

syntheses especially lies the danger that the synthetic chemist can become channeled into one line of thinking and overlook more efficient methods, simply because the number of combinatorial possibilities for synthetic routes is so great. The challenge of designing a computer package to direct a long-range search, then, is to be able to handle a very large diversity of target structures without becoming polarized into overly restrictive antithetic channels. The Robinson annulation package described in this paper represents a highly effective approach to this problem.

It is not possible, and certainly not desirable, for the search-table writer to "lead the computer by the hand" back antithetically from an arbitrary target structure to a preselected key intermediate. The aim of the long-range search package is rather to provide a framework wherein the computer program can use its own subgoal capabilities to arrive at desired precursors in an efficient fashion. It

is in such an unbiased reduction of the combinatorial explosion that the computer has an advantage over the chemist and has a potential for making a very positive contribution to the solution of synthetic problems in years to come.

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Molecular Orbital Theory of Supernucleophiles: Complementary Criteria and Supporting Evidence

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Molecular orbital (MO) theory is used to show that the two commonly invoked and apparently different electronic structure criteria for supernucleophilic propensity are complementary. The complementary character is realized through the inherent flexibility of MO wave functions. Canonical MO's express the Ingold criteria. Localized MO's express the lone-pair-repulsions criterion. A consequence of the complementarity is that more extensive models of the α effect may be based on either electronic structure criterion. A simple treatment of the electronic structure of supernucleophiles is likewise a consequence of the complementarity. Supernucleophilic propensity may be characterized by the numbers of valence electrons and α atoms that are associated with the nucleophilic moieties. The concepts of enhanced supernucleophilic and moderated nucleophilic propensities are proposed on the basis of electronic structure arguments. It is found that both types of nucleophilicity are observed in potential supernucleophiles. Experimental evidence is presented in support of the proposed degree of nucleophilic character for the dichloroamide anion and trichloroamine.

Canonical molecular orbitals are the usual delocalized molecular orbitals (MO's).¹ Localized MO's are MO counterparts of valence bond (VB) concepts such as lone pairs.² Canonical MO's and localized MO's are completely equivalent descriptions because of the well-known arbitrariness of MO wave functions.³ A consequence of the equivalence is that apparently different valence models may be essentially the same. For example, Walsh's rules⁴ in terms of canonical MO's are equivalent to Gillespie's rules⁵ in terms of localized MO's.⁶

Two commonly invoked and apparently different criteria for supernucleophilicity have been proposed on the basis of the electronic structure of nucleophilic moieties. The lone-pair-repulsions criterion^{7,9-11} is based on repulsions

between lone-pair electrons on the nucleophile and the α atom. The Ingold criterion¹² requires the highest energy occupied MO to be antibonding with a node that is normal to the bond between the nucleophile and the α atom. We show that the two criteria are quantum mechanically equivalent. The lone-pair-repulsions criterion can be expressed with localized MO's, and the Ingold criterion can be expressed with canonical MO's. Consequently, extensive models of supernucleophilicity, such as reaction schemes and catalytic arguments, may be based on either electronic structure criterion. This is the spirit of Klopman's approach,⁸ which requires the highest occupied orbital to have an especially high energy.

Given the equivalence of the two electronic structure criteria, a systematic analysis of the electronic structure of supernucleophiles can be achieved. Two numbers are necessary to characterize potential supernucleophiles, the

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number of valence electrons and the number of α atoms. A particular α coordination determines the number of valence electrons that may be associated with a potential supernucleophile.

The unified treatment suggests two novel implications that are consequences of the electronic structure. Enhanced supernucleophilicity is associated with potential 2-coordinate supernucleophiles. We discuss the experimental results for NCl_2^{-13-15} and *N*-chlorobenzenesulfonamide anion¹⁶ which are evidence for enhanced supernucleophilicity. Moderated nucleophilicity is associated with some potential 3-coordinate supernucleophiles. The sulfite ion is a known 3-coordinate supernucleophile.¹⁷ We report new experimental results which demonstrate the reduced nucleophilicity of NCl_3 .

Electronic Structure of Supernucleophiles

A. Molecular Orbitals and Molecular Orbital Configurations. Two types of MO's are commonly used. Canonical MO's are obtained as solutions of the canonical MO Hartree-Fock-Roothaan equations.¹ They correspond to delocalized bonds, antibonds, etc. Localized MO's are obtained by applying localization criteria.¹⁸ They satisfy the localized MO equations¹⁹ and correspond to the bonds, lone pairs, etc. of valence bond theory.²

Canonical and localized MO's are occupied according to different Aufbau principles. We shall show that electronic configurations in terms of localized MO's may be derived by using valence bond theory and that electronic configurations in terms of canonical MO's are quantum mechanically equivalent to electronic configurations in terms of localized MO's.

1. Aufbau Principles and Electronic Configurations. An Aufbau principle is used to enumerate configurations for a given set of orbitals. Consider the first excited state of carbon atom. The hydrogenic atomic orbital Aufbau principle enumerates the electronic configuration as in eq 1, where the 2s and 2p atomic orbitals are



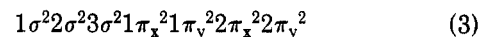
each singly occupied. The hybrid atomic orbital Aufbau principle can be used to describe the same state in terms of the four equivalent sp^3 tetrahedral hybrids as in eq 2,



where t_i denotes a singly occupied sp^3 hybrid. Equations 1 and 2 are quantum mechanically equivalent, as will be shown below.

