

Steric and electronic effects in S_N2 reactions*

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Abstract: This article gives an overview of recently published literature on the factors that govern S_N2 reactivity. By comparing reactivity in solution with that in the isolated gas phase, it has become possible to dissect the contribution of the solvent from that of the intrinsic molecular properties. This has proven to be an extremely important and fruitful step forward in obtaining key knowledge not available before. The gas-phase studies have made it clear that organic chemists need to revise radically their concepts and ideas about this crucial reaction type. This is particularly true with regard to the commonly used term “steric effect”.

Keywords: S_N2 ; steric effect; reaction mechanism; nucleophilic substitution reactions; solvent effects.

INTRODUCTION

The acronyms S_N1 , S_N2 , E1, and E2 were introduced by Ingold to describe the mechanistic landscape that is relevant to a wide range of situations where a base reacts with an organic substrate $R^1R^2CHCXR^3R^4$ [1]. At the molecular level, the relative distribution between substitution (S) and elimination (E) is determined by whether the base under the given conditions may act either as a Lewis base attacking the carbon atom holding the X group or as a Brønsted base attacking the β -hydrogen atom. Likewise, the outcome of the reaction will depend on whether the proton acidic or carbon acidic property of the substrate is the dominating. Furthermore, the leaving group ability of X is of importance. Typically, the reaction is conducted in a solvent close to ambient temperature. Under these conditions the properties of both the base and the substrate will be strongly influenced by the solvent, both in general by its dielectric properties and more specifically through complex formation [2]. In many cases, the solvent is directly involved, acting as the base (solvolysis).

While elimination reactions appear to be reasonably well understood on the basis of the Brønsted acid/base properties of the reactants, both in solution and in the gas phase [3–9], nucleophilic substitution reactions turn out to be more complicated in the sense that the intrinsic factors that determine reactivity have been rather poorly understood. This paper will therefore deal with nucleophilic substitution reaction, with a strong emphasis on the S_N2 mechanism. In particular, the relationship between the nucleophilicity of the base and its Brønsted basicity has been unclear. The same is true with regard to the steric and electronic factors that control substrate reactivity. The only logical step to be made in order to better understand how the molecular properties determine base and substrate reactivity is to separate out the important and often decisive contribution of solvent effects on the rate and product distribution. This is conveniently obtained by studying the reaction in the isolated gaseous state—either by

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performing mass spectrometric experiments or by theoretical modeling. In addition to the obvious advantage this systematic and transparent approach provides, it gives a unique opportunity to clarify central concepts used in textbooks and publication. Unfortunately, parts of the language of organic chemistry are obscure and often provide little physical insight into the phenomena under study.

THE SUBSTRATE

Typically, in solution, substrates with large alkyl groups react slower in S_N2 reactions



than less bulky substrates, so there is strong experimental evidence in favor of the reactivity trend of the so-called α -series: $CH_3 > CH_3CH_2 > (CH_3)_2CH > (CH_3)_3C$. From the teachings of organic chemistry textbooks—dating back to the time of Ingold and Hughes—this trend is attributed to steric hindrance (steric retardation). By examining a large number of modern textbooks of organic chemistry, it seems that the original understanding of the physical background of steric hindrance has disappeared over the years. Instead, the typical textbook accounts for the phenomenon using an illustration showing how the backside entrance of the nucleophile becomes more difficult the more bulky the substituent is, hinting erroneously that steric hindrance to a large degree is an entropy effect. In order to understand this issue better, it is necessary to go back to the original literature. In stark contrast to the modern textbook, Ingold's book (Chap. 7) explains very carefully that the steric retardation is due to an enthalpy effect. This is based on the physical measurements providing reliable estimates of the Arrhenius activation energy. The author notes that the steric hindrance is the result of a larger compression of the transition state (beyond the van der Waals radii) than of the reactant state, implying that in rare cases where the opposite is true, there could even be steric acceleration. For the α -series, the hindrance, in enthalpy terms, is of the order of 20 kJ mol^{-1} in going from methyl to tertiary butyl. It was also suggested that the measured hindrance effect might also have a contribution from electronic (polar) effects, although it was difficult to assess this contribution 60 years ago.

