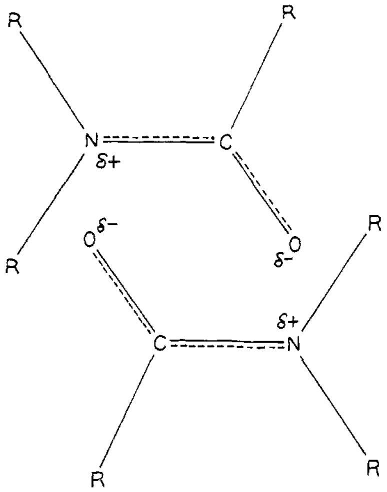
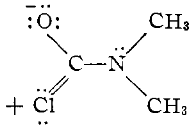


Fig. 3.—Structures favoring possible dimerization of N,N-disubstituted amides because of dipolar-type interactions.

progressive decrease in stability of the more polar ground state relative to the less polar excited state with increasing dilution. The barrier height would therefore be expected to decrease monotonically with dilution as is indeed found.

When DMP is dissolved in the polar solvent dibromomethane, a similar decrease in barrier height with increasing dilution might be anticipated, but the formation of hydrogen bonds of the type $HBr_2C{-}H.....O = CR' - NR_2$ between solvent and solute may stabilize the more polar ground state relative to the transition state and increase the barrier height. At higher dilutions the low dielectric constant of the dibromomethane, compared to that of pure DMP, presumably leads to the observed decrease in the barrier, although the values are always higher than for carbon tetrachloride solutions of the same concentration. Another factor that might give rise to the maximum in the concentration dependence of E_a is the competition between hydrogen-bond formation between solvent and amide and dimer formation between the amide molecules.

A rather similar result is found for the potential barrier restricting internal rotation about the central C–N bond of DMCC. The barrier is lower for pure DMCC (7.3 ± 0.5 kcal./mole) than for pure DMP, and the difference has been attributed[8] to a decrease in the relative contribution of structures analogous to II as a result of competition from the cross-conjugation represented by III. It might be expected that dilution with a non-polar solvent would again decrease the barrier height but less markedly than for DMP. This



III

apparently is true since the total variation of E_a for the solutions of DMCC in carbon tetrachloride is only 0.7 kcal./mole. Although the errors in E_a are of about the same order of magnitude, ±0.5 kcal./mole, as the total variation, we feel that the trend downward with dilution of the amide is significant. The barrier in DMCC shows an initial rise on adding dibromomethane followed by a decrease at greater dilutions just as was observed in DMP. It is interesting, but probably fortuitous, that the maximum value of E_a for both DMP and DMCC comes at a dilution corresponding to equal numbers of carbonyl oxygen atoms and of solvent hydrogen atoms available for hydrogen-bond formation. As suggested elsewhere,[8] the large free energies of activation ΔF^*, as compared to the activation energies E_a, probably are due to low transmission coefficients for the internal rotations involved. It is anticipated that more complex relationships will be observed with other solvents and other substituted amides, but the results should lead to further knowledge concerning intermolecular interactions in these mixtures.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND, AND NORTHWESTERN UNIVERSITY, CHICAGO, ILLINOIS]

The Factors Determining Nucleophilic Reactivities

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RECEIVED MAY 17, 1961

Three important factors determining the reactivity of nucleophilic reagents are considered. These are basicity, polarizability and the presence of unshared pairs of electrons on the atom adjacent to the nucleophilic atom, the alpha effect. The theoretical bases for these three factors are discussed. Experimental data for a number of substrates are given which make it clear that the reactivities of some substrates depend almost entirely on basicity of the nucleophile, and some substrate reactivities depend entirely on the polarizability. Substrates which resemble the proton in having a high positive charge and a low number of electrons in the outer orbitals of the central atom depend on basicity. Substrates with a low positive charge and with many electrons in the outer orbitals of the central atom depend on polarizability. The alpha effect appears to be general for all substrates.

There is now available in the literature a large amount of data on the rates of the generalized bimolecular substitution reaction

$$N + SX \longrightarrow NS + X \qquad (1)$$

Here N is a nucleophilic reagent (ligand in inorganic chemistry) and SX is a substrate containing a replaceable group X and an electrophilic atom S. Other groups, of course, may be bound to S. The

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nucleophilic reactivity of N is measured by the rate of reaction 1 for a given substrate.[2a] Often the relative rate with respect to a standard nucleophile such as water is used as a measure of reactivity. It is well known that the substrate, SX, determines not only the magnitudes of the rates but also the order for a series of nucleophiles. Information is available in cases where S is a carbon atom, either tetrahedral or trigonal, phosphorus, oxygen, boron, nitrogen or sulfur, and where S is a metal atom or ion in a complex. With such a wide range of information at hand, it seems desirable to discuss the following points in as fundamental a manner as possible: what factors make N a good nucleophilic reagent in general, and what specific factors in SX will tend to produce a certain order of reactivity among the various N groups.

To limit the problem somewhat, certain factors will be deliberately omitted from discussion. These include solvation effects, for it is known that different orders of reactivity can be found in different solvents.[2b] Also steric factors, such as strain in the transition state for reaction 1, will not be mentioned further nor will features such as hydrogen bonding or cyclic structures for the transition state. This means that entropies of activation will not be considered and the emphasis will be on the electronic factors which determine the energies of the ground states of N and SX and the activated complex N—S—X.

General Nucleophilic Reactivity.—Several approaches might be used to set up a normal scale of reactivity. For example, a standard substrate might be used as in the work of Swain and Scott.[2a] Or a correlation of rate data with quite independent properties of the nucleophile could be attempted as in the equation of Edwards,[3] wherein the reactivity of N is correlated with its ability to be oxidized (electrode potential) and to take up a proton (basicity). A correlation[4] of nucleophilicity with basicity and polarizability of the form

$$\log (k/k_0) = \alpha P + \beta H \qquad (2)$$

where (k/k_0) is the rate relative to water, P is defined as $\log (R_N/R_{H_2O})$ with R standing for molar refractivity,[5] and H is a function of basicity ($H = pK_a + 1.74$), has been given. The coefficients α and β are determined by experiment for each substrate, and with suitable choice of values the equation can be made to fit a large amount of rate data. Recently it has been shown[6] that a certain group of nucleophiles seem to react at rates invariably higher than can be accounted for by (2). These nucleophiles can be represented by the formula YN, where N is the nucleophilic atom and Y is an electronegative atom which contains one or more pairs of unshared electrons. Examples would be NH_2OH, ClO^- and $R_2C{=}NO^-$.

