Quantum Mechanical Studies of the α Effect

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Abstract: Ab initio self-consistent field calculations with extended basis sets were done to obtain wave functions for a variety of nucleophiles (Cl^-, OH^-, NH_3, CH_3NH_2, NH_2OH, NH_2NH_2, ClO^-, and OOH^-), to determine whether molecular energetics and/or electronic structure considerations could elucidate the α effect. In contrast to those of most of the standard nucleophiles, the wave functions of the α nucleophiles contained no lone-pair valence molecular orbitals. The highest occupied molecular orbital (HOMO) of OOH^- was highest in energy of all the HOMOs, but the orbital energies of the HOMOs of the other nucleophiles did not correlate well with reactivity, nor did the net electronic charge on the nucleophilic center. Characteristic of most of the α nucleophiles is an asymmetric antibonding HOMO in which the charge density is more diffuse on the nucleophilic center and which has a nodal plane perpendicular to the bond. Thus, the electrons of this HOMO are readily polarized by the approaching electrophile, and the donation of these antibonding electrons stabilizes the composite system along the potential energy surface.

Introduction

A certain class of nucleophiles was recognized by Edwards and Pearson[1] as exhibiting exceptionally high reactivity toward a variety of substrates relative to their basicity toward the proton. Considered characteristic of the group of "supernucleophiles" is the presence adjacent to the nucleophilic center of an electronegative atom having one or more pairs of unshared electrons. Edwards and Pearson[1] ascribed the enhanced reactivity to the unshared electron pair on the adjacent center and referred to the phenomenon as the "α effect." Among these "α nucleophiles" may be included hydrazine, hydroxylamine, the hypochlorite ion, and the anion of hydrogen peroxide. A survey of the factors that may influence nucleophilicity is presented by Bunnett[2] and a review of α nucleophilicity by Fina and Edwards.[3] Among experimental studies of α nucleophiles are those of Ibne-Rasa and Edwards,[4] Behrman et al.,[5] Zoltewicz and Deady,[6] Beale,[7] Wiberg,[8] Biggi and Pietra,[9] and Dixon and Bruice.[10] The latter authors postulate that the α effect is not associated with a single factor but may involve several factors depending upon the specific nucleophile. In addition, solvent effects and the nature of the substrate may also be contributing factors.

Of the various factors that may effect α nucleophilicity, one hypothesis has received considerable attention and is based upon lone pair–lone pair repulsions. As suggested early on by Ibne-Rasa and Edwards,[4] the electrostatic repulsions between the electron pair of the reacting atom and the free electron pair of the adjacent electronegative atom raise the ground-state energy of the nucleophile, thus lowering the energy of activation. This explanation is commonly referred to as "ground-state destabilization". Considerations of these interactions on the basis of perturbation theory appear in a series of papers by Aubort, Hudson, Klopman, and co-workers.[11] In one,[11a] the authors predicate that splitting of the lone-pair n orbitals accounts for α nucleophilicity, when the resultant n* orbital lies above the highest occupied π orbital. Within the framework of frontier orbital theory, Klopman et al.[11b,c] diagrammatically depict the orbitals of OH^- and ClO^- in a manner so that the interaction between the pπ orbitals of the oxygen and the chlorine atoms produces orbital splitting such that "the highest filled molecular orbital in ClO^- is much higher than in OH^-". As a result, the interaction of the substrate with ClO^- requires less energy and is faster than the reaction with OH^- as the nucleophile.

