ORGANIC CHARGE-TRANSFER COMPLEXES

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Preface

This book describes various aspects of interactions commonly termed "charge-transfer complexes". They comprise electron-donor–electron-acceptor associations for which an intermolecular electronic-charge-transfer transition (or transitions) is usually observed.

The expression "charge-transfer", used to describe these complexes, has been criticized on the grounds that in many systems the contribution of charge-transfer forces to the stabilization of the ground state is negligible, and that in any case the term presupposes a valence bond description of the complex. However, the term is widely used in this sense; other terminology tends to be either too general or too cumbersome. This problem of nomenclature is discussed further in Chapter 1 and elsewhere in the book.

The large amount of work which has been published in this field has meant that an effectively comprehensive study is impracticable. Although, therefore, some selection has been unavoidable, an attempt has been made to make the coverage reasonably wide within the field of *organic* charge-transfer complexes. Nevertheless, I am aware that the more detailed treatment of certain aspects reflects my particular interests.

There has been a general coverage of the literature up to the beginning of 1968, although a few more recent references are also included. The present rapid development of this field is indicated by the fact that at least 400 more papers relevant to this book have been published within the past year.

I am indebted to many colleagues and friends for their help and encouragement. My interest in charge-transfer complexes was initiated by the late Dr. D. Ll. Hammick, F.R.S., who was one of the pioneers in the study of these systems. My thanks are particularly due to the research students who have collaborated with me and have helped so much to maintain the interest in this work. Individual references to their published and unpublished contributions are made throughout the book.

Finally, I should like to thank Academic Press for their helpfulness, consideration and patience at all stages of publication.

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Acknowledgements

List of Commonly Used Symbols

A = electron acceptor

D = electron donor

AD = 1:1 charge-transfer complex

ν_{CT} = frequency of intermolecular charge-transfer band

E_{CT} = energy of intermolecular charge-transfer band

I^D = ionization potential of an electron donor

E^A = electron affinity of an electron acceptor

A = absorbance [optical density]

ϵ = molar absorptivity [molar (decadic) extinction coefficient]

δ = chemical shift with reference to some non-interacting species

Δ = population-averaged chemical shift involving a component in the free and complexed states with reference to the same nucleus in the uncomplexed component

Δ_0 = chemical shift in a completely complexed component with reference to the same nucleus in the uncomplexed state

K = association constant

K^{AD} = association constant for the equilibrium $A + D \rightleftharpoons AD$

$K_c^{AD} = K^{AD}$ (*molar* concentration units)

$K_x^{AD} = K^{AD}$ (*mole-fraction* concentration units)

$K_m^{AD} = K^{AD}$ (*molal* concentration units)

$K_r^{AD} = K^{AD}$ (mol/kg solution concentration units)

Contents

Chapter I

General

1.A. Introduction

The historical development of chemistry has led to the concept of the molecule. Although this idea has been vital, not all associations of atoms conform to the concept. The anomalous "unsaturated valencies" or "residual affinities" of an earlier phase in organic chemistry are a reflection of our inadequate description, rather than the implied peculiarities of chemical interaction. All molecules interact with other molecules, but for the most part the intermolecular forces involved are small compared with the inter-atomic forces within molecules, and there is no problem in defining the molecule and concluding that intermolecular forces are "non-chemical" in the sense that they do not require a description in terms of classical covalent or ionic bonding. Nevertheless, while not being immediately amenable to description in terms of classical chemical bonds, interactions between molecules may be sufficiently strong or show such features as to make it impossible to provide an explanation in terms of dispersion, dipole–dipole, dipole–induced-dipole and suchlike van der Waals forces. The recognition of the usefulness of the concept of the molecule, and subsequently of chemical bonding within molecules, has led to a reluctance to recognize the possibility of graded interaction between the extremes of the classical covalent or ionic bond and the weakest van der Waals interactions.

Even when we do recognize this possibility, there is a danger of further compartmentalizing the systems of intermediate interaction into various distinct types, members of each group being expected to conform to type. There may be many apparently obvious representations of a particular type—for example hydrogen-bonded complexes. However, this does not

mean that an interaction which only marginally conforms necessarily needs a separate special explanation.

I.B. Definition of the Term "Complex" in Organic Chemistry

It is difficult to find an adequate definition of the term "complex" because its usage has been so varied. On the one hand it has been used to describe the product of the weak reversible interaction between two or more components to account for small deviations from ideality. It has also been used as the description of the product of strong interactions where new covalent (σ) bonds are formed. The terminology is further confused by the use of the expression "molecular compound" by some authors as a synonym of (molecular) complex.

