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REACTION AND SUBSTITUENT CONSTANTS FOR PYRAMIDAL INVERSION
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We wish to show that from a Hammett $\rho$ for the nitrogen inversion of 1-aryl-2,2-dimethylaziridines, where the correlation is with $\sigma_p^-$ of the p-substituent in the phenol, substituent constants for pyramidal inversion ($\sigma_{inv.}$) can be derived for substituents directly on the inverting atom.

In order to determine the Hammett $\rho$ at 25°, the inversion rates of these 1-arylaziridines at 25° were determined from the experimental $\Delta G^\ddagger$ values adjusted to 25° by assuming $\Delta S^\ddagger = 0$. A plot of these log $k$ values vs $\sigma_p^-$ gave a $\rho$ of 2.5 (Fig. 1). This value was used in Fig. 2 to determine $\sigma_{inv.}$ constants for the substituents on the nitrogen atom. The $\sigma_{inv.}$ constants so determined were used to determine $\rho$ values for other series as shown in Fig. 3, using experimentally determined rate constants adjusted to 25°. From these $\rho$ values, a number of $\sigma_{inv.}$ constants were determined for substituents that were not present in the aziridine series. The data in Fig. 2 and 3 are summarized in Table 1. Substituents that were common to more than one series were $\text{Si(CH}_3\text{)}_3$, $\text{COCH}_3$, $\text{SiH(CH}_3\text{)}_2$, $\text{SC}_6\text{H}_5$, $\text{C}_6\text{H}_5$, $\text{H}$, $\text{C(CH}_3\text{)}_3$, cyclohexyl, $\text{CH(CH}_3\text{)}_2$, $\text{CH}_3$, $\text{N}_2$, $\text{Br}$, $\text{Cl}$, and $\text{OH}$.

The other substituents occurred in only one series and those $\sigma_{inv.}$ constants are, therefore, subject to greater error. The $\sigma_{inv.}$ constants are many times larger in value than the Hammett $\sigma$ constants. This can be attributed to the fact that the substituent is directly on the reacting center in inversion. There are three well-known factors evident in the order of the $\sigma_{inv.}$ constants: electronegativity, conjugative and steric effects.

In the acyclic amine series, the $\sigma_{inv.}$ constants appear to be additive.

*Fig. 1. Log $k$ for N inversion vs $\sigma_p^-$; solvent, CF$_2$Cl$_2$.*

*Fig. 2. Log $k$ for nitrogen inversion in aziridines vs $\sigma_{inv.}$; see Table 1 for the data. The x's represent the points in Fig. 1 adjusted to solvent C, Table 1; $\sigma_{inv.}$ for aryl = $\sigma_{inv.}$ for phenyl + $\rho$ for the p-substituent. Four substituents, which were present in the 2,2-dimethyl series, determined the $\rho$ of the carbon unsubstituted aziridine series. The H substituent, which was present in this series, determined the position of the $\sigma_{inv.} = 0$. 
Fig. 3. Log k for pyramidal inversion vs $\sigma_{\text{inv}}$ constants. The points on the dashed lines are for the sum of $\sigma_{\text{inv}}$ constants of the substituents on the inverting atom.

Differing $\sigma_{\text{inv}}$ constants, the sum of which is -4.9. The log k corresponding to $\sigma_{\text{inv}} = -4.9$ determined from the H$_2$N- line in Fig. 3 is 4.6, nearly the same as the 4.7 determined experimentally$^{10}$ and adjusted to 25°.

From Fig. 3 can be seen that the cyclic amine series$^{12}$ converge to a point where log k = 12.8 and $\sigma_{\text{inv}} = 4.9$. This indicates that a substituent with $\sigma_{\text{inv}}$ of 4.9 would cause the amine to be effectively planar irrespective of ring constraints.$^{13}$ The substituent, difluorophosphine, appears to have a $\sigma_{\text{inv}}$ constant of 4.3 or greater, because it has been shown to give a planar amine.$^{14}$