An alternative explanation has been presented by Ingold,[12] who postulated that the effect is due to "inhomogeneous, directed polarizability in the nucleophilic orbital at the reaction site". As stated by Ingold: "The real condition for the 'α effect' is that the highest occupied orbital centered largely on the nucleophilic atom is antibonding, with a node normal to the bond between that atom and the 'α' atom". As a result of this inhomogeneous polarizability, the interaction of the electrons of this orbital with the substrate is facilitated. This concept was also presented in a slightly different manner by Edwards and Pearson[1] in their discussion of the influence of polarizability in the behavior of the nucleophile. Because in some studies[5] the macroscopic evidence (molar refractivity) concerning the polarizability of some α nucleophiles did not indicate any extraordinary polarizability, not as much attention has been paid to the Ingold hypothesis as to lone pair repulsion theory. A third theory is that postulated by Liebman and Pollack.[13] They assert that a major flaw in the explanation based upon lone pair–lone pair splitting is the assumption that this splitting necessarily raises the energy of the highest occupied molecular orbital (HOMO). They show that the HOMO of ClO^- lies lower in energy than that of O^- but higher than that of Cl^-. They advance the theory that the two lone-pair nonbonding orbitals of the α nucleophile together with the π system of the electrophile form a six-electron cyclic transition state. The extra stability of these transition states over the corresponding acyclic transition states formed by non-α-nucleophiles is due to the aromatic character of the six-electron cyclic array. The latter theory requires the presence of two lone pairs on the nucleophile.

In a consideration of "ground-state destabilization", two incongruities appear. First, it should be recognized that the HOMOs of the anions must be higher in energy than those of the neutral species. The added electron in the anions naturally is less tightly bound than the outer electrons of the neutral species. Thus, ground-state destabilization per se cannot account for an enhancement in the reactivity of a species such as NH_2NH_2 with respect to a species such as OH^-. Secondly, in accordance with perturbation theory,[14] the zero-order approximation to the wave functions in the case of degenerate orbitals, e.g., in NH_2NH_2, or near-degenerate orbitals, e.g., in NH_2OH, is a pair of orbitals which are linear combinations of the unperturbed orbitals, one corresponding to a lower energy bonding orbital and the other to a higher energy antibonding orbital. Owing to the perturbation, changes occur not only in the energy but also in the nature of the unperturbed orbitals, the original lone-pair orbitals forming a bonding and antibonding pair. Thus, perturbation theory is compatible with Ingold's definition of the electronic structure of the α nucleo-

Table I. Atomic Coordinates for Nucleophile Wave Functions[a]

		x	y	z			x	y	z
OH⁻	O	0.0	0.0	0.0	ClO⁻	O	0.0	0.0	0.0
	H	0.0	0.0	1.781		Cl	0.0	0.0	2.967
NH₂OH	N	0.0	0.0	0.0	O₂H⁻	O₁	0.0	0.0	0.0
	O	0.0	0.0	2.7590		O₂	0.0	2.5323	0.0
	H₁	1.5923	−1.0610	−0.5127		H	1.7584	3.0365	0.0
	H₂	−1.5923	−1.0610	−0.5127					
	H₃	0.0	1.7677	3.1671	NH₃	N	0.0	0.0	0.0
						H₁	−0.8841	1.5313	−0.7186
						H₂	−0.8841	−1.5313	−0.7186
CH₃NH₂	C	0.0	0.0	0.0		H₃	1.7682	0.0	−0.7186
	N	0.0	0.17	2.78					
	H₁	1.6864	−0.9746	−0.682					
	H₂	−1.6864	−0.9746	−0.682	NH₂NH₂	N₁	0.0	1.37	0.0
	H₃	0.0	1.9492	−0.682		N₂	0.0	−1.37	0.0
	H₄	1.5282	−0.7208	3.504		H₁	1.5290	2.0873	0.9017
	H₅	−1.5282	−0.7208	3.504		H₂	−1.5290	2.0873	0.9017
						H₃	0.9017	−2.0873	1.5290
						H₄	0.9017	−2.0873	−1.5290

[a] Coordinates given in au of length (1 au = 0.52917 Å).

Table II. Total Energies and Orbital Energies for Nucleophile Wave Functions[a]

