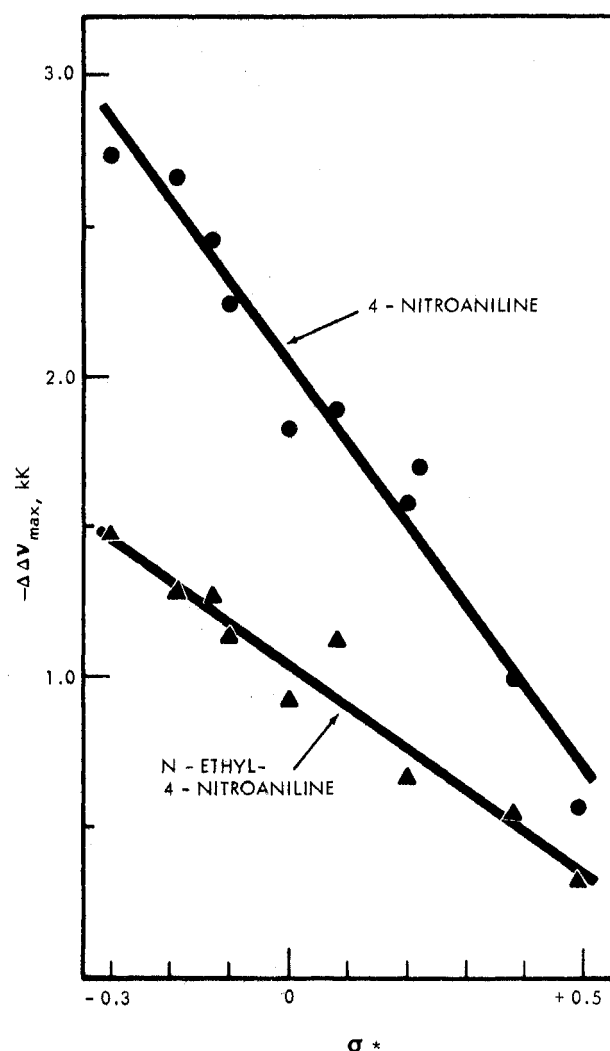


Figure 1.— $-\Delta\Delta\nu_{\max}$  for 4-nitroaniline and *N*-ethyl-4-nitroaniline relative to *N,N*-diethyl-4-nitroaniline *vs.*  $\sigma^*$  of R in ROH.

ductive order and, with the exception of one out-of-line data point,<sup>10</sup> is near linear with  $\sigma^*$  of R in ROH as is shown by the lower plot in Figure 1. The result fit the least-squares correlation equation

$$-\Delta\Delta\nu_{\max} = 1.03 - 1.41 \sigma^* \quad (2)$$

(10) If the point for 2-phenylethanol (in which solvent the absorption peak is very dissymmetric about the maximum) is excluded, the correlation equation becomes  $-\Delta\Delta\nu_{\max} = 1.01 - 1.43 \sigma^*$ , with  $r = 0.99$  and  $s = 0.06$  kK (excellent correlation).<sup>9</sup>