The three properties of basicity, polarizability and unshared pairs on the neighboring atom are sufficient for a fundamental discussion of nucleophilic reactivity. Each of these properties now will be considered in detail and the mechanism of their contribution to the stability of the transition state in a substitution reaction discussed.

Basicity.—The relationship of basicity to nucleophilic character is implicit in the fact that substitution reactions are generalized acid–base reactions. Reaction 1 where S is a proton is one example of the more general class and hence N is always a base. Basicity is measured in terms of an equilibrium constant for a reaction like (3) or (4). Ideally the gas phase proton affinities would be most desirable to avoid solvation difficulties.[7]

$$N(g) + H(g)^+ \rightleftarrows NH(g)^+ \qquad (3)$$

In the absence of values for most proton affinities, the base constant in water is ordinarily used.

$$N(aq) + H(aq)^+ \rightleftarrows NH(aq)^+ \qquad (4)$$

The large number of such constants and their precision make them valuable for correlation of rate data. The rate constants of reactions such as (3) and (4) are sometimes available, but they are no more fundamental than the equilibrium constants.

In the case of basicity to the proton, N is clearly interacting with a positive center. In substitution reactions, N is interacting with the atom S most directly. In the ground state SX, it is conceivable that S has a net negative charge. However in the transition state for reaction 1 it may be assumed that S has developed a positive charge of some magnitude since the leaving of X would always remove negative charge from S. We now seek the relationship between the charge on S in the transition state, the basicity of N to the proton and the rate of the substitution reaction.

First it is necessary to examine the process of binding a proton to a base in more detail. Consider the ground state of N, the base. It is characterized by a certain distribution of nuclei and electrons with a wave function, ϕ_0, the square of which represents the spatial density of the electron cloud. The proton is now added to this system. It will seek out the position in the molecule which has the greatest negative potential. This negative potential will be partly the result of the original charge distribution and partly the result of the redistribution caused by the presence of the proton. An important point, however, is this: for the electronegative atoms with which nucleophilicity is concerned, the perturbation of the original charge cloud by proton is not great.

For example, a number of calculations of the proton affinities of simple molecules and ions have been made by quantum mechanical perturbation methods recently.[8] Surprisingly good results can

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(2) (a) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953). (b) For examples see E. A. S. Cavell, *J. Chem. Soc.*, **4217** (1958); S. Winstein, *et al.*, *Tetrahedron Letters*, No. **9**, 24 (1960); R. G. Pearson and D. C. Vogelsong, *J. Am. Chem. Soc.*, **80**, 1048 (1958); J. Miller and A. J. Parker, *ibid.*, **83**, 117 (1961).

(3) J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954).

(4) J. O. Edwards, *ibid.*, **78**, 1819 (1956).

(5) There is an inconsistency in this equation in that theory predicts the form $P = R_N - R_{H_2O}$. The logarithm is better empirically, probably because only a fraction of the total refraction is concerned with the nucleophilic center.

(6) W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 1778 (1960).

(7) R. G. Pearson and D. C. Vogelsong, *ibid.*, **80**, 1038 (1958).

(8) H. Hartmann, *et al.*, *Z. Naturforsch.*, **2a**, 489 (1947); *Z. physik. Chem.*, **19**, 29 (1959); *ibid.*, **22**, 305 (1959); R. Gaspar, *et al.*, *Acta Phys. Acad. Sci. Hung.*, **7**, 151, 44 (1957); *Ann. Physik*, **2**, 208 (1958); *Acta Phys. Acad. Sci. Hung.*, **10**, 149 (1959); A. F. Saturno and R. G. Parr, *J. Chem. Phys.*, **33**, 22 (1960).

be derived by simply burying the proton in the charge cloud of the base without any change in the electron wave function.[9] Better results can be obtained if the wave function ϕ_0 is modified to move the electron cloud towards the proton. There are two ways of producing this electronic distortion. One is to add to ϕ_0 a wave function ϕ_H which is centered on the proton. This is the usual linear combination of atomic orbitals method as applied to polar, covalent bonds. The other method is to add to ϕ_0 one or more terms which represent additions to the wave function still centered on the nucleophilic atom of N but distorted toward the proton. As an example, in HF only wave functions centered on fluorine are used. The reason for the success of this method is that the final wave function for HF is not greatly different from that for F^-.[10]

One concludes from the above that basicity is determined chiefly by the original distribution of charge and, to a lesser degree, by the redistribution of charge caused by the proton. A high negative potential can be caused by a large negative charge on N over-all, by an electronegative atom which concentrates much of the charge near it, and/or by a favorable arrangement of the other nuclei and electrons. This last point is illustrated by the presence of base-strengthening or acid-weakening dipoles in the molecule N.

As a simple example of some of the principles mentioned, fluoride ion is much more basic than iodide ion in aqueous solution. In the gas phase fluoride ion is more basic by some 50 kcal./mole, the difference between the proton affinities. The total charge is the same but is concentrated near the nucleus in the case of F^- and widely dispersed in the case of I^-. A high negative potential is produced near the fluorine nucleus by this tight charge cloud. The diffuse charge cloud of iodine produces a less negative potential. The redistribution of charge caused by the proton is more extensive for the less electronegative, more polarizable iodide ion. However the energy gain from redistribution fails to compensate for the lower energy due to the diffuse, original charge distribution.

The effect of favorable arrangement of nuclei is shown by the fact that the basicities of the ions F^-, OH^-, NH_2^- and CH_3^- increase markedly in the order given.

