

Generation of Radical-cations from Naphthalene and Some Derivatives, both by Photoionization and Reaction with $\text{SO}_4^{\cdot-}$: Formation and Reactions Studied by Laser Flash Photolysis

Steen Steenken*

Max-Planck-Institut für Strahlenchemie, Mülheim, Federal Republic of Germany

Cathryn J. Warren and Bruce C. Gilbert*

Department of Chemistry, University of York, Heslington, York YO1 5DD

Radical-cations from naphthalene and some derivatives have been generated in aqueous acetonitrile both by direct photolysis (with λ 248 nm light *via* biphotonic ionization) and *via* reaction with $\text{SO}_4^{\cdot-}$. The radical-cation reacts rapidly with the parent substrate (k ca. 10^8 dm³ mol⁻¹ s⁻¹) and with nucleophiles (*e.g.* with N_3^- $k = 4.2 \times 10^9$ dm³ mol⁻¹ s⁻¹ or with water, k 4×10^4 s⁻¹). The radical-cation from 1-naphthylethanoic acid undergoes rapid decarboxylation (k 5×10^5 s⁻¹). The radical cations from 4-methyl- and 4-methoxy-phenylethanoic acid also rapidly decarboxylate to yield the corresponding benzyl radicals.

The complexity of the products obtained and of the intermediates detected (by ESR) in the oxidation of some arylalkanoic acids with both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ in acid has been interpreted in terms of the initial formation of arene radical-cations or zwitterions $^{+\cdot}\text{Ar}(\text{CH}_2)_n\text{CO}_2\text{H}/^{+\cdot}\text{Ar}(\text{CH}_2)_n\text{CO}_2^-$. For example, with $n > 2$ rapid decarboxylation is believed to follow long-range electron-transfer from the carboxylate to the ring. However, no direct evidence for the intermediate radical-cations has so far been obtained and the rate constants for fragmentation processes (derived by kinetic simulation of steady-state concentrations) can only be regarded as estimates.

A flash photolysis study was therefore undertaken with the aims both of generating arene radical-cations and of monitoring their behaviour directly. The majority of the experiments were carried out using a pulsed KrF laser (with λ 248 nm), both to generate $\text{SO}_4^{\cdot-}$ (from peroxydisulphate) as a primary oxidant and also in an attempt to bring about direct photoionization of the substrates. Photoionization, which constitutes an important step in many photochemical reactions, may occur by monophotonic or biphotonic processes (in the latter of which a first-formed excited state is ionized by interaction with a second photon).² The ease with which photoionization occurs (and its mechanism) should be influenced by the oxidation potential of the substrate and the nature of the solvent.³ The energy associated with a photon of λ 248 nm is 5 eV and the free energy of hydration of an organic radical-cation and of e^- is 3–3.5 eV;^{2,4} this implies that only those molecules with a gas-phase ionization potential below ca. 8.5 eV would be expected to undergo monophotonic ionization in water under these conditions. Though this suggests that for benzene (E_i 9.2 eV), for example, monophotonic ionization would not be expected, for naphthalene (E_i 8.15 eV)^{5,6} and its derivatives this might constitute a significant mechanism for ionization.

The occurrence of mono- and bi-photon processes, as well as reaction with $\text{SO}_4^{\cdot-}$, has thus been explored for a variety of benzene and naphthalene derivatives, chosen to include those which may be susceptible to oxidative fragmentation.

Results and Discussion

(a) *Laser Flash Photolysis Studies.*—(i) *Phenylethanoic acids.* Initial experiments involved some phenylethanoic acids, the facile oxidative decarboxylation of which (to give benzyl radicals) has previously been demonstrated.^{1,7} Aqueous

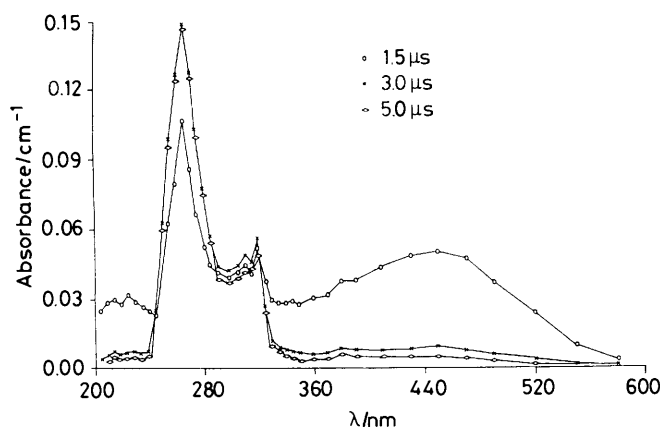


Figure 1. Absorption spectra recorded 1.5, 3, and 5 μs after flash photolysis (λ 248 nm) of an aqueous solution of 4-methylphenylethanoic acid (10^{-3} mol dm⁻³) and potassium peroxydisulphate (0.1 mol dm⁻³) at pH 1.8.

solutions typically contained the substrate (10^{-3} mol dm⁻³) and potassium peroxydisulphate (0.1 mol dm⁻³), conditions which give an absorbance at 247 nm of ca. 2.6 cm⁻¹ (and with the majority of the light absorbed by the peroxydisulphate ion, to minimize any photoionization): solutions were thoroughly degassed to remove oxygen before irradiation.

Photolysis of a solution of peroxydisulphate in the presence of 4-methylphenylethanoic acid at pH 1.8 resulted in the absorption spectra shown in Figure 1 (recorded 1.5, 3 and 5 μs after the flash). The broad peak centred at 450 nm characterizes $\text{SO}_4^{\cdot-}$; the absorbance with λ_{max} 270 nm which grows in intensity is assigned to the 4-methylbenzyl radical [see reactions (1) and (2)] on the following basis. Photolysis of an aqueous solution of peroxydisulphate (0.1 mol dm⁻³) in the presence of 1,4-dimethylbenzene (*p*-xylene, 10^{-3} mol dm⁻³) gave a spectrum which 0.3 μs after the flash showed absorption from $\text{SO}_4^{\cdot-}$ (λ_{max} 450 nm) and an absorption with λ_{max} 290 nm, attributed to the 1,4-dimethylbenzene radical-cation (see ref. 9); after 5 μs both had decayed, leaving a spectrum identical with that observed from 4-methylphenylethanoic acid and attributed to the 4-methylbenzyl radical, formed in this case *via* rapid deprotonation [reaction (3)].

