Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Mulliken's Charge-Transfer Theory and its Application to Chemical Reactions

Saburo Nagakura [a]
[a] Institute for Molecular Science, Myodaiji, Okazaki, 444, Japan

To cite this article: Saburo Nagakura (1985): Mulliken's Charge-Transfer Theory and its Application to Chemical Reactions, Molecular Crystals and Liquid Crystals, 126:1, 9-18

To link to this article: http://dx.doi.org/10.1080/15421408508084150

Mol. Cryst. Liq. Cryst. 1985, Vol. 126, pp. 9-18
0026-8941/85/1261-0009/$15.00/0

Printed in the United States of America

MULLIKEN'S CHARGE-TRANSFER THEORY AND ITS APPLICATION TO CHEMICAL REACTIONS

SABURO NAGAKURA
Institute for Molecular Science, Myodaiji, Okazaki
444, Japan

Abstract The charge-transfer mechanism of aromatic substitution reaction is discussed, much importance being attached to the relative height of the highest occupied orbitals of electron donors to those of the lowest unoccupied orbitals of electron acceptors. Electron transfer processes have been studied with solutions having N,N,N',N'-tetramethyl-p-phenylenediamine as an electron donor.

INTRODUCTION

Mulliken's charge-transfer (hereafter abbreviated to CT) theory[1] has been widely and successfully applied to the interpretation of various properties of electron donor-acceptor (hereafter abbreviated to EDA) complexes such as their stabilities, geometrical structures, and spectroscopic, electric and magnetic properties. The existence of CT states characteristic of EDA complexes has been demonstrated by the measurements of dipole moments and absorption and electron spin resonance spectra of their excited states[2]. In particular, the electron spin resonance and triplet-triplet absorption studies of excited EDA complexes of 1,2,4,5-tetracyanobenzene as an electron acceptor with hexamethylbenzene and other electron donors quantitatively determined the CT character of their excited triplet states[3,4]. This may be the most direct experimental evidence of Mulliken's CT Theory.

Mulliken's conception of intermolecular resonance interaction between the no-bond and CT structures has been shown to be important in studying systematically organic reaction mechanisms. In the present paper, the CT mechanism of organic reactions is explained.

CT MECHANISM OF AROMATIC SUBSTITUTION REACTIONS

According to the simple molecular orbital theory, Mulliken's concept of interaction between the CT and no-bond structures

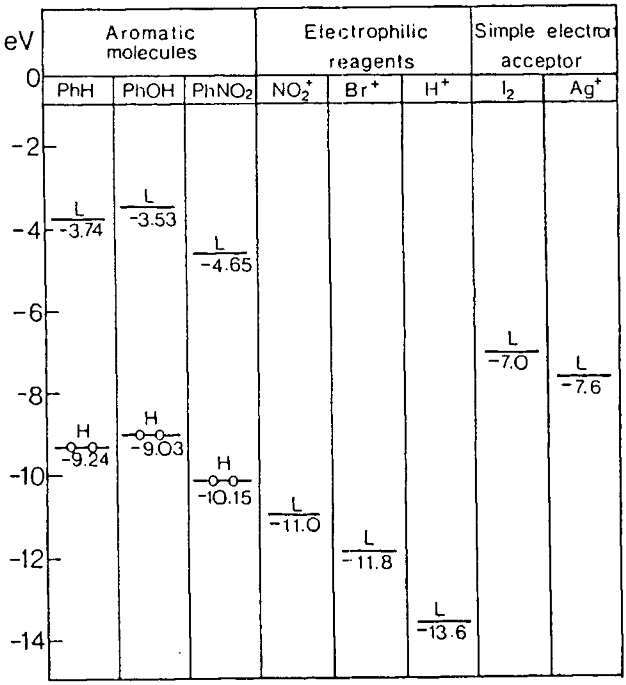
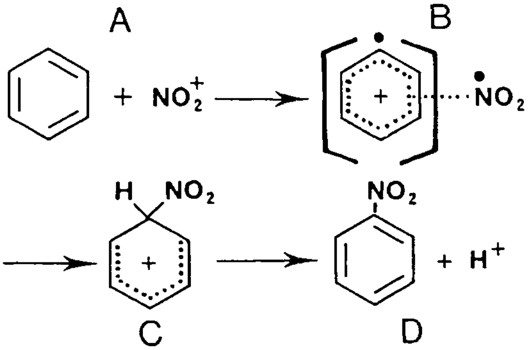


FIGURE 1. Molecular orbital diagrams for aromatic molecules, reagents, and electron acceptors.

is replaced by the interaction between appropriate molecular orbitals of an electron donor and those of an electron acceptor, in particular by the interaction of the highest occupied molecular orbital (HOMO) of the former with the lowest unoccupied orbital (LUMO) of the latter. The HOMO of some aromatic substrates estimated from their ionization potential and the LUMO's of electrophilic reagents estimated from their electron affinities are shown in Figure 1 together with the LUMO's of usual electron acceptors[5].

