with the generally accepted mechanism of the reaction. It is hoped that further discussion and experimentation will result which will either prove or disprove these conclusions. Furthermore, because of the importance of the acyloin reaction as a synthetic tool in organic chemistry, more work is needed to describe (1) adsorption and desorption of organic molecules on alkali metal surfaces and (2) steric, conformational, and electronic effects on the electron transfer to esters.

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A Suggestion for the Revision of Mechanistic Designations

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A simple system for the designation of chemical reaction mechanisms is suggested. The new system represents each bond-making and bond-breaking step in symbolic form and requires only two symbols plus atomic symbols for the elements to represent all heterolytic and homolytic reactions including electron-transfer reactions. Minor modification of the system allows the designation of ion-paired intermediates and caged radical pairs. An approach to the designation of photochemical reaction mechanisms is also suggested. The new system can serve as a digital code which, when applied to a set of reagents, will generate both mechanism and products. Its application to information retrieval is anticipated.

In the past 30 years chemistry has become increasingly mechanistic. The term mechanism has many peripherally different definitions but basically means a description of the sequence of bond-making and bond-breaking steps occurring as a set of starting molecules, atoms, or ions is converted to a new set. When mechanisms are grouped for classification, extramechanistic information is included to indicate the outcome of the reaction, *i.e.*, substitution, elimination, or addition. This procedure gives more information than would be available from the purely mechanistic part of the classification symbols, but it still leaves important parts of the known details of the mechanism to be associated with the symbols by memorization.

As an example, consider the classification S_N2. The most descriptive part of the symbol gives the information that the eventual outcome of the reaction is substitution of one group for another but it does not convey the important fact that the reaction is concerted. To the uninformed beginner it might seem redundant that the attack of a nucleophile would have to be designated as bimolecular. The symbol SN1 would completely baffle a beginning student until he was told that this is a two-step reaction and the designations nucleophilic and unimolecular apply to different steps. Even the most mechanistically organized textbooks invariably group SN1 and SN2 reactions together, implying a nonexistent similarity in the events leading to products. Mechanistically, an SN2 reaction is more closely related to the attack of base on a carbon acid to form a carbanion than to an SN1 reaction and the factors which facilitate the first two reaction types are closely related. It is not uncommon to find other nucleophilic substitutions, such as those involving addition–elimination, which is still a third mechanistic type, incorporated in discussions of SN1 and SN2 reactions.

It is not the main purpose of this paper to support a mechanistic approach to teaching organic chemistry. Some chemical educators feel that students find the mechanistic approach more difficult than the functional-group or reaction-outcome approaches. We would, however, suggest that a completely mechanistic approach has never been given a chance. The nomenclature system we will suggest has the pedagogic advantage of having reaction-type symbols that directly describe molecular events. The new system also provides a number of more general benefits and directives.

Chemical Reactions as Bond-Making and Bond-Breaking Processes

Background. Almost all chemical reactions involve bond making and bond breaking. These processes are the lowest common denominators of all reaction mechanisms. A reasonable system of mechanistic nomenclature should therefore start with a system for labeling the distinguishable types of bond making and bond breaking and continue by indicating the sequence of such steps which occur as reactants are converted to products. The first section of this paper is essentially a description of the method previously suggested by Mathieu and coworkers.[1] We have altered the symbolism slightly and made a few extensions.

Association Processes. Association processes may be separated into three categories, *i.e.*, homolytic (A·), nucleophilic (AN), and electrophilic (AE), *i.e.*

$$\mathrm{X\cdot + R\cdot \longrightarrow R{:}X \qquad (A\cdot)}$$
$$\mathrm{X{:} + R \longrightarrow R{:}X \qquad (A_N)}$$
$$\mathrm{X + R{:} \longrightarrow R{:}X \qquad (A_E)}$$

These categories subdivide into various charge types when the substrate (R) and reagent (X) structures are specified. As in previous systems, ambiguity arises when it is not clear which reactant should be considered the reagent and which the substrate.[2] This difficulty can produce two descriptions of the same mechanism. However, the problem may be avoided in a manner to be described later in this paper.