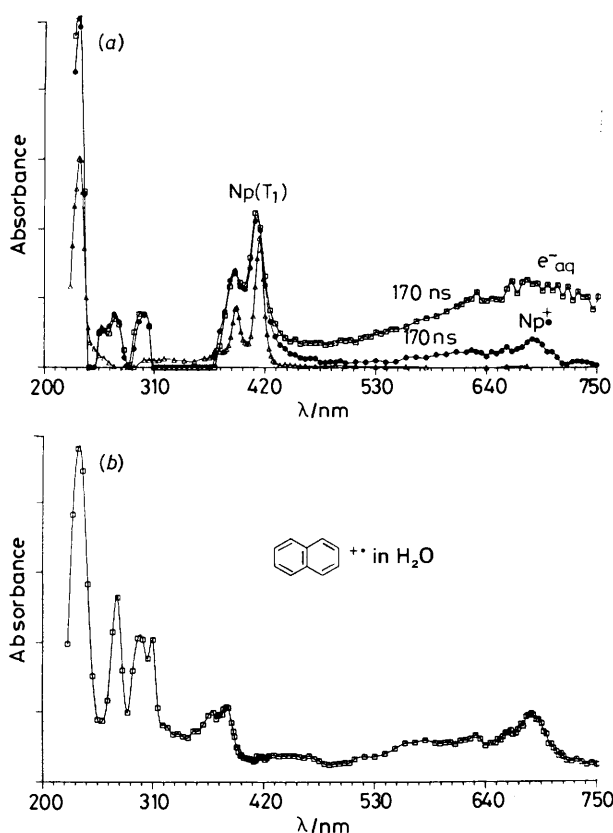
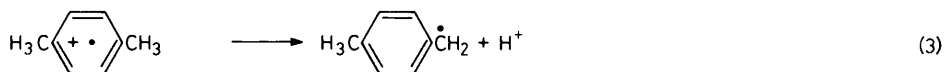
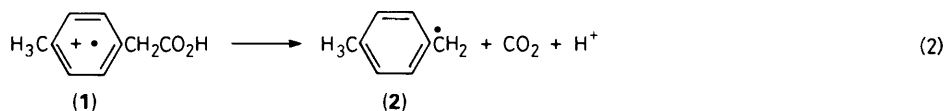
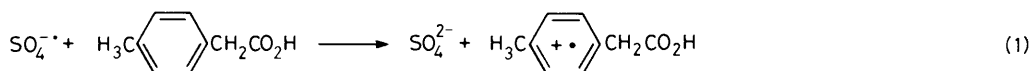


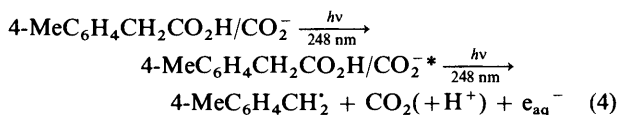
Figure 2. (a) Absorption spectra of transients produced on 248 nm photolysis (100 mJ/pulse) of a deoxygenated saturated solution of Np in water, recorded 170 ns after the pulse (squares and circles). The spectrum characterized by the circles was recorded after addition of 0.37 mol dm^{-3} 2-chloroethanol as an e_{aq}^- scavenger. For comparison, the triangles identify the spectrum of $\text{Np}(\text{T}_1)$ recorded at $17 \mu\text{s}$ after the pulse in a 0.1 mmol dm^{-3} solution of Np in cyclohexane, using 10 mJ/pulse for excitation. (b) Absorption spectrum of the transient $\text{Np}^{\cdot+}$ produced on photolysis (100 mJ/pulse) of an aqueous solution saturated with Np and O_2 , and containing 0.37 mol dm^{-3} 2-chloroethanol to scavenge e_{aq}^- . The spectrum was recorded at $3.3 \mu\text{s}$ after the pulse. At this time, $\text{Np}(\text{T}_1)$ has quantitatively disappeared due to reaction with O_2 .

First-order rate constants (k_{obs}) for the decay of $\text{SO}_4^{\cdot-}$ and build up of the absorption from (2) were recorded in experiments in which different concentrations of the parent acid were employed. Plots of k_{obs} against substrate concentration yielded a second-order rate constant of $4.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the oxidation of the substrate [reaction (1)]. When acetonitrile was employed as the solvent a significant decrease

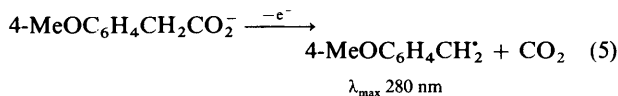
in reaction rate (k_1 $3.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) was determined. This solvent effect is indicative of a strongly polar transition state in the reaction of $\text{SO}_4^{\cdot-}$ with the substrate. Similar observations have been made in the reaction of $\text{SO}_4^{\cdot-}$ with phenylacetaldehyde acetals¹⁰ and with allyl alcohol.¹¹

Our experiments indicate that the decay of the radical-cation of 4-MeC₆H₄CH₂CO₂H (if indeed formed) is fast compared with its rate of formation by reaction with $\text{SO}_4^{\cdot-}$, so only a lower limit for k_2 of $ca. 5 \times 10^6 \text{ s}^{-1}$ can be given.

