

# Photochemical Study of the Reactions of the 2-Naphtoxide Ion with Haloadamantanes

Juan E. Argüello, Marcelo Puiatti and Alicia B. Peñeñory

Departamento de Química. Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria. (5000) Córdoba, Argentina

E-mail: jea@dqo.fcq.unc.edu.ar, penenory@dqo.fcq.unc.edu.ar

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**Abstract:** The fluorescent excited state of 2-naphtoxide ion is quenched by haloadamantanes (**X-Ada**) as electron acceptors according to an electron-transfer mechanism. This mechanism is proposed on the basis of: 1) decreasing quenching rate constant as the reduction potential of **X-Ada** is made more negative and 2) the analysis of reaction products.

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## Introduction

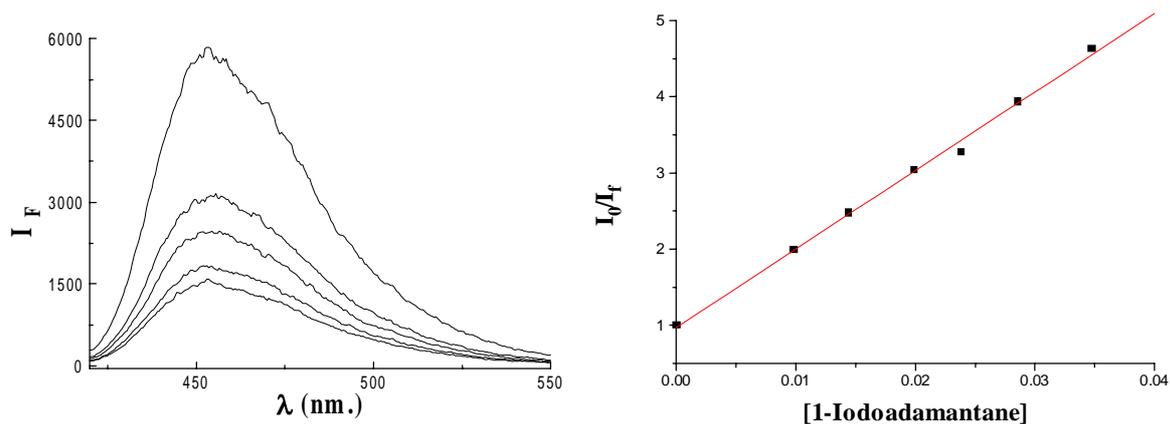
It is known that the 2-naphtoxide ion reacts with a variety of aryl halides under photostimulation in liquid ammonia yielding 1-aryl-2-naphtoxides as substitution products.[1] It was proposed that these reactions occur by the  $S_{RN}1$  mechanism, and involve the participation of radicals and radical anions as intermediates. However, no quantitative photochemical studies of these reactions have been performed. Considering that the photophysics of 2-naphtoxide ion was determined by Soumillion and co-workers, [2] we undertook a systematic study of the photoinduced reaction of this ion with haloadamantanes.

## Results and Discussion

The deactivation of the singlet excited state of 2-naphtoxide ion by haloadamantanes, **X-Ada**, was studied in dimethylsulfoxide (DMSO) by fluorescence stationary techniques. The results obtained from the inhibition of the fluorescence of 2-naphtoxide ion by 1-iodo, 1-bromo and 1-chloroadamantane showed Stern-Volmer linear plots. The quenching rate constants from these plots show a good correlation with the reduction potentials of the adamantyl halides. (Table 1).

**Table 1.** Fluorescence quenching of the 2-naphtoxide ion by X-Ada.

<i>X-Ada (Q)</i>	$k_{SV}$	$kq (10^9 M^{-1}s^{-1})$	$\log kq$	$E_{red}$ [3]
1-Iodoadamantane	103	5.7	9.8	-2,20
1-Bromoadamantane	2.2	0.12	8.1	-2,54
1-Chloroadamantane	0.81	0.045	7.65	-2,64

**Figure 1.** Quenching of 2-naphtoxide ion by 1-Iodoadamantane.

1-Iodoadamantane quenches the fluorescence of 2-naphtoxide ion with a rate constant near the diffusion limit ( $k_{diff}$  for DMSO =  $3,3 \times 10^9 M^{-1}s^{-1}$ ) [4]. A plot of the logarithm of the rate constants vs. the change in free energy follows a typical behavior for an electron transfer reaction. From the photochemical study we performed a detailed analysis of the reaction products. Thus, the photoinduced reaction of 2-naphtoxide ion with 1-iodoadamantane in DMSO rendered a mixture of adamantane (coming from the reduction of the adamantyl radical intermediate), substitution products (which arise from the addition of the adamantyl radical to the 3, 6 and 8 positions of the ion) as well as 1-adamantanol and minor amounts of 1-adamantyl-2-naphthylether.

## References and Notes

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