# Brønsted Catalysis Law Plots for Heterolytic, General Base-Catalyzed Smiles Photorearrangement

Gene G. Wubbels,* W. Donald Cotter,
Houston Sanders, and Constance Pope

*Departments of Chemistry, Grinnell College,
Grinnell, Iowa 50112 and Washington College,
Chestertown, Maryland 21620*

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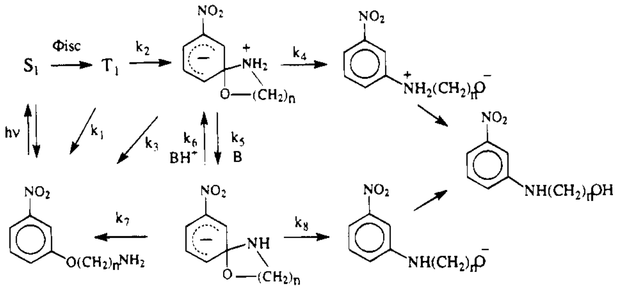
The reactions known as nucleophilic aromatic photosubstitutions continue to provide challenges for mechanistic understanding.[1,2] Our discoveries of a Smiles photorearrangement,[3] an intramolecular nucleophilic aromatic photosubstitution, and of general base catalysis of this photochemical reaction,[4,5] have clarified several mechanistic features of this class of reactions. Displacement via $S_N2Ar^*$ by an amine of an alkoxy group situated meta to a nitro group involves a kinetically significant deprotonation of a reactive intermediate postulated[4] to be a high energy $\sigma$-complex.

These findings contrast with those for a Smiles photorearrangement discovered by Mutai and co-workers[6–8] that is regiospecific for the ring carbon atom para to the nitro group. The Mutai reaction is general base catalyzed,[9] and we reported the Brønsted Catalysis Law plot for this reaction,[10,11] showing that the proton donor is a nitrogen-centered cation radical with a $pK_a$ of approximately 7. We now report mechanistically informative Brønsted plots for two examples of Smiles photorearrangements studied earlier[3–5] that are regiospecific for the ring position meta to the nitro group.

Quantum yields at 313 ± 10 nm for bases with $pK_a$'s from 5 to 11 were determined in 1.00 cm cuvettes at 25 °C with a monochromator illuminated by a 75 W xenon lamp. The actinometer was Aberchrome 540 in toluene.[12] Quantum yields for bases with $pK_a$'s from 2 to 5, which afforded only weak catalysis, required greater precision of measurement. These were obtained by use of reaction solutions in 1.3 cm diameter Pyrex tubes in a merry-go-round illuminated by a single 350 nm lamp (Rayonet RPR-208). We attempted to use several amines in the $pK_a$ range of 3 to 5, but found pyrazoles to quench the photorearrangement and 4-chloropyridine to interfere because of a thermal hydrolysis reaction. Reaction solutions contained 0.0010 M reactant, 0.10 M amine, KCl to an ionic strength of $\mu = 0.10$, carbonate-free water, dissolved air, and various pH's as noted. Reactions were monitored at low conversion at 405 nm ($\epsilon_{\text{product}}$ is 1110).

**Scheme 1**



A Brønsted Catalysis Law plot requires the $pK_a$ of the base and the logarithm of the rate constant for its proton transfer reaction (see eq 1). In order to obtain these data

$$\log k_b = \beta\, pK_a + C \qquad (1)$$

from the raw kinetic data in the form of quantum yields at various base concentrations, we postulate the mechanism shown in Scheme 1, for which the quantum yield expression shown in eq 2 has previously been shown[13] to be suitable.

$$\frac{1}{\Phi} = \frac{1}{\Phi_{isc}}\left(1 + \frac{k_1}{k_2}\right)\left(1 + \frac{k_3}{k_4 + \sum k_{5i}[B_i]}\right) \qquad (2)$$

