π COMPLEXES AS REACTION INTERMEDIATES

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Contents

I. Introduction

Organic complexes in which the components are not covalently linked have been known for many years and have been proposed as intermediates in additions to olefins and in aromatic substitutions.[1,2] A large number of such adducts have been isolated or have been detected by the optical or solubility properties of mixtures of suitably chosen interactants and have been named molecular, donor–acceptor, inner, outer, charge-transfer, or π complexes, the variety being indicative of the uncertainty as to the nature of the bonding. In this review the generic term *molecular complexes* will be used. Another type of adduct called a π *complex*, which will be so named here, has been proposed as an intermediate in many reactions and has also been claimed to describe the bonding in certain carbonium ions and organic molecules.[3,4] In contradistinction to molecular complexes, the components of these π complexes were considered to be covalently linked. Unfortunately, the two types have been widely confused as to name and nature, particularly in discussions of reaction mechanisms.

Usually when reaction intermediates such as carbonium ions or radicals are postulated, it is possible to show that analogous stable substances of the same type as the hypothetical intermediates exist and that these more accessible substances have the chemical and physical properties of the hypothetical ones. Some evidence of this type is available for molecular complexes, but that for π complexes is more tenuous, or more subtle, according to the point of view. Unambiguously recognizable π complexes cannot be isolated, and their presence in reaction schemes often has no consequences for kinetics or products that differ from those of conventional mechanisms.

The purpose of this review is to assess the present status of π complexes in organic chemistry. Such an assessment is necessary, as π-complex theory has been repeatedly and vigorously advocated, although many of its applications have been refuted; and it has often been accepted in the absence of detailed criticism as an established part of mechanistic thought. Consequently, reaction schemes including π complexes have proliferated with little or no supporting evidence. A secondary aim is to attempt to clear misconceptions concerning the role of molecular complexes that have often been

(1) P. Pfeiffer and R. Wizinger, *Justus Liebigs Ann. Chem.*, **461**, 132 (1928).
(2) G. Briegleb, "Elektronen-Donator-Acceptor Komplexverbindung," Springer-Verlag, Berlin, 1961.
(3) M. J. S. Dewar, *Nature*, **156**, 784 (1945).
(4) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949.

named and considered synonymous with π complexes. The structures and reactions of organometallic compounds will not be discussed.

No detailed objective review exists on these topics. Selected applications of π-complex theory have been repeatedly presented,[4-7] but contrary opinions and facts have been largely ignored. Several excellent reviews[2,8,9] deal with the preparation and with the chemical and physical properties of molecular complexes but only briefly or indirectly mention π complexes, and a detailed discussion of the importance of molecular (so-called charge-transfer) complexes as reaction intermediates is available.[10] The literature reviewed in the present article has been scanned up to May 1969, but complete coverage is not attempted as many claims that are not backed by evidence for π complexes as reaction intermediates are ignored. As the discussion traverses a wide range of organic mechanisms, most accepted reaction schemes that do not involve π complexes are merely outlined and often reviews or recent papers containing leading references are cited.

II. Molecular and π Complexes

A. MOLECULAR COMPLEXES

Aromatic molecules readily complex with a variety of compounds, e.g., halogens, metal ions and salts, nitro compounds, tetracyanoethylene and related compounds, quinones, triphenylmethane dyes, and halogen acids, often yielding deeply colored products from colorless reactants.[2,8,9] Unsubstituted arenes apparently only form dimers when one component is in an excited state[11] or when a dimer cation can be achieved.[12] Often the conditions for complex formation are critical; there is no evidence for complexing of benzene or anisole with halogens in acetic acid although such interactions occur in carbon tetrachloride.[13] Usually 1:1 adducts are formed; some, e.g., quinhydrone or the p-iodoaniline-s-trinitrobenzene complex, are stable solids, whereas others can only be detected in solution by physical techniques. Typically the heat of formation lies in the range 2–10 kg cal mole^{-1}, and a low heat of activation ensures that complexes are usually rapidly and reversibly formed on mixing the components at room temperature and can only be isolated when insoluble. These adducts are quite different from clathrate compounds.

An early speculation concerning the bonding[14] was that electron transfer between donor (D) and acceptor (A) components gave radical ions held together by electrostatic forces. This concept has been developed into a detailed theory based on the possibility of resonance of a no-bond structure (D, A) with a dative structure (D$^+$-A$^-$) formed by charge transfer, or, in general, with several dative structures as well, perhaps as

locally excited structures.[15-17] In this model the ground state of the complex is an aggregate, essentially nonbonded in character, receiving a minor and usually rather uncertain contribution from the dative form, but which nevertheless in suitable solvating media may form a radical ion pair.[18] The ground state of the complex is described by wave function 1, and a low-lying excited state exists, described by eq 2, that is largely dative in character. Excitation 1 $\rightarrow$ 2 leads to characteristic charger-tansfer spectra in the visible or near-ultraviolet, and the complex is said to be held by charge-transfer forces in both ground and excited states. This theory has been

$$\Psi = a\Psi_0(D, A) + b\Psi_1(D^+-A^-) \qquad (1)$$

$$\Psi' = a^*\Psi_1(D^+-A^-) - b^*\Psi_0(D, A) \qquad (2)$$

$$(|a| > |b|;\ a \simeq a^*;\ b \simeq b^*)$$

widely used to interpret the spectra of complexes[19] and is applicable to all types of adducts. A similar conclusion can be reached using molecular orbital theory: overlap of donor and acceptor orbitals generates two new molecular orbitals as a linear combination of these, and occupation of the lower orbital gives partial cationic character to the donor and partial anionic character to the acceptor.

Information about charge-transfer forces can probably best be obtained by measurements of stability constants, and this approach has shown that there is no major contribution by such forces to the bonding in adducts of many arenes with tetracyanoethylene.[20] Consequently, following earlier suggestions,[4] van der Waals interactions of dipole–dipole, dipole-induced dipole, and dispersion type were held responsible for the stability of these adducts, and of charge-transfer complexes in general. Although the spectrum of such a complex can be interpreted in terms of charge transfer, it does not follow that the ground state is a charge-transfer complex or that charge transfer plays a dominant or even a significant role in the bonding. In fact, so-called contact charge-transfer spectra can be observed for complexes that are generally agreed to be stabilized by van der Waals interactions, the only requirement for a transition to occur with significant intensity being that the components are held closely together.[21,22] On the other hand, nmr studies reveal complexing due to van der Waals interactions when no charge-transfer bands can be observed.[23] The theoretical treatment that leads to the concept of charge-transfer forces applies the valence-bond method to the situation of electron transfer but neglects extension to the van der Waals forces. This leads to the linking of the term charge transfer to a particular and incomplete quantum-mechanical model. The predominance of van der Waals interactions in stabilizing

(5) M. J. S. Dewar in "Theoretical Organic Chemistry" (The Kekulé Symposium), Butterworth and Co. Ltd., London, 1959, p 179.

(6) M. J. S. Dewar in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 296.

(7) M. J. S. Dewar and A. P. Marchand, Ann. Rev. Phys. Chem., 16, 321 (1965).

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(22) W. N. White, ibid., 81, 2912 (1959).

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these complexes is revealed by more general calculations[24-26] and has been accepted by the proponent of the charge-transfer theory.[27]

Contemporaneous with this work, measurements of the solubilities of hydrogen halides in mixtures of olefins or aromatics with aprotic solvents gave convincing evidence for two types of complexes.[28-30] Olefins formed colorless complexes with heats of formation about 3 kg cal mole⁻¹; these were nonconducting and largely dissociated even at −70°, and dissociation did not lead to isomerization of labile substrates. In contrast, addition of small quantities of gallium trichloride or other Lewis acids gave conducting solutions from which rearranged olefins could be isolated. For the former conditions, formation of a so-called π complex was proposed that had inappreciably perturbed π orbitals and was held together by electrostatic hydrogen bonding. This was represented by 1; structure 2 was ruled out by the lack of conductivity. A σ complex equivalent to an open carbonium ion paired to its counter anion, 3, was considered to be formed in the presence of Lewis acids.
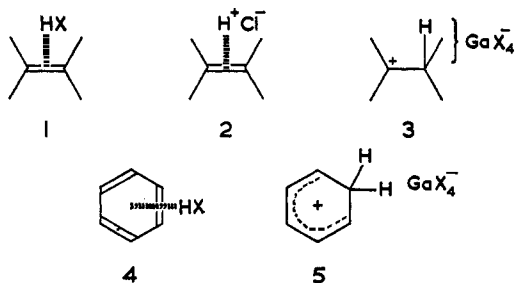

The solubilities of protonic and Lewis acids in aromatics likewise indicated the formation of 1:1 and less usually 1:2 adducts, some of which were isolable solids.[29,30] With protonic acids colorless, largely dissociated complexes resulted, and in the presence of deuterated acid the recovered aromatic did not contain tracer. Combinations of protonic and Lewis acids led to complexes that could be obtained in much higher equilibrium concentration, were colored and conducting, and provided a pathway for the exchange of hydrogen isotopes. Again the two types were classed as π and σ complexes and were represented by 4 and 5, respectively.

This work was the first to draw a clear distinction between these two classes of complexes, although equivalent species had previously been proposed as intermediates in aromatic substitution.[31] Aromatic σ complexes, which will be further discussed in section VI.A, are essentially similar to the structures used in the localization method for the treatment of aromatic reactivity[32] except that they receive a more literal representation as actual species rather than as structures in the sense of resonance theory. Hydrogen bonding of polar mole-

cules to olefins, acetylenes, cyclopropanes, and aromatics to form transient complexes of the π type has been detected by spectral and other physical means.[29,33-35]

B. DEWAR'S π COMPLEXES

Following a suggestion[36] that the structures of boron hydrides and the stability of olefin–salt complexes could be rationalized if cations were held embedded in the π orbital of an unsaturated system, Dewar introduced a different type of π complex from that previously described.[3,4,37,38] He pointed out that the π orbital of an olefin or an aromatic ring resembled the filled p orbital of an atom and so should be able to overlap and coalesce with an atomic orbital or a localized molecular orbital to give a three-centered orbital equivalent to a so-called *molecular bond*. This bond can hold two electrons only, so bonding between a filled π orbital and a potential adduct is only possible if the latter has a vacant low-lying orbital or each component of the potential complex has a half-filled orbital. Typically, filled π orbitals donate to unfilled p or d and sometimes hybrid orbitals of electrophiles. Similarly, but less commonly, two π orbitals may overlap provided the same conditions apply. π complexes were initially believed to be nonlocalized in the sense that the bonded electrophile could move freely over the π system with only minor constraints in the form of shallow potential energy wells at the apices of the underlying framework: such species are represented by 6 and 7. The p orbital of a complexed electrophile must have its axis perpendicular to the plane of an aromatic ring in order to overlap efficiently with the appropriate orbital of the latter, and must be situated on the periphery, for the symmetry of the available occupied π molecular orbitals of the aromatic ring does not allow overlap if the electrophile is located on the sixfold axis. An electrophile with a vacant d orbital can, however, occupy this latter position, as the symmetry requirements of the overlapping orbitals can now be met. Subsequently the idea of localized π complexes, 8 and 9, was introduced,[6,39-41] in which the electrophilic component of the complex was oriented near a particular electron-rich or sterically favorable site on the π system.
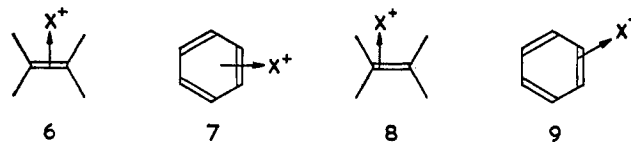
van der Waals interactions are not considered responsible to any significant extent for the stability of these complexes. Electrons are transferred from donor to acceptor to create a dative covalency, albeit of an unusual kind, that has a heat of formation probably greater than 30 kg cal mole⁻¹, although the exact value for any particular organic complex is uncertain.[7] As a consequence, Dewar π complexes, in contrast to

(24) K. E. Shuler, *J. Chem. Phys.*, 20, 1865 (1952).
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(32) G. W. Wheland, *J. Amer. Chem. Soc.*, 64, 900 (1942).

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(34) W. Lüttke and R. Mecke, *ibid.*, 53, 241 (1949).
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(36) K. S. Pitzer, *J. Amer. Chem. Soc.*, 67, 1126 (1945).
(37) M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946).
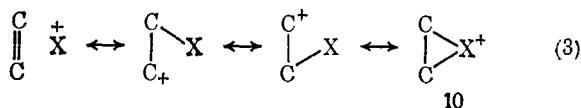(38) M. J. S. Dewar, *ibid.*, 777 (1946).
(39) L. Melander, *Ark. Kemi*, 2, 213 (1950).
(40) H. C. Brown and H. Jungk, *J. Amer. Chem. Soc.*, 77, 5579 (1955).
(41) H. C. Brown and H. Jungk, *ibid.*, 78, 2182 (1956).

molecular complexes, were considered to be formed essentially irreversibly in many reactions. This covalent nature of the molecular bond has been repeatedly stressed and has been compared with that of the bond between nitrogen and hydrogen in ammonium chloride. The electrostatic bonding in the π complexes discussed in the last section is, on the other hand, considered to be analogous to that between oxygen and hydrogen in the unstable adducts of ethers and hydrogen halides.[6,7] The stability of the ground state in Dewar's π complexes is accompanied by a large destabilization of the first excited state, and typically the separation of the two states is too large for charge-transfer spectra to occur at wavelengths higher than where the components of the complex absorb. As a result characteristic spectra are only found in weakly bonded π complexes, e.g., where π-d rather than π-p overlap occurs, as in the adducts of halogens and aromatics.

Dewar's π complexes can be represented in valence-bond terms as a hybrid of four canonical forms, eq 3. This description has not been developed, however, as it obscures the ob-

$$\begin{matrix} C \\ \parallel \\ C \end{matrix} \overset{+}{X} \leftrightarrow \begin{matrix} C \\ | \\ C_+ \end{matrix} \diagdown X \leftrightarrow \begin{matrix} C^+ \\ | \\ C \end{matrix} \diagup X \leftrightarrow \begin{matrix} C \\ | \\ C \end{matrix} \diagup X^+ \qquad (3)$$

10

servational requirement for an electrophile to complex with an unsaturated system, since equivalent valence-bond structures can be written for π-anion complexes.[42]

The theoretical justification for Dewar's π complexes is unsatisfactory. A three-centered cation can be qualitatively rationalized on the basis of simple Hückel molecular orbital theory.[43] The calculation is that of an altered cyclopropenyl cation, and for parameters reasonable for the partial bonds, the secular equations have only one negative root; hence, for most examples of interest the π complex has only one bonding molecular orbital which is occupied by two electrons. Anions or radicals would not readily form such complexes, which could only occur if highly electronegative or other modified substituents alter the parameters drastically and allow a second molecular orbital to become bonding to accept the additional electron(s). A quantitative development of these ideas is, however, difficult. The calculated heats of formation of complexes of the types (Ph, X^+), (C=C, X^+), and (Ph$^+$, Ph$^+$) gave values (depending on the choice of parameters) in the range 30–80 kg cal mole^{-1} which, although approximate, were considered to justify belief in the existence of these species as intermediates rather than transition states.[44] Similar calculations supported a π-complex mechanism for benzidine rearrangements.[45] Nevertheless, because of the many assumptions used in both these sets of calculations,[46] the results are indicative of a general situation rather than being descriptive in any precise way of any actual one, and their validity as to the conclusions drawn is questionable.

Carbonium ions have been formulated as π complexes (section IV) and similar calculations have indicated that the

latter is a preferable[47,48] or, conversely, a less favored[49] description for particular examples. However, the calculation of resonance energies of conjugated systems by these methods is questionable,[50] and their use to compare energies of classical ions and π complexes of different geometries is invalid, as approximations that are permissible for molecules break down completely for ions. In calculating the total bond energy, a term $(B - A)$ is introduced, where A is the mutual repulsion of the electrons in the molecule minus their repulsion in separate atoms and B is the mutual repulsion of the nuclei. For molecules, A and B are usually approximately equal and the term can be neglected, but for ions $|B - A|$ may be ca. 100 kg cal mole^{-1}. If ions of different geometries are compared, the corresponding terms for each are neither individually negligible nor equal in size, and so cannot be ignored. A and B cannot be estimated with any confidence, and calculations which equate these quantities give results so incorrect as to be valueless even in a qualitative sense.[7] A full self-consistent-field treatment would have to be applied to obtain meaningful results in these and more complicated examples, and at the moment this is impracticable.

C. NOMENCLATURE

Much confusion has arisen concerning the nature and naming of the various types of complexes, particularly when they are considered as transiently formed reaction intermediates. As stated in section I, it is convenient to use the terms *molecular complexes* and *π complexes* for species that owe their stability to van der Waals interactions and dative covalencies, respectively.[5,6] The fundamentally different character of the latter class has been continually ignored and misunderstood, although much of this misrepresentation has undoubtedly arisen because many examples originally chosen as illustrations of π complexes[4] were obviously at the time, or were later shown to be molecular complexes as defined here. Although the generally accepted meanings of these terms overlap considerably and the degree of covalent bonding in a complex must vary continuously over a spectrum encompassing examples of the two types as extremes, the adoption of the dual classification is useful and convenient. Furthermore a clear distinction between the two classes can usually be maintained: thus, 11 represents the π complex from iodinonium ion and pyridine, whereas 12 ↔ 13 is a resonance formulation of the
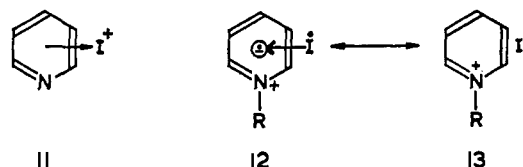
so-called charge-transfer complex formed by N-alkylpyridinium iodide.[10] We prefer to describe the latter in terms of 13 as a molecular complex, i.e., an ion pair held by van der Waals interactions; but if electron transfer to the aromatic ring does take place, it can only be to an empty, high-energy orbital to give an unstable species. Structure 11 may not be achieved in

(42) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, C71 (1951).