Since textbooks have a strong impact on the way many chemists think, we may assume that the everyday use of the term "steric hindrance" is at best vague and intuitive—more likely it is incorrect. The purpose of this section is to uncover the physical origin of the observed reactivity trends, thereby casting a critical light on the usual explanation. Moreover, it has been difficult applying experimental methods, both in principle and in practice, to dissect a steric effect term from an electronic effect term. One part of the enigma is the evident fact that increasing the size of the alkyl group of the substrate influences both the geometric features of the molecule and the electronic structure at the reactive central carbon atom. However, as will be demonstrated below, it is possible, by applying accurate and reliable electronic structure calculations, to improve our understanding of this relationship in a manner almost unthinkable in the Hughes/Ingold era.

Electronic property of alkyl compounds

Before proceeding to our discussion on the origin of the molecular origins for reactivity, it may be of value to see how the electronic effect of the alkyl group alone influences the properties of a molecule, i.e., in the absence of steric effects. We will use the row of alcohols as the example, although our point is general.



Figure 1 shows the relationship between the gas acidity and gas basicity (for definitions, see eqs. 2 and 3, respectively) in the series water, methanol, ethanol, isopropanol, and tertiary butanol. From

these data it is evident that the alcohol both becomes a stronger acid and a stronger base upon increasing the size. The linear correlation suggests a common origin. Gasteiger and Hutchings were able to correlate proton affinity with two essential molecular parameters, namely, electronegativity and polarizability [10]. Leaning to this fact, it seems clear that the molecular polarizability is the common factor that provides the rationale for the similar stabilization of the charged forms of the deprotonated and protonated alcohol. In quantitative terms, the electronic stabilization is slightly higher for the positive ion than for the negative ion. This well-known inductive effect is a general phenomenon, found for a wide range of alkyl substituted systems [11–13].

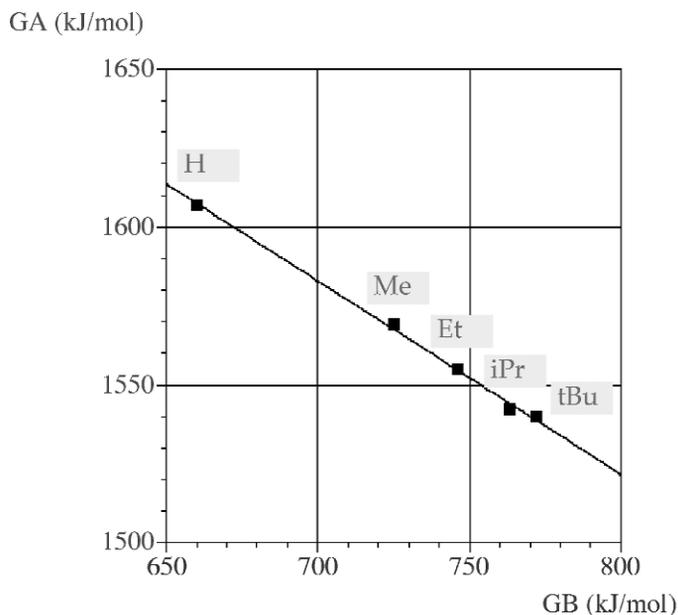


Fig. 1 Gas acidity as function of gas basicity for a series of alcohols, ROH. Thermochemical data have been taken from the NIST compilation [14].

Protonated alcohols: An exceptional case providing insight

The rate of an S_N2 reaction is determined by the barrier height, which is the energy difference between the transition structure (TS) and the reactant structure (RS). The normal reactivity trend, described above, means that the TS becomes more destabilized relative to the RS with increasing size of the alkyl group. The question I will address here, is to which degree this destabilization is due to an increasingly negative inductive effect with alkyl size, and to what degree it comes from increasing steric repulsion in the TS as the alkyl group grows larger. Our own study of identity S_N2 reactions of protonated alcohols with water