Dissociation Reactions. The reverse of these associations will be called homolytic dissociation (D·), nucleophobic dissociation (DN), and electrophobic dissociation (DE) and are illustrated as

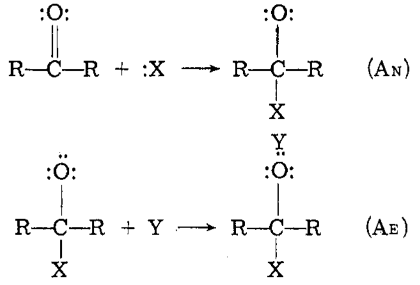
$$\mathrm{R{:}X \longrightarrow R\cdot + X\cdot \qquad (D\cdot)}$$
$$\mathrm{R{:}X \longrightarrow R + X{:} \qquad (D_N)}$$
$$\mathrm{R{:}X \longrightarrow R{:} + X \qquad (D_E)}$$

Use of the term nucleophobic to describe a process in which an electron pair is repelled by the nucleus has the advantage that both forward and reverse reactions are identically subscripted and are therefore easily remembered.[3]

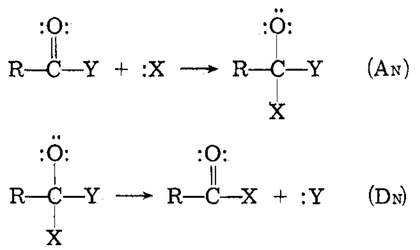
Nonconcerted Combinations of Two Processes. If two or more bond-forming or bond-breaking processes, or two sets thereof, are not synchronous, a plus sign will be introduced between the terms describing each separate step. For example, an SN1 reaction becomes DN + AN

$$\mathrm{RX \longrightarrow R + {:}X \qquad (D_N)}$$
$$\mathrm{R + {:}Y \longrightarrow R{:}Y \qquad (A_N)}$$

Nucleophilic addition to C=O could be AN + AE



or AE + AN for the corresponding electrophilic addition. With a leaving group attached to C=O, the reaction could be AN + DN



In all, there are 16 possible combinations. Of these, eight are unlikely because they usually increase or decrease charge by 2. These are either combinations of identically labeled A's or D's (AN + AN) or a sum of two different processes with different labels (AN + DE). Thus, for a two-term combination, the probable processes are those for which only two of the symbols are identical. Exceptions to this arise when the part of the molecule being designated as substrate changes between steps as in the abstraction of some group.

The four remaining probable processes not discussed above all involve DE terms. For uncharged molecules this denotes expulsion of a cation and there is fairly general agreement that, for most examples of this process, a base or nucleophile assists in removal of the cation, probably *via* a concerted process. An E1 reaction, for example, is probably never a DN + DE type because some base, however weak, is involved in removal of the proton, even though this often is omitted in textbook representations. Decarboxylation of a carboxylate anion more closely approximates a true DE process, but this representation simply reflects ignorance of the changes in solvation as the carbon dioxide is being formed. The same objection can be raised to all of the four single-term descriptions: AN, DN, AE, DE. This is not a weakness of the system but rather a lack of experimentally demonstrated facts. As will be seen below, a great strength of this scheme is a flexibility which allows a mechanism's designation to keep pace with increasing awareness of its complexity.

Concerted Combinations of Two Processes. If two or more bond-making or bond-breaking processes occur in a concerted, synchronous fashion, the plus sign will be removed. An SN2 reaction then becomes ANDN. Certain types of SE2 may be AEDE. Cycloadditions could be AEAN and their reverse DEDN. The order of the terms is obviously unimportant for a concerted reaction so that only eight combinations are possible. As in the nonconcerted cases, combinations with more or less than two different symbols indicate group abstraction.

Use of the System to Describe Common Reaction Types

Comparison of Systems. Before proceeding to a discussion of nomenclature for other common mechanistic types, a brief comparison of the information provided by the existing and proposed systems is in order. Consider, for example, the relative merits of SN2 *vs.* ANDN as a description of the reaction of CH_3I and ^-OH. The numerical part of the former symbol is unnecessary in the proposed system because every dissociation reaction is unimolecular and, with the exception of intramolecular reactions, for which we will later suggest distinguishing symbols, associations are always bimolecular. Thus, the molecularity of each step in a reaction is obvious from its symbol. The uninformed student might assume that ANDN meant nucleophilic displacement on iodine or on hydrogen. Both of these alternatives are more properly considered ANDE reactions. Although neither of these reactions compete when this particular substrate is treated with hydroxide ion, the origin of the classification difference is illustrative. In the association step, the hydrogen or iodine atom is considered part of the substrate, but in the dissociation step it is not. The arbitrary change in frame of reference results in a designation for which the number of different symbols is other than 2.