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practice in the particular example but it is clearly distinguishable from 12 ↔ 13 in principle.

Structure 10 represents a bridged species that has been proposed to represent certain halogenated cations (cf. section V). It is generally considered to be essentially equivalent to the π complex 6, especially as the olefin moiety in the latter must be distorted from planarity,[7] thereby enforcing a hybridization intermediate to sp[2] and sp[3] on the apical carbons,[51] and d-orbital feedback (cf. section III.B) from the electrophile can result (in certain cases) in direct bonding to these carbons in the π complex. Nevertheless a distinction between 10 and 6 has been claimed[52] in that the latter alone retains unsaturation. Such a fine difference is difficult to verify by experiment or to specify in principle.

The well-authenticated phenonium ions (10, X = Ph) (section IV.A) can similarly be regarded[7] as π complexes, as also can bridged alkyl and hydrogen cations (10, X = alkyl, H) that have been proposed as transition states or intermediates in many reactions. From the valence-bond viewpoint, the π complex representation of the two last types is most attractive, as the bridging group or atom can remain formally univalent, whereas the fully bridged structure 10 requires forbidden expansion of valence shells. However, the molecular orbital description of the same situation provides suitable orbitals to accommodate the bridging species in a triangular arrangement, although whether of stability characteristic of intermediates or transition states cannot be determined.[43] Following precedent,[7] we will regard all these bridged ions as π complexes. This classification may be disputable, but it does permit a unified discussion for these closely related species.

There is general agreement that, in the contexts under discussion, σ complexes include carbonium ions (3) or four π-conjugated systems such as 5. π and σ complexes have also been classified together as inner complexes, using a term originally applied to types of so-called charge-transfer complexes. There can be very little difference in either geometry or energy between σ complexes and localized π complexes such as 9.

III. Formulation of Molecules as π Complexes

A. ORGANIC COMPOUNDS

Early in the development of π-complex theory, proposals were made that ethylene oxide, cyclopropane, and ozone be regarded as such complexes and be represented by 14 (X = O and CH_2) and 15, the last structure possessing a double molecular bond.[4,53] Graphite oxide, peroxides of polynuclear


14   15   16
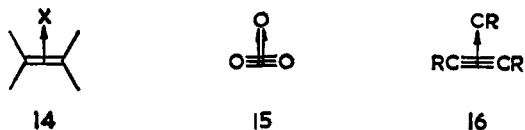
hydrocarbons, e.g., coronene, and certain other strained or unsaturated compounds were considered similarly.[4] After a short but very sharp controversy in which structure 14 for ethylene oxide was claimed to be consistent with data on force

constants[54] but in turn was considered to be completely at variance with the chemical[55] and spectral[56,57] properties, the idea was dropped. Recently the ir spectrum of cyclopropanone has been interpreted[58] on the basis of structure 14 (X = CO), but the consensus considers such models unnecessary and the conventional structures are invariably adopted. The spectra and other physical properties of cyclopropenes might well be regarded with profit on the basis of a model 16, as here conventional valence-bond descriptions present difficulties.

B. ORGANOMETALLIC COMPOUNDS

In contrast to the situation just described, bonding in olefin-metal complexes was first rationalized by application of the π-complex theory. It was pointed out[42] that in the well-known silver ion–olefin adducts the molecular bond between the π orbital and an unfilled orbital of the metal ion could be augmented by reverse dative bonding, owing to overlap of an occupied d orbital of the metal with the empty antibonding π* orbital of the olefin. The d orbital has the correct symmetry to accomplish such overlap, whereas occupied s and p orbitals have not. The reverse bonding is illustrated in 17, and the total molecular bonding in 18. Similar use of atomic or hybrid d

17   18   19
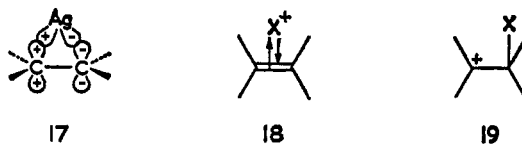
orbitals to feed back electrons from metal to olefin and to additionally stabilize the complex is believed to be responsible for the existence, sometimes as isolable species, of many complexes. As an example, overlap of an olefinic π orbital with one of the vacant $5d6s6p^2$ hybrid orbitals of the platinum(II) ion cannot alone account for the stability of the complex that is formed, but back-donation of a filled 5d6p hybrid metal orbital confers the additionally required bonding.[59] Such examples could be multiplied[60] and generally d–p hybrid orbitals of the metal are employed; presumably d orbitals alone do not provide sufficient overlap. Many scores of π complexes of different metals with olefins, acetylenes, dienes, and arenes have been isolated and their chemistry elucidated.[60-62]

In complexes of aromatics with halogens, d → π* back-donation may also augment the π–d bonding; ir studies suggest that the halogen here lies on the sixfold axis of the ring,[63] as is expected from the symmetry requirements of the orbitals involved in both molecular bonds. Many claims have also been made for π complexes of organic compounds and nonmetals. Some are undoubtedly valid but others need reappraisal; e.g., adducts of boron trichloride with substituted anilines were assigned thus on minimal ir evidence,[64] but more

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(63) E. E. Ferguson, J. Chem. Phys., 25, 577 (1956); 26, 1357 (1957).

(64) W. Gerrard and E. F. Mooney, J. Chem. Soc., 4028 (1960).

detailed studies supplemented by nmr prove the formation of σ complexes.[65]

C. REACTION INTERMEDIATES

There is little doubt that in addition to describing ground states π complexes are intermediates in many organometallic processes, such as organic reactions catalyzed by metals or their ions, e.g., the Ziegler–Natta polymerization of olefins,[66] hydrogen exchange of aromatics over metal catalysts,[67] oxidations of olefins catalyzed by mercuric ions,[68] the Ullmann synthesis of biaryls,[69] and many others.[70]

There is also a plethora of claims for π-complex intermediates in organic reactions not involving such catalysts, but the situation is here much more obscure. In these reactions the formation of molecular complexes can often be demonstrated under conditions that lead to the overall products, but it is not easy to prove that the products are formed from the complexes or that unambiguously distinguishable π complexes are present. The formation of either type of complex can have no consequences on kinetics or products if the complexes lie at low-energy levels relative to intermediates or transition states that occur further along the reaction coordinate, nor can kinetics or the dependence of rate on medium distinguish between, for example, a bimolecular reaction and a unimolecular reaction of a preformed complex of the same components. Similarly, substituent effects are never sufficient to show that a reaction necessarily involves the preliminary formation of a complex, but a close similarity between substituent effects on rate and those on the formation of a related complex does suggest that the transition state of the reaction is similar to the complex. However, despite these problems, good cases have been made that many organic and biochemical reactions proceed through the formation of molecular complexes,[10] although some wildly improbable schemes involving these species have had to be refuted.[10] A typical reaction for which molecular complexes have been proposed is the hydrolysis of derivatives of carboxylic acids with hydroxide ion;[71] added heterocyclics inhibit this, presumably because of the formation of unreactive species similar to 12 ⟷ 13.

Dewar has repeatedly advocated the intermediate formation of π complexes in a variety of reactions, but his views have been often misquoted and misunderstood. For example, his proposals for electrophilic aromatic substitution have been rejected because the supposed (by his critics) low heat of activation for formation of a π complex was deemed incompatible with the high heat of activation of the reaction, and so the π complex was dismissed as a poor model for the transition state.[72] Irrespective of the reality of π-complex theory, such arguments, although valid for molecular complexes, are totally inapplicable to π complexes.

In general, a scheme (eq 4) can be postulated where A, B, and P are reactants and products and π and σ are the respec-

tive complexes. Molecular complexes may be present either in prequilibrium with A and B or after the rate-determining step. Dewar prefers schemes where, according to the reaction, either (a) step 1 is fast and step 2 is slow, both being irreversible, or

$$A + B \underset{-1}{\overset{1}{\rightleftharpoons}} \pi \underset{-2}{\overset{2}{\rightleftharpoons}} \sigma \overset{3}{\longrightarrow} P \qquad (4)$$
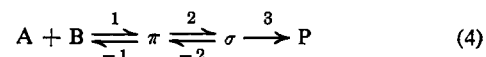
(b) step 1 is slow and step 2 is fast, again both being irreversible. Step 3 is fast in both schemes. Other combinations of fast, slow, irreversible, and reversible steps are possible, some of which would result in a build-up of π or σ during reaction. On the basis of these mechanisms, certain predictions can be made for particular routes that differ from predictions for routes where π is not formed.

The evidence for π complexes in different types of reactions will be assessed in the following sections. Certain proposed intermediates that are demonstrably or probably molecular complexes using our dual classification, but which have been considered as π complexes synonymous with the type proposed by Dewar, will also be discussed. For convenience the terms π- and σ-complex routes will be used for mechanisms in which the respective complexes are formed in rate- or product-determining steps. In all these considerations Occam's razor must be applied: hypothetical intermediates must not be introduced unless the accepted mechanisms based on well-authenticated intermediates (such as carbonium ions, carbanions, and radicals of the classical open type) prove inadequate.

IV. Formulation of Carbonium Ions as π Complexes

A. CLASSICAL IONS

Following the interpretation of the structure of diborane and related compounds,[73] the importance of many-centered bonds in electron-deficient molecules became apparent and parallel developments led to the description of the bonding in carbonium ions by molecular bonds of the type postulated for π complexes. The generally accepted open classical ions 19 were formulated as π complexes[4] (6, X = alkyl or H) or similar (but not fully specified) structures.[74,75] The nonlocalized π complex 8 is so close in energy and geometry to 19 that its separate consideration does not seem worthwhile.

Although quantitative or even qualitative calculations of the relative stabilities of 19 and 6 cannot be made, the factors favoring the occurrence of each structure can be simply assessed.[76] In 19 the positive charge resides on a carbon atom (if distribution of charge to the peripheral hydrogens by inductive and electromeric effects is ignored), whereas in 6 a fraction δq is situated on X. If ΔH is the heat of formation for the interconversion of 19 and 6, E_{C-C}, $E_{C=C}$ and E_{C-X} are bond energies, E_π is the bond energy of the molecular bond in 6, and I_C and I_X are the ionization potentials of C and X, eq 5 can be set up which reduces to eq 6, where A is a constant for attack on a particular π system by different reagents. Conse-

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(70) C. W. Bird, "Transition Metal Intermediates in Organic Chemistry," Logos, London, 1967.

(71) F. M. Menger and M. L. Bender, J. Amer. Chem. Soc., 88, 131 (1966).

(72) G. S. Hammond, ibid., 77, 334 (1955).

(73) H. C. Longuet-Higgins, J. Chim. Phys., 46, 268 (1949).

(74) H. Eyring, H. M. Hulburt, and R. A. Harman, Ind. Eng. Chem., 35, 511 (1943).

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(76) M. J. S. Dewar and R. C. Fahey, Angew. Chem. Intern. Ed. Engl., 3, 245 (1964).

quently, **6** will be favored thermodynamically if the C–X bond is weak and X is of low electronegativity, because the mo-

$$\Delta H = E_{C=C} + E_\pi - E_{C-C} - E_{C-X} + \delta q(I_C - I_X) \quad (5)$$

$$\Delta H = A + E_\pi - E_{C-X} + \delta q I_X \quad (6)$$

lecular bond, although of covalent character, will be relatively weak in comparison with normal C–C covalencies and variations in its energy are unlikely to be important. **6** may also be relatively stabilized if X has π or unbonded p or d electrons that can back-donate to the π* orbitals. Generally, however, empty orbitals in **6** are strongly antibonding, in contrast to those in benzyl and allyl cations which are nonbonding, so that conjugation with α- or β-located substituents will be unimportant and the presence of such groups will relatively stabilize **19**. This approach suggests that if X is alkyl or particularly hydrogen structure **6** is much less likely than **19**. Recent calculations[49,77] and the lack of neighboring group participation by such groups[78] favor this (the open ethyl cation is calculated to be more stable than a bridged species by *ca*. 24 kg cal mole⁻¹), although (*cf*. section II) the validity of such treatments is extremely doubtful. Cations containing halogens bonded adjacent to the positive center will be considered in section V.

The physical and chemical evidence for carbonium ions has been examined in very great detail, and descriptions of acyclic and of most carbocyclic ions as π complexes are quite unnecessary.[79,80] Not only can all the data applicable to these structures be very satisfactorily interpreted in terms of open classical ions, but in certain instances π complexes can be definitely ruled out. An example of the latter was the
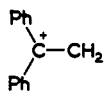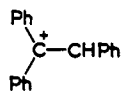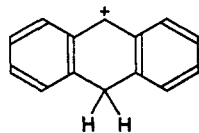

20 **21** **22**

observation that the uv spectra of solutions of 1,1-diphenylethylene, triphenylethylene, and anthracene in concentrated sulfuric acid were only consistent with protonation at those carbons which were predicted by simple molecular orbital theory to lead to the most stable open ion, *i.e.*, to form **20–22**. As each ion possessed a benzhydryl cation residue, similar spectra for the trio were expected and were indeed observed;[81] such similarity would not fit other structures for the ions. Intense absorption bands, attributed to π complexes, have also been observed when certain 1,1-diarylethylenes were dissolved in acids,[82] but closely comparable spectra result from similar treatment of benzhydrol and the explanation was considered untenable.[83,84]

A classical open ion, rather than a π complex, is undoubtedly favored in all these examples by the presence of the

aryl substituents, but similar conclusions as to the preference for an open ion are generally held for aliphatic cations. The close similarity of the spectrum of the supposed *t*-butyl carbonium ion generated by treatment of *t*-butyl alcohol or isobutylene with acid to that of the isoelectronic trimethylborine was considered[85] to indicate the same type of planar open structure for the former as that of the latter, but this argument is now known to be invalid, as a cyclic trimer cation was actually formed under the reaction conditions.[86] Nevertheless, the conclusion has been verified and extended to many other structures by detailed spectroscopic studies. Treatment of alkyl fluorides with antimony pentafluoride or hydride abstraction from an alkane by strong acid gave solutions that were shown by nmr to contain open primary, secondary, and tertiary carbonium ions.[87-89] For example, **23** possessed five spectrally equivalent methyl groups even at −180°, and although the barrier for methyl shift appeared less than 2–3 kg cal mole⁻¹, there was no detectable tendency to form a static π complex. In another investigation all four methyl groups of **24** were found to be equivalent and so all must have been coupled equally to the lone tertiary hydrogen atom; a π complex in which the bridging hydrogen either carried a fraction of the positive charge or was partially bonded to a positively charged carbon could be ruled out by comparing the observed deshielding of the methyl and methine hydrogens with that expected for an open ion, and rapidly equilibrating open ions were preferred. Most of these and similar results were obtained at low
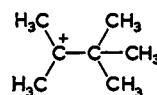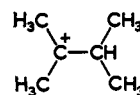
23 **24**

temperatures where an equilibrium between **6** and **19** could favor the latter, but a similar pattern is found at higher temperatures, and the ir and uv spectra at various temperatures were all in agreement with those predicted by theory for open ions.[87,88] In summary, despite much speculation, no evidence has been presented for π complexes in this context and there is no reason to believe that classical carbonium ions exist as other than open species.

B. NONCLASSICAL IONS

Much recent effort in bicycloalkane chemistry has been directed to determine whether mesomeric nonclassical carbonium ions or equilibrated systems of open classical ions are intermediates in certain reactions; in the latter situation the nonclassical species can only have the status of transition states. The majority view favors nonclassical ions as intermediates,[80,90,91a] typically represented as **25** (for the ion formed from isobornyl chloride). Bicyclics have important advantages over acyclics or monocyclics in forming such ions, for the last

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(78) B. Capon, *Quart. Rev.* (London), 18, 45 (1964).

(79) D. Bethall and V. Gold, "Carbonium Ions, an Introduction," Academic Press, London, 1967.

(80) G. A. Olah and P. von R. Schleyer, Ed., "Carbonium Ions," Vol. I, Interscience Publishers, New York, N. Y., 1968.

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(87) G. A. Olah, "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, p 21.

(88) G. A. Olah and C. U. Pittman, *Advan. Phys. Org. Chem.*, 4, 305 (1966).

(89) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, 89, 4739 (1967).

(90) G. D. Sargent, *Quart. Rev.* (London), 20, 301 (1966).

(91) (a) J. A. Berson in ref 6, p 111; (b) A. D. Walsh, *J. Chem. Soc.*, 89 (1947).

pair must sustain a large entropy loss when the chain or ring aligns to allow three-center interaction, whereas the interacting centers in the first-named are rigidly held in fixed orientation with no interposed solvent molecules. Nonclassical ions can be represented as internal π complexes,[7,44,91b] e.g., **26** or in

25 **26**
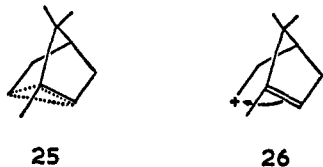
general **6**, $X^+ = CR_3^+$. A good example of this approach is the application to the equilibrium mixture of three isomeric nonclassical bicyclobutonium ions, **27**, that are believed to be formed in reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl compounds. The alternative picture is of π complexes with an apical vinyl group which is stabilized by back-donation; cf. **28**, the probable stereochemistry of which is outlined in **29**. The π complex **30** is almost certainly too strained to make an important contribution.[7] In these internal π complexes the weaker bond between the basal carbons and the apical atom readily allows the distortion necessary for a molecular bond to be formed with little expenditure in energy;[7]

27 **28** **29** **30**

31
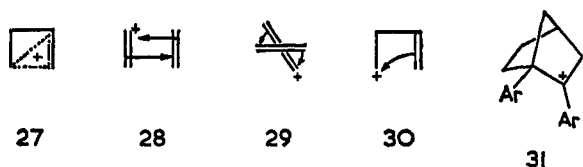
thus a distortion that would halve the energy of a C–C σ bond would cost ca. 40 kg cal mole^{-1}, whereas a similar perturbation in a π complex might not cost more than ca. 15 kg cal mole^{-1}.

