

Kinetics of *cis-trans* Isomerization of *para*-Substituted N-Benzylideneanilines

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Kinetic data are reported for the thermal *cis-trans* relaxation of photoisomerized ethanol solutions of two series of N-benzylideneanilines, substituted in the *para* position of either the benzaldehyde or aniline ring. The isomerization followed first-order kinetics. For each series, log *k* values appear to correlate with the Hammett σ constants. At 30.0°, ρ (the proportionality constant) = 0.40 for the substituent on the benzaldehyde ring and $\rho = 2.00$ for the substituent on the aniline ring. Thermodynamic properties of the reactions are also given.

Introduction

The *cis-trans* isomerization of organic compounds containing a carbon-nitrogen double bond has been studied relatively little in comparison to the extensive investigations dealing with isomerizations about carbon-carbon and nitrogen-nitrogen double bonds.² This situation apparently arises from the difficulty in observing isomerizations in these compounds owing to the faster thermal *cis-trans* transformation around the C=N bond in comparison to the corresponding isomerizations around the C=C or the N=N bond. However, by ultraviolet irradiation of ethanolic solutions of N-(α -naphthylidene)- α -naphthylamine and of N-benzylideneaniline cooled to about -100° Fischer and Frei³ were able to observe the photoproducted *cis* isomers spectrophotometrically. More recently, Bell, Conklin, and Childress⁴ reported the separation of the geometric isomers of the Schiff base formed by the condensation of 2-amino-5-chlorobenzophenone and aminoethylmorpholine.

By using flash photolysis and fast recording techniques, studies on the isomerization of Schiff bases at room temperature were carried out in this laboratory.^{5,6} In the present investigations these techniques were applied to the study of substituent effects on the kinetic and thermodynamic properties of the thermal *cis-trans* isomerization of two series of *para*-substituted N-benzylideneanilines.

Experimental

Materials. The preparation and purification of the *para*-substituted benzylideneanilines were described

previously.⁷ Other chemicals were ethanol (U.S.I., U.S.P.), acetic acid (Allied Chemical and Dye Corp., reagent grade), and sodium acetate (Merck, reagent).

Method and Calculations. Test solutions were prepared with absolute ethanol as solvent, water content less than 0.04%, and with the concentration of compound about 10⁻⁴ M. The solutions were also buffered with acetic acid and sodium acetate in a molar ratio of 1.40:1. Two buffer concentrations were used, one 2.09 × 10⁻⁴ M in acetic acid and another 1.05 × 10⁻³ M.

A high-energy, fast flash photolysis unit⁸ was used in accordance with the specifications given in ref. 9 with the following exception: thermostating (to an accuracy of ±0.2°) was accomplished with a 10% acetic acid solution which also served as a cutoff filter.

Changes in optical density, $\Delta O.D.$, were followed vs. time for the thermal relaxation of flashed solutions. k_{exptl} equals the slope of a straight line fitted to a plot

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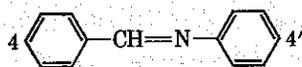
(9) G. Wettermark and R. Ricci, *J. Chem. Phys.*, **39**, 1218 (1963).

of $-\ln |\Delta O.D.|$ vs. time according to the method of least squares.

A and E_a in the Arrhenius equation $k = A \exp(-E_a/RT)$ were calculated from the regression line fitted by the method of least squares to a plot of $\log k_{\text{exptl}}$ vs. T^{-1} . ΔS^* was determined from the transition state theory applying the equation $\Delta S^* = (\ln A - 1 - \ln(k/h) - \ln T)R$ for $T = 303^\circ\text{K}$. (k stands for the Boltzmann constant and h for the Planck constant in this relation).

Results and Discussion

The compounds investigated were anils of the general structure



They were substituted in either the 4- or 4'-position with the groups $\text{N}(\text{CH}_3)_2$, OCH_3 , CH_3 , Cl , Br , and NO_2 .

All compounds absorbed in the near-ultraviolet region of the spectrum with the absorption extending into the visible. With all compounds except 4'- NO_2 , exposure to a pulse of ultraviolet light, "flash," caused transient changes in the light absorption in the region 300–450 $\text{m}\mu$. The original optical density was restored in the dark. Some solutions showed increased transient absorption, others decreased absorption; with some compounds a solution showed increase over one part of this wave length region and decrease over the remaining part. The solutions were transparent in the region 450–600 $\text{m}\mu$ both before and after flashing.

The thermal relaxation after flashing followed in every case the kinetics of a first-order reaction and was followed for two to three half-lives. Arrhenius plots of the rate constants are shown in Figure 1. No transient changes in light absorption with a half-life exceeding 20 μsec . were observed in solutions of the 4'- NO_2 compound, over the wave length region 350–600 $\text{m}\mu$. All compounds except the 4'- $\text{N}(\text{CH}_3)_2$ and 4'- OCH_3 derivatives yielded rate constants which did not show any systematic dependence on the concentration of acetate buffer. No distinction was therefore made between the data at the two different buffer concentrations. For the 4'- $\text{N}(\text{CH}_3)_2$ and 4'- OCH_3 anils the rate constants were substantially higher for the higher buffer concentration, and with these compounds separate Arrhenius plots were made for the two buffer concentrations. The values of A and E_a from the regression lines in Figure 1 are collected in Table I. The rate constants, k , at 30.0° , as obtained from the regression lines, entropies of activation, and σ -values^{10,11} are also included in the table.

