

## **DIAZONIUM SALTS IN PHOTOCHEMISTRY III: ATTEMPTS TO CHARACTERIZE ARYL CATIONS**

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### **Summary**

Nanosecond laser photolysis techniques were used to examine the photodecomposition of diazonium tetrafluoroborates. Only bleaching signals at the characteristic absorption wavelength of the diazonium salts were observed; aryl cations could not be detected directly, even for those samples with ground state triplets.

Chromate ions were found to react efficiently with the protons generated in the reaction of aryl cations with water. The reaction leads to the bleaching of chromate and is a convenient probe to examine the behaviour of aryl cations in water. Examination of this process in the presence and absence of inorganic anions enables the lifetime of the phenyl cation in water to be estimated as about or slightly shorter than 500 ps.

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### **1. Introduction**

Aryl cations remain among the most evasive organic reaction intermediates. The only technique that has successfully detected a few cations has been low temperature electron paramagnetic resonance (EPR) [1 - 6] which is limited to those systems such as *p*-dialkylaminophenyl cations leading to ground state triplets [2 - 4]. An earlier report of the detection of aryl cations using flash photolysis techniques in which the lifetimes were well in excess of 10  $\mu$ s was later shown to be incorrect [7, 8].

Laser flash techniques have been widely used in recent years to examine the behaviour of numerous organic reaction intermediates. We have examined the possibility of using nanosecond laser techniques in an attempt to improve our understanding of the behaviour of aryl cations. While we were unable to detect these species directly, our results provide some insight into the behaviour of aryl cations and for the first time yield approximate lifetime values. Some experiments in matrices at 77 K were also carried out.

## 2. Experimental details

The preparation and purification of diazonium tetrafluoroborates was the same as described in earlier papers in this series [9, 10]. Laser photolysis experiments were carried out in deaerated solutions employing a flow system and using the pulses from a nitrogen laser (337.1 nm; pulse length, about 8 ns; energy per pulse, up to 10 mJ) or an excimer laser (308 nm with Xe-HCl mixtures; pulse length, about 5 ns; energy per pulse, up to 80 mJ) for excitation. Further details of our computerized facility have been reported elsewhere [11].

UV-visible spectra at 77 K were obtained using a Hewlett-Packard 8450-A spectrometer whose open table design allows the irradiation of the samples without moving them from the spectrometer cell compartment.

## 3. Results

Laser photodecomposition of aqueous solutions of the diazonium tetrafluoroborates 1 - 5 led, as the only significant signals in the nanosecond time scale, to the bleaching of the diazonium precursor:

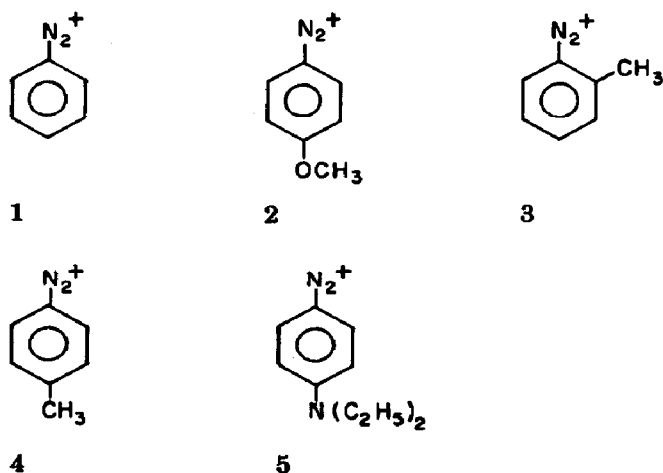


Figure 1 illustrates this behaviour for substrate 5.

