

Exergonic fragmentations in photogenerated zwitterions

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The competition between the fluorescent back-electron transfer and the exergonic fragmentation of radical anions in photogenerated intramolecular zwitterions showed that the rate of fragmentation followed the driving force of the reaction, with the notable exception of the most exergonic case.

Mesolytic cleavages¹ provide an excellent opportunity to experimentally investigate the functional dependence of the reaction rate (kinetics) on the driving force (thermodynamics) for an elementary reaction. Several theoretical and experimental studies have shown² that quadratic (Marcus-type) free-energy relationships may account for the main features of such fragmentation reactions. Indeed, in many instances the cleavage may be viewed as a dissociative intramolecular electron transfer, and analyzed in similar terms.²

To date, most of the fragmentation data have been obtained in the endergonic (or weakly exergonic) region. However, to better define the curvature of the free-energy function for the cleavage and to probe for the existence of an inverted region (similar to that found in electron-transfer reactions), data in the highly exergonic region are required. To probe such a regime, high-energy radical ions have to be generated rapidly, and once generated, they should be able to undergo fragmentation of a homolytically weak bond, giving a stable ionic fragment.³

Based on work of Singer⁴ *et al.*, we have designed an experimental system (Scheme 1) wherein the radical ion pairs (zwitterions) are generated by an intramolecular electron-transfer from the excited state of the aminophenyl moiety to the naphthyl ring bearing a suitable leaving group in a benzylic position. The fluorescent back-electron transfer within the

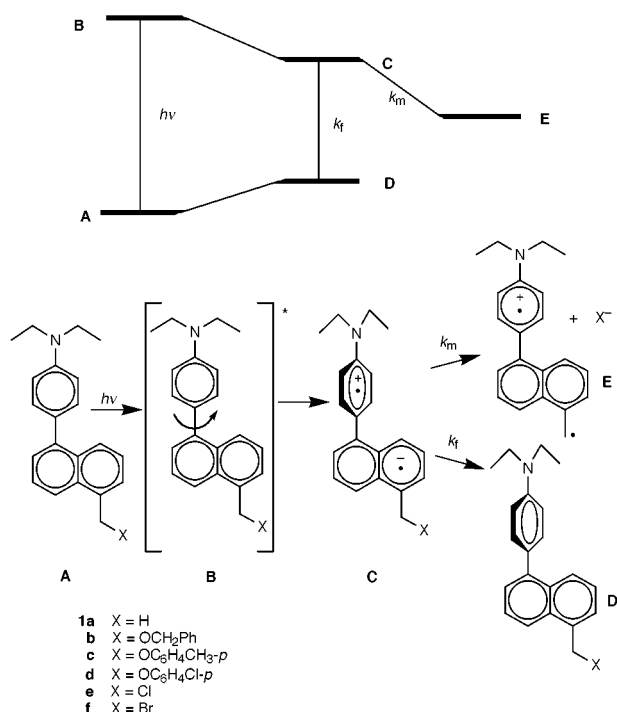
zwitterion competes with the fragmentation of the benzylic bond in the naphthyl radical anion, providing a sensitive handle on the dynamics of the system.

UV-Visible spectra of all compounds⁵ in MeCN were very similar, with the low-energy absorption band maxima at 325–330 nm. These bands were red-shifted (*ca.* 15 nm) and significantly more intense than the corresponding band of 4-bromo-*N,N*-diethylaniline, suggesting some charge-transfer nature of the transition (**A** → **B**). The degree of twist between the phenyl and the naphthyl moieties in **A** in solution is unknown and, therefore, the extent of the electronic coupling between the donor (aminophenyl) and the acceptor (naphthyl) could not be easily determined. The energy separation between the ground state (**A**) and the Franck-Condon state (**B**) is *ca.* 87 kcal mol⁻¹.

All compounds showed fluorescence with λ_{max} around 475 nm (**1a** has λ_{max} of 454 nm). All the fluorescence bands had identical shapes (widths) when recorded on the energy scale, but their intensity varied strongly with the nature of the substituent X (Fig. 1). The fluorescence corresponds⁴ to the transition from the zwitterionic state (**C**) to the neutral state **D** (wherein the twist and solvation status is that of **C**, rather than that of the fully relaxed **A**). It is believed⁴ that degree of twisting in **C** should approach 90°, but is probably somewhat less, leading to only a partial electron transfer between the donor and acceptor moieties.⁶ The energy separation between **C** and **D** is *ca.* 60 kcal mol⁻¹ (68 kcal mol for **1a**).

The oxidation potential of the donor part is 0.74 V vs. SCE, and the reduction potential of the acceptor component is -2.38 V vs. SCE.⁷ The difference (3.12 eV) corresponds to the energy separation between the neutral state (**A**) and the zwitterionic state (**C**), assuming that the coulombic interactions (in MeCN) between the cation and the anion and the electronic coupling between them^{4,6} (which depends on the twist angle) are relatively small. This approximation suggests that **B** → **C** and **D** → **A** relaxation processes (solvent and internal) correspond to *ca.* 15 and 12 kcal mol⁻¹, respectively (Scheme 1).

