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Nonchain Processes in Nucleophilic Substitutions Triggered by Electron Transfer ($S_{RN}1$). Photochemical and Electrochemical Induction of the Substitution of 1-Iodoadamantane by Arenethiolate Ions

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Abstract: Photochemical induction of the reaction of 1-iodoadamantane with arenethiolate ions provides a clear-cut example of nonchain $S_{RN}1$ substitutions. With 4-methoxy-, 4-methyl-, and 4-cyanobenzene and benzenethiolate ions, excellent yields (over 85%) are obtained in spite of efficient electron transfer quenching of the very easily oxidized anion radical of the substituted product by quaternary ammonium countercations. The production of the corresponding disulfides is used to determine the number of chains. Absorption and fluorescence spectroscopy and laser pulse irradiation experiments indicate that the electron which triggers the substitution process is generated by photoejection from the nucleophile, with an efficiency that decreases in the order 4-methoxybenzene > 4-methylbenzene > 4-benzene > 4-cyanobenzenethiolate. Electron photoejection does not occur with naphthalenethiolate ions. However substitution can be entrained by addition of benzenethiolate ions. The two nucleophiles were found to have comparable reactivities toward the 1-adamantyl radical. Rather than the formation of its anion radical, the first step of the $S_{RN}1$ process is a dissociative electron transfer to 1-iodoadamantane, yielding directly the adamantyl radical. This is the reason that direct electrochemical induction of the substitution was not observed. Induction by electrogenerated aromatic anion radicals could be observed. It was much less efficient than photoinduction because the amount of electron donor species required to trigger the reaction is much larger.

Many nucleophilic substitutions at sp^2 and sp^3 carbons are induced by light, by solvated electrons, or by electrons from an electrode or from homogeneous outersphere electron donors.[2–12] The radical mechanism depicted in Scheme 1 (the "$S_{RN}1$" mechanism[13]) is commonly accepted for these reactions.[2–12]

The existence of all three steps has been proved by direct or indirect electrochemistry for aromatic substrates giving rise to fast-cleaving anion radicals, $RX^{\bullet-}$ (cleavage rate constants of $\geq 10^5$ s^{-1}).[4,8,12] In these experiments the chain process is initiated by single electron transfer from an electrode surface or from an homogeneous outersphere electron donor generated at the electrode. These studies have also allowed the determination of many rate constants for cleavage of substrate anion radicals and for formation of anion radicals by coupling of aromatic radicals with nucleophiles.[4,8,14,15] A model based on an extension of the dissociative electron transfer theory has been recently proposed relating the reactivity for these two essential steps of the $S_{RN}1$ process to the structure of the reactants.[10–12,16]

Scheme 1

$$RX^{\bullet-} \rightleftharpoons R^{\bullet} + X^{-} \tag{1}$$

$$R^{\bullet} + Nu^{-} \rightleftharpoons RNu^{\bullet-} \tag{2}$$

$$RX + RNu^{\bullet-} \rightleftharpoons RX^{\bullet-} + RNu \tag{3}$$

In most cases, the direct and indirect electrochemical determinations of coupling rate constants between aryl radicals and nucleophiles were based on the observation of its competition with electron transfer reduction of the aryl radical by the electrode or by electrogenerated homogeneous electron donor. The latter reactions are fast since the standard potentials of aryl radicals are much more positive than the reduction potentials of usual $S_{RN}1$ substrates. They are, together with the reduction of the radical by the anion radical of the substituted product (eq 4), efficient termination steps in electrochemically induced

$$R^{\bullet} + RNu^{\bullet-} \rightarrow RNu + R^{-} \tag{4}$$

$$R^{-} + \text{proton donor} \rightarrow RH$$

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$S_{RN}1$ substitutions. In organic solvents, H-atom abstraction by the aryl radical may be an additional termination step leading to the same reduction product.

Similar chain processes and termination steps should also be present when the $S_{RN}1$ reaction is triggered in the same media by light or solvated electrons. The chain character of photochemically induced reactions has been demonstrated in a few cases by the observation of quantum yields greater than one.[17] However, the most widely employed means of testing the chain character of the reaction has been the observation that the introduction of a redox trap or of a radical scavenger depresses the reactivity.[5] It should be borne in mind however that a negative observation does not prove that propagation chains are absent. Such an observation may indeed result from reaction 3 being faster than electron transfer from $RNu^{\bullet-}$ to the redox trap or reaction 2 being faster than reaction of $R^{\bullet}$ with the radical trap.

The concept that $S_{RN}1$ reactions necessarily involve a chain process is so widespread that the absence of reactivity depression upon addition of a redox trap or of a radical scavenger has often been taken as evidence for a different mechanism. Namely, steps 1 and 2 and the photochemical initiation step in the conventional $S_{RN}1$ reaction Scheme 1 would then be replaced by reaction 5,[17] where, owing to cage recombination of radicals

$$RX + Nu^- \xrightarrow{h\nu} [RX^{\bullet-}, Nu^{\bullet}] \rightarrow [R^{\bullet}, X^-, Nu^{\bullet}] \rightarrow RNu + X^- \quad (5)$$

$R^{\bullet}$ and $Nu^{\bullet}$, the key intermediate of an $S_{RN}1$ process, $RNu^{\bullet-}$, does not transpire along the reaction pathway. However, a nonchain $S_{RN}1$ mechanism has been proposed to explain the photomethylation of triphenylmethyl anion in dimethyl sulfoxide.[18]

We will address this question in the following report, trying to establish whether or not a photochemically induced true $S_{RN}1$ reaction (true in the sense that the $RNu^{\bullet-}$ anion radical resulting from the coupling of the $R^{\bullet}$ radical with the nucleophile is an intermediate) can be a nonchain process. In this connection, an advantage of using arenethiolate ions (ArS^-) as nucleophiles is that the reaction gives rise, as a side product, to the easily identifiable dimer ArSSAr whose yield provides a measure of the number of chains involved.

Another problem is the nature of the initiation step in photoinduced $S_{RN}1$ reactions. Direct photolysis of the R−X bond and photoinduced electron transfer within a substrate−nucleophile charge transfer complex have been evoked as possible means to generate the $R^{\bullet}$ radical or the $RX^{\bullet-}$ anion radical, respectively, therefore triggering the chain process represented in Scheme 1.[17,19,20] The photoinduced reaction of 1-iodoadamantane with arenethiolate ions was the occasion of investigating another initiation pathway, namely electron transfer from an excited state of the nucleophile to the substrate.

In several instances, photochemical induction appears as more efficient than induction by solvated electrons or by electrons from an electrode or from an electrogenerated homogeneous outersphere electron donors: substitution occurs with an excellent yield with no or little formation of the hydrogenolysis product in contrast with what is observed for the same substrate−nucleophile couples with other modes of induction. For example, the light-stimulated reaction of 1-bromoadamantane with diphenyl phosphide ions in liquid ammonia yields 70% substitution product and 16% adamantane, whereas with solvated electron induction, the respective yields are 6% and 67%.[21,22] The comparison between photochemical and direct as well as indirect electrochemical induction of the reaction of 1-iodoadamantane with arenethiolate ions provides a striking example of such different efficiencies. Reasons causing this strong dependence of the product distribution upon the mode of induction will be analyzed in the following discussion.

Scheme 2

$$R^{\bullet} + Nu^- \rightleftharpoons RNu^{\bullet-} \quad (2)$$

$$RX + RNu^{\bullet-} \longrightarrow R^{\bullet} + X^- + RNu \quad (3')$$

Another source of interest of haloadamantanes as $S_{RN}1$ substrates is that the anion radical $RX^{\bullet-}$ cannot be an intermediate since electron transfer from heterogeneous or homogeneous outersphere sources is concerted with bond breaking[23] as in all aliphatic halides investigated so far.[8] These substrates may thus offer examples where the three-step propagation process in Scheme 1 is replaced by the two-step mechanism represented in Scheme 2.

Another difference with aryl substrates concerns the location of the electron that is transferred concertedly with bond formation. With aryl substrates, it is transferred into the π^* orbital of the aryl moiety of the substituted anion radical.[8,10-12,16] In the present case, it goes to the π^* orbital of the Nu moiety of $RNu^{\bullet-}$.[24]

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[22] (a) For aromatic substrates, two examples may serve to illustrate this difference between photochemical induction and induction by solvated electrons. Photostimulated substitution by acetone enolate ions in liquid ammonia of a series of substituted benzenes bearing as a leaving group I, Br, Cl, F, SPh, or OPh produces mono- and diphenylated acetone in high yields with very little formation of benzene.[22b] When the reaction is triggered by solvated electrons, benzene is found among the reaction products in amounts that vary with the nature of the leaving group and may be as high as 80%.[22c,d] Reaction of acetone enolate ions with 2-bromopyridine in liquid ammonia under photostimulation leads nearly quantitatively to the substitution product with no detectable formation of pyridine.[22e] In contrast, when the reaction is triggered by solvated electrons in the same solvent the yield in substitution product is very low and pyridine is formed.[22e] (b) Rossi, R. A.; Bunnett, J. F. *J. Org. Chem.* **1973**, *38*, 1407. (c) Bard, R. R.; Bunnett, J. F.; Creary, X.; Tremelling, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2852. (d) Tremelling, M. J.; Bunnett, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7375. (e) Komin, A. P.; Wolfe, J. F. *J. Org. Chem.* **1977**, *42*, 2481. (f) It has been noticed at a qualitative level that, with aromatic substrates, direct and even indirect electrochemical induction is less efficient than photochemical induction.[22g] (g) See ref 8 and references cited therein.

