Fluorescent Quenching of the 2-Naphthoxide Anion by Aliphatic and Aromatic Halides. Mechanism and Consequences of Electron Transfer Reactions

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The fluorescent excited state of the 2-naphthoxide ion (**1**) is quenched by aliphatic and aromatic halides according to an electron-transfer mechanism, with generation of the corresponding alkyl and aryl radicals by a concerted or consecutive C−X bond fragmentation reaction. Whereas bromo- and iodobenzene follow a concerted ET mechanism (C−X, BDE control), 1-bromonaphthalene exhibits a stepwise process (π LUMO control). The photoinduced reaction of anion **1** with 1-iodoadamantane (**2**) in DMSO affords substitution products on C3, C6, and C8, 1-adamantanol, 1-adamantyl 2-naphthyl ether, and adamantane (3.2, 13.2, 12.2, 2.8, 2.5, and 14.1% yields, respectively). A complex mixture is also observed in the photochemical reaction of neopentyl iodide (**3**) with anion **1**, which renders substitution on C1, C3, C6, C8, and 2-naphthyl neopentyl ether (8.1, 1.3, 19.1, 31.1, and 2.8% yields, respectively). The absence of reaction in the dark and the inhibition of the photoinduced reaction by the presence of the radical traps di-*tert*-butylnitroxide (DTBN) and 1,4-cyclohexadiene are evidence of a radical chain mechanism for these substitutions. On the other hand, only coupling at C1 is achieved by the photostimulated reaction of anion **1** with iodobenzene (**5**), to afford 41.9% of 1-phenyl-2-naphthol and 5.4% of disubstitution product. The regiochemistry of these reactions can be ascribed to steric hindrance and activation parameters.

Introduction

Photoinduced electron transfer (PET) stimulates wide interest in areas that range from biological to technological processes.[1] The rate of the process and the formation of free fragments are strongly dependent on the nature of the donor−acceptor pair. Aliphatic and aromatic free radicals produced in electron-transfer processes can initiate a chain reaction mechanism of substitution ($S_{RN}1$ mechanism) to afford substitution in aromatic (ArX) and aliphatic halides (RX) where the classical mechanisms, i.e., S_N1, S_N2, and S_NAr, are not possible for steric hindrance or energetic reasons.[2]

It is known that the 2-naphthoxide ion reacts with a variety of aryl halides under photostimulation in liquid ammonia to yield 1-aryl-2-naphthoxides as substitution products.[3] These reactions have been proposed to occur by the $S_{RN}1$ mechanism, and involve the participation of radicals and radical anions as intermediates (eq 1).

Ar = *p*-CH₃OC₆H₄, 1-naphtyl
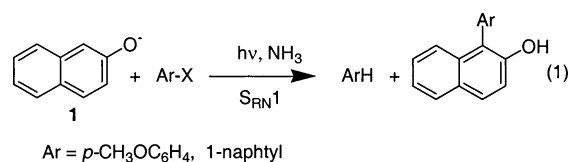
On the other hand, an efficient *O*-alkylation occurs in the $S_{RN}1$ reaction of 1-methyl-2-naphthoxide ions[4] with α,*p*-dinitrocumene and α-chloro-*p*-nitrocumene and phenoxide ions[5] with α,*p*-dinitrocumene. The change in the regiochemistry of the coupling reactions of these ambident anions depends on the radical nature. This was ascribed to differences in the activation energy for the two possible pathways. Thus, the C−C coupling route is faster than the C−O route for aryl radicals, and the inverse occurs for the radicals with EWG.[6] To the present,

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(6) Pierini, A. B.; Borosky, G. L.; Baumgartner, M. T. *Int. J. Quantum Chem.* **1992**, *44*, 759−772.
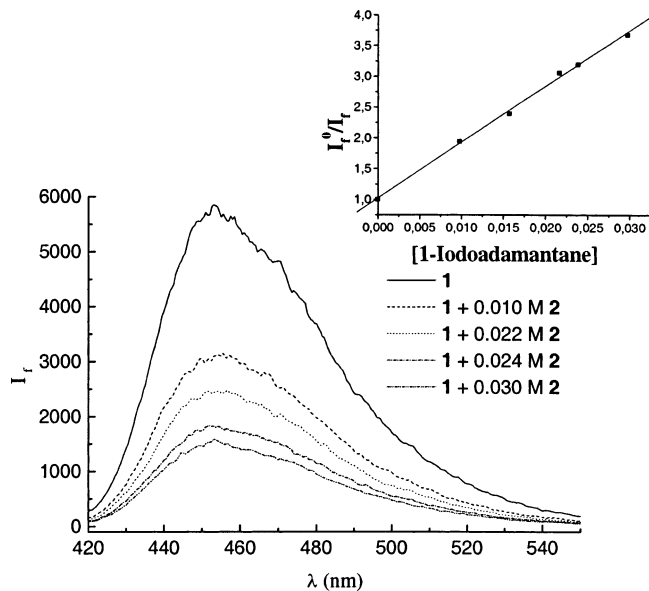
FIGURE 1. Fluorescent quenching of ion **1** by **2**.

there are neither reports on the reactivity of these anions with aliphatic halides without EWG nor quantitative photochemical studies of these reactions. Considering that the photophysics of the 2-naphthoxide anion (**1**) was determined by Soumillion and co-workers,[7] we undertook a systematic study of the photoinduced reaction of ion **1** with 1-adamantyl and neopentyl halides. The product distribution as well as the regiochemistry of the coupling reaction between the radicals and anion **1** was determined.

