

In analogy with the case of the lines seen earlier, where their scalar combination represented the family of lines passing radially through their point of intersection, in this case the scalar combination would represent the family of all planes passing radially through their *line* of intersection, as shown in *Figure 3*, by rotating P_1 or P_2 about L . The reader is encouraged to verify this geometric intuition algebraically by using α and β as the multipliers for P_1 and P_2 and proving that P_3 passes through L for any combination of α and β . P_3 thus represents the planes generated by rotating either P_1 or P_2 about L_1 through the complete range of 0 to 360 degrees.

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Illustrating the Reactivity-Selectivity Principle and the Iso-Selectivity Rule through Ring Substituted α -Azidobenzyl Carbocations

V Jagannadham
 Department of Chemistry
 Osmania University
 Hyderabad 500 007, India
 Email:
 jagannadham1950@yahoo.com

It is axiomatic in organic chemistry that a compound or intermediate which is *highly unstable* in a thermodynamic sense is *highly reactive* in a kinetic sense and the one which is *highly stable* in a thermodynamic sense is *highly unreactive* in a kinetic sense. In this context reactivity represents the capacity of a species to react and selectivity is a mere number that represents the ratio of reaction rates.

‘Reactivity’ of a species describes how fast it reacts compared to the other species. Comparing two reactants A_1 and A_2 , it is apparent that A_1 is more reactive than A_2 towards B , if $k_1 > k_2$ for the reactions:



and



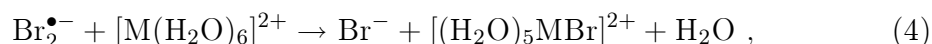
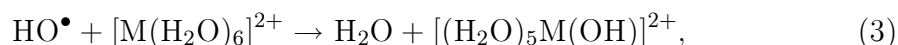
where k_1 and k_2 are rate constants.

Keywords

Benzyl azide,
 reactivity-selectivity,
 α -azidocation.



‘Selectivity’ of a species is a measure of the extent to which its rates of reaction with various substrates differ. It measures something quite different from reactivity. Consider the reactions of HO• and Br₂^{•-} with Fe²⁺(H₂O)₆ and Cr²⁺(H₂O)₆ as examples.



where M stands for Fe or Cr.

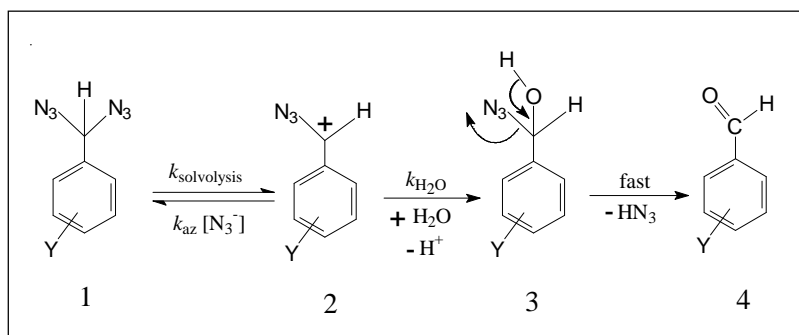
In *Table 1* the second order rate constants for the reactions in (3) and (4) are given [1–4]. The rate constants of HO• with Fe²⁺ and Cr²⁺ are greater than those of Br₂^{•-}, which means that HO• is more reactive than Br₂^{•-} towards the metal ions. HO• is less discriminating than Br₂^{•-} towards the two metal ions. The result is that the rate constants of HO• with the two metal ions differ only by a factor of ten, whereas the rate constants of Br₂^{•-} differ by a large factor of about 500. It is clear that the more reactive HO• is less selective and the less reactive Br₂^{•-} is more selective.

This concept can also be applied to organic reactive intermediates and their neutral adducts [5] such as the three benzyl-*gem*-diazides (**1**) and their α-azidobenzyl carbocations (**2**). Benzyl-*gem*-diazides (**1**) were synthesized by the reported procedure [5]. Treating benzaldehyde (16 mmol) with azidotrimethylsilane (2.5 equivalents added over a period of 2h) in presence of SnCl₂·2H₂O (0.06 equivalents) in dichloromethane (10 ml) at 0 °C under argon and then stirring for 20 h at room temperature (72 h in the case of 4-nitrobenzaldehyde). Purification by column chromatography on basic alumina using solvent mixtures of 5–25% ethyl ether and hexane as eluents gave the diazides as clear oils. (Caution! These compounds are explosive when dealing in large quantities. Of course it is safe when small amounts of the order of mmols are handled). The cations (**2**) are formed by solvolysis of the neutral compounds in water by an S_N1 mechanism (*Scheme 1*).

Table 1. Second order rate constants for the reactions of hydroxyl and bromine radicals with Fe²⁺ and Cr²⁺.

Radical	<i>k</i> , mol ⁻¹ sec ⁻¹	
	Fe ²⁺ (H ₂ O) ₆	Cr ²⁺ (H ₂ O) ₆
HO•	4.3 × 10 ⁸	4.8 × 10 ⁹
Br ₂ ^{•-}	3.6 × 10 ⁶	1.9 × 10 ⁹





Scheme 1.

The formation of the carbocation intermediate (**2**) is supported by measuring the effect of added azide common ion on the rates of solvolysis ($k_{\text{solvolysis}}/\text{sec}$). The final product benzaldehydes (**4**) are formed through highly unstable α -azidohydrin intermediates (**3**) by the elimination of hydrazoic acid.

