



11. Internationales Farbensymposium 11th International Colour Symposium

September 23–26, 1991
Montreux – Switzerland

Chimia 45 (1991) 277–281
© Schweiz. Chemiker-Verband; ISSN 0009–4293

Charge-Transfer Activation of Electron Donor-Acceptor Complexes and Their Role in Electrophilic Aromatic Substitution

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Abstract. Electron donor-acceptor or EDA complexes are common precursors leading to a variety of organic reactions, as indicated by the appearance of characteristic charge-transfer absorption bands. Structural effects of HOMO-LUMO interactions extant in donor-acceptor pairs, established by X-ray crystallography, are critical to the charge-transfer excitation of various types of weak molecular complexes in which time-resolved picosecond spectroscopy identifies the nature of charge-transfer ion pairs. Their relevance to the transition state description of electrophile/nucleophile interactions is underscored in the detailed study of electrophilic aromatic nitration.

1. Introduction

The color changes attendant upon the exposure of various arenes to halogens prior to electrophilic aromatic halogenation are attributed to the formation of weak complexes [1]. The idea that such colors derive directly from the charge-transfer excitation of the 1:1 complex is due to *Mulliken* [2]. In a much more general context, charge-transfer absorption bands result whenever intermolecular complexes [D,A] are formed from the association of an electron donor (D) with an electron acceptor (A) [3]. Indeed electron donors can also be characterized as reducing agents as well as nucleophiles [4]. Furthermore, nucleophiles are often the most effective as negatively-charged anions, and they are also referred to sometimes as *Brønsted*

and *Lewis* bases or in terms of their softness on the HSAB scale [5]. Since each of these classifications relates in some way to a molecular property that is qualitatively considered in degrees of electron-richness [6], the more inclusive designation of electron donors, as originally defined by *Mulliken* [7], is preferable. Thus, the description of an aromatic nucleophile as a relatively electron-rich donor (D) is to be contrasted to the halogen electrophile as an electron-poor acceptor (A).

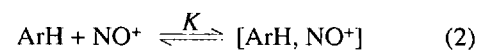
Electron donors and acceptors constitute reactant pairs that are traditionally considered with more specific connotations in mind – such as nucleophile and electrophile in bond formation, reductant and oxidant in electron transfer, base and acid in adduct production, anion and cation in ion-pair annihilation, etc. [8]. As such, the preequilibrium formation of a nonbonded electron donor-acceptor (EDA) complex, *i.e.*



has its counterparts that are variously described as an encounter complex, a precursor complex, a contact charge-transfer complex or a contact ion pair [9]. Despite the limited values of the formation constant $K < 10M^{-1}$ in *Eqn. 1*, a number of charge-transfer complexes have been isolated and structurally characterized by X-ray crystallography [10]. Thus, *Fig. 1* depicts the myriad of crystallographic structures derived from the CT complexes of a simple (arene) donor with different electron acceptors selected from the list of common electrophiles, including bromine, tetracyanobenzene, carbon tetrabromide, chloranil, tetracyanoethylene, together with nitrosonium, silver(I), alkyltin, and lead cations [11]. Although several structural types of arene complexes are included, the linear correlations in *Fig. 2* typify the direct correspondence of the charge-transfer absorptions ($h\nu_{CT}$) with various types of acceptors, irrespective of whether they are involved in a η^2 or η^6 bonding relationship with the arene donor.

