STABILIZATION OF CARBENIUM IONS BY AN Q-AZIDO GROUP

Shmaryahu Hoz^{*} and J. L. Wolk Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel 52900.

Abstract. The ability of the azido group to stabilize an α carbenium ion was calculated to be intermediate between that of OH and NH₂. The barrier for the decomposition of the title compound into N₂ and H₂C=N⁺ is 4.6 kcal/mol.

Organic azides exhibit a rich and colorful chemistry and are very useful in modern synthesis.¹ However, because of their high reactivity, relatively, little is known about the azido group as a substituent affecting the reaction center as opposed to being the reaction center itself.² Even less is known about its ability to stabilise a neighboring carbenium. Resonance structures of alkyl azides indicate that the azido group is capable of stabilizing an adjacent positive center since in one of these structures a negative charge is placed on N₁.

 $R - N_1 - N_2 = N_3$ <-----> R - N = N = N

Reactions such as electrophilic bromination of azidobenzene (which is faster from that of toluene),³ the facile electrophilic attack on vinyl azides,⁴ and the successive substitution of Cl in CH_2Cl_2 by N_3^{-} ,⁵ are only a few examples which also point to this effect. However, unlike the thio, oxo and amino groups, the ability of the azido group to stabilize an α carbenium ion is not well recognised.

In this study, we were primarily interested in quantitative comparison of the stabilization of a carbenium ion by the azido group with that of other more common substituents. Such a comparison can be performed by using the isodesmic reaction shown in equation 1 for azide.

	N ₃ CH ₃	+ сн ₃ +	> N ₃ CH ₂ ⁺	+	CH4	(1)
	(1)		(2)			
Energy au.	-202.86738	-39.23064	-202.00740	-	40.19517	

Using Gaussian 86^6 and the $6-31G^*$ basis set,⁷ we have calculated the structures and energies of the four species in equation 1. The geometrical parameters for 1 and 2 along with their Mulliken atomic charges are given in scheme 1.

As expected, in 2, the N_1-N_2 bond becomes longer and the C-N₁ bond shorter compared to 1 as a result of the introduction of the positive

charge. This is associated with an increase in the double bond character in the latter bond at the expense of the former. Less expected is the N-N-N bending in the carbenium by 12° , showing some resemblance to butadiene in its S-trans conformation. An additional contribution to the observed inplane bending of the N₃ array comes most probably from electrostatic repulsion between the neighboring hydrogen and the terminal nitrogen atom. These two atoms are positively charged (0.31 and 0.12 charge unit respectively) and the electrostatic repulsion between them amounts to 0.12*0.31*300/3.3=3.7 kcal/mol⁸. The presence of electrostatic interactions in the system is also evident from comparison of the two H-C-N angles in 2. The difference between these two angles is affected even to a larger extent by the repulsion from the central nitrogen atom.

Using the energies of the species in equation 1, it was found that the methyl cation stabilization energy of the azido group is 65.6 kcal/mol. This stabilization energy is compared in Figure 1 with that of other substituents whose methyl cation stabilization energies were calculated by Hopkinson and Lien⁹ using the same basis set.

The location of the azido group between OH and NH_2 , which are the known to be the best groups to stabilize an α carbenium ion in solution, is remarkable. Although crossover can and most probably will occur upon moving from the gas phase to solution due to the high polarizability of the azido group (which is more important in the gas phase),¹⁰ this result is unanticipated.

Finally, we have calculated the transition state for the decomposition of the azidocarbenium and confirmed its identity by force constant analysis. Its geometrical parameters are given in scheme 1. From its energy (-201.99999 au) and that of 2, one obtains an activation energy of 4.6 kcal/mol for its decomposition into N_2 and $H_2C=N^+$. This low activation barrier is highly surprising since, in spite of the general instability of azides, their derivatives have rather high activation energies for the expulsion of N_2 . These could be in the range of 30 to 45 kcal/mol for Me, Et and similar azido derivatives.¹¹ This difference of an order of magnitude in activation energy between for example methyl azide and 2, most probably stems from the difference in the N-N bonding in the two species. In the former, one of the resonance structures (see above) has a double bond character between these two atoms, whereas in 2 the lone pair on N₁ is delocalised onto the carbenium center and accordingly does not strengthen the N-N bond. This is evident from the comparison of C-N and N-N bond