While the system discussed above is satisfactory for the designation of simple mechanistic types and is superior to the existing method, ambiguities develop in the description of more complex reactions. Moreover, while the system conveys some extramechanistic information, this feature is dependent on the availability of a consistent method for making the substrate–reagent assignment. We will now develop a different subscriptive procedure which not only avoids the substrate–reagent decision but which also describes the mechanistic events in sufficient detail to allow the determination of product structure.

A Modification Which Avoids the Substrate–Reagent Decision. In order to give complete reaction-outcome information, the two atoms involved in each bond-making and bond-breaking process must be specified in the designation. This can be easily done by subscripting the atomic symbols of the two atoms after each A or D notation. Conveniently, it is not necessary to employ the designations N or E provided that a standard direction for electron flow is chosen. We will subscript the atomic symbols so that the *first subscripted atom is the one carrying the electron pair in a heterolytic process.* A homolytic process will be designated by placing a dot between the two atomic symbols.

Nucleophilic and Electrophilic Substitutions. The three processes referred to in the preceding section now become

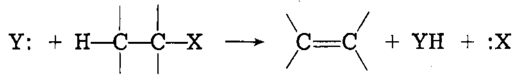
$$\mathrm{HO{:}} + \mathrm{CH_3I} \longrightarrow \mathrm{CH_3OH} + \mathrm{{:}I} \qquad (\mathrm{A_{OC}D_{IC}})$$

$$\mathrm{HO{:}} + \mathrm{CH_3I} \longrightarrow \mathrm{HOH} + \mathrm{{:}CH_2I} \qquad (\mathrm{A_{OH}D_{CH}})$$

$$\mathrm{HO{:}} + \mathrm{CH_3I} \longrightarrow \mathrm{HOI} + \mathrm{{:}CH_3} \qquad (\mathrm{A_{OI}D_{CI}})$$

The designations are clearly distinguishable and completely specified. This modified system has the pedagogic drawback that mechanistic classes are not so easily identified, but with some practice the general categories can be recognized. In the foregoing set of reactions, for example, all of the designations have the form $A_{XZ}D_{YZ}$ where X and Y represent the entering and leaving groups, respectively, and Z is an atom on which concerted nucleophilic displacement is occurring. An electrophilic displacement would have the common atom subscripted first and have the general form $A_{ZX}D_{ZY}$. Nonconcerted nucleophilic and electrophilic substitutions will have the forms $D_{XZ} + A_{YZ}$ and $D_{ZX} + A_{ZY}$, respectively.

Elimination Reactions. The most commonly encountered elimination reaction is the loss of HX



$$\mathrm{Y{:}} + \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X} \longrightarrow \mathrm{{>}C{=}C{<}} + \mathrm{YH} + \mathrm{{:}X}$$

The accepted mechanistic alternatives are

$$\mathrm{E1} = \mathrm{D_{XC}} + \mathrm{A_{YH}D_{CH}}$$

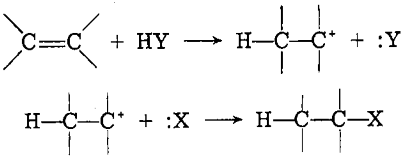
$$\mathrm{E2} = \mathrm{A_{YH}D_{CH}D_{XC}}$$

$$\mathrm{E1cB} = \mathrm{A_{YH}D_{CH}} + \mathrm{D_{XC}}$$

The presence of identical terms indicates that the reaction outcome is the same for all three mechanistic variations. It should be noted that insofar as the "substrate" is concerned, it is possible to obtain the same reaction outcome with different symbols. In the case of elimination reactions, there is a set of possible mechanisms whose representations contain the terms A_{HY}, D_{CX}, and D_{HC}, which lead to the same products. It is generally true that, for any mechanistic representation, reversal of the subscript order for one term will require that all the others be either reversed or replaced. This has the effect of reversing the direction of electron flow and may or may not lead to a realistic mechanistic alternative. In the present example, the combination $A_{HY}D_{CX}D_{HC}$ is, in fact, observed as a component part of the mechanism for reduction of hindered ketones by isopropyl Grignard reagents (X = Mg, Y = C). A more complete representation of this mechanism would be $A_{HY}D_{CX}D_{HC}A_{OX}$. The absence of a balancing A term in our representation of the common elimination types simply ignores the fate of the departing nucleophobe.