There are two widely used Aufbau principles for molecules. The canonical MO Aufbau principle specifies the electronic configuration in terms of canonical (delocalized) MO's. The valence bond Aufbau principle specifies the electronic configuration in terms of valence bond structures. Consider F_2 as an example. The canonical valence MO's for first-row (nonhydride) diatomics are 1σ - 4σ , $1\pi_x$, $1\pi_y$, $2\pi_x$, and $2\pi_y$. (We have suppressed the gerade-ungerade symmetry characteristic of the homonuclear dia-

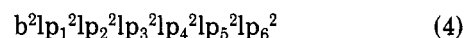
tomics.) The 1σ , 2σ , and 1π are bonding MO's; 3σ , 4σ , and 2π are antibonding MO's. The canonical MO Aufbau principle describes the ground state of F_2 as in eq 3.



The valence bond Aufbau principle described the ground state of F_2 as the valence bond structure



This structure denotes six doubly occupied lone pairs (lp_i) and one doubly occupied bond (b). The electronic configuration is written as in eq 4.



Equations 3 and 4 are apparently different descriptions of the same electronic states. We conclude, therefore, that descriptions of states in terms of electronic configurations are not necessarily unique. In the next two subsections, we shall describe how the different descriptions are related.

2. Valence Bond Theory and Localized MO's. MO theory and valence bond theory are *not* strictly equivalent in a mathematical sense. Therefore, we cannot use valence bond and MO theories interchangeably, and we cannot strictly compare electronic configurations such as those given by eq 3 and 4. This is inconvenient and can be circumvented with the localized representation of MO theory.

Localized MO's may be defined with symmetry criteria (equivalent orbitals),²⁰⁻²² chemical criteria,²³ or mathematical criteria.^{18,19,24} They satisfy MO equations¹⁹ and are identified with the bonds, lone pairs, etc. of valence bond theory.² For example, the F_2 localized MO's consist of one bond and six lone pairs.²⁵ These correspond to the b and lp_i of eq 4. Consequently, eq 4 represents the electronic configuration of F_2 in terms of localized MO's.

This provides the desired method for comparing MO and valence bond electronic configurations. We use the valence bond Aufbau principle to define valence bond structures. The orbitals associated with the valence bond structures are taken to be localized MO's. This is accomplished straightforwardly because localized MO's are the MO counterparts of valence bond theory.² Thus, the valence bond Aufbau principle leads to electronic configurations whose occupied orbitals are localized MO's. These may be rigorously compared with the electronic configurations which arise from the canonical MO Aufbau principle and canonical MO's. This is demonstrated in the next subsection.

3. The Quantum Mechanical Equivalence of Electronic Configurations in Terms of MO's. There is a many-to-one correspondence between configurations of electrons and MO wave functions. Since there is a well-known arbitrariness associated with MO wave functions,³ an electronic configuration in terms of MO's is also arbitrary. The particular statement of the arbitrariness which we employ at present is that a MO wave function that consists of a single Slater determinant is invariant against unitary transformations of the occupied MO's. We shall exploit this to point out that an electronic configuration in terms of canonical MO's is quantum mechan-

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ically equivalent to an electronic configuration in terms of localized MO's.

Let Γ be an electronic configuration in terms of MO's $\{\psi_i\}$, e.g., eq 5 where n is the number of occupied MO's. The

$$\Gamma = \psi_1^2 \psi_2^2 \dots \psi_n^2 \quad (5)$$

configuration Γ gives rise to a MO wave function $\Psi(\Gamma)$. A second set of MO's, $\{\lambda_i\}$, may be constructed from the $\{\psi_i\}$ according to eq 6, where the $\{T_{ij}\}$ are elements of a unitary

$$\lambda_i = \sum_{j=1}^n T_{ij} \psi_j \quad (6)$$

matrix and $1 \leq i \leq n$. Equation 6 transforms a given set of occupied MO's, $\{\psi_i\}$, into a second set of occupied MO's, $\{\lambda_i\}$, and a given MO wave function, $\Psi(\Gamma)$, into a second MO wave function, $\Psi(\Lambda)$. All physical observables are unchanged by the transformation defined by eq 6. The two MO descriptions are quantum mechanically equivalent.

The MO wavefunction $\Psi(\Lambda)$ is associated with an electronic configuration λ in terms of the $\{\lambda_i\}$ (eq 7). Since

$$\Lambda = \lambda_1^2 \lambda_2^2 \dots \lambda_n^2 \quad (7)$$

$\Psi(\Lambda)$ and $\Psi(\Gamma)$ are quantum mechanically equivalent, the electronic configurations Λ and Γ are quantum mechanically equivalent; thus, Λ and Γ are equally valid physical descriptions. If Λ corresponds to localized MO's and Γ corresponds to canonical MO's, then we have the desired result.