Analogous π complexes can be visualized for all nonclassical ions that have been proposed. As significant resonance interactions between suitably situated aryl groups and the molecular bond are not expected, it is not surprising that the ion **31**, in contrast to the situation for other norbornyl derivatives, exists as two isomeric rapidly interconverting classical ions rather than as a π complex.[92] The π-complex model for nonclassical ions seems reasonable and can account for such evidence, mainly spectral, that has been put forward to define the structure of nonclassical ions. In fact, differences in the two models may be largely semantic. Nevertheless, the view has not been generally accepted and the conventional bridged structures with partial bonds, as **25**, are usually preferred, although the π-complex model may be useful in designing experiments utilizing the π route to nonclassical ions, involving double bond participation at an incipient cationic center.

Phenonium ions, i.e., cations with a bridging phenyl group (**32**), are well authenticated from kinetic and stereochemical studies on β-phenylethyl compounds.[79,80] These would not be considered nonclassical on the definition that the latter possess ground states with delocalized σ electrons,[93] but it is convenient to discuss them here. These ions have been considered to be equivalent to π complexes,[7] i.e., **6** (X = Ph), but other

32 **33** **34** **35**

36
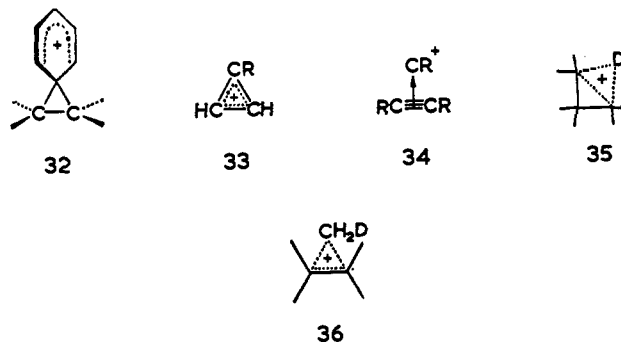
workers have distinguished between π complexes and bridged species. Thus a choice in favor of the former has been made on the basis of kinetic studies of the formolysis of β-arylethyl tosylates,[94] whereas the nmr spectrum of solutions produced by treating β-(p-methoxyphenyl)ethyl chloride with antimony pentafluoride in sulfur dioxide at $-70°$ has given claimed evidence[95,96] for a bridged species (**32**). In the latter work, three types of protons belonging to cyclopropyl groups, methoxy groups, and an AB ring quartet were found at the expected shifts, and the highly deshielded ring pattern was that of a phenonium ion rather than of the aromatic ring expected for **6** (X = Ar);[1] such results were considered to exclude a pair of equilibrating classical ions or a π complex. Similar ions with more than one α or β phenyl group definitely formed classical open ions rather than bridged species.[97] Chemical and nmr evidence[98] was also claimed to favor the structure of cyclopropenium ion, **33**, rather than the π complex **34**; but, as for the studies with phenonium ion, the nmr spectrum expected from the π complex is somewhat uncertain, and this intermediate cannot be ruled out on spectral evidence alone. The empty orbitals of cyclopropenium ion are strongly antibonding as is proved by the ineffectiveness of phenyl groups in stabilizing the species. Certainly this orbital structure is similar to that predicted for π complexes.

Treatment of cyclopropanes with electrophiles has been proposed[4] to give π complexes (**6**, $X^+ = CH_2^+X$). The scrambling of tracer to all carbon atoms of isopropyl alcohol isolated from hydrolysis of cyclopropane with deuterated acid was interpreted[99] in terms of a nonclassical edge-protonated ion (**35**) that was converted into edge-protonated isomers via the formation of **36**, and similar intermediates have been proposed in other reactions.[49,100] These isotopic data can be rationalized in terms of π complexes[7] and differences between the two descriptions must be largely semantic.

C. IN ALIPHATIC REARRANGEMENTS

π complexes have been advocated[4,101] in place of the generally accepted carbonium ions or analogous species in a variety of intramolecular aliphatic rearrangements that involve migrations of atoms or groups to electron-deficient centers, e.g., the

(92) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, J. Amer. Chem. Soc., **85**, 479 (1963).
(93) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965, p V.

(94) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, J. Amer. Chem. Soc., **89**, 370 (1967).
(95) G. A. Olah, E. Namanworth, M. B. Comisarow, and B. Ramsey, ibid., **89**, 711 (1967).
(96) G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, ibid., **89**, 5259 (1967).
(97) W. A. Bonner and C. J. Collins, ibid., **78**, 5587 (1956).
(98) R. Breslow, J. T. Groves, and G. Ryan, ibid., **89**, 5048 (1967).
(99) A. A. Aboderin and R. L. Baird, ibid., **86**, 2300 (1964).
(100) H. Hart and R. H. Schlosberg, ibid., **90**, 5189 (1968).
(101) M. J. S. Dewar, Annu. Rep. Progr. Chem., **48**, 118 (1951).

Wagner–Meerwein, pinacol, benzilic acid, Beckmann, Hofmann, Curtius, and Lossen rearrangements, and also for certain isomerizations, e.g., of nitro and nitrito or cyano and isocyano compounds, that probably proceed through the formation of ion pairs. These proposals have aroused little interest, as the details of these rearrangements can be adequately accommodated within the framework of the existing theory. Certain 1,2 hydride and alkyl group shifts have nevertheless been discussed subsequently in terms of π complexes,[7] despite the lack of evidence for these species in SN1 reactions that has been outlined in section IV.A.

Most 1,2 shifts that have been so examined take place with racemization or inversion of configuration at the migration termini, but the hydride shift accompanying solvolysis of certain cyclic tosylates proceeded with retention at the migration origin.[102,103] To account for this, the intervention of the equivalent of a hydrogen-bridged π complex was proposed that was bonded electrostatically through the hydrogen to a solvent molecule and directed attack of this solvating molecule from the side of the bridge so as to destroy the ion. Alternatively, formation of an open carbonium ion that partitioned to products faster than undergoing ring inversion can also lead of the observed stereochemistry. The latter view is supported by a recent nmr study of the kinetics of similar hydride shifts;[104] the rate did not correlate with the basicity of the olefin moiety of the proposed π complex, and the factors which stabilized the open carbonium ion were also operative in the transition state of rearrangement, which thus almost certainly resembled the open rearranged ion rather than a π complex.

D. IN ELIMINATION

π-Complex routes have been proposed for certain E1 reactions. Here the proton is considered not to be directly lost from the β carbon atom but is first transferred to the π orbital of the developing double bond and is either removed in a stereospecific anti elimination or migrates to form a rearranged open ion that can rotate, re-form a π complex, and ultimately lose the proton in an overall nonstereospecific manner. A detailed analysis of the olefinic products from the acetolysis of threo- and erythro-3-phenyl-2-butyl tosylate revealed that, although a phenonium ion (or phenyl-bridged π complex) was a major intermediate en route to acetate esters, it was not important in elimination. Part of the latter reaction was believed to result from nonstereospecific loss of a proton from a classical open ion, and the remainder arose from a proposed hydrogen-bridged π complex in a stereospecific anti fashion.[105] A similar π complex has been invoked to account for the formation of the Hofmann product (1-ene) rather than the expected 2-ene from solvolysis of 3-p-anisyl-2-butyl brosylate.[7] The probability of forming a phenyl-bridged π complex in both these examples may introduce electronic and stereochemical control that is absent in eliminations from alkyl compounds.

Several claims have also been made for π-complex routes in the dehydration of alcohols by aqueous mineral acids. These

E1-like processes are the reverse of heterolytic additions of water to olefins, so that any evidence for π complexes that is adduced for the latter reactions can be applied to the former by the principle of microscopic reversibility. Such evidence will be discussed in section V.B. Comparison of the rates of ^{18}O exchange and dehydration of primary, secondary, and tertiary alcohols suggested heterolysis to cations,[106] and detailed data for the first type were argued to support the formation of a π complex after the heterolysis.[107] Here, the rates of dehydration were linear in the Hammett h_0 acidity function and a mechanism was proposed in which a carbonium ion encumbered with the leaving water molecule was converted into a π complex in the rate-determining step. Direct isomerization of an open carbonium ion to the complex was considered to be ruled out by the dependence on the h_0 rather than the j_0 acidity function. This interpretation has been severely criticized,[108] and more recently the general use of acidity-function correlations to assign mechanisms and to infer particular intermediates has been questioned (cf. section V.B). The currently accepted view is that all the available data are consistent with the reversible formation of an open carbonium ion followed by rate-determining loss of the proton.[106] This is reiterated in a recent study of dehydrations of 1,2-diarylethanols,[109,110] although here the occurrence of open ions would be especially favored. d_1-1,2-Diphenylethanol gave trans-stilbene with all tracer retained at one carbon, thus ruling out hydride shift that would arise from the formation of a (presumably symmetrical) π complex. Moreover rates of dehydration from this and other substrates with two identical aryl groups showed no deviation from the Hammett σ–ρ relationship that was obeyed by unsymmetrically substituted arylethylenes. Accelerated rates would have been expected if a symmetrical π complex had been formed after heterolysis.

Characterization of the kinetically controlled products of dehydration of a variety of alcohols over alumina and other solid catalysts has led to the proposal of π-complex routes with apical aryl, alkyl, and hydrogen groups.[111] Similar intermediates were believed to account for the large preference for the formation of cis olefins, rather than the more stable trans isomers, under the same conditions. The pathway to the former was considered to be facilitated by analogy with the generally greater stability of complexes of cis olefins than those of trans olefins with Lewis acids. The incidence of π complexes in these probably heterolytic processes, which involve complexing to metal ions of the lattice, is reasonable, as neighboring group participation may be evoked to assist sluggish proton loss, but there is no justification for the extrapolation of these mechanisms to the very difficult conditions in homogeneous solution. It is significant that E1 reactions in solution do not lead to an abnormal ratio of geometrical isomers or, in general, to the skeletal rearrangements that intrude over solid catalysts.[106]

(102) S. Winstein and N. J. Holness, J. Amer. Chem. Soc., 77, 5562 (1955).
(103) D. J. Cram and J. Tadanier, ibid., 81, 2737 (1959).
(104) D. M. Brouwer, C. MacLean, and E. L. Mackor, Discuss. Faraday Soc., 39, 121 (1965).
(105) D. J. Cram, J. Amer. Chem. Soc., 74, 2137 (1952).

(106) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., Amsterdam, 1963, p 145.
(107) R. H. Boyd, R. W. Taft, A. P. Wolf, and D. R. Christman, J. Amer. Chem. Soc., 82, 4729 (1960).
(108) J. F. Bunnett, ibid., 83, 3978 (1961).
(109) D. S. Noyce, D. R. Hartter, and R. M. Pollack, ibid., 90, 37 (1968).
(110) D. S. Noyce, D. R. Hartter, and F. B. Miles, ibid., 90, 3794 (1968).
(111) H. Pines and J. Manassen, Advan. Catal., 16, 49 (1966).

E. IN DEAMINATION

The relatively unsolvated carbonium ion generated by deamination of primary alkylamines with nitrosating agents differs from the formally identical but solvated species usually formed, in particular by showing an enhanced tendency to rearrange.[112] Consequently the dearth of evidence for π complexes in carbonium ion producing reactions might not here apply.

Deamination of isobutylamine mainly yielded t-butyl alcohol, and when the reaction was conducted in deuterated water, no carbon-bonded tracer was found in the products.[113] This observation led to the proposal of a bridged cation, equivalent to a π complex, as an intermediate from which the apical proton did not exchange with the medium, but the data do not require this complex to be other than a transition state. A π-complex route can be ruled out for deamination of 1-^{14}C-ethylamine, as over 98% of tracer was retained at the C_1 position in the product ethanol,[114] but as expected 2-phenylethylamines, capable of forming π complexes of the phenonium ion type, gave[112] products with almost equal scrambling of tracer between C_1 and C_2. Surprisingly, reaction of 1-^{14}C-n-propylamine under comparable conditions led to scrambling of tracer, purportedly through the formation of methyl and hydrogen-bridged π complexes or edge-protonated nonclassical ions.[115] The stereospecificity of rearrangements that followed deamination of 2-amino-3-phenylbutane was also attributed to a methyl-bridged π-complex intermediate, but the possibility of this result arising from sterically controlled attack on an open carbonium ion was also allowed, although not favored.[116] In these, as in many other reactions, π complexes have been considered to be intermediates, but their occurrence as transition states linking classical open ions cannot be ruled out. The available data are consistent with both possibilities.

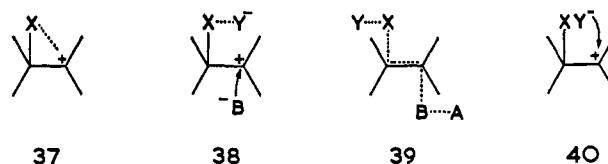## V. π Complexes in Addition to Unsaturated Systems

π complexes can only occur in S$_N$1 and E1 reactions if they are either generated from the initially formed open carbonium ion at a rate comparable to that of the destruction of the latter by a nucleophile or are directly formed by neighboring group participation of a β-linked group assisting the heterolysis and by passing the free ion. Their direct formation by addition of electrophiles to unsaturated systems, however, has been repeatedly advocated on the basis of the following five lines of evidence.

(a) It is argued that the much greater ease of electrophilic, compared with nucleophilic, addition is only consistent with π-complex theory.[4] These observations are, however, also consistent with the much greater stability of open carbonium ions than of carbanions in the common reaction media.

(b) Olefins are stated to act as bases in a way consistent with the formation of π complexes.[4,37,42] But, in contrast, the rates of addition (when measurable) do not correlate with the

stability constants of the substrate toward silver ion[117] and none of the cited evidence is inconsistent with the formation of σ complexes or open carbonium ions.

(c) The oft-quoted stereospecificity or stereoselectivity for $anti$ addition to olefins has been asserted to be consistent only with the formation of a π complex and consequent nucleophilic attack from the unhindered side. Nevertheless, this is not a unique interpretation of the facts. Although certain halogen-containing cations may be cyclic, $cf.$ 10, and can be regarded essentially as π complexes, an alternative intermediate, that also leads to $anti$ addition, is an open ion where rotation about a C–C bond is prevented by the electrostatic interactions shown in 37. Another possible explanation is that neutralization of the initially formed classical open ion is faster than rotation about the newly formed single bond, so the anion is directed to give overall $anti$ addition by steric hindrance to syn attack caused by the bulk of the recently added electrophile and its counter species, $cf.$ 38. A third, and per-

haps the most probable explanation of the stereochemical results, is concerted termolecular $anti$ addition with bypassing of the free cation (see section V.A), $cf.$ 39.

(d) The kinetics of certain hydrations and the dependence of rate on substitution for certain halogenations have been claimed to indicate π-complex routes. These will be discussed in sections V.B and C.

(e) Nmr evidence has been put forward for cyclic halogen-containing cations that can essentially be regarded as π complexes. Such species were present at low temperatures in strongly acidic media but the relevance of such observations to typical reaction conditions is not clear.

A. HYDROHALOGENATION

Addition of hydrogen chloride to isobutylene in aprotic media was much faster if the mixture was cooled and then allowed to warm to room temperature than if the whole procedure was carried out under the latter conditions,[118] and the addition of hydrogen bromide and of bromine was similar. A claim that these observations support a π-complex route[119] has been disputed,[120] and molecular complexes such as can be detected spectroscopically on adding hydrogen bromide to allyl chloride at $-177°$ are probably formed.[121] The high kinetic orders in acid and the complicated kinetics generally observed for addition of hydrogen halides to olefins in nonpolar media[118,122,123] have also been quoted as evidence for the formation of π complexes but, if chain processes can be excluded as an explanation of these kinetics (which is not cer-

(112) D. V. Banthorpe in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1968, p 585.
(113) L. G. Cannell and R. W. Taft, $J. Amer. Chem. Soc.$, 78, 5812 (1956).
(114) J. D. Roberts and J. A. Yancey, $ibid.$, 74, 5943 (1952).
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tain), the formation of molecular complexes must be again inferred.