Cl⁻		OH⁻		NH₃		CH₃NH₂	
−459.521 207		−75.352 464 −75.417 54[b]		−56.176 588		−95.183 266 −95.112 68[c]	
1s	−104.3378	1σ	−20.1047	1a₁	−15.5415	1a′	−15.536
2s	−10.0724	2σ	−0.8626	2a₁	−1.1523	2a′	−11.246
2p	−7.5386	3σ	−0.1956	1e$_{x,y}$	−0.6295	3a′	−1.1722
3s	−0.6428	1π$_{x,y}$	−0.0610	3a₁	−0.4187	4a′	−0.8994
3p	−0.068 81					1a″	−0.6622
						5a′	−0.6061
ClO⁻		OOH⁻		NH₂NH₂		6a′	−0.5494
						2a″	−0.5221
−534.214 646 −534.318 86[d]		−150.130 986		−111.148 915 −111.074 34[e]		7a′	−0.3785
1σ	−104.550	1a′	20.2926	1a	−15.5753		
2σ	−20.217	2a′	−20.1785	2a	−15.5749	NH₂OH	
3σ	−10.283	3a′	−1.1572	3a	−1.2546	−130.962 709 −130.897 42[e]	
4σ	−7.752	4a′	−0.772 83	4a	−1.0237	1a′	−20.589
1π$_{x,y}$	−7.747	5a′	−0.3818	5a	−0.670 02	2a′	−15.620
5σ	−1.047	1a″	−0.2975	6a	−0.660 14	3a′	−1.395
6σ	−0.6965	6a′	−0.2571	7a	−0.6172	4a′	−1.0825
2π$_{x,y}$	−0.2845	7a′	−0.0822	8a	−0.4130	1a″	−0.6806
7σ	−0.2422	2a″	−0.0510	9a	−0.4006	5a′	−0.668
3π$_{x,y}$	−0.092 73					6a′	−0.603
						2a″	−0.484
						7a′	−0.4246

[a] Energies reported in atomic units (1 au = 27.21 eV = 627.3 kcal mol⁻¹). [b] Reference 22. [c] Reference 19. [d] Reference 20. [e] Reference 18.

philes and tends to discount the cyclic transition state theory, which is based upon the presence of the two lone-pair orbitals.

Because the nature of α nucleophilicity does not seem completely elucidated and because in the present "state of the art" high-quality ab initio wave functions can be calculated for relatively small molecules, a series of self-consistent field (SCF) calculations was made on several species (NH₂NH₂, NH₂OH, ClO⁻, and OOH⁻) associated with the α effect and on other nucleophiles (NH₃, CH₃NH₂, OH⁻, and Cl⁻) which are not. In this way, a comparison of the wave functions could clarify the role of energetics and/or electronic structure in the α effect. Although, with the exception of OOH⁻, previous ab initio calculations had been done for all species, the calculations varied widely in the size and choice of basis sets and properties reported and thus could not be compared directly. Advantage

was taken of this previous research in that, as specified later, no attempt was made to determine in the present work the minimum-energy geometry, reliance instead being placed on the results of the previous work.

Computational Details

The calculations were performed by using the POLYATOM series of programs,[15] designed to handle a symmetry-adapted Gaussian basis. In all the calculations "extended basis sets" were used.[16] The functions used for the second-row atoms were the Dunning[17] 4s/3p contractions of 9 s and 5 p Gaussian primitives, his 2s contraction being used for hydrogen. For chlorine, the 4s/3p contractions (14 s and 10 p primitives) of Huzinaga and Arnau[18] were split to give a 6s/5p basis for better balance with the 4s/3p contractions used for the lighter atoms. The atomic coordinates used were those given by Allen

Table III. Net Atomic Charges on Nucleophiles[a]

OH⁻	ClO⁻	OOH⁻	NH₃	NH₂OH	NH₂NH₂	CH₃NH₂
O −1.2	O −0.78	O₁ −0.73	N −0.88	N −0.50	N −0.59	N −0.70
H +0.2	Cl −0.22	O₂ −0.55	H +0.29	O −0.53	H₁,₃ +0.27	C −0.42
		H +0.28		H₁,₂ +0.31	H₂,₄ +0.31	H₁,₂ +0.17
				H₃ +0.41		H₃ +0.21
						H₄,₅ +0.29

[a] atoms numbered as shown in Table I.