4. ⁵S State of Carbon. A compact example of the quantum mechanical equivalence of electronic configurations is provided by the all-spins-parallel ⁵S state of carbon. Equation 1 describes its electronic configuration in terms of hydrogenic valence atomic orbitals. The wave function corresponding to eq 1 is the Slater determinant given in eq 8, where the $\alpha(i)$ are one-electron spin configurations.

$$\Psi(\Gamma) = \frac{1}{8} |2s(1)\alpha(1)2p_x(2)\alpha(2)2p_y(3)\alpha(3)2p_z(4)\alpha(4)| \quad (8)$$

The unitary transformation that corresponds to eq 6 is the transformation from the hydrogenic atomic orbitals to the sp^3 atomic hybrids of eq 2. This is given by eq 9a-d. The

$$t_1 = \frac{1}{2}(2s + 2p_z) + (\frac{1}{2})^{1/2} 2p_x \quad (9a)$$

$$t_2 = \frac{1}{2}(2s + 2p_z) - (\frac{1}{2})^{1/2} 2p_x \quad (9b)$$

$$t_3 = \frac{1}{2}(2s - 2p_z) - (\frac{1}{2})^{1/2} 2p_y \quad (9c)$$

$$t_4 = \frac{1}{2}(2s - 2p_z) + (\frac{1}{2})^{1/2} 2p_y \quad (9d)$$

wave function corresponding to eq 2 is the Slater determinant shown in eq 10.

$$\Psi(\Lambda) = \frac{1}{8} |t_1(1)\alpha(1)t_2(2)\alpha(2)t_3(3)\alpha(3)t_4(4)\alpha(4)| \quad (10)$$

The wave functions $\Psi(\Gamma)$ and $\Psi(\Lambda)$ are equivalent descriptions of ⁵S. The physical observables calculated by using $\Psi(\Gamma)$ are identical with the physical observables calculated by using $\Psi(\Lambda)$. An exactly parallel discussion can be given for the canonical and localized MO's of F_2 . The electronic configurations are listed in eq 3 and 4. The unitary transformation from canonical to localized MO's corresponds to eq 6 and 9. The transformation coefficients are available in the literature.^{25,26}

B. Electronic Structure Criteria for Supernucleophilic Propensity. An important consequence of the quantum mechanical equivalence of localized and canonical MO's is that apparently different valence descriptions may be equivalent or complementary. For example, Thompson⁶

showed that Walsh's rules,⁴ using canonical MO's, are equivalent to Gillespie's rules,⁵ using localized MO's.

Two apparently different basic electronic structure models have been proposed to account for supernucleophilic propensity, the Ingold criterion and the lone-pair criterion. In this section, we shall derive alternative statements of the criteria which are easily systematized and establish the condition for their complementary character. We shall apply the results to classes of potential supernucleophiles in the following three sections.

1. The Ingold Criterion as a Specification of the Total Number of Valence Electrons According to the Canonical MO Aufbau Principle. The Ingold criterion¹² is worded in the language of canonical MO's (delocalized MO's). The criterion requires the HOMO to be antibonding, with a node that is perpendicular to the bond between the nucleophile and the α atom. (The HOMO is the occupied canonical MO which has the largest orbital energy.) Thus the Ingold criterion specifies the HOMO to be an antibonding π -type MO. We refer to this as the π^* -HOMO or π^* .

We can deduce an implication of the Ingold criterion which is convenient for present purposes. For a particular coordination, the π^* -HOMO requirement defines the MO configuration according to the canonical MO Aufbau principle. That is, the Aufbau principle enumerates the canonical MO's which must be occupied in order for π^* to be the HOMO. Therefore, an implication of the Ingold criterion is that it specifies the number of valence electrons that are available to potential supernucleophiles, according to the canonical MO Aufbau principle.

2. The Lone-Pair-Repulsions Criterion as a Specification of the Total Number of Valence Electrons According to the Valence Bond Aufbau Principle. The lone-pair-repulsions criterion^{7,9-11} is stated in the language of valence bond theory. It states that potential supernucleophiles exhibit lone pairs on the nucleophile and the α atom which engage in strong nonbonded repulsions across the bond.

An implication of this formulation can be deduced which is convenient for present purposes. For a particular coordination, the lone-pair-repulsions requirement defines the valence bond structure according to the valence bond Aufbau principle. That is, the Aufbau principle enumerates the structures which exhibit lone pairs that undergo strong nonbonded repulsions across the bond. This defines the total number of available electrons. Therefore, an implication of the lone-pair-repulsions criterion is that it specifies the number of valence electrons that are available to potential supernucleophiles, according to the valence bond Aufbau principle.