Direct photolysis of 4-methylphenylethanoic acid led to the delayed formation (during 0.7 μs) of an absorption with a maximum at 270 nm and a weaker band at $ca. 320 \text{ nm}$, identified as the 4-methylbenzyl radical, and a further band increasing in intensity from 500–750 nm. Addition of dichloromethane, N_2O or O_2 removed the latter which indicates that this absorption is due to the hydrated electron, scavenged by these electron traps. The delayed appearance of the absorption from (2) was followed at 300 nm (because of interference from fluorescence at 270 nm) as a function of pH: its rate constant for formation [*i.e.* the rate constant for decarboxylation of (1)] was found to be $1.5 \times 10^7 \text{ s}^{-1}$ at pH 0.3. At higher pH, the rate constant increased (to $k_{\text{obs}} \geq 5 \times 10^7 \text{ s}^{-1}$ at pH ≥ 2.5): this indicates that decarboxylation is faster when the carboxy group is ionized. The yield of 4-MeC₆H₄CH₂ was higher when the ionized acid was photolysed. From the dependence on the 248 nm light intensity of the yield of e_{aq}^- and 4-MeC₆H₄CH₂, it is concluded that the ionization requires two 248 nm photons (is biphotonic).



4-Methoxyphenylethanoic acid was studied in an analogous way. From experiments using $\text{SO}_4^{\cdot-}$ to oxidize the compound *via* removal of one electron, it is estimated that the rate of decarboxylation of the radical zwitterion (which has the carboxyl group ionized) is $\geq 5 \times 10^7 \text{ s}^{-1}$ [see equation (5)].



The 4-methoxybenzyl radical produced in reaction (5) could also be generated from 4-methoxytoluene by reaction with $\text{O}_4^{\cdot-}$, produced¹² *via* radiation [see reaction (6)].



(ii) *Photoionization of naphthalene.* Photolysis of a saturated solution of naphthalene in water ($[\text{Np}] ca. 10^{-4} \text{ mol dm}^{-3}$) gave

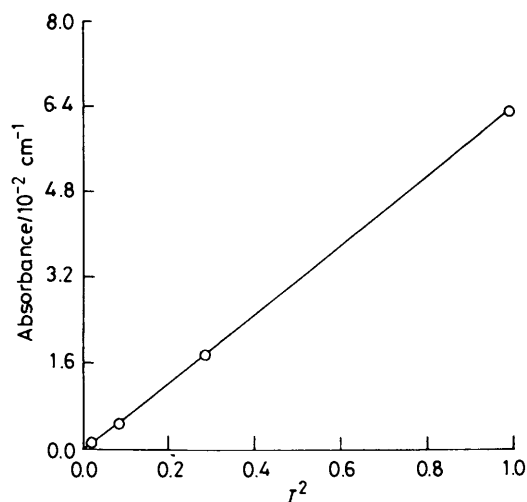


Figure 3. Variation of the absorbance due to the hydrated electron at 650 nm (corrected for any contribution from the radical-cation, *via* experiments with CH_2Cl_2) with the square of the relative laser intensity following flash photolysis of an aqueous solution of naphthalene. The energy per pulse varied from 5 to 40 mJ.

a spectrum 170 ns after photolysis which comprised bands at 233, 275, 300, 390, and 410 nm with a further broad band commencing at 500 nm and increasing to a maximum of *ca.* 700 nm [see Figure 2(a)]. On the ≤ 500 ns timescale, the spectral region between 310 and 365 nm is masked with respect to absorption measurements by the intense fluorescence of naphthalene, due to emission from the first excited singlet state [$\text{Np}(\text{S}_1)$]. The half-life of this state in aqueous solution was measured to be 31 ns, considerably shorter than the 70 ns found¹³ in cyclohexane. The value of λ_{max} of the fluorescence in aqueous solution was determined to be 325 nm, which means that the energy of $\text{Np}(\text{S}_1)$ is 3.81 eV above the ground state. The rate of the fluorescence decay could be enhanced by the addition of O_2 . Analysis of this effect led to the rate constant $k[\text{Np}(\text{S}_1) + \text{O}_2] = 1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, a value higher than that for reaction of triplet Np with O_2 (see below). The fluorescence decay was also increased in the presence of cyclohexa-1,3-diene (1,3-CHD). From this fluorescence decay enhancement, $k[\text{Np}(\text{S}_1) + 1,3\text{-CHD}] = 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Addition of CH_2Cl_2 or $\text{HOCH}_2\text{CH}_2\text{Cl}$ as electron scavengers caused a decrease in the intensity of the 500–750 nm band (due to removal of e_{aq}^-) and revealed absorption bands with λ_{max} 630 and 680 nm [see Figure 2(a)]. On addition of oxygen (1 mmol dm^{-3}) the fluorescence intensity and lifetime (see above) were considerably reduced and the absorptions at 390 and 410 nm were weakened in intensity or removed [see Figure 2(b)]. Since oxygen is known to be a triplet scavenger it is concluded that these peaks are due to triplet naphthalene [$\text{Np}(\text{T}_1)$]. This was confirmed by exciting naphthalene in ethanol or cyclohexane with low-intensity radiation (10 mJ/pulse, conditions under which triplet formation should be encouraged¹⁴): the spectrum recorded in cyclohexane 17 μs after the pulse is also shown in Figure 2(a). The spectrum with

bands at λ_{max} 233, 390, 410 nm is in excellent agreement with those previously recorded and assigned to $\text{Np}(\text{T}_1)$.¹⁵ The half-life of $\text{Np}(\text{T}_1)$ in pure deoxygenated water was measured to be 7.2 μs , and its rate of reaction with O_2 , $k_q(\text{O}_2) = 3.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (from the rate of decrease of the band at 410 nm).

The absorptions at these wavelengths could also be scavenged by cyclohexa-1,3-diene (1,3-CHD), another well-known triplet scavenger. From the dependence on [1,3-CHD] of the first-order rate of decay of the absorption at 410 nm, the rate constant for the quenching of the naphthalene triplet by 1,3-CHD was determined as $k_q = 2.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. On the basis of phosphorescence measurements,¹⁶ the energy of the triplet is 2.64 eV above the singlet ground state.

