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CHARGE TRANSFER THEORY AND THE ACTIVATED COMPLEX

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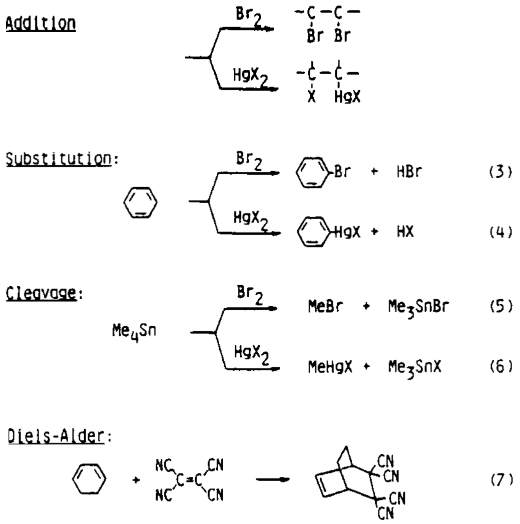
Abstract For a wide variety of organic and organometallic reactions, the observed correlation of the second-order rate constant (log k) with the charge transfer transition energy ($h\nu_{CT}$) directly relates the activated complex for the adiabatic process to the ion pair derived from the vertical CT excitation of the electron donor-acceptor complex as experimentally observed by time-resolved spectroscopy.

INTRODUCTION

Transient charge transfer (CT) absorption bands are often observed during the reactions of many organic and organometallic compounds with electrophiles.[1,2] These are associated with intermediate complexes formed in such common examples as:



In these reactions, the organic or organometallic compound serves as the electron donor in measure with its low ionization potential.[3] Correspondingly, the electron-deficient partner such as bromine is usually designated as the electrophile which cannot be distinguished from its capacity as an electron acceptor.[4]

The concept of charge transfer also applies to divers donor and acceptor pairs such as:

Donor Acceptor

(8)

$$Et_3N + CCl_4 \longrightarrow Et_3N^{+\cdot} + CCl_4^{-\cdot} \qquad (9)$$

$$RMgX + O_2 \longrightarrow RMgX^{+\cdot} + O_2^{-\cdot} \qquad (10)$$

Donors	I_D(eV)	Acceptors	E_A(eV)
$CH_2{=}CH_2$	10.5	O_2	0.7
$(CH_3)_2C{=}C(CH_3)_2$	8.4	CCl_4	2.1
Et_3N	7.7	Quinone	2.6
$PhOCH_3$	8.5	TCNE	3.1

More broadly speaking, charge transfer forms a part of a continuum of oxidation-reduction processes which are mechanistically distinguished by the extent to which the interpenetration of coordination spheres of the reactant pair has taken place in the activated complex.[5] The two mechanistic extremes have been designated as outer-sphere and inner-sphere prototypes as schematically represented below.

OXIDATION-REDUCTION REACTIONS

$$\underset{\text{(Oxidant)}}{A} + \underset{\text{(Reductant)}}{D} \longrightarrow A^- + D^+$$

- Outer-sphere Transition State:

- Inner-sphere Transition State:

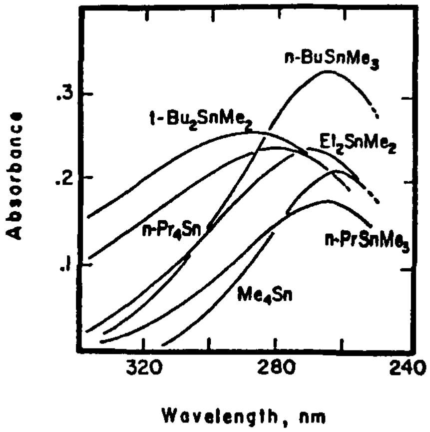
It is important to emphasize the caveat that any kinetics investigation of oxidation-reduction processes must specifically address the question of reversibility in the electron-transfer step[6] i.e.