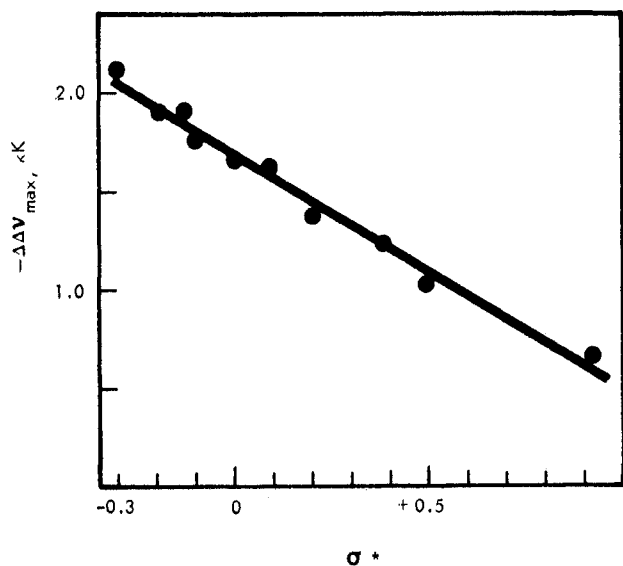
TABLE II

SPECTRAL DISPLACEMENTS FOR *N*-ETHYL-4-NITROANILINE

Solvent, ROH, R =	$\sigma^*$ of R	$\lambda_{\max},$ nm	$\nu_{\max},$ kK	$-\Delta\nu_{\max},$ kK	$-\Delta\Delta\nu_{\max},$ kK
(CH <sub>3</sub> ) <sub>3</sub> C-	-0.30	388	25.77	3.25	1.46
(CH <sub>3</sub> ) <sub>2</sub> CH-	-0.19	387	25.84	3.18	1.29
<i>n</i> -C <sub>4</sub> H <sub>9</sub> -	-0.13	386.5	25.87	3.15	1.26
C <sub>2</sub> H <sub>5</sub> -	-0.10	385	25.97	3.05	1.13
CH <sub>3</sub> -	0.00	386.5	25.87	3.15	0.91
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> -	+0.08	393	25.45	3.57	1.11
HO-CH <sub>2</sub> CH <sub>2</sub> -	+0.20	399	25.06	3.96	0.66
Cl-CH <sub>2</sub> CH <sub>2</sub> -	+0.38	398	25.13	3.89	0.54
H-	+0.49	407.5	24.54	4.48	0.31

TABLE III  
 SPECTRAL DISPLACEMENTS FOR 4-NITROPHENOL AND 4-NITROANISOLE

Solvent, ROH, R =	$\sigma^*$ of R	4-Nitrophenol			4-Nitroanisole			$-\Delta\Delta\nu_{\max}$ , kK
		$\lambda_{\max}$ , nm	$\nu_{\max}$ , kK	$-\Delta\nu_{\max}$ , kK	$\lambda_{\max}$ , nm	$\nu_{\max}$ , kK	$-\Delta\nu_{\max}$ , kK	
(CH <sub>3</sub> ) <sub>3</sub> C-	-0.30	315	31.74	3.35	304	32.89	1.24	2.11
(CH <sub>3</sub> ) <sub>2</sub> CH-	-0.19	312.5	32.00	3.09	303.5	32.94	1.19	1.90
<i>n</i> -C <sub>4</sub> H <sub>9</sub> -	-0.13	313	31.95	3.14	304	32.89	1.24	1.90
C <sub>2</sub> H <sub>5</sub> -	-0.10	311.5	32.10	2.99	304	32.89	1.24	1.75
CH <sub>3</sub> -	0.00	311.5	32.10	2.99	305	32.79	1.34	1.65
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> -	+0.08	317.5	31.50	3.59	311	32.15	1.98	1.61
HO-CH <sub>2</sub> CH <sub>2</sub> -	+0.20	317	31.55	3.54	313	31.95	2.18	1.36
ClCH <sub>2</sub> CH <sub>2</sub> -	+0.38	316.5	31.60	3.49	314	31.87	2.26	1.23
H-	+0.49	317.5	31.50	3.59	317	31.55	2.58	1.01
CF <sub>3</sub> CH <sub>2</sub> -	+0.92	312	32.05	3.04	315	31.75	2.38	0.66
Cyclohexane		285	35.09		293	34.13		
CCl <sub>4</sub>		289	34.60	(0.49)	298	33.56	(0.57)	
ClCH <sub>2</sub> CH <sub>2</sub> Cl		301.5	33.17	(1.92)	309	32.36	(1.77)	


 Figure 2.— $-\Delta\Delta\nu_{\max}$  for 4-nitrophenol relative to 4-nitroanisole vs.  $\sigma^*$  of R in ROH.

with  $r = 0.97$  and  $s = 0.09$  kK (good correlation).<sup>9</sup>

It is of some interest that both the slope and the intercept for 4-nitroaniline in eq 1 come very near to being twice the corresponding values for *N*-ethyl-4-nitroaniline in eq 2. This finding suggests to us that 4-nitroaniline forms *two* hydrogen bonds to the ROH solvents and that these hydrogen bonds are very nearly equal in strength to each other and to the single hydrogen bond in *N*-ethyl-4-nitroaniline.<sup>11</sup>

The above results also help to explain some seeming variations in the effects of *N*-alkyl groups on the spectra of nitroaromatic amines depending on the solvent. In cyclohexane the bathochromic displacement on *N,N*-diethylation of 4-nitroaniline is 42.5 nm; in methanol the shift amounts to 26.5 nm; and in *tert*-butyl alcohol 13 nm. This decreasing trend can now be rationalized on the basis that, on *N,N*-dialkylation, we are excluding progressively stronger bathochromic effects of hydrogen bonding in the more basic solvents. The fact that the solvent effect is almost as great as the substituent

effect emphasizes the need to take such hydrogen bonding phenomena into account in spectra-structure correlations for compounds of the types discussed here.

