Control of reaction course of the excited state of charge-transfer complexes by the free energy of backward electron transfer

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Selective excitation of charge-transfer (CT) complexes between acenaphthylene and various electron acceptors gives net reaction products when the resulting radical ion pairs lie at sufficiently higher energy than the ground state (large $-\Delta G_{BET}$); however, with decrease of $-\Delta G_{BET}$, these tend to become less reactive and finally non-reactive.

During active works on photoinduced electron transfer reactions, attention has been paid to the behavior of the excited states of charge-transfer complexes.[1–9] It was found that, for the combination of aromatic hydrocarbons with electron acceptors, contact radical ion pairs (CIPs) produced on excitation of their charge-transfer complexes facilely undergo backward electron-transfer (BET), the rate constant of which, k_{BET}, increases with decrease of the net free energy difference, $-\Delta G_{BET}$, between the ground state and the radical ion pair, whereas solvent separated radical ion pairs (SSIPs) resulting from encounters of excited states of either donors or acceptors with counterparts follow a bell-shaped k_{BET} *versus* $-\Delta G_{BET}$ relationship.[1–5] The above difference in behavior between CIPs and SSIPs might reflect a much smaller reorganization energy for BET from the former than from the latter.[8] However, the above energy gap effect on the reactivity of CT complexes has been investigated mostly by means of transient absorption spectroscopy, therefore whether the excited states of the CT complexes do or do not give the final reaction products remains unclear. Previously, we found that selective excitation of the CT complex of acenaphthylene (ACN) and TCNE with 546.1 nm light in acetonitrile or dichloroethane did not give any product, whereas excitation of ACN with 435.8 nm light in the presence of TCNE afforded products by way of electron transfer.[10,11]

This finding has led us to examine how $-\Delta G_{BET}$ affects the net chemical reactivity of the excited states of CT complexes between ACN and a series of electron acceptors such as nitriles, acid anhydrides, and quinones,† and we found that the $-\Delta G_{BET}$ value very dramatically controls the net reactivity of the excited state as reported below. The CT complexes‡ were selectively excited in dichloromethane with 546.1 nm light to determine the quantum yields of the reaction, or with >500 nm light to investigate the reaction products, since the CT complexes show absorption at wavelengths longer than 500 nm but ACN shows absorption at wavelengths shorter than 500 nm.

Fig. 1 plots the quantum yields of reaction, Φ_R, against $-\Delta G_{BET}$.§ This indicates that CT complexes with large $-\Delta G_{BET}$ values give net products; however, with lowering of $-\Delta G_{BET}$, Φ_R tends to decrease and finally reaches zero when $-\Delta G_{BET}$ is lower than 1.7 eV.¶ When $-\Delta G_{BET}$ is lower than the threshold, excitation of the CT complexes of ACN with acceptors did not result in any reaction products but excitation of ACN in the presence of the same acceptors afforded reaction products. In these cases, for the same combination of ACN and an acceptor, the SSIP resulting from excitation of ACN is reactive but either the excited state of the CT complex or the CIP resulting therefrom is unreactive. On the other hand, the CIP resulting from the excited CT complex, when lying with $-\Delta G_{BET}$ larger than the threshold, can undergo charge separation to give definite products *via* SSIPs competing with BET.

The Φ_R is composed of efficiencies for charge separation from the excited CT complex, Φ_{CS}, and for the generation of products from the dissociated radical ions, Φ'_R, according to $\Phi_R = \Phi_{CS} \times \Phi'_R$. Therefore, the above results certainly indicate that charge separation practically does not occur when $-\Delta G_{BET}$ is smaller than the above threshold, and the efficiency for charge separation tends to increase with increase of $-\Delta G_{BET}$ as shown in Scheme 1, since the radical ions, once produced from the SSIP, can give reaction products; *i.e.* Φ'_R is always > 0. In fact, excitation of ACN in the presence of the electron acceptors examined afforded reaction products and these were essentially the same as those resulting from excitation of CT complexes when they gave net reaction products.‖ In Scheme 1, A and A′ represent, for example, TCNB and TCNE, respectively.