We can see from this Figure that the LUMO's of typical electrophilic reagents such as NO_2^+, Br^+ and H^+ lies below the HOMO's of aromatic molecules which are susceptible to the electrophilic substitution reaction. On the other hand, the LUMO's of the iodine molecule and the silver cation which can not cause substitution reaction but form stable EDA complexes are higher than the HOMO's of the aromatic molecules. This means that an extremely large electron transfer from the aromatic substrate toward the reagent is necessary for the occurrence of electrophilic substitution reaction. In other words, the electrophilic substitution proceeds through a stage at which the reagent robs almost one electron from the aromatic substrate molecules.

For the nucleophilic aromatic substitution, the HOMO of the reagent is generally very high. This means that one electron transfer occurs from the reagent towards the aromatic molecules at an intermediate stage of the reaction. This CT mechanism of heterolytic aromatic substitution can be schematically represented as follow:



Here NO_2^+ is taken as an example of the electrophilic reagent. Stage C corresponds to the inner complex as an reaction intermediate.

The CT mechanism mentioned above can be described by the aid of Mulliken's concept of the resonance interaction between the CT and no-bond structures. According to this, the heterolytic aromatic substitution is interpreted as transfer processes between the no-bond and CT structures[6]. Approximate formulae for the activation energy derived on the basis of this mechanism show that the orientation of substitution is determined by localization energies or free valencies of aromatic cations and anions for electrophilic and nucleophilic substitution, respectively. Furthermore, the necessary condition for the occurrence of the aromatic substitution is deduced with regard to ionization potentials and electron affinities of aromatic molecules and reagents, and also with regard to binding energies between two components in intermediate inner complexes. This treatment can well explain the experimental results. In future, however, this should be elaborated by considering the contribution of locally excited structures and solvent effects.

Since the proposal of the CT mechanism of heterolytic substitution in 1954, we have studied the detailed mechanism for various organic reactions by detecting unstable intermediates and have succeeded in detecting radical ions and inner complexes as intermediates for various aromatic substitution reactions including photo-Smiles rearrangement[7], nucleophilic substitution reactions of p-benzoquinone and chloranil with aliphatic and aromatic amines[8,9] and in demonstrating the validity of the CT mechanism.

CHARGE TRANSFER INTERACTION BETWEEN N,N,N',N'-TETRAMETHYL-p-PHENYLENEDLAMINE (TMPD) AND CHLORANIL

We have observed the absorption spectrum of a system containing TMPD and chloranil in an ethyl ether-isopropyl alcohol(3:1) mixed solvent at various temperatures[10]. At low concentrations of both components (1.75 - 1.25 x 10^{-4} M for TMPD, 1 - 20 x 10^{-4}M for chloranil), a color cycle shown in Figure 2 is observed. Both components which are almost completely free at room temperature. The colorless solution at room temperature turns greenish yellow at 193K and shows an absorption band at 830nm which is due to the outer complex. The color becomes deeper by lowering the temperature to 77K. The solution color changes from greenish yellow to reddish

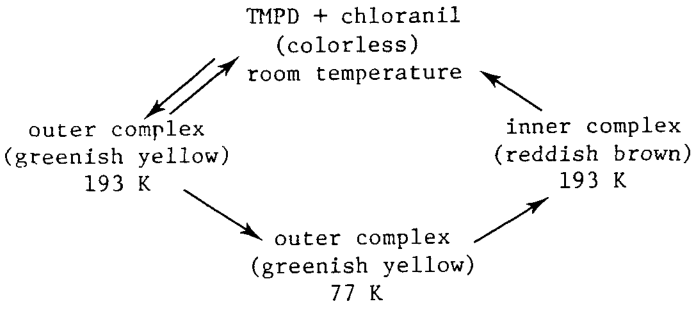


FIGURE 2. A color cycle observed with the TMPD-chloranil system.

brown by raising temperature from 77K to 193K. The reddish brown solution shows absorption peaks at 1100, 635, 520 and 434nm. The 1100nm band corresponds to a reverse CT band of the inner complex (ion pair) observed by Sato et al. for the solid TMPD-chloranil[11]. By raising further the temperature, the solution returns to the initial colorless state. This color cycle can be repeated many times.