Results

Fluorescent Quenching of the 2-Naphthoxide Ion (1) by RX and ArX. A solution of ion **1** in DMSO has a pale yellow color and absorbs maximally at 396 nm, whereas most of the alkyl and aryl halides show absorption below 300 nm. When different RX or ArX are added to a solution of **1**, no changes are observed in the absorption spectra.

On the other hand, the fluorescent excited state of anion **1** ($\phi_F = 0.93$ in DMSO)[7] is quenched by RX and ArX following Stern–Volmer linear plots, which allow us to evaluate the quenching rate constants (k_q) and the quantum yield for the fluorescent quenching (ϕ_q). As an example, the effect of adding increasing concentrations of 1-iodoadamantane (**2**) on the fluorescent spectra of anion **1** is shown in Figure 1. The quenching rate constants have a good correlation with the reduction peak potentials for the halides measured by cyclic voltametry and with the theoretical values of their LUMO energy calculated by using the AM1 method (Table 1). Thus, iodide **2** inhibits the fluorescence of anion **1** with a rate constant near diffusion (k_{diff} for DMSO = 3.3×10^9 M^{-1} s^{-1}).[8] For the alkyl halides the LUMO orbital is the σ^*

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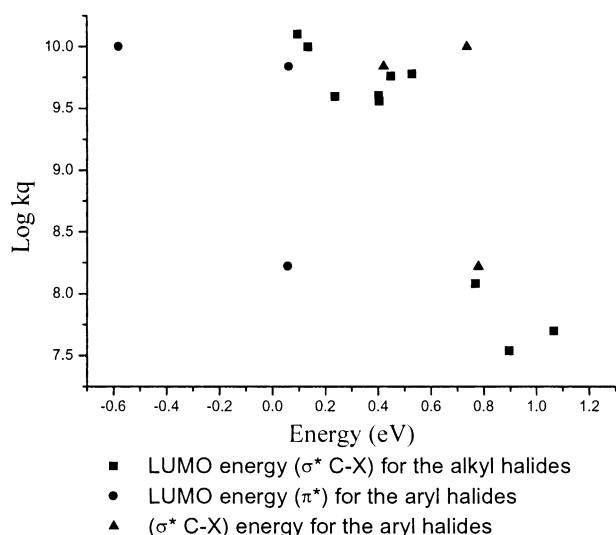
TABLE 1. Fluorescent Quenching of Anion 1 by Alkyl and Aryl Halides

Q	E (V)[a] vs SHE	LUMO[b]	Ksv[c]	kq x10^{-9} (M^{-1}s^{-1})[d]	Log kq	Φ_q[e]
	-1.57	0.1342	178.5 ± 8.0	9.92	10.0	
	-1.70	0.0949	229.6 ± 5.7	12.9	10.1	
	-1.81[f]	-0.581 0.736[g]	187.2 ± 2.9	10.4	10.0	
	-1.93	0.0620 0.4207[g]	123.7 ± 2.6	6.95	9.84	0.77
	-2.16	0.5279	106.8 ± 1.5	6.00	9.78	0.75
	-2.01	0.4472	103.0 ± 2.8	5.78	9.76	0.75
	-2.01	0.2361	70.8 ± 2.1	3.98	9.60	
	-2.21	0.4014	71.9 ± 2.8	4.04	9.61	
	-2.24	0.4035	64.8 ± 7.5	3.64	9.56	
	-2.46	0.0588 0.779[g]	2.96 ± 0.24	0.166	8.22	
	-2.45	0.7672	2.16 ± 0.19	0.121	8.08	
	-2.75	0.896	0.61 ± 0.03	0.034	7.54	
	--	1.067	0.87 ± 0.05	0.049	7.70	

[a] Reduction peak potential at 0.1 V s^{-1}, 0.1 M Bu$_4$NBF$_4$ in DMSO. [b] LUMO energy in eV obtained by using the AM1 method. [c] Stern–Volmer constant. [d] $k_q = Ksv/\tau_0$; τ_0 = lifetime of the excited singlet of **1**. [e] Quenching Φ for [Q] = 0.04 M. [f] Jaworski, J. E.; Leszczynski, P.; Kalinowski, M. K. *Pol. J. Chem.* **1995**, *69*, 688–692. [g] Energy of the σ^* C–X bond.

C–X, which is not the case for aryl halides. However, for all the monohalide substrates studied with the exception of 1-bromonaphthalene, a parabolic correlation is found between the quenching rate constant and the calculated σ^* C–X, including the phenyl derivatives (Figure 2). Whereas bromobenzene exhibits a quenching rate constant of 1.66×10^8 M^{-1} s^{-1} (C–X BDE control), 1-bromonaphthalene shows a k_q of 10.4×10^9 M^{-1} s^{-1} (π LUMO control).

Under similar conditions chlorobenzene was unreactive.

Photoinduced Reactions of Ion 1 with RI and PhI. From stationary photolysis experiments we performed a detailed analysis of the reaction products. Thus, the photoinduced reaction of **1** with R–X = 1-iodoadamantane (**2**), 1-iodo-2,2-dimethylpropane (**3**), and 1-iodo-2,2-dimethyl-3-phenylpropane (**4**) in DMSO rendered a mixture of the respective alkanes R–H (from the hydrogen abstraction of the radical intermediates), substitution products (which arise from the addition of the radicals to the 3, 6, and 8 positions of the ion), as well as

FIGURE 2. Correlation between the rate constant for the quenching and the MO energy.

