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Absorption Spectra of the Radical Ions of Quinones: A Pulse Radiolysis Study

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The formation of quinone radical ions was observed at room temperature using pulse radiolysis. The following quinones were investigated: *p*-benzoquinone, *p*-naphthoquinone, 5,8-dihydroxy-1,4-naphthoquinone, anthraquinone and 1,4-dihydroxyanthraquinone. The radial cations were produced in freon-113 solutions and the radical anions were produced in methanol solutions. The absorption spectra of the radical ions were found in the near-UV–VIS range. The spectra of the radical cations were blue shifted compared with the spectra of the corresponding radical anions.

Whereas semiquinone radicals and radical anions have been extensively investigated, there are few papers concerning radical cations of quinones. The EPR spectrum assigned to a symmetric σ-radical cation was recorded after irradiation of *p*-benzoquinone in a $CFCl_3$ matrix at 77 K.[1] Earlier reports on EPR detection of a symmetric π-cation radical generated by *in situ* UV photolysis of *p*-benzoquinone in trifluoroacetic acid at room temperature[2,3] were questioned.[1]

This study was undertaken in order to generate radical cations of several quinones [*p*-benzoquinone, *p*-naphthoquinone, 5,8-dihydroxy-1,4-naphthoquinone (naphthazarin), anthraquinone and 1,4-dihydroxyanthraquinone (quinizarin)] and to record their absorpion spectra. We chose freon-113 ($CF_2ClCFCl_2$) as the solvent because it is a strong electron acceptor and its ionization potential is high (11.99 eV). The electrons are immobilized by the solvent and electron-transfer processes are unlikely to occur.[4] Because of these properties freon-113 is an excellent host for radiolytic generation of cations, even for compounds with relatively high ionization potentials.[4] For comparison the absorption spectra of the corresponding radical anions were recorded after pulsed irradiation of deaerated methanol solutions. Cations and anions of the quinones were investigated in the liquid phase.

Experimental

The quinones used were synthesized and purified in the Institute of Dye Chemistry (Technical University of Łódź). *p*-Benzoquinone (BQ) was used as received. *p*-Naphthoquinone (NQ) and naphthazarin (NZ) were additionally purified by vacuum sublimation. Anthraquinone (AQ), quinizarin (Q) and methanol (MeOH; POCh, Poland, puriss grade), were purified as described earlier.[5,6] Freon-113 (FR) was dried over molecular sieve 4A and fractionated. The absorption spectra of the solutions were recorded using a Hewlett Packard 8452A diode array spectrophotometer. Methanol solutions were deaerated by bubbling argon through them for 30 min prior to irradiation.

An ELU-6 linear accelerator delivering 17 ns electron pulses was employed. The doses were in the range 30–65 Gy as calibrated by thiocyanate dosimetry. The samples were placed in a Spectrosil A cell of either 10 or 14 mm pathlength. The monitoring light, having passed through the sample and Bausch and Lomb monochromator, was detected with Hamamatsu R-928 photomultiplier. Transient signals were recorded by a 400 MHz storage oscilloscope Tektronix 7834 with attached TV camera, Datalab DL912 transient recorder and Philips 3320A digital scope. All instruments were linked to an IBM PC AT computer. The computer programs for data aquisition and analysis were developed in our institute. The pulse radiolysis system used is described in detail elsewhere.[7,8]

Results and Discussion

The initial products of radiolysis of liquid FR are cations (positive holes), FR^+, electrons and various excited states. After thermalization the electrons immediately attach themselves to FR molecules to form anions, FR^-. These then dissociate into FR radicals ($C_2F_3Cl_2^{\bullet}$) and Cl^-, as expected for chlorine-substituted hydrocarbons.

The transient spectra recorded after pulse irradiation of FR were very similar to those reported by Hurni and Bühler.[4] According to their interpretation the spectrum of irradiated FR probably consists of overlapping bands of the FR cation at 380 nm and of the FR anion at 440 nm. The third component of the spectrum, a broad band at *ca.* 380 nm extending to 440 nm, corresponds to an unknown radical product.