Table 1 summarizes the quantum yields and proton transfer rate constants for the photorearrangements. The rate constants were calculated by use of eq 3 for the case of $n = 2$ and eq 4 for the case of $n = 3$. The parameters in these equations were determined as described and reported earlier.[13] The rate constants are based on the

$$\frac{1}{\Phi} = 2.36\left(1 + \frac{1.16 \times 10^8}{1.93 \times 10^7 + (1.4 \times 10^{10})[OH^-] + k_{5b}[\text{base}]}\right) \qquad (3)$$

$$\frac{1}{\Phi} = 2.78\left(1 + \frac{1.90 \times 10^8}{3.8 \times 10^7 + (1.4 \times 10^{10})[OH^-] + k_{5b}[\text{base}]}\right) \qquad (4)$$

assumption that proton transfer from the intermediate to hydroxide ion occurs at the diffusion rate, which we assume to be $1.4 \times 10^{10}\ M^{-1}\ s^{-1}$, the rate constant for proton transfer to hydroxide ion from the zwitterionic form of glycine.[14]

As shown in Figure 1 and 2, both the $n = 2$ and the $n = 3$ homologs show a break in their Brønsted Catalysis Law plots at a $pK_a$ in the range of 4 to 6.[15] The work of Eigen[14] suggested that in the absence of complications, Brønsted plots for elementary proton transfers involving

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[15] For both the $n = 2$ and $n = 3$ cases, the ratios of the variances (mean square residuals) for one-line and two-line fits of the data in Table 1 were calculated. The ratios are 20 and 3.7, respectively, which demonstrate the existence of a break in the Brønsted plot (two-line fit) in each case at greater than the 95% confidence level, which corresponds to a ratio of 3.677.

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**Table 1. Reaction Efficiency and Rate Constants of Proton Transfer to Amine Bases from the Intermediate $\sigma$-Complex from $m$-$O_2NC_6H_4O(CH_2)_nNH_2$**

| | | $n = 2$ | | | | $n = 3$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| base | p$K_a$[a] | pH | $\Phi$ | $k_5 \times 10^{-8}$ $M^{-1} s^{-1}$ | log $k_5$ | pH | $\Phi$ | $k_5 \times 10^{-8}$ $M^{-1} s^{-1}$ | log $k_5$ |
| 3-chloropyridine | 2.84 | 10.04 | 0.0683 | 0.153 | 7.18 | 10.04 | 0.0632 | 0.100 | 7.01 |
| 2-methoxypyridine | 3.06 | 10.04 | 0.0713 | 0.268 | 7.43 | 10.04 | 0.068 | 0.476 | 7.68 |
| pyridine | 5.17 | 10.04 | 0.112 | 2.08 | 8.32 | 10.04 | 0.868 | 2.09 | 8.32 |
| 4-picoline | 6.00 | 10.00 | 0.121 | 2.57 | 8.41 | 11.15 | 0.116 | 3.27 | 8.51 |
| 2,4,6-collidine | 7.43 | 10.04 | 0.144 | 3.89 | 8.59 | 11.13 | 0.120 | 3.82 | 8.58 |
| hydrazine[b] | 7.64 | 11.53 | 0.218 | 2.81 | 8.45 | | | | |
| glycinamine | 8.03 | 10.00 | 0.152 | 4.53 | 8.66 | 11.44 | 0.173 | 9.95 | 8.99 |
| diethanolamine | 8.88 | 11.21 | 0.182 | 4.54 | 8.66 | 11.29 | 0.131 | 4.35 | 8.64 |
| ethanolamine | 9.50 | | | | | 11.13 | 0.153 | 8.37 | 8.92 |
| 3-amino-1-propanol | 9.96 | 10.85 | 0.173 | 5.71 | 8.76 | 11.20 | 0.145 | 7.10 | 8.86 |
| n-butylamine | 10.64 | 10.04 | 0.097 | 6.80 | 8.83 | 11.36 | 0.153 | 8.40 | 8.92 |
| *tert*-butylamine | 10.68 | 11.51 | 0.217 | 6.57 | 8.82 | 11.17 | 0.171 | 15.0 | 9.17 |

[a] p$K_a$ values taken from D. Perrin. *Dissociation Constants of Organic Bases in Aqueous Solution,* London; Butterworth, 1965 and Supplement, 1972. [b] The $K_a$ and rate constant for hydrazine have been halved because of a statistical correction owing to its two equivalent basic sites.