2. Colored Aromatic EDA Complexes with Nitrosonium Ion

A nitrosonium salt like a nitronium salt can serve effectively either as an oxidant or as an electrophile toward different aromatic substrates. Thus, the electron-rich polynuclear arenes suffer electron transfer with $NO^+ BF_4^-$ to afford stable arene cation radicals [12]. Other activated aromatic compounds such as phenols, anilines, and indoles undergo nuclear substitution with nitrosonium species that are usually generated *in situ* from the treatment of nitrites with acid. It is less well-known, but nonetheless experimentally established [13] that NO^+ forms intensely colored charge-transfer complexes with a wide variety of common arenes (ArH), *i.e.*, *e.g.*, benzene, toluene, xylenes,



and mesitylene generate yellow to orange vivid hues when added to colorless solutions

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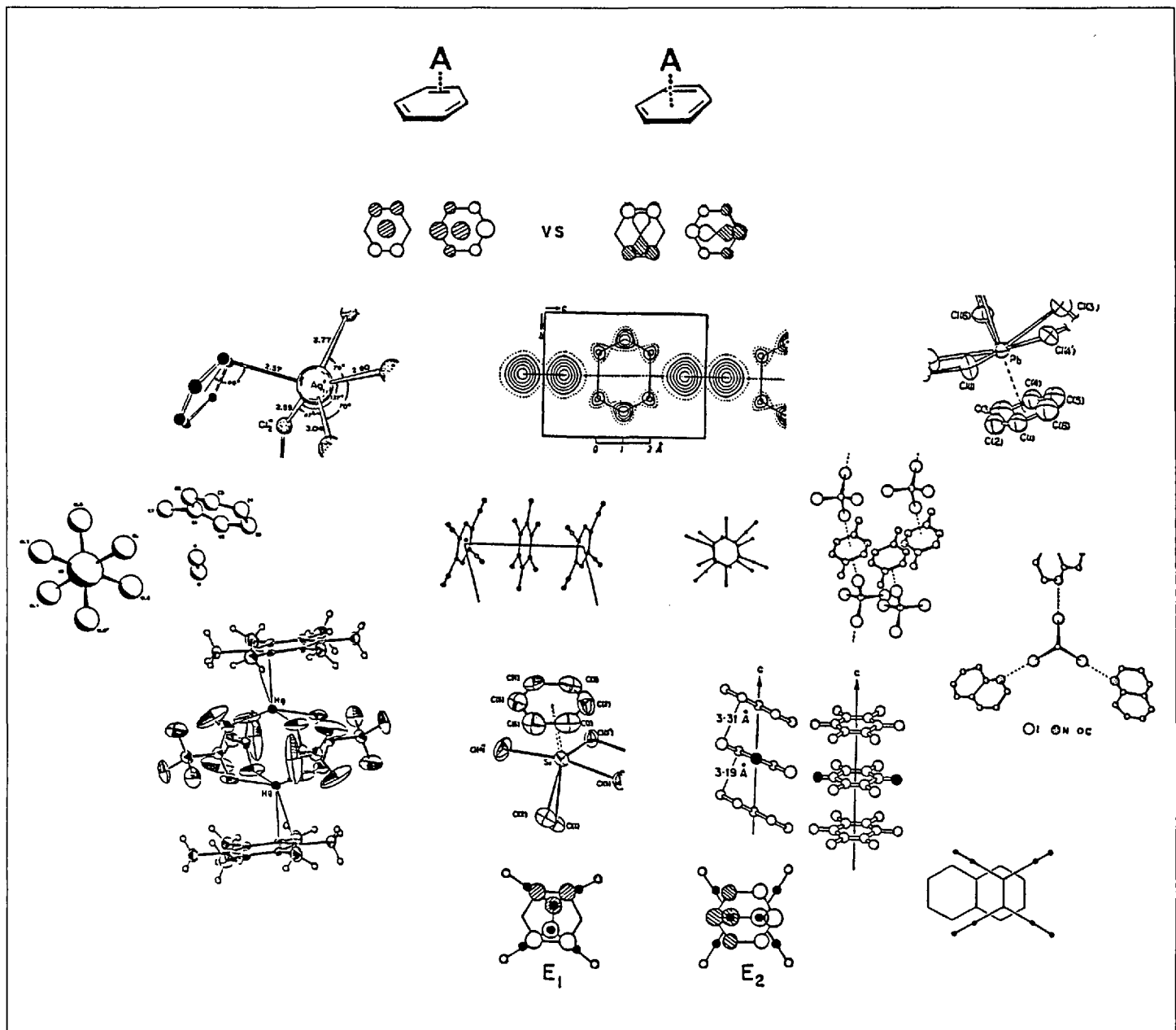