provides the first clue to the answer of this question. Quite surprisingly, the experimentally found reactivity order $[\text{CH}_3 > \text{CH}_3\text{CH}_2 < (\text{CH}_3)_2\text{CH} < (\text{CH}_3)_3\text{C}]$ for these gas-phase reactions is almost the opposite of the normal trend [15]. In addition, high-level quantum chemical calculations reproduce the experimental results very accurately [15,16]. In other words, increasing steric repulsion seems not to be the determining factor explaining reactivity in this particular example. For the analogous reactions of protonated amines the normal trend is observed [17], while for protonated fluorides the barriers are low and close to constant throughout the series [18]. With regard to the protonated alcohols, it appears that

gas-phase and solution reactivity are diametrically opposite. From quantum chemical calculations of reaction 4 in the presence of water, either in the form of a supermolecule with four extra water molecules or with a polarizable continuum model, the normal reactivity trend was found [15]. These examples do not of course prove that the steric effect is without relevance, but the electronic effect seems to be more important. The question is therefore if this is a general situation, or only relevant to some sub-classes of S_N2 reactions.

Substituted allyl substrates

A wider database of reaction data, also including the more common anionic class ($Y^- + RX$), is needed to study the relationship between the steric and the electronic effect on reactivity trends. It was suggested that allylic substrates are suitable model systems for this purpose, and the following reactions were studied by applying reliable ab initio methods: $X^- + YCHCHCZ_2X \rightarrow YCHCHCZ_2X + X^-$ ($X = H, CH_3, NH_2, F, Cl$; $Y = F, OH, H, CHO, BH_2$; $Z = H, CH_3$) [19]. In this model system, it is possible to fine-tune the electronic properties by systematic variation of the remote substituent Y , not affecting the steric situation at the reaction center. In agreement with the normal reactivity trend, the barrier height increases by bringing in two methyl groups ($Z = CH_3$) directly at the reaction center, but it is notable that the consequence of this substitution is by far smaller than changing the remote substituent from $Y = CHO$ to OH .

Energy decomposition analysis (EDA)

EDA provides a mathematical approach to disentangle the different contributions to the energy difference between the TS and the RS. By applying an EDA scheme originally suggested by Morokuma [20] and later developed by Ziegler [21], it becomes possible to identify energy terms appropriate to our discussion. The steric effect has its counterpart in the Pauli repulsion term of this EDA. Recently, we performed this type of analysis to selected but very typical S_N2 reactions along the respective reaction coordinates all the way from reactants to products [22]. Contrary to the common notion—as it is expressed in the textbooks—it appeared that the Pauli repulsion between the fragments decreases in the vicinity of the TS. The effect becomes more pronounced when the central alkyl group of the substrate becomes bigger and more bulky. In other words, the extraordinary observation is that the steric effect one can identify is the opposite of the reactivity trend. This is also in line with the observation of the TS geometries reported here and elsewhere, namely, that the TSs show no obvious signs of being more compressed than the RS. As a matter of fact, the situation proves to be the opposite, leaving no support for the idea of Hughes and Ingold on steric hindrance.

Having made this progress in our endeavour to improve our insights of the factors that control the substrate S_N2 reactivity, we will now for a while turn our attention to the other reactant, namely, the nucleophile.

THE BASE (NUCLEOPHILE)

A straightforward etymological examination of the term “nucleophile” indicates that it describes a molecule with affinity to positive electric charge. The name stems from Ingold, but the concept can be dated back to Lapworth (1925) [23]. Nucleophilicity is nowadays a quantitative measure of nucleophile strength. Swain and Scott were early in suggesting how this could be done in 1953 by linking nucleophilicity of Y^- to the relative rate of the reaction