The spectrum recorded after completion of the scavenging of $\text{Np}(\text{T}_1)$ by O_2 is shown in Figure 2(b). It has bands with λ_{max} 235, 275, 297, 310, 368, 384, 630, and 685 nm and is very similar to that detected^{17–21} following γ -radiolysis of naphthalene in frozen matrices at 77 K and to that obtained²² from pulse-radiolysis studies of the reaction of naphthalene with $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$; on the basis of the spectroscopic and mechanistic evidence this absorption is attributed to the naphthalene radical-cation, $\text{Np}^{+\cdot}$. The $\text{Np}^{+\cdot}$ peak at 235 nm is reported here for the first time.

The possibility that production in aqueous solution of the radical cation is monophotonic, as has recently been suggested for anthracene and 1-methylnaphthalene²³ or biphenyl derivatives²⁰ in acetonitrile [where e^- is scavenged to produce $(\text{MeCN})_2^{\cdot-}$]²⁴ was investigated *via* variation of the laser intensity (with the use of filters placed in the beam). As judged by the yield of e^- (monitored at 630 nm) and $\text{Np}^{+\cdot}$ (monitored at 275 and 685 nm in experiments in the presence of CH_2Cl_2), both of which increased in proportion to the square of the light intensity, the production of $\text{Np}^{+\cdot}$ (and e^-) is a biphotonic process (see *e.g.* Figure 3).^{*} The dependence of the yield of $\text{Np}^{+\cdot}$ on photon density was also studied (monitoring the absorbance at 685 nm) in water: acetonitrile (1:1) (the absorption spectrum being identical with that obtained in aqueous solution) and in pure acetonitrile in the range 5–40 mJ per 20 ns pulse. In every case the concentration of $\text{Np}^{+\cdot}$ increased with the square of the energy per pulse, indicating that ionization of Np requires two photons (is biphotonic). At > 40 mJ per pulse, saturation phenomena were prominent.

In order to identify the electronically excited state[†] that, upon further excitation, gives rise to the radical-cation, the fluorescence intensity at λ_{max} 325 nm and the triplet concentration, monitored by the absorption at λ 410 nm, were measured as a function of the incident light intensity in the same range as that used for determination of [$\text{Np}^{+\cdot}$]. The results are shown in Figure 4. The concentrations of both $\text{Np}(\text{S}_1)$ and $\text{Np}(\text{T}_1)$, after an initial strictly linear rise [shown for $\text{Np}(\text{T}_1)$ in the inset], pass through a maximum as the incident laser power is further increased. In contrast, the concentration of $\text{Np}^{+\cdot}$, after an initial parabolic rise (reflecting its biphotonic formation), further increases with increasing photon density, although saturation effects are clearly visible as the power per pulse increases. These dependencies are interpreted in terms of depletion of both $\text{Np}(\text{S}_1)$ and $\text{Np}(\text{T}_1)$ by 248 nm photons to yield ionized naphthalene molecules, *i.e.* $\text{Np}^{+\cdot}$, and e_{aq}^- . Photoionization of $\text{Np}(\text{S}_1)$ has previously been observed in argon matrices.²¹ By comparing the absorbance due to $\text{Np}^{+\cdot}$ and e_{aq}^- at 650 nm with that from an aqueous KI solution [$\phi(e_{\text{aq}}^-) = 0.29$ upon excitation at λ 254 nm²⁵], the quantum yield for photoionization of Np at an incident laser power of 40 mJ/pulse was determined as $\phi(\text{Np}^{+\cdot}) = 0.07$.

The energetics of photoionization of $\text{Np}(\text{S}_1)$ (3.81 eV above ground state) are favourable: with the additional 5 eV provided by the 248 nm photon, the available energy is clearly above the

^{*} For a discussion of the parameters important in determining photonity, see: U. Lachish, A. Shafferman and G. Stein, *J. Chem. Phys.*, 1976, **64**, 4205.

[†] For information on the electronically excited states of Np see *e.g.* ref. 20 and J. M. O. Matos and B. O. Roos, *Theor. Chim. Acta*, 1988, **74**, 363, and I. Baraldi and G. Ponterini, *Gazz. Chim. Ital.*, 1988, **118**, 109, and references therein.

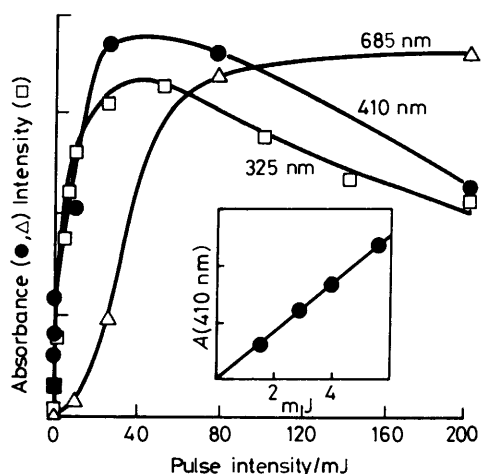


Figure 4. Dependence on pulse intensity (in mJ) of the yield of $\text{Np}^{+\bullet}$ (measured at 685 nm, triangles), of $\text{Np}(\text{T}_1)$ (measured at 410 nm, circles) and of $\text{Np}(\text{S}_1)$ (measured as the fluorescence intensity at 325 nm, squares) in aqueous solutions. $\text{Np}^{+\bullet}$ and $\text{Np}(\text{T}_1)$ were measured at 50 ns after the pulse. The fluorescence was recorded at 90 ns. The absorbance scale for $\text{Np}^{+\bullet}$ and $\text{Np}(\text{T}_1)$ is the same. The scale for the fluorescence has been adjusted to make the curve fit in with the other curves. The inset shows the strictly linear dependence of $[\text{Np}(\text{T}_1)]$ on the photon flux in the region of low laser power. The argon-bubbled saturated Np solution contained $0.37 \text{ mol dm}^{-3} \text{ HOCH}_2\text{CH}_2\text{Cl}$ to scavenge e^-_{aq} .