Fig. 1. Collage of X-ray crystallographic structures of aromatic EDA complexes showing η^2 and η^6 interactions to various electron acceptors (see text)

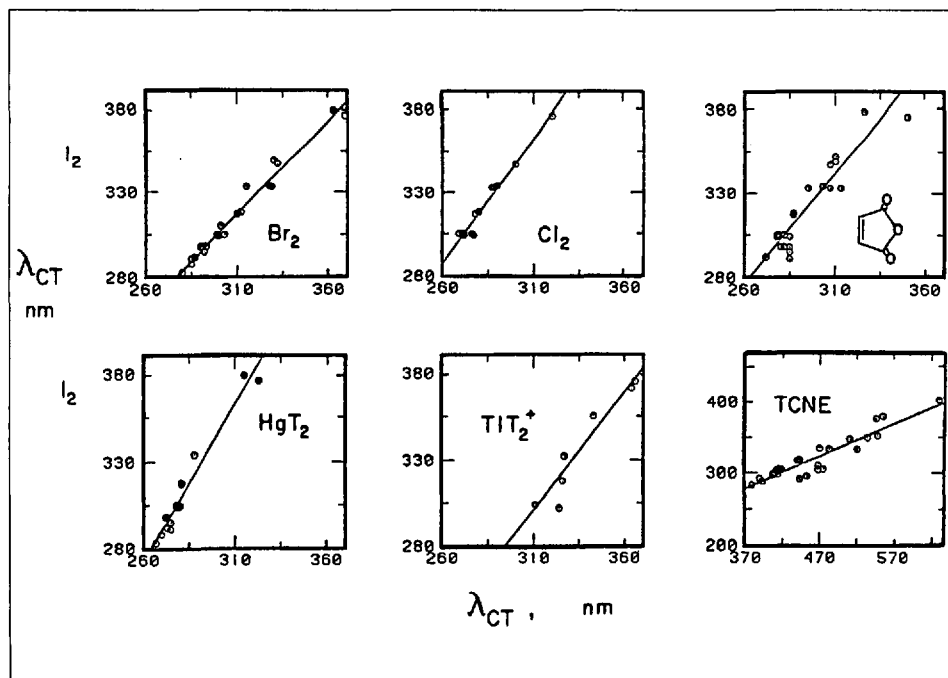
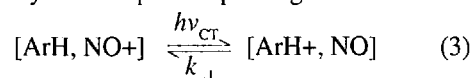


Fig. 2. Direct relationship of the charge-transfer absorption bands of various arene-iodine complexes (ordinate) with those of the corresponding aromatic complexes with different acceptors (abscissa) as indicated

of $NO^+PF_6^-$ in acetonitrile. Analogously, the more electron-rich durene, pentamethylbenzene, hexamethylbenzene, and naphthalene afford dark red solutions when exposed to NO^+ . These highly colored solutions upon standing at -20° , deposit crystals of the CT complexes. In this manner, the 1:1 arene complexes $[ArH, NO^+PF_6^-]$ are isolated with $ArH =$ mesitylene, durene, pentamethylbenzene, and hexamethylbenzene, and the ORTEP diagram from the X-ray crystallography of the mesitylene complex is presented in Fig. 3 [14]. Indeed the relevant CT interaction clearly derives from the centrosymmetric (η^6) structure of the arene- NO^+ pair reminiscent of the other aromatic EDA structures presented in Fig. 1. However, the NO^+ complexes are unusual in two important ways. First, the formation constant K is strongly dependent on the donor strength (i.e., ionization potential) for the arene-increasing dramatically from $0.5M^{-1}$ with benzene to $31\ 000M^{-1}$ with hexamethylbenzene (HMB). Second, the frequency of the N-O stretching band in the IR spectrum