3. Localized MO's and the Condition for the Complementary Character of the Electronic Structure Criteria. We shall prove the following statement: If, for a given coordination of the nucleophile, the Ingold criterion and the canonical MO Aufbau principle give rise to the same number of electrons as do the lone-pair-repulsions criterion and the valence bond Aufbau principle, then the Ingold criterion and the lone-pair-repulsions criterion are complementary. We cannot prove this statement until we formulate both criteria in the same theory. This is accomplished with the following corollary. A valence bond structure corresponds to a MO configuration in terms of localized MO's. The application of the corollary leads to the following statement. The lone-pair-repulsions criterion and the valence bond Aufbau principle give rise to a MO configuration in terms of localized MO's. We refer to this MO configuration as Λ . A certain number of electrons is

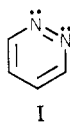
associated with Λ , say M . It is clear that the Ingold criterion and the canonical MO Aufbau principle give rise to a MO configuration in terms of *canonical* MO's, say Γ . A certain number of electrons is associated with Γ , say N . If $N = M$, then Γ and Λ are quantum mechanically equivalent, because *any* MO configurations that are associated with the same number of electrons are quantum mechanically equivalent. If Γ and Λ are quantum mechanically equivalent, then the two criteria used to deduce them are complementary. Hence, if $N = M$, then the two electronic structure criteria for supernucleophilic propensity are complementary.

4. Nature of Electronic Structure Criteria. It is important to appreciate that each criterion is essentially based on the electronic structure of an isolated molecule. The implication is this: if the criteria are satisfied, then the molecule is potentially a supernucleophile; whereas, if the criteria are not satisfied, then the molecule is probably not a supernucleophile. Exceptions are to be expected, because electronic structure criteria typically do not preclude several chemical tendencies. For an obvious example, which is relevant to the present case, F_2 satisfies the Ingold criterion and the lone-pair criterion. However, F_2 chemistry is typically dominated by its oxidizing propensities, and hence F_2 is not expected to behave chemically like a supernucleophile. The real purpose of electronic structure criteria is to help unify what would otherwise appear to be isolated chemical results.

s-p Supernucleophiles

The present work considers nucleophilic centers and α atoms that are bonded together by atomic s and p orbitals. We call these s-p supernucleophiles. Two numbers are useful for classifying these species. The α coordination number is defined as the number of α atoms. The number of valence electrons is defined as twice the number of electron pairs that are associated with the nucleophilic center and the α atoms.

Consider the example of pyridazine (I). The nitrogens



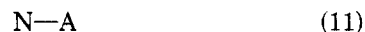
are simultaneously nucleophilic centers and α atoms, so the α coordination number is 1. Six pairs of electrons are associated with the N-N supernucleophilic moiety. (Two pairs are associated with the N=N and one pair is associated with each N-C bond.) This gives 12 valence electrons.

The α coordination number of s-p supernucleophiles may be 1, 2, or 3. The nucleophilic center has four atomic orbitals available for coordination. According to the Ingold criterion, there must be at least one π antibonding HOMO between the nucleophilic center and the α atoms. According to the lone-pair-repulsions criterion, there must be at least one lone pair on the nucleophilic center. In either case, the maximum α coordination number is 3. We shall refer to the α coordination numbers as 1-coordination, 2-coordination, and 3-coordination.

The α coordination number and the number of valence electrons together specify the electronic structures that we associate with supernucleophilic propensity. We classify supernucleophiles according to their α coordination. The Ingold criterion is invoked to determine the MO configurations that are associated with a given α coordination, i.e., the number of valence electrons that are associated with a given α coordination. The lone-pair-repulsions criterion

is invoked to determine the valence bond structures that are associated with a given α coordination, i.e., the number of valence electrons that are associated with a given α coordination. If the Ingold and lone-pair-repulsions criteria predict the same number of valence electrons, then complementarity for that α coordination follows from the results of the Electronic Structure of Supernucleophiles section and this section. The necessary derivations are given in the next three subsections.

A. 1-Coordinate Supernucleophiles. If N is the nucleophile and A is the α atom, then a 1-coordinate nucleophile is denoted by the structure in eq 11. Their electronic structure is characteristic of diatomic molecules.



1. The Ingold Criterion and Canonical MO's. Canonical MO's of diatomic molecules exhibit σ , π , δ , etc. symmetry. The canonical MO's of 1-coordinate s-p supernucleophiles exhibit σ and π symmetries only. As in the Electronic Structure of Supernucleophiles section, we suppress the gerade-ungerade cases and denote the valence MO's by $1\sigma-4\sigma$, $1\pi_x$, $1\pi_y$, $2\pi_x$, and $2\pi_y$. The antibonding π MO's are $2\pi_x$ and $2\pi_y$. The last MO to be occupied according to the Aufbau principle is 4σ . The next-to-last MO's to be occupied are $2\pi_x$ and $2\pi_y$. Therefore, every potential 1-coordinate supernucleophile must exhibit the occupancy

$$\Gamma_1 = \gamma_1 \cdot 2\pi_x^m 2\pi_y^n \quad (12)$$

where

$$\gamma_1 = 1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2 \quad (13)$$

This occupancy is imposed by the Ingold criterion; i.e., the HOMO must be an antibonding π MO.

The configuration γ contains ten valence electrons. The $2\pi_x$ and $2\pi_y$ MO's may contain up to four electrons. Configurations with unpaired electrons are radicals or biradicals, and this character dominates their chemistry. It is therefore unnecessary to consider them as potential supernucleophiles. This leaves two possibilities for the potential supernucleophiles, namely, eq 14 and 15. Thus,

$$\Gamma_1(12) = \gamma_1 \cdot 2\pi_x^2 \text{ or } \gamma_1 \cdot 2\pi_y^2 \quad (14)$$

$$\Gamma_1(14) = \gamma_1 \cdot 2\pi_x^2 2\pi_y^2 \quad (15)$$

according to the Ingold criterion, 1-coordinate supernucleophiles have either 12 or 14 valence electrons.