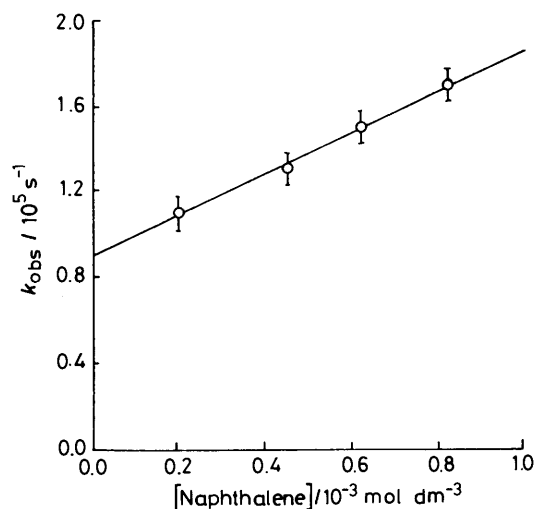


Figure 5. Variation of k_{obs} for the decay of the naphthalene radical-cation [measured from the absorbance at 650 nm following photolysis of a solution of naphthalene and $\text{S}_2\text{O}_8^{2-}$ (0.1 mol dm^{-3}) in H_2O -MeCN] with the naphthalene concentration.

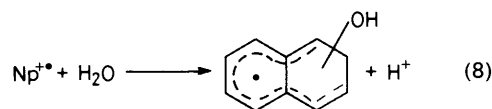
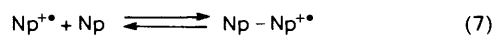
ionization threshold (8.15 eV).⁶ When $\text{Np}(\text{T}_1)$ (2.6 eV above ground state) is excited, 7.6 eV are available. Since hydration of the ions provides 2.5–3.5 eV,⁴ ionization is also thermodynamically possible in this case.

From the absorption spectrum (not corrected for depletion of parent) of $\text{Np}(\text{T}_1)$ as shown in Figure 2(a) it appears as if the triplet has only a low extinction coefficient at 248 nm, the wavelength of the exciting laser light [the extinction coefficient of $\text{Np}(\text{T}_1)$ at λ 415 nm is $20\,000$ – $40\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; see ref. 15]. The extinction coefficient of $\text{Np}(\text{S}_1)$ at 248 nm appears to be unknown.

Spectra from $\text{Np}^{+\bullet}$ were also obtained *via* the photolysis of solutions of $\text{S}_2\text{O}_8^{2-}$ (0.1 mol dm^{-3}) and naphthalene ($5 \times 10^{-4} \text{ mol dm}^{-3}$) in aqueous acetonitrile (1:1). The rate of

electron-transfer to $\text{SO}_4^{\bullet-}$ was determined as $2.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (as described above).

The decay of the naphthalene radical-cation in MeCN- H_2O (1:1) was studied utilizing that part of the spectrum with λ_{max} 630 and 685 nm (since this was considered to be most likely to be free from interference from other transients, such as the triplet and ring-adducts). The decay of the radical-cation produced by reaction with $\text{SO}_4^{\bullet-}$ was monitored and found to be first order and independent of laser intensity. However, the value of k_{obs} was found to depend upon the concentration of naphthalene, as shown in Figure 5. The linear dependence of rate on concentration indicates that there is a second-order reaction between radical-cation and parent: the intercept is believed to correspond to hydration of the radical-cation [reaction (8)]. This reaction, in which water reacts as a nucleophile towards the radical cation, is analogous to that²⁶ involving acetate as the nucleophile. Values of the rate constants for reactions (7) and (8) are derived as $9.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $8.4 \times 10^4 \text{ s}^{-1}$, respectively. Experiments in pure aqueous solution, *i.e.* in the absence of acetonitrile, showed a lower rate of hydration of the radical-cation [reaction (8)], *i.e.* $4 \times 10^4 \text{ s}^{-1}$ (see Table 1).



The dimer radical-cation expected²⁷ to result from the reaction of the radical-cation with parent, was directly detected in experiments in which the photomultiplier was replaced as a detector by a photodiode (to provide the greater sensitivity needed to detect absorptions at higher wavelength, *e.g.* 1 100 nm, see Figure 6). The broad band at *ca.* 1 100 nm is in good agreement with that^{17,18,28,29} previously described.

Reaction (8) was also monitored by conductance. As seen from Figure 7, in acid solution there is an increase of conductance due to replacement of $\text{Np}^{+\bullet}$ by the much more mobile H^+ ion. In basic solution, the conductance decreases since the proton produced in reaction (8) is neutralized by an OH^- ion whose concentration is thereby reduced. Close inspection of the conductance traces shows that the build-up of conductance is not mono-exponential as required by reaction (8) but that, in addition to a fast component (with k *ca.* $2.5 \times 10^4 \text{ s}^{-1}$), there is a slower component the rate of which is roughly an order of magnitude lower. This is interpreted in terms of the dimerization reaction (7) being reversible, with the dissociation of the dimer being rate-determining.

The observation [see Figure 7(b)] that the rate of conductance change at pH 10.1 (decrease) is somewhat faster than that at pH 4.5 (increase) is due to the fact that in basic solution $\text{Np}^{+\bullet}$ decays not only by reaction with H_2O but also with OH^- ($k = 2.4 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, see Table 1). The fact that the optically detected rate of decay of $\text{Np}^{+\bullet}$ ($4 \times 10^4 \text{ s}^{-1}$) is larger than the initial rate for (the dominant) formation of H^+ ($2.5 \times 10^4 \text{ s}^{-1}$) is in support of reaction (7), since this pathway constitutes an additional path of depletion of $\text{Np}^{+\bullet}$.