Returning to the common elimination types, $D_{XC} + A_{YH}D_{CH}$, $A_{YH}D_{CH}D_{XC}$, and $A_{YH}D_{CH} + D_{XC}$, it will be noted that not all of the possible sequences are represented. An inquisitive student might ask, "Why not $A_{YH} + D_{CH}D_{XC}$ (hydrogen bonding followed by concerted elimination) or $D_{XC}A_{YH} + D_{CH}$ (hydrogen-bond formation concerted with loss of nucleophobe)?" We feel that, by systematizing thought, adoption of our scheme might stimulate the search for evidence of new mechanistic types. Some apparently complex mechanistic distinctions can be represented in simple terms by this system. The question of anchimeric assistance, for example, reduces to a consideration of the validity of a single plus sign in the mechanistic designation.

Addition Reactions. The general form of acid-catalyzed addition of HX to a double bond is



$$\mathrm{{>}C{=}C{<}} + \mathrm{HY} \longrightarrow \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^{+}} + \mathrm{{:}Y}$$

$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^{+}} + \mathrm{{:}X} \longrightarrow \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X}$$

The addition is seen to be the reverse of an E1 reaction and this relationship is apparent from the symbolic representation $A_{CH}D_{YH} + A_{XC}$. The A's and D's are simply interchanged and the order of the terms reversed. Addition of HX, where HX itself serves as the proton source, is a special case of the reaction above (Y = X).

A similar relationship exists between nucleophilic addition to a multiple bond and the E1cB reaction and this is evident using the new terminology. The reverse of an E2 reaction would be designated $A_{XC}A_{CH}D_{YH}$. The combination $\mathrm{A_{XQ}A_{QY}}$ is representative of a termolecular reaction unless X and Y are atoms in the same molecule. Reverse E2 reactions are highly improbable.

It is probably worth mentioning at this point that for reactions involving formation or destruction of multiple bonds, the π bond is not indicated in the designation. This means that for β-elimination reactions, the species generated is formally a zwitterion

$$\mathrm{H{-}C{-}C{-}X} \longrightarrow \mathrm{{}^{+}C{-}C^{-}} + \mathrm{HX}$$

As this species is a very minor resonance contributor to most carbon–carbon double bonds, the double bond may be regarded as formed at this point and inclusion of an additional $\mathrm{A_{CC}}$ term seems superfluous. We would reserve this abbreviation of the system for cases in which the plus and minus charges are generated on adjacent carbons. All other cases should specifically designate bond formation if that is intended.

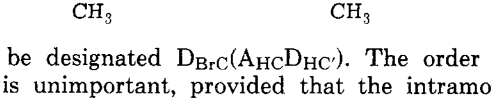
A related problem is that our system does not indicate the hybridization of the atom involved in a particular bond-making or -breaking process. Nucleophilic attack at carbon is $\mathrm{A_{XC}}$ regardless of whether C is present as tetrahedral carbon, C=Y, C≡Y, etc. We considered including a method for designating this in the system, but it seemed to open the door for inclusion of a variety of structural distinctions of increasing subtlety, the logical extension of which was a complete designation of the structures of all reagents. A reviewer has suggested $\mathrm{A_{OH^-,CH_3}} + \mathrm{D_{I^-,CH_3}}$ for the SN2 reaction of methyl iodide with hydroxide. We have no objection to this and feel that the capacity for such extension is a strength of the system. For simplicity in this paper, however, we will confine our subscripting to the two atoms directly involved. We would point out that a considerable amount of implicit structural information is contained in the mechanistic designation because of structural exclusion of certain mechanistic types. $\mathrm{A_{XC}} + \mathrm{D_{YC}}$ is not an observed mechanism for nucleophilic displacement at saturated carbon and the designation therefore implies trigonal or digonal carbon.