Table IV. Population Analysis for Highest Occupied Orbitals of the Nucleophiles

OH⁻	$1\pi_{x,y}(n)$	NH₃	3a₁(n)	ClO⁻	$3\pi_{x,y}(\pi^*)$
O x,y	2.000 00	N 1s	−0.000 64	O x,y	1.144 52
		N 2s	0.154 57	Cl x,y	0.855 47
		H s	0.015 54		
OOH⁻	2a″(π*)	N z	1.799 44		
O₁ z	1.467 02			NH₂OH	7a′(σ)
O₂ z	0.532 99	NH₂NH₂	9a(σ*)	N 1s	−0.000 51
		N₁,₂ 1s	−0.000 17	N 2s	0.130 65
CH₃NH₂	7a′(σ)	N₁,₂ 2s	0.051 15	N y	1.179 67
N 1s	−0.000 46	N₁ x	0.031 03	N z	0.201 21
N 2s	0.103 96	N₁,₂ y	0.125 93	O 1s	−0.000 11
N y	1.406 74	N₁ z	0.722 89	O 2s	0.034 55
N z	0.112 96	N₂ x	0.722 89	O y	0.219 32
C 1s	−0.000 01	N₂ z	0.031 01	O z	0.156 80
C 2s	0.004 11	H₁,₃ s	0.017 61	H₁,₂ s	0.020 03
C y	0.107 03	H₂,₄ s	0.051 18	H₃ s	0.039 07
C z	0.010 82				
H₁,₂ s	0.047 59				
H₃ s	0.131 15				
H₄,₅ s	0.014 26				

et al.[19] for hydroxylamine and hydrazine, by Fink and Allen[20] for methylamine, by O'Hare and Wahl[21] for the hypochlorite ion, by Buenker and Peyerimhoff[22] for the hydroperoxyl radical, and by Cade[23] for the hydroxide ion. For ammonia, the experimental geometry was used. Hydrazine, for convenience, was treated as if it belonged to the C_1 point group; with the geometry used, its molecular orbitals can consist of linear combinations of all the basic functions. Hydroxylamine, the hydroperoxide ion, and methylamine have a molecular plane of symmetry and transform according to C_s symmetry. Their molecular orbitals consist of a′ orbitals (σ type) and a″ orbitals (π type). The atomic coordinates for all wave functions are given in Table I. Mulliken population analyses were calculated by using the POLYATOM program, and probability distribution maps were calculated by a modified version of the program MOPLOT.[15]

Results of the Calculations

In Table II are summarized the energetics of the calculated wave functions. The energies of the highest occupied molecular orbitals increase in the order $NH_2OH < NH_3 < NH_2NH_2 < CH_3NH_2 < ClO^- < Cl^- < OH^- < OOH^-$. The net atomic changes are reported in Table III. Excess negative charge on the nucleophilic center increases in the order $NH_2OH < NH_2NH_2 < CH_3NH_2 < OOH^- < ClO^- < NH_3^- < OH^-$. The population analysis of each of the HOMOs is given in Table IV, the more familiar σ, π, and n notation specified in addition to the symmetry notation of the orbital. The OH^- and NH_3 molecular orbitals are clearly lone-pair molecular orbitals. Inspection of the molecular orbital coefficients[24] showed the HOMOs of OOH^-, ClO^-, and NH_2NH_2 to be of an antibonding nature, whereas those of CH_3NH_2 and NH_2OH comprise a bonding combination of the p_z atomic orbitals and

Table V. Population Analysis of π-Type Orbitals[a] of Nucleophiles

	CH₃NH₂			OOH⁻ [b]	
	1a″(π)	2a″(π*)		1a″(π)	
H₁, H₂	0.105 53	0.354 21	O₁ z	0.532 65	
H₄, H₅	0.284 01	0.134 33	O₂ z	1.467 35	
C x	0.373 52	0.721 10			
N x	0.847 38	0.301 84			
	ClO⁻ [b]			NH₂OH	
				1a″(π)	2a″(π*)
			H₁, H₂	0.309 96	0.107 57
	1πx,y(n)	2πx,y(π)	N x	1.015 87	0.164 52
Cl x,y	1.999 99	1.161 25	O x	0.364 23	1.620 34
O x,y		0.838 74			

[a] Orbitals perpendicular to molecular plane of symmetry in nondiatomics. [b] Other π-type orbital is highest occupied molecular orbital; population analysis given in Table IV.