In the presence of a solute (S) the solute cations can be produced by resonant charge transfer:

$$FR^+ + S \rightarrow FR + S^+ \qquad (1)$$

The possibility of solute anion formation in freon-113 can be excluded due to dissociation of FR^-. However, if we assume a slow rate of Cl^- detachment, then electron transfer from FR^- to the solute molecule seems improbable. The solute anions will not be formed if the matrix anion has a slow electron-transfer rate.[9] This assumption seems to be quite probable in the case of freons. Electron transfer between perfluorocarbons and other electron-affinic compounds was found to proceed at an unusually slow rate even for quinones, for which electron affinities are higher than that of the perfluorocarbon used.[9–11]

The spectral changes recorded after pulse irradiation of AQ solution in FR are very complex owing to competition between the recombination of matrix ions and the transfer of the positive charges to AQ molecules. No absorption above 540 nm is observed, so the product must absorb in the same range as the products of FR radiolysis. After *ca.* 1 µs some absorption remains while in FR alone it is negligible [Fig. 1(*a*), insets 1 and 2]. Fig. 1 shows the corresponding spectrum assigned to $AQ^{\bullet+}$. The spectrum does not change for tens of µs, so $AQ^{\bullet+}$ is stable at least on this timescale. The spectrum is very similar to that of $AQ^{\bullet-}$ recorded in deaerated methanol[5] [Fig. 1(*b*)]. The absorption maxima of $AQ^{\bullet+}$ (350,

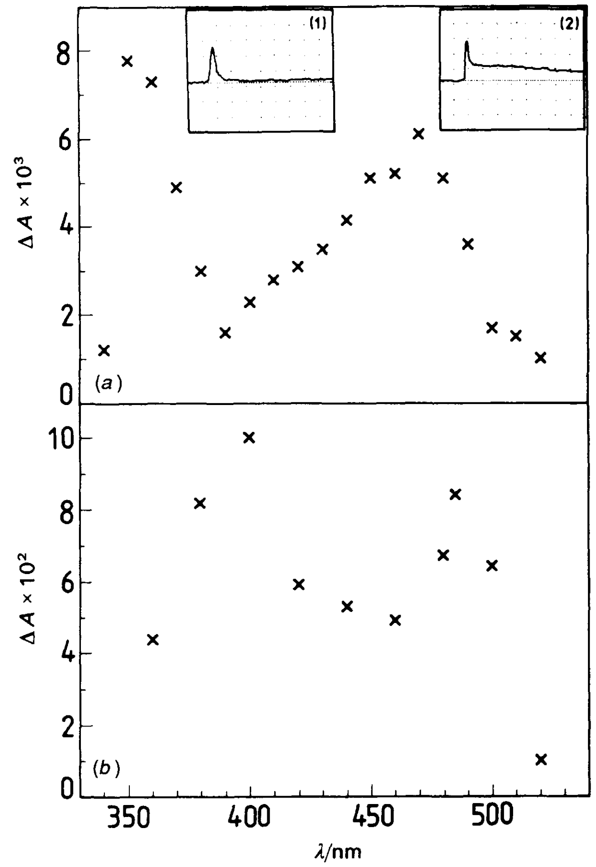

Fig. 1 (*a*) Absorption spectrum of $AQ^{\bullet +}$ in FR solution of AQ (1×10^{-4} mol dm^{-3}) 1 µs after the 17 ns pulse, taken at room temperature, dose 61.5 Gy. Insets: decay of absorption at 470 nm in FR, 200 ns per division, 2.0% per division (1), and in the solution of AQ (1×10^{-4} mol dm^{-3}), 200 ns per division, 1.9% per division (2). (*b*) Absorption spectrum of $AQ^{\bullet -}$ in deaerated alkaline (0.02 mol dm^{-3} NaOH) MeOH solution of AQ (2×10^{-5} mol dm^{-3}) 40 µs after the 17 ns pulse, at room temperature, dose 29 Gy (taken from ref. 5)