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[24] (a) Besides the photostimulated reaction of 1-bromoadamantane with diphenyl phosphide and diphenyl arsenide ions in liquid NH_3,[21] 1-iodoadamantane has been shown to react with benzenethiolate, benzeneselenate, benzenetellurate, 1-naphthaleneselenate,[24b] Se^{-2}, and Te^{-2} [24c] ions under the same conditions, whereas diethyl phosphite, amide, 2-picolyl, and acetone enolate ions, as well as other carbanions which react on aromatic substrates, are unreactive.[24c] Diphenyl phosphide and benzenethiolate ions and carbanions also react with 1-bromoadamantane under irradiation in DMSO at room temperature.[24d,e] A $S_{RN}1$ mechanism has also been proposed for the spontaneous reaction of lithium and sodium trimethylstannanes with 1-halo- and 1,3-dihaloadamantanes.[24f,g] The reactions of other bridgehead halides with nucleophiles have been reviewed.[9] (b) Alonso, R. A.; Palacios, S. M.; Rossi, R. A. *Tetrahedron* **1985**, *41*, 4147. (c) Palacios, S. M.; Santiago, A. N.; Rossi, R. A. *J. Org. Chem.* **1984**, *49*, 4609. (d) Bornancini, E. R. N.; Alonso, R. A.; Rossi, R. A. *J. Org. Chem.* **1987**, *52*, 2166. (e) Rossi, R. A.; Pierini, A. B.; Borosky, G. L. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2577. (f) Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833. (g) Adcock, W.; Clark, C. I. *J. Org. Chem.* **1993**, *58*, 7341.

Chart 1

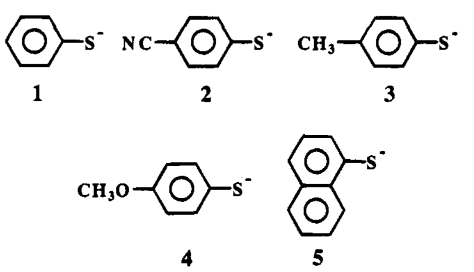

Table 1. Direct and Mediated Electrolyses of 1-Iodoadamantane in the Presence of Arenethiolate Ions[a]

nucleo-phile[b]	mediator [E^0 (V vs SCE); conc (mM)]	conc of AdI (mM)	electro-lysis potential[c]	AdSAr (%)	AdH (%)
1	none	5	−2.00	0	96
	none	4	−2.10	0	95
	terephthalonitrile	3.5	−1.60	0	95
	[−1.60; 0.5]				
	anthracene	10	−1.90	0	96
	[−1.96; 0.5]				
	9,10-diphenylanthracene	14	−1.84	0	95
	[−1.86; 1]	14	−1.82	0	95
		14	−1.80	15	77
		14	−1.78	6	86
2	terephtalonitrile	3.35	−1.56	0	95
	[−1.60; 0.5]				
	9,10-diphenylanthracene	14	−1.82	0	95
	[−1.86; 1]	14	−1.80	0	95
		14	−1.82	5	88
		14	−1.78	5	88
3	terephtalonitrile		−1.59	0	94
	[−1.60; 2]	9			
	perylene		−1.70	0	95
	[−1.70, 1]	6.7			
	9,10-diphenylanthracene	6	−1.80	0	94
	[−1.86; 1]	14	−1.78	0	94
4	9,10-diphenylanthracene	5	−1.80	0	94
	[−1.86; 1]	7	−1.78	0	94
5	9,10-diphenylanthracene	14	−1.80	0	93
	[−1.86; 1]	14	−1.78	0	94

[a] Exhaustive electrolysis in acetonitrile + 0.1 M n-Bu_4NBF_4 at 20 °C. [b] 100 mM tetramethylammonium salt. [c] In V vs SCE.

Results and Discussion

Direct and Mediated Electrochemical Induction. The cyclic voltammetry of 1-iodoadamantane (AdI) at a glassy carbon electrode in acetonitrile at low scan rates gives rise to an irreversible wave (peak potential: −2.20 V vs SCE at 0.1 V/s). No trace of reversibility appears upon raising the scan rate. As discussed in detail elsewhere, the characteristics of the wave indicate than electron transfer and breaking of the carbon−iodine bond are concerted, i.e., the anion radical $AdI^{\bullet-}$ is not an intermediate in the reduction.[23]

As seen with aromatic halides, the occurrence of $S_{RN}1$ substitution manifests itself by a decrease of the reduction wave, until total disappearance, upon addition of increasing amounts of the nucleophile.[8,25] No such observation was made with AdI: addition of various arenethiolate ions (Chart 1) up to a concentration of 0.1 M did not affect noticeably the cyclic voltammetric current-potential curves.

The absence of substitution by benzenethiolate was confirmed in preparative-scale electrolysis at a potential located at the foot of the voltammetric wave: adamantane was the only product of exhaustive electrolysis (Table 1).

These negative results can be interpreted as follows. An estimation of the standard potential of the $Ad^\bullet/Ad^-$ couple in DMF from redox catalysis experiments gave a value of −1.81 V vs SCE.[26] The adamantyl radical is thus reduced at the potential where it is produced from AdI. A similar sequence of potentials does not hamper substitution in the case of aromatic halides in spite of the fact that aryl radicals (reduction potentials within −0.3/−0.5 V vs SCE[16]) are much easier to reduce than the adamantyl radical. However, the anion radicals of aromatic substrates are intermediates in the reduction. The radical $R^\bullet$ is thus produced away from the electrode surface allowing its coupling with the nucleophile during the time it diffuses toward the electrode where it is reduced on its way back. In the present case, the adamantyl radical is produced, through dissociative electron transfer to AdI, at the electrode surface where it is immediately reduced. Therefore, even if it were intrinsically fast, coupling with the nucleophile could not compete with electron transfer from the electrode. Adamantane then arises from the protonation of Ad^- by proton donors present in the solution (residual water, quaternary ammonium cations of the supporting electrolyte, solvent).

Scheme 3

A B

$$P + e^- \rightleftharpoons Q^{\bullet -} \quad (6)$$

$$Q^{\bullet -} + RX \rightleftharpoons RX^{\bullet -} + P \quad (7) \qquad Q^{\bullet -} + RX \longrightarrow R^\bullet + X^- + P \quad (7')$$

$$RX^{\bullet -} \longrightarrow R^\bullet + X^- \quad (1)$$

$$R^\bullet + Nu^- \rightleftharpoons RNu^{\bullet -} \quad (2)$$

$$RNu^{\bullet -} + P \longrightarrow RNu + Q^{\bullet -} \quad (8)$$

$$Q^{\bullet -} + R^\bullet \longrightarrow R^- + P \quad (9)$$

$$R^- + \text{proton donor} \longrightarrow RH$$

$$Q^{\bullet -} + R^\bullet \longrightarrow RQ^- \quad (10)$$

Redox mediators, such as stable aromatic or heteroaromatic anion radicals, have been used to obviate the reduction of aryl radicals formed close to the electrode surface from fast-cleaving anion radicals, thus leading to more efficient substitution according to Scheme 3A.[8,27] In cyclic voltammetry, one starts from the reversible wave of the mediator couple ($P/Q^{\bullet -}$). Addition of the substrate triggers a catalytic increase of the cathodic peak and a loss of reversibility, indicating that the reduction of the substrate is initiated by the reduced form of the mediator, $Q^{\bullet -}$, rather than by the electrode. When efficient substitution occurs, progressive addition of the nucleophile decreases the catalytic wave, eventually restoring the height and reversibility of the initial $P/Q^{\bullet -}$ wave thanks to reactions 2 and 8. Compared to direct electrochemical induction, more efficient substitution then results from a more favorable competition of reaction 2 with reaction 9 than with reduction of $R^\bullet$ at the electrode surface.

We followed the same strategy with AdI using as mediators terephthalonitrile, perylene, and anthracene, which have standard potentials ranging from −1.60 to −1.96 V vs SCE (Table 1), positive to those of the mediators used in a previous redox catalysis estimation of the $Ad^\bullet$ reduction potential with 1-bromo (AdBr)- and 1-chloroadamantane.[26] It was hoped that reaction 2 would compete favorably with reaction 9 in the framework of Scheme 3B. With these mediators, however, no sign of a decrease of the catalytic wave could be detected upon addition of the arenethiolate nucleophiles up to a concentration of 0.1

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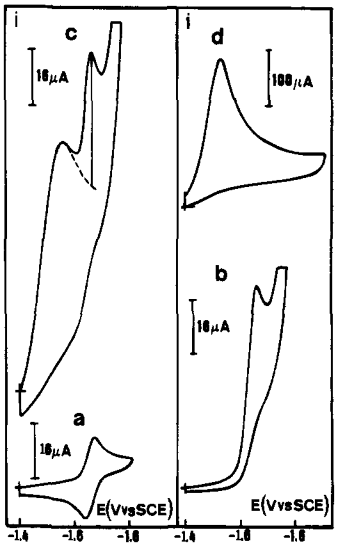

Figure 1. Cyclic voltammetry of 9,10-diphenylanthracene (0.5 mM) at a glassy carbon electrode in acetonitrile + 0.1 M n-Bu_4NBF_4: (a) alone, (b) in the presence of 7 mM AdI, and (c) in the presence of 7 mM AdI and 120 mM **1**, (d) Cyclic voltammetry of 7 mM PhSSPh alone. Scan rate 0.1 V/s. Temperature: 20 °C.