an antibonding combination of the p_y atomic orbitals. These features are evident in the probability distribution plots shown in Figures 1–5. To determine whether other molecular orbitals are of n type, population analyses were made for several lower lying molecular orbitals of π type (Table V) for CH_3NH_2, ClO^-, OOH^-, and NH_2OH. With the exception of the 1π orbital of ClO^-, identifiable as the 2p lone pair of chlorine, all these molecular orbitals are characterized by greater or lesser electron delocalization among the atoms. In summary, the wave functions of the non-α-nucleophiles do contain lone-pair molecular orbitals among the higher energy molecular orbitals, with the exception of CH_3NH_2. The wave functions of the α nucleophiles do not contain lone-pair molecular orbitals among the higher energy molecular orbitals. The 7a′ molecular orbitals (HOMOs) of CH_3NH_2 and of NH_2OH are characterized by a high participation of the basis functions on the ni-
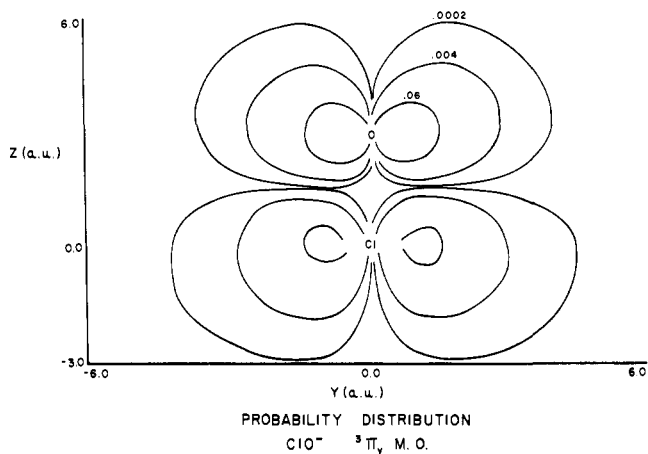
PROBABILITY DISTRIBUTION
ClO⁻ ³π_y M. O.

Figure 1.

PROBABILITY DISTRIBUTION
OOH⁻ 2a″ M.O.

Figure 2.

PROBABILITY DISTRIBUTION
N₂H₄ 9a M.O.

Figure 3.

PROBABILITY DISTRIBUTION
NH₂OH 7a′ M.O

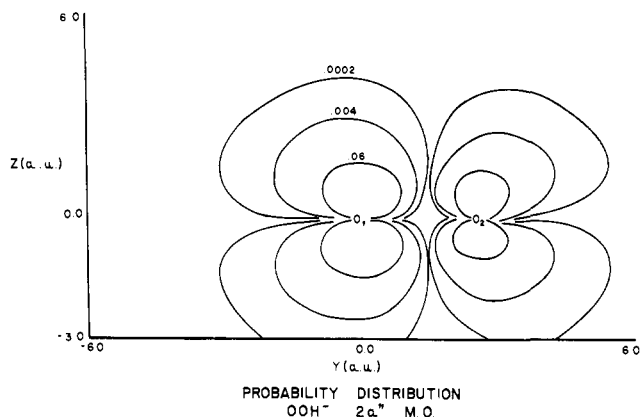**Figure 4.**

PROBABILITY DISTRIBUTION
CH₃NH₂ 7a′ M.O.

Figure 5.

trogen atom; the lower lying 2a″ molecular orbitals are antibonding orbitals with electronic charge polarized to the nonnucleophilic center.