Early indications suggested that additions of hydrogen chloride and iodide to simple olefins were stereospecifically *anti*, whereas hydrogen bromide predominantly, although not exclusively, followed this route.[124] Such orientation was considered good evidence for π-complex formation and the assumed universal preponderance of *anti* addition was considered indicative of the universal preponderance of π complexes in addition reactions. Recently this simple orientational pattern has been spoiled. Addition of deuterium chloride and bromide (the heavy isotope was used to allow distinction to be made between the products of *anti* and *syn* addition to acenaphthylene,[125,126] indene,[127] and *cis*- and *trans*-1-phenylpropene[128] in methylene chloride, acetic acid, and pentane led to 80–89% *syn* addition under kinetically controlled conditions. This orientation cannot be rationalized by steric effects, and the protagonists of the π-complex theory concluded that in these poorly dissociating conditions, with reactive substrates containing aryl groups suitably substituted to stabilize open ions, the initially generated cation was an open carbonium ion which was destroyed by the counterion of the electrophile in a *syn* process, *cf*. 40, before an external nucleophile could intervene.[76] Others[124] have asserted that such observations do not exclude π complexes as intermediates, as the π orbitals of the substrate only undergo a slight change of geometry on attachment of a proton and *syn* attack by the counterion breaks up the complex. Such *syn*-directed decomposition has not been otherwise postulated and it seems unlikely, especially for the additions of electrophiles other than hydrogen (see section V.B) which would greatly perturb the π orbital. Nevertheless it has been conceded[124] that these additions and the accompanying rearrangements cannot be wholly described in terms of π complexes. At best such species must isomerize to open ions en route to products.

A recent proposal throws an entirely new light on the significance of *anti* addition. Kinetic evidence was adduced that addition of hydrogen chloride to cyclohexene in acetic acid was termolecular and gave predominantly *anti* addition.[129] A transition state 39 resembling that of E2 was proposed for a concerted process that was essentially similar to that suggested much earlier[130] for the iodination of acetylene. The unramified substrates for which this mechanism applies and the entirely typical reaction conditions support the general validity of this route; consequently great caution must be exercised in assuming addition to proceed *via* a cationic species and then deducing the nature of this species from the observed stereochemistry. A theoretical justification for concerted *anti* addition has been available since it was recognized that the first excited state of acetylene was *anti* bent,[131] and quantum mechanical calculations have also supported the adoption of this route.[132] Orbital symmetry requires *anti* addition for many concerted reactions, but even when nonconcerted such orientation can still predominate because the shape impressed by the sym-
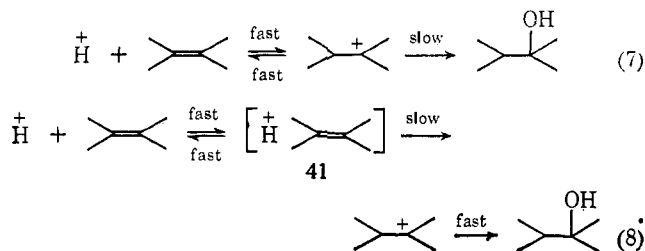
metry requirements can be retained to the point at which a succeeding reaction step produces the stereospecific result.[133]

Previous to this work, predominantly *anti* addition of hydrogen bromide to cyclohexene[134] and of hydrogen chloride to 1,2-dimethylcyclohexene[135] in acetic acid and pentane had been observed. Addition to the latter and to the isomeric 2,3-dimethylcyclohex-1-ene and 1-methyl-2-*exo*-methylenecyclohexene gave different proportions of *anti* and *syn* addition in the same conditions, despite reasonable preconceptions that each would form the same open carbonium ion; as a result this family of reactions was considered to procede either by the formation of (different) π complexes or by concerted additions. The latter view now seems very attractive.

Hydrohalogenation of norbornene and its homologs has been favored to follow π-complex routes, but addition of deuterium bromide to the parent compound[136] and of various acids to other bicyclic olefins under conditions where radical reactions were suppressed gave *syn–exo* addition that could only be rationalized if open carbonium ions were intermediates.[137–141]

B. HYDRATION

This special case of the addition of hydrogen ion and a nucleophile is one of the few reactions for which specific kinetic evidence for a π-complex route has been proposed. Preconceptions that eq 7 represented the mechanism were dispelled by the discovery that 2-methylbut-2-ene and 2-methylbut-1-ene, which formed the same products under similar conditions from presumably the same carbonium ion, were not interconverted during the reaction,[142,143] nor was tracer incorporated into unreacted substrate when the reaction was conducted in deuterated solvent.[144] This implies that either the carbonium ion was not formed in preequilibrium or a cation (41, eq 8)

$$\overset{+}{H} + \;\;>\!\!=\!\!< \;\; \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} \;\; >\!\!\overset{+}{\underset{}{}}\!\!< \;\; \overset{\text{slow}}{\longrightarrow} \;\; >\!\!\overset{\text{OH}}{\underset{}{}}\!\!< \qquad (7)$$

$$\overset{+}{H} + \;\;>\!\!=\!\!< \;\; \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} \;\; \left[\overset{+}{H}\;>\!\!=\!\!<\right] \;\; \overset{\text{slow}}{\longrightarrow}$$
$$\text{41}$$

$$>\!\!\overset{+}{\underset{}{}}\!\!< \;\; \overset{\text{fast}}{\longrightarrow} \;\; >\!\!\overset{\text{OH}}{\underset{}{}}\!\!< \qquad (8)$$

was generated in which the added proton did not become structurally equivalent to the adjacent hydrogens derived from the olefin. As the first alternative required a rate-determining transfer of protons from acid to substrate, which was considered unacceptable both on general grounds owing to the usual rapidity of such transfers and because of the linear dependance of the rate of hydrations of several olefins on Ham-

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mett's h_0 function rather than on stoichiometric pH, the second explanation was preferred and a mechanism (eq 8) was proposed.[145,146] Various speculations as to the structure of 41 were made, of which a π complex was most popular.

Later, several lines of evidence accumulated against eq 8. (a) Usually hydrations show specific proton catalysis,[147] but the discovery of examples of general acid catalysis[148] implied rate-determining transfer of protons to the substrate. Specific catalysis would be found for a mechanism involving slow proton transfer if the catalytic constant for hydroxonium ion was much greater than that of the undissociated acid. (b) A dependence of rate on h_0 is now believed not to exclude rate-determining proton transfer to the substrate, but rather to signify that the proton is largely transferred in the transition state of a step that may be either slow or fast compared with subsequent steps.[149-152] Any reaction in which the proton is essentially free from its counterion or encumbering solvent shell will have a rate correlating with the thermodynamic acidity and hence with h_0; whereas, when there is little proton transfer to the substrate in the rate-determining step, the rate is largely determined, in a bimolecular process, by the probability of encounters, i.e., by the stoichiometric acidity of the medium. The transition state for the formation of a carbonium ion from an olefin in a slow proton transfer should certainly resemble a carbonium ion,[72] and the value of the Brønsted α exponent (ca. 0.9) for certain hydrolyses leads to the same conclusion, for α is believed to be equivalent to the mean charge on the incipient anion of the acid molecule in the transition state of a slow proton transfer.[153] (c) The solubilities of several olefins in acids under conditions where hydration is rapid indicate no measurable complex formation.[154,155] (d) Measurement of both the volume and entropy of activation for several hydrations suggests that in the rate-determining step the transition state contained at least one firmly bonded molecule of water[156] and excludes this step being the unimolecular isomerization of a π complex to an open ion, eq 8. (e) Preequilibrium transfer of a proton requires a solvent isotope effect, k_{D_2O}/k_{H_2O} of 2–3, whereas typical hydrations have values less than 1, which are consistent with slow proton transfers.[144,148,157-159]

These and other observations relating both to aliphatic olefins and to styrene and its derivatives are all consistent with a mechanism in which a proton is transferred to the olefin in a slow step followed by rapid capture of the resulting open carbonium ion by the solvent. Such a proton transfer involves extensive electronic reorganization and rehybridization and is quite reasonably different in activation energy from the rapid,

reversible proton transfers to lone pairs of bonded oxygen or nitrogen. Mechanisms with "encumbered" carbonium ions (cf. section IV.D) have been proposed in attempts to overcome some of the objections to the π-complex route,[107] but there is no reason to adopt these speculations or mechanisms that invoke the formation of π complexes after the rate-determining step (cf. section IV.D).

One of the few extant investigations of the stereochemistry of hydration is the acid-catalyzed addition of water to 1,2-dimethylcyclohexene: under kinetically controlled conditions nearly equal quantities of the products of syn and anti addition were reported.[160] Acid-catalyzed addition of methanol to bicyclo[3.1.0]hex-2-ene was syn stereospecific.[161] These results are as expected if the product-determining step is capture of an open carbonium ion with no hindrance and with restricted access to the attacking solvent, respectively, in the two examples.

Hydration of acetylenic acids, ethers, and thioethers and of furans show the same pattern of behavior as olefins and undoubtedly involve similar mechanisms.[162,163] Hydrations of acetylenes in the presence of mercuric and other metal ions lead to the rapid formation of colored complexes that have been reasonably claimed to be π complexes,[164] but these are undoubtedly only formed in the presence of such ions. A few studies have been made of the proton-catalyzed addition of weak acids to olefins. The rate addition of ethanol and formic acid to menth-3-ene correlated with h_0 of the medium and as the rate of racemization of the substrate was approximately the same as the rate of addition there was no evidence for preequilibrium proton transfer.[165] Although novel at the time, this observation fits into the currently accepted mechanism. More recently, product analyses have been made for the addition of acetic acid to norbornadienes under a variety of conditions of solvent and ionic strength; a multiplicity of steps was indicated without the need to invoke π complexes.[166]

C. HALOGENATION

Addition of certain halogens to olefins is widely accepted as proceeding through cyclic ions 10, which can be considered equivalent to π complexes, as intermediates, except when phenyl or analogous substituents are so located to stabilize open ions. Such halogenonium ions can only be opened by nucleophilic attack so as to give overall anti addition; but, as previously pointed out, the observation of this mode of addition is consistent with, but does not prove, the intervention of these ions. π complex formation could be favored by back d $\rightarrow$ π^* donation from electrophilically added bromine and iodine, and these halogens show neighboring group participation consistent with such an interaction in many reactions,[78] although direct physical evidence for such species under the reaction conditions is not forthcoming. Similar cyclic struc-

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tures for cations containing electrophilically added chlorine or fluorine are most unlikely.

Four main sets of evidence have been cited in support of the occurrence of π complexes in bromination.[167] (a) *anti* addition to a variety of olefins was found[124, 168] except where phenyl substituents biased the system in favor of an open ion and resulted in nonstereospecificity.[168] (b) The rate of addition to tetrasubstituted ethylenes correlated with the sum of the Taft σ* substituents for the alkyl substituents, thus implying that the positive charge was equally divided between the two olefinic carbons in the transition state.[169] Also the rates of addition to styrenes with electron-withdrawing substituents obeyed the Hammett equation with a ρ value (−2.2) much larger than those (*ca.* −4.0) found for the analogous additions of chlorine to cinnamic acids or for solvolyses that were considered typical for reactions involving open ions.[170] The former evidence could be accounted for on the basis of a bimolecular mechanism, and unfortunately the latter argument is weakened by exceptions;[183] one solvolysis that undoubtedly involves an open ion has a high ρ value (−2.2) and one bromination has a low ρ value (−4.0). It is also surprising that the aromatic groups in styrenes do not direct the formation of an open rather than a bridged ion. (c) The nmr spectra of bromine-containing cations are consistent with the π-complex structure,[171] but the conditions under which they were observed (very low temperatures and strongly acid media) are far removed from those of additions. (d) The similar rate of attack by anions and the solvent on the initially formed cation was best understood, for a particular series of brominations, if the cation was a π complex, as it was considered unlikely that the low concentration of anions could have competed with the solvent for the capture of open primary or secondary carbonium ions.[172] However, it is an open question whether a π complex could show sufficient discrimination toward the two competing nucleophiles, and this explanation overlooks the possibility of reaction of the substrate with the components of an ion pair, as in **40**, or an ion aggregate.

Although (a) and (b) can be alternatively rationalized (*cf.* section V.A) and the other arguments are weakened by the objections pointed out, it has been generally concluded that these four types of evidence present a conclusive case for the occurrence of π-complex routes.

Bromine–olefin complexes have been spectroscopically identified in aprotic solvents at low temperature.[173] A correlation of their stability with rate of addition was considered to be consistent with their rate-determining interconversion into either a π complex or an open ion,[174] and they are undoubtedly molecular complexes.

Although few reactions have been adequately investigated, electrophilic addition of iodine is generally found to be *anti* stereoselective[124] and as for bromination, a π-complex route has been widely assumed and backed by similar nmr[175] and

kinetic[176, 177] evidence. As before, other explanations seem equally valid.

Chlorine adds to butenes and other simple olefins exclusively *anti*,[168, 178] and π complexes have been forcefully advocated to account for such addition to *cis-di-t*-butylethylene.[170] For the latter compound this route is calculated to have a heat of activation some 9 kg cal mole⁻¹ lower than that involving open ions, but this is difficult to reconcile with the marginal nature of the neighboring group participation shown by chlorine in solvolysis,[78] and concerted termolecular *anti* addition is an attractive alternative.

Chlorinations of stilbene and phenylpropenes are nonstereospecific[168, 178] as expected owing to the preference for formation of an open carbonium ion, and some stereoselective *syn* additions, which are rationalized as for the analogous hydrohalogenations, have recently been reported mainly for cyclic systems such as acenaphthylene and phenanthrene.[179, 180] On the other hand, addition of chlorine to 1,2-disubstituted ethylenes and norbornenes is asserted to involve π-complex mechanisms, both to account for the *anti* stereospecificity and for the correlation of rate with Taft's σ* values for the alkyl substituents, regardless of their orientation on the double bond.[181] As mentioned before, neither argument is compelling. Although neighboring group participation of chlorine is normally insignificant, nmr evidence has been claimed, as in bromine cations, for π complexes.[147]

A very extensive investigation of the additions of chlorine, hypochlorous acid, and other carriers of positive chlorine to a variety of olefins was best interpreted by open ion routes.[182–184] Prop-1-ene gave 1-chloro-2-hydroxypropane on treatment with hypochlorous acid under conditions where radical addition was suppressed, whereas a π-complex route would have been expected to give the other chlorohydrin by analogy with the direction of ring opening in the corresponding epoxide. In this, and in related reactions, neighboring group participation of electrostatic origin, *cf.* **37**, was preferred, although π-complex routes were conceded to be relatively more important for the additions of the corresponding positive bromine and iodine compounds.[185] Fluorine adds to olefins at low temperatures probably in a four-center transition state after formation of a molecular complex.[186, 187] Neighboring group participation of fluorine is almost invariably quite insignificant[187] and π complexes are most unlikely.

D. OTHER ADDITIONS

Additions of various arylsulfenyl halides to cyclohexene and substituted styrenes have Hammett ρ values and entropies of

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activation very similar to those for the bromination of the same substrates and so have been considered to proceed by similar mechanisms.[188,189] Additions of these reagents to norbornene, acenaphthylene, and butenes were exclusively *anti*,[190,191a] and these two sets of results led to the postulation of cyclic episulfonium ions (**10**, X = SAr) as intermediates. Such cyclic ions have also been indicated by other evidence.[191b] The formation of an open ion which was destroyed before rotation was considered to be excluded by the finding of complete *anti* stereospecificity for additions to butenes over the temperature range -34–$146°$; it was stated that to account for this on the open-ion model the unlikely assumptions were necessary that the heats of activation for rotation within the ion and for its destruction by nucleophiles were identical, and that the preexponential term for the bimolecular step was very large; however, the fraction of any minor products could have been changed manyfold over this temperature range while remaining too small to be detected, and concerted termolecular *anti* addition was also not ruled out.

π-Complex routes have often been postulated in reactions where molecular complexes can be inferred or sometimes directly indicated by the rapid and reversible formation of colored adducts at low temperatures and by solvent effects on rate. A typical example is 1,2 cycloaddition of tetracyanoethylene to olefins to yield tetracyanocyclobutanes.[10] Complexes of unspecified nature have been proposed to account for color phenomena, the steric consequences, and solvent and substituent effects on Diels–Alder reactions,[192] but such species may be merely formed in competition rather than as intermediates.[193] The thermal equilibration of the ^{14}C-labeled *endo* complex of maleic anhydride and cyclopentadiene to the *exo* isomer in the presence of unlabeled maleic anhydride gave a product containing too much tracer to be derived from dissociation and recombination; the results suggested that internal isomerization proceeded by fragmentation, and that the two components must have been held in a complex as their restriction within a solvent cage could be ruled out.[194a] A π complex rather than a molecular complex has been preferred,[9] but more recent investigations[194b] have shown that the reaction was intermolecular when carried out under conditions where the reagent was completely soluble; the apparent intramolecularity was attributed to the presence of undissolved solid.

Addition of ozone to olefins has also been proposed to follow a π-complex route,[195,196] a species **6**, $X^+=O^+$—O—O^-, being postulated that rearranged to a covalently linked cyclic adduct. Although this scheme was claimed to account for certain details of the reactions, it is not clear if π or molecular complexes were intended, and more than one mechanism may well be possible for reactions of this type. Similar doubts apply

to similar intermediates proposed in hydroboration[197] and epoxidation[198] of olefins. Oxymercuration[199] and oxidative rearrangement of olefins induced by lead tetraacetate[200] may involve π complexes stabilized by the presence of the heavy metal, but addition of acetyl nitrate was nonstereospecific, and for this and other reasons was believed to proceed through open ions.[201]

In summary, much of the evidence that has been adduced and widely accepted for π-complex routes or for routes containing the closely related, probably equivalent, cyclic "onium" ions is consistent with but does not require these mechanisms. Such routes are most likely to occur for electrophilic addition of bromine or iodine where efficient d → π* donation is possible or for addition of sulfur electrophiles which are well disposed to form sulfonium compounds. Alternatively, concerted termolecular *anti* addition may account for most, if not all, of the available data. Kinetic studies are urgently needed to explore the generality of this last mechanism.