Table I: Rate Parameters for the Thermal Relaxation of Photoisomerized Solutions of N-Benzylideneanilines

4-Substituent	σ -Value ^a	Rate constant at 30° , k , sec. ⁻¹	Pre-exponential factor, A , sec. ⁻¹	Activation energy, E_a , kcal. mole ⁻¹	Entropy of activation, ΔS^* , cal. mole ⁻¹ deg. ⁻¹
O^-	-1.00	0.40	1.0×10^{12}	17.2	-6
$\text{N}(\text{CH}_3)_2$	-0.600	0.67	2.8×10^{12}	17.5	-4
OH^b	-0.357	0.72	1.6×10^{11}	15.7	-10
OCH_3	-0.268	1.12	5.9×10^{12}	17.6	-2
CH_3	-0.170	1.30	1.4×10^{13}	18.1	-1
H^b	0	1.67	3.0×10^{10}	14.2	-13
Cl	0.226	1.75	5.7×10^{12}	17.3	-2
Br	0.232	1.72	2.5×10^{12}	16.9	-4
NO_2	0.778	2.17	1.4×10^{12}	16.4	-5
4'-Substituent					
$\text{N}(\text{CH}_3)_2$	-0.600	{ 0.25 ^c 0.79 ^d	{ 2.1×10^8 1.9×10^6	{ 12.4 8.8	{ -22 -32
OCH_3	-0.268	{ 0.24 ^c 0.42 ^d	{ 3.5×10^{10} 2.6×10^9	{ 15.5 13.6	{ -12 -18
CH_3	-0.170	0.59	3.5×10^{12}	17.7	-3
H^b	0	1.67	3.0×10^{10}	14.2	-13
Cl	0.226	3.12	4.6×10^{12}	16.9	-3
Br	0.232	3.41	9.4×10^{12}	17.3	-1
NO_2	0.778	No transient change			

^a The σ -values are taken from ref. 10 and are essentially the same as those given by Jaffé.¹¹ ^b Data obtained from ref. 6. ^c Acetic acid concentration: $2.09 \times 10^{-4} M$. ^d Acetic acid concentration: $1.05 \times 10^{-3} M$.

Table I shows that the relaxation, when not catalyzed by the buffer, has an activation energy of 14–18 kcal. mole⁻¹ and a pre-exponential factor of 10^{12} to 10^{13} sec.⁻¹. However, for the two samples showing buffer catalysis, 4'- $\text{N}(\text{CH}_3)_2$ and 4'- OCH_3 , E_a and A are significantly lower.

Assuming that the buffer catalysis is linearly dependent on buffer concentration obeying the law

$$k_{\text{exptl}} = k_s + k_{\text{buffer}}[\text{HOAc}] \quad (1)$$

it is possible to evaluate the uncatalyzed portion of the rate constant, k_s , and the buffer-catalyzed portion, $k_{\text{buffer}}[\text{HOAc}]$. The concentration of acetic acid, $[\text{HOAc}]$, is arbitrarily chosen to represent the buffer concentration. For the 4'- $\text{N}(\text{CH}_3)_2$ and 4'- OCH_3 anils eq. 1 was applied to calculate k_s and k_{buffer} at any temperature where k_{exptl} had been measured at both buffer ratios. The values of k_s and k_{buffer} were used separately in the Arrhenius equation to obtain

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Table II: Rate Parameters Obtained by Separating the Thermal Relaxation into an Uncatalyzed Portion and a Catalyzed Portion

Substituent	Uncatalyzed portion				Buffer-catalyzed portion		
	k_s (30°), sec. ⁻¹	A , sec. ⁻¹	E_a , kcal. mole ⁻¹	ΔS^\ddagger , cal. mole ⁻¹ deg. ⁻¹	k_{buffer} (30°), l. mole ⁻¹ sec. ⁻¹	A , l. mole ⁻¹ sec. ⁻¹	E_a , kcal. mole ⁻¹
4'-N(CH ₃) ₂	0.094	6×10^{11}	17.8	-7	7.9×10^2	3.1×10^7	6.5
4'-OCH ₃	0.17	3×10^{11}	16.9	-8	2.3×10^2	2.0×10^8	9.7

