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CATALYSIS BY THE FORMATION OF MOLECULAR COMPLEXES

BY

P. A. CHOPARD¹

RÉSUMÉ

Les phénomènes de catalyse sont caractérisés, selon la définition classique, par l'altération de l'état de transition d'une réaction chimique, sans modification de l'énergie libre de réaction.

Bien que rarement satisfaites, ces conditions sont cependant approchées dans les cas de catalyse homogène par formation de complexes moléculaires. Certains exemples typiques de ce mode de catalyse sont passés en revue, par exemple les réactions d'hydrogénation, d'oxydation et de polymérisation catalysées par les métaux de transition. En chimie purement organique, la situation est plus confuse du fait que les potentiels d'ionisation et les affinités électroniques des participants sont moins variés que ceux des composés minéraux. Ainsi les rapports fournis par la littérature dans ce domaine apparaissent peu nombreux. Il est cependant très probable que de nombreux processus biologiques sont catalysés grâce à l'intervention de complexes de transfert de charge de faibles variations d'affinité pouvant mener à une grande variété de processus.

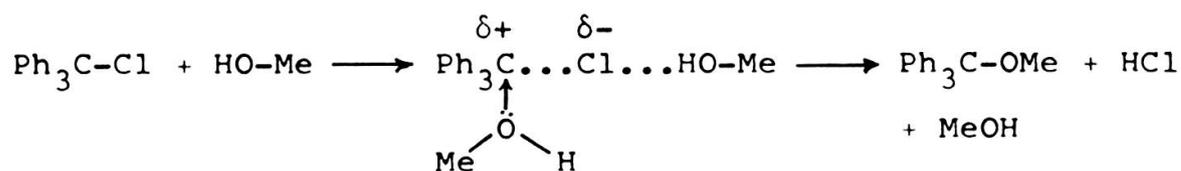
De plus, certains transferts de charge (électrons thermiques) peuvent conduire à des états d'excitation similaires à ceux observés en photo ou électrochimie. L'oxydation luminescente de certains anions radicalaires aromatiques, produits par transfert de la charge d'un métal alcalin, en fournit un exemple typique. Le mécanisme de cette réaction étant comparable en de nombreux points à ceux de la bioluminescence, ce qui précède laisse donc entrevoir l'importance considérable que revêt l'étude de la catalyse par formation de complexes moléculaires à l'égard de la nature fondamentale des processus vitaux.

1. INTRODUCTION

According to classical definitions, when catalysis of a chemical reaction is involved, the catalyst should only participate to the structure of the transition state and ultimately separate from the products. Thus, only rate controlling factors (activation parameters) should be modified while the final equilibrium should remain unchanged. Hence, general acid and base catalysis can be considered as true catalysis processes while solvent effects (catalysis by the solvent) [1] in solvolysis or

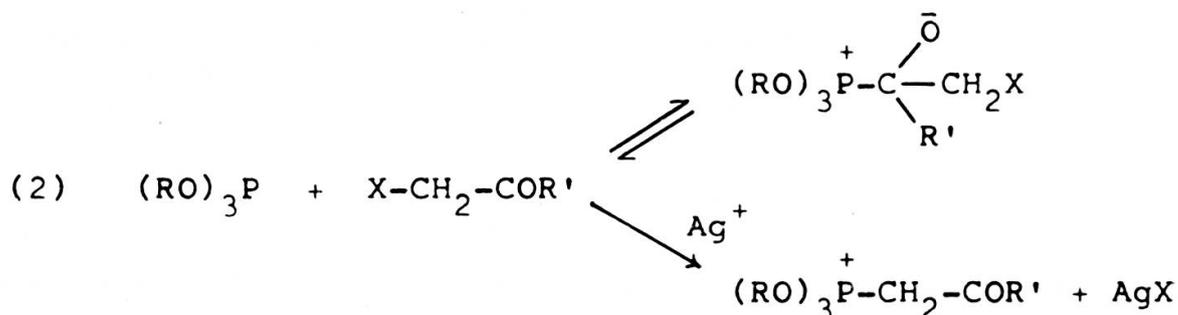
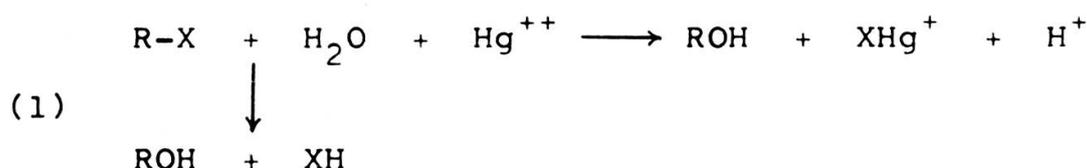
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multiorder reactions may not necessarily be so. Thus, the pseudo-termolecular reaction of trityl chloride and methanol in benzene [2] can be described as a 2nd order displacement, catalyzed by methanol,