VI. π Complexes in Aromatic Substitution

A. GENERAL

Aromatic electrophilic substitution (ArSE2) is usually considered to follow a σ-complex route (eq 9, although either step can be reversible and the second can become rate limiting in certain reactions), but an alternative scheme, eq 10, has been advanced.[4] The latter mechanism requires interconversion of two π complexes through an intermediate σ complex. The formation of a nonlocalized π complex from the reactants was

$$\text{(9)}$$

$$\text{(10)}$$
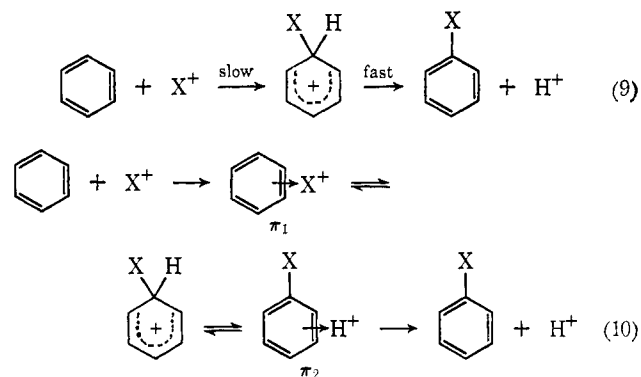
at first considered to be rate determining; on this basis the rate should be substantially independent of the nature of the substituents in the ring, although the distribution of the products should be governed by the same factors as in the σ-complex route. Later this rate-determining step was only considered likely for strongly exothermic reactions,[7] and the slow step was suggested to be the conversion of a localized π complex into the σ complex.[7] Now both rate and products would be dependent on the substituents in a manner similar to that for the σ complex.

Several alleged lines of evidence were marshalled to support the π-complex route.[4] (a) The adducts of hydrofluoric acid and

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benzene were asserted to be π complexes. (b) The formation of such complexes was supposed to account for the dipole moment of aluminum trichloride in benzene and also for certain cryoscopic data. (c) The alleged exclusive *para* coupling of amines and phenols with diazonium ions was held to contrast sharply with the *ortho–para* mixture obtained with other electrophiles and to indicate a different reaction mechanism. As the relatively stable diazonium ion has no empty bonding orbitals in its classical formulation, it was considered to show no tendency to form a π complex and therefore should react as in eq 9, whereas other electrophiles should follow eq 10. (d) It was concluded that only the occurrence of π complexes could satisfactorily account for the migrations of substituents that are sometimes observed during ArSE2 reactions. Some of these examples, such as (a) and (b), were singularly ill-chosen to prove the occurrence of π complexes in general, let alone as specialized reaction intermediates; all are consistent with the formation of σ complexes and the adoption of the classical scheme, eq 9. Another argument put forward to support the π-complex route[4] was that localization of the electrophile into a σ complex would destroy the aromatic character of the substrate, but a molecular orbital investigation of the σ complex of a proton with benzene has convincingly shown that interaction of the methylene hydrogen with the residual π orbital creates appreciably large bond orders between the tetrahedral carbon and its trigonal neighbors, and restores the otherwise lost aromatic character of the ring to a very considerable extent.[202]

Several theoretical approaches related to π-complex theory have been propounded. Following an analysis of aromatic reactivity that emphasized the role of the highest occupied molecular orbitals of the substrate,[203,204] a theory was developed for ArSE2 that posited two unsymmetrical adducts formed in sequence with the incoming electrophile and the displaced proton, respectively, held by so-called charge-transfer forces.[205] These presumably molecular complexes were nevertheless emphasized to be inner complexes with strong, although unspecified binding, and their actual structure seems quite obscure. Detailed calculations based on this model were claimed to account for selected experimental results, but nevertheless the significance and validity of the theory is not clear. Although more accurate predictions of the isomer ratio in, *e.g.*, the nitration of aromatic hydrocarbons, can be claimed than result from the calculation of atom localization energies of a σ complex, this fit results from using two disposable parameters to characterize the nature of the electrophile and the transition state. Undoubtedly the calculation based on a σ complex would be much improved by the introduction of additional parameters. Another theoretical treatment based essentially on the formation of a molecular complex has been offered.[206]

These novel approaches have not been generally accepted and it is difficult to see how weakly bonded complexes possibly in rapid equilibrium with their components at ordinary temperatures can be good models for the transition state of a reac-

tion requiring very considerable activation energy. Calculations of the stability of complexes of aromatics with tropylium ion[207] imply that only relatively stable ions will form π or molecular complexes with aromatic donors; usually the interactions between the reactants lead directly to σ complexes.

Considerable effort has been expended on searching for stable complexes that can be implicated as intermediates in ArSE2. If indeed π complexes are intermediates, physical evidence would be expected for their existence in conditions that did not lead to substitution, although the fine distinction between localized π complexes and σ complexes must be borne in mind. Conclusive proof has been obtained that many aromatics form cations with electrophiles.[208] Numerous proton-addition complexes have been characterized, mainly by systematic applications of eq 11–13 (M = Pb or Sb; Ar = benzene and homologs), and nmr analysis of the resultant solutions at −50° revealed signals due to methylene hydrogen

$$Ar + HF + MF_5 \rightleftharpoons ArH^+MF_6^- \qquad (11)$$

$$Ar + AgMF_6 + HCl \rightleftharpoons ArH^+MF_6^- + AgCl \qquad (12)$$

$$Ar + FSO_3H + MF_5 \rightleftharpoons ArH^+MF_6^- + SO_3 \qquad (13)$$

that could be unambiguously assigned to σ complexes.[87,209–211] The ir and uv spectra at low temperatures were all consistent with those predicted using correlation rules and molecular orbital theory respectively for σ complexes,[212–214] although uv spectra assignable to certain molecular complexes could be detected at low temperature if rigorously dried systems were used.[214] Analysis of the uv spectrum of proton–anthracene complexes indicated the unique formation of σ complexes (section IV.A) and a similar complex resulted from hydride-ion extraction from 9,10-dihydroanthracene[215] and has been further characterized as possessing a ¹³C–H coupling constant for the C₉ position characteristic of sp² hybridization.[216] Several of the aromatic components of proton-addition complexes have been found to exchange hydrogen for deuterium in the presence of deuterated acid. This is consistent with the formation of a σ complex that can lose either hydrogen isotope to revert to starting material.[217]

σ complexes have also been characterized from treatment of aromatics with alkyl or acyl fluorides and hydrogen fluoride, with nitrosyl fluoride and boron trifluoride, and with ethyl fluoride and boron trifluoride to form species such as ArR⁺-BF₄⁻ (where R = alkyl, acyl, NO, etc.), and in some examples[210] these readily decompose to the normal products of ArSE2. Other σ complexes have been assigned by nmr spectroscopy to the products of exhaustive methylation of ben-

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zene[218] and other aromatics[219,220] or have been postulated on the basis of spectral[221] and kinetic[221-223] evidence for desulfonations and decarboxylations.

Although adducts of molecular halogens and aromatic compounds that can probably be classed as π complexes have been obtained,[224,225] there is no physical evidence for such complexes with the reactive electrophiles believed to intervene in ArSE2. The present position, which will be outlined in the light of chemical evidence in the next sections, is not so much whether σ or π complexes are mechanistically significant, for it is increasingly evident that in almost, if not all, ArSE2 reactions the former plays a dominant role in controlling the rate and products, but whether there is evidence for the existence of π complexes on the reaction path. Excellent reviews on both general[208,226,227] and specific aspects, i.e., nitration,[228] halogenation,[228] sulfonation,[229] and Friedel–Crafts reactions,[230] of ArSE2 are available.

B. ELECTROPHILIC HALOGENATION

The rates of chlorination and bromination of a number of substituted benzenes[29,226,231-232] and polycyclic hydrocarbons[208,233] did not correlate with the stability of the complexes formed with hydrogen chloride (section II.A) but rather with that of σ complexes. The relative basicities toward hydrogen chloride of a series of alkylated benzenes only varied over a range of 1.5-fold, whereas the relative stabilities of the σ complexes with hydrofluoric acid–boron trifluoride steadily increased 3000-fold under similar conditions and the rates of halogenation similarly steadily increased 80,000-fold. A more spectacular effect was found for polycyclic hydrocarbons; again the so-called π basicity with respect to hydrogen chloride varied little over the series, but there was a good correlation of the logarithm of the equilibrium constant for σ-complex formation with the logarithm of the rate constant for chlorination and bromination (and also for nitration and deuteration) over a range of ten powers of ten in the respective variables.[43,208] Such linear correlations can only mean that the transition state of the rate-determining steps closely resembled σ complexes and there was no similarity to either molecular or π complexes.

Detailed analysis of the relative reactivities of specific positions in isomeric alkylbenzenes could also be convincingly interpreted in terms of σ-complex routes,[226] as could be the observation (unusual for ArSE2) of kinetic isotope effects, k_H/k_D, of considerably greater than unity for deuterium-substituted substrates in certain iodinations and brominations.[208] The latter results prove that a C–H bond is broken in the rate-determining step and are inconsistent with π-complex routes where either formation of the complex or an interconversion of a π to a σ complex is rate determining. Theoretical treatments have been presented for conveniently estimating the disparity of the intermediate from a fully developed σ complex.[234]

Halogenations of many series of substrates have not been investigated and the practice has arisen of using the relative rates of substitution of toluene and benzene, k_T/k_B, as an index to mechanism. For a σ-complex route, this ratio should be considerably greater than unity as the influence of the substituent should be felt to differing, but significant, degrees depending on the resemblance of the transition state to the σ complex; values of 30–100 are typically found. For a π-complex route, on the contrary, this ratio should be close to unity if the slow step is the formation of the initial π complex. If the π → σ interconversion is rate limiting, values similar to that for the σ-complex route are expected. Ratios of 1 to 3 have been deemed consistent with the former variation of the π-complex route. k_T/k_B should fall from the values typical of σ-complex routes if reactive reagents are used, for a low heat of activation implies similarity of the transition state to the reactants, and thence to a π complex, rather than to a σ complex. However, a selectivity relationship has been discovered connecting the rates and the proportions of isomeric products in both fast and slow reactions that is believed to apply to all σ-complex routes and to be diagnostic of them.[227]

The aluminum bromide catalyzed bromination and chlorination of aromatics in dipolar aprotic solvents and the direct chlorination in the same media had k_T/k_B values that were similar and supported σ-complex routes.[230] Bromination in trifluoroacetic acid as solvent (which, compared with the similar reaction in acetic acid, shows uncomplicated kinetics), however, gave k_T/k_B of about 2500, the highest recorded for ArSE2; this anomalously high value may be due to the presence of a more complicated mechanism than was suspected.[235] Prima facie evidence for a π-complex route is the low k_T/k_B ratios for the chlorination and bromination of aromatics in nitromethane catalyzed by iron trichloride;[236] here the presence of the metal ions may favor such routes.

The evidence summarized above and certain other similar data[230] have resulted in the consensus that electrophilic halogenation involves σ-complex routes, with a few possible exceptions. An early advocacy of a π-complex route[44] based on an analysis of the relative bromination rates of anisole and 1,2-dimethoxybenzene was refuted after an evaluation of the cited data.[237]

High kinetic orders in the reagent have been observed for certain halogenations in solvents such as acetic acid and have been considered to indicate complexing between the reac-

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tants.[31,238,239] Some complexes have been either isolated or detected spectroscopically from mixtures of aromatic[240,241] or heterocyclic bases[242,243] with halogens at room temperature. The low heats of formation and the characteristic contact charge-transfer spectra[244] imply molecular complexes. As would be expected, σ complexes cannot be isolated or detected in typical reacting systems except under the special conditions described in the previous section, but **42** can be isolated on bromination of 2,6-di-*t*-butylphenol,[245] and analogous dienones[246] have been characterized when proton loss from a phenolic hydroxyl group in a σ complex can stabilize these structures. An intermediate with a uv spectrum different from, but an nmr spectrum similar to, the reactants accumulated during iodination of G-salt.[247,248] This intermediate
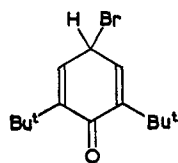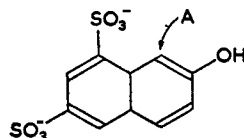
42   **43**

had spectral properties quite different from the well characterized σ complex that accumulated in the analogous bromination. The former intermediate was almost certainly a molecular complex, indicating that apparently the bulky electrophile cannot penetrate to the hindered 1 position of the substrate, *cf.* **43**. This does not prove that a molecular complex is formed when a direct route to the σ complex is available but it does suggest that both types are possible intermediates on the reaction path.

C. ELECTROPHILIC NITRATION

The selectivity of certain nitrations indicates a σ-complex route.[249] A variety of nitrating agents, *e.g.*, N-nitropyridinium tetrafluoroborate in acetonitrile, nitric–sulfuric acid in sulfolane, and nitric acid in acetyl nitrate, all result in k_T/k_B in the range 27–37. However, reactions have been discovered where such selectivity does not occur; rates of nitrations with nitronium salts, $NO_2^+X^-$ with $X^- = BF_4^-$, ClO_4^-, PF_6^-, etc., in nitromethane, sulfolane, and other dipolar aprotic solvents[250–253] were too fast to measure by conventional means,

but use of the competition method showed low selectivity, *e.g.*, k_T/k_B of 1–2. On the basis of the selectivity rule, if these fast reactions pursued σ-complex routes they would have a predictably low positional selectivity in forming products, but the observed low substrate selectivities were all accompanied by high discrimination between the available positions; typically an isomer ratio of *ortho*:*meta*:*para* = 66:1:33 was found. As a consequence of this breakdown in the expected behavior other anomalies appeared: although alkylbenzenes were always more reactive, albeit by only small total rate factors, than benzene, the *meta* positions were uniformly deactivated and their partial rate factors were all less than 1. These observations are inconsistent with any mechanism in which the individual nuclear positions compete for the reagent. In explanation, formation of a π complex in the rate-determining step was proposed and the subsequent rapid conversion into a σ complex allowed discrimination in orientation of products. A small kinetic isotope effect (*ca.* 1.2) was found for the nitration of deuterated substrates, which was an embarrassment for the π-complex mechanism but was interpreted as a secondary effect.[253,254]

Other observations have also suggested the formation of complexes in nitration: colors were formed on mixing aromatics with nitric acid in nitromethane, which were reasonably proposed to signal the formation of molecular complexes,[255] and anomalously high (compared with those found in typical nitrations) ratios of *ortho* to *para* products from biphenyl have been attributed to electrophilic attack by π-complexed nitronium ion on the nearest activated carbon of the neighboring ring.[256] However, these last results may derive from the dipolar aprotic solvents used, for isomer ratios in nitration are known to be highly sensitive to the reaction medium.[257]

The technique of the competition experiments on which the evidence for π-complex routes depends have been severely criticized. Some objections[258] have been convincingly rebutted,[259,260] but others have not been answered in a satisfactory manner. Nitration with nitronium salts under conditions similar to those in the definitive experiments were claimed to give different results with four rather than with two competing substrates,[261] and certain reactions were stated to be brought to the substrate selectivity that was normal for σ-complex routes if low concentrations of the nitrating agent and a very efficient mixing system were used.[262] The inference was that in the earlier work the reaction occurred shortly after mixing before a uniform distribution of the reactants could be achieved. Consequently the solution was depleted of the more reactive substrate in the zone of mixing and the less reactive competitor was nitrated to a very considerable extent before more of the reactive species diffused into this area. The finding of appreciable quantities of dinitrotoluenes in the competition between benzene and toluene taken to a few per cent interconversion[262] is consistent with this interpretation. Most of

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this criticism was demolished by the demonstration that nitronium ion, under the conditions leading to high substrate selectivity, had reacted with a demonstrable impurity in the solvent to generate an unspecified nitrating agent,[263] and also by the low, less than 3%, yield of *meta* isomer from toluene, whereas greater than 40% of this isomer would have been expected if the reactions were diffusion controlled. In addition, use of a high-speed flow system in attempts to directly measure nitration rates led to the conclusion that there was little spread of rates between benzene and its alkyl homologs, although only rough comparisons of reactivity rather than reproducible absolute rates could be obtained.[263] Nevertheless, no effective explanation has been given of the unexpected dinitration, which intrudes to a greater extent than would have been expected for a quite indiscriminate reagent. A similar unexplained example of dinitration under competitive conditions was the recovery of mainly unreacted substrate and its dinitro derivative from the reaction of dibenzyl and nitronium tetrafluoroborate in sulfolane.[264]

The likelihood that the competition method leads to erroneous conclusions for these nitrations can be inferred from the results of several other investigations in which the method was applied for nitronium salts and aromatics in dipolar aprotic media. Thus, (a) when the reagent in one solvent was added to a solution of benzene and mesitylene in another, the apparent reactivities depended upon the initial solvent used for the reagent rather than upon the final composition of the mixture.[265] (b) If benzene and pentamethylbenzene were put into competition,[266] the latter reacted with nitronium ion preferentially and no nitrobenzene was formed unless the benzene was present in molar excess, although when the substrates were reacted separately benzene nitrated at much the faster rate. (c) In contrast to its rapid reaction with benzene, nitronium tetrafluoroborate reacted very slowly with anthracene in sulfolane, and an intermediate with a uv spectrum consistent with a σ complex accumulated.[267] Similar results were obtained for nitration of naphthalene derivatives.[268] (d) A detailed analysis which allowed for the concentration of nitronium ion in various nitrating media has suggested that diffusion control is likely for aromatics of barely greater reactivity than benzene,[269,270] so the innate reactivity of alkylbenzenes may be underestimated by any kinetic method.