With this concept of the mechanism for basicity in hand, an answer can be given to the question of the relation between the charge on the substrate atom S, the basicity of N and the rate of reaction. A high positive charge on S in the transition state can lead to a strong interaction with the high negative potential of a basic reagent N. This will lower the energy of the activated complex and cause a high rate of reaction. Thus basicity will be an increasingly important factor in rate of substitution as the positive charge on the electrophilic atom in the substrate increases. The coefficient β in equation 2 thus will increase as the charge on the substrate increases.

There is an important restriction to the conclusion derived in the above paragraph. In order for a strong lowering of the energy by electrostatic effects to occur, it is necessary that either the positive charge be situated in the region of negative potential or the negative charge be situated in the region of positive potential. The proton is unique in that it always can be placed in the most favorable region without restrictions. Any other possible atom S will be seriously restricted by the additional electrons that it has. Repulsion between these electrons and the electrons of N will raise the energy rapidly as S and N are brought together. It should be noted that this repulsion is due to the operation of the Pauli exclusion principle and is far greater than simple electrostatic repulsion.

The importance of this repulsion is summarized by pointing out that the equilibrium bonding distance of the proton to the first row atoms contained in N is about 1.0 Å., whereas the transition state distance between S and the basic atom of N usually is estimated to be of the order of 1.5 to 2.0 Å. The greater separation is partly compensated for by some of the electronic charge of N drifting closer to S. However, as pointed out, this has had the effect of partly destroying the basicity of N.

Polarizability.—It is known that polarizable molecules and ions such as thiourea, iodide ion and unsaturated systems are more nucleophilic than their basicities would warrant. Indeed, often such species have negligible basicity. The reason for the beneficial effect of high polarizability on rate has not been well understood. Two factors have been considered by various writers. One is that polarization of the bonding electrons in the direction from N toward S occurs. This permits better electrostatic interaction without bringing in Pauli exclusion effects due to the rest of the N molecule as explained above. The other factor considered[2a] is the polarization of non-bonding electrons on N away from S. This has the desirable effect of reducing electrostatic repulsions between N and the leaving group X. However, since it also has the effect of reducing the electrostatic attraction between N and S, it is not clear that the over-all balance is a favorable one. A more important consideration is that such removal of non-bonding electrons away from the S–N bonding region diminishes repulsions due to Pauli exclusion. This makes closer approach of S to N possible.

Quantum mechanical calculations of polarizability involve putting the atom or molecule in a weak, homogeneous electric field and carrying out a second-order perturbation calculation of the energy.[11] The lowering of the energy in the field is proportional to the polarizability. The procedure is to mix in to the ground state wave function ϕ_0 excited wave functions which combine with

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[9] J. R. Platt, *J. Chem. Phys.*, **18**, 932 (1950); H. C. Longuet-Higgins, *J. Inorg. Nuclear Chem.*, **1**, 60 (1955); also R. Gaspar, *et al.*, ref. 8.

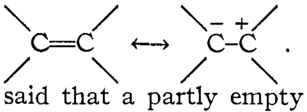
[10] There are examples of bases in which the electronic distribution is markedly changed on adding a proton. The pseudo-acids, such as nitromethane, obviously form such anions.

[11] For an elementary discussion see K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, New York, N. Y., 1953, p. 69; for recent calculations see A. Dalgarno and D. Parkinson, *Proc. Roy. Soc. (London)*, **A250**, 422 (1959), and R. M. Sternheimer, *Poly. Rev.*, **115**, 1198 (1959).

ϕ_0 to give a resultant which corresponds to a shift of the electronic charge distribution toward more positive potential. For example, an atomic p orbital can be mixed with an s ground state orbital to form a hybrid with the center of the electron cloud moved away from the nucleus. An atomic d orbital can be mixed with a ground state p orbital, and so on.

The conclusions from the above calculations are that *high polarizability results from the existence of low-lying excited states which, when mixed with the ground state, produce polarity.* Only the electrons in the highest energy atomic or molecular orbitals of the ground state are affected. Weakly held electrons are most easily distorted because the energy required to excite them is small. It may be noted that basicity and polarizability generally do not go together since they depend on quite different factors. The factors are really somewhat incompatible as shown by the different properties of F^- and I^-; however, it is possible to have both factors in the same molecule as typified by the sulfide ion $S^=$.

For the purpose of understanding nucleophilic reactivity, the important result from the above discussion is that certain highly reactive nucleophiles are characterized by having empty orbitals available which are relatively low in energy. These empty orbitals can be used to accommodate some of the electrons of the molecule N in the transition state. The additional possibility exists that in some cases these empty orbitals can be used to hold some of the electrons on the substrate S. Consider the case of an iodide ion attacking a substrate in which the electrophilic atom is oxygen (as in peroxide). There will be Pauli repulsion between the non-bonded *p* electrons on oxygen and on iodine. By forming a p–d hybrid on iodine, two new orbitals will be formed, one oriented away from oxygen and holding an oxygen electron pair. This is illustrated in Fig. 1. The net result is a lower energy than if both pairs of electrons tried to occupy the same region in space.

The high polarizability of unsaturated systems is evidenced by the exaltation of the molar refraction for such compounds. This can be explained by stating that the anti-bonding molecular orbital of the π-system is mixed in with the bonding orbital. This creates a polar structure, *e.g.*,  . In a crude way it can be said that a partly empty atomic orbital has been created. It should be noted that there are definite directional properties for polarization in molecular systems. This can affect that possibility of using such empty, excited orbitals in the transition state.

The efficiency of high polarizability in the nucleophile in lowering the energy of the activated complex will be a function of the substrate SX. It will always produce some lowering of the energy because of the flexibility it gives to the system. In the case of bonding to the proton, it is not very effective as has already been discussed. Polarizability will be of the greatest help in the case of a substrate which has many electrons in the outer orbitals of S, particularly if these orbitals project well out from the atom S and form an obstruction to the close approach of N.