The azide ion is a very reactive nucleophile and reacts at diffusion level rate constants (k_{az}) with almost all carbocations as determined by flash photolysis technique [6].

The selectivities $\frac{k_{\text{az}}}{k_{\text{H}_2\text{O}}}$ were determined for the cations by studying the common ion inhibition on rates of solvolysis by added azide ion, using the following equation derived for the mechanism given above and applying steady state treatment to the intermediate α -azidobenzyl cation.

$$\frac{k_{\text{solvolysis}}}{k_{\text{obsd}}} = \left(\frac{k_{\text{az}}}{k_{\text{H}_2\text{O}}} \right) [\text{N}_3^-] + 1.$$

Here $k_{\text{solvolysis}}$ is the rate constant in the absence of added azide ion and k_{obsd} is that observed in the presence of added azide ion.

For $\text{Y} = 4\text{-CH}_3\text{O}$, $\frac{k_{\text{az}}}{k_{\text{H}_2\text{O}}} = \frac{5 \times 10^9}{5.8 \times 10^5} = 8,600 \text{ mol}^{-1}$, so this cation is highly selective in reacting with the two nucleophiles, i.e., azide ion and water. For $\text{Y} = 4\text{-NO}_2$, $\frac{k_{\text{az}}}{k_{\text{H}_2\text{O}}} = \frac{5 \times 10^9}{8.6 \times 10^8} \approx 6 \text{ mol}^{-1}$, indicating little selectivity towards the two nucleophiles.

For $\text{Y} = 4\text{-H}$, this ratio is 86 and its selectivity lies between selectivities of the other two (see Table 2). The selectivity and reactivity of the three cations are not only dependent on the high differences of reactivity of the two nucleophiles, azide ion and water, but also on the differences in the stabilities of the three cations (**2** with $\text{Y} = 4\text{-NO}_2$, 4-H and $4\text{-CH}_3\text{O}$) which is attributable to the differences in

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Y	$k_{\text{solvolysis}}$ sec^{-1}	k_{az} $\text{mol}^{-1} \text{sec}^{-1}$	$K_{\text{eq}} =$ $k_{\text{solvolysis}}/k_{\text{az}}$ mol	$k_{\text{H}_2\text{O}}, \text{sec}^{-1}$	$\frac{k_{\text{az}}}{k_{\text{H}_2\text{O}}}, \text{mol}^{-1}$
4-NO ₂	4.9×10^{-7}	5×10^9	9.8×10^{-17}	8.6×10^8	≈ 6
4-H	3.9×10^{-4}	5×10^9	7.8×10^{-14}	5.8×10^7	86
4-CH ₃ O	0.62	5×10^9	1.2×10^{-10}	5.8×10^5	8,600

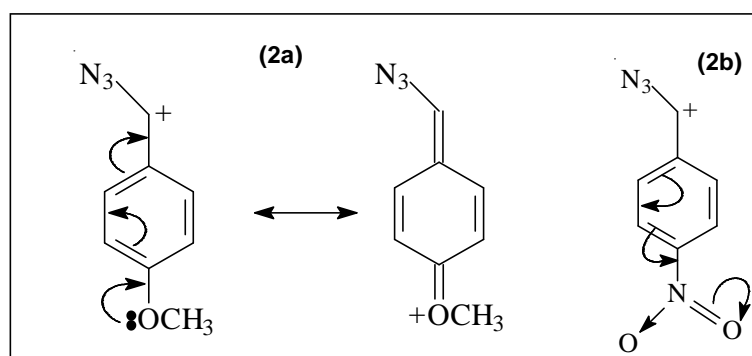
Table 2. Rate and equilibrium constants for the formation and reactions of azidobenzyl cations (2) from their neutral compounds (1) in water at 25 °C. The data are from [5].

the resonance effects of the substituents, the methoxy and the nitro groups, as shown below.

The lone pair of electrons on oxygen of the methoxy group stabilizes the cation and hence, 4-methoxyazidobenzyl cation (**2a**) is more selective (*Scheme 2*). In this case the selectivity between azide ion and water is 8,600:1.

In 4-nitroazidobenzyl cation (**2b**) the magnitude of the positive charge increases due to -M effect of nitro group, hence it is more reactive and so less selective. Here the selectivity between azide ion and water is only 6:1.

The unsubstituted cation lies in between these two, whose selectivity between azide ion and water is moderate, i.e., 86:1.



Scheme 2.

The Iso-Selectivity Rule: It is known that there is often a linear correlation between the values of ΔH^\ddagger and ΔS^\ddagger for a given reaction series. This is usually written as:

$$\Delta H_i^\ddagger = \beta \Delta S_i^\ddagger,$$

where the slope β is known as the iso-kinetic temperature.

Now, considering a series of species like azidobenzyl cations the iso-kinetic rule can be explained. As k_{az} is diffusion controlled rate constant ($5 \times 10^9 \text{ mol}^{-1}\text{s}^{-1}$) it is not affected by temperature. But $k_{\text{H}_2\text{O}}$ is temperature dependent. As we increase the temperature, $k_{\text{H}_2\text{O}}$ ($5.8 \times 10^5 \text{ sec}^{-1}$) for methoxy substituted azidobenzyl cation (**2a**) increases and tends to equal the rate constant of nitro-substituted azidobenzyl cation (**2b**) (8.6×10^8). Hence all the ring-substituted azidobenzyl cations may react at the same rate with nucleophilic water at a particular temperature. This temperature is called the iso-selective (kinetic) temperature at which all the cations become non-selective and react with every nucleophile with equal facility.

Suggested Reading

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