The concentration of the outer complex increases at 77K compared with that at 193K. Consequently, the microscopic polarity of the solution becomes larger at 77K and the activation energy for the inner complex formation is lowered as is shown in Figure 3. This phenomenon is interesting in the sense that the reaction system itself enhance the inner complex formation by increasing the polarity of microscopic chemical environment.

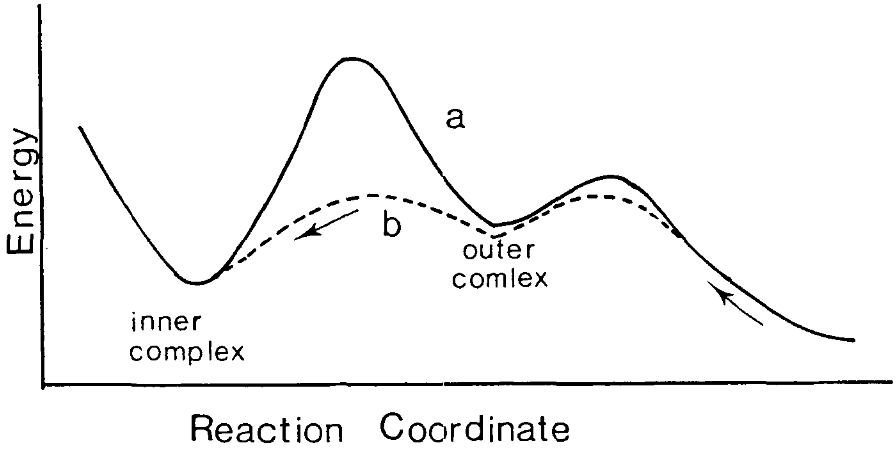


FIGURE 3. Potential energy curves for the TMPD-chloranil system.

MAGNETIC FIELD EFFECTS ON PHOTOIONIZATION OF TMPD

Magnetic field effects upon the photoionization yield of TMPD in deaerated 2-propanol solution has been studied[12]. Transient photoconductivity has been measured in the absence and in the presence of magnetic fields. The result observed in the presence of the magnetic field of 720mT is shown in Figure 4 compared with that in the absence of the magnetic field. We can see from this Figure that the maximum photocurrent increases by ~ 15%. Furthermore it is concluded from sensitizing experiment using acetone as a triplet sensitizer and also from the laser intensity dependence of photocurrent that the photoionization occurs through an excited singlet state.

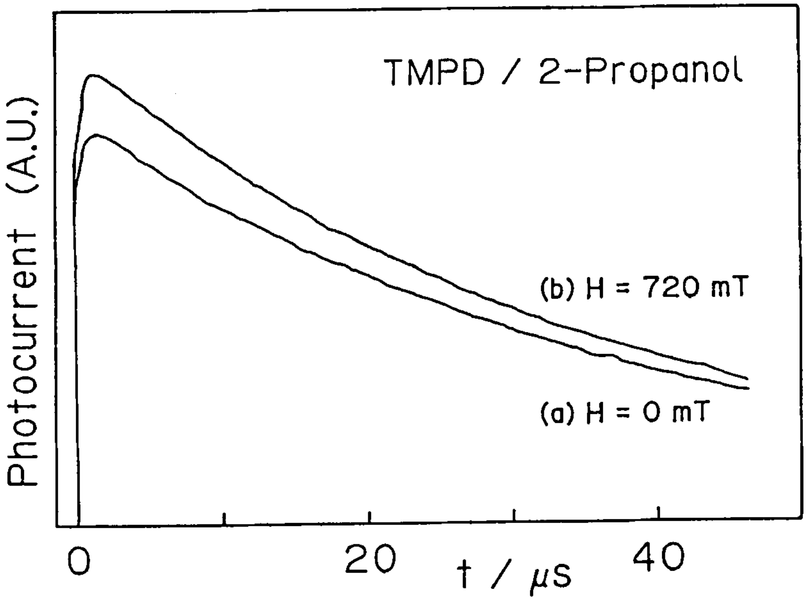
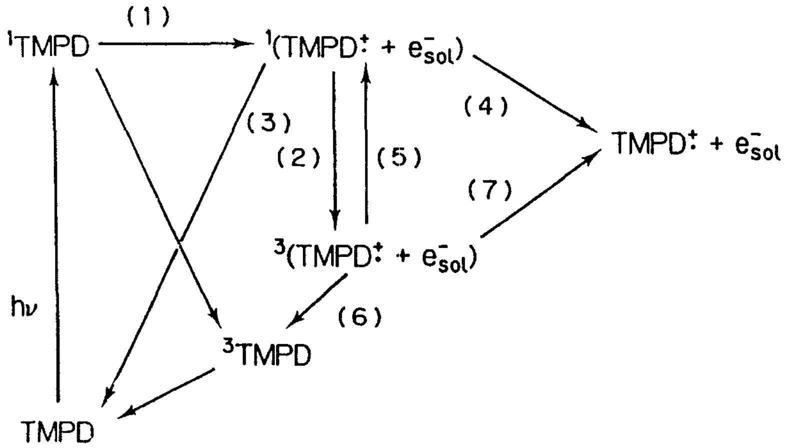