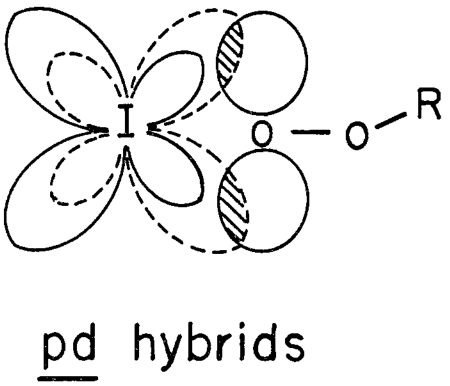


Fig. 1.—Polarization of pd orbital hybridization in the reaction of iodide ion with a peroxide. The solid line hybrid is filled and the dotted line hybrid is empty.

The Unshared Pair on the Adjacent Atom. The Alpha Effect.—If basicity is used as a criterion, a certain group of nucleophiles is found to react more rapidly than expected with a number of substrates. The nucleophilic reagents include hydroxylamine, hydrazine, hydroxamic acids, N-hydroxyphthalimide, isonitrosoacetone, the anions of peroxides and hydrogen peroxide, hypochlorite ion, oxime anions and others. The substrates which show the effect include activated esters,[6] peroxides,[12] nitriles,[13] tetrahedral phosphorus,[14] activated double bonds[15] and, possibly, acetaldehyde hydrate[16] (in a proton transfer reaction). The one common feature that can be distinguished in these nucleophiles is the presence of an electronegative atom containing one or more pairs of unshared electrons adjacent to the nucleophilic atom. For reasons that will be brought out in the discussion that follows, it is proposed that the excess reactivity shown by this class of reagents be called the "alpha effect." The reference is to the pairs of electrons on the alpha atom.

The mechanism by which these alpha electrons can influence the rate has been discussed, but it cannot be said that it is understood.[6] A reasonable explanation can be given by considering the limiting case of a nucleophilic substitution. Imagine a pair of electrons leaving the nucleophile for a substrate a large distance away. This would resemble the ionization of a halide ion from an organic halide to form a carbonium ion. By analogy any factor

$$N^{m} \longrightarrow N^{m+2} + 2e^- \qquad (5)$$

$$RX \longrightarrow R^+ + X^- \qquad (6)$$

which would stabilize the carbonium ion R^+ should also stabilize the denuded nucleophile N^{m+2}. This would include the presence of an unshared pair of

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[12] D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).

[13] K. B. Wiberg, *ibid.*, **77**, 2519 (1955).

[14] L. Larsson, *Acta Chem. Scand.*, **12**, 723 (1958); A. L. Green, G. L. Sainsbury, B. Saville and M. Stansfield, *J. Chem. Soc.*, 1583 (1958); J. Epstein, M. M. Demek and D. H. Rosenblatt, *J. Org. Chem.*, **21**, 796 (1956).

[15] C. A. Bunton and C. J. Minkoff, *J. Chem. Soc.*, 665 (1949); H. O. House and R. S. Ro, *J. Am. Chem. Soc.*, **80**, 2428 (1958); H. E. Zimmerman, L. Singer and B. S. Thyagarajan, *ibid.*, **81**, 108 (1959).

[16] R. P. Bell, *J. Phys. Chem.*, **55**, 885 (1951).

electrons on the adjacent atom. An α-halo ether would be an example of the stabilization for a carbonium ion.

$$\text{R-O-CH}_2\text{-Cl} \longrightarrow \text{R}{-}\overset{+}{\text{O}}{=}\text{CH}_2 + \text{Cl}^- \qquad (7)$$

So, in a similar fashion, one can write

$$\text{Cl-O}^- \longrightarrow \overset{+}{\text{Cl}}{=}\text{O} + 2e \qquad (8)$$

To the extent to which the transition state represents some removal of an electron pair from the reactive atom, the π-bonding shown in 8 should make some contribution to the stability of the system. In the same way, removal of chloride ion in the transition state for 7 is not complete, but the enhancement in rate by the oxygen atom, compared to a methylene group, is many powers of ten.[17]

Since excess reactivity for these special reagents such as NH_2OH is referred to basicity as a standard, the possibility of stabilization of the conjugate acid, such as NH_3OH^+ or HOCl, must also be considered. Because the proton polarizes some of the electrons toward itself, some effect of π-bonding must be expected. To have enhanced nucleophilic reactivity, it is necessary that removal of sigma electrons be more complete in the activated complex of the nucleophilic reactions than in the normal state of the acid. In view of earlier remarks on the small perturbation of the electron cloud of the base due to the proton, this probably is always the case. The available rate data do not indicate any substrate for which this special group of nucleophiles does not show enhanced reactivity. Some important substrates, such as saturated carbon, have not as yet been investigated quantitatively.

A further prediction from the theory advanced above is that other carbonium ion stabilizing factors should create better nucleophiles.[18,19] Such factors could be alkyl and aryl substitution and unsaturation. To be effective such groups must be on the alpha atom; however, in these cases there are complications by other phenomena. Increased steric strain and significant electronic arrangement on proton addition to the nucleophile are two possible factors which would render the above prediction invalid.

Orders of Nucleophilic Character.—In a displacement reaction, the order of nucleophilic strength is a marked function of the nature of the substrate. It is the purpose of this section to discuss the orders of nucleophilic strength for a number of substrates. In most cases, we shall not give numerical data, often because of their incomplete nature; references from which the results were obtained will be given, however. The data presented in this section will be discussed later in relation to the conclusions of the previous section.

Hydrogen.—In general, rates of nucleophilic displacement on hydrogen (as given by general base catalyzed reactions) follow the equilibrium basicity scale moderately well. There are, however, significant exceptions some of which are discussed by Bell.[16,20,21] For example, hydroxide ion often is kinetically less reactive than one would expect from a Brønsted plot,[20] while oximate ions react more rapidly than would be expected[16]; the latter nucleophile is one which has a free electron pair on the alpha atom. The adverse effect that strong electron delocalization in anions can have on rates is pointed out by Bell[16,20]; this is particularly noteworthy in the case of the anions of pseudo-acids like nitromethane.