Discussion

As observed by Dixon and Bruice,[10] several factors may enter into α nucleophilicity, as evidenced by changes in relative reactivity of the nucleophiles with changes in substrate. For example, the data of Biggi and Pietra[9] show the following decrease in reactivity of the nucleophiles when chloro-2,4-dinitrobenzene is the substrate: $CH_3NH_2 > NH_2NH_2 > OH^-$ > NH_3. Behrman and co-workers report the rate constant for OOH^- reacting with this substrate to be 300 times greater than for OH^-, whereas Dixon and Bruice[10b] report that the ratio is of the order of 10^5 for the substrate. As presented by Edwards and Pearson[1] reactivities decrease in the order OOH^- > $ClO^- > OH^- > NH_2OH > NH_3$ for carbonyl carbon and $OOH^- > OH^- > ClO^- > NH_2OH$ for tetrahedral phosphorus. The data of Dixon and Bruice[10a,b] show the following decrease in reactivity with respect to malachite green: OOH^- > NH_2NH_2, $ClO^- > C_2H_5NH_2 > NH_2OH > OH^-$. In these comparisons, only OOH^- shows consistently highest reactivity. On the other hand, the other α nucleophiles sometimes are more reactive and sometimes less reactive than the other nucleophiles, depending upon the substrate. On the assumption, then, that OOH^- possesses all of the characteristics leading to α nucleophilicity, whereas the other α nucleophiles do not, it is constructive to identify those characteristics of the OOH^- wave function which may influence α nucleophilicity. First, of all the HOMOs of the nucleophiles studied, the HOMO of OOH^- lies highest in energy. Secondly, of the anionic nucleophiles, OOH^- had the least excess negative charge on the

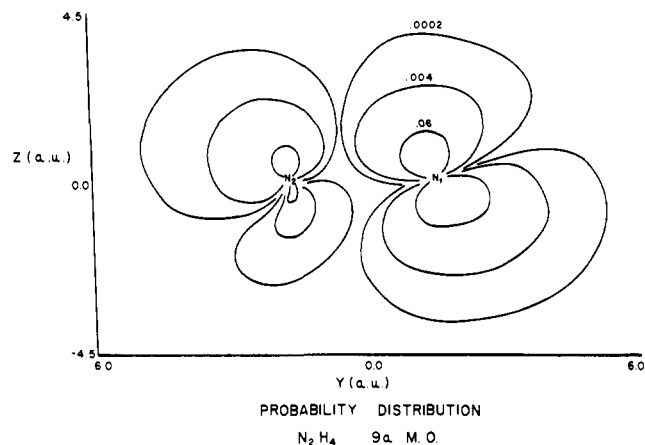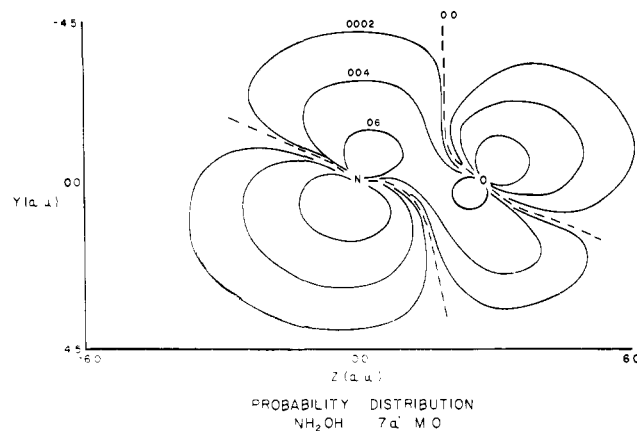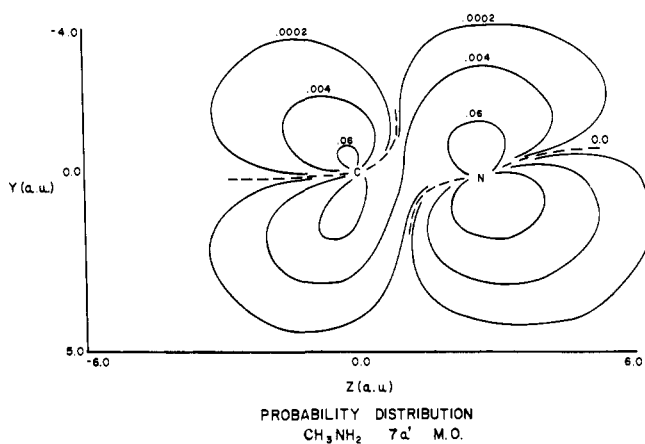nucleophilic center. Third, the HOMO of OOH^- can be clearly identified (see Figure 2) as an asymmetric antibonding combination of the p_z orbitals of the two oxygens, the charge density being more diffuse on the nucleophilic oxygen, with a nodal plane perpendicular to the O–O bond. This first feature certainly is in accord with the ground-state destabilization theory of α nucleophilicity. However, little correlation is apparent between the ordering of the orbital energies and the relative reactivities with the exception of OOH^-. The second factor most likely can be dismissed as an influence in α nucleophilicity, more probably being a function of the electronegativity of adjacent atoms. The net charges on the neutral nucleophiles exhibit the same behavior. Perhaps the most