2. The Lone-Pair-Repulsions Criterion and Localized MO's. The nucleophile and α atom of 1-coordinate supernucleophiles may be bonded together by single, double or triple bonds. The corresponding valence bond structures are given as eq 16-18, respectively, where



the lines indicate paired electrons, i.e., bonds and/or lone pairs. The triple bond structure of (18) does not satisfy the lone-pair-repulsions criterion. The reason is that the lone pairs are directed away from each other along the N-A bond and therefore cannot engage in strong nonbonded repulsions across the bond. The valence bond structures of (16) and (17) both satisfy the lone-pair-repulsions criterion.

Fourteen valence electrons are associated with (16), and 12 valence electrons are associated with (17). Thus, (16)

Table I. Complementarity of the Electronic Structure Criteria in the Case of 1-Coordinate Supernucleophiles

supernucleophile	π^* HOMO	valence bond structure and localized MO's
14 Valence Electrons		
hypochlorite ion ^a	$3\pi^{c,d}$	
hydroperoxide ion ^a	$2a''^d$	
hydrazine ^a	$9a^{d,e}$	$H_2\ddot{N}-\ddot{N}H_2^i$
hydroxylamine ^a	$7a'^{d,e}$	$H_2\ddot{N}-\ddot{O}H^i$
12 Valence Electrons		
pyridazine ^b	$8b_2^f$	

^a Jencks, W. P. "Catalysis in Chemistry and Enzymology"; McGraw-Hill: New York, 1969; Chapter 2. ^b Zoltewicz, J. A.; Deady, L. W. *J. Am. Chem. Soc.* 1972, 94, 2765. ^c O'Hare, P. A. G.; Wahl, A. C. *J. Chem. Phys.* 1971, 54, 3770. ^d Heaton, M. M. *J. Am. Chem. Soc.* 1978, 100, 2006. ^e Contour plots are given in ref *d* and show the essential antibonding character of π^* . ^f Popkie, H. E.; Kaufman, J. J. *J. Chem. Phys.* 1977, 66, 4827. The π HOMO lies in the plane of the ring and has nodes perpendicular to the N-N bond. Similar remarks apply to cinnoline. ^g The isovalent F_2 molecule's localized MO's are reported in: Edmiston, C.; Ruedenberg, K. *J. Chem. Phys.* 1965, 43, S97. ^h The H_2O_2 localized MO's are reported in: England, W.; Gordon, M. S.; *J. Am. Chem. Soc.* 1972, 94, 4818. ⁱ England, W.; Gordon, M. S., unpublished calculations.

corresponds to an electronic configuration in terms of localized MO's that occupies 14 valence electrons, and (17) corresponds to an electronic configuration in terms of localized MO's that occupies 12 valence electrons. The conclusion is that, according to the lone-pair-repulsions criterion, 1-coordinate supernucleophiles have either 12 or 14 valence electrons. This shows that the Ingold criterion and the lone-pair-repulsions criterion are complementary in the case of 1-coordinate supernucleophiles.

3. Examples. The complementarity of the electronic structure criteria is illustrated in Table I. All species that are listed in the first column of the table are known to be supernucleophiles. Column two identifies the π^* HOMO of each supernucleophile as determined by MO calculations. Column three lists their complementary valence bond and localized MO descriptions.

Consider the hypochlorite ion as an example. The 3π HOMO has nodes that are perpendicular to the Cl-O bond. Three lone pairs occur on the nucleophile and on the α atom.

B. 2-Coordinate Supernucleophiles. Let N be the nucleophile, and let A and B be the α atoms. A 2-coordinate supernucleophile is represented as in (19). Its

$$A-N-B \quad (19)$$

electronic structure is characteristic of triatomic molecules. According to Walsh's rules⁴ and Gillespie's rules,⁵ the potential supernucleophiles exhibit bent geometries.

1. The Ingold Criterion and Canonical MO's. The canonical MO's of bent triatomic molecules exhibit a and a' symmetry. (We consider the general case of C_s symmetry, or $A \neq B$. All results apply to the $A = B$ case.) The a' MO's correspond to π MO's. Suppose the z axis is perpendicular to the plane of the molecule. The a' MO's have the general form given in eq 20, where $p_z(N)$, etc.

$$a' \approx C_N p_z(N) \pm [C_A p_z(A) + C_B p_z(B)] \quad (20)$$

denote p_z atomic orbitals on the nucleophilic center, etc.

The a' MO's are characteristically bonding or antibonding with respect to both α atoms.