Carbonyl Carbon.—Jencks and Carriuolo[6] discuss the reaction of *p*-nitrophenyl acetate with a large number of nucleophiles. To a large extent, the nucleophilic strength correlates with basicity, although there are some deviations[6,22] as may be seen in Table I. The influence of a spare pair of electrons on the alpha atom is shown by perhydroxyl ion, hypochlorite ion and others. It was also found that polarizable, non-basic nucleophiles such as iodide ion and thiourea are not reactive to this ester. The results obtained are explained in terms of a tetrahedral intermediate[22] which may go on to product or revert to starting material, but there can be no question that nucleophilic character in this case is primarily dependent on

TABLE I

RATES OF NUCLEOPHILIC REPLACEMENTS[a]

Nucleophile	pK_{HA}	Substrates: Carbonyl carbon[b]	Substrates: Tetrahedral phosphorus[c]
HOO^-	11.5	2×10^5	1.0×10^5
Acetoximate	12.4	3.6×10^3	....
Salicylaldoximate	9.2	3.2×10^3	1.5×10^3
OH^-	15.7	9×10^2	1.6×10^3
$C_6H_5O^-$	10.0	1×10^2	34
NH_2OH	6	1×10^2	1.3
OCl^-	7.2	1.6×10^3	7×10^2
$CO_3^=$	10.4	1.0	75
NH_3	9.2	16	....
CN^-	10.4	11	....
$C_6H_5S^-$	6.4	....	7.4×10^{-3}
$C_6H_5NH_2$	4.6	1.5×10^{-2}	....
C_5H_5N	5.4	0.10	....
NO_2^-	3.4	1.3×10^{-3}	....
$CH_3CO_2^-$	4.8	5×10^{-4}	....
F^-	3.1	1×10^{-3}	Very reactive[d]
$S_2O_3^=$	1.9	1×10^{-3}	Unreactive
H_2O	−1.7	6×10^{-7}	1×10^{-6}

[a] Rate constant units are l. mole^{-1} min.$^{-1}$. [b] *p*-Nitrophenyl acetate as substrate (ref. 6). [c] Isopropoxy-methylphosphoryl fluoride (Sarin) as substrate (ref. 24). [d] Estimated from other similar substrates.

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(17) P. Ballinger, P. B. D. de la Mare, G. Kohnstam and B. Prestt, *J. Chem. Soc.*, 3641 (1955).

(18) By similar reasoning one also could predict that any factor which stabilizes free radicals would also create stronger nucleophilic reagents. This stems from the relationship between nucleophiles and reducing agents (C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 5).

(19) R. G. Pearson and F. V. Williams, *J. Am. Chem. Soc.*, **76**, 258 (1954); R. P. Bell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1286 (1949).

(20) R. P. Bell, "Acid–Base Catalysis," Clarendon Press, Oxford, 1941, page 92.

(21) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

(22) (a) M. L. Bender, *Chem. Revs.*, **60**, 53 (1960); especially pages 62–64; (b) M. L. Bender and W. A. Glasson, *J. Am. Chem. Soc.*, **81**, 1590 (1959).

basicity. Bruice and Lapinski[23] have found Brønsted slopes of about 0.8 in the reaction of *p*-nitrophenyl acetate with several series of nucleophiles, even though each series fell on a different line. The high value of the slope implies that basicity is an important factor.

This conclusion is not limited to activated esters nor to esters only. Data in the literature indicate that ordinary esters show an even greater dependence on basicity.[22] Acyl halides and acid anhydrides also show a high sensitivity to basicity in their reactions with nucleophiles.[22a]

Tetravalent Phosphorus.—The literature data on displacements in neutral four-coördinate phosphorus compounds are scattered, thus it is difficult to prepare a list of nucleophiles in order of relative strength. Some numerical data are presented in Table I,[14,24] and the order in water appears to be $OOH^- > OH^- \simeq OCl^- > NH_2OH > NO_2^- > N_3^- > H_2O$. In ethanol, the order $F^- > C_2H_5O^- > C_6H_5O^-$ was found.[25] Sulfur nucleophiles such as $S_2O_3^{=}$ and $C_6H_5S^-$ do not seem to be particularly reactive. The conclusion that nucleophilic strength to four-coördinate phosphorus primarily follows basicity seems certain. The reactivity of fluoride ion is surprisingly high, however, as are the reactivities of nucleophiles with unshared electrons on the alpha atom.

Individual phosphorus compounds show considerable variation in the extent to which basicity plays a role in nucleophilic strength. The slopes of plots of log k_2 against pK_a (of conjugate acid of nucleophile) are 0.9, 0.7 and 0.5 for the substrates Sarin (isopropoxy-methyl-phosphoryl fluoride), TEPP (tetraethyl pyrophosphate) and Tabun (dimethylamide-ethoxy-phosphoryl cyanide), respectively, all with substituted hydroxamic acids.[14]

This selectivity order does not result from a reactivity order of Tabun > TEPP > Sarin. Similarly it has been shown[24b] that in compounds of the type R_3PX, the importance of basicity in the nucleophile decreases as alkyl R is converted to alkoxyl OR. Such variations are understood in terms of increasing π-bonding(donation of electrons from oxygen in OR to phosphorus) which cuts down on the positive charge on the phosphorus atom. Nevertheless, even in strongly π-bonded systems, there is no good evidence that polarizable, but non-basic, nucleophiles become effective.

Trigonal Boron.—Not many data are available. In a series of reactions of R_2BX compounds with various reagents, it was found[26a] that the rate order was $OH^- > OR^- > NH_3 > R_2NH \simeq SR^-$. Thus basicity rather than polarizability seems the important factor.

Tetrahedral Boron.—The breaking of the boron-nitrogen bond in H_3NBF_3 has been found to be catalyzed by anions.[26b] The order of nucleophilic strength appears to be $OH^- > F^- > H_2O$ with Cl^- showing no influence. Although the amount of data is limited, we conclude that nucleophilic attack on tetrahedral boron is primarily a function of basicity.