When the CT complexes afford net reaction products, the resulting products are classified into two classes, *i.e.* those derived from benzoquinones (BQs) and those from non-BQs as shown in Scheme 2. Selective excitation of the CT complexes between ACN and non-BQs, namely acid anhydrides or nitriles, gave mainly two isomeric dimers of ACN, *cisoid*-**1** and *transoid*-**1**, in a ratio of 3–7 : 1, as observed in the excitation of ACN in the presence of electron acceptors such as TCNE which results in electron transfer from the excited ACN to the acceptors followed by the formation of a dimeric radical cation of ACN ($ACN_2^{+\cdot}$) affording *cisoid*- and *transoid*-**1** in the same ratio as above (Scheme 2).[10]

Excitation of the CT complexes of BQs, when affording products, gave addition products (**2**, **3**, and **4**), together with *cisoid*-**1** and *transoid*-**1** (Scheme 2), but no reduction products of BQs such as hydroquinones. For example, selective excitation of the CT complex between ACN and 2-CBQ gave **2**, **3**, and **4** in 13, 32, 7% yields, respectively, together with 20% of **1** with a *cisoid* : *transoid* ratio of 4.0 : 1 on consumption of 21% of

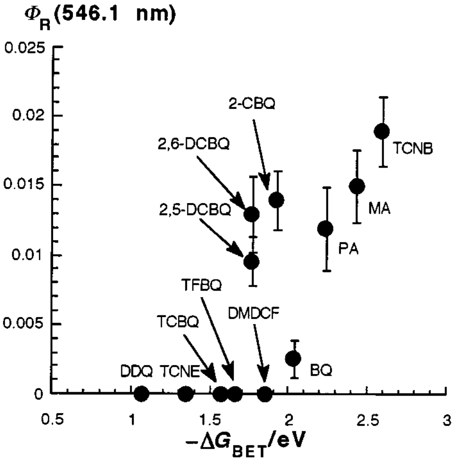
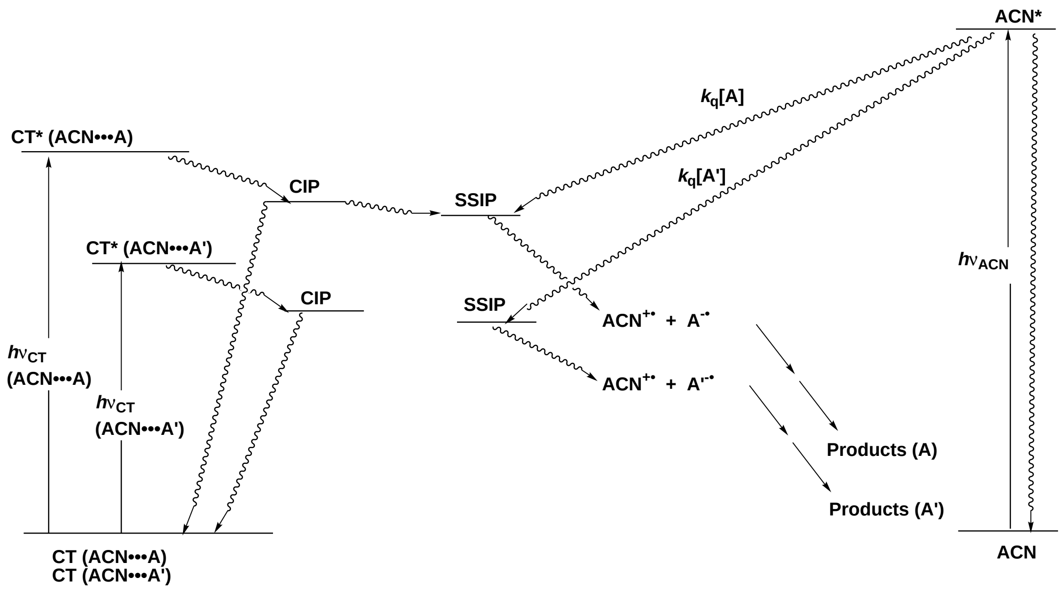
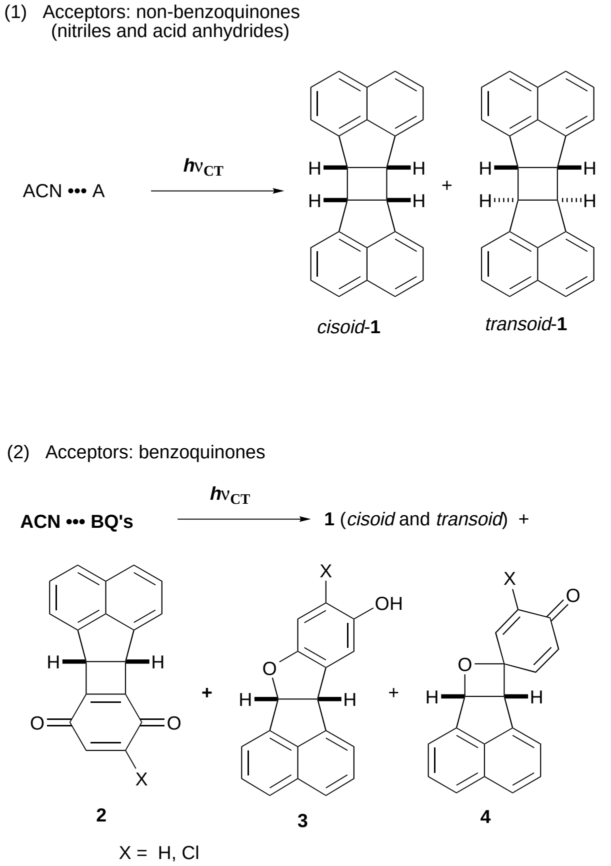