The valence MO's of s-p supernucleophiles are denoted as $1a-10a$, $1a'$, and $2a'$. The $2a'$ is the π^* MO and corresponds to the minus sign in eq 20. The $9a$ and $10a$ MO's are the last ones occupied, according to the Aufbau principle. The $2a'$ MO is occupied just before $9a$ and $10a$. Therefore, a potential 2-coordinate supernucleophile exhibits the occupancy

$$\Gamma_2 = \gamma_2 (2a')^2 \quad (21)$$

where

$$\gamma_2 = 1a^2 2a^2 3a^2 4a^2 5a^2 6a^2 7a^2 8a^2 (1a')^2 \quad (22)$$

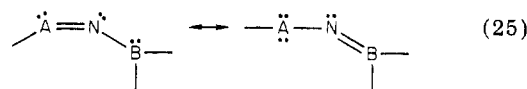
Thus, according to the Ingold criterion, 2-coordinate supernucleophiles have 20 valence electrons.

Walsh's rules⁴ predict that triatomic molecules which have 20 valence electrons exhibit bent geometries.

2. The Lone-Pair-Repulsions Criterion and Localized MO's. The nucleophile and α atoms of 2-coordinate moieties may be bonded together by single or double bonds. The corresponding valence bond structures are given by (23) and (24), respectively, where the lines indicate paired electrons.



The double bond structure of (24) does not satisfy the lone-pair-repulsions criterion. There is appreciable resonance of the type given in eq 25. The consequence is that



the lone pair on the nucleophile has appreciable bonding character and hence does not satisfy the lone-pair-repulsions criterion. A specific example is the case of nitrite ion.

Twenty valence electrons are associated with the valence bond structure of (23). The lone-pair-repulsions criterion is satisfied relative to both α atoms. Thus, 2-coordinate moieties that have 20 valence electrons are potential supernucleophiles, according to the lone-pair-repulsions criterion.

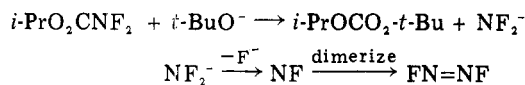
Structure (23) corresponds to a configuration in terms of localized MO's that occupies 20 valence electrons. Consequently, the Ingold and lone-pair-repulsions criteria are complementary in the case of 2-coordinate supernucleophiles.

Gillespie's rules⁵ predict that triatomics which have 20 valence electrons exhibit bent geometries.

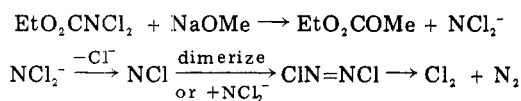
3. Enhanced Supernucleophilicity. It is reasonable to expect that the presence of two α atoms would further enhance nucleophilicity, perhaps by a substantial amount. In this connection, our attention was drawn to the dichloroamide anion NCl_2^- . Walsh's rules⁴ predict that the NCl_2^- $3b_1$ HOMO is π antibonding along both α bonds; i.e., the Ingold criterion is satisfied along both bonds. Correspondingly, there are two lone pairs on N and three lone pairs on each Cl. All exhibit strong nonbonded repulsions; i.e., the lone-pair-repulsions criterion is satisfied relative to both α atoms.

There are a number of literature reports dealing with this type of species. It appears that there is a large driving force for α elimination, i.e., conversion of NX_2^- to halo-

Scheme I



Scheme II



Scheme III



nitrene, NX.²⁷ For example, Klopotek and Hobrock proposed²⁸ the pathways outlined in Scheme I for reaction of isopropyl *N,N*-difluorocarbamate with potassium *tert*-butoxide. In addition, reactions were carried out between the generated fluoronitrene and various substrates.

In a related study²⁹ with *N,N*-dichlorourethane and sodium methoxide, the main products were ethyl methyl carbonate and nitrogen, presumably formed via displacement of NCl_2^- followed by α elimination (Scheme II).³⁰ Further indication of the transitory nature of NCl_2^- is provided by the behavior of dichloroamine in basic solution.³¹ Decomposition to nitrogen is observed, most likely with NCl_2^- acting as an intermediate (cf. Scheme II).

In recent years, we found that the combination of trichloroamine and aluminum chloride can function as an aminating reagent for alkanes,³¹ alkyl halides,³¹ aromatics,³¹ and alkenes.³¹ According to the mechanistic interpretation, the indicated coordination and polarization take place (Scheme III). Apparently, dichloroamide anion, complexed with AlCl_3 , is generated when positive chlorine is lost by interaction with the organic substrate. An unusual result is obtained with toluene, namely, meta orientation. Scheme IV has been postulated.³¹ To our knowledge, this is the only example of an addition-elimination pathway involving toluene. Since loss of a proton from the σ complex is generally preferred, the substitution pathway may reflect the supernucleophilicity of NCl_2^- . The absence of α elimination is probably due to stabilization of NCl_2^- by association with AlCl_3 .