- ■ LUMO energy (σ^* C–X) for the alkyl halides
- ● LUMO energy (π^*) for the aryl halides
- ▲ (σ^* C–X) energy for the aryl halides

TABLE 2. Reactions of the 2-Naphthoxide Ion (1) with Iodides in DMSO[a]

| | | | | product distribution (%)[c] |
| | | | | | | substitution products on |
entry	substr RI	reac cond	I$^-$ (%)[b]	RH	ROH	O	C1	C3	C6	C8
1	2	*hv*	85	14.1	2.8	2.5		3.2	13.2	12.2
2		dark	<2							
3[d]		*hv*	27		13.4					
4	3	*hv*	83	*e*	*e*	2.8	8.1	1.3	19.1	31.1
5		dark	<2							
6	4	*hv*	89	8.9	*e*	*e*	*e*	*e*	*e*	*e*
7	5	*hv*	54				41.9[f]			
8		dark	<2							

[a] Substrates 0.04 M, 2-naphthoxide ion (**1**) 0.12 M, irradiation for 1 h with a medium-pressure Hg lamp under nitrogen atmosphere. [b] Determined potentiometrically. [c] Determined by GC, using the internal standard method, error 5%. [d] Without the presence of ion **1**. [e] Not quantified. [f] Together with 5.4% yield of a disubstitution product.

minor amounts of the corresponding alcohols (R–OH) and 1-alkyl-2-naphthyl ether derivatives. The photoinduced reaction of anion **1** with iodobenzene (**5**) was also studied in DMSO.

Reactions of Anion 1 with 1-Iodoadamantane (2). The photoinduced reaction of anion **1** with iodide **2** yields after 1 h a mixture of products: adamantane (**6**), 1-adamantanol (**7**), 1-adamantyl 2-naphthyl ether (**8**), and the substitution products on carbons 3, 6, and 8 of the naphthyl ring (**9**–**11**) (eq 2). This reaction does not occur in the dark (Table 2, entries 1 and 2).
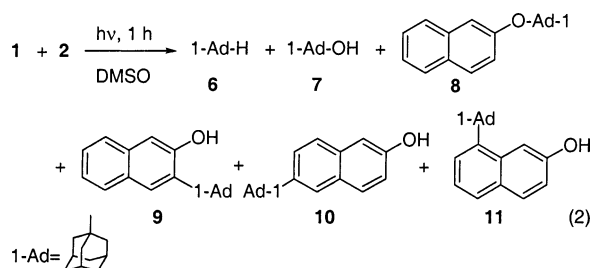
As a control experiment, a solution of iodide **2** was irradiated for 1 h in DMSO to give 1-adamantanol in

TABLE 3. Quantum Yields of the PET Reactions of Ion 1 with 2[a]

| | added compd | | Φ[c] |
entry	(M)	I$^-$ [b]	6	8	9	10	11
1		1.08	0.071	0.076	0.103	0.222	0.304
2[d]	DTBN (0.04)	*e*		0.078	0.006	0.040	0.017
3[f]	DTBN (0.08)	*e*		0.014	0.004	0.024	0.012
4	1,4-cyclohexa-diene (0.12)	*e*	0.222	0.057	0.049	0.183	0.061

[a] Performed under nitrogen atmosphere, using 0.04 M solutions of substrate and 0.12 M solutions of the anion, irradiation at λ_{max} 350 nm. [b] Determined potentiometrically. [c] Determined by GC, using the internal standard method, error 5%, with potassium ferrioxalate as actinometer. [d] In this reaction the Φ of the adduct **12** is 0.147. [e] Not quantified. [f] Φ of the adduct **12** is 0.094.

13.4% yield (Table 2, entry 3). It was previously reported[9] that the photolysis of **2** in polar solvents affords solvolytic products coming from a carbocation intermediate. Thus, 1-adamantanol is the main product observed in DMSO.[9]

The quantum yield determined ($\lambda = 350$ nm) for the reaction of ion **1** with iodide **2** was near 1, evaluated as the quantum yield for the iodide ion formation or as the addition of the quantum yields for the formations of products **6**–**11** (Table 3, entry 1). This photochemical reaction is inhibited by a radical trap as di-*tert*-butylnitroxide (DTBN) with formation of adduct **12**. In the
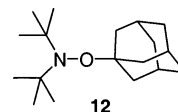
presence of 1,4-cyclohexadiene as hydrogen atom donor, the quantum yields for the reaction products **8**–**11** decrease whereas the formation of adamantane considerably increases (Table 3, entries 2–4). For the quantum yield determination the reactions are performed at very low conversion, and not even traces of 1-adamantanol are observed.
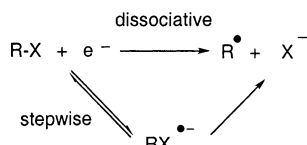
Reaction of Anion 1 with 1-Iodo-2,2-dimethylpropane (3). When a solution of anion **1** with iodide **3** was irradiated for 1 h, a mixture of the substitution products on carbons 1, 3, 6, and 8 of the naphthoxide anion and the ether derivative were formed with 83% yield of iodide ion (eq 3) (Table 2, entry 4).
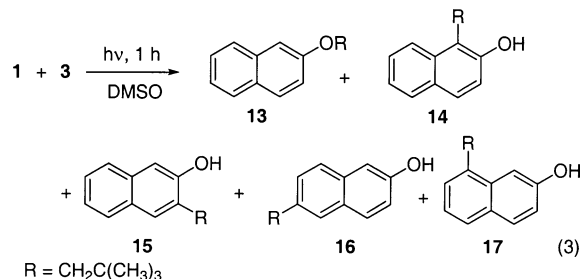
There is no reaction in the dark between **1** and **3**. To improve the mass balance by quantification of the product from hydrogen atom abstraction of the radical intermediate, the photoinduced reaction was performed with 1-iodo-2,2-dimethyl-3-phenylpropane (**4**), a heavier