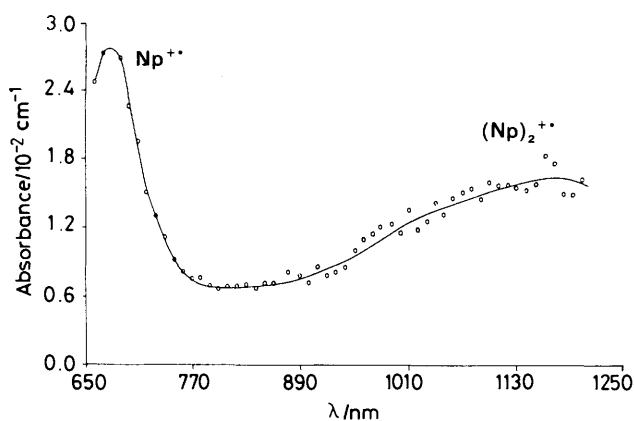
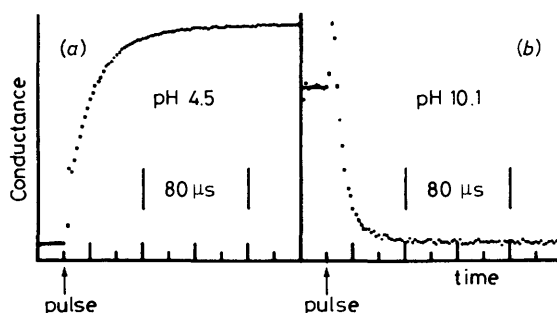
Experiments were also designed to measure rate constants for the reaction of the naphthalene radical-cation with a series of other nucleophiles (OH^- , N_3^- , SO_3^{2-} , and piperidine) by measuring the pseudo-first-order rate constant for the decay of the absorbance at 630 nm from $\text{Np}^{+\bullet}$ (generated by direct photoionization in H_2O and H_2O -MeCN). These values (Table 1) are discussed below.

(iii) *Naphthalene derivatives.* Table 2 contains details of the absorption spectra of some substituted-naphthalene radical-

Table 1. Rate constants for reaction of a series of nucleophiles with the naphthalene radical-cation.

Nucleophile	$k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ^a	Solvent ^b
H ₂ O	4.0×10^4 ^c	A
H ₂ O	8.4×10^4 ^c	B
HO ⁻	2.4×10^8	A
HO ⁻	2.8×10^8	B
N ₃ ⁻	4.2×10^9	B
SO ₃ ²⁻	1.65×10^9	B
Piperidine	2.9×10^8	B
Naphthalene	9.5×10^7	B

^a $\pm 10\%$. Calculated from the rate of decay of the absorbance from Np⁺ at 650 nm. ^b A, water; B, 1:1 water-acetonitrile. ^c s^{-1} , $\pm 20\%$.

**Figure 6.** Absorption spectrum of the naphthalene monomer and dimer radical-cations recorded 35 μs after photolysis of a solution of naphthalene in H₂O-MeCN (1:1).**Figure 7.** Photolysis-induced change of conductance of a deoxygenated aqueous solution saturated with Np and containing 0.3 mol dm^{-3} 2-chloroethanol: (a) pH 4.5; (b) pH 10.1.

cations, obtained *via* reaction with photochemically generated SO₄²⁻ in MeCN-H₂O. The rate constants for the formation of the radical-cations (Table 3) were determined *via* the build-up of the absorption from the radical-cation at 650 nm (and checked *via* monitoring of the decay of the absorbance from SO₄²⁻ at 450 nm).

The decay of the radical-cations was also monitored by following the decrease with time of the absorbance at 650 nm as a function of substrate concentration. Plots of k_{obs} against substrate concentration revealed the occurrence of both concentration-dependent and -independent modes of decay (presumably corresponding to reaction with parent compound and hydration, respectively, for which results are summarized in Table 3).

In contrast with the spectra obtained from other substrates, 1-naphthylethanoic acid gave a spectrum which showed only one main absorbance, at λ_{max} 330 nm, except for a very weak absorbance at *ca.* 700 nm (when recorded after 0.3 μs). That this may be attributed to the 1-naphthylmethyl radical (3) (see ref. 30) was confirmed by generating the latter by reaction of 1-methylnaphthalene with O^{·-} (itself generated by reaction of SO₄²⁻ with OH⁻ at high pH).¹² We conclude that the reaction of SO₄²⁻ with 1-naphthylethanoic acid (but not the 2-isomer which gave a typical naphthalene-type radical-cation spectrum) leads to rapid decarboxylation [reaction (9)] of a first-formed radical-cation as observed for the other analogues (see above). Direct photolysis of the parent also gave the absorption at 330 nm from 1-naphthylmethyl³⁰ together with a sharp band at 410 nm (assigned to the triplet) and absorption from e⁻. [Experiments with low-intensity photolysis and propan-2-ol as the solvent gave a clear spectrum assigned to the triplet, with λ_{max} 390, 410 nm, but no evidence of (3), which indicates that the latter does not derive from the triplet itself]. By monitoring the build-up of the absorption at λ 330 nm in the direct photoionization experiments we calculate that the rate of decarboxylation of the radical cation of 1-naphthylethanoic acid is $5 \times 10^5 \text{ s}^{-1}$ (at pH 3.5).

(b) *ESR Results.*—Initial experiments were carried out in which the reactions of naphthalene and some derivatives (including the methylnaphthalenes and naphthylethanoic acids) with both [·]OH and SO₄²⁻ in aqueous solution were studied by ESR spectroscopy (as described previously for phenylethanoic acid and its derivatives¹). Despite use of a rapid flow-system (for the generation of these intermediates from the Ti^{III}-H₂O₂ and Ti^{III}-S₂O₈²⁻ couples, respectively) and photosensitized photolysis of S₂O₈²⁻ for the generation of the latter, no signals from organic free radicals could be directly detected. This may reflect lack of solubility (*e.g.* for the hydrocarbons) as well as the expected multiplicity of hyperfine splittings *e.g.* cyclohexadienyl adducts and naphthylmethyl radicals. A spin-trapping technique was therefore employed.