- Ion-Pair Intermediate:

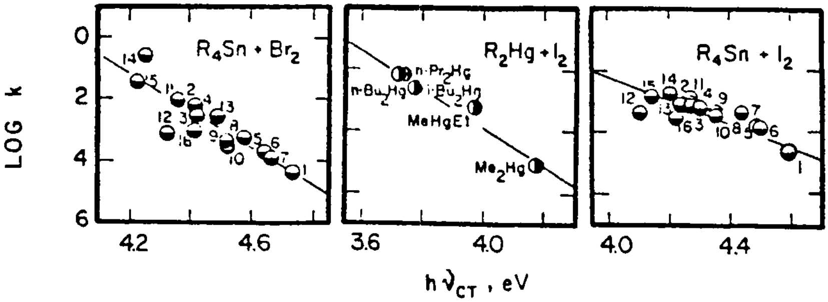
$$\begin{tikzcd} A + D \arrow[r, shift left, "k_1"] \arrow[rr, bend right, "k_{obs}"'] & {[A^- D^+]} \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] & \text{Products} \end{tikzcd}$$

CHARGE TRANSFER EXCITATION AND THE ACTIVATED COMPLEX

Although the theoretical basis for outer-sphere electron transfer is provided by Marcus theory, no such paradigm is available for inner-sphere electron transfer.[7] We have presented a phenomenological approach to this problem which can be summarized as follows.[8] Consider the halogenolysis of alkylmetals as represented in eq 5 above. Typical transient charge transfer spectra (obtained by a spectral difference method) are shown below for a series of alkyltin compounds with bromine.[9]



For a variety of systems consisting of different alkylmetals with halogens, the second-order rate constants (log k) are experimentally found to vary linearly with the CT transition energy ($h\nu_{CT}$) of the 1:1 electron donor-acceptor (EDA) complex as shown below.



If we proceed from Mulliken theory,[10] the transition energy represents the energetics for the charge transfer process given in eq 11,

$$D + A \rightleftharpoons [D,A] \xrightarrow{h\nu_{CT}} [D^+A^-]^* \qquad (11)$$

where D and A represent the organometal donor and the halogen acceptor, respectively, and the asterisk identifies the ion pair derived from vertical excitation in the EDA complex. As such, it is related to the adiabatic ion pair $[D^+A^-]_s$ which is formed in the thermal reaction by a contribution from solvation (s).[11] The interrelationship among the three species is schematically represented by the thermochemical cycle below.

Activation Process for Inner-Sphere Oxidation.

Energetics of Ion-Pair Formation

$$\begin{tikzcd}
 & & {[D^+A^-]^*} \arrow[dd, "\Delta G^s"] \\
D + A \arrow[r, phantom, "\overset{K}{\rightleftharpoons}"] & {[D,A]} \arrow[ur, "h\nu_{CT}"] \arrow[dr, "\Delta G^{\ddagger}"'] & \\
 & & {[D^+A^-]_s}
\end{tikzcd}$$

When a comparative method is used to evaluate the energy changes, the thermochemical cycle predicts the following equivalent relationships,

$$\underline{\Delta G_r^{\ddagger}} = \underline{-RT \ln k/k_0 = \Delta h\nu_{CT} + \Delta G_r^{s}} \tag{12}$$

$$\text{Since } \Delta h\nu_{CT} = \Delta w_p^{*} + \Delta I_D,$$

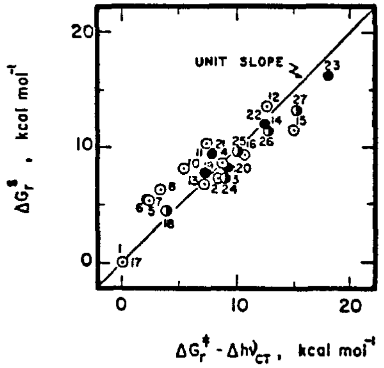
$$\underline{\Delta G_r^{\ddagger}} = \underline{\Delta w_p^{*} + \Delta I_D + \Delta G_r^{s}} \tag{13}$$

$$\underline{\Delta G_r^{\ddagger}} = \underline{\Delta w_p^{*} + \Delta G_r^{0}} \tag{14}$$

where all quantities relate to energy differences relative to those of the reference alkylmetal. The work term w_p in the ion pair derives from the first order Mulliken formulation:

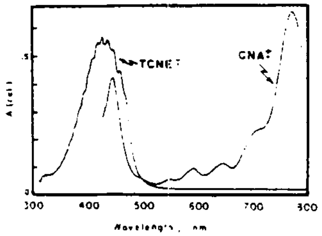
$$h\nu_{CT} = I_D - E_A - w_p$$

where I_D is the vertical ionization energy of the alkylmetal donor. [Note the electron affinity E_A of the acceptor drops out in the comparative procedure]. The success of this formulation is shown by the figure below which graphically illustrates the fit of eq 12 to the three independently determined experimental variables, viz., $\Delta G_r^{\ddagger}$, $\Delta h\nu_{CT}$, and ΔG_s. Note that all the points in the three plots of log k vs $\Delta h\nu_{CT}$ shown above are included in this unified picture.

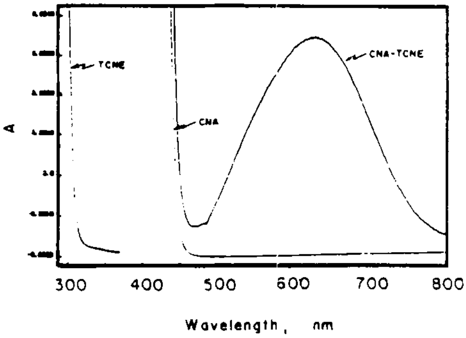


EXPERIMENTAL VERIFICATION OF MULLIKEN THEORY

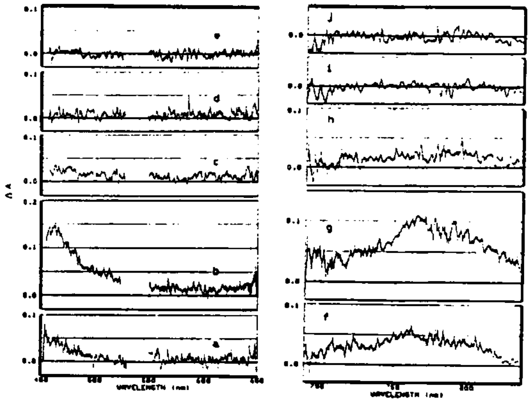
The validity of the generalized formulation of reaction rates as presented by eqs 12-14 depends critically upon the ion pair as the CT excited state according to eq 11. However there has been heretofore no direct and unambiguous experimental verification of Mulliken theory. Accordingly our next task was to establish this important point. We initially chose for study the EDA complexes of substituted anthracenes (R-An) with tetracyanoethylene (TCNE) for two reasons. First, we could independently generate the corresponding donor cation radicals and the acceptor anion radical by electrochemical methods, e.g.[12]



Second, in these EDA complexes the CT absorptions are clearly separated from the absorption bands of either reactant, as illustrated below in a represented example (CNA = 9-cyanoanthracene).[13]

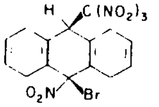


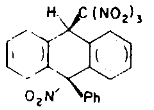
Thus irradiation with the available 532-nm laser pulse ensures that only the CT band is specifically excited in these complexes. The series of time-resolved spectra below (taken at ~25-ps intervals) demonstrates that $R\text{-}An^{+\cdot}$ and $TCNE^{-\cdot}$ are formed concomitantly within the rise time of the initial 25-ps laser pulse.