M. Likewise, in preparative-scale electrolysis, no substitution product could be detected while formation of adamantane was nearly quantitative (Table 1). However, an additional side reaction that consumes the radical $R^•$ exists in the case of adamantyl and not in the case of aryl radicals, namely the coupling with the aromatic anion radicals serving as mediator (reaction 10 in Scheme 3B),[26] as with all aliphatic radicals investigated so far.[8] With the mediators used above, this coupling is fast, with a rate constant around 10^9-10^{10} M^{-1} s^{-1}.[26]

We therefore tried another mediator, namely 9,10-diphenylanthracene, in hope that steric hindrance by the 9,10 phenyl groups would slow down reaction 10. This is indeed what we observed with benzenethiolate ions in cyclic voltammetry. As seen in Figure 1, the catalytic wave shows a small but distinct decrease upon addition of the nucleophile. Quantitative exploitation of the variation of this small decrease as a function of the nucleophile concentration is precluded by the unavoidable presence of the dimer PhSSPh in the nucleophile solutions which gives rise to an overlapping wave in front of the mediator wave (Figure 1c,d). No clearly detectable decrease of the catalytic wave was observed with any of the other four arenethiolate nucleophiles, for which the dimer wave was likewise present.

Using the same mediator in preparative-scale electrolysis, a small but distinct amount of substitution product was detected, besides adamantane in the case of benzenethiolate ions (Table 1). This is also the case with **2**, although the substitution yield was even smaller. With all three remaining nucleophiles no substitution product could be detected.

The fact that, with **1** and **2**, the substitution yield shows some dependence upon the electrolysis potential indicates that the reduction of AdI simultaneously involves the mediator and the electrode (at least a part of its surface; due to ohmic drop, the potential difference between working and reference electrodes is not necessarily constant over the whole surface).

The attempts of direct and indirect electrochemical induction have proved negative in most of the investigated cases. However, the observation that, with 9,10-diphenylanthracene anion radical as mediator, substitution takes place, even in very modest yields, is important. It proves that single electron donors are able to trigger the $S_{RN}1$ substitution of 1-iodoadamantane according to the mechanism depicted in Scheme 3B. The rate constants of the competing reactions may be estimated to lie around 10^9 M^{-1} s^{-1}. Taking into account the concentrations of mediator and nucleophile in the preparative-scale experiments, it follows that the rate constants of coupling of the adamantyl radical with arenethiolate nucleophiles should not be larger than ca. 10^7 M^{-1} s^{-1}.

Table 2. Substitution of 1-Iodoadamantane by Arenethiolate Ions by Continuous White-Light Irradiation in Acetonitrile[a]

	nucleophile[b]				
	1	**2**	**3**	**4**	**5**
AdSAr (%)[c]	91	95	80	86	0
AdH (%)[d]	5	3	12	8	0

[a] 300 W tungsten filament lamp. Pyrex cell. AdI concentration: 20 mM. Temperature: 20 °C. Deaereated solutions kept under a nitrogen stream. 10–20 h irradiation. [b] 60 mM of the tetramethylammonium salt. [c] Determined by HPLC. [d] Determined by GPC (see the Experimental Section).

Table 3. UV–Vis Characteristics[a] of 1-Iodoadamantane and of the Arenethiolate Ions[b] in Acetonitrile[c]

	compd					
	AdI	**1**	**2**	**3**	**4**	**5**
λ_{max} (nm)	262	302	354	302	296	330, 394
$\epsilon_{max}\times 10^{-3}$ (l mol^{-1} cm^{-1})	0.79	14.7	20.0	14.0	20.0	16.4, 2.5

[a] Main bands. [b] Tetramethylammonium salt. [c] Temperature: 20 °C.

Photochemical Induction. Efficiency and Number of Propagating Chains. Strikingly different results were obtained by photochemical induction. As seen in Table 2, continuous white-light irradiation of acetonitrile solutions of AdI and the arenethiolate ions (see the Experimental Section) gave excellent substitution yields, accompanied by the formation of a small amount of adamantane (with the exception of **5** which does not react at all).

The spectral characteristics of AdI and of the five nucleophiles are summarized in Table 3. Mixtures of AdI with the arenethiolate ions did not exhibit, in between 190 and 820 nm, any new band in addition to those of the two components that could be attributed to the formation of a charge transfer complex. We are thus led to conclude that the photochemical induction of the observed substitutions results from the excitation of the arenethiolate ion. The mechanism by which the electron that triggers substitution is generated from this excitation process will be discussed in the next section and shown to involve photoejection from the thiolate ion.

The quantum yield of the overall substitution reaction was determined in a laser flash experiment at 308 nm in which a mixture of AdI (17 mM) and **1** (30 mM) was irradiated with a 205 mJ energy pulse corresponding to the injection of 1 mM concentration of photons (see the Experimental Section). The resulting concentration of 1-adamantyl phenyl sulfide was 0.12 mM, corresponding to a quantum yield of 0.12. This low value of the quantum yield matches the observation that the reaction times in the continuous irradiation experiments are large (10–20 h). Such a low quantum yield points to a rather inefficient chain process. However, several chains could be operating if the quantum yield of the initiation process happened to be low.

The number of chains was determined from continuous irradiation experiments in the following manner on the basis of the reaction scheme (Scheme 4) (it must be emphasized however that the foregoing analysis does not depend upon the exact mechanism by which the electron that triggers substitution is generated). We first noticed that the anion radicals of the adamantyl aryl sulfides resulting from substitution are potent

Scheme 4

$$\mathrm{Nu^-} \xrightarrow{h\nu} \mathrm{Nu^{\bullet} + e^-} \tag{11}$$

$$\mathrm{RX + e^-} \longrightarrow \mathrm{R^{\bullet} + X^-} \tag{12}$$

$$\mathrm{R^{\bullet} + Nu^-} \rightleftharpoons \mathrm{RNu^{\bullet -}} \tag{2}$$

$$\mathrm{RNu^{\bullet -} + RX} \longrightarrow \mathrm{RNu + R^{\bullet} + X^-} \tag{3'}$$

$$\mathrm{RNu^{\bullet -} + R^{\bullet}} \longrightarrow \mathrm{R^- + RNu} \tag{13}$$

$$\mathrm{R^- + proton\ donor} \longrightarrow \mathrm{RH}$$

$$\mathrm{RNu^{\bullet -} + Nu^{\bullet}} \longrightarrow \mathrm{Nu^- + RNu} \tag{14}$$

$$\mathrm{2\,Nu^{\bullet}} \longrightarrow \mathrm{NuNu} \tag{15}$$

$$\mathrm{RNu^{\bullet -} + NuNu} \longrightarrow \mathrm{Nu^{\bullet} + Nu^- + RNu} \tag{16}$$

$$\mathrm{RNu^{\bullet -} + NR'_4{}^+} \longrightarrow \mathrm{NR'_3 + (R'R' + R'H + R'\_H) + RNu} \tag{17}$$

$$\mathrm{R^{\bullet} + CH_3CN} \longrightarrow \mathrm{RH + {}^{\bullet}CH_2CN} \tag{18}$$

reducing species. 4-Cyanophenyl and 1-naphthyl adamantyl sulfides exhibit cyclic voltammetric waves that become reversible above 1 and 20 V/s, respectively, from which standard potentials of −2.22 and −2.45 V vs SCE can be derived. Adamantyl phenyl sulfide exhibits a wave overlapping the discharge of the supporting electrolyte with a peak at ca −2.8 V vs SCE whereas 4-methylphenyl and 4-methoxyphenyl adamantyl sulfides do not exhibit any detectable wave before the supporting electrolyte discharge, in line with the electron-donating properties of these substituents. We may thus envisage that the anion radical $\mathrm{RNu^{\bullet -}}$ transfers one electron not only to the substrate RX in the chain-carrying reaction (3′) but also to the quaternary ammonium cations of the supporting electrolyte and to the tetramethylammonium cations introduced stoichiometrically with the arenethiolate ions according to reaction 17. That this is indeed the case was proved by the detection of an important amount (see Table 5 for quantitative data) of tributylamine among the reaction products.[28]

At the start of the continuous irradiation experiments, the solution unavoidably contains some ArSSAr dimer deriving from dioxygen oxidation of the arenethiolate nucleophiles. We have noticed that the ArSSAr concentration increases as the reaction proceeds. Dimerization of $\mathrm{ArS^{\bullet}}$ radicals in the present series is a fast reaction close to the diffusion limit.[29] The disulfides thus obtained are easier to reduce than AdI (see Figure 1). From the potentials at which the anion radicals $\mathrm{RNu^{\bullet -}}$ are generated, both reactions 3′ and 16 can be assumed to be governed by diffusion ($k_{\mathrm{dif}} = 2 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$ in acetonitrile). As shown below, the increase in NuNu dimer concentration at any time of the reaction is a measure of the competition between reactions 3′ and 17 and therefore of the number of chains involved in the substitution process.