applying a linear free energy relationship. Their definition is the one approved by IUPAC. It is obvious that nucleophilicity and basicity are related—the question is how. The answer is not right at hand since, for example, the relative order of nucleophilicity of the halide anions in protic solvents is opposite to that of the basicity. Before proceeding, we note that basicity is an equilibrium property while nucleophilicity is a kinetic property. To put these two concepts on common ground we will need to apply a two-step process for our analysis. The first step is to find out how nucleophilicity is related to carbon basicity. The second is to look for how carbon and proton basicities relate. We will start with the first. Bordwell et al. demonstrated that an approximate Brønsted-type relationship exists between carbon basicity and rates of S_N2 reactions in dimethyl sulfoxide (DMSO) solution [24], and it is highly relevant to this discussion to mention that Streitwieser wrote that “the free energies of activation for reaction of six anionic nucleophiles with methyl iodide in dimethyl formamide correlate linearly with the overall heats of reaction in the gas phase” [25]. For gas-phase reactions, it was suggested by Pellerite and Brauman that the barrier height, and thereby the rate, is determined by two factors, the average *intrinsic* nucleophilicity of X and Y (eq. 1) and the reaction exothermicity, expressed in the form of a Marcus-type relationship [26,27]. Both their own analysis of experimental data, and later computational tests of the hypothesis suggest that it is generally valid, at least approximately [28–31]. Having established this relationship, the second step is then to consider the relationship between carbon (Lewis) and hydrogen (Brønsted) basicity. It has been known since 1985 that there exists a good linear correlation between methyl cation affinity and proton affinity [32,33]. More recently, a similar linear relationship was shown also to exist for other alkyl group affinities (ethyl, *iso*-propyl, and *tert*-butyl) [12]. In all cases, the alkyl cation affinities (ACAs) span a smaller range of values, and the larger the alkyl group is, the more narrow is the range. This has an interesting consequence. For a general S_N2 reaction, eq. 1, the reaction exothermicity is equal to the difference in alkyl affinity of X^- and Y^- . In other words, the larger the alkyl group, the smaller is the relative effect of exothermicity on the rate of the reaction. The effect of the thermodynamic driving force will be discussed in more detail later on.

Periodic trends

The Marcus-type relationship discussed immediately above includes knowledge of intrinsic nucleophilicities of X and Y. To obtain these for a series of nucleophiles and nucleofuges (leaving groups) it is necessary to study identity reactions, and for simple gas-phase reactions this type of data is nowadays conveniently obtained through accurate quantum chemical calculations. To obtain a sufficiently reliable and representative database, the potential energy profiles of 18 identity S_N2 reactions, both anionic and cationic, were estimated using the composite quantum chemical method G2 (for X = NH_2 , OH, F, PH_2 , SH, Cl, AsH_2 , SeH, Br) [34]



and



The periodic variation in the strengths of these nucleophiles shows an interesting pattern. Firstly, intrinsic nucleophilicity decreases (barrier height increases) as one passes downwards in a group of the periodic table [34,35]. Secondly, nucleophilicity increases from left to right within a period [34]. These trends appear on first sight to be contrary to general observation. For example, it is well known that F^- in general is a rather poor nucleophile in protic solvents, in particular in water. However, at this point of the discussion we need to remind ourselves that the trends reported here are from the gas phase, and that the nucleophilicity of F^- in solution is significantly enhanced upon changing to a more nonpolar solvent [36].

Taking the thermodynamical driving force into account

In addition to the intrinsic nucleophilicities of X and Y, the barrier height for a gas-phase reaction is determined by the reaction exothermicity through the Marcus-type relationship discussed in the previous two sections—the more exothermic the reaction, the lower is the barrier. Since exothermicity is determined by the relative carbon basicities of X and Y, i.e., the difference in their ACAs, it is clear that a base with a higher ACA is a stronger nucleophile. Very interestingly, the periodic trend in ACA is the exact opposite to the trend in intrinsic nucleophilicity [34]. While this may seem a bit puzzling at first sight, it explains why it has taken so long time to understand how nucleophilicity and basicity are connected. Our original description of the paradox was that there are two opposing forces at work, since a strong base will be a poor nucleophile in terms of having a high intrinsic barrier but will be a good nucleophile by shifting the barrier to a lower level by stabilizing products relative to reactants [34]. For strongly exothermic reaction, the latter will be the dominating. In these situations, basicity and nucleophilicity correlate. A recent example of this was given by Bento and Bickelhaupt [37]. By realizing the complex relationship between nucleophilicity on the one hand, and basicity and intrinsic nucleophilicity on the other—we now understand why nucleophilicity and basicity sometimes correlate and sometimes do not correlate.

It is relevant to mention *en passant* that alternative nucleophilicity scales to that of Swain and Scott exist. For example, there exists a vast body of experimental data, to a large degree derived by systematic investigations between various nucleophiles and electrophiles (in particular benzhydrylium ions) in solution by Mayr and coworkers. These data have been analyzed in the light of several definitions of nucleophilicity supporting consistency between solution cation affinity and Swain/Scott nucleophilicity [38]. On the background of our present discussion we realize that the good consistency is probably due to the thermodynamic driving force dominating the reactions investigated.