Tetrahedral Sulfur.—There are no data available from which a quantitative scale of nucleophilic character can be derived. It is possible, however, to gain some idea of nucleophilic character from available data on competitive reactions.[27-29] Bunnett and Bassett[27] treated *p*-nitrophenyl *p*-toluenesulfonate with various nucleophiles and isolated the products in high yield. The most striking result obtained was that very basic nucleophiles preferred to attack tetrahedral sulfur whereas more polarizable (albeit still somewhat basic) nucleophiles attacked the aromatic carbon atom. Similar results had been found in the reaction of neopentyl *p*-toluenesulfonate,[28] wherein the competition for the nucleophile is between saturated carbon and tetrahedral sulfur. From such data, we conclude that the rough order of nucleophile strength in attack on tetrahedral sulfur is $OH^- \simeq CH_3O^- > C_6H_5O^- > RNH_2 >$ Piperidine $> C_6H_5NH_2 > C_6H_5S^-$. Thus basicity is of prime importance for nucleophilic character in this case, although there may well be some dependence on polarizability also.

Bivalent Sulfur.—Parker and Kharasch[30] in their review on the breaking of the sulfur–sulfur bond have compiled lists from which orders of nucleophilic strength may be obtained. Since many of the data are qualitative in nature and since both rate and equilibrium data are considered, the order given below is at best a rough one. The order is $RS^- > R_3P > C_6H_5S^- \simeq CN^- > SO_3^{=} > OH^- > S_2O_3^{=} > SC(NH_2)_2 > SCN^- > Br^- > Cl^-$. From this order it would seem that nucleophilic attack on bivalent sulfur requires both polarizability and basicity.

There is evidence that polarizability is more important than basicity in at least one case, sulfur in the form of S_8 and S_6 species in solution. Here it has been shown by Bartlett[31] that triphenylphosphine, HS^- and HSO_3^- are powerful nucleophiles for sulfur, whereas tertiary amines are not.

Aromatic Carbon.—From the studies of Bunnett[27,32] and Huisgen[33] it is possible to list the nucleophiles in order of relative strength. The order observed is $C_6H_5S^- \simeq CH_3O^- > C_5H_{10}NH > C_6H_5O^- > N_2H_4 > OH^- > C_6H_5NH_2 > Cl^- > CH_3OH$. Also the order $C_6H_5NH_2 > NH_3 > I^- > Br^-$ is known. Apparently nucleophilic attack requires both polarizability and basicity. The discrimination between nucleophiles by the substrate is very large; for example, methoxide ion is 10^4 times as reactive as aniline which, in turn, is 10^9 times as reactive as the solvent methanol.

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Saturated Carbon.—The reaction of nucleophiles with tetrahedral carbon atoms has been studied often and, at least in major detail, is well understood. The order of nucleophilic strength is $C_4H_9S^- > C_6H_5S^- > S_2O_3^{=} > SC(NH_2)_2 > I^- > CN^- > SCN^- > OH^- > N_3^- > Br^- > C_6H_5O^- > Cl^- > C_5H_5N > CH_3CO_2^- > H_2O$; these data are collected from several sources[2a,3,4,34] and refer primarily to reactions in aqueous solution at room temperature. This order follows electrode potentials for oxidation of nucleophiles[2b] surprisingly closely. In Table II, calculated rate constants for displacement on saturated carbon by a variety of nucleophiles are presented.

TABLE II

RATES OF NUCLEOPHILIC REPLACEMENTS[a]

Nucleophile	Saturated[b] carbon	Peroxide[c] oxygen	Platinum (II)[d]
$SO_3^{=}$	2.3×10^{-4}	2×10^{-1}	......
$S_2O_3^{=}$	1.7×10^{-4}	2.5×10^{-2}	......
$SC(NH_2)_2$	2.5×10^{-5}	Very fast	8×10^{-1}
I^-	1.2×10^{-5}	6.9×10^{-1}	2×10^{-1}
CN^-	1×10^{-5}	1.0×10^{-3}	......
SCN^-	3.2×10^{-6}	5.2×10^{-4}	4×10^{-1}
NO_2^-	1.8×10^{-6}	5×10^{-7}	4×10^{-3}
OH^-	1.2×10^{-6}	[e]	[e]
N_3^-	8×10^{-7}	....	8×10^{-3}
Br^-	5×10^{-7}	2.3×10^{-5}	(5×10^{-3})[f]
NH_3	2.2×10^{-7}	....	(8×10^{-4})[f]
Cl^-	1.1×10^{-7}	1.1×10^{-7}	9×10^{-4}
C_5H_5N	9×10^{-8}	....	3×10^{-3}
H_2O	1×10^{-10}	[e]	5×10^{-7}

[a] Rate constant units are l. $mole^{-1}$ sec^{-1}. [b] Substrate is hypothetical methyl compound whose rate with Cl^- is same as peroxide rate with Cl^-. [c] Substrate is hydrogen peroxide (ref. 41). [d] Substrate is $Pt(dien)Br^+$ (where dien is diethylenetriamine) ref. 42. [e] Rate too low to measure. [f] Estimated from other similar substrates.

The observed order can be considered to be made up of a combination of polarizability and basicity factors with the former being more significant. The importance of polarizability is demonstrated by the fact that malonate ion reacts several times more rapidly with ethyl bromide than does ethoxide ion, even though ethoxide is 500 times more basic.[35] The high rate of reaction of the anions of pseudo acids in general is noteworthy in view of the slowness of proton transfers involving these anions. Similarly tri-substituted phosphines are more reactive in displacements on carbon than are trisubstituted amines, even though the amines are more basic.[36]

Trivalent Nitrogen.—Compounds of the type NH_2X will react with nucleophiles by displacement at nitrogen[37,38] when X is a good leaving group such as Cl^- or $SO_4^{=}$. Some of the nucleophiles are NH_3, RNH_2, R_3N, R_3As, R_2S, OH^- and $C_2H_5O^-$. The phosphines react moderately rapidly,[39] the amines at a measurable rate[40] and the oxygen bases somewhat more slowly. Hence polarizability is important and basicity probably less so.