A dilemma thus arises. There is considerable evidence that diffusion control exists in these nitrations, but this cannot account for the positional selectivity; conversely, if the low substrate selectivities shown by the competition experiments are meaningful, it is difficult to account for previously reported results that clearly indicate appreciable discrimination toward substrates by reagents that definitely generate nitronium ion as the attacking species in protic media; the evidence for this particular nitrating species is too strong to be discounted.[265]

Attempts have been made to rationalize the differences in substrate discrimination for nitrations in protic and dipolar aprotic media by postulating a rate-determining break-up of a solvated ion pair containing nitronium ion in the latter medium with direct transfer of the cation to form a π complex, whereas free nitronium ion is considered to be present in the protic medium.[271] The present situation is uncertain and more data must be accumulated before firm conclusions concerning the occurrence of π complexes in these reactions can be convincingly claimed.

D. FRIEDEL-CRAFTS REACTIONS

Complex formation is an aid to solubility of the reactants in these reactions, especially when nonpolar solvents are employed, and a variety of adducts of catalysts, substrates, reagents, and products have been reported.[230] Here only those of the reagent and substrate will be considered.

Early studies of alkylation and benzylation of aromatics with gallium tribromide as catalyst[272,273] showed low substrate selectivities, typically k_T/k_B = ca. 3.2, accompanied by a low selectivity, e.g., ortho:meta:para = 41:19:40, in product-forming steps. The selectivity rule was obeyed and σ-complex routes were inferred. On the other hand, although the alkylation and benzylation of substituted benzenes with aluminum trichloride–nitromethane complex in nitromethane as solvent and with other catalyst solvent systems gave a low substrate selectivity from the competition method, e.g., k_T/k_B was in the range 1.7–4.0 and the rates for other aromatics correlated with the stability constants for complexes with silver ions, halogens, picric acid and tetracyanoethylene, these were accompanied by a high orientational selectivity, and the selectivity rule was not obeyed. Similar results were obtained for other Friedel-Crafts alkylations. The *meta* positions of all these substrates were uniformly deactivated and small, presumed secondary, kinetic isotope effects were sometimes found, all this closely resembling the situation for nitrations in dipolar aprotic solvents.[87,210,274,275] Measurement by fast reaction techniques of the rates of benzylation, isopropylation, and *t*-butylation of benzene and toluene in nitromethane was bedevilled by impurities in the solvent, which prevented reproducible results, but, as for nitration, approximate comparisons were achieved that were claimed to confirm the results obtained in the competition experiments.[276]

These sets of results were interpreted in terms of a π-complex mechanism similar to that proposed for nitration, but the doubts concerning the technique and interpretation of competition exponents again apply. In particular, there are large discrepancies between the relative reactivities obtained by competition for Friedel-Crafts halogenation (k_T/k_B = ca. 3.6) and those obtained by direct kinetic methods (k_T/k_B = ca. 30) under otherwise identical conditions,[277,278] which have led to the preference for σ- rather than π-complex routes.[278]

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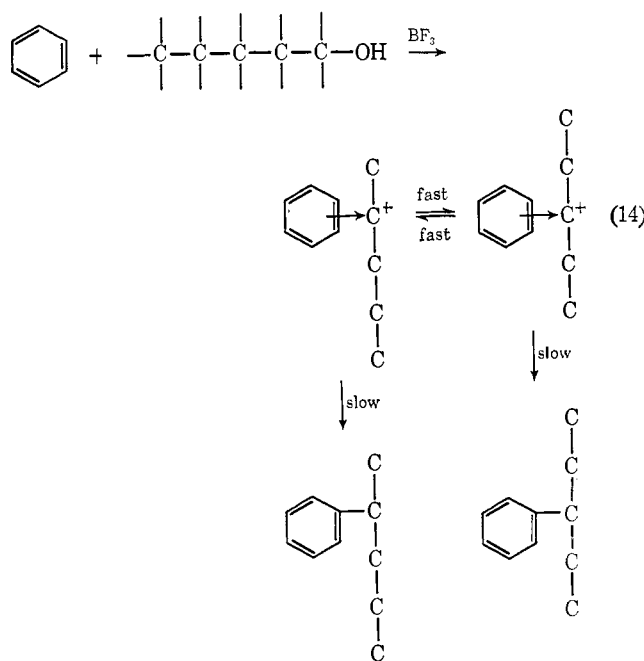(275) G. A. Olah, S. H. Flood, and M. E. Moffatt, ibid., 86, 1060 (1964).
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When the alkylating agent generated, or acted as a carrier for, relatively stable carbonium ions, the selectivity toward substrates significantly increased and a σ-complex route was probable. Thus t-butylation of mono- and polymethylbenzenes in nitromethane gave $k_T/k_B = \sim 15$, compared with ~ 2 for isopropylation.[275] As expected from the weakly electrophilic nature of acylium ions in Friedel–Crafts reactions, reagents such as $CH_3CO^+SbF_6^-$ showed a high discrimination toward substrates, e.g., $k_T/k_B = \sim 120$, coupled with a distinct preference for one particular product, e.g., ortho:meta:para = 1:1:98. Appreciable primary kinetic isotope effects, e.g., $k_H/k_D = \sim 3.0$, were also observed.[230, 279]

π complexes have also been proposed to account for the extent of racemization in the alkylation of aromatics with optically active butan-2-ol and for the isomerization observed in similar reactions with pentan-2-ol, both reactions being catalyzed by boron trifluoride. Racemization and isomerization were both less important than in other reactions believed to involve the cations as free ions.[280, 281] The alcohols were unchanged on treatment with the catalyst and the isomerization was believed to occur within a complex, eq 14, the inter-

$$\bigcirc + \; -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OH \xrightarrow{BF_3}$$

conversion of the two π complexes being rapid to allow for the formation of the same proportions of isomers from either pentan-2-ol or pentan-3-ol. As a spectacular illustration of the proposed mechanism it was found that although hexamethylbenzene, which cannot undergo substitution, was recovered unchanged after treatment with pentan-2-ol and Lewis acids in pentane, the alcohol was extensively polymerized, presumably due to the formation of a complex and equilibration to a free ion. It is not clear whether molecular or π complexes are involved in these reactions, nor how general for other reactants the isomerizations might be. The boron trifluoride catalyzed alkylation of benzene with optically active $[1,1,1\text{-}^2H_3]$-propan-2-ol proceeded with at least 93% racemization of the

alkyl groups and implied the formation of an almost free carbonium ion with no complexing at its stage of formation.[282] (1,1,1) complexes of aromatics with boron trifluoride and alkyl and acyl halides have been detected at low temperatures; these may be molecular complexes and decompose to σ complexes and products of ArSE2 on warming.[210, 283-285]

E. HYDROGEN EXCHANGE

The σ-complex route, eq 9, would be expected for this, the simplest of all aromatic substitutions, with the special conditions that both steps must be reversible and so generally a single rate-determining step cannot be pinpointed. Isotope exchange must be studied in order to follow the reaction and the usual technique has been to measure the rate of dedeuteration or detritiation of the aromatic, when, owing to the low concentration of tracer cations, the exchange is essentially irreversible. An alternative π-complex route, eq 10, has been proposed in which π_1 is converted into the σ complex, and the latter is subsequently converted into π_2 in slow and fast steps, respectively.[286, 287]

The π-complex route was proposed to account for the dependence on the Hammett h_0 function of exchange catalyzed by protic and Lewis acids, in regions of acidity where h_0 and pH diverge, for anisole, phenols, toluene, and other aromatics.[286-289] According to views accepted at the time, such correlations required a preequilibrium protonation of the substrate which was conceivable for the π-complex route (eq 10 with the first step at equilibrium), but not for the σ-complex route. A Hammett dependence is now considered to be also consistent with a kinetically slow irreversible step with extensive proton transfer from the acid to the substrate in the transition state[290] (section V.B) and considerable evidence against a π-complex route has been accumulated. This can be summarized as follows. (a) The rates of several exchanges, including those in azulenes and trimethoxybenzenes,[289, 291-293] were proportional to h_0 in certain acidity ranges but yet exhibit general acid catalysis in buffers at lower acidities. The latter observations indicate that the rate-determining step is the slow transfer of proton to substrate and a difference in mechanism in the different conditions seems unlikely. Proof of general acid catalysis is difficult in the moderately concentrated acids used in h_0 correlations, but 1,2-dimethoxybenzene exchanged threefold faster in sulfuric acid than in perchloric acid of the same h_0 value; and catalysis due to undissociated acid or particularly bisulfate ion was probable,[294] as it is well established that the latter species has a catalytic coefficient, derived from the Brønsted law, comparable with that of hydroxonium ion

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under similar conditions.[295] (b) General acid catalysis has also been demonstrated for exchange in other di- and trimethoxybenzenes and some methylindoles.[296-298] (c) Certain exchanges in substituted benzenes have curved h_0 plots or non-Hammett dependences,[288,299,300] which are considered to rule out π-complex routes.[301] (d) The relative reactivities of the *ortho* and *para* positions of alkylbenzenes toward different catalyzing acids varied markedly with the number and position of substituents and also with the activity of the undissociated acid, in a manner consistent only with the formation of σ complexes in a step involving slow proton transfer.[288,301,302] Finally, (e) the rate of proton transfer from concentrated acid to azulene has been directly measured[303] in a flow system and, after necessary corrections were made for medium, isotopic, and statistical effects, was found to agree with the value derived from tritium exchange data calculated on the basis of eq 9.

The demonstration of a slow proton transfer rules out the preequilibrium formation of a π complex, but fits well[296,298] the classical ArSE2 mechanism, eq 9. Slow proton transfer to give a π complex of the nonlocalized type has been considered unlikely[286,287] and is inconsistent with the excellent correlations established between exchange of a variety of substrates and both the stability constants for σ complexes formed by protonation with hydrogen fluoride[288] and the rates of chlorination,[227] the latter reaction being reasonably considered (section VI.B) to proceed by a σ-complex route. The currently accepted view is that eq 9 describes hydrogen exchange as it does other aromatic substitutions. It has been suggested that an increase in either acidity of the reaction media or in reactivity of the substrate could lead to a π-complex route,[304,305] but such a situation has not been achieved in practice.

The more rapid detritiation of [o-³H]-p-cresol in deuterium oxide than in water of the same acidity by a factor of 1.6 and the profile of the variation of rate of the same compound in differing mixtures of the two solvents[306] is not that expected for the σ-complex mechanism, but the significance of this in view of the amassed contrary data is unclear, and doubt has been expressed concerning the general validity of mechanistic conclusions that are drawn from rate measurements in isotopically mixed solvents.[295] The detritiation of [o-³H]-p-xylene is slower in deuterium oxide than in water.[307]

F. MISCELLANEOUS ELECTROPHILIC SUBSTITUTIONS

Nitrosations effected by nitrosonium salts, NO^+X^-, in dipolar aprotic solvents, *i.e.*, in conditions similar to those leading to the alleged π-complex mechanisms in nitration, obey the selectivity relationship and show kinetic isotope effects

($k_H/k_D = 1.9$–3.6) that are entirely consistent with a σ-complex route in which proton loss is kinetically significant.[230,308] However, substituent effects on the nitrosation step of diazotization of amines at moderate acidities have been interpreted as showing the formation of an unspecified (covalent or molecular) π complex followed by migration of the nitrosonium ion to the amino group;[309] the detailed data cannot accommodate direct SE2 attack on the amino group. The range of this mechanism is bounded at low acidities by the much faster conventional reaction *via* a free amine and at high acidities by the low mobility of the protons of the amino group. The colored intermediates observed in the reaction of nitrosulfuric acid with aromatic hydrocarbons and phenols have been assigned as π complexes, $ArNO^+$ and Ar_2NO^+, on the basis of spectral studies.[310] These species were rapidly decomposed by water to liberate the starting materials and were undoubtedly molecular complexes. π complexes have also been postulated for sulfonations[311] but the dependence of rate on the activity of sulfur trioxide favored σ-complex routes,[226,312,313] and in line with the general evidence for ArSE2, their reactions are now generally considered to follow the latter routes.

Metalations might reasonably be expected to proceed through π-complex mechanisms, as the electrophiles usually have filled d orbitals capable of back-donation, although the actual atom hybridization in any particular case is often obscure, but there is no evidence for such routes.[226] Mercuration has been the best studied,[314] and this obeys the selectivity relationship and for one example, at least, exhibits a large kinetic isotope effect ($k_H/k_D = 6.0$). π complexes have been opined to intervene in the positional rearrangements of *p*-alkylmercuric acetates but no evidence has been produced to support this view.[314]

Protodeboronation of *p*-mercuroxybenzeneborinic acid was slower in deuterium oxide than in water, exhibited general acid catalysis, and so was assigned a σ-complex route despite a good correlation of rate with h_0 that at the time was considered to be inconsistent with this mechanism.[315] Protodeacylation[316] and protodeiodination[317,318] of other aromatics showed similar kinetic characteristics and undoubtedly followed the same mechanism. Protodesulfonation showed an h_0 dependence and was conversely considered to follow a π-complex route,[311] but the acceptance of the σ-complex alternative in the reverse sulfonation in addition to the other circumstantial evidence makes this unlikely. σ-Complex routes are also very probable for the acid cleavages of aryl silicon, germanium, tin, and lead compounds.[319] Rate data for iododestanylation of several compounds favor formation of a nonlocalized π complex in the rate-determining step, presumably as a result of the capacity of iodine to use d orbitals in back-donation, followed

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by formation of a localized π complex and the bond reorganizations shown in eq 15. The details of the kinetics are inconsistent with any other route.[320] The only other important candidate for a π-complex mechanism in ArSE2 is the substitution

(15)
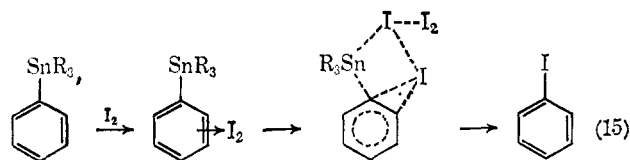
didate for a π-complex mechanism in ArSE2 is the substitution of the solvent that takes place on thermal decomposition of benzene 1,4-diazooxide: this reaction has a low substrate but high positional selectivity akin to that met with in nitration.[321]

G. NUCLEOPHILIC SUBSTITUTION

Aromatic compounds that are activated by nitro or other electron-withdrawing groups are predisposed to undergo nucleophilic displacement of a suitably situated leaving group and also to form molecular complexes with electron donors. However, the participation of the latter complexes in the course of the former reactions usually seems unimportant. Although the molecular complexes are logical intermediates for substitution they are not obligatory,[322,323] and several nmr studies have shown that although highly colored complexes (showing contact charge-transfer spectra) may be formed in reaction mixtures, they are not kinetically significant intermediates, this role being taken by σ complexes of the so-called Meisenheimer type.[324–326] An elegant study of the reaction of tetracyanoethylene with dimethylaniline,[327] which is a model for its kind, has dissected the mechanism in terms of σ and π complexes, but the latter were of the rapidly, reversibly formed type and must be molecular complexes.

The evidence for molecular complexes in these reactions and the influence of complexing by added aromatics on aliphatic nucleophilic reactions has been admirably reviewed.[10] All the data can be interpreted in terms of such complexes. There is no role to be ascribed to π complexes.

VII. π Complexes in Aromatic Rearrangements

It has been repeatedly claimed[4–7] that only π-complex routes can account for the intramolecularity and for details of products and kinetics of a variety of aromatic rearrangements. This assertion is invalid.

A. BENZIDINE REARRANGEMENT

This celebrated reaction will be discussed at length for two reasons. First, its interpretation in terms of π complexes was the first application of Dewar's theory[3] and has been claimed to be the greatest triumph of that theory.[6] Secondly, this rearrangement is one of the few reactions where an extensive series of predictions differing from those of rival theories

concerning kinetic form, relative rates, and nature of products can be made on the basis of the π-complex theory and put to the test of experiment.

The rearrangement, which is actually a family of reactions, can be formulated as eq 16; the benzene rings can be substituted and naphthalene or heterocyclic rings may be present in the hydrazo compound. The main products are p-benzidines (44), diphenylines (45), o-semidines (46), and p-semidines (47), together with azo compounds and fission amines (the products

(16)
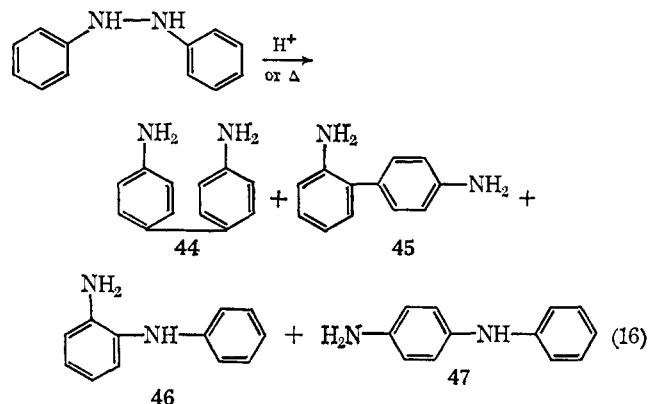
of disproportionation), although all types are not usually formed in quantity from any particular example.[328] Rearrangements of several substrates have been shown to be strictly intramolecular for both acid- and thermal-catalyzed rearrangements,[329,330] and in this the benzidine and nitroamine rearrangements (section VII.B) share a unique place among aromatic rearrangements.