Experiments were typically conducted with a small quantity of the spin-trap 2-methyl-2-nitrosopropane (Me₃CNO, Bu¹NO) together with the substrate in aqueous solution or aqueous acetonitrile to which either hydrogen peroxide or potassium peroxydisulphate had been added. Photolysis led in most cases to the detection of ESR signals which characterize the formation of Bu₂NO[·] [from decomposition of the trap, and with $a(\text{N})$ 1.60 mT, g 2.006] and [·]ON(Bu¹)CH₂CN [with $a(\text{N})$ 1.50, $a(2\text{H})$ 0.913 mT, g 2.006].

However, when 1-naphthylethanoic acid (but not the corresponding 2-isomer) was employed in experiments with either S₂O₈²⁻ or H₂O₂ (at low pH), as well as in experiments involving direct photolysis in MeCN, strong signals resulted from a radical with $a(\text{N})$ 1.60, $a(2\text{H})$ 1.14 mT, g 2.006. This is assigned the structure (4), and it is believed to be formed by the rapid formation and fragmentation of an intermediate radical-cation, as suggested in the flash-photolysis results described above.

(c) *Mechanistic Implications.*—The results presented here establish that radical-cations of some naphthalene derivatives are produced both by reaction with SO₄²⁻ and by direct photoionization with radiation of λ 248 nm (in a biphotonic process). It is interesting that 248 nm photolysis of 1,3-dioxoles, which have an E_i of *ca.* 8 eV (similar to that of Np), leads to nonphotonic ionization.³¹ The difference in behaviour may be related to the smaller size of the dioxole molecule, which leads to a larger energy of hydration of the radical-cation. Another reason may be that in the case of Np, the state reached by the absorption of a 248 nm photon (the S₂ state ¹B_{2u})

Table 2. Characteristics (λ_{\max}) of the absorption spectra of the radical-cations of naphthalene and its derivatives.^a

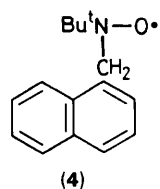
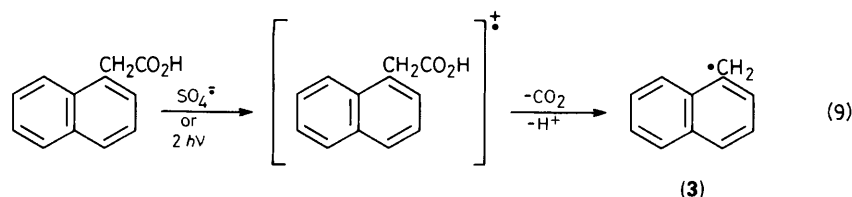
Compound	λ_{\max}/nm					
Naphthalene	235, 275	300, 310	370	630	685	
1-Chloronaphthalene		330	390	690	750	
2-Chloronaphthalene		300	400	630	690	
2-Fluoronaphthalene		310	380	610	670	
1-Methylnaphthalene		310	390	640	700	
2-Methylnaphthalene		310	400	630	680	
1-Ethylnaphthalene		320	400	630	690	
2-Ethylnaphthalene	270	300	370	620	670	
1-(2-Hydroxyethyl)naphthalene		310	390	650	700	
2-(2-Hydroxyethyl)naphthalene	290	310	390	630	680	
2-Naphthylethanoic acid	280	310	380	630	680	

^a Generated by photolysis of substrate (1×10^{-4} mol dm⁻³) with peroxydisulphate (0.1 mol dm⁻³) at pH 3.5 in 1:1 acetonitrile–water.

Table 3. Rate constants for the formation and reactions (with parent and with water) of some naphthalene radical-cations.

Substituent	$10^{-9} k(\text{Np} + \text{SO}_4^{\cdot-})^a$	$10^{-7} k(\text{Np}^{\cdot+} + \text{Np})^b$	$10^{-4} k(\text{Np}^{\cdot+} + \text{H}_2\text{O})^c$
H	2.9	9.5	8.4
1-Cl	1.3	—	10
2-Cl	1.1	23	25
2-F	1.4	27	5.5
1-Me	2.8	4.0	3.0
2-Me	2.3	—	4.5
1-Et	2.1	2.0	3.8
2-Et	2.0	2.0	5.0
1-CH ₂ CH ₂ OH	2.8	—	3.8
2-CH ₂ CH ₂ OH	2.9	—	4.7
1-CH ₂ CO ₂ H	1.5 ^d (3.5) ^{d,e}	<i>f</i>	<i>f</i>
2-CH ₂ CO ₂ H	3.6 ^{d,e}	—	—

^a dm³ mol⁻¹ s⁻¹, $\pm 10\%$; measured from the build-up in absorbance at 650 nm following photolysis of a solution of substrate and peroxydisulphate (0.1 mol dm⁻³) in 1:1 H₂O–MeCN at pH 3.5. ^b dm³ mol⁻¹ s⁻¹, $\pm 10\%$; determined from the slope of a plot of k_{obs} for the decay of the radical-cation against substrate concentration (in H₂O–MeCN). ^c s⁻¹, $\pm 10\%$; determined from intercept of plot of k_{obs} for the decay of the radical-cation against substrate concentration (in H₂O–MeCN). ^d Measured from the decay of the SO₄^{•-} absorption at 450 nm. ^e In water. ^f Decarboxylation occurs: see the text.



relaxes rapidly to the fluorescent ¹B_{3u} state, and this process competes with ionization.*

The rate constants for the reaction of the parent compounds with SO₄^{•-} approach the diffusion-controlled limit (see Table 3) and, for a given solvent composition (MeCN–H₂O), are not very sensitive to the nature of the substituent. Evidence from 1-naphthylethanoic acid suggests that the reaction is acceler-

ated in aqueous solution, indicating an ionic transition state.