(9) Perkins, P. R.; Pincock, R. E. *Tetrahedron Lett.* **1975**, *11*, 943–946.

SCHEME 1

$$R\text{-}X + e^- \xrightarrow{\text{dissociative}} R^\bullet + X^-$$

$$\text{stepwise} \searrow \quad \nearrow$$

$$RX^{\bullet-}$$

derivative of **3**. Thus, after 1 h of irradiation a solution of anion **1** with **4** renders 89% yield of iodide ion with 8.9% yield of 2,2-dimethyl-3-phenylpropane determined by GC, with a complex mixture of substitution products, which were not isolated (Table 2, entries 5 and 6).

Reactions of Anion 1 with Iodobenzene (5). The photostimulated reaction of anion **1** with iodide **5** affords mainly the substitution product at C1 (**18**) together with a minor amount of a disubstitution product **19** (41.9% and 5.4% yield respectively) (eq 4). Due to the complexity of the signals in the proton and carbon NMR spectra, it was not possible to assign the structure of product **19**. This reaction does not occur in the dark (Table 2, entries 7 and 8).

$$\mathbf{1} + \mathbf{5} \xrightarrow[\text{DMSO}]{h\nu, 1\text{ h}} \mathbf{18} + \mathbf{19} \quad (4)$$
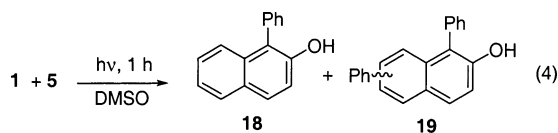
Discussion

Mechanism for the PET Reductions of RX and ArX. The formation of a CTC between the naphthoxide anion and the halides was not observed by UV–vis spectroscopy, which allowed us to disregard this possibility as a mechanism for the ET reaction.

However, the rate constant for the fluorescent quenching of anion **1** by the halides shows a good correlation with their reduction potential or the LUMO energies. Thus, as the reduction potential of RX is made more negative or the LUMO energy is higher, a decrease in the quenching rate constant is found. On the basis of the observed correlation we propose an electron-transfer mechanism for this fluorescent quenching of anion **1** by the electron acceptors (RX and ArX).

Two different mechanisms are possible for the ET: a stepwise process with consecutive ET and fragmentation of the C–X bond in which the radical anion is an intermediate, or a concerted one, namely dissociative ET. This dichotomy is presented in Scheme 1.

Both mechanisms are well described in the literature for homogeneous and heterogeneous (electrochemical) reactions.[10] For aromatic halides such as iodo-, bromo-, and chlorobenzene it was considered that the ET affords a π radical that after an intramolecular ET to the σ state dissociates into a Ph$^\bullet$ radical.[11] On the other hand, for alkyl halides such as 1-iodo- and 1-bromoadamantane and iodo- and bromoneopentane, the ET and fragmentation is proposed to occur simultaneously in a concerted mechanism.

(10) (a) Savéant, J. M. *Adv. Phys. Org. Chem.* **1990**, *26*, 1–130. (b) Savéant, J. M. *Adv. Electron-Transfer Chem.* **1994**, *4*, 53–116. (c) Savéant, J. M. *Acc. Chem. Res.* **1993**, *26*, 455–461. (d) Lund, H.; Daasbjerg, K.; Lund, T.; Occhialini, D.; Pedersen, S. U. *Acta Chem. Scand.* **1997**, *51*, 135–144.
(11) Pierini, A. B.; Duca, J. S., Jr.; Baumgartner, M. T. *THEOCHEM* **1994**, *311*, 343–352 and references therein.

A dissociative mechanism[12] is assumed for the ET from the exited state of anion **1** to aliphatic halides without electron-withdrawing groups such as 1-iodoadamantane (eq 5 and eq 6), as evidenced by the observed good correlation between the log k_q and the values of σ^* C–X for most of the compounds studied (Figure 2).

$$S^0 \xrightarrow{h\nu} S^1 \quad (5)$$

$$S^1 + \mathbf{2} \xrightarrow{k_{ET}} \mathbf{20} + 1\text{-Ad}^\bullet + I^- \quad (6)$$
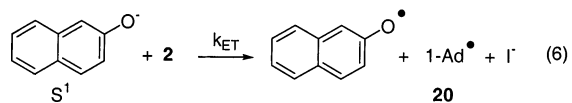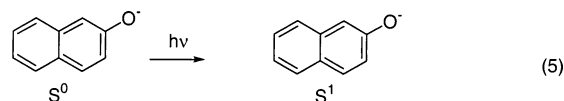
The fact that for the bromo- and iodobenzene k_q correlates with the σ^* C–X values and not with the LUMO energy (for which a higher k_q should be expected) allows us to propose a concerted mechanism for the ET and the fragmentation of the C–X bond for both halides (C–X BDE control). Whereas 1-chlorobenzene was unreactive, 1-bromonaphthalene showed a faster quenching rate constant than bromobenzene, which correlates with the aromatic LUMO. This result suggests a stepwise behavior for the naphthalene bromide (π LUMO control).