The reaction was followed by direct cyclic voltammetric determination of the decay of RX and the increase of ArSSAr as shown in Figure 2. Since the waves of RX and ArSSAr overlap, we constructed, from solutions of original samples of ArSSAr, not only a current-concentration calibration straight line at the ArSSAr peak potential for determining the ArSSAr concentration but also another one corresponding to the RX peak potential that was used to obtain the RX concentration by difference.

The results of a set of experiments in which the concentration of n-$\mathrm{Bu_4NBF_4}$ was varied are summarized in Table 4. For a quantitative treatment of these results according to Scheme 4, we define the number of chains as

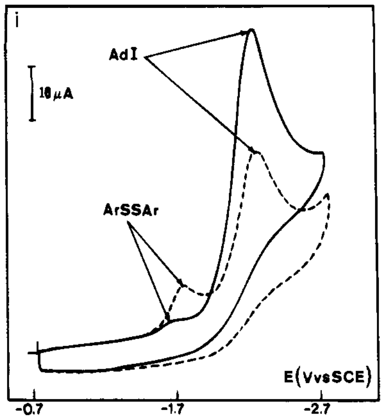

Figure 2. Cyclic voltammetry of a solution of AdI (1.5 mM) in acetonitrile + 0.1 M n-$\mathrm{Bu_4NBF_4}$ in the presence of 6 mM **1** under continuous irradiation by a 300 W sunlamp: solid line, before irradiation; dashed line, after 30 min of irradiation. Scan rate: 0.1 V/s. Temperature: 20 °C.

$$\nu = [\mathrm{X'^-}]/[\mathrm{X^-}] \tag{i}$$

where $\mathrm{X^-}$ is the amount of iodide ions produced by the initiation reaction 12 and $\mathrm{X'^-}$ the amount of iodide ions produced by the chain-carrying reaction (3′). Reactions 13 and 18 can be neglected in this analysis since adamantane was shown to be a very minor side product.

As shown in the Appendix, Scheme 4 predicts that the product distribution at any time is a function of a single dimensionless competition parameter

$$\sigma = (k_{17}/k_{\mathrm{dif}})([\mathrm{NR'_4{}^+}]/[\mathrm{RX}]^0) \tag{ii}$$

where $[\mathrm{RX}]^0$ is the initial concentration of RX. The decay of RX and the production of the dimer NuNu are related to σ according to eq iii.

$$\sigma \ln \frac{2([\mathrm{RX}]/[\mathrm{RX}]^0) + 2([\mathrm{NuNu}]/[\mathrm{RX}]^0) + \sigma}{2 + 2([\mathrm{NuNu}]^0/[\mathrm{RX}]^0) + \sigma} + 2\{([\mathrm{NuNu}] - [\mathrm{NuNu}]^0)/[\mathrm{RX}]^0\} = 0 \tag{iii}$$

When σ is small, i.e. when reaction 3′ overcomes reaction 17, $[\mathrm{NuNu}] - [\mathrm{NuNu}]^0 \approx 0$. A large number of chains thus corresponds to a vanishingly small production of the dimer.

Conversely, when σ is large, $2([\mathrm{NuNu}] - [\mathrm{NuNu}]^0) \approx [\mathrm{RX}]^0 - [\mathrm{RX}] = [\mathrm{RNu}]$. The absence of chains thus corresponds to a maximal production of the dimer, equal to one-half the consumption of RX and one-half the production of RNu.

σ could thus be determined for each of the continuous irradiation experiments in Table 4 by iterative resolution of eq iii. The rate constant of electron transfer between the anion radical of the substituted product and the tetraalkylammonium cation of the supporting electrolyte, k_{17}, is then obtained by application of eq ii.[30] As seen in Figure 3, the rate constant thus determined is satisfactorily constant over the whole set of experiments leading to the conclusion that Scheme 4 is a reasonable representation of the substitution process. Analysis of Scheme 4 also predicts (see Appendix) that the chain number

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(28) The formation of H-atom disproportionation and dimerization products from n-$\mathrm{Bu^{\bullet}}$ (eq 17) were not investigated. Coupling of n-$\mathrm{Bu^{\bullet}}$ with the thiolate ion should not be important since anion radicals of alkyl aryl sulfides have been shown to be unstable in experiments where aryl radicals were reacted with alkyl thiolate ions.[5]

(29) (a) See ref 29b and references therein. (b) Andrieux, C. P.; Hapiot, P.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1993**, *115*, 7783.

(30) In the calculation of k_{17}, the concentration of tetrabutylammonium cations was taken as the sum of the n-$\mathrm{Bu_4N^+}$ from the supporting electrolyte and the $\mathrm{Me_4N^+}$ countercations of the $\mathrm{PhS^-}$ ions, assuming that k_{17} is about the same in both cases. The contribution of the latter cations relative to the former is small, 12% at most.

Table 4. PhSSPh Production as a Function of the Progression of the Reaction in White-Light Continuous Irradiation[a] of Mixtures of AdI[b] and PhS^- [c] in Acetonitrile for Increasing Concentrations of the Quaternary Ammonium Salt[d]

$[PhS^-]^0$ = 3 mM			irradiation time (min) [AdI] (mM) [PhSSPh] (mM)							
$[n\text{-}Bu_4N^+]$ (M)	$[PhSSPh]^0$ (mM)	half-reaction time[e]								
0.05	0.08	48	10	15	20	25	35	45	62	70
		(42)	1.28	1.19	1.10	1.04	0.92	0.75	0.57	0.46
			0.12	0.14	0.16	0.17	0.20	0.21	0.23	0.25
0.10	0.05	49	7	15	20	26	32	40	51	60
		(57)	1.42	1.28	1.19	1.11	0.98	0.84	0.69	0.57
			0.08	0.12	0.13	0.15	0.17	0.20	0.21	0.23
0.25	0.06	61	12	21	28	40	50	60	71	82
		(71)	1.45	1.33	1.25	1.11	0.91	0.78	0.60	0.53
			0.09	0.13	0.15	0.20	0.23	0.24	0.27	0.29
0.50	0.05	62	7	17	25	32	42	52	62	72
		(91)	1.47	1.36	1.29	1.15	1.00	0.88	0.77	0.69
			0.10	0.13	0.17	0.21	0.25	0.29	0.32	0.35

$[PhS^-]^0$ = 6mM			irradiation time (min) [AdI] (mM) [PhSSPh] (mM)							
$[n\text{-}Bu_4N^+]$ (M)	$[PhSSPh]^0$ (mM)	half-reaction time[e]								
0.05	0.12	36	10	16	22	30	40	51	65	
		(26)	1.18	1.05	0.93	0.84	0.70	0.48	0.39	
			0.18	0.21	0.23	0.24	0.27	0.30	0.32	
0.10	0.10	41	5	11	17	27	37	47	57	71
		(35)	1.31	1.22	1.13	1.01	0.77	0.67	0.61	0.47
			0.15	0.16	0.19	0.21	0.26	0.27	0.29	0.31
0.25	0.08	46	5	24	32	40	54	64	75	
		(46)	1.32	1.03	0.90	0.81	0.66	0.55	0.44	
			0.14	0.27	0.30	0.31	0.33	0.34	0.36	
0.50	0.12	55	16	25	31	40	45	55	65	
		(54)	1.21	1.07	1.02	0.92	0.80	0.75	0.64	
			0.24	0.29	0.31	0.35	0.40	0.43	0.48	

[a] 300 W lamp. [b] 1; 5 mM. [c] Tetramethyl ammonium salt. [d] Temperature 20 °C. [e] Observed and (in parentheses) predicted (min).

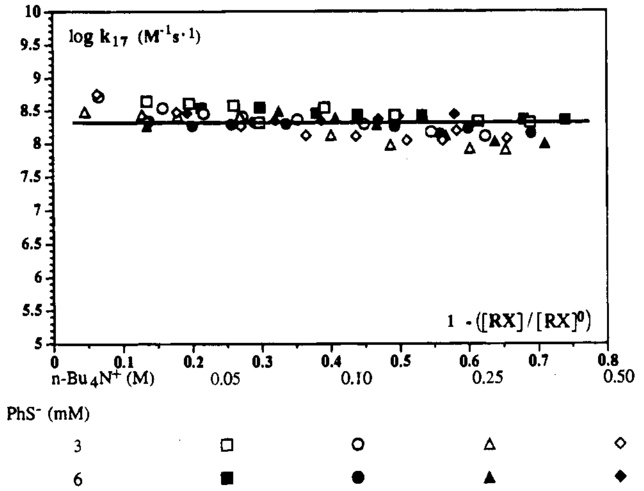

Figure 3. Photochemical induction of the reaction of AdI with PHS^-. Determination of the rate constant of reaction 17 in Scheme 4 from the experiments in Table 4 using eqs ii and iii.

is given by the function of $[NuNu]/[RX]^0$, $[NuNu]^0/[RX]^0$, and σ defined in eq iv.

$$\nu = \left[\sigma\left(1 + \frac{[NuNu]^0}{[RX]^0} + \frac{\sigma}{2}\right) \times \left[1 - \exp\left\{-\frac{2}{\sigma}\left(\frac{[NuNu]}{[RX]^0} - \frac{[NuNu]^0}{[RX]^0}\right)\right\}\right] - \sigma\left(\frac{[NuNu]}{[RX]^0} - \frac{[NuNu]^0}{[RX]^0}\right) - \left(\frac{[NuNu]}{[RX]^0}\right)^2 - \left(\frac{[NuNu]^0}{[RX]^0}\right)^2\right] \Bigg/ \left[2\,\sigma\left(\frac{[NuNu]}{[RX]^0} - \frac{[NuNu]^0}{[RX]^0}\right) + \left(\frac{[NuNu]}{[RX]^0}\right)^2 - \left(\frac{[NuNu]^0}{[RX]^0}\right)^2\right] \qquad \text{(iv)}$$

Figure 4 shows the variation of the chain number in the experiments reported in Table 4 and Figure 3 as a function of the progression of the reaction for the four concentrations of supporting electrolyte. The curves were generated using the average value of k_{17} determined in Figure 3 (log k_{17} = 8.3). We see that the number of chains is extremely small, between 0 and 2. In the experiment with a 0.1 M $n\text{-}Bu_4N^+$ concentration, we have also determined the yield of substitution product, AdSPh, and of tributylamine as a function of the progression of the reaction (Table 5).