In the zwitterion **C** bearing a potential leaving group (**1b–f**) the unimolecular fragmentation reaction (k_m) of the naphthyl-centered radical anion (mesolysis) competes with the fluorescent decay (k_f). Such an additional reaction leads to a non-radiative depletion of **C**, and to the apparent change in the fluorescent life-time and the quantum yield as compared to that of the non-reactive model **1a** (Fig. 1).



Scheme 1

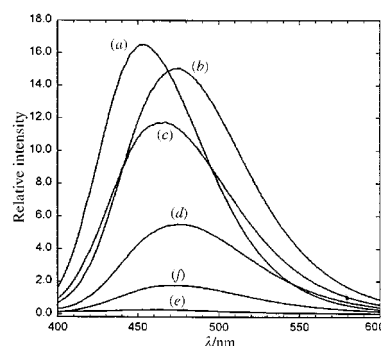


Fig. 1 Steady-state fluorescence spectra of (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d** and (e) **1e** recorded in acetonitrile under identical experimental conditions.

Table 1 Thermodynamic and kinetic data for mesolytic fragmentation

Compound	$\Delta G_h(\text{C-X})^a/$	$E^{\text{ox}}(\text{X}^-)^b/$	$\Delta G_m^c/$	Φ_{rel}^d	k_m^e/s^{-1}
	kcal mol ⁻¹				
1a	77	-0.12	25	1.00	—
1b	70	0.77	-3	0.83	3.6×10^7
1c	51	0.28	-10	0.71	7.2×10^7
1d	51	0.38	-13	0.34	3.4×10^8
1e	65	1.62	-27	0.02	8.6×10^9
1f	53	1.28	-31	0.10	1.6×10^9

^a Free energy of homolysis of the benzylic bond in the neutral molecule, from ref. 10. ^b Oxidation potential of the anion formed in the cleavage, from ref. 11 and 12. ^c Free energy of the mesolysis as calculated from the formula in the text. ^d Relative quantum yields for fluorescence determined in deoxygenated MeCN under argon, under identical experimental conditions for all the compounds. ^e The rate constant for radical anion fragmentation calculated as described in ref. 8.

Using the relative quantum yield data, and the fluorescence lifetime of the model compound (**1a**), values for the rate of the mesolysis (k_m) can be determined for each of the reactive compounds⁸ (**1b–f**). In general, the lower the relative quantum yield for fluorescence, the faster the rate of mesolysis. The results of such calculations are collected in Table 1.

The thermodynamics of mesolytic cleavage was calculated on the basis of a simple thermodynamic cycle (Table 1).^{1a,9} The free energy of mesolysis (ΔG_m) is a function of the free energy of homolysis (ΔG_h) of the scissile bond in the radical ion precursor, and the difference (ΔE) in the redox potentials of the radical ion and the ionic fragments produced. Specifically, in this case ΔE is the difference between the oxidation potential of the anion formed [$E^{\text{ox}}(\text{X}^-)$] and the reduction potential of the naphthyl moiety ($E^{\text{red}} = -2.38$ V vs. SCE). Thus, $\Delta G_m = \Delta G_h - 23.06 (E^{\text{ox}} - E^{\text{red}})$. The homolytic bond free energies are available from the literature.¹⁰ The oxidation potentials of various ions can be obtained from thermodynamic cycles¹¹ or from direct measurements.¹²

The obtained data clearly show that the fragmentation rate of the radical anion correlates with the driving force for the reactions. In general, the more exergonic the reaction, the faster the cleavage of the radical anion, with the notable exception of the bromide **1f**. In this case the fragmentation reaction is five times slower than that of the less exergonic chloride (**1e**).

The sub-nanosecond lifetimes observed for these cleavage reactions are in general agreement with the reaction rates observed for other radical anion fragmentations with similar driving forces,^{2b,d,13} and are, perhaps, only slightly slower than what would be expected for such exergonic processes based on other literature data.^{2,13} This observation suggests that the electronic coupling does not drastically diminish the electron density in the naphthyl radical anions with the radical cation moiety in the zwitterion.⁶

The molecules studied here provide rates for the most exergonic mesolytic fragmentations studied so far. In this context, the inversion in the free-energy profile that is observed for the bromide (**1f**) suggests a possible existence of an inverted region analogous to that observed in electron-transfer reactions.¹⁴ To the best of our knowledge this would be the first example of a reaction where bonds are broken (or made) showing such a behavior. More data are necessary before any firm conclusions can be reached, but the position of the inversion point on the free-energy plot suggests that these reactions have rather small intrinsic barriers.

According to the classical Marcus formulation,¹⁵ the top of the parabola in the ($\log k$) vs. ΔG plot should be located at the ΔG value equal to four times the intrinsic barrier (with the negative sign). In our case the maximum rate at best can be halfway between the ΔG_m values for the chloride and the

bromide. Such simplified analysis suggests that the intrinsic barrier for the mesolytic cleavages of this type of radical anions is ca. 7 kcal mol⁻¹ or less. This estimate is in very good agreement with previous observations,^{2b,d,13} where the intrinsic barrier was postulated to be between 8–4 kcal mol⁻¹.