A transition between a concerted and stepwise mechanism is possible by changing the driving force of the experimental conditions.[13,14] For example, by increasing the scan rate of cyclic voltametry[15] or by modifying the temperature.[16] For iodobenzene the mechanism passes from concerted to stepwise as the driving force increases. In contrast, bromobenzene and 1-iodonaphthalene follow a stepwise mechanism over the whole range of scan rate.[17]

The fluorescent quenching of the 2-naphthoxide ion by the aromatic halides showed a clear change of mechanism from concerted to stepwise going from bromobenzene to 1-bromonaphthalene, by changing the driving force of the reaction, that is making the process more exergonic.

Our experimental results also indicate that the calculated energy order for the virtual molecular orbitals obtained by AM1 is erroneous. This statement is in agreement with the recently ab initio theoretical studies with electronic correlation, showing that the LUMO for iodobenzene has σ symmetry (σ^* C–I) and that for chlorobenzene is of π nature, whereas for bromobenzene both orbitals σ (σ^* C–Br) and π have similar energy.[18]

Quantum Yield for Fluorescent Quenching. For the photochemical initiation by an excited donor, the occurrence of a concerted ET/bond-breaking reaction

(12) (a) Savéant, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 6788–6795. (b) Savéant, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10595–10602.
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(15) Andrieux, C. P.; Robert, M.; Saeva, F. D.; Savéant, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 7864–7871.
(16) Andrieux, C. P.; Savéant, J. M.; Tardy, C. *J. Am. Chem. Soc.* **1997**, *119*, 11546–11547.
(17) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1999**, *121*, 7158–7159.
(18) Vera, M. PhD Thesis, adviser Prof. Dra. Adriana B. Pierini, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, 2001.

intuitively appears as an ideal situation in which the quantum yield quenching of fragmentation should be unity. This view is based on back ET between the fragments in the solvent cage having an activation barrier too high to compete with their diffusion out of the cage.[13,19] On the other hand, quenching quantum yields are expected to be lower for a stepwise photo-induced ET due to the higher probability of back ET from the intermediate radical anion formed.[13,19] However, it has been shown on theoretical grounds that photoinduced dissociative ETs do not necessarily mean a quantum yield equal to unity. Partition between back ET and fragmentation when the upper first-order potential energy of the system intersects the reactants and fragments zero order surfaces is the main reason for observing a less than unity quantum yield.[13,19] Thus, the experimental quenching quantum yields measured for the reduction of CCl_4 by the excited singlets of perylene and 2-ethyl-9,10-dimethoxyanthracene (EDA) are 0.70 and 0.77, respectively.[20a] Similarly the experimental quenching quantum yields measured for the ET from the excited singlets of perylene to 4-cyano-trifluoromethyl-benzene and from EDA to dimethylphenyl sulfonium, to 4-cyanobenzyl-methylphenyl sulfonium, and to 4-cyanobenzyl chloride were 0.25, 0.35, 0.77, and 0.55, respectively.[20b] On the basis of electrochemical and photochemical experimental results, the first two values are assigned to a stepwise ET mechanism; the last one (0.55) is assigned to a concerted mechanism and a value of 0.77, corresponding to 4-cyanobenzylmethylphenyl sulfonium, a situation in which both mechanism are considered competitive.[20b]

Our results are consistent with the statement that a concerted photoinduced electron transfer is not necessarily endowed with a unity quantum yield.[13,19] In fact, a quantum yield as low as 0.5 can be envisaged from theoretical calculations.[19a] Thus, for the dissociative PET reactions between anion **1** and iodides **2**, **3**, and **5** the quantum yields measured are 0.75, 0.75, and 0.77, respectively.

Nucleophilic Substitutions Reactions of Anion 1 with Alkyl and Aryl Halides. There is no reaction between anion **1** and iodide **2** in the dark whereas a mixture of substitution on C3, C6, and C8 (**9**–**11**), reduction (**6**), and the solvolytic 1-adamantanol and the ether derivative (**7** and **8**) are produced in the photo-stimulated process, which is strongly inhibited by DTBN. Also, inhibition in the formation of the substitution products is observed in the presence of a hydrogen atom donor such as 1,4-cyclohexadiene, with an increase in the yield of adamantane. These results can be rationalized by a radical chain mechanism of substitution ($S_{RN}1$) as follows.

The adamantyl radical (**20**) formed by a dissociative PET (eqs 5 and 6) reacts with **1** at the 3, 6, and 8 positions to yield the radical anion intermediates. No addition to C1 is observed. These radical anions transfer their odd electron to the substrate to continue the propagation cycle to give the radical **20** and the products

SCHEME 2
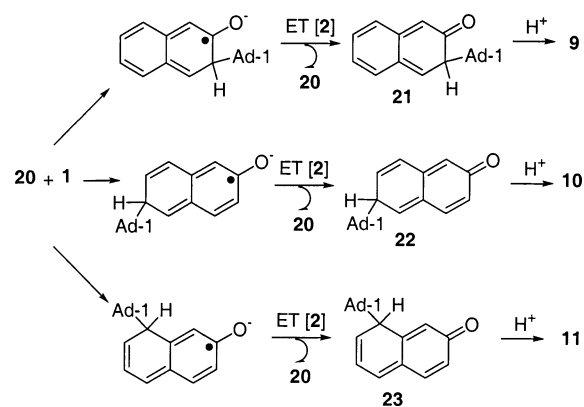
21–**23**. Under the basic reaction conditions, the latter yield the more stable enol tautomers (products **9**–**11**) (Scheme 2).