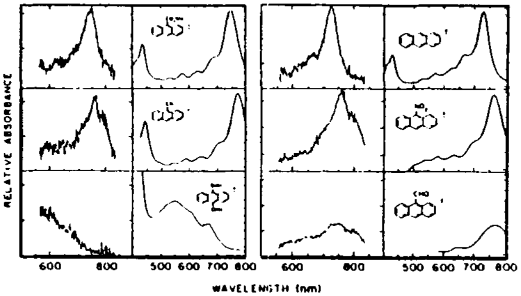
The following figures (c,h above) show that these ions subsequently undergo mutual annihilation by back electron transfer within ~50-ps to regenerate the original EDA complex. This conclusion is supported by independent photochemical experiments which confirm the fact that no chemistry results from CT excitation; viz., the quantum yield for reaction is nil in this system.

By way of contrast, the EDA complexes of the same series of anthracenes with tetranitromethane (TNM) as the common acceptor are found to undergo efficient photochemistry.[14] The meso adducts shown below are formed with an almost unit quantum yield upon the specific excitation



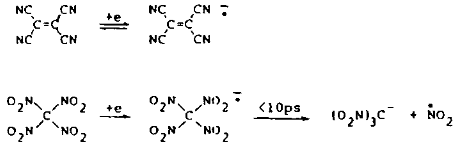


of the CT bands of the 9-bromo and 9-phenylanthracene complexes. These EDA complexes also afford the same series of transient aromatic cation-radicals within the 25-ps pulse as shown below.



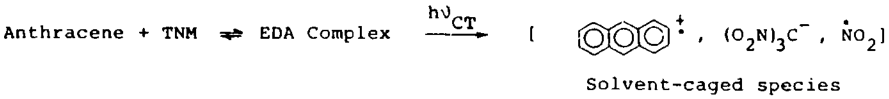
Thus the striking difference between the behavior of the TCNE and the TNM complexes upon CT excitation must lie in the relative rates of back electron transfer, i.e., $[D^{+}A^{-}]^{*} \rightarrow [D, A]$. Indeed such a conclusion accords with the known stability of $TCNE^{\bar{\cdot}}$ but dissociative character to the electron capture by TNM, i.e.[15]

STABILITY OF ACCEPTOR RADICAL-ANIONS



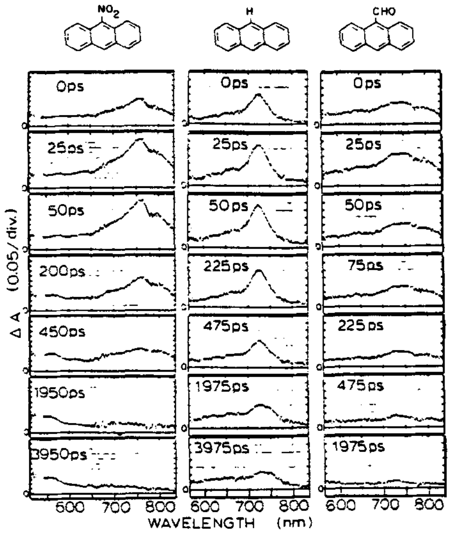
The metastable character of $TNM^{\bar{\cdot}}$ would thus preclude this mode of ion-pair deactivation. Accordingly the CT excitation can be described by a fragmentation process such as:

CHARGE-TRANSFER PHOTOCHEMISTRY OF ANTHRACENE-TNM COMPLEXES

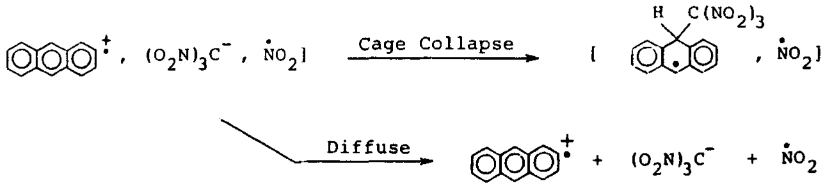


(15)

Time-resolved spectroscopy again provides detailed information as to how the solvent-caged species in eq 15 lead to the meso adducts. Thus the series of spectra below show that most of the aromatic cations disappear on the ps time-scale.