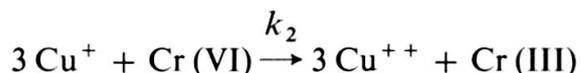
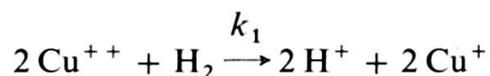


but in general, the energy of the initial and the final state are not the same in the presence or in the absence of the solvent catalyst (entropy and solvation factors) and the free energy of the catalyzed reaction will be different from that of the uncatalyzed reaction.

Strong differences between the final states of catalyzed and uncatalyzed reactions are exemplified by the electrophilic action of some metal salts, i.e.



In case (1) [3] the reaction has shifted from mechanism SN_2 to mechanism SN_1 because of the strong interaction between the catalyst and the leaving group. In case (2) [4], the course of the reaction has been completely modified, since the relative electrophilic power of the saturated carbon and the carbonyl group toward the nucleophile have been changed by the catalyst. After the reaction, regeneration of the metal ions is not straightforward and both the above cases provide typical examples of a drastic interaction of the catalyst with reactants. In many other cases, however, substances having participated and having been modified in a reaction can be returned to their initial state in a very simple way, for example, in the copper (II) catalyzed oxidation of H_2 with chromates [5], the concentration of



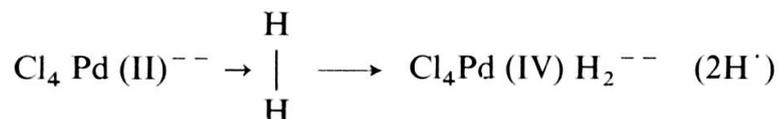
the catalyst is practically not depleted since $k_2 \gg k_1$. Consequently, the classical definition of catalysis, rather applies to systems where the interaction of the catalyst with the reactants in the transition state is relatively weak and where the energy factors governing the extent of bonding of the catalyst with the reactants are of the same order as those between the reactant themselves. Homogeneous systems fitting these requirements are well represented by molecular adducts (charge transfer or other species) since the interactions between donors and acceptors are of a very wide order of magnitude [6]. These interactions may range from simple dipole-induced dipole forces to energies as large as those of strong covalent bonds. It is true that solvation energy factors can also be very large; however in complex adducts the ratio of donor to acceptor (or vice-versa) remains generally quite small (< 2 or 3).

Although this aspect of catalysis, that is the influence of donor-acceptor interaction on the reactivity (of any reactive function) of one of the complex moieties is attracting now much interest, it appears to be relatively unexplored; at least with regard to the above concept. It is the purpose of this review to discuss a few of the observations reported in the literature and associated with this subject and tentatively correlate them with other processes involving non thermal excitation.

2. HOMOGENEOUS CATALYSIS WITH MOLECULAR COMPLEXES

Inorganic Complexes.