decreases markedly from $\nu_{\text{NO}} = 2037 \text{ cm}^{-1}$ in the toluene complex to $\nu_{\text{NO}} = 1880 \text{ cm}^{-1}$ in the HMB complex. Such a large change in ν_{NO} parallels the difference between the uncomplexed acceptor [$\nu(\text{NO}^+) = 2280 \text{ cm}^{-1}$] and free nitric oxide [$\nu(\text{NO}) = 1876 \text{ cm}^{-1}$]. The unusually pronounced dependence of both the formation constant K and N–O stretching frequency of the aromatic EDA complexes with NO^+ with the aromatic donor strength (as evaluated by the ionization potential) point to a sizeable change in the CT component in the ground state of these complexes.

The irradiation of the charge-transfer band of the aromatic EDA complexes with NO^+ can be carried out at $\lambda = 355 \text{ nm}$ using a 30-ns laser pulse [15]. The time resolved spectrum in Fig. 4 shows the typical bleaching of the CT absorption band and the appearance of the aromatic cation radical with $\lambda_{\text{max}} \sim 500 \text{ nm}$. Since no photochemistry occurs upon the prolonged irradiation of



the CT absorption band, the subsequent first-order decay of the ArH^+ absorption clearly relates to back electron transfer (k_{-1}). It is significant that the trend in k_{-1} accords with the expected increase in driving force for back electron transfer in proceeding from HMB ($IP = 7.71 \text{ eV}$) to benzene ($IP = 9.23 \text{ eV}$). Moreover, it is interesting to note that the magnitudes of these rate constants are in line with those found for the collapse of $[\text{ArH}^+, \text{NO}_2]$ in charge-transfer nitration (*vide infra*). The time-resolved spectral studies thus support the notion that ion radical pairs can be held together by CT interactions sufficient to retard their diffusive separation.

3. Aromatic EDA Complexes as the Unifying Theme in Electrophilic Aromatic Substitution. Charge-Transfer Activation in Nitration

The role of charge-transfer complexes in aromatic nitration with nitronium ion was first suggested by *Kenner* [16], who envisaged an initial step that ‘involves transference of a π -electron...’ Later *Brown* [17] postulated charge-transfer complexes as intermediates, and *Nagakura* provided further theoretical support for one-electron transfer between an aromatic donor (ArH) and an electrophile such as NO_2^+ [17]. Despite notable elaborations by *Pederson, Perrin* and coworkers [18], this formulation has not been widely accepted for nitration and related electrophilic aromatic substitutions. As broadly conceived, the seminal question focuses on the activation process(es) leading up to the well-established *Wheland* or σ -intermediate [19]. In the electron-transfer mechanism, the formation of the ion radical pair **I** is the distinctive feature, as summarized in *Scheme 1*.

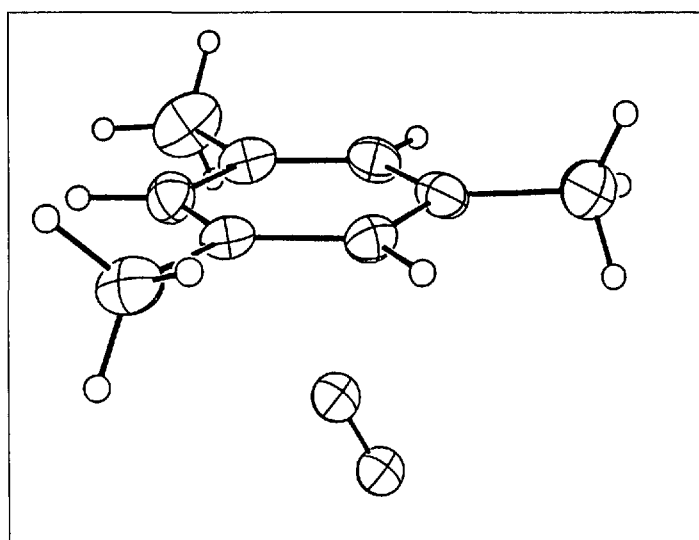


Fig. 3. ORTEP diagram of the mesitylene EDA complex with NO^+ (PF_6^- omitted for clarity)