Parallel effects on [ $^+X=C_1 \rightarrow C_4=NO_2^-$ ] transition maxima as occur on *N*-alkylation of 4-nitroaniline should also take place on *O*-alkylation of 4-nitrophenol, *i.e.*, a bathochromic effect on replacing hydrogen by alkyl in nonpolar solvents,<sup>12</sup> partially or completely offset in alcoholic or aqueous media, by a hypsochromic displacement resulting from exclusion of a hydrogen bond to the solvent.

It would follow in a similar manner, then, that  $-\Delta\Delta\nu_{\max}$  values, obtained by comparing red shifts from cyclohexane to ROH solvents for 4-nitrophenol and 4-nitroanisole, should be measures of  $ArOH \cdots O < \frac{H}{R}$

hydrogen bond strengths.<sup>13</sup> We have carried out such a comparison; the results, in terms of  $\lambda_{\max}$ ,  $\nu_{\max}$ ,  $-\Delta\nu_{\max}$ , and  $-\Delta\Delta\nu_{\max}$ , are given in Table III and a plot of  $-\Delta\Delta\nu_{\max}$  vs.  $\sigma^*$  is shown in Figure 2. As was anticipated, the  $-\Delta\Delta\nu_{\max}$  values again arrange the alcohols and water in the inductive order and the trend with  $\sigma^*$  is near linear. The least-squares correlation equation is

$$-\Delta\Delta\nu_{\max} = 1.68 - 1.20 \sigma^* \quad (3)$$

with  $r = 0.99$  and  $s = 0.06$  kK (excellent correlation).<sup>9</sup>

It is of some interest that in this series the hypsochromic effect of excluding the hydrogen bond in some instances outweighs the "normal" bathochromic effect of *O*-alkylation. The consequence is that 4-nitroanisole absorbs at the longer wavelengths in cyclohexane, carbon tetrachloride, 1,2-dichloroethane, and trifluoroethanol, but 4-nitrophenol absorbs at the longer wavelengths in water and the more basic alcohols.

It should be noted in conclusion that we have represented these  $-\Delta\Delta\nu_{\max}$  values as being measures of relative solvent proton affinity, rather than intrinsic basicity. Hydrogen bond strength is only one of many possible criteria for proton acceptor ability and, as we have mentioned in earlier papers,<sup>4,7,14</sup> proton acceptor

(12) The red shift in cyclohexane on going from 4-nitroaniline to *N*-ethyl-4-nitroaniline ( $\lambda_{\max}$  343 nm) is -1.86 kK; the corresponding shift for 4-nitroanisole relative to 4-nitrophenol is -0.97 kK.

(13) As was the case earlier, shifts on going from cyclohexane to carbon tetrachloride or 1,2-dichloroethane are reasonably similar for both compounds (Table III).

(14) J. W. Eastes, M. H. Aldridge, R. R. Minesinger, and M. J. Kamlet, *J. Org. Chem.*, in press.

(11) An alternative possibility, that 4-nitroaniline forms a single hydrogen bond to solvent and that this is somehow sterically weakened on *N*-ethylation to give about half the enhanced bathochromic effect, seems ruled out by the fact that  $-\Delta\Delta\nu_{\max}$  values in all ROH solvents are almost identical for *N*-methyl-, *N*-ethyl-, and *N*-isopropyl-4-nitroaniline.

ability is in turn only one of the many complex interacting factors influencing  $pK_a$ 's.

### Experimental Section

Ultraviolet absorption spectra were determined on a Cary Model 14 recording spectrophotometer with matched 1-cm silica cells. Concentrations were  $3-5 \times 10^{-5} M$ . The reported data represent the average of two determinations for each spectrum, with occasional checks that  $\lambda_{max}$  did not vary with concentration. All solvents were Spectro Grade or the best grade com-

mercially available and were checked by glpc to confirm the absence of significant impurities.

**Registry No.**—4-Nitroaniline, 100-01-6; *N,N*-diethyl-4-nitroaniline, 2216-15-1; *N*-ethyl-4-nitroaniline, 3665-80-3; 4-nitrophenol, 100-02-7; 4-nitroanisole, 100-17-4.