Similarly, irradiation of  $10^{-3}$  M solutions of 1 - 5 in ether-isopentane-ethanol glasses at 77 K led to bleaching with the generation of only weak signals in the UV region. For example, for 5 these signals had  $\lambda_{max} = 262$  nm and were still present after thawing and refreezing; they were therefore assigned to final stable products and not to transient intermediates. The spectrometer used allowed the recording of the complete spectrum (200 - 800 nm) just a few seconds after irradiation. No evidence for absorption due to aryl cations could be obtained for any of the substrates; even 5,

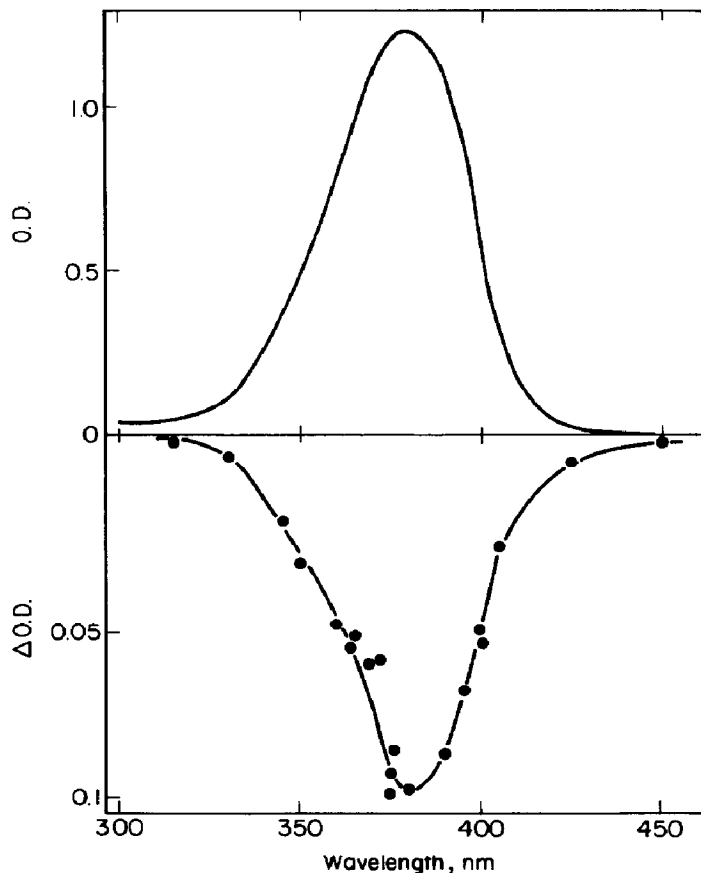


Fig. 1. Absorption spectrum of the tetrafluoroborate of **5** (0.04 mM) (upper curve) in water at 300 K and bleaching of **5** during the laser flash photolysis of a 0.11 mM solution using 337 nm light for excitation (lower curve).

which is known from EPR studies to produce a detectable ground state triplet aryl cation [2 - 4], gave no signal.

In several of our laser flash experiments we added inorganic anions in an attempt to trap the corresponding aryl cations. Attempts with anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{SCN}^-$  failed to lead to any significant signals. When we added  $\text{CrO}_4^{2-}$  we observed clear well-resolved bleaching traces; one such example is shown in Fig. 2. These results were particularly encouraging since there are several reports in the literature where organic chromates have been proposed as reaction intermediates [12]. However, our experiments (see below) eventually led us to conclude that the observed bleaching reflects the protonation of the chromate dianion which has  $\text{p}K_a = 6.49$  [13]. The kinetics of the bleaching process are dependent upon the chromate concentration, as shown in Fig. 3, and lead to a rate constant for protonation of  $(2.66 \pm 0.56) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  which was obtained using **3** as a precursor (the errors are reported as  $\pm 2\sigma$ ). We propose that the proton is produced by reaction of the aryl cation with water:

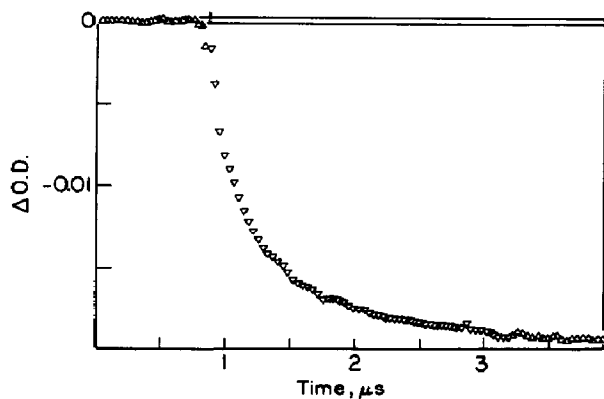


Fig. 2. Bleaching of  $\text{CrO}_4^{2-}$  observed in a solution of **1** (0.13 mM) and  $\text{K}_2\text{CrO}_4$  (0.21 mM) in water at 300 K upon laser excitation at 308 nm.

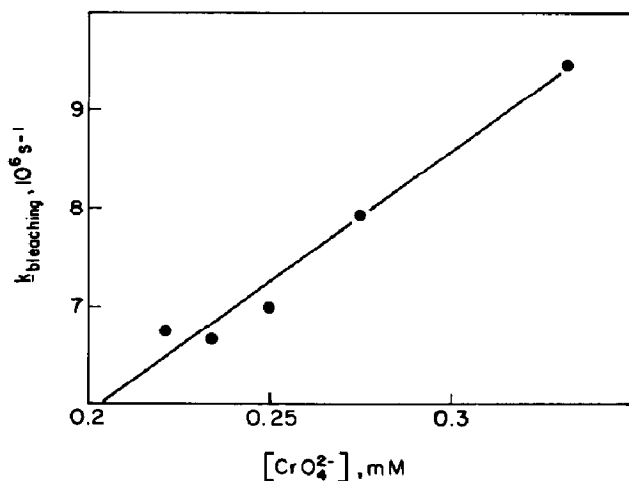


Fig. 3. Plot of the rate of chromate bleaching (monitored at 370 nm) during the laser photolysis (308 nm) of 0.403 mM **3** in water at 300 K.



The bleaching of  $\text{CrO}_4^{2-}$  was usually monitored at 370 nm, and was permanent in millimolar unbuffered solutions as indicated by spectra obtained several minutes after irradiation. However, the bleaching could be reversed by the addition of small concentrations of base. For example, Fig. 4 illustrates the effect of adding 1.34 mM NaOH. It should be noted that, in addition to the recovery, the change in optical density (ordinate) is also reduced by NaOH, reflecting the direct reaction of  $\text{OH}^-$  and  $\text{H}^+$ . In

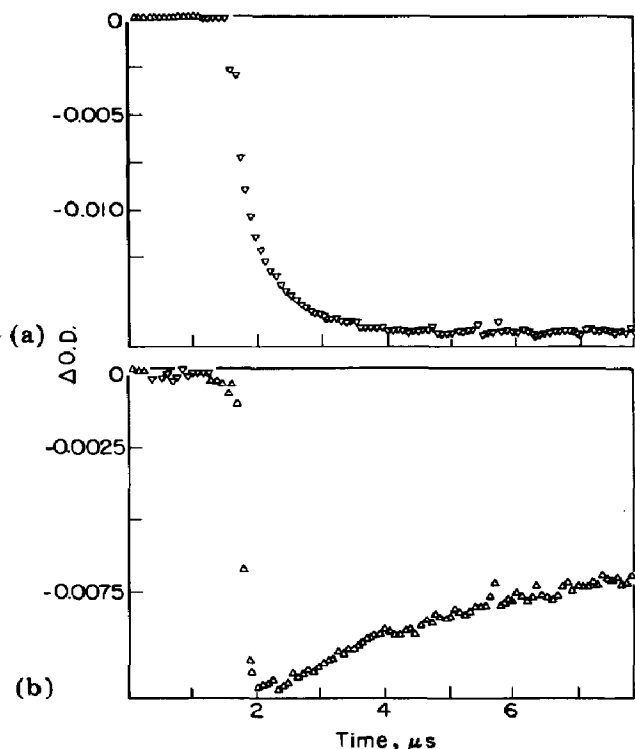
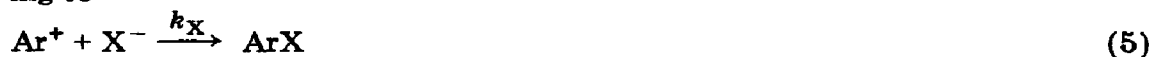