Bivalent Oxygen.—Data for nucleophilic displacements on oxygen in peroxide have been collected.[41] The order observed with hydrogen peroxide is presented in Table II. Also known are the facts that (a) trialkyl phosphines react rapidly even at low temperature, (b) olefins and organic sulfides react as nucleophiles and (c) oxygen anions (except peroxides which have unshared electrons on the alpha atom) are extremely poor nucleophiles. The observations lead to the conclusion that nucleophilic displacements on oxygen follow the polarizability scale closely, with little if any contribution from basicity. Explanations for the observed order of nucleophile reactivity have recently been given.[41]

Platinum(II) Compounds.—In a recent study, Gray[42] found that nucleophiles will react with many planar platinum (II) compounds by what is most certainly a nucleophilic displacement mechanism. Quantitative data are shown in Table II. The order is similar to that observed with peroxide oxygen, and this similarity is confirmed by the facts that olefins and phosphines are good nucleophiles while hydroxide ion and ethoxide ion are very poor nucleophiles.[43] Accordingly polarizability is dominant for platinum(II) and basicity seems to play no important role.

The nature of the platinum complex does determine nucleophilic order to some extent, however. In the case of $PtCl_4^{=}$ and $PtNH_3Cl_3^-$, nitrite ion is over 1000 times as reactive as chloride ion.[44] For $Pt(dien)Cl^+$, as shown in Table II, the reactivity ratio is about 5. From this, and other observations, it is likely that polarizability enhances nucleophilic character toward platinum(II) to a greater extent as the positive charge on platinum diminishes. Ignoring this effect, the general order of reactivity toward platinum(II) seems to be $R_3P \simeq$ thiourea $\simeq SCN^- \simeq I^- > N_3^- > NO_2^- >$ pyridine $>$ aniline $>$ olefin $\simeq NH_3 \simeq Br^- > Cl^- >$ glycine $\simeq OH^- \simeq H_2O \simeq F^-$.

Halogen Compounds.—It is rather surprising to find that nucleophilic displacements on fluorine are possible, but such is apparently the case in the compound perchloryl fluoride $FClO_3$. Enolate ions, nitronate ions, enamines, vinyl ethers and related organic compounds (all of which have a canonical form with a free electron pair on carbon) attack the fluorine in perchloryl fluoride to give products containing carbon–fluorine bonds.[45] Bases such as ethoxide ion and ammonia attack the chlo-

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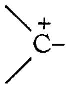
rine to form substituted perchlorates, but there is no evidence found for these basic nucleophiles attacking the fluorine atom. We conclude that attack on covalent fluorine requires a highly polarizable nucleophile and basicity is of no importance. Conversely attack on tetrahedral chlorine seems to require basicity.

Discussion

The three sources of high nucleophilicity mentioned in the first section are basicity, polarizability and the alpha effect. They seem to be essentially independent of each other. As far as can be ascertained at present, the alpha effect is common to all substrates, though it is expected that the magnitude of the effect will be found to vary over a wide range eventually. From the examples of the previous section, it is seen that different substrates show marked differences with respect to susceptibility toward basicity and polarizability. Stated another way, the values of α and β in equation 2 show large variations with the substrate.

The particular cases of the substrates of carbonyl carbon, tetrahedral phosphorus, tetrahedral sulfur, trigonal boron and the proton seem to depend almost entirely on basicity. The examples of oxygen, bivalent sulfur, fluorine and platinum seem to depend almost entirely on polarizability. Aliphatic tetrahedral carbon, aromatic carbon and trivalent nitrogen depend on both factors with polarizability rather dominant.

The theoretical discussion of the first section enables these variations to be understood in a very satisfactory way. To the extent that the interaction between S and N in the transition state of reaction 1 resembles the interaction of a proton with N, we should find basicity important. The characteristics of the proton are a high positive charge and an absence of outer electrons. It is just those substrates which most nearly fulfill these requirements for which basicity is indeed dominant. In the case of ester hydrolysis, it is structure  $>\overset{+}{C}-\overset{-}{O}$ which is available for the transition state. This presents a more positive carbon to the incoming nucleophile and, equally important, one less pair of electrons attached to carbon, in comparison to a substrate such as an alkyl halide. In the compounds of tetrahedral phosphorus and sulfur, there is both a high positive charge and a set of empty d orbitals of some stability on the central atom. As π-bonding from oxygen to the central atom reduces the positive charge and fills up these orbitals, so the susceptibility to basicity decreases as expected. Trivalent boron is positive in nature and has an empty p orbital as well. The function of the empty orbitals in all these cases is two-fold: to reduce the number of repelling electron pairs on the substrate atom and to provide a positive site for the acceptance of electrons from N.

The cases where polarizability is the chief factor show a common pattern. The central element is electronegative, often negatively charged in the ground state and has a number of outer orbital electrons. The first two factors cause basicity to play a minor role and the last factor insures that polarizability will be important. Recall that the important property of a highly polarizable nucleophile is that it can provide a low-energy, empty orbital to accommodate electrons from the substrate. In the cases of oxygen, bivalent sulfur and fluorine, the central atom S has a full set of p orbital electrons. In the case of platinum(II), there is a full set of d orbital electrons except for one vacant d orbital in the plane of the complex. The eight d electrons project in all directions from which a nucleophile could reasonably approach the central atom.