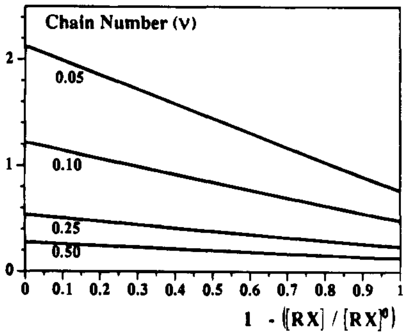

Figure 4. Photochemically induced reaction of AdI with PHS^-. Variation of the chain number with the progression of the reaction in the experiments reported in Table 4 for four concentrations of $n\text{-}Bu_4NBF_4$ (number on each curve in M).

Table 5. Production of AdSPh and $n\text{-}Bu_3N$ as a Function of the Progression of the Reaction in White-Light Continuous Irradiation[a] of Mixtures of AdI (1.5 mM) and PhS^- (6 mM)[b] in Acetonitrile in the Presence of 0.1 M $n\text{-}Bu_4NBF_4$[c]

	irradiation time (min)		
	30	60	90
$[AdSPh]/([AdI]^0 - [AdI])$	0.97	0.97	0.97
$[n\text{-}Bu_3N]$ (mM)	0.30	0.60	0.72
$2([PhSSPh] - [PhSSPh]^0)$ (mM)	0.24	0.64	0.80

[a] 300 W lamp. [b] Tetramethylammonium salt. [c] Temperature: 20 °C.

It is clearly apparent that the occurrence of a true $S_{RN}1$ mechanism, involving the coupling between the $R^\bullet$ radical and the nucleophile, is compatible with a negligible number of

Table 6. White-Light Irradiation^a of Mixtures of AdI with **5** and **1**^{b}

[**5**] (mM)^c	[**1**] (mM)^c	[AdI]^0 (mM)	[PhSSPh]^0 (mM)	1 − [AdI]/[AdI]^0	[PhSSPh] (mM)	yield^d in AdSNaph (%)	yield^d in AdSPh	rate ratio ρ^e
2.9	4.5	1.5	0.26	0.47	0.42	21	76	0.43
5.5	6.0	1.5	0.15	0.45	0.30	26	71	0.40
4.1	3.1	1.4	0.20	0.44	0.44	36	60	0.42
2.7	1.3	1.5	0.20	0.61	0.60	45	51	0.42

^{a} 300 W lamp. ^{b} In CH_3CN + 0.1 M n-Bu_4NBF_4. Temperature: 20 °C. ^{c} Tetramethylammonium salt. ^{d} vs AdI consumed. ^{e} Defined in eq v.

Scheme 5

$$PhS^- \xrightarrow{h\nu} PhS^{\bullet} + e^- \qquad (11)$$

$$e^- + AdI \longrightarrow Ad^{\bullet} + I^- + \qquad (12)$$

$$Ad^{\bullet} + PhS^- \rightleftharpoons AdSPh^{\bullet -} \quad (2) \qquad Ad^{\bullet} + NaphS^- \rightleftharpoons AdSPNaph^{\bullet -} \quad (2')$$

$$AdSPh^{\bullet -} + NR'_4{}^+ \longrightarrow AdSPh + prod.\ (17) \qquad AdSNaph^{\bullet -} + NR'_4{}^+ \longrightarrow AdSPNaph + prod.\ (17')$$

chains. In other words, efficient photoinduced $S_{RN}1$ reactions need not be chain processes.[31]

In the framework of Scheme 4, the decrease of the chain number upon raising the supporting electrolyte concentration should be accompanied by a slowing down of the whole process. We indeed observe that the half-reaction time increases with the supporting electrolyte concentration (third column in Table 4). Simulation of the kinetics with a constant average value of 1.4×10^{-4} s^{-1} for the rate of production of $R^{\bullet}$ in the initiation process (reactions 11 and 12) leads to half-reaction times that do increase with the supporting electrolyte concentration (third column in Table 4), albeit somewhat more rapidly than the experimental values. The difference is larger for 3 mM than for 6 mM PhS^-. Since the Pyrex vessel cut the wavelengths bellow 350 nm, only a small tail of the PhS^- spectrum is used in the irradiation process, suggesting that not all incident photons are absorbed; the more so, the lower the initial concentration of PhS^- and the greater the irradiation time, in line with the trends exhibited by the experimental data.

The production of *n*-Bu_3N provides a further test of the reaction mechanism. Scheme 4 predicts (see the Appendix) that the concentration of *n*-Bu_3N produced should be equal to twice the production of PhSSPh. As seen in Table 5, this prediction is satisfactorily verified by the experimental results.

With direct or indirect electrochemical induction, the predominant formation of adamantane is a consequence of the facile reduction of the $R^{\bullet}$ radical by the electrode or by the mediator. The strikingly different yields observed with photochemical induction results from the following reasons. In the photochemical reaction, the only reducing species present is the anion radical $RNu^{\bullet -}$. This is a strong reductant, potentially able to reduce $R^{\bullet}$ at the diffusion limit. However, $RNu^{\bullet -}$ competitively undergoes fast reactions (3′, 14, 16, and 17) with species present in concentrations many orders of magnitude larger than the steady-state concentration of $R^{\bullet}$. Thus, reaction 13 can only produce a tiny amount of adamantane. It may well be that the formation of RH arises predominantly from H-atom abstraction from the solvent (reaction 18) rather than from reaction 13.[32]

Another remarkable feature of the photochemically induced reactions is the total lack of reactivity of **5** (Table 2) in spite of more favorable spectral characteristics for the production of an excited state during white-light irradiation through a Pyrex vessel (Table 3).

Is this due to the inability of **5** to act as a photoinitiator or as a nucleophile? The answer resides in successful entrainment experiments (Table 6) in which irradiation of mixtures of AdI with **5** *and* **1** yielded both substitution products, thus showing that **5** is a good nucleophile but a poor photoinitiator. As in the preceding experiments, with the same concentration of supporting electrolyte, PhSSPh increases as the reaction proceeds, indicating that the number of chains is also small. The reaction scheme can thus be simplified as depicted in Scheme 5, which shows the competition of the two nucleophiles for the adamantyl radical.

Under these conditions

$$\frac{[\mathrm{AdSNaph}]}{[\mathrm{AdSPh}]} = \rho \frac{[\mathrm{NaphS}^-]}{[\mathrm{PhS}^-]} \quad \text{with}$$

$$\rho = \left(k'_2 \frac{k'_{17}}{k'_{17} + k'_{-2}}\right) \Big/ \left(k_2 \frac{k_{17}}{k_{17} + k_{-2}}\right) \quad \text{(v)}$$

allowing the derivation of the rate ratio ρ from the yields in AdSPNaph and AdSPh, the constancy of ρ over a variation of the concentration ratio [**5**]/[**1**] from 0.6 to 2 justifies the above approximation. The driving forces of reactions 2 and 2′ are given by eq vi[10−12,16] (energies in electronvolts, potentials in volts), in which the dominant term is the standard potential for generation of the anion radical, $E^0_{\mathrm{RNu/RNu^{\bullet -}}}$.

$$\Delta G^0_{\mathrm{R^{\bullet}+Nu^- \rightarrow RNu^{\bullet -}}} = -D_{\mathrm{RNu}} - E^0_{\mathrm{RNu/RNu^{\bullet -}}} + E^0_{\mathrm{Nu^{\bullet}/Nu^-}} - T(\bar{S}_{\mathrm{RNu}} - \bar{S}_{\mathrm{Nu^{\bullet}}} - \bar{S}_{\mathrm{R^{\bullet}}}) \quad \text{(vi)}$$

From the values of the cyclic voltammetric peak potentials given earlier, its variation can be estimated as ca. 0.35 V in favor of the naphthyl derivative. The standard potential for the oxidation of the nucleophile, $E^0_{\mathrm{Nu^{\bullet}/Nu^-}}$, slightly disfavors the naphthyl derivative (0.16 V vs SCE[33] against 0.10[29] for the phenyl derivative) and so does the bond dissociation energy term, D_{RNu}, by analogy with what has been previously observed with benzyl halides[34a] and sulfonium cations,[34b] whereas the entropic term should not vary significantly from one derivative to the other. The activation free energies of forward reactions 2 and 2′ obey the quadratic equation vii, where the intrinsic barrier free energy, $\Delta G^{\ddagger}_{0,\mathrm{RNu^{\bullet -} \rightarrow R^{\bullet}+Nu^-}}$, is given by eq viii.[10−12,16] The first term is slightly in favor of the naphthyl derivative. $E^0_{\mathrm{RNu/RNu^{\bullet -}}}$ repre-