Fig. 4. Bleaching of 0.21 mM CrO<sub>4</sub><sup>2-</sup> (monitored at 370 nm) upon laser excitation (308 nm) of a 0.13 mM solution of 1 in (a) the absence and (b) the presence of 1.34 mM NaOH at 300 K.

buffered solutions (pH 7) the recovery was extremely rapid or totally undetectable, depending on the buffer concentration. As the chromate concentration was increased the rate of bleaching increased up to the point where for all practical purposes it was concurrent with the laser excitation. All these data point unambiguously to the proton as the species responsible for the bleaching. From this information we conclude that all the precursors of the proton must have lifetimes of less than 5 ns; this applies to the aryl cations as well as to any excited state of the diazonium salt involved in its photodecomposition.

The magnitude of the bleaching of chromate ions is a measure of the number of aryl cations reacting with water to release protons. This process can be used as a probe for the reactivity of aryl cations towards inorganic anions such as Cl<sup>-</sup> and SCN<sup>-</sup> in a Stern–Volmer type of approach. Thus if we add the anion X<sup>-</sup> such that its only effect is the trapping of Ar<sup>+</sup> according to



the equation

$$\frac{\text{OD}_{\text{bleach}}^0}{\text{OD}_{\text{bleach}}} = 1 + k_X \tau [\text{X}^-] \quad (6)$$

holds where the lifetime  $\tau$  refers to the aryl cation in the absence of  $X^-$ . Figure 5 shows the plots for the reaction of **1** with  $Cl^-$  and of **3** with  $SCN^-$  which lead to  $k_X\tau$  values of  $5.3\text{ M}^{-1}$  and  $2.9\text{ M}^{-1}$  respectively. The plots show some tendency to level off at higher  $X^-$  concentrations. In addition to the changes in  $OD_{\text{bleach}}$  we observed a moderate decrease in the observable rate constant for bleaching  $k_{\text{exptl}}$  upon addition of large concentrations of salts. We presume that this may be an ionic strength effect on the protonation of chromate ions, and it may also have some effect on the efficiency of bleaching. The concentration range employed in Fig. 5 is relatively free from these problems, and the Stern-Volmer slopes given above should be reasonably accurate.

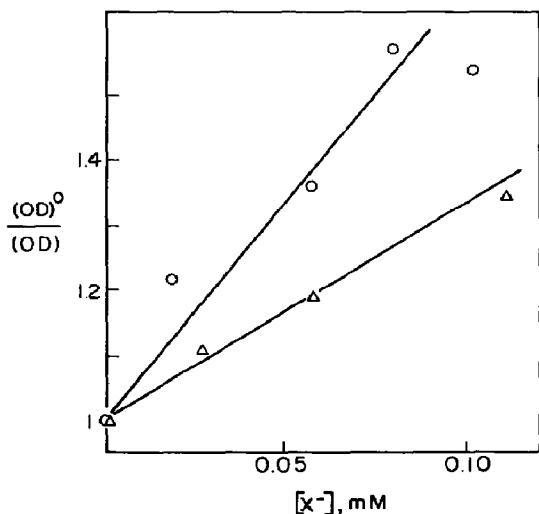


Fig. 5. Dependence of  $OD^0/OD$  for the bleaching signal at 370 nm on the concentration of added anion according to eqn. (6) for 0.42 mM **3** and 0.24 mM chromate reacting with  $SCN^-$  (○) and for 0.11 mM **1** and 0.09 mM chromate reacting with  $Cl^-$  (△) at 300 K using 308 nm laser excitation.