The difference in barrier between the cyclic amines and the oxaziridines at $\sigma_{\text{inv}} = 4.9$ is 6.5 kcal/mol, an increase due to the presence of the oxygen atom. Although there is only limited data for the 5 and 6 membered rings containing both O and N atoms as in the oxaziridines, the intersection of the line for the 6 membered ring with the oxaziridine line at $\sigma_{\text{inv}} = 4.9$ gives a $\rho$ of 0.9 which is the same as for the acyclic amines and homopiperidines. Also on this same line would be the acyclic hydroxylamine series assuming additive $\sigma_{\text{inv}}$ constants. Therefore, it appears that the N-O ring series also converge at $\sigma_{\text{inv}} = 4.9$. 
The data for acyclic phosphines and arsines are very limited for any one series. However, by plotting the log k vs the sum of the $a_{inv.}$ constants, reasonably straight lines can be obtained.\textsuperscript{15} The ratio of the $\rho$ values for the acyclic amines, phosphines, and arsines is 0.5: 1.0: 1.25 compared to the 0.34: 1.0: 1.4 ratio of sensitivities for calculated barriers.\textsuperscript{16}

From the correlation of data reported here, predictions can be made for rates of inversion of many compounds not yet measured. As more experimental data becomes available, the values of the $a_{inv.}$ constants reported here may need to be revised.

Table 1. Substituent Constants for Pyramidal Inversion.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$a_{inv.}$</th>
<th>log $k^a$ (25°)</th>
<th>Substituent</th>
<th>$a_{inv.}$</th>
<th>log $k^a$ (25°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-$Si(CH$_3$)$_3$</td>
<td>+ 4.4</td>
<td>-1.2b,c, -5.9D,b,c</td>
<td>$-$C(CH$_3$)$_3$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$-$CO$_2$H</td>
<td>+ 3.8</td>
<td>&gt;8.7v</td>
<td>$-$SCl$_2$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$-$SiH(CH$_3$)$_2$</td>
<td>+ 3.5</td>
<td>3.9r,b,g, -0.2,b,g</td>
<td>$-$H</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$-$COH</td>
<td>+ 3.5</td>
<td>12.0n$^h$</td>
<td>$-$CH(CH$_3$)$_2$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$-$CO$_2$CH$_3$</td>
<td>+ 3.1</td>
<td>7.8v</td>
<td>$-$CH$_2$C$_6$H$_5$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$-$PO(C$_6$H$_5$)$_2$</td>
<td>+ 2.7</td>
<td>6.9M</td>
<td>$-$CH$_3$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$-$CONH$_2$</td>
<td>+ 2.6</td>
<td>11.3N$^j$</td>
<td>$-$OH$_2$</td>
<td>-1.6</td>
<td></td>
</tr>
<tr>
<td>$-$CON(CH$_3$)$_2$</td>
<td>+ 2.3</td>
<td>5.7v</td>
<td>$-$NH$_2$</td>
<td>-1.6</td>
<td></td>
</tr>
<tr>
<td>$-$SCl$_3$</td>
<td>+ 2.3</td>
<td>6.3M$^k$</td>
<td>$-$Br</td>
<td>-2.2</td>
<td></td>
</tr>
<tr>
<td>$-$NO$_2$</td>
<td>+ 2.1</td>
<td>10.8N$^j$</td>
<td>$-$Cl</td>
<td>-2.5</td>
<td></td>
</tr>
<tr>
<td>$-$As(CH$_3$)$_2$</td>
<td>+ 1.9</td>
<td>5.4M$^l$</td>
<td>$-$I</td>
<td>-2.2</td>
<td></td>
</tr>
<tr>
<td>$-$SO$_2$C$_6$H$_5$</td>
<td>+ 1.6</td>
<td>3.8C$^i$</td>
<td>$-$SCl$_2$</td>
<td>-2.3</td>
<td></td>
</tr>
<tr>
<td>$-$SO$_3$C$_6$H$_5$</td>
<td>+ 1.5</td>
<td>3.5C$^d$</td>
<td>$-$Br$_2$</td>
<td>-2.2</td>
<td></td>
</tr>
<tr>
<td>$-$SC$_6$H$_5$</td>
<td>+ 1.4</td>
<td>4.2M$^k$, 3.3C$^i$</td>
<td>$-$OCCl$_3$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$-$SC$_6$F$_5$</td>
<td>+ 1.3</td>
<td>4.4K$^m,n$, 3.2d,n, -4.4R$^s$</td>
<td>$-$OCH$_3$</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>$-$Si(CH$_3$)$_3$</td>
<td>+ 1.2</td>
<td>2.8C$^i$</td>
<td>$-$OCONH$_2$</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>$-$H</td>
<td>0</td>
<td>8.5N$^x$, -0.5R$^y,n$</td>
<td>$-$OH$_2$</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$-$F</td>
<td>7.8</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculated from the Eyring equation assuming a transmission coefficient of unity; $\Delta G^\ddagger$ was calculated from $\Delta G^\ddagger = \Delta S^\ddagger F + RT - RT25^\circ$, assuming $\Delta S^\ddagger = 0$. Log $k = \log k_0 + a_{inv.}$, where log $k_0$ is for the H substituent. Solvents: A, (CD$_3$)$_2$CO; B, C$_6$H$_6$; C, DCD$_3$, CHClF$_2$, CHFCl$_2$; D, dicalin, toluene, bromonaphthalene; M, CH$_2$Cl$_2$; N, no solvent; R, CCl$_4$, CF$_2$Cl$_2$, CFCl$_3$; S, CS$_2$; T, C$_2$Cl$_4$; V, CCl$_2$ = CDC. b R.D. Bacchini, J.P. Casey, R.J. Cook, G. Senkler and K. Mislow, J.Amer.Chem. Soc., 91, 2850 (1972). c Sum of $a_{inv.}$ for (C$_6$H$_5$)(C$_3$H$_2$)Cl(Si(CF$_3$)$_2$) = 5.4. d F.A.L. Anet and J.N. Ozyany, J.Amer.Chem. Soc., 89, 352 (1967). e H. Eton and K. Mislow, ibid., 95, 1805 (1973); sum of $a_{inv.}$ for (C$_6$H$_5$)(C$_3$H$_2$)Cl(C$_6$H$_5$)$_2$ = 4.8. f G. Senkler in K. Mislow, Trans.N.Y. Acad.Sci., 35, 227 (1973); sum of $a_{inv.}$ for (C$_6$H$_5$)(C$_3$H$_2$)$_2$C$_6$H$_5$ = 8.9. g Sum of $a_{inv.}$ for (C$_6$H$_5$)(SiH(CF$_3$)$_2$) = 8.3.
REFERENCES AND FOOTNOTES