In this book the term "complex" will be taken to mean, experimentally, a substance formed by the interaction of two or more component molecules (and/or ions), which may have an independent crystal structure and which will reversibly dissociate into its components, at least partially, in the vapour phase and on dissolution. This definition suggests that there is no, or only a very small, contribution from covalent binding in the ground state. However, it must be recognized that there is a gradation from these weaker interactions to classical covalent (σ) bond formation.

I.C. Charge-Transfer (Electron Donor–Acceptor) Complexes

The complexes presently discussed are formed by the weak interaction of electron donors with electron acceptors. Using valence-bond theory, a rational explanation of many of the ground-state properties has been given in terms of a structure which involves mainly dispersion, dipole and similar forces together with a usually small contribution from a covalent dative structure in which one electron has been transferred from the donor to the acceptor component of the complex (see Chapter 2). The observed electronic absorption spectra, characteristic of the complex as a whole, are accountable as intermolecular charge-transfer transitions (Chapter 3).

There is not complete agreement concerning a general term to describe these interactions. Mulliken[1-3] has called all electron donor–electron acceptor interactions (*electron*) *donor–acceptor complexes*, and has emphasized the range of component sub-types by a detailed terminology. Interactions in which covalent (σ) bonds are formed are automatically included. In other contexts such products would simply be considered as new covalent compounds.

A criticism of the term "charge transfer" is that it reflects the particular valence-bond description.[4] In many so-called "charge-transfer" complexes, charge-transfer forces do not provide the major contribution to the binding forces in the ground state. This point has been made strongly by Dewar and his co-workers.[5, 6] Similar conclusions have been drawn from recent considerations of the measured dipoles of "charge-transfer" complexes in the ground state.[7] Measurements of halogen pure-electrical quadrupole resonances for complexes of p-xylene with carbon tetrabromide and with carbon tetrachloride, and for the benzene–bromine complex suggest that there is little or no transfer of charge in the ground states of these complexes.[8] Nevertheless, the term has a wide common usage to describe the weak interactions between electron donors and electron acceptors which are the subject of this book. This terminology will be retained, although it must be emphasized that the term cannot be taken to imply that transfer of charge is the major mode of binding in these complexes.

Charge-transfer complexes usually involve simple integral ratios of the components,* the enthalpy of formation is usually of the order of a few kcal/mol or less, and the rates of formation and decomposition into the components are so high that the reactions appear to be instantaneous by normal techniques. An electronic absorption extra to the absorption of the components is often observed. This is the result of an intermolecular charge-transfer transition involving electron transfer from the donor to the acceptor (see Chapters 2 and 3). Consequently, for many so-called charge-transfer complexes it would be semantically more correct to speak of "complexes showing charge-transfer absorption". However, this expression lacks the facileness of "charge-transfer complexes". Furthermore, there are many cases of complexes so classified in which it is experimentally difficult to demonstrate the presence of the supposed charge-transfer absorption.

It should be emphasized that charge-transfer interaction in the ground state is not an exclusive process. The description of a particular complex as, for example, a hydrogen-bonded or a charge-transfer complex is, on occasion, only one of differing terminology.

I.D. Electron Donors and Electron Acceptors

The components of the complex have been described as electron donors and electron acceptors. This description is preferred to *Lewis* bases and acids, since Lewis's concept originally applied to the donation or

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* Exceptions are known: for example, the iodine complexes of perylene, violanthrene and p-phenylenediamine (see Chapter 9).
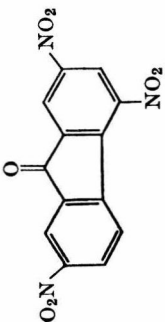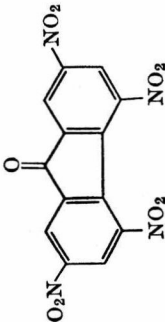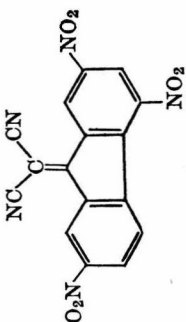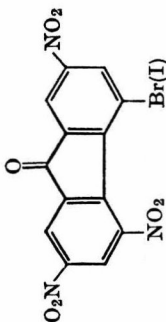
acceptance of *pairs* of electrons,[9] whereas we shall not wish to make such a restriction.