Such rapid processes must result from cage collapse such as:

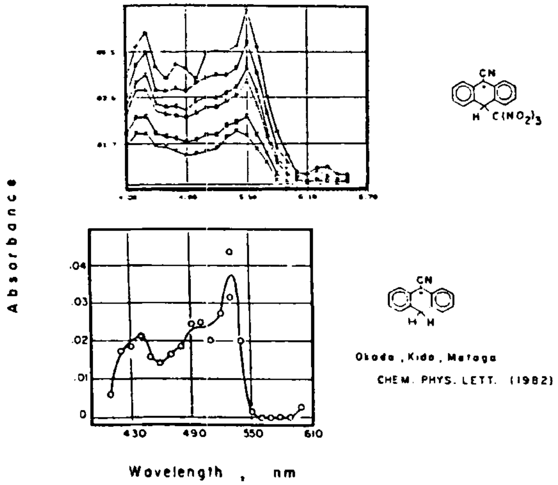


(16a)

(16b)

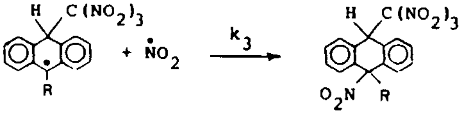
In this formulation, the diffusional processes in eq 16b are responsible for the residual cations observed at relatively long times (ns) after irradiation.

The appearance of the adduct radical on the ns time-scale in CH_2Cl_2 solution is shown in the spectrum below by a comparison with an earlier spectral observation by Mataga and coworkers.[16]



Okada, Kida, Mataga
CHEM. PHYS. LETT. (1982)

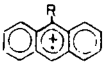
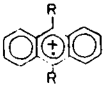
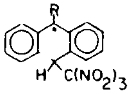
The series of spectra above also illustrate the slower decay of the radical to the meso adduct, i.e.,



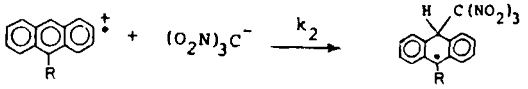
(17)

Analysis of this data indicates that the adduct radical disappears with second-order kinetics. The rate constant k_3 for this process is listed below for several derivatives.

KINETICS OF THE DISAPPEARANCE OF FREE RADICAL-IONS AND FREE RADICALS

Transient Species	R	max (nm)	Log k_2 ($A^{-1}s^{-1}$)		
			CH_2Cl_2	(0.1M TBAP)	MeCN
	CHO	730			5.6
	H	710	7.62	(5.4)	5.6
	Ph	720	7.59	(5.5)	5.7
	Br	725	7.64	(5.5)	5.5
	$CH=CH_2$	690	7.1	(5.5)	5.3
	Br,Br	710	5.7	(3.8)	-
	Ph,Ph	660	3.6	-	-
	CH_3,CH_3	650	5.3	-	-
			Log k_3 (A^{-1} s^{-1})		
			CH_2Cl_2		MeCN
	NO_2	540	5.5		5.6
	CN	550	5.8		5.8
	CHO	540	5.7		5.7

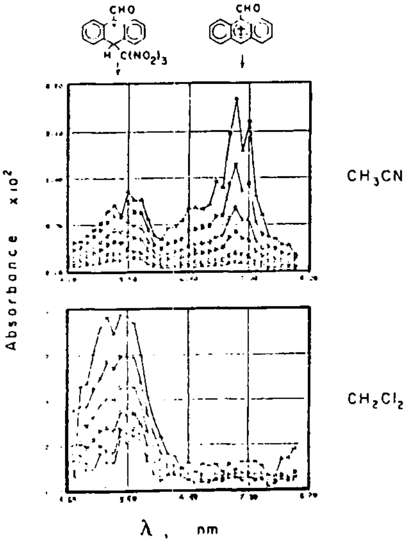
There is also evidence in the ns studies for residual, longer lived cations which also decay with second-order kinetics.