FIGURE 4. Time dependence of photocurrent for the deaerated 2-propanol solution of TMPD (5 x 10^{-4}M):(a) in the absence of a magnetic field; (b) in the presence of the magnetic field.

From the experimental results mentioned above and also from an analogy with other photoinduced electron transfer reactions, we can propose a reaction mechanism for this reaction:



TMPD in the excited singlet state ejects an electron to a solvent molecule to generate a singlet radical pair of the TMPD cation and the solvated electron (process(1)). From the singlet pair, there are three competing processes,i.e., intersystem crossing (ISC) to a triplet radical pair (process (2)), recombination to the ground state TMPD (process (3)), and separation into free radicals (process (4)). The triplet radical pair may undergo ISC to the singlet one (process (5)), recombination to the excited triplet TMPD (process (6)), and separation into free radicals (process (7)).

Here we represent the rate constant of process i as k_i. On the assumption of $k_6 \gg k_3, k_5, k_7$, the yield of dissociated radical ion is proportional to $k_4/(k_2 + k_4)$. According to the radical pair model, the singlet-triplet ISC of the radical pair ((2) and (5)) occurs via electron-nuclear hyperfine interaction. At zero field, all triplet sublevels are degenerate with the singlet state. In the presence of a magnetic field, the degeneracy between the singlet state and two triplet sublevels is removed because of the elctronic Zeeman effect. Therefore, singlet-triplet ISC rates (k_2 and k_5) is reduced in the presence of a magnetic field. The reducation of k_2 results in the increase in the yield of the dissociated ionic species at the expense of that of the excited triplet yield.

REFEREBCES

1. R. S. Mulliken and W. B. Person, Molecular Complexes (Wiley, New York, 1969).
2. S. Nagakura, in Excited States, Vol. 2, edited by E. C. Lim (Academic Press, New York, 1975) pp. 321-383.
3. H. Hayashi, S. Iwata, and S. Nagakura, J. Chem. Phys., 50, 993 (1969);
4. S. Matsumoto, S. Nagakura, S. Iwata, and J. Nakamura, Mol. Phys., 26, 1465 (1973).
5. S. Nagakura and J. Tanaka, J. Chem. Phys., 22, 563 (1954); Bull. Chem. Soc. Japan, 32, 734 (1959).
6. S. Nagakura, Tetrahedron, 19 Suppl. 2, 361 (1963).
7. K. Yokoyama, R. Nakagaki, J. Nakamura, K. Mutai, and S. Nagakura, Bull. Chem. Soc. Japan, 53, 2472 (1980).
8. T. Yamaoka and S. Nagakura, Bull. Chem. Soc. Japan, 44, 2971 (1971).
9. T. Nogami, T. Yamaoka, K. Yoshihara, S. Nagakura, Bull. Chem. Soc. Japan, 44, 380 (1971).
10. T. Nogami, K. Yoshihara, and S. Nagakura, Bull. Chem. Soc. Japan, 44, 295 (1971).
11. Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, Bull. Chem. Soc. Japan, 43, 2370 (1970).
12. Y. Tanimoto, T. Watanabe, R. Nakagaki, M. Hiramatsu,

and S. Nagakura, to be published in Chem. Phys. Lett.