important characteristic of the OOH^- wave function with respect to α nucleophilicity is the nature of the HOMO, which conforms to Ingold's[12] condition for the α effect. In the context of frontier orbital theory, one rationalizes the interaction of the nucleophile with the substrate via the HOMO of the nucleophile. In OOH^-, this molecular orbital is more diffuse at the nucleophilic site and thus its electrons are more easily polarized by the approaching electrophile. Moreover, donation of these *antibonding* electrons to the electrophile has a stabilizing effect on the composite nucleophile–electrophile system. This feature reflects an inhomogeneous polarizability of the HOMO not of the total charge distribution of the molecule and, thus, is not discernible when the macroscopic polarizability is examined. Indeed, the probability distribution plots of the total NH_2NH_2 wave function in the xy and yz planes are very symmetric even though the corresponding plots of the HOMO of NH_2NH_2 are not (Figure 3). The formation of the antibonding, and concomitant bonding, molecular orbital from the lone pairs of the separated atoms can be rationalized on the basis that the consequent electronic delocalization stabilizes the molecule by reducing the electronic repulsion between the two electrons constituting the lone pair, as well as by perturbation theory.

Accepting, therefore, two criteria for α nucleophilicity, (1) a HOMO high in energy and (2), more importantly, an antibonding HOMO of inhomogeneous polarizability, an analysis can be made of the other nucleophiles. Of the anionic nucleophiles, the HOMO of ClO^- is the lowest lying in energy (15 kcal mol^{-1} more stable than that of Cl^-). This HOMO displays the antibonding character requisite to the second criterion, but because the valence electrons of the chlorine atom are further from the nucleus than those of second-row atoms, the charge density is more diffuse about the chlorine than about the nucleophilic center (Figure 1). Thus, ClO^- does not display consistently the α effect, being more reactive to carbonyl carbon than OH^- and less reactive to tetrahedral phosphorus than OH^-. With respect to malachite green, ClO^- and NH_2NH_2 show about the same degree of reactivity, even though the ClO^- HOMO is higher in energy than that of NH_2NH_2. Of the neutral nucleophiles, hydrazine is the only one with a HOMO purely antibonding in character, but this molecular orbital is lower in energy than that of methylamine. The latter factor may be responsible for the higher reactivity of methylamine over hydrazine with respect to the chlorodinitrobenzene. On the other hand, the HOMO of NH_2NH_2 is more diffuse and more polarizable than that of ClO^- at the nucleophilic site, which may enhance the reactivity of the former over the latter with respect to malachite green. The highest occupied orbitals of both CH_3NH_2 and NH_2OH are similar in character (Figures 4 and 5), the charge density in the nucleophilic center being slightly more polarizable for hydroxylamine. Both molecular orbitals are slightly bonding in nature, and, therefore, the donation of these electrons to the electrophile does not stabilize the composite system to the same

extent as does the donation of purely antibonding electrons. Indeed, one would expect a rather similar behavior for these two nucleophiles, ethylamine and hydroxylamine exhibiting about the same order of reactivity to malachite green.

Obviously, the α effect arises from several factors, some of which have been dealt with in the present work, and the extent of the α effect is related to the substrate. Any analysis of the nucleophiles as isolated molecules cannot represent the reality of the interacting species in a macroscopic system and, of necessity, ignores solvent effects, kinetic vs. thermodynamic factors, and the like. The present work, however, strongly supports the Ingold[12] definition of α nucleophilicity and to a lesser extent the "ground-state destabilization" theory.[4,11] The results of the work do not support the cyclic transition state theory,[13] the α nucleophiles being distinguished by the absence of lone pair orbitals.

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