Free-Radical Reactions. As mentioned above, homolytic reactions require special notation. For simple association and dissociation of radicals, the order of subscripting is arbitrary, but if a free radical is bonding to or separating from a diamagnetic species, it is informative to *subscript the atom carrying the unpaired electron first.* The reaction

$$\mathrm{RS\cdot} + \mathrm{H_2C{=}CH_2} \longrightarrow \mathrm{RSCH_2{-}CH_2\cdot}$$
$$\mathrm{RSCH_2{-}CH_2\cdot} + \mathrm{RSH} \longrightarrow \mathrm{RSCH_2CH_3} + \mathrm{RS\cdot}$$

will be designated $\mathrm{A_{S\cdot C}} + \mathrm{A_{C\cdot H}D_{S\cdot H}}$

Rearrangements. In rearrangement processes where bonds are broken and new bonds formed without separation of any parts of the molecule or ion, increased clarity is obtained if the intramolecular processes are placed within parentheses. For example, the reaction



$$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle H}{C}}{-}CH_2{-}Br} \longrightarrow \mathrm{CH_3{-}\underset{\displaystyle CH_3}{\overset{+}{C}}{-}CH_3} + \mathrm{:Br}$$

would be designated $\mathrm{D_{BrC}(A_{HC}D_{HC'})}$. The order of the terms is unimportant, provided that the intramolecular processes are adjacent for bracketing. We have chosen to indicate the bonds made or broken in the order of their increasing number of bond distances from one reaction terminus (arbitrarily taken as the C–Br bond). *If the same atomic symbol is used more than once in a designation, a prime notation will be affixed each time the symbol refers to a new atom.* In more elaborate cases, it might be desirable to number the different atoms of the same element but this is usually unnecessary.

Complex Reactions

General Considerations. For complex reactions these mechanistic designations can become quite lengthy. For example, acid-catalyzed ester hydrolysis can be represented as $\mathrm{A_{OH}D_{XH}} + \mathrm{A_{O'C}} + \mathrm{A_{XH'}D_{O'H'}} + \mathrm{A_{O''H'}D_{XH'}} + \mathrm{D_{O''C}} + \mathrm{A_{XH}D_{OH}}$. This is clearly too unwieldy for oral communication of mechanistic thought. Its value lies in the fact that the groups of terms present are readily related to the component parts of other mechanisms. To illustrate, the first two terms are of the same general form as all electrophilic additions to multiple bonds. The combination $\mathrm{A_{OH}D_{XH}} + \mathrm{D_{OC}}$ will be common to all acid-catalyzed dehydrations, ether cleavages, etc. The relationship to acid-catalyzed amide hydrolysis is evident in the replacement of $\mathrm{A_{OH}D_{XH}} + \mathrm{D_{OC}}$ by $\mathrm{A_{NH}D_{XH}} + \mathrm{D_{NC}}$, thus allowing ready recognition of the mechanistic similarity. In general, mechanisms which are too complex or unique to warrant a special designation in the system presently in use are easily named in the new system and their relationship to more common types becomes apparent.

Reactions Involving Electron-Transfer Steps. As an example, consider the "SRN1" mechanism recently studied by Bunnett[4]

$$\mathrm{M}^n + \mathrm{ArX} \longrightarrow [\mathrm{ArX}]\cdot^- + \mathrm{M}^{n+1} \quad (1)$$
$$[\mathrm{ArX}]\cdot^- \longrightarrow \mathrm{Ar\cdot} + \mathrm{X}^- \quad (2)$$
$$\mathrm{Ar\cdot} + \mathrm{R:} \longrightarrow [\mathrm{ArR}]\cdot^- \quad (3)$$
$$[\mathrm{ArR}]\cdot^- + \mathrm{ArX} \longrightarrow \mathrm{ArR} + [\mathrm{ArX}]\cdot^- \quad (4)$$

The first and fourth steps present a problem in that no bond-making or -breaking steps are required. Electron-transfer reactions are generally thought to proceed by complex formation prior to the electron-transfer step and can be treated as A + D processes within the framework of the proposed nomenclature system.

If the electron transfer were an inner-sphere process, such as

$$\mathrm{ArX} + \mathrm{M}^n \longrightarrow \mathrm{ArXM} \longrightarrow [\mathrm{ArX}]\cdot^- + \mathrm{M}^{n+1}$$

the designation would be $\mathrm{A_{M\cdot X}} + \mathrm{D_{XM}}$ or $\mathrm{A_{MX}} + \mathrm{D_{X\cdot M}}$. We prefer the former representation if the donor (M) is paramagnetic and the latter when it is diamagnetic.