Electrostatic TS model

The periodic trends in intrinsic nucleophilicity can be rationalized on the basis of an electrostatic model [34]. In this model, we compare the electronic structure of the TS with that in the substrate for the reaction between X^- and CH_3X , and we will compare the strong intrinsic nucleophile F^- with the much weaker NH_2^- . The plots of the Laplacian of the electron density for the species in question are illustrative (Fig. 2).

In both cases there is a strong and polar C–X bond in the substrate, CH_3X . The poorest electron donor, F^- , gives rise to little electron donation to the carbocationic center, and the C–F bond has a stronger electrostatic character than the corresponding C–N bond. Inspection of the electron densities shows that the TSs possess less covalent and more electrostatic character than their substrate counterparts, and this difference is most pronounced for NH_2^- . The result is that the electronic rearrangement necessary to reach the TS will be the least for F^- , suggesting why the barrier is lower in this case.

This model has support from an analyses by Joubert et al., who showed that electron density is transferred from the nucleophile to the nucleofuge without involving the central carbon atom in the reaction between chloride and methyl chloride [40]. Furthermore, the analysis of the factors responsible for S_N2 reactivity in allylic [19] and benzylic [41] substrates are also in support of this electrostatic model. Normally, one would not consider helium to be a nucleophile, except that it has electron pairs in its valence, but in this connection it is interesting that the symmetrical structure typical for a TS, $[He\cdots CH_3\cdots He]^+$, instead is a potential energy minimum [42].

Even more support for the electrostatic model comes from the study of S_N2 reactions with non-carbon central atoms. Substituting carbon by a more electronegative element (N, O) increases the barrier height [43,44], while substituting by a more electropositive atom (Si, S, P) decreases the barrier, in many cases to the extent that the symmetrical central TS becomes the potential energy minimum [45–49].

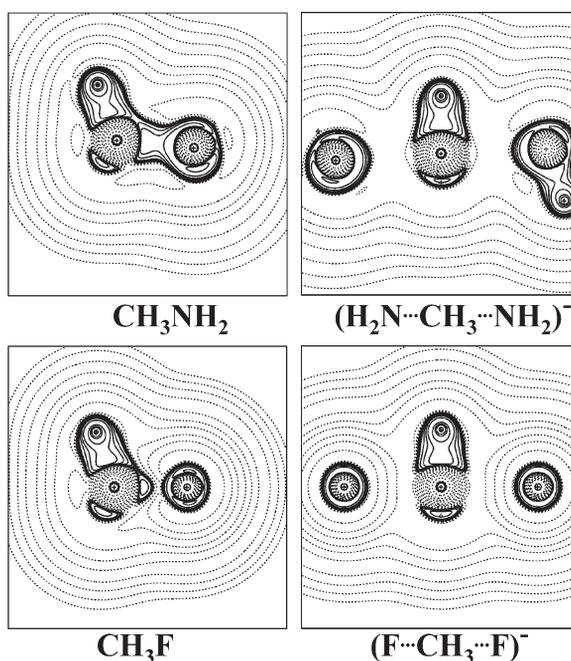


Fig. 2 Cross-section of the Laplacian of the one-electron density calculated in a plane containing the nucleophile, the central carbon, and the leaving group, obtained using the program AIMPAC [39]. A more pronounced electrostatic character of the bond is revealed by a lower value of the Laplacian between nuclei.

CONCLUSION

A clear picture of the S_N2 reaction emerges from the discussion above. By comparing solution and gas-phase reactivity, and from the analysis of the inherent molecular factors that determine the reactivity we may draw two important conclusions.

- The “steric effect” does not account for reaction trends with changing the alkyl group of the substrate. The electronic (essentially inductive effect) is by far the dominating one.
- Basicity and nucleophilicity correlate only for strongly exothermic reactions only. For identity reactions they are anti-correlated.

These conclusions are at odds with conventional ideas, and textbooks in organic chemistry need to be revised.

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