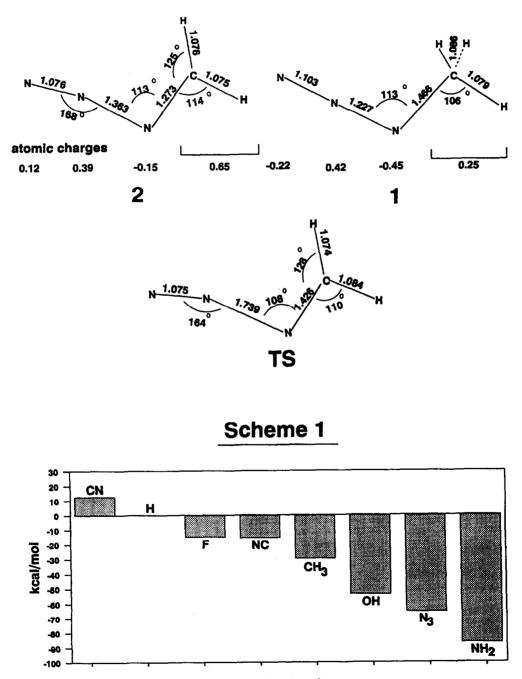


Figure 1. Energies of the isodesmic reaction (eq 1). negative numbers indicate stabilization.

lengths in 1 and 2 (scheme 1). Thus, it can be anticipated that higher stability of azidocarbenium with respect to a split of N_2 can be achieved by substituting the hydrogens in 2 by carbenium stabilizing groups, such as MeO, thereby enabling observations of azidocarbenium derivatives in solution.

References and notes.

 (a) Patai, S. Ed. "The Chemistry of the Azido Group"; Wiley: New-York, 1971; (b) Patai, S. and Rappoport, Z. editors, Supplement D to the series "The Chemistry of the Functional Group"; Wiley: New-York 1983; (c) Scriven, E. F. V.; Turnbull, K. Chem. Rev. 1988, 88, 297.

See however: Biffin, M. E. C.; Miller, J.; Paul, D. B. in ref. 1a p 203.
 Smith, P. A. S.; Hall, J. H.; Kan, R. O. J. Am. Chem. Soc. 1962, <u>84</u>, 485.

4. Hassner, A.; Levy, A. B. J. Am. Chem. Soc. 1971, <u>93</u>, 5469 and references cited therein.

5. Hassner, A. personal comunication.

6. Frisch, M.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Stewart, J.J.P.; Bobrowitz, F.; DeFrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fluder, E.; Pople, J.A. GAUSSIAN-86, Release C, Carnegie Mellon University.

7. Hariharan, P. C.; Pople, J. A. Chem. Phys. Let. 1972, <u>16</u>, 217.

8. Kosower, E. M. in "An Introduction to Physical Organic Chemistry" Wiley: New-York, 1968, p. 39.

9. Hopkinson, A. C.; Lien, M. H. Can. J. Chem. 1985, 63, 3582.

10. See for example the carbenium stabilization by thio- and oxo- groups in solution and in the gas phase: Bernardi, F.; Csizmadia, I. G.; Schlegel, H. B.; Wolfe, S. Can. J. Chem. 1975, <u>53</u>, 1144; Bernardi, F.; Mangini, A.; Epiotis, N. D. Larson, J. R.; Shaik, S. S. J. Am. Chem. Soc. 1977, <u>99</u>, 7465; Casserio, M. J. Am. Chem. Soc. 1978, <u>100</u>, 4242; Jensen, J. L.; Jencks, W. P. J. Am. Chem. Soc. 1979, <u>101</u>, 1476; Hoz, S.; Aurbach, D. J. Org. Chem. 1984, <u>49</u>, 1984 and references cited therein.
11. Abramovitch, R. A. Kyba, E. P. Ref. 1a, p 221.

(Received in UK 29 May 1990)