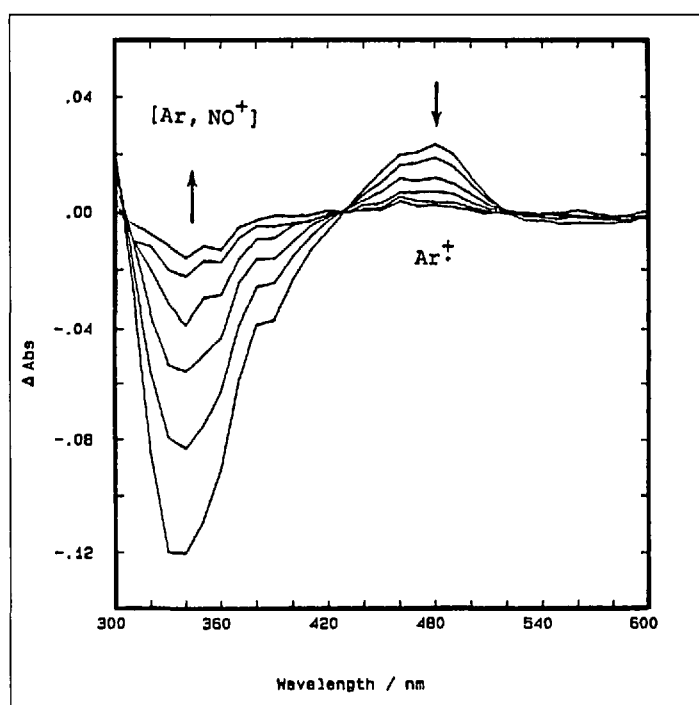
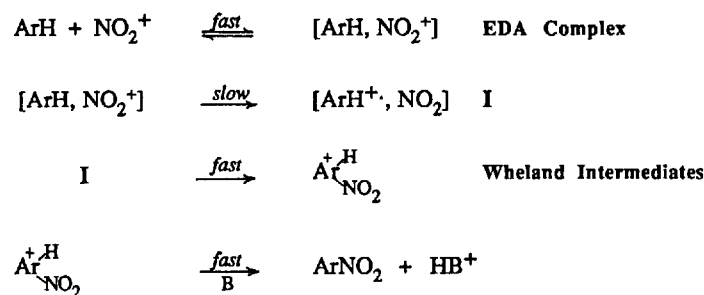


Fig. 4. Typical time-resolved absorption spectrum following the CT excitation of nitronium EDA complexes with arene (hexamethylbenzene) showing the bleaching of CT absorption and growth of the donor cation radical (HMB^+)

Scheme 1



Accordingly, the properties and behavior of the intimate ion radical pair are crucial to establishing its relationship with the numerous facets of electrophilic aromatic nitration [20]. For these reasons it is especially important to know whether the ion pair **I** will actually lead to the appropriate *Wheland* intermediate, and in the amounts necessary to establish the isomer distributions commonly observed in aromatic nitrations. However, the independent proof of the ion radical

pair **I** has not been forthcoming owing to its expectedly transitory character.

Picosecond time-resolved spectroscopy has defined the relevant photophysical and photochemical processes associated with the charge-transfer excitation of an arene complex such as anthracene with tetranitromethane [21]. As applied to benzenoid donors ArH , the formation of the pertinent ion radical pair by charge-transfer excitation is summarized below.

