

Kinetic study of charge transfer interaction of substituted pyridines and substituted 4-styrylpyridines with *p*-bromanil

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Kinetics of charge transfer interaction of various 3- and 4-substituted pyridines and 4'-substituted 4-styrylpyridines with *p*-bromanil has been studied spectrophotometrically in carbon tetrachloride at three different temperatures and thermodynamic parameters have been evaluated. The reaction between pyridine and *p*-bromanil follows second order kinetics, first order in each reactant. Electron-releasing substituents in pyridine ring increase the rate of the charge-transfer interaction while electron-withdrawing substituents retard it. Good Hammett correlations have been observed in both the reaction series. The ratio of effectiveness of transmission of substituent effect in styrylpyridine system relative to pyridine system in this reaction is computed to be 0.167.

Aza-aromatics form charge transfer complexes with halogens^{1,2}, 1, 3, 5-trinitrobenzene³ and 2, 3-dichloro-5, 6-dicyano-*p*-benzoquinone⁴ in non-polar solvents. Recently the spectroscopic and kinetic studies of interaction of *p*-xylene and *p*-bromanil⁵, aliphatic amines with chloranil^{6,7} and aromatic hydrocarbons with chloral⁸ in non-polar solvents have been reported. The present study was undertaken to test the ability of pyridines and styrylpyridines as electron donors, to gain information about the substituent effect on the donors and to examine the transmission of substituent effect through the styryl group to the pyridine ring.

Materials and Methods

p-Bromanil was prepared in the laboratory. Pyridine, 3-methylpyridine, 4-methylpyridine, 4-ethylpyridine and 3-acetylpyridine were commercial samples and were purified by distillation. Nicotinic acid and isonicotinic acid were also commercial samples and recrystallised from light petroleum (40-60°C). 4'-Substituted 4-styrylpyridines were prepared in the laboratory⁹. The solvent carbon tetrachloride (BDH, AR) was dried and distilled before use.

The kinetics were followed upto 60% completion or more, under pseudo-first order conditions with excess of [pyridine] spectrophotometrically at 410 nm where the absorbances of the reaction mixtures continue to increase with time. The con-

centration of *p*-bromanil was 1×10^{-4} mol dm⁻³. The concentration of pyridines ranged from 0.003 to 0.08 mol dm⁻³. Optical density measurements were made using HITACHI 200-20 UV-visible spectrophotometer. The reaction mixture was kept in the cell for 15 min. to attain thermal equilibrium. The optical density values were noted at zero time (A_0) and at regular time intervals (A_t). The infinity values (A_∞) were noted at the end of the reaction. Pseudo-first order rate constants, k , at the product bands were calculated using Eq. (1),

$$k = \frac{2.303}{t} \log \frac{(A_\infty - A_0)}{(A_\infty - A_t)} \quad \dots (1)$$

The second order rate constants (k_2) were evaluated from the relation $k_2 = k_1/[\text{pyridine}]$ and the precision of k_2 values is given in terms of 95% confidence limits of the 'student t '.

Product analysis

When the reaction mixture was left overnight a brown solid product appeared and was isolated by filtration. This was washed with carbon tetrachloride. The IR spectrum (Perkin-Elmer 783; KBr disc) was taken^{7,10} for parent compounds and the product. The NMR spectrum (JNM-GSX-400 FT NMR; CDCl₃) was taken for 4-styrylpyridine and the product. The IR and NMR

spectra of the product show marked variations from those of the parent compounds. Further analysis of the product is in progress.

Results and Discussion

The reaction between *p*-bromanil and pyridine follows second order kinetics, first order in each reactant. Rate coefficients at various initial [*p*-bromanil] and [pyridine] are presented in Table 1. Plots of $\log (A_\infty - A_t)$ versus t are linear indica-

ting first order dependence in *p*-bromanil. Constant values of second order rate constants at different initial [pyridine] show that the order in pyridine is unity.

The second order rate constant for the reaction of *p*-bromanil with 3- and 4-substituted pyridines and 4'-substituted 4-styrylpyridines measured at 35°, 40° and 45°C and the activation parameters calculated are listed in Tables 2 and 3. The rate data in Tables 2 and 3 reveal that the reaction is accelerated by electron-releasing substituents and retarded by electron-withdrawing substituents present in the pyridine ring or in the phenyl ring of the styryl group.

The rate data were correlated with various substituent constants and Table 4 summarizes the results of correlation analysis. Correlation of $\log k_2$ at 35°C with σ_m and σ_p substituent constants for 3- and 4-substituted pyridines respectively and σ_p constants of Katritzky *et al.*¹¹ for styrylpyridines is good as has been observed in the earlier studies on styrylpyridines¹²⁻¹⁴.