Most studies have concerned the acid-catalyzed reaction. Here the π-complex theory supposes that the N–N bond in the protonated substrate heterolyzes and is replaced by a delocalized molecular bond between the rings which holds them in parallel planes with the possibility of mutual rotation, eq 17. The highest filled orbital of the aniline moiety acts as a donor and the corresponding empty molecular orbital of the

(17)
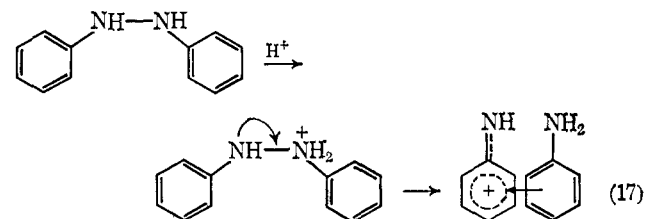
other as an acceptor to give good overlap, as the orbitals are similar in shape. Products follow from replacement on the molecular bond by a localized interatomic σ bond which, in some cases, is formed after rotation of the components of the complex and leads to diphenylines or semidines. This theory is superficially very attractive, particularly as it accounts for the strict intramolecularity of a reaction that requires an unprecedented convolution of the original molecular geometry. Unfortunately, it fails to accommodate the experimental facts that have been accumulated over the past decade.

Application of π-complex theory was originally based on the preconception that the rearrangement was always first order

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in acid. The discovery that the parent hydrazobenzene and several derivatives underwent reactions that were second order in acid[328,331] whereas 2,2'-dimethylhydrazobenzene showed transitional kinetics with an order of 1.6 over a small range of acidity[332] proved an embarrassment to the theory, as diprotonated π complexes had been deemed unlikely. Consequently the theory was adapted as in eq 18, where B is substrate, π is a π complex, and P represents products. Application of the steady-state approximation to π gave a rate (eq 19, where a and b are constants) that allows the extremes of

$$B + H^+ \underset{t}{\rightleftharpoons} BH^+ \underset{s}{\rightleftharpoons} \pi \xrightarrow{H^+} P \qquad (18)$$
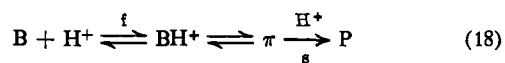
$$\frac{-d(B)}{dt} = \frac{a(B)(H^+)^2}{1 + b(H^+)} \qquad (19)$$

$$\frac{-d(B)}{dt} = k_2(H^+)(B) + k_3(H^+)^2(B) \qquad (20)$$

first- or second-order dependence on acid or transitional kinetics, depending on the size of b. Equation 18 requires rate-determining transfer of a proton to break up the π complex. This is inconsistent with both the specific acid catalysis and the solvent isotope effects, k_{D_2O}/k_{H_2O}, of $ca.$ 4, 3, and 2 for two-proton, transitional, and one-proton mechanisms, respectively, that have now been observed for several substrates.[333] A more crucial failure of the π-complex mechanism is its prediction that for reactions exhibiting transitional kinetics the order in acid should change from 2 to 1 as the acidity is increased. In the event, all such reactions that have been investigated[333,334] showed the opposite trend and the rate eq 20 was quantitatively obeyed for a plot of $-d(B)/dt$ $vs.$ H$^+$ was linear in (H$^+$). This latter rate law corresponds to the coexistence of a pair of independent mechanisms, one first order and the other second order in acid.

π-Complex theory also fails to accommodate three other groups of kinetic observations. (a) When the adjustments were introduced to allow for the second catalytic proton, it was pointed out[101] that whereas formation of p-benzidines should be second order in acid, that of semidines should be linear, because nonproton-assisted rotation of the initially formed complex would have to be faster than proton-assisted breakdown of the same complex. Contrary to this prediction semidine formation is second order in several examples and always has the same kinetic form as the accompanying reactions, leading to the products of rearrangement or disproportionation from the same substrate.[334] An analogous, but unnoticed discrepancy between prediction and experiment at this time was the identical kinetic form for formation of p-benzidine and diphenyline from hydrazobenzene itself; since the latter is supposed to originate from a rotated π complex it should also follow one-proton kinetics, whereas it followed the two-proton mechanism characteristic of benzidine formation.[331,333] (b) Any π complex formed from the three isomeric hydrazonaphthalenes should be more stable than the corresponding

species from hydrazobenzene. This follows from rough calculations[44] and experimental data for metal ion and halogen complexes.[2,9] Consequently, if rearrangement of hydrazobenzene is induced by attack by a proton on a π complex, as is postulated to account for the two-proton kinetics, the naphthyl compounds should require the second catalytic proton even more strongly, whereas they reacted much more readily and followed one-proton kinetics.[333] (c) The one-proton or transitional kinetics found for various 4,4'-disubstituted hydrazobenzenes have been attributed to bulky substituents interfering with the developing π complex and causing its components to rotate into a more sterically favorable relative orientation.[7] Specific examples of this effect were claimed for 4-chloro-4'-t-butyl- and 4-methyl-4'-chlorohydrazobenzenes, which had kinetic orders of 1.5 to 1.6 in acid over unspecified ranges of acidity,[335] but a previously recorded[336] quadratic dependence on acidity of the rearrangement of the equally hindered 4,4'-dimethylhydrazobenzene was overlooked. Recently, the 4-chloro-4'-t-butyl compound has been reinvestigated and shown to follow approximately two-proton kinetics in the range studied.[337] The corresponding di-t-butyl compound, which should be an outstanding example of one-proton kinetics on the π-complex theory, was also found to have the same kinetic form.[337]

The transition states of formation and decompositions of the postulated π complexes have never been defined, and assumptions could still be built into the theory to account for the extensive data on salt and solvent effects that have been reported.[333]

The π-complex theory is no more successful in accommodating the products of rearrangement. Thus, (a) a literature survey led to the proposal[4,5] of a set of rules for predicting products from variously substituted hydrazo compounds which were claimed only to be consistent with the π-complex theory. A detailed reappraisal of this claim in the light of all the available data has shown that there is no observational basis for the rules.[333] Nevertheless, it is persistently stated that the "Dewar rules" describe the experimental situation.[7] (b) The π-complex mechanism cannot account for the products from hydrazo compounds with one benzo and one naphtho residue. The explanation proposed[4,5,7] for the predominance of 2,2'- and 4,4'-linked products from hydrazonaphthalenes required a locking effect of extended π orbitals preventing relative rotation of the rings, unlike the situation for hydrazobenzenes, where overlap between only two benzene rings takes place and free rotation is possible. Thus when one naphthalene ring is replaced by a benzene group the possibility of free rotation should be introduced; however, the pattern of products found in the hydrazonaphthalenes persists.[333] (c) One of the firmest props of the π-complex mechanism is the claimed lack of rearrangement products from 4,4'-diphenylhydrazobenzene,[338] which is attributed[5,7] to steric interactions between the extended π orbitals, preventing complexing and thus rearrangement, but permitting disproportionation. This was contrasted to the entirely normal rearrangement of the 2,2'-diphenyl isomer where such steric control was absent. Reinvestigation of the former compound has shown that about 20% rearrangement does occur under the usual reaction con-

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ditions,[339] this proportion being not atypical for 4,4'-disub-stituted substrates.[334] (d) Claims that colored salts, which were observed and isolated on treatment of hydrazo compounds with acids in aprotic media, were π complexes[4] have been disproved.[328] These species are mixtures of disproportionation and rearrangement products, and N-protonated substrates. Finally, (e) a specific test was devised by isolating unreacted 3,3'-diaminohydrazobenzene initially labeled with ^{15}N in the hydrazo groups after 50% reaction. Rotation within a π complex would have led to scrambling of the tracer between the hydrazo and amino groups, but none was detected.[340]

Recently this theory has been adapted in an attempt to incorporate two-proton kinetics without introducing general acid catalysis.[7] Now a diprotonated π complex was introduced, despite previous categorical statements[6] that such a species could not be formed, but that the monoprotonated π complex would rearrange on the approach of the second proton.[5,6,45] This change reduces the theory to a tenuous description of little predictive value. The contrary evidence notwithstanding, the π-complex mechanism persists and has been postulated for recently investigated rearrangements and disproportionations.[337,340,341] The intermediate formation of a novel type of π complex, with one catalytic proton sandwiched between and holding together the two aromatic rings of a rearranging hydrazo compound,[342] has been soundly criticized as being unphysical and being unable to accommodate the observed kinetics and products.[7]

An alternative theory of the rearrangement, a so-called polar-transition-state theory, has been proposed[333] that meets the challenge of the available data on the basis of essentially σ-complex routes. It is not disputed that some van der Waals or other weak interactions can occur between the rings during rearrangement, but it is very clear that such species have no consequences as to products or kinetics, and it does not seem profitable to speculate on their existence. This mechanism can also be readily extended to the thermal (or no-proton) rearrangement, whereas the π-complex mechanism appears conceptually unable to deal with this situation.[333]

Two acid-catalyzed rearrangements closely related to the benzidine rearrangement are those of p-quinamines to p-aminodiphenyl ethers[343] and of O,N-diarylhydroxylamines to p-hydroxy-p'-aminobiaryls.[344] These are probably intramolecular and have been assigned π-complex mechanisms, but with no supporting evidence.

The mechanism of the disproportionation sometimes accompanying the benzidine rearrangement is less well understood, although the kinetic form suggests that the two types of reactions share a common rate-determining step.[334] The first-order dependence on substrate invalidates the opinion[4] that this step is the reaction of a protonated π complex with a neutral hydrazo molecule. A mechanism in which disproportionation arises from bifurcation of the route to rearrangement at certain σ-complex intermediates seems likely.[334]

B. NITROAMINE REARRANGEMENT

The acid-catalyzed conversions of N-nitroarylamines into o- and p-nitroarylamines (eq 21) is also intramolecular over a wide range of acidities and conditions and has been re-

$$\text{(21)}$$
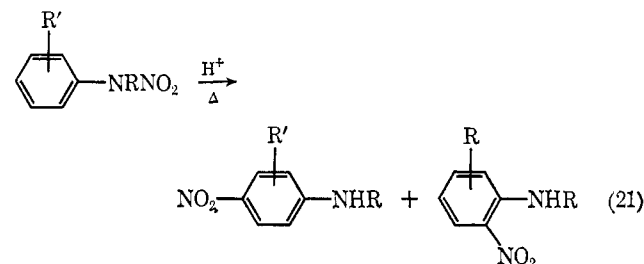
peatedly quoted as an example of a π-complex mechanism.[4–7] The protonated substrate that is formed in preequilibrium is supposed to heterolyze to incipient nitronium ion and amine which form a π complex within which the nitro group migrates without becoming kinetically free.

No evidence has been produced to support this hypothesis, but several different sets of data refute it. Thus, (a) the rates of reaction of a series of para-substituted N-methyl-N-nitroanilines showed a good correlation with the σ^+ values of the substituents, ρ −3.9, and so, under these reaction conditions the amino nitrogen becomes electron deficient in the transition state and fission to incipient nitrite ion rather than nitronium ion, must occur.[345] (b) This direction of heterolysis appears universal as nitrous acid, diazonium ions, quinones, and imines were formed as side products of several rearrangements, but nitrate ion that would result from scission to nitronium ion has never been found.[346,347] (c) The π complex is believed to collapse to form σ complexes identical with those typically formed in aromatic nitration en route to products,[6] so the effect of ring deuteration on the proportions of ortho and para products should be similar in the two types of reactions. In fact, although such effects have never been detected in the latter reaction, primary isotope effects were found for rearrangement,[346,347] and can be interpreted by a mechanism that bypasses both σ and π intermediates and leads to concerted bond making and breaking at the site of substitution. And (d) a π-complex route would be expected to lead to considerable, perhaps predominant, meta substitution or to migration into the unsubstituted ring of N-nitronaphthylamines, especially at high acidities. Rigorous chromatographic screening of products from several types of substrate did not detect these products; 2 and 4 isomers only were formed as were expected from the alternative (vide supra) route.[346,347]

A major conceptual shortcoming of the π-complex mechanism is that if it is proposed to account for the strictly intramolecular rearrangements of nitroamines there is no reason why the acid-catalyzed rearrangements of N-halogenoamines, N-phenylhydroxylamines, and N-nitrosoamines should not follow suit, and indeed they were specifically claimed to do so.[4] However, all these reactions are essentially completely intermolecular (cf. section VII.D) under typical experimental conditions. The non-π-complex mechanisms that have been proposed for the benzidine and nitroamine rearrangements[333,346]

(339) H. J. Shine and J. P. Stanley, Chem. Commun., 294 (1965).
(340) G. S. Hammond and J. S. Clovis, J. Org. Chem., 28, 3283 (1963).
(341) J. Kenner, Nature, 219, 153 (1968).
(342) L. L. Ferstandig, Tetrahedron Lett., 1235 (1963).
(343) B. Miller, J. Amer. Chem. Soc., 86, 1127 (1964).
(344) J. R. Cox and M. F. Dunn, Tetrahedron Lett., 985 (1963).

(345) W. N. White, J. R. Klink, D. Lazdins, C. Hathaway, J. T. Golden, and H. S. White, J. Amer. Chem. Soc., 83, 2024 (1961).
(346) D. V. Banthorpe, E. D. Hughes, and D. L. H. Williams, J. Chem. Soc., 5349 (1964).
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are unique on account of the structure of the migrating groups in the two cases, and similar mechanisms would not be expected to apply to the other rearrangements.

C. OTHER INTRAMOLECULAR REARRANGEMENTS

Only the benzidine and nitroamine rearrangements have been proved to be intramolecular over a wide range of conditions using several different criteria. Several others have been considered to be so on minimal evidence.[348] These can be conveniently itemized.

(1) π-Complex mechanisms have been suggested for the rearrangement of alkyl aromatics promoted by mixtures of protonic aids and Lewis acids under conditions similar to those of Friedel–Crafts reactions, e.g., the hydrogen fluoride–boron trifluoride catalyzed conversion of p-xylene into the meta isomer[349] and the migration of the alkyl group of o-fluoro-isopropylbenzene on treatment with hydrogen chloride and aluminum trichloride.[350] Analysis of the rate of passage of tracer into the various ring positions of several compounds showed that a series of 1,2 shifts rather than random migration occurred,[351,352] the only rearrangement product from 1-^{14}C-methylnaphthalene, for example, being the 1-[14]-C-2-methyl isomer.[353] Nonlocalized π complexes are consequently excluded but localized complexes have been proposed.[348] Intermolecular cross alkylation, e.g., the formation of benzene and dialkylbenzene from monoalkylbenzene, often with rearrangement of the transferred group, has also been assigned to π-complex routes.[348] In eq 22, tracer labeling (denoted by an asterisk) of the n-propyl group revealed that after treatment with acid the proportions of 48, 49, 50, and 51 were

(22)

(23)
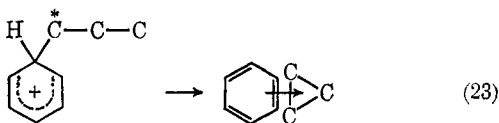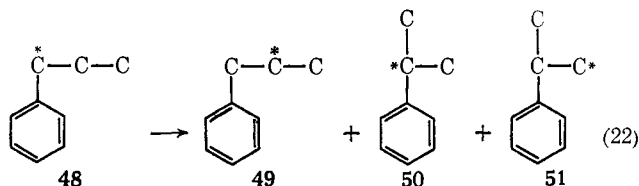
49, 48, 1.5, and 1.5%, and a σ → π interconversion, eq 23, was proposed to lead to the rearrangement;[354] however, it was not explained why isopropylbenzene was not preferentially formed from this π complex. Migratory aptitudes for similar claimed intramolecular shifts fell in the order, Me > Et > i-Pr > t-Bu, which was the reverse of the tendency for intermolecular group migration and for the stability of free ions;[355]

such trends were considered to indicate π-complex rather than σ-complex routes.

Most of the scattered available data,[348] only a fragment of which can be mentioned here, can be equally well rationalized on π-complex routes or by 1,2 shifts to form a sequence of σ complexes or, for intermolecular alkylation, by the formation of kinetically free ions or of incipient ions in molecular aggregates, followed by ArSe2 of the classical type. Too little evidence is available to infer the outline of these mechanisms, let alone to elucidate the fine distinctions between π- and σ-complex routes. Indeed, recent tracer studies of intermolecular alkylation had led to a mechanism, which may have general validity, that dispenses with σ or π complexes altogether.[294,356]

(2) Closely related to the above is the Jacobson rearrangement, whereby alkyl aromatics (especially tetrasubstituted benzenes) are warmed with concentrated sulfuric acid to form a sulfonic acid which decomposes to a rearranged hydrocarbon on dilution and heating. This last step is a consequence of the general reversibility of sulfonation. The only "acceptable" mechanism has been claimed[6,357] to involve the formation of a π complex, as eq 24, but a σ-complex route with 1,2 shifts to give an intermediate product with minimum steric crowding

(24)
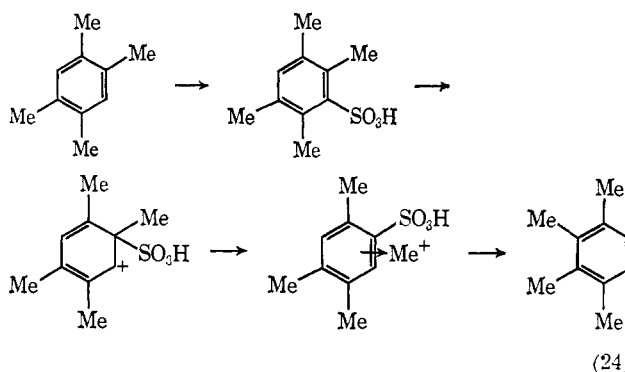
about the sulfonic acid group is highly probable.[348,358] Intramolecular migration of the sulfonic acid group in alkylsulfonic acids may follow similar pathways;[359,360] if a π-complex route were used a symmetrically situated migrating group may be formed with d–π overlap that permits direct 1 → 4 migration. A recent proposal bypasses π- or σ-complex routes for the Jacobson rearrangement in favor of isomerization of cation radicals,[361] but the generality and validity of this is not clear.