Hydrogenation with activated hydrogen is one of the most studied processes with regard to catalysis. The activation of hydrogen by some transition metal ions [7] can be regarded as involving initially a charge transfer; for example with palladium chloride, the following reaction

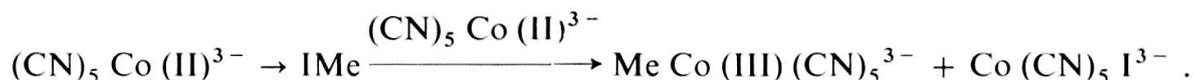


may be followed by heterolytic splitting,

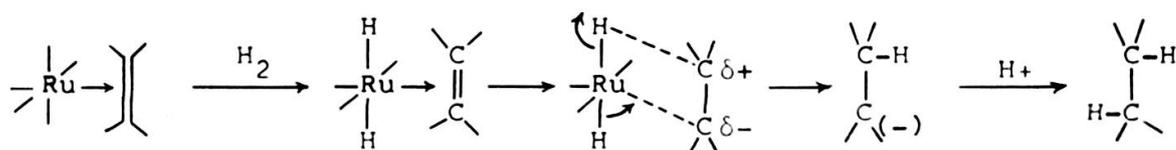


which, consecutively to hydride consumption, will restore the metal to its original valency state.

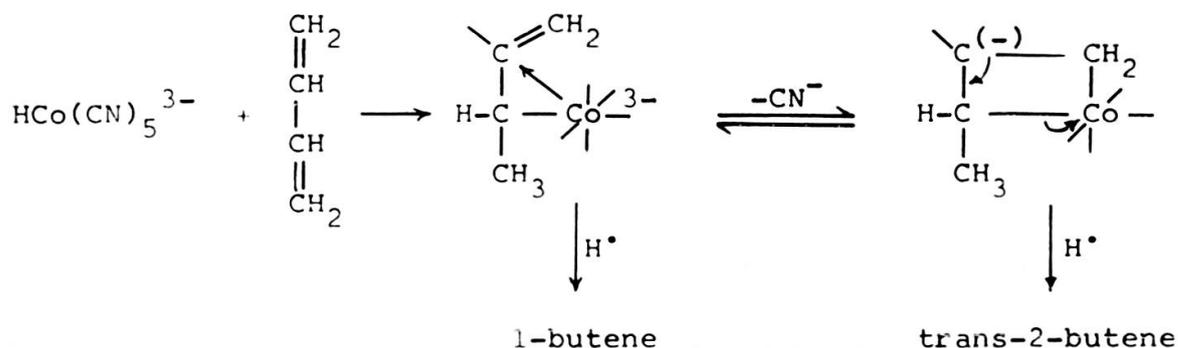
This activation of the H_2 bond is reminiscent of the activation of the $C - X$ bond [8] ($X = \text{halogen}$) which probably proceeds by initial interaction with the halogen atom,



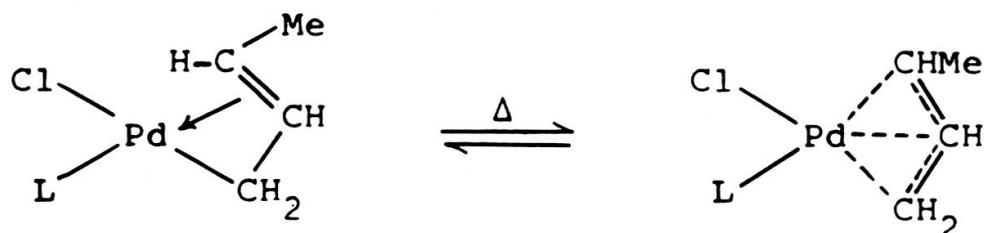
In some cases of catalyzed hydrogenation, the catalyst not only activates the hydrogen but also complexes with the substrate. For example in the hydrogenation of activated olefins [9] (unsaturated carboxylic acids) by ruthenium (II) salts, the reaction is 2nd order relatively to the initial metal-olefin complex and hydrogen; the mechanism postulated above suggests stereospecificity.



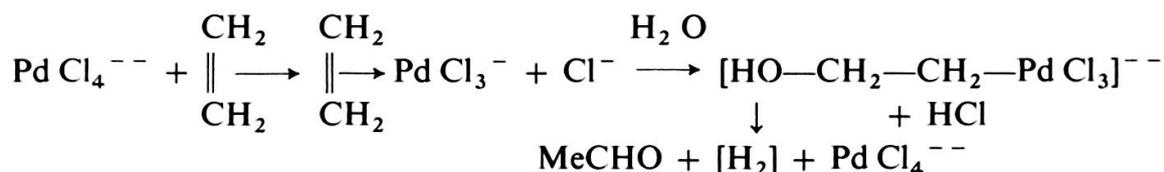
Steric control has been demonstrated in the hydrogenation of butadiene [10] with cobaltic salts and the mechanism interpreted on the basis of the rearrangement of an initial covalent metal-organic compound, via the formation of an internal donor-acceptor complex,