The observation of a possible inversion point on the free-energy function also suggests that the maximum rate for the cleavage reaction of radical anions is up to two magnitudes lower than what would be expected from transition state theory with a transmission coefficient of unity. Such a result would suggest that the electronic coupling between the π -system bearing the unpaired electron and the σ^* orbital of the scissile bond is not very strong.

We thank the NSF and PRF for support of this research.

Notes and references

- Mesolysis is defined as a unimolecular fragmentation of a radical ion into a radical and ion. See: (a) P. Maslak and J. N. Narvaez, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 283; (b) P. Müller, *Pure Appl. Chem.*, 1994, 1077.
- (a) J.-M. Savéant, *J. Phys. Chem.*, 1994, **98**, 3716; (b) P. Maslak, T. M. Vallombroso, W. H. Chapman Jr. and J. N. Narvaez, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 73; (c) A. Anne, S. Fraoua, J. Moiroux and J.-M. Savéant, *J. Am. Chem. Soc.*, 1996, **118**, 3938; (d) M. L. Andersen, W. Long and D. D. M. Wayner, *J. Am. Chem. Soc.*, 1997, **119**, 6590.
- For a review see: P. Maslak, *Top. Curr. Chem.*, 1993, **168**, 1.
- J. C.-C. Tseng, S. Huang and L. A. Singer, *Chem. Phys. Lett.*, 1988, **153**, 401; J. C.-C. Tseng and L. A. Singer, *J. Phys. Chem.*, 1989, **93**, 7092; M. J. Foley and L. A. Singer, *J. Phys. Chem.*, 1994, **98**, 6430.
- The reactive compounds for these studies were prepared from **1b**. Both **1a** and **1b** were synthesised following the literature procedure (ref. 4). All compounds were stable for several weeks at -10 °C under argon in the dark. Each compound was prepared and studied independently at least twice.
- The electronic coupling between the radical cation and the radical anion in **C** (if the twist angle is less than 90°) would lead to a shift of electron density from the radical anion moiety to the radical cation site, diminishing the degree of electron transfer, and affecting somewhat the thermodynamic calculations presented here.
- The reversible redox potentials were obtained using cyclic voltammetry on **1a**.
- Quantum yield of the model compound (**1a**) is $Q^{\circ} = k_f/(k_f + k_{\text{other}})$, where k_{other} includes all non-radiative decay paths of **C**. Quantum yield of the reactive compounds (**1b–f**) is $Q = k_f/(k_f + k_{\text{other}} + k_m)$, and therefore, $k_m = (Q^{\circ}/Q - 1)\tau^{\circ}$, where τ° is the fluorescent life-time of the model [$\tau^{\circ} = 1/(k_f + k_{\text{other}})$] determined by time-resolved fluorescence to be 5.6 ns.
- D. D. M. Wayner and V. D. Parker, *Acc. Chem. Res.*, 1993, **26**, 287.
- S. W. Benson, *Thermochemical Kinetics*, Wiley, New York, 1976; S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev.*, 1969, **69**, 279; S. E. Stein, *Structure and Properties*, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, 1994.
- The data for halogen ions (and H⁻) are based on the gas phase ionization potentials, hydration energies, and solvation energies for transfer from water to MeCN, and are adjusted for the reference electrode used here (SCE): R. G. Pearson, *J. Am. Chem. Soc.*, 1986, **108**, 6109; Y. Marcus, *Pure Appl. Chem.*, 1985, **57**, 1103.
- P. Hapiot, J. Pinson and N. Yousfi, *New J. Chem.*, 1992, **16**, 877; E. M. Arnett, K. Amarnath, N. G. Harvey and S. Venimadhavan, *J. Am. Chem. Soc.*, 1990, **112**, 7346; F. G. Bordwell and J.-P. Cheng, *J. Am. Chem. Soc.*, 1991, **113**, 1736; F. G. Bordwell, X.-M. Zhang, A. V. Satish and J.-P. Cheng, *J. Am. Chem. Soc.*, 1994, **116**, 6605; J. Lind, X. Shen, T. E. Eriksen and G. Merenyi, *J. Am. Chem. Soc.*, 1990, **112**, 479; G. Merenyi, J. Lind and M. Jonsson, *J. Am. Chem. Soc.*, 1993, **115**, 4945.
- P. Maslak, J. Kula and J. E. Chateaufneuf, *J. Am. Chem. Soc.*, 1991, **113**, 2304.
- See for example: P. F. Barbara, T. J. Meyer and M. A. Ratner, *J. Am. Chem. Soc.*, 1996, **100**, 13 148.
- R. A. Marcus, *Discuss. Faraday Soc.*, 1960, **29**, 21; R. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155; R. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265.

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