(3) Both π- and σ-complex routes have been proposed for the acid-promoted rearrangements of halogeno aromatics, such as the interconversions of dihalobenzenes.[362–364] Bromine shows a propensity for 1 → 4 shifts, perhaps via a direct span in a symmetrical π complex, but an intermolecular mechanism remains very probable. The Reverdin rearrangement,[365] e.g., the formation of 1-methoxy-2-iodo-4-nitrobenzene from nitra-

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(362) G. A. Olah and M. W. Meyer, J. Org. Chem., 27, 3464 (1962).

(363) G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, ibid., 27, 3441 (1962).

(364) G. J. P. Augustijn, E. C. Kooyman, and R. Louw, Rec. Trav. Chim. Pays-Bas, 82, 965 (1963).

(365) D. V. Nightingale, Chem. Rev., 40, 117 (1947).

tion of p-iodoanisole, has also been considered to follow a π-complex route.[6,7] This reaction is completely analogous to the Jacobson rearrangement, but here iodine migrates, rather than an alkyl group, and the added electrophile is not removed on work-up. The same possibility of 1,2 shifts between σ complexes is open. Some details of mechanism cannot be satisfactorily explained on either π- or σ-complex routes, and it is possible that intermolecular routes may intrude or even predominate.

(4) Claims and counter-claims for π- and σ-complex routes have been made for a variety of other acid-catalyzed and a few thermally induced rearrangements. A selection includes the methyl shifts accompanying the Fischer indole synthesis,[6] the Fries rearrangement of aryl esters to *ortho* and *para*-acylated phenols,[366] the conversion of aryl alkyl ethers to alkylated phenols,[5,6,367] the dienone–phenol rearrangement[6] and the similar reaction of quinols and their esters,[368] and the conversion of the alkali salts of o-phthalic acid to those of *meta* and *para* acids.[348,369] Few details are available for any of these reactions, their intramolecularity is usually in doubt, and their mechanism is obscure. If they are indeed intramolecular, σ-complex routes are equally, perhaps more, probable. Suggested π-complex routes[6] for the thermal Claisen rearrangement of allyl aryl ethers to o- and p-allylphenols and analogous reactions where sulfur and nitrogen replace oxygen have been definitely ruled out in favor of cyclic six-membered transition states that lead to *para*-linked products *via ortho* migration, with the formation of dienone intermediates.[348,370]

D. INTERMOLECULAR REARRANGEMENTS

An important group of acid-catalyzed rearrangements involves the formal migration of a cation, eq 25. When this cation was a relatively stable species, *e.g.*, in the diazoamino-

$$(25)$$

o and *p*
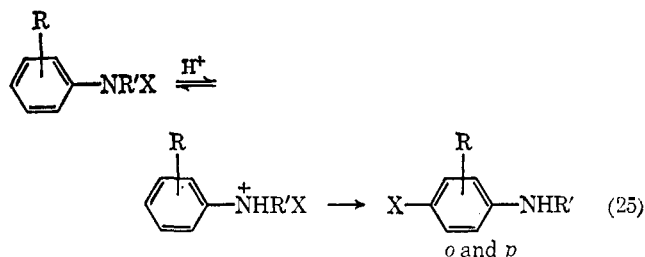
benzene rearrangement (R′ = H; X = N₂Ar), an intermolecular pathway was proposed.[4] But when it was reactive, as in the Hofmann–Martius rearrangement (R′ = alkyl, H; X = alkyl), the Fischer–Hepp rearrangement (R = alkyl; X = NO), the Orton rearrangement (R = acyl; X = hal), and the phenylhydroxylamine rearrangement (R = alkyl, H; X = OH), heterolysis was proposed to lead smoothly to a π complex and thence to intramolecular rearrangement. Various arguments were adduced in favor of this mechanism; thus, the π route was supposed to explain the alleged lack of that polyalkylation in the Hofmann–Martius reaction which was claimed to be expected on an intermolecular route, due to the activating effects of the alkyl group on benzenoid reactivity.[4]

In fact, polyalkylation *does* occur to some extent,[371] but probably does not predominate in these processes, because the most reactive *para* position is blocked first, and the *ortho* positions, probably for steric reasons, are much less susceptible to attack.

It was generally agreed by most workers at the time of the above proposals that these rearrangements, especially when carried out in protic media, were strictly intermolecular; *i.e.*, fission to an aromatic fragment and a kinetically free electrophile was followed by recombination, and so the question of π complexes could only have arisen in the final ArSE2 step.

The mechanisms of those reactions that have been studied in aprotic media are more obscure. The Orton rearrangement is promoted by carboxylic acids in chlorobenzene and an intramolecular π-complex route was proposed[4,372] to accommodate the observation that free halogen could not be detected in quantities sufficient to sustain the observed rates. Kinetic evidence for intermolecularity with O-halogenated acid species as the halogen carrier has, however, been offered,[373,374] and the π-complex mechanism cannot account for the very ready isomerizations of 2,6-disubstituted N-bromoacetanilides, as the extension of the π orbitals to the amino nitrogen would here have been sterically inhibited.[375] More recent tracer studies of the concurrent rearrangements of two N-bromoacetanilides in aprotic media suggest that cations occur in aggregates consisting of brominating agent, bromine acceptor, and acid catalyst and no role is assigned to π complexes.[5,376] Molecular complexes have been proposed as mechanistically significant intermediates in the thermal Ladenburg rearrangement of N-alkylpyridinium iodide,[377] but it is difficult to see how these low-energy species can have the influence claimed.

VIII. π Complexes in Radical Reactions

A. GENERAL

A description of radicals as π complexes is much less attractive than that of carbonium ions, as the extra electron must occupy a nonbonding molecular orbital of high energy. Nevertheless, early proposals were that radicals from organic peroxides could be so described,[4] but this view was neither developed nor accepted. Hexaphenylethane forms numerous colorless complexes with ethers, nitriles, esters, carbon disulfide, etc., usually 1:1 in stoichiometry, but these are probably not complexed radicals, as is often assumed, but crystal lattice compounds;[378] and the solid complexes of diphenylpicrylhydrazyl and α,γ-bisdiphenylene-β-phenylallyl radical with benzene,[379,380] which are more stable than the uncomplexed radicals, are probably similar. The dimer, formed from Würster's blue perchlorate at −80 to −180° and detected by measurements of magnetic susceptibility,[381] has been widely quoted as a radical π complex. This shows a strong charge-transfer band in the visible and is probably indistinguishable

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(367) M. J. S. Dewar and N. A. Puttnam, *J. Chem. Soc.*, 4086, 4090 (1959).

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from a molecular complex, for radical complexes in general must lie in the borderline region where distinction between π and molecular complexes cannot be drawn. Spectral and magnetic properties of N-ethylphenazyl at low temperatures are similar and have been similarly interpreted.[381]

B. AROMATIC SUBSTITUTION

These reactions have been rarely discussed in terms of radical π complexes, and reactivity has generally been correlated with the free valence index or the localization energies of σ complexes. A "π-extension" model has been developed[43] for the radical methylation of benzene (and also for the radical copolymerization of olefins); this incorporates some of the ideas of π-complex theory, but is a computational device rather than a structural proposal.

The phenylation of toluene[382] has been claimed to involve a complex with a π–π bond that is presumably equivalent to a π-complex intermediate, which leads to a mixture of methylbiphenyls, whereas at higher temperatures such complexing is considered unfavored and bibenzyl results. Phenylation of benzene with benzoyl peroxide[383] gives an enhanced yield of products if minute traces of transition metal salts are present; under the same conditions substituted benzenes also gave high yields, but as there was no significant change in the ratio of isomeric products in the presence or absence of the metal salts, it was argued that there was no formation of a radical π complex, the oxidation of which to a cation π complex by electron transfer to the metal ion would have led to a different isomer distribution from that for the uncatalyzed reaction, i.e., one typical of electrophilic substitution. The incidence of radical π complex cannot, however, be similarly dismissed for other radical substitutions,[384] and it may be significant that traces of transition metal ions are often required for hydroxylations,[385] although esr data are consistent with radical hydroxylation proceeding through a σ complex.[386] The status of the few claims for π-complex routes is doubtful, although several loose complexes have been reported,[387] and the consensus is that such routes are unimportant.[388,389]

Different positional selectivities for free radical chlorination of aliphatic hydrocarbons were found in aromatic and aliphatic solvents,[390,391] and these were reasonably attributed to π complexing in the former media with consequent deactivation of the reagent. The weak nature of the complexing was indicated by the lack of substitution of the solvent, nor was there correlation of the solvent effect with the reactivity of the aromatic in phenylations considered almost certainly to proceed through σ complexes. There was a good correlation between the ability of the solvent to complex with the radical reagent and its stability in a molecular complex with hydrogen chloride. Similar, but generally smaller, solvent effects on reactivity are reported for the additions of hydrogen bromide

and iodofluoroform to a series of olefins in aromatic solvents[392] and for other additions in certain ethereal and alcoholic media.[393]

C. ADDITION TO UNSATURATED SYSTEMS

Several homolytic additions of bromine to olefins were anti stereospecific,[394] as was that of hydrogen bromide to the isomeric 2-bromobut-2-enes and 2-butenes at $-78°$. For the latter reactions the stereospecificity fell rapidly with increasing temperature, and at room temperature both cis and trans isomers gave the same product mixture.[395,396] Addition of hydrogen bromide and bromochloroform to other acyclics at room temperature were also nonstereospecific,[397,398] whereas addition of hydrogen bromide to substituted cyclohexenes at $-80°$ were anti stereospecific.[396,399]

Three explanations have been proposed for the anti stereospecificity. (a) Bridged radicals similar to the cyclic ions postulated in heterolytic addition that can be considered practically equivalent to π complexes may occur. Such complexes would be much less stable than their cationic counterparts and would only exist at low temperatures, but would lead to anti addition for the same reasons.[396,400,401] Objections have been made to the expansion of the valence octet in these complexes,[402] but on the molecular orbital description suitable orbitals, albeit of a high-energy kind, can be provided to accommodate the "extra" electron. (b) For addition of hydrogen bromide, a π complex is supposed to be formed between the olefin and the undissociated acid, with the result that addition of a bromine atom is directed to the other side to form a radical which then collapses with abstraction of hydrogen from the complexed acid to result in anti addition. This mechanism has, however, been rejected.[399] When the reaction is conducted in the presence of a large molar excess of ether the stereospecificity is unimpaired, whereas this additive should break up any π complex by preferentially bonding to undissociated acid. (c) For the addition of bromine or hydrogen bromide, atomic bromine was considered to add to form an open classical radical that abstracted hydrogen or bromine, respectively, before rotation, so that the newly acquired atom was added in the most sterically favored fashion on the far side of the molecule from the first added.[394] As hydrogen bromide is a particularly good chain-transfer agent in radical reactions it is very reasonable that radicals generated in its presence would rapidly abstract hydrogen, but that at higher temperatures rotation could be faster and the anti stereospecificity would disappear. Methanethiol is a less efficient chain-transfer agent and cannot sustain anti addition; thus its addition to but-2-enes and cyclohexenes is nonstereospecific even at $-70°$. Addition of a mixture of the thiol and hydrogen bromide gives

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(398) P. S. Skell and R. G. Allen, ibid., 81, 5383 (1959).
(399) H. L. Goering and L. L. Sims, ibid., 77, 3465 (1955).
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(401) C. Walling and E. S. Huyser, Org. React., 13, 91 (1963).
(402) J. I. G. Cadogan and M. J. Perkins in "Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, p 585.

anti addition, presumably due to the acid acting as a chain-transfer agent following initial addition of a thiol radical.[398,403] Steric control of addition can similarly account for the *anti* stereospecificity for other reagents and substrates.[404–410]

π complexes have rarely been mentioned in context with addition of other halogens, although their occurrence as intermediates to account for both the induction period and the distribution of products from the iodination of styrene has been proposed.[411] The decomposition of acetyl peroxide in cyclohexene to yield a mixture of cyclohexyl mono- and diacetate has been considered to involve a π-complex route, and in support it was shown that the efficiency of competition for acetoxy radicals by several added olefins correlated with their so-called π basicity,[412] but it is not clear whether this is a unique interpretation. A general survey of related additions led to the conclusion of nonstereospecific addition to form an open radical.[401]

The only physical evidence for what are claimed to be radical π complexes is that derived from esr of the products of addition of hydrogen bromide to a number of symmetrically substituted olefins at −196°; symmetrical radicals were inferred,[413] whereas unsymmetrically substituted olefins did not give the same type of spectrum and the nature of the complex was unclear. Molecular complexes held by van der Waals interactions may well have been observed. As previously pointed out, distinction between the classes of π and molecular complexes must be blurred when radicals are considered.

D. MISCELLANEOUS

Radical polymerizations of olefins, induced by heavy metals, *e.g.*, silver and mercuric ions, have been claimed to follow π-complex routes,[414] but although many examples are known of potentially polymerizable olefins complexing with Lewis acids, as shown by spectroscopic studies, there is no good reason to suppose them capable of initiating a chain process. In dry solvents such complexes appear stable for long periods and polymerization, presumably of a heterolytic nature, is only initiated on addition of traces of water.[415]

1,2 shifts in radicals can be regarded as passing through π complexes, where the latter have the status of transition states, but (*cf.* section II.B) it is unlikely that such complexes are intermediates. There is no evidence for 1,2 shifts of hydrogen,[416] and although such shifts of alkyl groups are known, the intermediate formation of open radicals is likely.[417,418]

IX. Conclusions

Organic complexes can be conveniently grouped into two classes, molecular complexes held by van der Waals forces and π complexes involving molecular covalent bonds, usually of the π–p type, between the adducts. Despite their wide currency, charge-transfer forces are probably of little consequence in stabilizing the former type. Usually a fairly clear distinction can be drawn between molecular and π complexes, although they have often been considered synonymous in mechanistic discussions.

Many organometallic compounds possess molecular bonds with the π–p bonding supplemented by π*–d or similar overlap, but there is no evidence for analogous bonding of either type in stable organic molecules. Although π complexes are undoubtedly intermediates in many organometallic reactions, including formally organic processes catalyzed by metal ions, their occurrence as transient intermediates in purely organic reactions, in which efficient back-donation of the π*–d type is either not possible or is ineffective due to the sizes of the interacting orbitals, has been the subject of much dispute. π complexes have been vigorously and repeatedly advocated to be reaction intermediates in a wide range of such processes, but, unfortunately, π-complex mechanisms usually have no consequences as to kinetics and products that differ from those of conventional mechanisms; consequently, tests of the theory are generally not possible. In addition, molecular orbital theory at its present state of development is too primitive to allow meaningful conclusions to be drawn concerning the proposed mechanisms.

The following main conclusions can be inferred concerning the role of π complexes in organic reactions. (a) Nonclassical carbonium ions may be reasonably formulated as π complexes, and any differences between the well-established cyclic phenonium ions and the oft-proposed cyclic halogenonium ions and the respective π-complex descriptions of the same species must be small; for most purposes the two formulations can be considered equivalent. It is only for these types of cations that any consistent physical evidence can be obtained that can be interpreted, however tenuously, and with extrapolations to different conditions, to support the existence of π complexes as reaction intermediates. Nevertheless, there appears to be no particular advantage in adopting the π-complex formation, rather than the conventionally accepted descriptions of any of these cations.

(b) There is no evidence that open classical carbonium ions, whether formed in substitution, elimination, deamination, or aliphatic rearrangements, can exist as π complexes. Certain physical and chemical observations have been adduced to favor these complexes, but alternative interpretations are always possible and usually are more probable. All the data can be systematically and satisfactorily interpreted in terms of conventional open ionic intermediates.

(c) Analysis of rate and product data often allows π-complex routes to be definitely excluded in aromatic substitution, and no physical evidence has been obtained, despite extensive search, that requires the postulation or accumulation of π complexes during these reactions. The chemical evidence for the route in a particular iodostannylation seems reasonable, but there is considerable controversy as to the experimental design and the interpretation of the results of the few nitrations and Friedel–Crafts alkylations that appear, on the basis of chemical evidence, to involve π-complex routes. Judgment on this must await the advent of much new data.

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(418) L. K. Montgomery and J. W. Matt, *J. Amer. Chem. Soc.*, 89, 934 (1967).

(d) The greatest triumph of the π-complex theory has been claimed to be the interpretation of the mechanism of the intramolecular benzidine rearrangement. This reaction is one of the few where detailed predictions can be made from this theory that differ from those of the more conventional theories, and the recent accumulation of a large body of data allows crucial tests to be made. The answer is unequivocal. The π-complex theory fails to accommodate the facts concerning rates, kinetic form, and products in all cases where a unique prediction can be made, whereas the rival theory based on σ complexes can account for all the available facts. The π-complex approach similarly fails for the nitroamine rearrangement, and although it has been advocated for many other aromatic rearrangements, none of these has been studied in sufficient detail to define the broad outlines, much less the fine details, of mechanism. All appear, at their present state of understanding, to be adequately interpreted in terms of the intervention of σ complexes.

(e) Radical π complexes would be expected to be much less stable than the proposed cationic species and indeed to be more akin to molecular complexes in properties, the dual classification as to types of complexes here breaking down. Although there is some evidence for complexes of a loose type being found in certain homolytic reactions there is no unique evidence requiring so-called π-complex routes in a variety of additions, substitutions, and rearrangements.

In summary, there is no justification for the continued advocacy of π complexes as obligatory intermediates in the range of organic reactions discussed here. There is no compelling evidence for their existence as discrete isolable species outside the realm of organometallic chemistry.