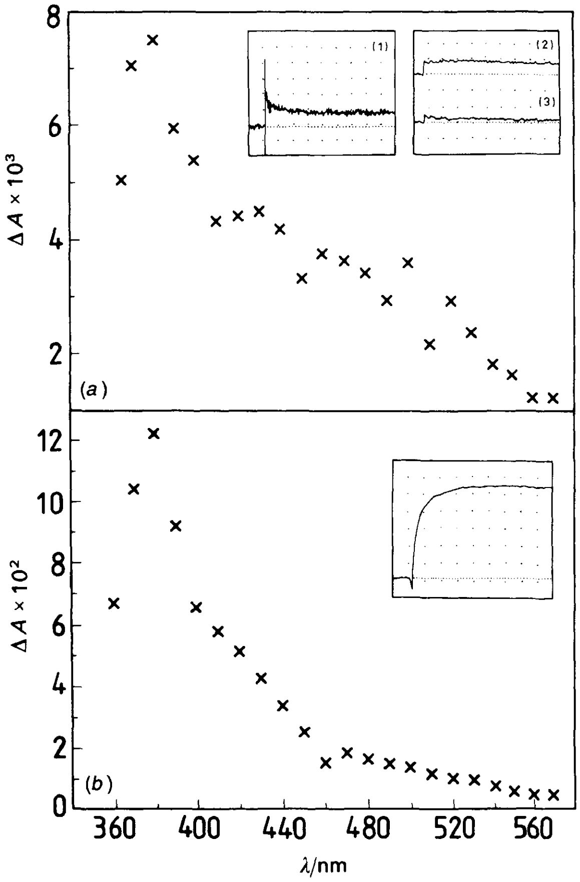

Fig. 2 (*a*) Absorption spectrum of $NQ^{\bullet +}$ in FR solution of NQ (1.38×10^{-3} mol dm^{-3}) at 1.5 µs after the 17 ns pulse, at room temperature, dose 52.1 Gy. Insets: the absorption changes at 380 nm, dose 65 Gy: 500 ns per division, 2.0% per division (1), 20 µs per division, 2.0% per division (2), in the presence of 0.1 mol dm^{-3} pent-1-ene, 20 µs per division, 2.0% per division (3). (*b*) Absorption spectrum of $NQ^{\bullet -}$ in deaerated MeOH solution of NQ (5.25×10^{-4} mol dm^{-3}) 20 µs after the 17 ns pulse, at room temperature, dose 32.5 Gy. Inset: growth of absorption at 380 nm, 2.5 µs per division, 5.4% per division

470 nm) are close to the maxima of $AQ^{\bullet -}$ (400, 480 nm) but are slightly blue shifted. The recorded absorption of $AQ^{\bullet +}$ is very weak, possibly because of the low efficiency of the positive charge transfer to AQ molecules. An alternative explanation is that the absorption coefficients of $AQ^{\bullet +}$ are very small compared with those of $AQ^{\bullet -}$.

The analogous spectra were recorded in solutions of NQ in FR. The spectrum recorded 1.5 µs after irradiation and ascribed to $NQ^{\bullet +}$ shows a single absorption band with a maximum at *ca.* 380 nm [Fig. 2(*a*)]. For comparison the spectrum of $NQ^{\bullet -}$ was obtained by pulsed irradiation of a deaerated methanol solution of NQ [Fig. 2(*b*)]. The absorption band of $NQ^{\bullet -}$ has a maximum at 380 nm, close to the maximum at 390 nm for $NQ^{\bullet -}$ in aqueous solution.[12]

The spectrum corresponding to $BQ^{\bullet +}$ recorded 4 µs after the pulse in FR solution, is shown in Fig. 3(a). Contrary to the previous radical cation spectra it shows no distinct maxima. The absorption band in the range below *ca.* 440 nm strongly increases towards the UV and reaches a limit determined by strong absorption of the parent compound. The spectrum of $BQ^{\bullet -}$ recorded in deaerated methanol shows a single band with a maximum at 415 nm [Fig. 3(*b*)], close to the maximum at 425 nm for $BQ^{\bullet -}$ in aqueous solution.[12] In this case the absorption spectrum of $BQ^{\bullet +}$ is shifted far towards the UV compared with the $BQ^{\bullet -}$ spectrum.

The spectra of $NQ^{\bullet +}$ and $BQ^{\bullet +}$ were calculated from very noisy traces like those shown in inset 1 in Fig. 2(*a*) and 3(*a*). After microseconds the signals were of much better quality [inset 2 in Fig. 2(*a*) and 3(*a*)] and in both cases decreased in the presence of a positive charge scavenger such as pent-1-ene [0.1 mol dm^{-3}, inset 3 in Fig. 2(*a*) and 3(*a*)]. Using a higher concentration of pent-1-ene (1 mol dm^{-3}) the cation absorption signals decreased by half compared with the 0.1 mol dm^{-3} pent-1-ene solution and the residual absorptions were comparable with those obtained for pulse-irradiated FR–pent-1-ene (1 mol dm^{-3}) solution.