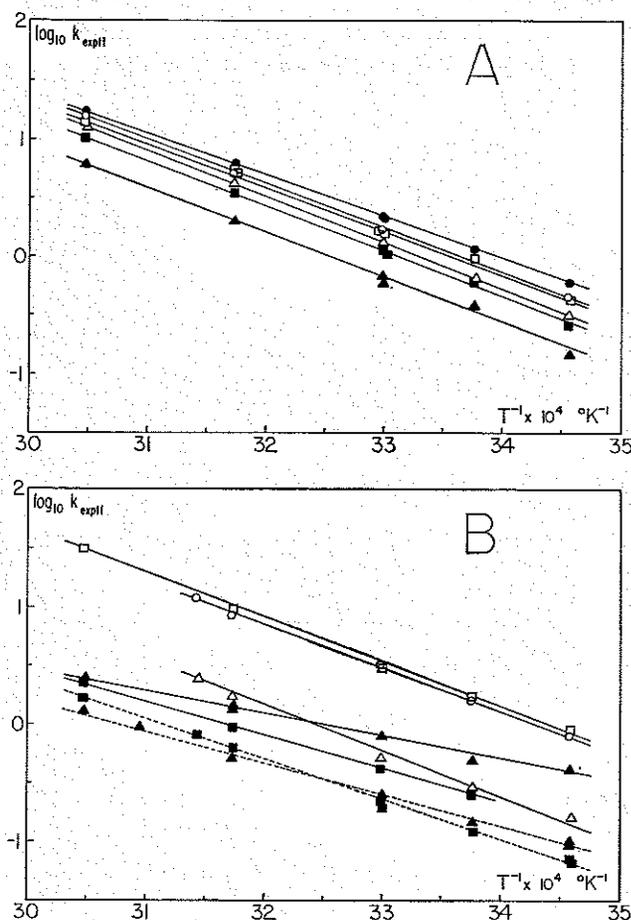


Figure 1. Activation energy plots of the rate constants for the thermal relaxation of photoisomerized solutions of N-benzylideneanilines in acetate-buffered ethanol. Substituent: \blacktriangle , N(CH₃)₂; \blacksquare , OCH₃; \triangle , CH₃; \circ , Cl; \square , Br; \bullet , NO₂. A: substituent in 4-position. B: substituent in 4'-position. For the 4'-N(CH₃)₂ and 4'-OCH₃ compounds: (---) connects rate constants obtained in buffer with [HOAc] = 2.09×10^{-4} M; (—) connects rate constants obtained in buffer with [HOAc] = 1.05×10^{-3} M.

the values of A and E_a given in Table II. Also presented in this table are the constants k_s and k_{buffer} at 30° obtained from the regression lines of the Arrhenius plots.

The Hammett equation

$$\log k = \rho\sigma + \log k_0 \quad (2)$$

was tested for the rate constants at each of the three temperatures 15, 30, and 45°. For the 4'-N(CH₃)₂ and 4'-OCH₃ only the buffer-uncatalyzed portion of the rate, k_s was used. The data for 4-O⁻ substitution were not included in these calculations. Plots of $\log k$ vs. σ -values are shown in Figure 2. Least-square fits give the characteristic constants presented in Table III.

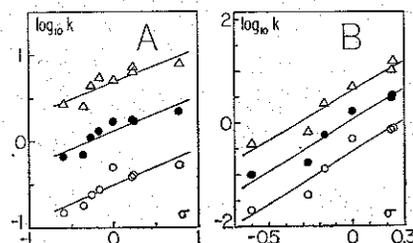


Figure 2. Test of the Hammett equation for the thermal isomerization of N-benzylideneanilines (*cis-trans* isomerization): \circ , 15.0°; \bullet , 30.0°; \triangle , 45.0°. A: substituent in 4-position. B: substituent in 4'-position.

Table III: Test of the Hammett Equation

	Temp., °C.	ρ	Correlation coefficient (r)	Std. error ^a
Substitution in 4-position	15	0.42	0.89	0.09
	30	0.40	0.90	0.08
	45	0.38	0.88	0.08
Substitution in 4'-position	15	2.05	0.97	0.16
	30	2.00	0.97	0.14
	45	1.95	0.97	0.13

^a Root mean square of the deviations along the $\log k$ axis about the fitted regression line.

It is noted that the correlation coefficients are relatively poor. The data do not show any obvious correlation between E_a and σ or A and σ . This could be due to insufficient accuracy in the determination of

E_a , but de Wolfe¹² also found that no such correlation exists in the case of hydrolysis of N,N'-diarylformamidines.

The thermally stable form of N-benzylideneanilines is the *trans* configuration. The observed transient changes are attributed to photochemical formation of the *cis* isomer followed by the thermal re-formation of the *trans* form.

The ρ -values in the Hammett equation are positive indicating that the reaction is facilitated by low electron density at the C=N bond.

The rate constant for the *cis-trans* isomerization of

the anion of the 4-OH compound from ref. 6 falls in the sequence predicted by the Hammett equation although one might have expected that resonance interaction with the reaction site would be important for this substituent. It should be noticed, however, that the data for this 4-O⁻ derivative were obtained from alkaline solutions and that environmental factors may be of importance when taking this value into account. It was therefore excluded in the present calculations.

(12) R. H. de Wolfe, *J. Am. Chem. Soc.*, **82**, 1585 (1960).