To measure the efficiency and chain length of the $S_{RN}1$ reactions, it is necessary to know the quantum yield for the initiation step as well as the quantum yield for the formation of the substitution products (Φ_{global}). Thus, it is possible to obtain the $\Phi_{propagation}$ (that is, the chain length) from the ratio of the overall quantum yield and the quantum yield of the initiation step.[21]

In an ideal situation, the photochemical efficiency of the initiation process will be the fluorescent quenching quantum yield measured. To evaluate only the quantum yield of the initiation process, it was necessary to carry out the reactions in the presence of a radical trap such as DTBN, which inhibits the propagation steps. Although the concentration of DTBN was enhanced from 0.008 to 0.08 M, the complete inhibition of the chain reaction was not observed. Considering the value obtained for a concentration of 0.08 M as the photochemical efficiency of the initiation process (Table 3, entry 3), it is possible to estimate an approximate value of 7 for the chain length or $\Phi_{propagation}$ for the reaction of 2-naphthoxide ion **1** with iodide **2**.

The formation of 1-adamantanol (**7**) and 1-adamantyl 2-naphthyl ether (**8**) is evidence of the presence, although in a lower proportion, of the 1-adamantyl cation (**25**) as an intermediate in this reaction. This cation can be generated by photolysis of **2** (Table 2, entry 3); nevertheless, a decrease in the quantum yield of **8** is observed by the addition of DTBN and 1,4-cyclohexadiene (Table 3, entries 3 and 4). These latter results can be ascribed to the participation of 1-adamantyl radicals (**20**) in the formation of the corresponding cation. Thus, **25** can be produced by photolysis of **2** or by ET from radical **20** to a good acceptor such as the naphthoxyl radical (**24**) (Scheme 3).

The photoinduced reaction of anion **1** with neopentyl iodide (**3**) yields substitution products on C1, C3, C6, C8, and the oxygen. However, not even a trace of the alcohol derivative is formed, which allows us to disregard the participation of the neopentyl cation in this reaction. On the other hand, it is well-known that the neopentyl cation gives a very fast rearrangement to the 2-methyl-2-butyl cation. These results indicate that the reaction proceeds

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SCHEME 3

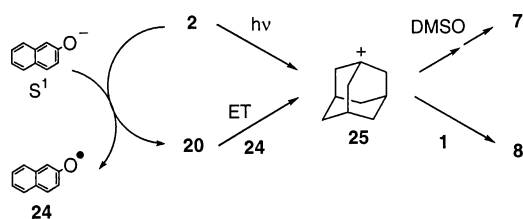**TABLE 4. AM1 (kcal/mol) Heat of Formation for the Radical Anion Product in the Reaction of Anion 1 with Phenyl, Adamantyl, and Neopentyl Radicals**

radical	position at anion **1**				
	C1	C3	C6	C8	O
phenyl	−1.729	0.297	5.665	2.206	14.730
1-adamantyl (**20**)	−58.611	−57.412	−51.968	−54.575	−44.275
neopentyl	−53.001	−51.123	−43.802	−49.824	−38.025

by a radical chain mechanism with the neopentyl radical as the intermediate. Coupling of this radical on the oxygen or the C1, C3, C6, and C8 results in the observed products **13**−**17**.

Iodobenzene reacts with anion **1** under irradiation to yield only monosubstitution on C1 (**18**) and disubstitution as a minor product (**19**). This reaction proceeds by the $S_{RN}1$ mechanism as previously reported, using liquid ammonia as solvent.[3,22] Deprotonation of **18** by anion **1** affords the 1-phenyl-2-naphthoxide anion, which is able to react further as a nucleophile with phenyl radicals to yield the disubstituted product **19**.

Regiochemistry of the Coupling Reaction. The regiochemistry observed in the reaction of phenyl radicals with anion **1** is in agreement with those previously reported,[22] although the concentrations used in DMSO are higher than those employed in liquid ammonia. Thus, in this reaction only coupling at C1 is observed for the monosubstitution.

On the other hand, 1-adamantyl radicals (**20**) generated by PET from anion **1** to **2** showed a very low reactivity yielding coupling at C3, C6, and C8. To rationalize the observed regiochemistry, preliminary theoretical results obtained from the AM1/UHF method[23] show that for all the cases studied the substitution on C1 yields the more stable radical anion (Table 4). This is also valid for the 1-adamantyl radical, which does not present reactivity at that position. Only the phenyl radical yields exclusive coupling at C1.