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## Substituent and Secondary Deuterium Isotope Effects for Hydrolysis of Schiff Bases<sup>1</sup>

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The inverse kinetic secondary deuterium isotope effect,  $k_D/k_H$ , for attack of hydroxide ion on the conjugate acids of substituted *N*-benzylidene-1,1-dimethylethylamines is near 1.22 and is independent of the nature of the polar substituent. The same isotope effect for the attack of water on the conjugate acid of *N*-4-methoxybenzylidene-1,1-dimethylethylamine is 1.20. Thus, transition states for these reactions resemble the adducts more closely than the substrates. Second-order rate constants for the attack of hydroxide ion on substituted *N*-(substituted)-benzylideneanilines are correlated by the Hammett  $\sigma$  constants. Values of  $\rho$  near 2.7 were obtained in all cases except for the Schiff bases derived from 4-nitrobenzaldehyde, for which a value of 1.9 was found. These large values are consistent with adduct-like transition states for Schiff base hydrolysis.

Previous studies of addition of nucleophilic reagents to Schiff bases derived from aromatic aldehydes have sufficed to establish a number of points pertinent to these reactions.<sup>3</sup> Some general conclusions include (i) the rate-determining step for hydrolysis changes from nucleophile attack to intermediate decomposition as the solution pH is lowered;<sup>4-9</sup> (ii) the conjugate acids of Schiff bases are very much more reactive toward nucleophilic attack than are the free bases;<sup>6-10</sup> (iii) the basicity of the departing amine has a marked influence on the kinetics of Schiff base hydrolysis—decreasing basicity decreases reactivity under basic but increases reactivity under acidic conditions;<sup>6,8,9</sup> and (iv) the addition of nucleophilic reagents to Schiff bases is subject to general acid-base catalysis.<sup>5,8,9,11,12</sup>

Having a general understanding of the course and kinetics of these reactions, it appears desirable to begin to probe the structure of the associated transition states and the variation in such structures with substrate reactivity in more detail. This manuscript reports the results of some efforts in this direction. Two approaches have been employed: kinetic secondary deuterium isotope effects and effects of polar substituents. The former have been studied em-

ploying *N*-benzylidene-1,1-dimethylethylamines deuterated at the aldehydic carbon as substrates and the latter using *N*-benzylideneanilines. In both cases the magnitude of the observed effects has been probed as a function of the nature of the polar substituent in the benzaldehyde moiety.

### Experimental Section

**Materials.**—Substituted *N*-(substituted)-benzylideneanilines were prepared by the direct condensation of the appropriate aldehydes and anilines. All such substrates were recrystallized to constant melting point or carefully redistilled prior to use. *N*-Benzylidene-1,1-dimethylethylamines were prepared as previously described.<sup>8</sup> Benzaldehyde-*1-d* was prepared by oxidation of benzoic-*1-d* in tetrahydrofuran at 17° by the slow addition of  $D_5IO_6$ , prepared by exchanging  $H_5IO_6$  with  $D_2O$ . Following completion of the reaction, the solvent was removed on a rotary evaporator and the benzaldehyde-*1-d* was isolated as the bisulfite complex. The deuterated benzoic substrate was prepared by refluxing for 24 hr a solution of 0.43 mol of benzoic, 1.00 mol of  $D_2O$ , and 0.001 mol of NaOH in 450 ml of dioxane. The dioxane-water azeotrope was removed by distillation and the exchange process was repeated. 4-Methoxybenzaldehyde-*1-d* was prepared in the same way, beginning with 4,4'-dimethoxybenzoic. 3-Bromobenzaldehyde-*1-d* was prepared by the bromination of benzaldehyde-*1-d*.<sup>13</sup> Proton magnetic resonance spectra of neat benzaldehyde-*1-d* samples revealed that each had an isotopic purity of at least 98%. Reagent grade salts and distilled water were employed throughout.

**Kinetic Methods.**—All reactions were followed spectrophotometrically employing Zeiss PMQ II spectrophotometers equipped with cell holders through which water from a constant-temperature bath was continuously circulated. Reactions were ordinarily monitored at wavelengths near the absorption maximum of the Schiff base under study. Spectra recorded at the conclusion of the hydrolysis reactions corresponded to those of a mixture of the appropriate aldehyde and amine. For those reactions not involving determination of secondary isotope effects, first-order rate constants were obtained from semilogarithmic plots of the difference in optical density and infinite time optical density

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(3) Two comprehensive reviews are available: W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964); "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, Chapter 10.

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