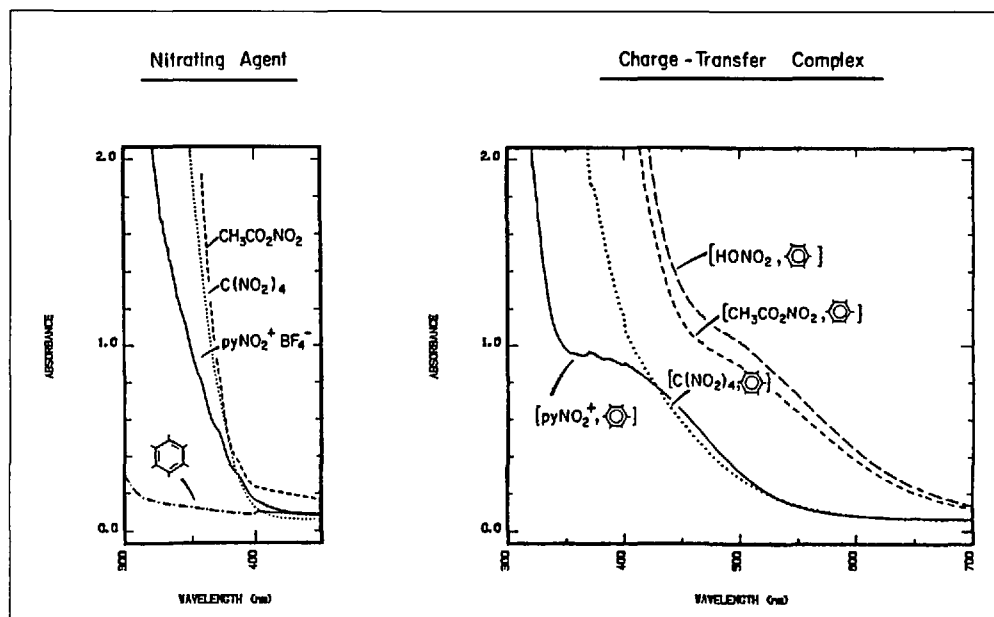


Fig. 5. Right: Comparative charge-transfer spectra of hexamethylbenzene-EDA complexes with various nitrating agents as indicated. Left: Absorption spectra of the uncomplexed donor and acceptors

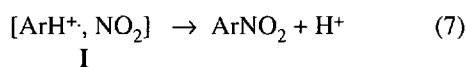
Scheme 2



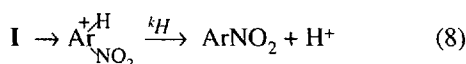
All the experimental observations with various benzenoid donors and tetranitromethane indeed coincide with the formulation in Scheme 2. Thus the exposure of ArH to a nitrating agent such as TNM as in Fig. 5 leads immediately to the EDA complex in Eqn. 5 [22]. It is singularly noteworthy that the charge-transfer spectrum of the aromatic EDA complex with TNM is not fundamentally distinguished from the CT spectra of other common nitrating agents shown in Fig. 5. Moreover, all of these EDA binary complexes are present in low steady-state concentrations owing to the limited magnitude of K as measured by the *Benesi-Hildebrand* method. Activation of the EDA complex by the specific irradiation of the CT band results in a photo-induced electron transfer in accord with *Mulliken* theory. The irreversible fragmentation following the electron attachment to TNM leads to the ion radical pair in Eqn. 6. The measured quantum yield of $\Phi \approx 0.5$ is similar to that ($\Phi \approx 0.7$) obtained for anthracene. Such high quantum yields relate directly to the efficiency of ion radical pair production in Eqn. 6 relative to energy wastage by back electron transfer of Eqn. 5. Moreover, the short lifetime (< 3 ps) of $\text{C}(\text{NO}_2)_4^-$ ensures that ArH^+ and NO_2 are born as an ion radical pair, initially trapped within the solvent cage, since this timescale obviates any competition from diffusional processes [21]. Charge-transfer excitation thus provides the experimental means of generating the intimate ion radical pair $[\text{ArH}^+, \text{NO}_2]$ for Scheme 1 in

sufficient concentrations and in a discrete electronic state as well as geometric configuration. Coupled with the observation of the fast kinetics allowed by the use of laser-flash photolytic techniques, we now focus on the pathways by which the ion radical pair collapses to nitration products with two series of aromatic ethers.