As expected from the above scheme, the extent of rearrangement leading to trans-2-butene decreases with increasing CN^-/Co ratio in the catalyst solution. The above interpretation is reasonable in view of the thermally controlled isomerization of the related palladium complexes which has been recently reported [11] (L is a donor ligand),

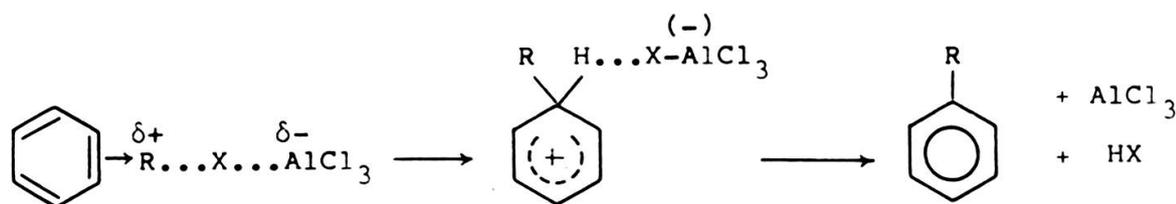


The existence of similar complexes has been postulated in the course of the catalyzed oxidation of olefins in presence of palladium salts [12],

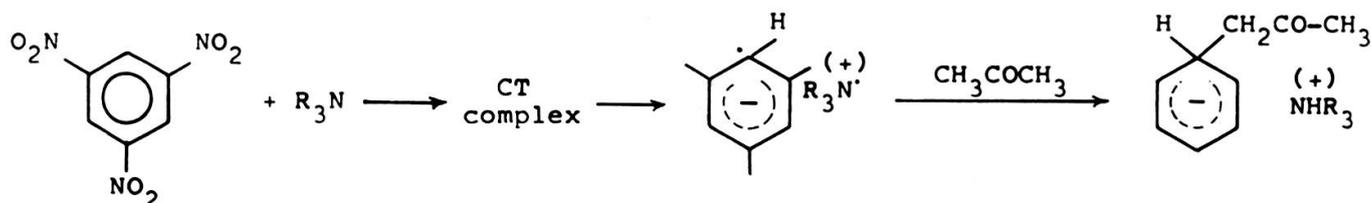


The extensive stereo control of some olefin polymerizations is one of the most striking aspects of molecular complex catalysis. However, the stereospecific control offered by catalyst of the Ziegler-Natta type has usually been interpreted [13] in terms of the structure of the solid catalyst and it is not clear whether these peculiar properties are linked to homogeneous as well as heterogeneous catalysis. Thus, it has been suggested that the homogenous polymerization of ethylene at low temperature [14] with mixed alkyl-titanium-aluminum catalysts is incompatible with either cationic or anionic mechanisms and the existence of an intermediate π -complex has been proposed; however, in this case, the reaction was found to be non-stereospecific while in another case [15], using rhodium (III) salts (rather different from typical Ziegler-Natta catalysts), butadiene gave crystalline trans-1,4-polybutadiene; also in this case, π -ene complexes were postulated as intermediates.

Finally, one should mention the close analogy existing between electrophilic substitution mechanisms and the Meisenheimer type complexes which often result from the decomposition of charge-transfer adducts, for example compare the mechanism of the classical Friedel-Craft reaction (catalyzed by aluminium chloride),



with the salt resulting from the decomposition, in presence of acetone [16], of a trinitrobenzene-trialkylamine charge-transfer complex,