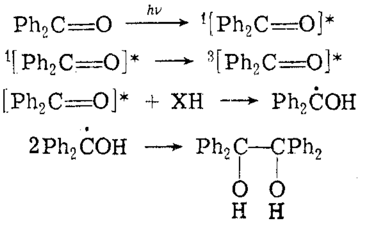
For an outer-sphere reaction, we suggest subscripting a symbol for the molecular orbital of the donor which carries the electron to be transferred followed by a symbol for the orbital in the acceptor which receives the electron. For the particular case of the SRN1 mechanism, the full designation will be $\mathrm{A_{M\cdot\pi}} + \mathrm{D_{\pi M}} + \mathrm{D_{XC}} + \mathrm{A_{C'C}} + \mathrm{A_{\pi\cdot\pi'}} + \mathrm{D_{\pi'\pi}}$. The symbol π is understood to represent a π molecular orbital. In the fifth and sixth terms of the representation, the electron is considered to be transferred to a new π system even though it is identical with the one involved in the first step. In other words, the reaction is considered to take place among a set of molecules which are all different even if the structures of some are identical.

The third and fourth terms present a new problem. Although the third term is $\mathrm{D_{XC}}$, a valid alternative is $\mathrm{D_{C\cdot X}}$. Both representations are correct because the reaction is both a nucleophobic and a homolytic dissociation. We have chosen to represent reactions involving attack or retreat of a nonbonded pair of electrons as heterolytic even if a free radical is formed or destroyed in the process. Thus the fourth term is $\mathrm{A_{C'C}}$ rather than $\mathrm{A_{C\cdot C'}}$.

Photochemical Reactions. These can be regarded as intramolecular electron-transfer reactions and treated within the framework of our scheme. For example, the basic reaction

$$A \xrightarrow{h\nu} A^*$$

can be designated $(A_{\Psi\Psi*}D_{\Psi*.\Psi})$. The parentheses indicate the intramolecular nature of the process. Intersystem crossing could be termed $A_{st}D_{t\cdot s}$ but this requires six symbols where two would suffice. We suggest that the combination ST be used for singlet to triplet interconversion. As an example, consider the photochemical preparation of benzpinacol



$$\begin{aligned} Ph_2C{=}O &\xrightarrow{h\nu} {}^1[Ph_2C{=}O]^* \\ {}^1[Ph_2C{=}O]^* &\longrightarrow {}^3[Ph_2C{=}O]^* \\ {}^3[Ph_2C{=}O]^* + XH &\longrightarrow Ph_2\dot{C}OH \\ 2Ph_2\dot{C}OH &\longrightarrow Ph_2C(OH){-}C(OH)Ph_2 \end{aligned}$$

We suggest the designation $2[(A_{\Psi\Psi*}D_{\Psi*.\Psi}) + ST + A_{O\cdot H}D_{X\cdot H}] + A_{C\cdot C}$. *When a series of steps occurs more than once in the formation of one molecule of product, the repeated series is enclosed in brackets and a coefficient indicating the number of occurrences placed in front of the brackets.* This bracketing technique can also be used for parallel sequences which generate intermediates that subsequently react with each other. For example, photochemical formation of mixed pinacol could be represented $[(A_{\Psi\Psi*}D_{\Psi*.\Psi}) + ST + A_{O\cdot H}D_{X\cdot H}] + [(A_{\Psi\Psi*}D_{\Psi*.\Psi}) + ST + A_{O\cdot H}D_{X\cdot H}]' + A_{C.C'}$. Note that the prime notation has been placed outside of the second bracketed sequence to avoid having to prime each atom and orbital in the second sequence. The use of brackets in this way should be regarded as an optional technique for increasing clarity. In the preceding mixed pinacol case, its use is convenient but not necessary.