The radicals anions calculated for coupling at C1 are presented in Figure 3. As can be seen from the figures the intermediate formed by coupling with radical **20** has a considerably steric hindrance between the methylene group of the radical and the oxygen and the hydrogen at position 8 of anion **1**. The primary neopentyl radical presents low regioselectivity with a minor steric hindrance as is shown by the formation of product from
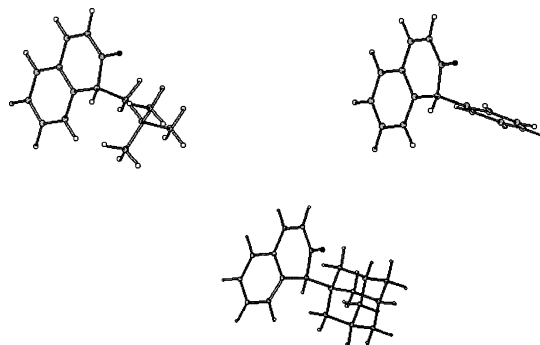
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FIGURE 3. Radical anion products for the coupling at C1 of the 2-naphthoxide ion with 1-adamantyl, phenyl, and neopentyl radicals.

coupling at C1. These factors could be responsible for a higher activation energy for coupling with these radicals, which will not be the case with the phenyl radicals.

On these basis coupling at position 1 with phenyl radicals will be under thermodynamic control while kinetic control will determine the coupling with the more sterically hindered radicals. Calculations with a higher theoretical level and with inclusion of solvent effects to clarify this regiochemistry are in progress.

Conclusions

The fluorescent excited state of the 2-naphthoxide ion (**1**) is quenched by aliphatic and aromatic halides as electron acceptors according to an electron-transfer mechanism, which is proposed on the basis of the following: (a) decreasing the quenching rate constant as the reduction potential of the halides is made more negative, following a typical behavior for an electron-transfer reaction, and (b) from a detailed analysis of the photochemical reaction products. The ET and the fragmentation of the C−X bond for 1-adamantyl, neopentyl, and phenyl iodide and bromide are assumed to be concerted due to the observed good correlation between the k_q with the σ^* C−X energies, whereas for 1-bromonaphthalene a stepwise behavior is suggested.

Aliphatic halides (such as 1-iodoadamantane and neopentyl iodide) and iodobenzene react with 2-naphthoxide ions by the $S_{RN}1$ mechanism in DMSO. Mechanistic evidence is provided by the stimulation of these reactions by light and the inhibition of the photoinduced reactions in the presence of 1,4-cyclohexadiene and DTBN. The photostimulated reactions of the 2-naphthoxide ion with different radicals afford a mixture of substitution products. The addition of the 1-adamantyl radical gives substitution at the 3, 6, and 8 positions of the ion as well as 1-adamantanol and minor amounts of 1-adamantyl 2-naphthyl ether. With a primary radical a similar behavior is observed as well as formation of the expected substitution at the one-position of the naphthyl moiety; meanwhile the aromatic radical renders almost exclusively the product coming from the substitution at the one-position. These last results can be rationalized in terms of steric effects.

Experimental Section

Methods. The fluorescent quenching study was performed by using stationary fluorescent techniques at room temperature (25 ± 1 °C). The reduction peak potentials were measured

by cyclic voltametry. The general methods and procedure for the photoinduced reaction are the same as previously published.[21]

Materials. *t*-BuOK, 2,2-dimethyl-3-phenyl-1-propanol, bromoneopentane, iodoneopentane, bromobenzene, iodobenzene, 1-bromoadamantane, 1-iodoadamantane, DTBN, and 1,4-cyclohexadiene were all high purity commercial samples which were used without further purification. The commercially available 2-naphthol was recrystallized from water. DMSO was distilled under vacuum and stored over molecular sieves (4 Å). The supporting electrolyte Bu₄NBF₄ was prepared following standard procedures. The 2-naphthoxide ion (**1**) was generated in situ by acid–base deprotonation with use of *t*-BuOK. 1-Iodo-2,2-dimethyl-3-phenylpropane[24] was synthesized by reaction of the corresponding tosylate with KI or LiCl in DMF. The tosylate and benzene sulfonate were prepared by standard procedures. The di- and trihaloneopentyl derivatives such as 1-iodo-2-iodomethyl-2-methylpropane, 1-bromo-2-bromomethyl-2-methylpropane, 1-chloro-2-chloromethyl-2-methylpropane, and 1-bromo-2,2-dibromomethylpropane were synthesized by reaction of the corresponding tosylates with KI, NaBr, or LiCl in diethylene glycol following a procedure similar to that reported in the literature.[25] 1,3-Diiodoadamantane and 1,3-dibromoadamantane were obtained by oxidation of the corresponding haloadamantane with CrO₃ and further reaction of the 3-hydroxy-1-haloadamantane with HI or HBr.[26]

1-Adamantyl 2-naphthyl ether (8) was isolated by radial chromatography with petroleum ether as eluent from the crude product reaction mixture of anion **1** and **2**: ¹H NMR (CDCl₃) δ 1.62 (6H, m), 1.95 (6H, m), 2.18 (3H, m), 7.15−7.82 (7H, m); ¹³C NMR (CDCl₃) δ 29.08, 37.11, 37.25, 40.75, 110.82, 123.84, 125.03, 125.81, 126.27, 127.83, 129.15, 132.74, 138.64, 153.62. MS (EI⁺) 279 (2), 278 (9), 135 (100), 93 (19), 79 (21). HRMS (EI⁺) calcd 278.1671, expt. 278.1672.