The procedure of Katritzky *et al.*¹¹ for obtaining σ_p values for the substituted styryl groups

Table 1—Effect on the rate of varying pyridine and *p*-bromanil concentration at 35°C

[pyridine] × 10 ³ (mol dm ⁻³)	[<i>p</i> -bromanil] × 10 ⁴ (mol dm ⁻³)	$k_1 \times 10^5$ (s ⁻¹)	$k_2 \times 10^3$ (dm ³ mol ⁻¹ s ⁻¹)
8.04	1.00	3.06 ± 0.33	3.80 ± 0.41
9.04	1.00	3.44 ± 0.33	3.81 ± 0.37
10.9	1.00	4.11 ± 0.66	3.77 ± 0.61
12.5	1.00	4.74 ± 0.57	3.80 ± 0.45
8.04	2.00	3.07 ± 0.72	3.82 ± 0.89
8.04	3.00	3.17 ± 0.49	3.94 ± 0.61
8.04	4.00	3.02 ± 0.01	3.76 ± 0.01

Table 2—Second order rate constants and activation parameters for the reaction of pyridine and 3- and 4-substituted pyridines with *p*-bromanil in carbon tetrachloride

substituent	$k_2 \times 10^4$ (dm ³ mol ⁻¹ s ⁻¹)			ΔH^\ddagger (kJ mol ⁻¹) (at 35°C)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹) (at 35°C)
	35°C	40°C	45°C		
4-Me	184 ± 3	213 ± 15	243 ± 17	20.3 ± 8.4	212 ± 28
4-Et	153 ± 4	174 ± 9	233 ± 17	31.4 ± 8.0	178 ± 26
3-Me	64.1 ± 3.7	119 ± 9	149 ± 7	66.1 ± 9.6	72.5 ± 31.8
H	38.0 ± 4.1	71.9 ± 0.9	87.0 ± 1.3	65.1 ± 7.4	80.1 ± 24.3
4-COOH	3.28 ± 0.06	4.38 ± 0.06	6.86 ± 0.41	57.4 ± 2.7	125 ± 9
3-COMe	2.15 ± 0.04	2.94 ± 0.04	4.08 ± 0.03	49.5 ± 2.1	155 ± 7
3-COOH	1.26 ± 0.10	1.69 ± 0.09	3.40 ± 0.06	77.9 ± 8.1	66.9 ± 26.6
4-CN	0.159 ± 0.004	0.289 ± 0.004	0.543 ± 0.003	97.4 ± 2.3	21.0 ± 7.5

Table 3—Second order rate constants and activation parameters for the reaction of 4'-substituted 4-styrylpyridines with *p*-bromanil in carbon tetrachloride

4'-substituent	$k_2 \times 10^4$ (dm ³ mol ⁻¹ s ⁻¹)			ΔH^\ddagger (kJ mol ⁻¹) (at 35°C)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹) (at 35°C)
	35°C	40°C	45°C		
OMe	285 ± 4	455 ± 46	618 ± 28	60.4 ± 5.2	78.8 ± 17.4
Me	239 ± 3	355 ± 8	523 ± 8	60.6 ± 2.0	79.5 ± 6.7
H	184 ± 2	275 ± 2	411 ± 1	63.3 ± 0.8	72.9 ± 2.7
Cl	132 ± 1	204 ± 1	312 ± 1	67.1 ± 0.8	63.2 ± 2.9
Br	126 ± 1	195 ± 1	295 ± 4	67.6 ± 1.3	62.2 ± 4.4
CN	67 ± 1	109 ± 1	173 ± 1	74.1 ± 2.1	46.2 ± 7.0
NO ₂	54 ± 10	92 ± 29	144 ± 7	76.1 ± 5.6	41.3 ± 18.4

Table 4—Linear correlation for the reaction of substituted pyridines and 4-styrylpyridines with *p*-bromanil

Parameters used in correlation		ρ/β	r	s	n
pyridines and styrylpyridines	vs σ_p/σ_m (Katritzky)	-4.22 ± 0.41	0.988	0.162	14
pyridines	vs σ (Hammett)	-4.01 ± 0.50	0.992	0.153	9
styrylpyridines	vs σ (Hammett)	-0.670 ± 0.04	0.999	0.001	7
pyridines and styrylpyridines	vs pK_a	-8.36 ± 0.116	0.958	0.138	13

from the pK_a values of the substituted pyridinium ions did not appear adequate as the effect of substituent on the pK_a values was very small. Therefore it was decided to correlate the rate data for 3- and 4-substituted pyridines and 4'-substituted 4-styrylpyridines separately with the Hammett σ constants. In both the cases the correlations were found to be good (Table 4).