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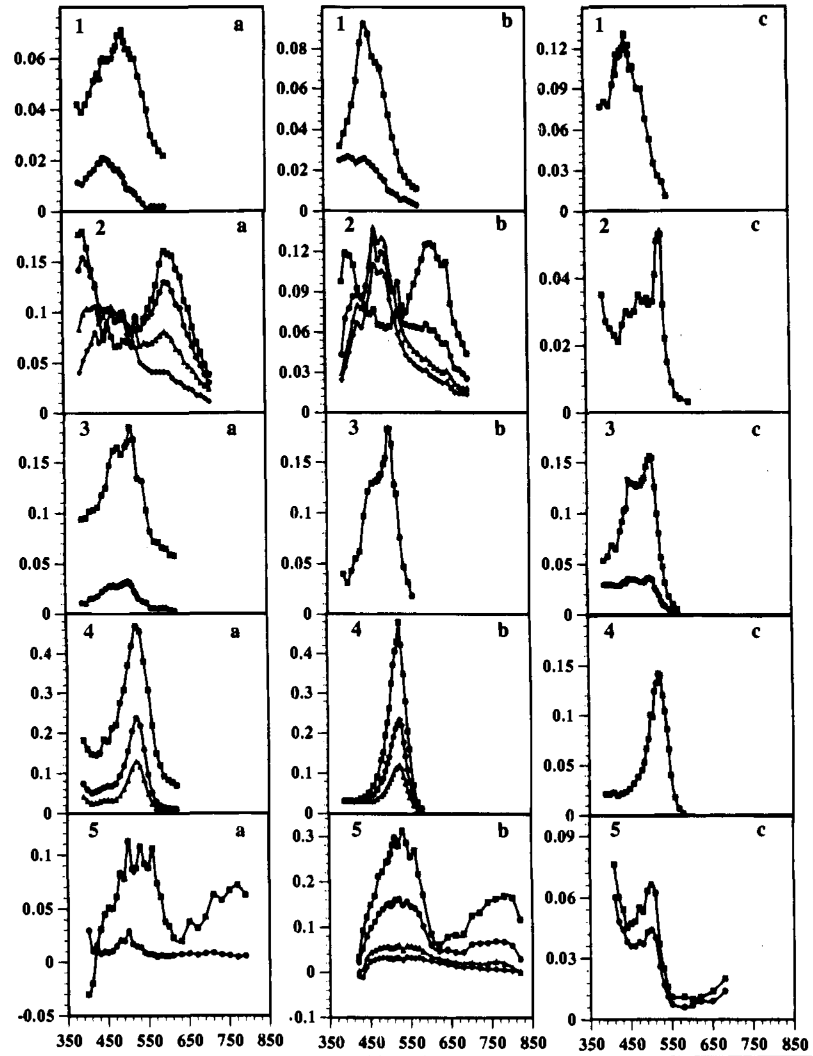
[31] A nonchain $S_{RN}1$ mechanism has been proposed previously for the photometalation of triphenylmethyl anion in CH_3SOCH_3.[18] However, the distinction between this mechanism and a coupling of methyl and triphenylmethyl radicals, based on the formation of *p*-coupling products besides α-coupling products requires the assumption that electron transfer from the $Ph_3CCH_3^{\bullet -}$ to CH_3SOCH_3 is a dissociative process leading to the formation of $CH_3^{\bullet}$ in the same solvent cage as $Ph_3CC^{\bullet}$. This assumption, which has not been established so far, was necessary for ruling out the radical coupling mechanism.

[32] (a) Evidence has been reported that adamantyl radicals readily abstract H-atoms from hydrocarbons[32b,c] and *t*-BuOH.[32b] (b) Engel, P. S.; Chae, W.-K.; Baughman, S. A.; Marschke, G. E.; Lewis, E. S.; Timberlake, J. W.; Luedtke, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 5030. (c) Lomas, J. S.; Briand, S. *Tetrahedron Lett.* **1989**, *30*, 707.

[33] Hapiot, P. Unpublished data.

[34] (a) Andrieux, C. P.; Le Gorande, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892. (b) Andrieux, C. P.; Robert, M.; Saeva, F. D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 7864.



		1	2	3	4	5
conc.	a	0.05	0.14	0.044	0.1	0.21
(mM)	b	0.075	0.1	0.075	0.1	0.2
	c	1	1.3	0.8	0.24	0.22
time after	a	■: 0.4, ●: 8.4	■: 0.4, ●: 2.8, ▲: 7.1, ◆: 17	■: 0.3, ●: 8.7	■: 0.4, ●: 3.9, ▲: 8.7	■: 0.4, ●: 8.4
laser pulse	b	■: 0.5, ●: 8.7	■: 0.4, ●: 2.8, ▲: 7.1, ◆: 17	■: 0.3	■: 0.4, ●: 3.9, ▲: 8.7	■: 0.8 ●: 3.7, ▲: 10.6
(μs)	c	■: 0.4	■: 0.3	■: 0.4, ●: 17	■: 1	■: 0.3, ●: 8

Figure 5. Spectra (absorbance vs wavelength, in nm) recorded after laser flash irradiation at 308 nm of acetonitrile solutions of tetramethylammonium salts of the nucleophiles (in the absence (a) and presence (b) of AdI (5 mM)) and of the corresponding disulfides (c).

sents the standard potential for injection of one electron into the π^* orbital of the nucleophile radical, i.e., the formation of an excited state of the nucleophile. Its variation should

$$\Delta G^{\ddagger}_{\mathrm{R\bullet+Nu^-\rightarrow RNu^{\bullet-}}} = \Delta G^{\ddagger}_{0,\mathrm{RNu^{\bullet-}\leftrightarrow R\bullet+Nu^-}} \times \left(1 + \frac{\Delta G^{0}_{\mathrm{R\bullet+Nu^-\rightarrow RNu^{\bullet-}}}}{4\Delta G^{\ddagger}_{0,\mathrm{RNu^{\bullet-}\leftrightarrow R\bullet+Nu^-}}}\right)^2 \quad \text{(vii)}$$

$$\Delta G^{\ddagger}_{0,\mathrm{RNu^{\bullet-}\leftrightarrow R\bullet+Nu^-}} = [D_{\mathrm{RNu}} + E^{0}_{\mathrm{RNu/RNu^{\bullet-}}} - E^{0}_{\mathrm{Nu\bullet(Nu^\bullet)^{\bullet-}}} + T(\bar{S}_{\mathrm{RNu}} - \bar{S}_{\mathrm{RNu^{\bullet-}}} + \bar{S}_{\mathrm{(Nu^\bullet)^{\bullet-}}} - \bar{S}_{\mathrm{Nu\bullet}})]/4 \quad \text{(viii)}$$

compensate the variation of the second term while the entropic term should remain about constant. Therefore, we expect forward reaction 2′ in Scheme 5 to be faster than forward reaction 2. However, as seen earlier, k_2 should not exceed 10^7 $\mathrm{M^{-1}\ s^{-1}}$, suggesting that reactions 2 and 2′ are up-hill processes. It is thus likely that the value of ρ is a reflection of a mixed kinetic control by reactions 2 (2′) and 17 (17′). Since, as seen earlier, AdSPNaph$^{\bullet-}$ is a weaker reductant than AdSPh$^{\bullet-}$, reaction 17′ should be slower than reaction 17. From the phenyl to the naphthyl derivative, the acceleration of the coupling of the nucleophile with the adamantyl radical is thus likely to be compensated by the slowing down of the electron transfer to the cation of the supporting electrolyte, resulting in comparable overall reactivities.

Photochemical Induction. Generation of the Electron That Triggers Substitution. The fluorescence yields of all five nucleophiles have been measured at two wavelengths (taking naphthalene as a reference[35]). They are listed in Table 7. The very low values thus found point to a rapid and irreversible transformation of the initial excited state at both excitation wavelengths. The species generated by flash photolysis at the same wavelengths have been investigated in acetonitrile in the absence and presence of iodoadamantane. The spectra thus recorded as a function of time are shown in Figures 5 and 6. At

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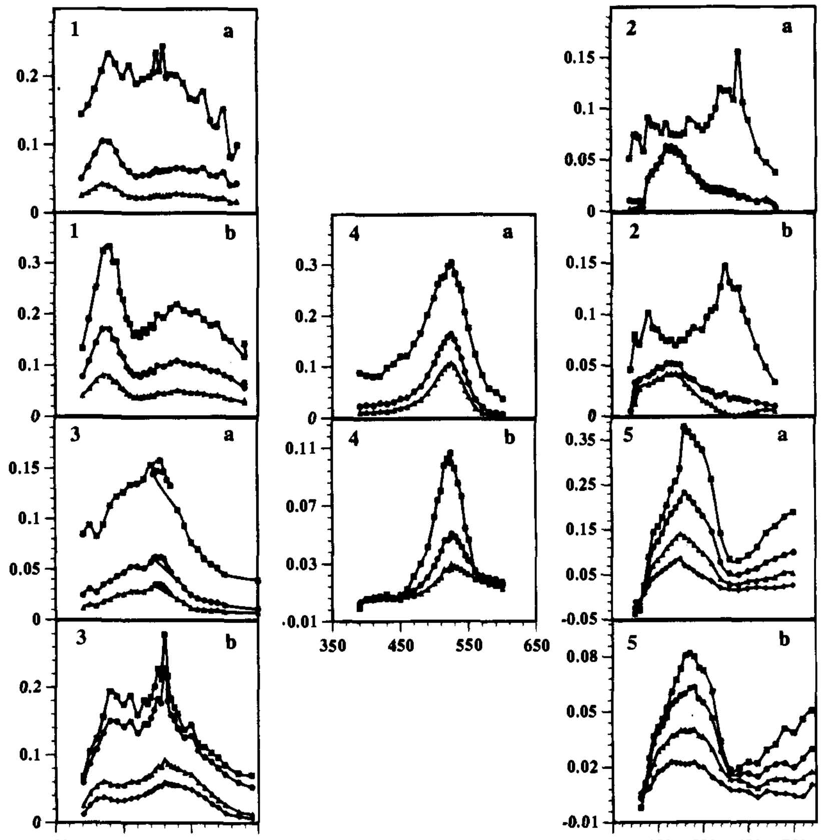
(35) Parker, C. A.; Rees, W. T. *Analyst* **1960**, *85*, 587.