3-(1-Adamantyl)-2-naphthol (9) was isolated by radial chromatography with petroleum ether/diethyl ether (98:2) as eluent from the crude product reaction mixture of anion **1** and **2**: ¹H NMR (CDCl₃) δ 1.82 (6H, m), 2.13 (3H, m), 2.23 (6H, m), 5.06 (1H, s), 6.99 (1H, s), 7.24−7.40 (2H, m), 7.64 (1H, s), 7.58−7.77 (2H, m); ¹³C NMR (CDCl₃) δ 29.67, 36.17, 42.90, 78.27, 120.96, 124.52, 125.59, 125.92, 127.21, 127.53, 128.29, 130.55, 134.00, 151.90; MS (EI⁺) 279 (21), 278(100), 221(37). HRMS (EI⁺) calcd 278.1671, expt. 278.1672.

6-(1-Adamantyl)-2-naphthol (10)[27] was isolated by several radial chromatography techniques with petroleum ether/diethyl ether (95:5) as eluent from the crude product reaction mixture of anion **1** and **2**: ¹H NMR (CDCl₃) δ 1.80 (6H, m), 2.00 (6H, m), 2.13 (3H, m), 4.91 (1H, s), 7.02−7.11 (2H, m), 7.49−7.73 (4H, m); ¹³C NMR (CDCl₃) δ 29.00, 36.14, 36.90, 43.18, 109.10, 117.48, 122.71, 124.81, 126.02, 128.99, 129.85, 132.79, 146.56, 152.92. MS (EI⁺) 279 (20), 278(100), 221(65). HRMS (EI⁺) calcd 278.1671, expt. 278.1668.

8-(1-Adamantyl)-2-naphthol (11) was isolated by several radial chromatography techniques with petroleum ether/diethyl ether (95:5) as eluent from the crude product reaction mixture of anion **1** and **2**: ¹H NMR (CDCl₃) δ 1.88 (6H, m), 2.19 (3H, m), 2.30 (6H, m), 5.38 (1H, s), 7.06 (1H, dd, *J* = 8.8, 2.2 Hz), 7.27 (1H, t, *J* = 7.7 Hz), 7.42 (1H, dd, *J* = 7.5, 1.3 Hz), 7.63 (1H, d, *J* = 8 Hz), 7.77 (1H, d, *J* = 8.7 Hz), 8.01 (1H, d, *J* = 2.2 Hz); ¹³C NMR (CDCl₃) δ 29.70, 37.19, 38.40, 42.34, 109.69, 116.21, 123.17, 123.98, 127.24, 130.53, 131.52, 132.44, 144.46, 151.79. MS (EI⁺) 279 (22), 278 (100), 221 (48). HRMS (EI⁺) calcd 278.1671, expt. 278.1670.

Coupling product from 1-adamantyl radical and DTBN (12) was isolated by radial chromatography with petroleum ether/diethyl ether (95:5) as eluent from the crude product reaction mixture of anion **1** and **2** in the presence of DTBN: ¹H NMR (CDCl₃) δ 1.06 (18H, s), 1.615 (6H, m), 1.76 (6H, m), 2.11 (3H, m); ¹³C NMR (CDCl₃) δ 27.19, 29.70, 30.56, 36.68, 41.13, 53.79. MS (EI⁺) 135 (100), 93 (30), 79 (26).

Neopentyl 2-naphthyl ether (13) was isolated by radial chromatography with petroleum ether as eluent from the crude product reaction mixture of anion **1** and **3**: ¹H NMR (CDCl₃) δ 1.08 (9H, s), 3.71 (2H, s), 7.11−7.44 (4H, m), 7.69−7.76 (3H, m); ¹³C NMR (CDCl₃) δ 26.71, 31.91, 77.92, 106.54, 119.13, 123.38, 126.24, 126.64, 127.62, 128.88, 129.21, 134.67, 157.59. MS (EI⁺) 215 (5), 214 (31), 145 (19), 144 (100), 116 (11), 115 (39).

1-Neopentyl-2-naphthol (14) was isolated by radial chromatography with petroleum ether/diethyl ether (98:2) as eluent from the crude product reaction mixture of anion **1** and **3**: ¹H NMR (CDCl₃) δ 1.09 (9H, s), 3.06 (2H, s), 7.11 (1H, d, *J* = 8.8 Hz), 7.31−7.39 (1H, m), 7.45−7.59 (1H, m), 7.68 (1H, d, *J* = 9.1 Hz), 7.79 (1H, dd, *J* = 8, 1.1 Hz), 8.06 (1H, d, *J* = 8.8 Hz); ¹³C NMR (CDCl₃) δ 30.53, 34.39, 37.30, 117.72, 117.91, 122.77, 124.52, 125.70, 128.02, 128.40, 151.63. MS (EI⁺) 215 (5), 214 (31), 158 (80), 157 (100), 129 (55), 128 (45), 127 (19).

1-Phenyl-2-naphthol (18) was isolated by radial chromatography with petroleum ether/diethyl ether (95:5) as eluent from the crude product reaction mixture of anion **1** and **4**: ¹H NMR (CDCl₃) δ 5.15 (1H, s), 7.18−7.82 (11H, m); ¹³C NMR (CDCl₃) δ 117.35, 120.96, 123.25, 124.57, 126.43, 127.97, 128.40, 128.91, 129.45, 129.56, 131.15, 133.25, 134.19, 150.12. MS (EI⁺) 221 (15), 220 (100), 219 (46), 191 (20), 198 (12), 189 (30). HRMS (EI⁺) calcd 220.0888, expt. 220.0886.

Supporting Information Available: ¹H NMR and ¹³C NMR spectra of compounds **8**−**14**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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