Reactions of the radical-cation which have been demonstrated include nucleophilic attack by, e.g. water and other nucleophiles (see Tables 1 and 3) as well as reaction with the parent to form dimer radical-cations, and, in one case, fragmentation *via* decarboxylation.

For the reaction of the radical-cations with the parent compounds, the substantially larger values of the rate constants for the 2-chloro- and 2-fluoro-substituted compounds than the parent and the correspondingly smaller values for the alkyl-substituted derivatives suggest that the rate is governed by the substituents' inductive effects. This behaviour is as anticipated since electron-donating (+I) substituents would be expected to stabilize a positively-charged species and hence to retard reaction (and *vice versa*); moreover since the product dimer radical-cation is believed to be a symmetrical, π - π bonded dimer, steric effects of substituents would not be expected to influence greatly the rate of reaction.

* See footnote (†) p. 337.

Table 4. Results of Hückel–McLachlan molecular orbital calculations on the singly-occupied molecular orbital (SOMO) in the naphthalene radical-cation and some derivatives.^a

Substituent	Energy (SOMO)	Spin density (excess charge)							
		1	2	3	4	5	6	7	8
2-Alkyl ^b	-0.6030	0.2026	0.0811	0.0490	0.1750	0.1706	0.0784	0.0597	0.1826
1-Alkyl ^b	-0.5815	0.1832	0.0904	0.0641	0.2006	0.1680	0.0604	0.0710	0.1608
H	-0.6180	0.1809	0.0691	0.0691	0.1809	0.1809	0.0691	0.0691	0.1809
2-X ^c	-0.6307	0.1620	0.0582	0.0892	0.1845	0.1886	0.0606	0.0778	0.1782
1-X ^c	-0.6536	0.1739	0.0501	0.0733	0.1606	0.1947	0.0782	0.0668	0.2001

^a HMO–McLachlan calculations with $\lambda = 1.2$, using the inductive model for 1- and 2-substituents (see the text). ^b k_e taken as -0.2 , to simulate the effect of an electron-donating inductive effect. ^c k_e taken as 0.2 , to simulate the effect of an electron-withdrawing inductive effect.

Compared with the reaction with water of the naphthalene radical-cation itself (for which k is $8.4 \times 10^4 \text{ s}^{-1}$ in MeCN–H₂O) the introduction of an electron-donating alkyl group appears to retard the rate of reaction, an effect which appears to be more marked for the 1- rather than the 2-isomer. This is as would be expected if the energy of the SOMO is raised by the incorporation of the alkyl groups, thus reducing the expected frontier-orbital interaction between the SOMO and the HOMO of the incoming nucleophile. The extra retardation for the 1-substituent may reflect an increased electronic effect [simple HMO calculations with an inductive model³² (see Table 4) confirm that the SOMO is more sensitive to changes in inductive effects at the α -position rather than the β -position] or an increased steric effect (if, as might be anticipated, attack is preferentially at position 1 and 8, as well as 4 and 5). However, in the absence of more detailed information on the products and their distribution, further speculation on the magnitude of k (and, in particular on the relatively low values obtained for the 1-Cl and 2-F substituents compared with 2-Cl) is not justified.

For the reactions of a range of nucleophiles with a single radical-cation ($\text{Np}^{\cdot+}$) the rate constants vary with their nucleophilicity, approaching the diffusion-controlled limit for N_3^- and SO_3^{2-} , which are known to be excellent nucleophiles.

Finally we draw attention to the facile decarboxylation of the 1-naphthylethanoic acid radical-cation (in contrast with its 2-isomer). Although this may reflect to a certain extent the relative stabilities of the products of the reaction (*i.e.* the 2-naphthyl *vs.* 1-naphthyl radical) it appears more likely to be explained largely in terms of the much greater positive charge density (and hence also unpaired electron density) at the 1- rather than the 2-position in the corresponding naphthalene radical-cation: simple HMO calculations (see Table 4) indicate that these are 0.1809 and 0.0691, respectively, in naphthalene^{•+} itself. The considerably greater concentration of positive charge expected on the ring carbon adjacent to the $\text{CH}_2\text{CO}_2\text{H}$ group in phenylethanoic acid and its derivatives compared with the naphthylethanoic acids would then account for the much more rapid decarboxylation reaction observed for these substrates.

Experimental

Solutions for flash photolysis were prepared by dissolving the substrate (10^{-3} – $10^{-4} \text{ mol dm}^{-3}$) in water (from a Millipore Milli-Q-system) or a 1:1 mixture of water–acetonitrile (spectroscopic grade). The concentration of substrate was determined from its absorbance and extinction coefficient at 248 nm. The concentration of added potassium peroxydisulphate (typically 0.1 mol dm^{-3}) was such that this component absorbed most of the radiation at 248 nm. Nucleophiles were added as solutions in the same solvent. The pH was adjusted by the addition of NaOH or HClO₄ as required and the solutions were saturated with oxygen. These solutions were photolysed by

pulses (*ca.* 20 ns, 100 mJ) of radiation (λ 248 nm) from a Lambda Physik EMG 103 MSC excimer laser. Light intensity was varied by the use of filters; the optical absorbance signals were digitized with a Tektronix 7612 or 7912 transient recorder interfaced with a DEC 11/73 computer which was also used for the analysis of data. Pulse radiolysis experiments were carried out as described previously.³³

ESR flow and photolysis experiments were carried out as described previously, except for the spin-trapping experiments which involved photolysis (with a Hanovia 1 kW mercury–xenon lamp) of solutions of the naphthylethanoic acids (typically 0.05 mol dm^{-3}) together with the peroxide (*ca.* 0.03 mol dm^{-3}) and the spin-trap Bu[•]NO (0.01 mol dm^{-3}) in aqueous acetonitrile.

All chemicals were commercial samples, used as supplied (except where stated otherwise).

The Hückel–McLachlan molecular orbital calculations were executed on a DEC 10 computer with a program in FORTRAN IV devised by Dr. D. R. Burnham.

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