Reactions Involving Ion Pairs. It is well established that *ion pairing of intermediates can affect the outcome of* chemical reactions. It is therefore useful to have a notation to distinguish these. For the sequence

$$RX \rightleftharpoons R^+X^- \rightleftharpoons R^+ \| X^- \rightleftharpoons R^+ + X^-$$

where the first intermediate is an intimate ion pair and the *second a solvent-separated ion pair, we suggest the designation* $D_{((RX))} + D_{(RX)} + D_{RX}$. The subscript R represents the atom bonded to X in RX. The same technique can be used in free-radical reactions to indicate caged pairs. It will be noted that no attempt has been made to indicate reversibility of steps. The system proposed describes the fate of the minimum number of molecules required by the stoichiometry. If there was more than one path to the product, we would regard the reaction as proceeding by more than one mechanism.

Use of the New Systems

Pedagogical Use. For the purpose of teaching mechanistic organic chemistry to beginners, we suggest that the N and E labels be used to designate mechanistic categories such as ANDN for SN2 reactions but that the atomic symbol subscripts be introduced when individual cases are compared: $A_{OC}D_{FC}$, $A_{OC}D_{ClC}$, $A_{OC}D_{BrC}$, etc., are all ANDN reactions with different nucleophobes but a common oxygen nucleophile.

Information Retrieval. Once translated into this system, mechanisms could be easily indexed. The main categories would be the A–D sequences and these would be subdivided into atomic variations. Further subdivision could be based on structural units (functional groups, ring systems, etc.) and, finally, each subcategory could be indexed by complete reactant structures. It would be a simple matter to determine whether a particular complete mechanism had been previously proposed. Finding the *component parts of mechanisms, on the other hand,* presents a formidable cross-indexing problem.

Suppose, for example, the goal was to find examples of nucleophilic displacement of fluoride from aromatic systems by the $A_{XC} + D_{FC}$ mechanism. Subdivision of A + D mechanisms would probably start with the first subscripted atom, so that search for examples involving a particular nucleophile would be much easier than the search for a nucleophobe. It would be necessary to examine each nucleophile subdivision for fluoride in the second term. All of these data would then be screened to remove nonaromatic substrates (acyl fluorides, vinyl fluorides, etc.). The situation is analogous to the search of a formula index for all compounds containing five oxygens.

A related problem arises if the search demands information not present in the mechanistic symbols alone. It is the nature of this system that a complete mechanism is not generated until the designation is applied to a particular substrate. Supposing that the search was for examples of nucleophilic addition of sulfur to double bonds, the term A_{SC} *does not include the bonding at carbon. A relatively* simple screening of substrates could be used for mechanisms where A_{SC} appeared as the first term. It would be more difficult to find those cases for which the double bond was generated in steps preceding that designated by A_{SC}.

We suggest that such complexities can be handled using high-speed computers. A suitable format would have to be devised for storage of both structural and mechanistic information. Much effort has been devoted to computer coding of molecular structure. Our system provides a workable approach to coding mechanistic information. Programs to interpret and screen the data in accord with the search goals can be envisioned to solve problems of the type discussed above.

We anticipate that in addition to its value for information retrieval, the computerized system would have predictive capability. The frequent appearance of certain mechanistic types and the absence of others would allow the computer to formulate mechanistic generalities. Perhaps new and useful reactions could be predicted.

Because the computerized system would be capable of generating the structures of reaction products from those of reactants, it also provides a source of synthetic information. Existing programs for chemical syntheses could possibly be adapted to use information abstracted in this form.

Summary of Advantages of the Proposed System

We have proposed a new system for the designation of reaction mechanisms. We feel that it has the following important advantages.

(1) Any mechanism can be designated, using only two mechanistic symbols and atomic symbols.

(2) Molecularity decisions are unnecessary.

(3) The mechanism is related to the symbols by logical rules so that no memorization is required. A beginning student can express a mechanism symbolically after a brief introduction to the rules.

(4) The system can be used to organize reactions into truly mechanistic categories.

(5) The system is an aid to mental organization, both for the reaction mechanician who would like to consider all possibilities in a system under study and for the beginner who can recognize similarities between mechanisms.

(6) The pedagogic potential is considerable. A student who is asked to translate mechanisms into symbols and *vice versa* is forced to blend structural change with electron movement. Memorization is discouraged and logical deduction is required. The system also should adapt well to computer-assisted instructional programs and automated examination grading.

(7) The system should be adaptable to information retrieval and would be easily computer coded.

(8) The basic framework provides possibilities for modernization. If, for example, a simple coding system for molecular orbitals were to become available, the atom-designating subscripts could be replaced by molecular orbital designations and possibly allow the incorporation of stereochemical information.