In each case the recorded spectra of quinone radical cations were very weak and were entirely situated in the range of absorption of matrix radiolysis products. A distinct growth in the product was not observed owing to the overlap with the considerably stronger absorption of the decaying FR ions. The traces of such growth may be found from analysis of signals such as those shown in Fig. 2(*a*) inset 2 and Fig. 3(*a*) inset 1. This does not apply to the spectra recorded in FR solutions of Q. In the region of intense Q absorption, 430–530 nm, bleaching on the timescale of several hundred ns was recorded. In the range of weak Q absorption (380–400 nm) and above 550 nm, where the parent compound does not absorb at all, the product absorption was observed. The spectrum recorded 1.5 µs after the pulse and assigned to $Q^{\bullet +}$ is shown in Fig. 4(*a*). In the spectrum of $QH_2^{\bullet -}$ in methanol solution there is a band in the range 550–700 nm[6] that is characteristic of 1,4-dihydroxysubstituted anthrasemiquinone

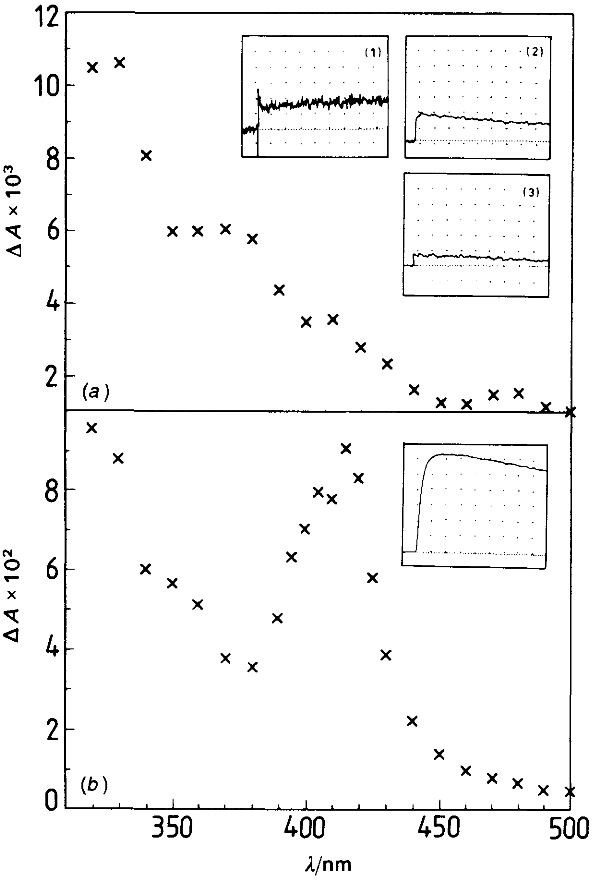

Fig. 3 (*a*) Absorption spectrum of $BQ^{\cdot +}$ in FR solution of BQ (3.82×10^{-3} mol dm^{-3}) 4 μs after the 17 ns pulse, at room temperature, dose 51 Gy. Insets: absorption changes at 330 nm: 500 ns per division, 1.8% per division (1), 20 μs per division, 1.8% per division (2), in the presence of 0.1 mol dm^{-3} pent-1-ene, 20 μs per division, 1.9% per division (3). (*b*) Absorption spectrum of $BQ^{\cdot -}$ in deaerated MeOH solution of BQ (4.89×10^{-4} mol dm^{-3}) 5 μs after the 17 ns pulse, at room temperature, dose 30.1 Gy. Inset: absorption changes at 415 nm, 2.5 μs per division, 3.9% per division