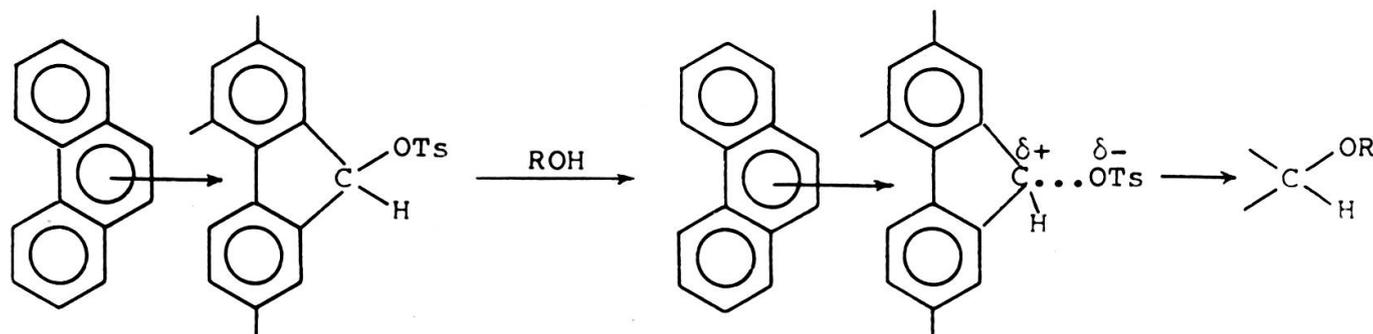
It can be seen from the above description that although there is a great number of reports concerning processes catalyzed via the intermediate formation of inorganic

or metal-organic donor-acceptor complexes (whatever type they are), they are not associated with a great variety of typical reactions. Recently, Klopman¹ has investigated the effect of complex formation between transition metals and aromatic compounds with regard to the reactivity of some ring substituents. Results have however not yet been disclosed.

Organic Complexes.

Donor-acceptor systems involving only organic molecules have been extensively studied on both practical and theoretical standpoints with regard to nature of bonding, extent of charge transfer and ultimate decomposition of participants, in a great variety of conditions. Many reviews have appeared on this subject [17] but very little appears to have been done concerning typical reactions of complex components with regard to their mutual interaction.

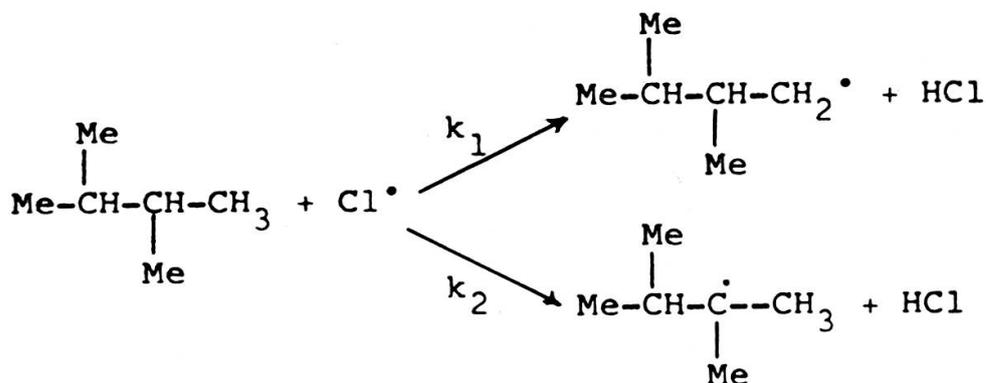
Thus, phenanthrene as a donor [18], has been shown to catalyze the solvolysis of 2, 4, 7-trinitro-9-fluorenyl tosylate, the rate being increased about 20 fold over the non catalyzed reaction. This effect seems to be quite small; however, one should keep in mind that, depending upon the



location of the donor with respect to the center which develops the positive charge in the transition state, one would expect some interference with the solvation necessary for the separation of charge to occur. It has been estimated then, that if these effects of desolvation were disregarded the overall increase in rate of this first order reaction by the donor should be about 300. In view of these results one may also expect that the extent to which a donor will change the rate of such displacement reactions should be related to the reaction order (that is to the extent of bond formation and bond break in the transition state). It is interesting to note that when the donor is covalently "held" together with the acceptor its importance may be markedly enhanced; thus paracyclophanyl 4-*p*-tosylate solvolyzes about 2×10^3 times more rapidly than cyclohexyl *p*-tosylate in acetic acid [19].