The dual nature of a polarizable nucleophile in both donating electrons to the substrate atom in a sigma bond and accepting electrons from the substrate atom in a π-bond has led to the suggestion that such nucleophiles be called biphilic reagents.[46] There is much evidence of fragmentary nature to indicate that biphilicity is important for complexes of the transition metal ions which are of relatively low positive charge and which have many d orbital electrons. For example, in the metal carbonyls it is only a biphilic reagent such as carbon monoxide itself, trialkyl phosphine and the like, which can easily displace an attached carbon monoxide molecule. This may be due to thermodynamic factors, but, in a few cases, it has been shown that simple nucleophilic displacements occur for these systems.[47] Hydroxide ion is often surprisingly poor as a reagent. For example, in the case of *cis* and *trans* $Rh(en)_2Cl_2^+$, the rate of reaction with hydroxide ion is hardly greater than the rate of reaction with water.[48] This is unexpected in view of the high positive charge for rhodium(III). The data for platinum(II) cited earlier again show hydroxide ion to be a poor reagent. For metal atoms with no outer d electrons and with a high charge, hydroxide ion becomes a good reagent again. This is true for chromium(VI), silicon(IV), germanium(IV) and tin(IV).

A biphilic reagent is not the same thing as an ambident reagent.[49] The latter has two different nucleophilic sites within it, such as the oxygen atom and the nitrogen atom in the nitrite ion. In any given transition state only one site is involved. Generally in an ambident reagent, one nucleophilic atom is more basic and one atom is more polarizable or presents a structure with an empty orbital. As explained by Kornblum and his co-workers,[49] if the substrate SX resembles a proton, the more basic atom will be the reactive one. This would be the case if a carbonium ion-like intermediate was formed. The more polarizable site would be the reactive one in the case of a substrate which favored polarizability over basicity, such as primary alkyl halide.

The reactions of alkyl halides and similar compounds require both basicity and polarizability, with the latter more important. This results naturally from the structure of the transition state

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in a displacement reaction. The central carbon atom is somewhat positive, but not greatly so. The orbitals surrounding carbon are all filled, but the electrons in them are somewhat removed from the critical region by bonding to other atoms or groups. The general situation is clearly intermediate between that of a proton as the substrate and an oxygen atom of a peroxide as a substrate, but rather closer to the oxygen atom case. As one goes from tetrahedral carbon compounds, R_3CX, across the periodic table to R_2NX, ROX and finally FX, one expects polarizability to become more important and basicity less important, as found. The fact that tetrahedral boron compounds, R_3BX, depend more on basicity than does R_3CX, is also expected.

It might also be predicted that as the groups surrounding carbon in R_3CX promote a mechanism with more carbonium ion-like character, the dependence on basicity should increase. This would follow from the increased positive charge on carbon in the transition state. It must be remembered, however, that groups that favor an S_N1 mechanism do so by processes which remove positive charge from the central carbon atom. This greatly reduces the expected effect, as was pointed out by Swain and Scott.[2a] The experimental facts are not quite enough at present to make the situation clear.

Acknowledgments. The authors are grateful to their colleagues, especially Myron L. Bender, John F. Neumer, William T. King and William P. Jencks, for their suggestions and comments. J.O.E. wishes to thank Brown University for sabbatical leave and Northwestern University for kind hospitality during the leave.

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Molecular Association of Nickel(II) Chelates. III. The Reaction of Nickel(II) Acetylacetonate with Pyridine

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RECEIVED JULY 7, 1961

The visible spectrum of anhydrous nickel(II) acetylacetonate in benzene containing pyridine is described. The data support the premise that the spectral and magnetic behavior of nickel(II) acetylacetonate is due to molecular association in solvents of low coördinating power. Furthermore, the data indicate that polymerization occurs in a fashion similar to that existing in the solid, namely, trimeric units of $Ni(AA)_2$ with six oxygens surrounding each Ni(II). The spectra show the formation of a species containing two $Ni(AA)_2$ units per pyridine and that the bis-pyridine product is formed only after the pyridine to nickel ratio exceeds 0.5. The preparation and characterization of the heretofore unknown compound $[Ni(AA)_2]_2 \cdot py$ is described. The equilibrium constant for the reaction $[Ni(AA)_2]_2 \cdot py + 3py = 2Ni(AA)_2 \cdot py_2$ has been determined from the spectra. An estimate is made for the equilibrium constant of the initial reaction, $2[Ni(AA)_2]_3 + 3py = 3[Ni(AA)_2]_2 \cdot py$.

Introduction

Molecular association of solute molecules in solvents of low coördinating power[1-4] and in the solid state has been invoked recently to explain the paramagnetism of some "quadricoördinate" Ni(II) chelates. In particular rather strong evidence has been presented[2,3] to suggest that the paramagnetism of Ni(II) acetylacetonate, $Ni(AA)_2$, is due to molecular association. In the solid state, X-ray crystal structure analysis has shown a trimeric arrangement of $Ni(AA)_2$ units with each Ni(II) atom surrounded by a distorted octahedron of oxygens.[5]

Diamagnetic molecules can be obtained if the methyl groups in acetylacetone are replaced by bulky residues which tend to prevent polymerization of the nickel(II) β-diketonate units. Some of the diamagnetic solids such as nickel(II) dibenzoylmethane and nickel(II) phenylacetylacetonate become partially paramagnetic in non-coördinating-solvents.[2,3] Nickel(II) diisobutyrylmethane, which is paramagnetic in the solid state, becomes less paramagnetic in solvents of low coördinating power as the temperature is increased and the concentration is decreased.[2] Polymerization in solution similar to that of the $Ni(AA)_2$ in the solid state apparently causes these peculiar magnetic effects. Molecular weight determinations in benzene[2] for the $Ni(AA)_2$ have suggested a trimer for the anhydrous material in this solvent. The association factor of 2.96 ± 0.2 is quite significant considering the difficulty in obtaining perfectly dry samples and solvent.

The trimeric units of Ni(II) acetylacetonate are broken by coördinating solvents. The dihydrate[6] and bis-pyridine[7] compounds are well known and easily obtainable. Changes in the ligand field surrounding the Ni(II) atom occur when the trimer is broken and the solvated material is formed. This field change produces a shift in the visible absorption spectrum of the material.[6] Since pyridine readily coördinates with $Ni(AA)_2$ in hydrocarbon solutions, producing a measurable spectral shift, it was hoped that additional information concerning the polymeric $Ni(AA)_2$ might be obtained by a spectrophotometric titration of the acetylacetonate in benzene with pyridine. Further interest in this

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