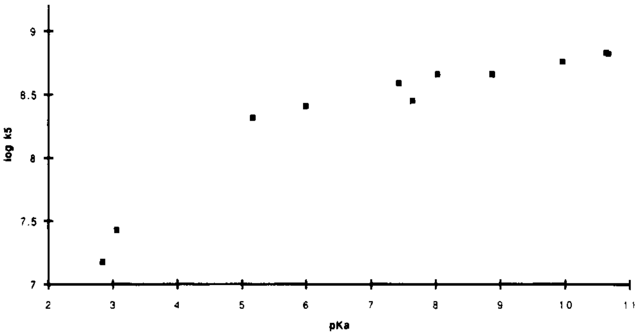


**Figure 1.** Log $k_5$ vs p$K_a$ for various amine bases in the photoreaction of $m$-$O_2N$-$C_6H_4OCH_2CH_2NH_2$.

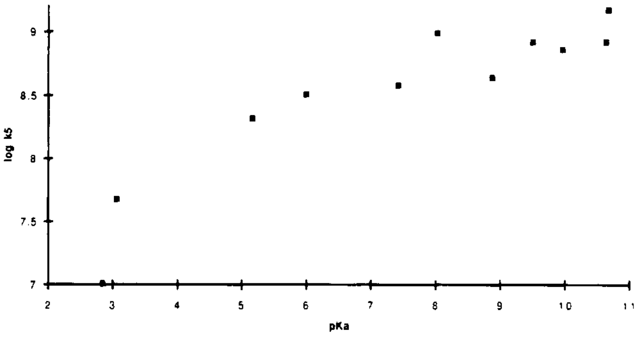
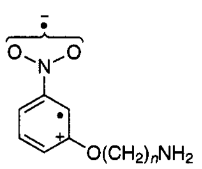


**Figure 2.** Log $k_5$ vs p$K_a$ for various amine bases in the photoreaction of m-$O_2N$-$C_6H_4OCH_2CH_2CH_2NH_2$.

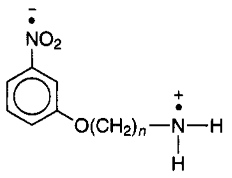
hydrogen bonding acids and bases should change from a slope of unity for bases with conjugate acid p$K_a$'s below that of the intermediate to a slope of 0 for bases with conjugate acid p$K_a$'s above that of the intermediate. The classic Eigen behavior shown by this Brønsted study finds precedent in the few cases reported for photoreactions[10,11] and several reported for excited state prototropy.[16]

These results can be readily interpreted. The p$K_a$'s of ammonium moieties of Meisenheimer complexes formed by ground state processes are estimated to be about three units lower than the corresponding open chain ammonium ion.[17] Although the $\sigma$-complex in the photochemical reaction lies some 20 kcal/mol higher than those formed by nucleophilic attack ortho or para to the nitro group,[18] its acidity would not be effected by this instability. The p$K_a$'s of the reactant conjugate acids are about 9 to 9.5, which suggests that the p$K_a$'s for the intermediates should be around 6, or slightly lower because of the proximity of the ionizing group to the nitro group and its lack of mesomeric negative charge for this case. This agrees well with the observed break points.

One can consider other possible interactions even in the absence of a reaction scheme for the intermediate that would rationalize the kinetics. Structure **1** is the simplest imaginable proton donor, that being the triplet $\pi,\pi^*$ excited state that gives rise to the reaction. Structure **2** is the species that would result from internal electron transfer, the primary event for the Mutai reactions.[6]



**1**



**2**

These can be ruled out as intermediates. The p$K_a$ expected for the aliphatic amine group of **1** is about 30, and a change of 25 p$K_a$ units stemming from the influence of any chemical species distant from the proton-bearing atom by five $\sigma$ bonds is not expected. The p$K_a$ expected for the aminium ion moiety of structure **2** would be about 7, based on the fact that the p$K_a$ of the aminium cation radical, $NH_3^{\bullet+}$, is 6.7.[19] This can be distinguished by the resolution of the experiments as not likely. The intermediate can be firmly ruled out because it would not give rise to the observed reaction product. The diradical configuration is associated with regiochemistry para to the nitro group, as shown by both intramolecular[7] and intermolecular[20] reaction systems.

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