3. The \( \alpha \) value used for \( -\text{OCH}_3 \) was -0.134 and for Cl, +0.25 calculated for both Cl and Br, then adjusted according to the experimental value for Br.4 The \( \Delta G^\ddagger \) for the p-nitrophenylaziridine was adjusted to \( \Delta G^\ddagger = 7.8 \text{ kcal/mol} \) for \( \text{ CF}_2 \text{Cl}_2 \) according to data in ref. 6. For the corresponding points in Fig. 2 and 3, the \( \Delta G^\ddagger \) values were adjusted for solvent C. Therefore, the log \( k \) values are slightly lower than in Fig. 1.
7. The log \( k \) of \( \text{CH}_3\text{NH}_2 \) and \( \text{PhCH}_2\text{Cl}\) (CH3)NCl deviated considerably; because of the latter deviation, the \( \alpha_{\text{inv.}} \) of \( -\text{OCH}_3 \) is subject to great uncertainty. Also, the log \( k \) of 2-(t-butyl)-3,3-diphenylazoniaziridine deviated considerably, probably because of steric interaction between the t-butyl group and the adjacent phenyl groups.
9. With increasing steric bulk at the inverting atom, \( \alpha_{\text{inv.}} \) constants may not be additive.
10. J. Cantacuzene, J. Leroy, R. Jantzen, P. Daudrago, J. Amer. Chem. Soc., 94, 7924 (1972); the \( \Delta G^\ddagger \) of 11.1 kcal/mol was attributed to rotation of the formyl group. However, it is reasonable that this barrier is an inversion-rotation barrier; the inversion and t-butyl rotation barriers have been shown to be identical in t-butylmethylbenzylamine.11
12. The \( \alpha \) values reflect the sensitivities to solvent constraints. The presence of substituents on the ring caused a decreased \( \alpha \) compared to the unsubstituted ring. The presence of the oxygen atom in the oxaziridine ring caused an increased \( \alpha \) compared to the aziridine series.
13. For log \( k = 12.8 \), \( \Delta G^\ddagger = 0 \) using the Eyring equation.
15. The t-buty1methylphenylphosphine and p-toly1methylphenylphosphine log \( k \)'s deviated considerably.
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