ArS⁻	conc.(mM)		time after laser pulse (μs)	
	a	b	a	b
1	0.3	0.3	■: 0.5, ●: 7.0, ▲: 17.0	■: 0.5, ●: 7.0, ▲: 17.0
2	0.05	0.05	■: 0.7, ●: 4.6, ▲: 8.6, ◆: 17.1	■: 0.7, ●: 4.6, ▲: 8.6, ◆: 17.1
3	0.095	0.5	■: 0.7, ●: 4.6, ▲: 8.6	■: 0.7, ●: 1.0, ▲: 4.6, ◆: 8.6
4	0.066	0.066	■: 0.7, ●: 4.6, ▲: 8.6	■: 0.7, ●: 4.6, ▲: 8.6
5	0.3	0.12	■: 0.8, ●: 3.7, ▲: 10.6, ◆: 17.0	■: 0.7, ●: 4.2, ▲: 9.2, ◆: 17.2

Figure 6. Spectra (absorbance vs wavelength, in nm) recorded after laser flash irradiation at 351 nm of acetonitrile solutions of tetramethylammonium salts of the nucleophiles in the absence (a) and presence (b) of AdI (5 mM).

Table 7. Fluorescence Yields (ϕ) of the Arenethiolate Ions[a]

	thiolate ion				
	1	2	3	4	5
ϕ_{308}[b]	$<10^{-6}$	$<10^{-6}$	$=0.7 \times 10^{-5}$	$=1.2 \times 10^{-5}$	$=0.4 \times 10^{-5}$
ϕ_{351}[c]	$=0.2 \times 10^{-3}$	$<10^{-6}$	$=0.5 \times 10^{-3}$	$=0.3 \times 10^{-3}$	$=0.4 \times 10^{-3}$

[a] From 0.1 mM solutions of the tetramethylammonium salt in acetonitrile. Temperature: 25 °C. [b] Excitation wavelength: 308 nm. [c] Excitation wavelength: 351 nm.

Table 8. Quantum Yields of Electron Photoejection (ϕ_e) as a Function of the Irradiation Wavelength and the Nature of the Thiolate Ion

	thiolate ion		
	1	3	4
$\phi_{e\text{-}308}$	0.43	0.50	0.75
$\phi_{e\text{-}351}$		0.20	0.14

308 nm, the initial spectra are very broad, pointing to the formation of several species. With **1**, **3**, and **4**, the spectra become narrower with time, then corresponding to the spectra of the corresponding arylthio radicals as was checked by generation of the same radicals by laser flash irradiation of the disulfides (Figure 5).[36a-c] This assignment was confirmed by generation of the arylthio radicals by laser flash irradiation of di-*tert*-butyl peroxide in the presence of each of the thiophenols.[36c,d] The spectra thus found by three different modes of generation were found to be similar to those previously recorded in water.[36e] With these three nucleophiles, the presence of iodoadamantane accelerates the formation of the thio radical. With **2**, the initial spectrum also becomes narrower in the presence of AdI but the thio radical is not the only species present. In this case, the presence of AdI does not modify noticeably the initial spectrum and its evolution with time. With **5**, the spectrum of the thio radical does not appear at all in the absence as well as in the presence of iodoadamantane.

Upon laser pulse irradiation at 351 nm, the initial spectra are also very broad (Figure 6). Overall, the generation of the thio radical is less efficient than upon irradiation at 308 nm. The radical is clearly visible with **3** and **4** in the presence of AdI, while with **1**, its spectrum is mixed with the spectra of additional species even in the presence of AdI. With **2** and **5** the initial spectra are the same as observed upon irradiation at 308 nm. The spectrum of the thio radical does not appear when AdI is present, even in the case of **2**, unlike what was observed upon irradiation at 308 nm.

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Table 9. White-Light Irradiation of ArS^- [a]/AdI[b] mixtures[c] at $\lambda \geq 351$ nm

	ArS⁻										
	1			**3**				**4**			
irradiation time (min)	40	80	100	10	20	40	60	5	10	15	20
unreacted AdI (%)	65	43	33	84	73	60	53	67	32	16	8
ArSAd (%)	31	53	61	8	17	31	38	28	58	75	82

[a] 3 mM tetramethylammonium salt. [b] 1 mM. [c] In CH_3CN + 0.1 M n-Bu_4NBF_4. Temperature: 20 °C.

The broad initial spectra observed at both irradiation wavelengths are reminiscent of those observed in pulse radiolysis of acetonitrile solutions.[37] This observation and the very low fluorescence yields observed for all arenethiolate ions point to photoejection of one electron from these ions.[38] However, efficiency of the reaction is larger at 308 nm than at 351 nm and decreases in the order **4** > **3** > **1** > **2** > **5** as the λ_{max} in the absorption spectrum undergoes a bathochromic shift and as the oxidability decreases. Since pure spectra of the radicals of **1**, **3**, and **4** are produced at 308 nm and that the same is true for **3** and **4** at 351 nm, the quantum yields of electron photoejection could be determined in these cases using the spectra of pure samples generated upon irradiation of the disulfides and the actinometric determination of the number of photons in the laser pulse. The ensuing data confirmed, on a quantitative basis (Table 8), the above-mentioned trends in the variations of electron photoejection efficiency with the irradiation wavelength and the nature of the thiolate ion.

As seen earlier, white-light irradiation of iodoadamantane/thiolate ion mixture gives rise to excellent substitution yields with the exception of **5**. The laser pulse experiments just described showed that the efficiency of the initiation process decreases upon raising the irradiation wavelength from 308 to 351 nm, thus indicating that, in white-light irradiation, the shortest wavelengths are the most efficient. We have checked this point in a series of white-light irradiation experiments where wavelengths below 350 nm were filtered off. As seen in Table 9, we indeed found that with **1**, **3**, and **4** the efficiency of substitution is significantly less than without filtering while no reaction occurs, not only with **5** but also with **2**.

Conclusions

In the reaction of benzenethiolate and para-substituted benzenethiolate ions with 1-iodoadamantane, electrochemical and photochemical induction led to strikingly different results. Direct electrochemistry yields adamantane with no trace of substitution product. The same is observed with the usual aromatic anion radical mediators. In the first case, the adamantyl radical being produced at the electrode surface through dissociative electron transfer is immediately reduced before reaction with the nucleophile. The reduction by the aromatic anion radical mediators in solution is likewise fast and, in addition, the adamantyl radical couples with the mediator, which also contributes to the inefficiency of the substitution process. Steric hindrance, as in the 9,10-diphenylanthracene anion radical mediator, slows down the coupling reaction, thus allowing the production of a small amount of substituted product with benzene and 4-cyanobenzenethiolate ions, proving the existence of an $S_{RN}1$ reaction.

In contrast, excellent substitution yields with very little adamantane are obtained upon photochemical induction. However, the quantum yield is very small, suggesting that the chain process is not very efficient. This conclusion is confirmed by the observation that the quaternary ammonium countercations of the arenethiolate ions or similar cations purposely added to the solution act as strong electron transfer quenchers of the anion radical of the substituted product in competition with the chain-carrying reaction. The production of disulfide from the dimerization of the nucleophile radical could be used to determine the number of chains, showing that it is very low, between 0 and 2.

A clear-cut example is thus provided that $S_{RN}1$ reactions, even leading to efficient substitution, are not necessarily chain processes. In the present studies the chains are quenched irreversibly by the tetraalkylammonium countercations. More generally, irreversible quenching by other irreversible acceptors, including the solvent, is anticipated when the anion radical of the substituted product is a strong reductant, as it is the case here. It follows that, in such circumstances, the lack of effect of redox traps is not a demonstrating criterion against an $S_{RN}1$ mechanism. The possibility of a cage radical recombination mechanism is ruled out by the formation of tributylamine, by the production of PhSSPh, and by the fact that they increase with the concentration of tetraalkylammonium cations.