Fig. 1 Plots of quantum yield (Φ_R) at 546.1 nm for the reaction of ACN with various acceptors *versus* the energy gap between the ground state and the CIP ($-\Delta G_{BET}$)



Scheme 1



Scheme 2

ACN. Similarly, direct excitation of ACN with > 400 nm light gave *cisoid*-**1**, *transoid*-**1**, **2**, **3**, and **4** in 9, 4, 18, 36, 8% yields, respectively, on consumption of 94% of ACN.

In conclusion, $-\Delta G_{\mathrm{BET}}$ clearly controls the reactivity of excited CT complexes by affecting the BET rate from the resulting CIP as schematically drawn in Scheme 1. Details of the present study will be published elsewhere.

To our knowledge, this is the first report to show, in a series of CT complexes between an electron donor with various acceptors, $-\Delta G_{\mathrm{BET}}$ dramatically controls the course of reaction leading to final isolable products.

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Notes and References

† Abbreviations of acceptors in this study: TCNB, tetracyanobenzene; DMDCF, dimethyl dicyanofumarate; MA, maleic anhydride; PA, pyromellitic dianhydride; BQ, 1,4-benzoquinone; 2-CBQ, 2-chloro-1,4-benzoquinone; 2,5-DCBQ, 2,5-dichloro-1,4-benzoquinone; 2,6-DCBQ, 2,6-dichloro-1,4-benzoquinone; TCBQ, chloranil; TFBQ, fluoranil.

‡ The CT complexes show absorptions extending to 400–700 nm in organic solvents depending on the acceptors. The equilibrium constants, K_{eq}, for formation of the 1 : 1 CT complex were spectrophotometrically[12] determined in DCE in the range 1.6–6.2 M^{-1} depending on the acceptors.

§ The quantum yields, Φ_{R}, for reaction on selective excitation of the CT complexes were determined based on the amount of converted ACN under irradiation by 546.1 nm monochromatic light in DCE.[13]

¶ In the threshold region, 2-CBQ ($-\Delta G_{\mathrm{BET}}$ 1.92 eV) showed higher Φ_{R} than BQ (2.03 eV), and moreover 2,6-DCBQ (1.76 eV) and 2,5-DCBQ (1.76 eV) exhibited much larger Φ_{R} values than DMDCF (1.85 eV). This fact might be attributed to the heavy atom effect of the chlorine atom in these chloroquinones to enhance conversion of the initially resulting singlet radical ion pair (RIP) to a triplet RIP which will more effectively lead to separation of free radical ions.

‖ An equimolar mixture (0.005–0.02 M) of ACN and an acceptor in DCE was irradiated using a 400 W high pressure mercury lamp in a merry-go-round apparatus at 20 °C as described for TCNE.[10] The products were isolated by flash column chromatography and identified by spectral properties and/or elemental analysis.

1 T. Asahi, M. Ohkohchi and N. Mataga, *J. Phys. Chem.*, 1993, **97**, 13132.
2 H. Miyasaka, S. Ojima and N. Mataga, *J. Phys. Chem.*, 1989, **93**, 3380, and references therein.
3 S. Ojima, H. Miyasaka and N. Mataga, *J. Phys. Chem.*, 1990, **94**, 5834.
4 N. Mataga and H. Miyasaka, *Prog. React. Kinet.*, 1994, **19**, 317.
5 N. Mataga, *Pure. Appl. Chem.*, 1997, **69**, 729.
6 G. Jones, II, W. A. Haney and X. T. Phan, *J. Am. Chem. Soc.*, 1988, **110**, 1922.
7 G. Jones, II, N. Mouli, W. A. Haney and W. R. Bergmark, *J. Am. Chem. Soc.*, 1997, **119**, 8788.
8 I. R. Gould and S. J. Farid, *Acc. Chem. Res.*, 1996, **29**, 522.
9 Y. Takahashi and J. K. Kochi, *Chem. Ber.*, 1988, **121**, 253.
10 N. Haga, H. Takayanagi and K. Tokumaru, *J. Org. Chem.*, 1998, **63**, 5572.
11 N. Haga, H. Nakajima, H. Takayanagi and K. Tokumaru, *Chem. Commun.*, 1997, 1171.
12 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.
13 J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, John Wiley & Sons, Inc, New York, 1966, p. 739.

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