p-Dimethoxybenzene (DMB) is the prototypical electron-rich aromatic donor owing to its reduced oxidation potential of only 1.30 V vs. SCE. Charge-transfer excitation of the 1:1 DMB complex with TNM proceeds quantitatively to the 2-nitro derivative and nitroform. The excellent material balance obtained in such a *charge-transfer nitration* of DMB demands that the ion radical pair in Eqn. 6 proceeds quantitatively to the nitration products according to the stoichiometry of Eqn. 7 [22].

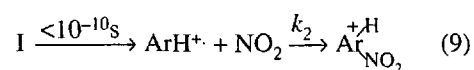


Indeed such cation radicals have been prepared from various arenes by other experimental methods, especially electrochemical oxidation [23]. The arene cation radicals related to DMB^+ are weak *Brønsted* acids, but they are highly susceptible to nuclear addition, and the σ -adduct in Eqn. 8 is the *Wheland* intermediate in electrophilic nitration, which is known to show no deuterium



kinetic isotope effect for k_H upon deprotonation [24]. Accordingly, the formation of the various isomeric *Wheland* intermediates will occur from the collapse of the ion radical pair in Eqn. 8. As such, the isomer distributions in the nitration products relate directly to the relative rates of addition to the various nuclear positions provided that it is irreversible and/or the adduct deprotonates rapidly. Thus, the strong correlation observed between the spin densities at the various nuclear positions of ArH^+ and the isomeric product distribution in aromatic nitration bears directly on the mechanism of such an ion radical pair collapse to the *Wheland* intermediate [25].

Although the *Wheland* intermediate in Eqn. 8 has not been separately observed, the time-resolved spectral changes of the cation radical ArH^+ do provide insight as to how it is formed. Thus, the relatively long lifetime of rather stable arene cation radical DMB^+ is sufficient to allow diffusive separation of the ion radical pair, ArH^+ and NO_2 , as essentially 'free' species [29]. The second-order process with the rate constant k_2 for the disappearance of DMB^+ then represents the 're'combination of these separated species to form the *Wheland* intermediate, *i.e.*



The anisoles (XA) with 4-fluoro, chloro and bromo substituents are substantially poorer electron donors as evidenced by their oxidation potentials E_{ox}^0 that are ~ 500 mV more positive than that of DMB (*vide supra*). As a result, the corresponding cation radicals XA^+ are significantly more susceptible than DMB^+ to nucleophilic addition. The latter can be circumvented in the CT nitration of haloanisoles by either the addition of neutral salt in dichloromethane or the use of acetonitrile as a polar medium. Most importantly the decay of the transient cation radical XA^+ formed by the CT excitation of the EDA consistently followed *first-order*