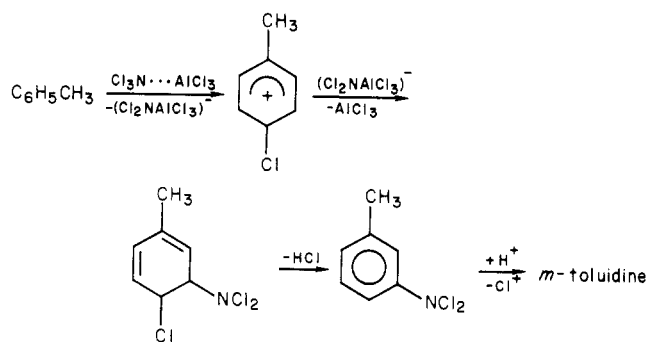
It is pertinent that Beale observed a dramatic example of the α effect with a related *N*-chloro anion.¹⁶ *N*-Chlorobenzenesulfonamide anion exhibited a second-order rate constant about 5 times larger than its *N*-methyl analogue in reaction with methyl methanesulfonate. A deceleration of 1000-fold was predicted on the basis of an extended Brønsted plot. We account for this in essentially the same way as for NCl_2^- .

C. 3-Coordinate Supernucleophiles. Let N be the nucleophile, and let A, B, and C be the α atoms. The 3-coordinate supernucleophiles have the coordination shown by (26). Their electronic structure is characteristic



of 3-coordinated tetraatomic molecules. This introduces an inherent imprecision into the application of the Ingold

Scheme IV



and lone-pair-repulsions criteria. A corresponding imprecision is associated with the nucleophilic propensity of the 3-coordinate moieties.

1. The Ingold Criterion and Canonical MO's. Consider a planar 3-coordinate moiety, and let the z axis be perpendicular to the molecular plane. The π -type MO's of this system are linear combinations of the atomic p_z orbitals on each center. In particular, the π^* MO of the Ingold criterion has the form given in eq 27. It is anti-

$$\pi^* \approx \text{C}_N \cdot p_z(\text{N}) - [p_z(\text{A}) + p_z(\text{B}) + p_z(\text{C})] \quad (27)$$

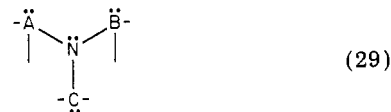
bonding with respect to each coordination. The canonical MO configuration that satisfies the Ingold criterion is written as eq 28. According to the Aufbau principle for

$$\Gamma_3 = \gamma_3(\pi^*)_2 \quad (28)$$

canonical MO's, γ_3 is a configuration of 12 doubly occupied valence MO's. Thus, the Ingold criterion predicts that planar 3-coordinate moieties which have 26 valence electrons are potential supernucleophiles.

Walsh's rules⁴ predict that 3-coordinate molecules which have 26 valence electrons exhibit pyramidal geometries. The MO of eq 27 acquires bonding character in this case and is no longer an antibonding π MO in the strict sense. The consequence is that the Ingold criterion does not precisely apply to 3-coordinate moieties. It is expected that 3-coordinate species will exhibit supernucleophilic propensity only if the MO of eq 27 retains appreciable antibonding π character in the pyramidal geometry.

2. The Lone Pair Repulsions Criterion and Localized MO's. The nucleophile and α atoms of a 3-coordinate supernucleophile are bonded together by single bonds. This is described by the valence bond structure given as (29), where the lines indicate paired electrons.



Twenty-six valence electrons are associated with this structure. If all atoms are coplanar, strong nonbonded repulsions are expected between the lone pair on N and the lone pairs on the α atoms. According to the lone-pair-repulsions criterion, planar 3-coordinate moieties with 26 valence electrons are potential supernucleophiles.

Gillespie's rules⁵ predict that 3-coordinate moieties which have 26 valence electrons exhibit pyramidal geometries. The lone pair on the nucleophile lies along the altitude of the pyramid formed by N, A, B, and C. That is, the lone pair on N is directed away from the lone pairs on the α atoms. This reduces the magnitudes of the lone-pair repulsions, relative to the planar case, perhaps by a substantial amount. An inherent imprecision is therefore introduced into the application of the lone-pair-repulsions criterion to the structure of (29). It is

(27) The nitrene may also bring about insertion reactions.

(28) Klopotek, D. L.; Hobrock, B. G. *Inorg. Chem.* 1967, 6, 1750.

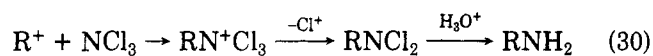
(29) White, R. E.; Kovacic, P. *J. Am. Chem. Soc.* 1974, 96, 7284.

(30) Other possible reaction pathways in this system are discussed in ref 29.

(31) Kovacic, P.; Lowery, M. K.; Field, K. W. *Chem. Rev.* 1970, 70, 639.

expected that 3-coordinate moieties will exhibit supernucleophilic propensity only if appreciable lone-pair repulsions occur in the pyramidal geometry. This is the localized MO analogue of the imprecision that was observed in the discussion of the Ingold criterion. Thus, the Ingold and lone-pair-repulsions criteria are complementary.

3. Moderated Nucleophilicity. It is reasonable to expect that the nucleophilic propensity of a 3-coordinate nucleophile may be reduced relative to other coordinations, perhaps by a substantial amount. Consider the case of NCl_3 , which has 26 valence electrons and is a potential supernucleophile. From a superficial examination of the electronic structure of NCl_3 , one might assume a high order of nucleophilicity, since three atoms possessing unshared electrons are bound to nitrogen. In addition, there is the possibility that in the aminations entailing $\text{NCl}_3\text{-AlCl}_3$, the electron-deficient carbon species are reacting with NCl_3 , not NCl_2^- (eq 30). The same end product would result



in either case. For these reasons, we carried out an experimental study aimed at determining the nucleophilicity of NCl_3 .