#### 4. Discussion

Our experiments with chromate ions indicate that aryl cations have a lifetime of less than 5 ns in aqueous systems at room temperature since the reaction leading to the bleaching of chromate can be made to occur essentially concurrently with laser excitation. These values contrast sharply with earlier estimates of lifetimes in excess of 10  $\mu s$ , which were believed to be incorrect [7, 8]. However, product studies and our own trapping experiments (*e.g.* Fig. 5) leave no doubt that at high anion concentrations (*e.g.* chloride) aryl cations can indeed be trapped [14, 15]; this sets the lower limit for the lifetime at 20 - 30 ps since it would be extremely difficult to scavenge a shorter-lived species with any significant efficiency. Thus these semiquantitative arguments put the lifetimes of typical aryl cations in

the 0.02 - 5 ns range. Further, our data also require the excited state of diazonium salts to have a lifetime of less than 5 ns. This seems more consistent with studies suggesting dissociative excited states [16] than with the low temperature phosphorescence from benzenediazonium tetrafluoroborate reported in alcohol glasses [17]. In fact experiments in our laboratory indicate that the reported phosphorescence is identical with that of anisole, thus casting serious doubts on the authenticity of the luminescence signals reported.

It is possible to obtain an estimate of the aryl cation lifetime from the Stern-Volmer slopes of  $5.3 \text{ M}^{-1}$  and  $2.9 \text{ M}^{-1}$  for the reactions of **1** with  $\text{Cl}^-$  and **3** with  $\text{SCN}^-$ . It is reasonable to assume that the combination of a positive and a negative ion, leading to a stable covalent product such as chlorobenzene, occurs near the diffusion limit, *i.e.*  $k_x \approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . Thus the lifetime of the phenyl cation would be around 500 ps, in agreement with the upper and lower limits established above. This value should be regarded as a rough estimate since short lifetimes of this type could imply that some of the scavenging occurs in static processes before the aryl cation leaves the primary solvent cage. Extensive discussions of problems of this nature have been reported [18]. When this type of error is important, the correct lifetime is usually shorter than that obtained from simple Stern-Volmer analysis of the data. It is also worth noting that the anion concentrations required in our experiments were somewhat lower than those employed in product studies [14, 15]. When the various error sources are critically examined the overall conclusion is that the phenyl cation lifetime in water is probably somewhat shorter than the value of 500 ps estimated above.

Our failure to detect the aryl cation **5** in solution or in glasses is particularly interesting in view of EPR studies [4, 5] which demonstrate that **5** has a ground state triplet as had been predicted by theoretical studies [19]. EPR studies of this type frequently involve relatively high diazonium salt concentrations and added salts such as lithium chloride. It is probable that the aryl cations are generated in microcrystalline environments under conditions which cannot easily be met (*e.g.* opaque glasses) using transmission optical spectroscopy [15]. There are also no estimates of the actual quantum yield of triplet aryl cation generation which may be quite inefficient, presumably reflecting low yields of intersystem crossing. A similar argument may apply in aqueous systems at room temperature where a short singlet lifetime could make intersystem crossing very inefficient. In fact even the expectation of a longer lifetime in the case of triplet aryl cations may be based more on intuition than on any documented facts.

An interesting observation in this study is the fact that the fast and efficient photodecomposition of diazonium salts can lead to large pH changes in just a few nanoseconds. In fact in millimolar unbuffered solutions the pH can change by as much as 3 units in a single laser pulse. Chromate ions are sensitive and adequate indicators for these pH changes ( $\text{p}K_a = 6.49$ ), and their spectrum has a convenient window near 308 nm (the laser

wavelength) which is well known to photochemists who frequently use chromate solutions to isolate the 313 nm mercury line [20]. We are currently examining the application of these observations as a "pH jump technique" that could be useful in the study of proton transport in organized and biological systems.

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