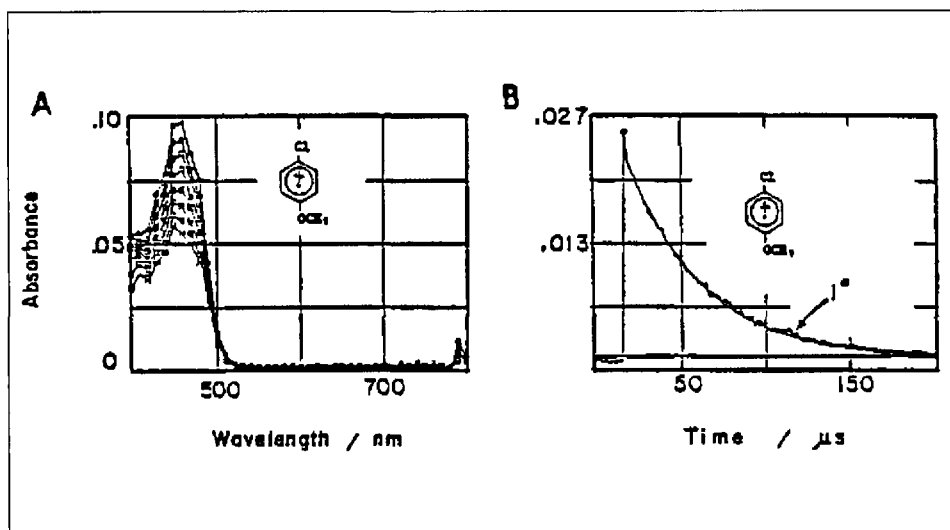
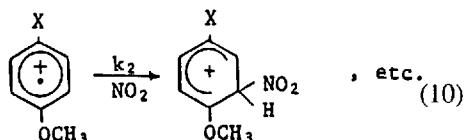


Fig. 6. A) Time-resolved absorption spectrum of the donor cation radical following the CT excitation of the tetranitromethane complex with arene (*p*-chloroanisole). B) First-order decay of the donor cation radical to the Wheland intermediate in aromatic nitration

kinetics [22]. The clean first-order rate processes are applicable to the complete disappearance of XA^+ as established by the return of the absorbance to the baseline in Fig. 6 for $X = Cl$. Since only CT nitration of XA occurs under these experimental conditions, the experimental first-order rate constant k_2 relates solely to the nuclear collapse of the ion radical pair in Eqn. 11. Indeed the regioselectivity of such an ion radical pair collapse yields the isomeric mixture of nuclear nitrations



tion products that is essentially indistinguishable from that obtained under conventional electrophilic conditions. It is also worth noting that the by-products from CT nitration are strongly reminiscent of the by-products reported in electrophilic nitration of the anisoles with nitric acid. In particular, the demethylation of the methoxy group to afford nitrophenols, and the *trans*-bromination of 4-bromoanisole to afford a mixture of 4-nitroanisole and 2,4-dibromoanisole are both symptomatic of radical-pair collapse at the *ipso* positions. These produce the σ -adducts which are akin to the Wheland intermediates known to undergo such transformations [26]. The kinetics of the collapse of the ion radical pair [ArH^+ , NO_2] from the representative arenes show that the decay of the spectral transients for nitration in Eqn. 8 is a reflection of the stability of the aromatic cation radical. E.g., the cation radical from *p*-methylanisole decays by second-order kinetics similar to the kinetic behavior of the long-lived cation radical from *p*-methoxyanisole. The large difference in the rates of diffusive combination with NO_2 corresponds to their relative stabilities as measured by $\Delta E^0 = 8.5 \text{ kcal mol}^{-1}$ of the parent arenes. There is a further, larger gap of $\Delta E^0 = 10.4 \text{ kcal mol}^{-1}$ which separates the stabilities of

the cation radicals of *p*-methylanisole and *p*-fluoroanisole, the least reactive haloanisole. Strikingly, every member of the family of *p*-haloanisole cation radicals reacts with NO_2 by first-order kinetics. This decay pattern strongly suggests that the CT nitration occurs by the cage collapse of the geminate radical pair [ArH^+ , NO_2] prior to diffusive separation, except when the anisole cation is a relatively stabilized species such as those with the *p*-methyl and *p*-methoxy substituents.

I gratefully acknowledge the numerous contributions of my collaborators mentioned in the references and especially S. Sankararaman, J. M. Masnovi, and E. K. Kim for their outstanding creative efforts. I also thank the National Science Foundation, the Robert A. Welch Foundation, and the Texas Advanced Research Program for financial support of this research.

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