There is also a striking difference between (direct or indirect) electrochemical and photochemical induction in the reaction of 1-naphthalene thiolate ions. Adamantane is formed quantitatively in the first case (for the same reason as with the other arenethiolate ions) whereas no reaction occurs in the second. This lack of reactivity derives from the inefficiency of initiation as revealed by successful entrainment experiments using the excitation of benzenethiolate ions to trigger substitution. The comparable overall substitution reactivity of the two ions is caused by a compensation between the better nucleophilic reactivity of the 1-naphthalenethiolate ion and the lesser reducing power of the anion radical of the corresponding substituted product.

Laser pulse and filtered white-light irradiation experiments indicate that initiation consists in the photoejection of one electron from the nucleophile ion.

Experimental Section

Chemicals. Acetonitrile (Merck Uvasol) and the supporting electrolyte, n-Bu_4NBF_4 (Fluka, puriss), were used as received. Adamantane, 1-adamantanol, and 1-bromoadamantane were purchased from the Aldrich Chemical Co., Inc. With the exception of 4-cyanothiophenol, all the aryl thiophenols were from commercial origin (Aldrich).

Literature procedures were followed in the preparation of 1-iodoadamantane (from 1-adamantanol):[39] mp 76 °C (lit. 75.3–76.4 °C); ^1H-NMR (200 MHz, $CDCl_3$) 1.60–1.94 (m, 9H, 3CH, $3CH_2$), 2.62 (s, 6H, $3CH_2$). 4-Cyanothiophenol (in three steps from 4-cyanophenol):[40] ^1H-NMR 7.50 (m, 4H, aromatic); MS (CI NH_3) 154 (M + 18, 100), 136 (M + 1, 12), 109 (M+ 1 − CN, 12), 103 (M + 1 − SH, 8). The five disulfides were obtained from the corresponding thiophenols as previously described.[40]

The substituted sulfides were obtained from the continuous irradiation experiments described earlier. After ether extraction and successive washing by a saturated Na_2SO_3 aqueous solution (aiming at reducing the disulfides into the corresponding sulfide ions and transferring them in the aqueous solution) and pure water, the sulfide was separated by

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flash chromatography on a silica column with pentane or a 75:25 pentane–dichloromethane mixture as the eluent. The sulfides thus obtained were characterized as follows. 1-Adamantyl phenyl sulfide: mp 72 °C (lit.[24b] 71.5–72 °C); ^{1}H-NMR (200 MHz, $CDCl_3$) 1.5–1.6 (m, 15H, adamantyl protons), 7.3–7.5 (m, 5H, aromatic protons); MS (CI NH_3) 244 (M), 135 (M − SC_6H_5). 1-Adamantyl 4-cyanophenyl sulfide: mp 138 °C; ^{1}H-NMR 1.5–1.6 (m, 15H, adamantyl protons), 7.25–7.6 (m, 4H, aromatic protons); MS 269 (M), 135 (M − SC_6H_4-CN). 1-Adamantyl 4-methylphenyl sulfide: mp 90 °C; ^{1}H-NMR 1.6–2.0 (m, 15H, adamantyl protons), 7.1–7.4 (m, 4H, aromatic protons), 2.35 (s, 3H, CH_3); MS 258 (M), 135 (M − $SC_6H_4CH_3$). 1-Adamantyl 4-methoxyphenyl sulfide: mp 69 °C; ^{1}H-NMR 1.6–2.0 (m, 15H, adamantyl protons), 6.8–7.4 (m, 4H, aromatic protons), 3.81 (s, 3H, OCH_3); MS 274 (M), 135 (M − $SC_6H_4OCH_3$). 1-Adamantyl naphthyl sulfide: ^{1}H-NMR 1.2–1.8 (m, 15H, adamantyl protons), 6.7–7.1 (m, 7H, aromatic protons); MS 294 (M), 135 (M − S − naphthyl).

The solutions of the thiolate ions were prepared under argon so as to minimize their oxygen oxidation to disulfides.

Instrumentation. The same double-jacketed cell (10-mL solution under an argon atmosphere) was used in cyclic voltammetry and in the continuous irradiation (with a 300 W tungsten lamp). In the latter case, disappearance of AdI and formation of the disulfide was followed by cyclic voltammetry. They were also followed, together with the formation of the sulfide, adamantane, and *n*-tributylamine, by GPC (Girdel 30, Delsi Instruments, flame ionization, 3m-5%-OV17 column, 100–280 °C with the injector and detector maintained at 200 and 280 °C, respectively, injected volume of 1.5–2 μL) and by HPLC (Gilson, UV-vis detector, 15- or 25-cm Hypersil C18 column, injected volume of 20 μL, H_2O–CH_3CN solvent gradient).

In cyclic voltammetry, the working electrode was a 3-mm-diameter glassy carbon disk (Tokai) frequently polished with a 1 μm diamond paste and ultrasonically rinsed in ethanol. The counter electrode was platinum wire and the reference electrode an aqueous SCE separated from the solution by a bridge filled with a 0.1 M acetonitrile solution of *n*-Bu_4NBF_4. The latter electrodes were also used in direct and indirect preparative-scale electrolyses, but the working electrode was a graphite crucible serving also as cell (50-mL solution). The potentiostat was a Taccussel ASA100 instrument, whereas in cyclic voltammetry, a home-built potentiostat and current measurer were used.[41]

An XeCl excimer laser (Questek 2310, λ = 308 and 351 nm) was used with a 0.4-cm^3 cell for laser pulse irradiation. The calibration of photon concentration vs pulse energy was carried out by actinometry.[42]

The fluorescence spectra were recorded on a Perkin Elmer LS50 spectrometer at 25 °C.

Appendix

After introduction of the following dimensionless time and concentration variables and rate constant parameters, $\tau = kt$ (k is first-order rate constant, depending on the number of photons absorbed, representing the production of $R^\bullet$ radicals in reaction 12), $a = [RX]/[RX]^0$, $z = [Nu^-]/[RX]^0$ ($z^0 = [Nu^-]^0/[RX]^0$), $c = [R^\bullet]/[RX]^0$, $v = [Nu^\bullet]/[RX]^0$, $x = [X^-]/[RX]^0$, $f = [RNu^{\bullet-}]/[RX]^0$, $x' = [X'^-]/[RX]^0$, $w = [NuNu]/[RX]^0$ ($w^0 = [NuNu]^0/[RX]^0$), and $y = [NR'_3]/[RX]^0$ ($\lambda_{\text{2nd order}} = k_{\text{2nd order}}[RX]^0/k$), the kinetics involved in Scheme 4 (simplified by the neglect of reactions 13 and 18) can be described by the following set of differential equations, steady-state equations and initial conditions:

$$\frac{da}{d\tau} = -a - \lambda_{3'}af, \quad \frac{dz}{d\tau} = -a - \lambda_2 cz + \lambda_{-2}f + \lambda_{16}fw,$$

$$\frac{dw}{d\tau} = \frac{\lambda_{15}}{2}v^2 - \lambda_{16}fw, \quad \frac{dx}{d\tau} = a, \quad \frac{dx'}{d\tau} = \lambda_{3'}af, \quad \frac{dy}{d\tau} = \lambda_{17}f$$

$$\tau = 0{:}\ a = 1, z = z^0, w = w^0, \quad \text{and all other concentrations are zero}$$

$$a + \lambda_{16}fw = \lambda_{15}v^2, \quad a + \lambda_{3'}af + \lambda_{-2}f = \lambda_2 cz,$$

$$\lambda_2 cz = \lambda_{3'}af + \lambda_{-2}f + \lambda_{16}fw + \lambda_{17}f$$

Thus, assuming that $k_{3'}$ and k_{16} are at the diffusion limit, k_{dif}, and introducing the competition parameter $\sigma = (k_{17}[NR'_4{}^+])/(k_{\text{dif}}[RX]^0)$

$$\frac{da}{d\tau} = -a\left(1 + \frac{a}{w + \sigma}\right) \quad \frac{dz}{d\tau} = -a\left(1 + \frac{a + \sigma}{w + \sigma}\right)$$

$$\frac{dw}{d\tau} = \frac{a}{2}\frac{\sigma}{w + \sigma} \quad \frac{dx}{d\tau} = a \quad \frac{dx'}{d\tau} = a\frac{a}{w + \sigma} \quad \frac{dy}{d\tau} = \frac{a\sigma}{w + \sigma}$$

It follows that

$$\frac{da}{dw} = -\frac{2(a + w + \sigma)}{\sigma}$$

and therefore, by integration,

$$\sigma \ln\left(\frac{2a + 2w + \sigma}{2 + 2w + \sigma}\right) + 2(w - w^0) = 0$$

i.e., eq iii in the text. Similarly

$$\frac{dx}{dw} = 2\frac{w + \sigma}{\sigma} \quad \text{and} \quad \frac{dx'}{dw} = 2\frac{a}{\sigma}$$

by integration of which, taking eq iii into account, one obtains

$$x = 2(w - w^0) + \frac{w^2 - w^{0^2}}{\sigma} \quad \text{and} \quad x' = \left(w^0 + 1 + \frac{\sigma}{2}\right) \times$$

$$\left[1 - \exp\left(-2\frac{w - w^0}{\sigma}\right)\right] - \left(w - w^0 + \frac{w^2 - w^{0^2}}{\sigma}\right)$$

and therefore eq iv in the text.

From the second expression of the $dw/d\tau$ and $dy/d\tau$ differential equations, it immediately appears that $y = 2(w - w^0)$, i.e., the production of amine is twice the production of NuNu.

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