¹ Cyanamid European Research Institute, Theoretical Organic Chemistry Group.

Very interesting results have been obtained with respect to the yields of chlorinated products in the reaction of atomic chlorine with some branched-hydrocarbons [20]



it has been found that the ratio of substitution at tertiary and primary carbon k_2/k_1 is not related to the polarity of the solvents used, but to their donating properties toward the strongly electronegative chlorine atom; the values of this ratio are approximately 4 in CCl_4 and nitromethane ($\epsilon \cong$ respectively 2 and 30) 10 in ether ($\epsilon \cong 4$) and 30 in benzene ($\epsilon \cong 2$). The interpretation of these results with regard to the nature of the transition state in this substitution is however difficult.

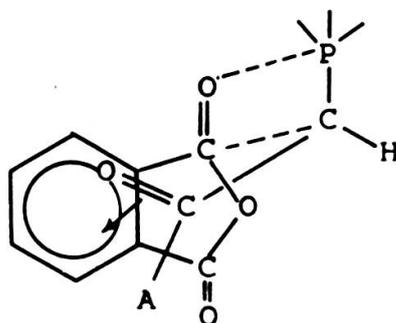
Reactions involving rearrangement processes or offering alternative routes to products may be expected to be among the most susceptible to be catalyzed by donor-acceptor interactions. Effectively, most rearrangement reactions involve concerted bond break and bond formation and the overall energy changes may be as low as a few kcal/mole. This can be compared with the stabilization energy of some charge transfer complexes [17f], see below,

Complex	— ΔH kcal/mole
Trinitrobenzene — hexamethyl benzene	4.7
Trinitrobenzene — naphthalene	4.3
Chloranil — hexamethyl benzene	5.4

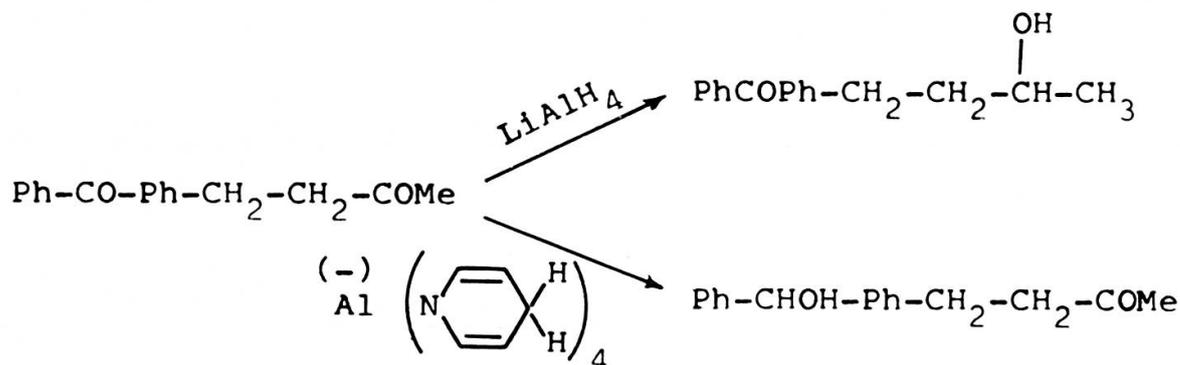
where ΔH has been derived from equilibria measurements.

The importance of charge transfer in rearrangement reaction has been recently discussed by Dewar and Marchand [21] in the description of the reactions and the nature of non classical carbonium ions. Thus, many structural changes observed with these types of compounds may be associated with the transient existence of internal π -complexes. Even very weak interactions may be, in some cases, orientation determinant. Thus we have recently reported evidence of stereochemical control in the reaction of carbonyl methylene phosphoranes and phthalic anhydride [22] and suggested that the orientation was determined by the extent of interaction between

the carbonyl π bond and the aromatic ring in the transition state. This extent is governed by the nature of substituent *A*.



This case, like many others, where a particular pathway is favoured because of complex formation between the reactants, is a typical example of intra-molecular catalysis. An example of interaction from an external agent is furnished by the reduction of 4-benzoylphenyl-2-butanone [23]. With LiAlH_4 the aliphatic carbonyl group is reduced while with lithium tetrakis (N-dihydropyridyl) aluminate, the benzoyl carbonyl is converted to hydroxyl. An interaction between the pyridyl groups and the conjugated aromatic part of the diketone is therefore probable.