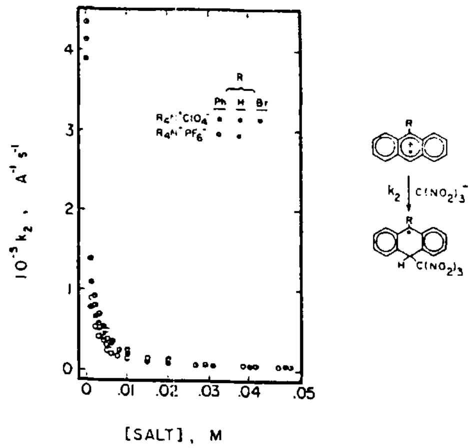
(18)

Values of the rate constants k_2 for these processes are included in the table above.

Solvent polarity plays an important but selective role in the time-resolved spectral changes of these reactive intermediates. For example with 9-formylanthracene, the lifetime of the cation is too short in CH_2Cl_2 to observe on the ns timescale as illustrated below. However, in the more polar CH_3CN, the absorption spectrum of the cation can be observed together with that of the adduct radical.

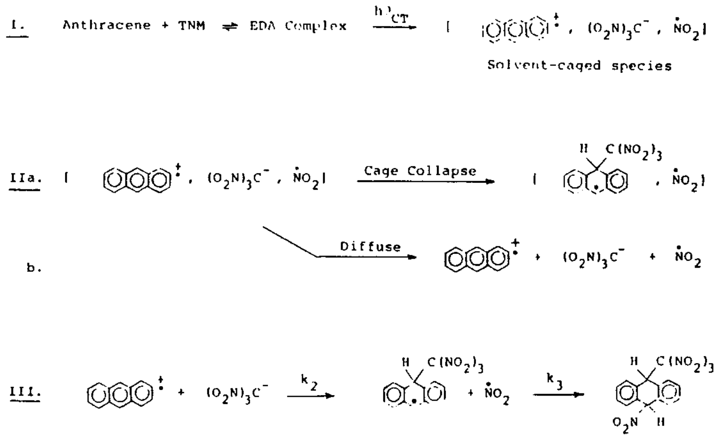


It is singularly noteworthy from the results listed in the table that solvent polarity has an important influence on the second-order rate of cation disappearance (eq 18), but it is essentially without effect on the rate of disappearance of the adduct radical (eq 17). Furthermore, only the kinetics of the cation decay is subject to a marked salt effect illustrated below.



Thus the CT excitation of the EDA complexes of the anthracenes and tetranitromethane provides an excellent opportunity to examine the more general problems relating to the dynamics of ion-pair and radical-radical interactions. These various processes are summarized below in the composite scheme showing the chemical routes which have been identified following CT excitation of the R-An/TNM complex.

CHARGE-TRANSFER PHOTOCHEMISTRY OF ANTHRACENE-TNM COMPLEXES



Important to Mulliken Theory, the use of time-resolved spectroscopy has allowed us to demonstrate the identity of ion pairs as the excited state of charge transfer transitions. The chemistry following CT activation relates to the properties of the ion pairs which are exemplified in this study by a comparison of TCNE and TNM complexes, viz.

THE FATES OF ION PAIRS FROM CHARGE TRANSFER EXCITATION OF EDA COMPLEXES

Anthracene + TCNE $\rightleftharpoons$ [EDA Complex] $\xrightleftharpoons[<50\,ps]{h\nu_{CT}}$ [Anthracene$^{\dot{+}}$ TCNE$^{\dot{-}}$] $\not\rightarrow$ Diels-Alder Adduct

(Φ_p = 0)

Anthracene + TNM $\rightleftharpoons$ [EDA Complex] $\xrightarrow{h\nu_{CT}}$ [Anthracene$^{\dot{+}}$ TNM$^{\dot{-}}$] $\longrightarrow$ 1:1 Meso Adduct

($\Phi_p \sim 1$)

We hope that further studies of the dynamics of CT ion pairs will provide the experimental basis for establishing their relationship with the activated complex as delineated in the title of this paper and summarized by eqs 12-14.

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