The observed ρ value of -4.01 ± 0.50 for the reaction of substituted pyridines shows that the effect of substituent is less pronounced as compared to that of protonated equilibrium of 3- and 4-substituted pyridines¹⁵ and more pronounced as compared to the reactions of methyl iodide¹⁶, phenacyl bromide¹³ and 2, 4-dinitrophenyl acetate¹⁴ with 3- and 4-substituted pyridines and also to the charge transfer equilibrium between pyridines and iodine, iodine monochloride and iodine monobromide as acceptors¹. The magnitude of ρ in comparison with the value -5.71 obtained for the ionisation of pyridinium ion in water suggests that only 70% of the positive charge carried by the pyridinium ion is developed in the transition state of the reaction of substituted pyridines with *p*-bromanil.

The application of the Hammett equation using σ values of 4'-substituents in styrylpyridines is used to calculate the reaction constant ρ for the styrylpyridines. The ρ value so calculated reflects not only the sensitivity of the reaction to the substituents but also the degree of the transmission of the substituent effect through the styryl group to the reaction centre. From the basicities of 4-styrylpyridines the value of ρ was found to be -0.85 . The ratio of effectiveness of transmission of substituent effect in styrylpyridine system relative to pyridine system in the protonated equilibrium was calculated to be 0.15. In the charge transfer complex formation between iodine and pyridines the ratio was found to be 0.18, for the

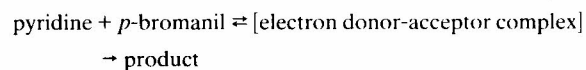
reaction between phenacyl bromide and pyridines¹³ the ratio was 0.104, while for the reaction between 2,4-dinitrophenyl acetate and pyridines¹⁴ the ratio was found to be 0.115. The ratio 0.167 obtained in the present study compares satisfactorily with the above values.

The non-bonding electrons of the nitrogen atom are involved in the acid-base reaction of these compounds and the conventional pK values of the respective compounds may be taken as a measure of the n -ionisation potential, provided the entropy effect is constant and steric effect is absent¹⁷. So if n -electrons are involved in the interaction of aza-aromatics with *p*-bromanil one may expect a direct proportionality between the logarithms of the rate constants and the pK_a values of the respective aza-compounds. In the present study a plot of $\log k_2$ at 35°C versus the pK_a values of the corresponding conjugate acids of substituted pyridines¹⁴ and styrylpyridines¹¹ is linear with $\beta_N = 0.836 \pm 0.116$ ($r = 0.958$; $s = 0.138$; $n = 13$; Table 4). A similar linear plot between $\log k$ against the pK_a in the charge transfer interaction of aza-aromatics with iodine, iodine monochloride and iodine monobromide was observed by Aloisi *et al.*¹ The present β_N value is comparable with that found in the nucleophilic reaction of substituted pyridines with *p*-nitrophenyl acetate ($\beta_N = 0.93$)¹⁸, 2,4-dinitrophenyl acetate ($\beta_N = 0.85$)¹⁹, 2,4-dinitrophenyl *p*-nitrobenzoate ($\beta_N = 0.9$)²⁰ and acetic anhydride ($\beta_N = 1.0$)²¹.

The entropies of activation are all negative (Tables 2 and 3) as expected for bimolecular reactions. Because of the development of charge in the transition state (formed from neutral molecules) the entropies of activation are more negative. There is fair correlation between ΔH^\ddagger and ΔS^\ddagger ($r = 0.998$). Exner plot of $\log k_2$ at 45°C versus $\log k_2$ at 35°C is also linear ($r = 0.999$). Existence of good correlation in isokinetic relationship

and compensation plot shows that in this reaction series all the substituted pyridines and 4-styryl-pyridines follow the same mechanism.

In line with the work of Dwivedi *et al.*^{4,22}, the following general scheme could be formulated for the reaction of *p*-bromanil with pyridine:



Pyridine and *p*-bromanil interact to form an electron donor-acceptor (EDA) complex in the first instance. It is generally believed that the formation of such EDA complex is instantaneous^{4,7,23}. The reaction may thus proceed through the EDA complex yielding the final solid product. This proposed scheme explains the second order kinetics, first order with respect to each reactant. The observed ρ value and negative values of entropies are also in accordance with this proposal.

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