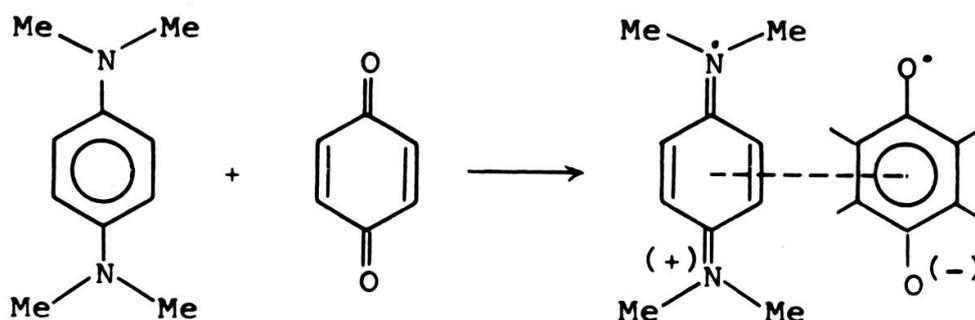


However it appears that very few examples comparable to the above are known at the present time. In view of their interest, it is probable that new developments will occur in the near future.

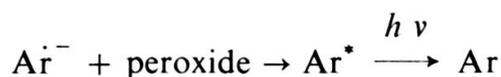
3. OTHER ASPECTS OF THE CHEMISTRY OF MOLECULAR COMPLEXES.

From the previous discussions it can be inferred that the systematic investigations of donor-acceptor interactions on typical organic reaction mechanisms is still in infancy. This is a surprising situation especially in view of the declining interest of the past decade in ground state electronic charge distribution and ground electronic

states in general, since it is realized that many of the most vital chemical properties must be associated in some way with excited states. It is therefore most instructive to draw a parallel between radiative and charge transfer excitation processes. It is true that most charge transfer absorptions are observed in the U.V. or visible region which correspond to transitions of roughly 50 to 150 kcal/mole. One might therefore conclude that the contribution of the excited state to the stabilization of the ground state of these adducts should be exceedingly small (cf. the stabilization energies given above) as predicted by Mulliken [17*d*]. However, many reactions involving the splitting of complexes formed by neutral donors and acceptors to their radical ions have been reported [17*g*] (thermal electron transfer) which suggests a non negligible charge transfer in the ground state (incidentally, many of these processes are also light catalyzed, as expected). Furthermore, strong evidence has recently been obtained, based on spectrographic methods, that the ground state of the tetramethyl *p*-phenylene diamine-chloranil complex is largely ionic in the solid state [26] and even in solution (acetonitrile, solvation energy estimated 5 kcal/mole).



The electrostatic contribution to the total energy of the complex must therefore be very large, an assumption which is somewhat surprising in cases where the existence of purely organic complexes is concerned. Estimations of these energy contributions have been presented [17*e*] and shown to be quite significant. It is thus possible to reach electronically excited states, by charge-transfer complexing, which are normally obtained only by photo- or electrochemical methods. This concept which is of obvious interest can be illustrated by the chemiluminescent oxidation of radical anions [24] derived from fluorescent hydrocarbons,



In this case the electron was furnished by an alkali metal but it is not impossible to imagine it being given by an organic donor. These possibilities have been discussed recently by Professor A. Weller in a lecture he gave at CERI.

To conclude this short review and to again stress the general importance of donor-acceptor phenomena, it is worth while reminding of their participation in biological processes. As a striking example, it has been postulated that the inhibition

("negative catalysis") of the infection of *E. Coli* by certain strains of bacteriophages [25] is due to charge transfer effects. The evidence presented was that inhibition and the association constant for the complex of the inhibitor with chloranil was parallel, in that the better the inhibitor, the higher the association constant.

Whether this interpretation is correct or not, it is obvious that molecular interactions play a predominant part in the complex reactions involved in living cells and that detailed investigations of related model systems should be among the main objectives of modern chemistry.

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