In a wider context Mulliken[2] has divided even-electron donor and acceptor species into increvalent and sacrificial types. Increvalent donors are lone-pair (n)-donors such as aliphatic amines, amine oxides, ethers, phosphines, sulphoxides, alcohols, iodides and the like. Some of these interact strongly with electron acceptors. Sacrificial donors are compounds which donate an electron from a bonding orbital. They include σ-donors such as hydrocarbons, especially small cyclic hydrocarbons. These are very weak electron donors. By contrast, sacrificial π-donors such as aromatics, particularly polycyclic systems and systems containing electron-releasing groups, may be strong donors. Some compounds such as aza-aromatics and aromatic amines may behave as n-donors towards some acceptors and π-donors towards others (see Chapters 3 and 7). Relatively little work has been reported on aliphatic π-donor hydrocarbons. It is doubtful whether the colours obtained by the addition of tetranitromethane to olefins are the result of charge-transfer complex formation (see Chapter 10).

Increvalent acceptors are of the vacant orbital (v) type. Many of these, for example B(hal)$_3$, Al(hal)$_3$, SnCl$_4$ are outside the scope of the present discussion. The binding of electron donors (particularly n-donors) to such acceptors is often so strong that covalent binding results. However, with other v-acceptors such as Ag$^+$, weak charge-transfer complexing may occur. Sacrificial acceptors may be of the σ- or π-type. σ-Acceptors include the hydrogen halides, the weakly accepting halo-substituted paraffins and the more strongly accepting halogens and pseudo-halogens, e.g. I$_2$, Br$_2$, ICl, ICN. π-Acceptors are the most common organic acceptors. They include aromatic systems containing electron-withdrawing substituents such as nitro, cyano and halo, also acid anhydrides, acid chlorides and quinones,[10] as well as planar aromatic cations (see Chapter 10). Some π-acceptors such as 1,3,5-trinitrobenzene, p-benzoquinone, chloranil (tetrachloro-p-benzoquinone) and picric acid (2,4,6-trinitrophenol) are well known as complexing agents. A list of some more novel π-acceptors is given in Table 1.1. Apart from these species, compounds with unpaired electrons may behave as electron donors or acceptors, e.g. I, O$_2$, diphenylpicrylhydrazyl (DPPH).
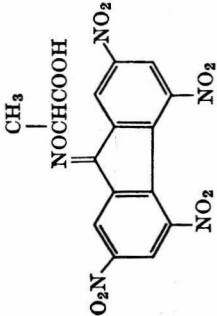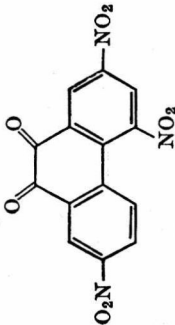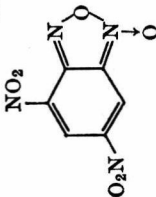
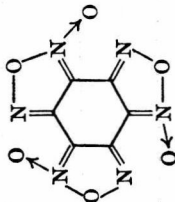Although this division into electron donor and electron acceptor species may be made, it must be emphasized that the terms are only relative. A single species may, for example, behave both as a donor and as an acceptor. This may possibly occur in self-complexes of benzene.[11] Similarly, it has been suggested that the larger condensed polycyclic aromatic hydrocarbons, which are good donors, should also be good

TABLE 1.1. Some π-electron acceptors

Formula	Name*	Reference†
	2,4,7-Trinitrofluorenone	M. Orchin and E. O. Woolfolk, *J. Am. chem. Soc.* **68**, 1727 (1946)
	2,4,5,7-Tetranitrofluorenone	M. S. Newman and H. Boden, *Org. Synth.* **42**, 95 (1962)
	9-Dicyanomethylene-2,4,7-trinitrofluorenone	T. K. Mukherjee and L. A. Levasseur, *J. org. Chem.* **30**, 644 (1965)
	4-Bromo- and 4-iodo-2,5,7-trinitrofluorenone	M. S. Newman and J. Blum, *J. Am. chem. Soc.* **86**, 5600 (1964)

TABLE 1.1.—continued

Formula	Name*	Reference†
	2-(2,4,5,7-Tetranitro-9-fluorenylideneaminoöxy)-propionic acid	M. S. Newman and W. B. Lutz, J. Am. chem. Soc. **78**, 2469 (1956)
	2,4,7-Trinitrophenanthraquinone (also 2,7-; 3,6- and 2,5-dinitro)	T. K. Mukherjee, J. phys. Chem., Ithaca **71**, 2277 (1967)
	4,6-Dinitrobenzofuroxan	P. Drost, Justus Liebigs Annln Chem. **307**, 49 (1899); A. S. Bailey and J. R. Case, Proc. chem. Soc. 176, 211 (1957); Tetrahedron **3**, 113 (1958)
	Benzotrifuroxan (sometimes described as hexanitrosobenzene)	A. S. Bailey and J. R. Case, Proc. chem.Soc. 176 (1957); Tetrahedron **3**, 113 (1958); A. S. Bailey, J. chem. Soc. 4710 (1960)