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References and Notes

(1) J. Mathieu, A. Allis, and J. Valls, *Angew. Chem.*, **72**, 71 (1960). We learned of this paper only after the first draft of our paper was completed. This is mentioned because it points out two important facts: (1) that a system based on the designation of each bond-making and bond-breaking step will be the logical outcome of any serious consideration of mechanistic nomenclature and (2) that chemists are extremely reluctant to accept new nomenclature systems regardless of their advantages.

(2) Common usage seems to be inorganic attacks organic and where both reagents are organic, charged attacks uncharged, but there are many exceptions and examples for which rules are not available.

(3) The terms nucleofugal and electrofugal have also been used: H. Zollinger, *Accounts Chem. Res.*, **6**, 335 (1973), and ref 1.

(4) (a) R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, **94**, 683 (1972); (b) *ibid.*, **96**, 112 (1974).

The Nature of the Ortho Effect. XI. Reaction Rates of Carboxylic Acids with Diazodiphenylmethane

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Rate constants for the reaction of diphenyldiazomethane with eight sets of ortho-substituted benzoic acids, six sets of phenylacetic acids, and seven sets of other acids were correlated with the equations

$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\upsilon_X + h$$
$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + h$$

to detect the presence of steric effects. All of the benzoic acids clearly showed the presence of a steric effect. This is the first time that a steric effect has been definitively demonstrated in sets of ortho-substituted benzene derivatives. The results obtained show that the electrical effect is definitely predominant, in good agreement with previous findings. Of the eight sets of benzoic acids studied, seven show steric acceleration of the rate; the eighth shows steric deceleration of the rate. Of the six phenylacetic acid sets studied, three showed steric effects. One these was rate accelerating; the other two were rate decelerating. Again, the electrical effect was predominant in these sets. Of the seven sets of other carboxylic acids studied, only the *cis*-α-phenylcinnamic acids showed a steric effect. Again, the electrical effect was predominant in this set. The composition of the electrical effect varied sufficiently to make impossible the use of a single set of ortho-substituent constants for the correlation of all sets studied. The values of α and β obtained in the correlations are linear in the $E_T(30)$ solvent parameters. New values of $E_T(30)$ have been calculated for *i*-BuOH and Me_2EtCOH. The possibility of hydrogen bonding in the case of hydroxyl substituents is evaluated. Hydrogen bonding definitely occurs in the case of salicylic acid; it may possibly occur in the case of 2-hydroxyphenylacetic acid.

In this paper we extend our previous work[1–5] on the nature of the ortho effect by a study of the rates of reaction of ortho-substituted carboxylic acids with diphenyldiazomethane by means of linear free energy relationships. The major objectives of this investigation are to detect the presence or absence of steric effects and to determine the composition of the electrical effect. The method which was employed in the study of steric effects is based on the correlation of the rate constants with linear free energy relationships. In order to carry out the analysis of the data it is necessary to examine four possible cases. 1. The steric effect may be represented by a steric parameter. Then the data will follow the equation

$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\upsilon_X + h \qquad (1)$$

where σ_I and σ_R represent the localized (field) and delocalized (resonance) electrical effects and υ is a steric parameter defined as[6]

$$\upsilon_X = r_{VX} - r_{VH} = r_{VX} - 1.20 \qquad (2)$$

In eq 2, r_{VX} and r_{VH} are the van der Waals radii of the X group and the hydrogen atom, respectively. We have chosen υ as a steric parameter in preference to the Taft E_S steric parameters[7] because we have previously demonstrated a linear relationship between E_S and the van der Waals radii.[1] 2. The steric effect cannot be represented by some steric parameter, and therefore the data do not obey a linear free energy relationship. In this case, the electrical effect of the X substituent remains a function of σ_{IX} and σ_{RX}. Whatever part of the rate constant is not represented by the electrical effect is dependent on the steric effect S_X. Then for the rate constant of the compound bearing the X substituent we may write

$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + S_X + h \qquad (3)$$

3. The steric effect is constant. Then υ_X is constant, and therefore $\psi\upsilon_X$ is constant. From eq 1

$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + h' \qquad (4)$$

where

$$h' = h + \psi\upsilon_X \qquad (5)$$