Ethyl bromide was used as the substrate in chlorobenzene solvent, and comparison was made with a standard nucleophile, triethylamine, at room temperature (ca. 22–24 °C). There is no reaction between NCl_3 and $\text{C}_6\text{H}_5\text{Cl}$ under these conditions. With the tertiary amine, substitution took place quickly, forming tetraethylammonium bromide in 12% yield after 6 h. The actual yields are slightly higher since the salt is somewhat soluble in the medium. In the case of trichloroamine, there was no evidence whatsoever for nucleophilic reaction at the end of 24 h. The positive chlorine content of the system remained at 91–100% of the original value. In addition, acid hydrolysis of the mixture yielded ammonium chloride in 88% yield, with no indication of the presence of ethylamine. Essentially the same positive chlorine content and ammonium chloride yield were observed with control systems containing no ethyl bromide. It should be noted that NH_4Cl was precipitated slowly in very minor amounts from the solutions, possibly resulting from inefficient free-radical reactions.

These data show that NCl_3 is a weak nucleophile and is definitely not in the supernucleophile category.

Moderated nucleophilicity is not always associated with potential 3-coordinate supernucleophiles. The sulfite ion (SO_3^{2-}) has 26 valence electrons and is a known supernucleophile.¹⁷ Its geometry is pyramidal in crystalline Na_2SO_3 ³² and in S-bonded unidentate sulfite complexes³³ but is planar in O-bonded unidentate sulfite complexes.³³ The geometry of the SO_3^{2-} supernucleophile in solution is not known. The cases of NCl_3 and SO_3^{2-} illustrate the inherent imprecision that is associated with applying the electronic structure criteria to 3-coordinate moieties.

Table II. Trichloroamine and Ethyl Bromide

time, h	amt Cl^+ , mmol	Cl^+ percentage of initial value
0	9.55	100
16	9.59	100
0	9.74	100
10	9.31	96
24	8.85	91
0	9.08	100
24	9.50	104
0 ^a	9.08	100
24 ^a	8.68	96

^a Control run, no ethyl bromide.

Table III. Ammonium Chloride from Trichloroamine-Ethyl Bromide

time, h	amt NCl_3 , mmol	NH_4Cl	
		amt, mmol	% yield
16	3.2	2.8	87
24	3.0	2.7	88
24 ^a	3.0	2.7	88

^a Control run, no ethyl bromide.

Experimental Section

Preparation of Trichloroamine. Trichloroamine solutions were prepared by a literature procedure³⁴ with chlorobenzene as solvent.

Analysis for Positive Chlorine. Iodometric determination of positive chlorine was made by a modification of the literature procedure:³² a mixture of ethanol or methanol (25 mL, 95%) and water (25 mL) served as solvent. Hydrochloric acid (10 mL, 1 N) was used for acidification.

Trichloroamine and Ethyl Bromide. A chlorobenzene solution (5.0 mL) of trichloroamine and ethyl bromide (5.0 mL) was mixed in a flask at room temperature and tightly stoppered. At intervals, aliquots were withdrawn and titrated for positive chlorine iodometrically (Table II). The acidic workup was performed by addition of HCl (16–20 mL, 6 N). The mixture was vigorously stirred in an ice bath for 4–6 h. After the aqueous phase was separated, the green organic phase was washed with cold HCl. The combined acid solution was washed with ether. Removal of water by rotoevaporation left a white precipitate shown to be ammonium chloride (Table III) by comparison of the IR spectrum with that of authentic material.

Triethylamine and Ethyl Bromide. A 2 N solution was prepared from 7.0 mL (50 mmol) of the amine diluted to 25.0 mL with chlorobenzene. When the amine solution (5.0 mL, 10 mmol) was mixed with ethyl bromide (5.0 mL, 67 mmol) at room temperature, the clear solution became turbid. Within minutes a precipitate formed. After the mixture had been allowed to stand 6 h, filtration yielded 256 mg of tetraethylammonium bromide (1.22 mmol, 12.1% yield). In another run for 8 h, 319 mg of the salt (1.52 mmol, 15.1% yield) was obtained. Rotoevaporation of the reaction mixture after 8 h in another run afforded 381 mg of product (1.81 mmol, 18% yield), indicating that the salt is slightly soluble in the medium. After 24 h, 834 mg (3.97 mmol, 40% yield) of salt resulted. The IR and NMR spectra were identical with those of authentic material.

Registry No. Trichloroamine, 10025-85-1; tetraethylammonium bromide, 71-91-0; ethyl bromide, 74-96-4; ammonium chloride, 12125-02-9.

(32) Wells, A. F. "Structural Inorganic Chemistry", 3rd ed.; Oxford University Press: London, 1962; p 431.

(33) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; p 248.

(34) Kovacic, P.; Goralski, C. T.; Hiller, J. J., Jr.; Levisky, J. A.; Lange, R. M. *J. Am. Chem. Soc.* 1965, 87, 1262.