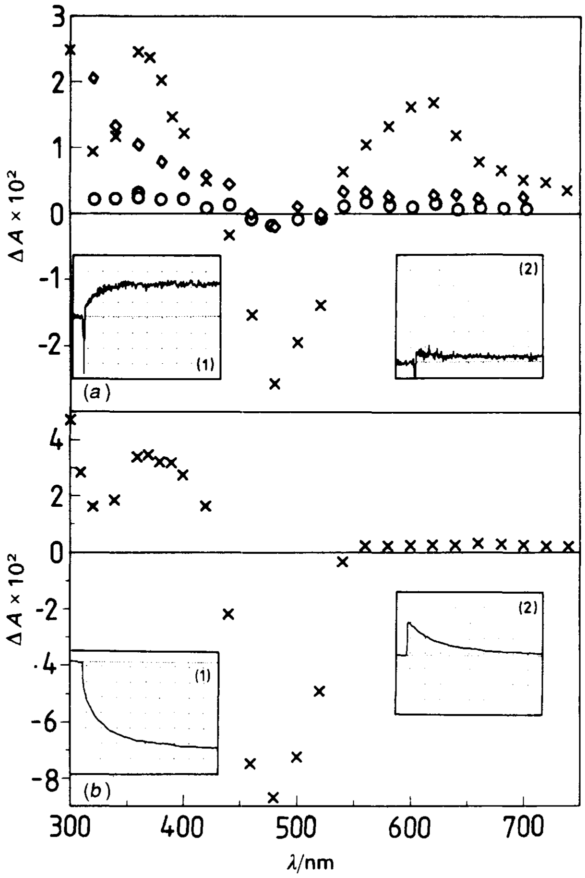

Fig. 4 (*a*) Absorption spectra recorded in FR solution of Q (1.12×10^{-4} mol dm^{-3}) taken 1.5 μs after the 17 ns pulse at room temperature, dose 60.2 Gy: spectrum of the radical cation $Q^{\cdot +}$, (×), and the spectra recorded in solution containing 3×10^{-3} mol dm^{-3} TEA (◇) and 0.01 mol dm^{-3} pent-1-ene (○), respectively. Insets: absorption changes recorded at 620 nm in solution without TEA or pent-1-ene (1) and in the presence of TEA (2), 200 ns per division, 1.8% per division. (*b*) Absorption spectrum recorded in FR solution of Q (1.12×10^{-4} mol dm^{-3}) taken at 150 μs after the 17 ns pulse at room temperature, dose 48.3 Gy. Insets: the bleaching at 480 nm, 20 μs per division, 4.1% per division (1), and the decaying absorption at 620 nm, 20 μs per division, 2.0% per division (2)

radical anions.[13] In the spectrum of $Q^{\cdot +}$ there is a similar band with a maximum at 620 nm [Fig. 4(*a*)]. This band disappears on the timescale of tens of microseconds while the bleaching band (430–550 nm) strongly increases [Fig. 4(*b*), insets 1 and 2]. The spectrum recorded after 150 μs [Fig. 4(*b*)] does not change in minutes and seems to correspond to the stable product of the cation decay.

In order to obtain direct evidence that the spectrum shown in Fig. 4(*a*) corresponds to the radical cation, we performed an experiment in the presence of triethylamine (TEA). The low ionization potential of TEA (7.50 eV) and the chosen concentration (3×10^{-3} mol dm^{-3}) assured practically complete scavenging of the positive charge. Under these conditions the spectrum attributed to the radical cation should not be observed. The experiment confirmed this expectation [Fig. 4(*a*)]. The absorption band at 620 nm in the presence of TEA is not observed [Fig. 4(*a*), insets 1 and 2]. This effect is even more distinct in the presence of another cation scavenger, pent-1-ene [Fig. 4(*a*)]. Neither TEA nor pent-1-ene act on anionic species so the possibility that the recorded spectrum corresponds to the radical anion can be excluded. It is worth mentioning that the absorption due to $NQ^{\cdot +}$ and $BQ^{\cdot +}$ cations also decrease in the presence of pent-1-ene, as described previously.

The results obtained for the second compound containing two hydroxyl groups in the *para*-position, NZ, were very similar to those of Q. The bleaching in the range of intense absorption of the parent compound (450–550 nm) is accompanied by a growing absorption with maxima at 330, 390 and 590 nm [Fig. 5(*a*), insets 1 and 2]. The spectrum assigned to $NZ^{\cdot +}$ is shown in Fig. 5(*a*), and it is similar to the spectrum of $NZ^{\cdot -}$, which was recorded after pulse irradiation of NZ solution in deaerated alkaline methanol.[14] A similar spectrum for $NZ^{\cdot -}$ was recorded by Land *et al.*[15] in aqueous solution. Two distinct maxima in the anion spectrum (at 390 and 440 nm) seem to correspond to the cation maxima at 330 and 390 nm, respectively. As in the case of Q at longer times the NZ cation takes part in a specific transformation. On the timescale of tens of microseconds the cation band at 590 nm disappears while the bleaching band and absorption with a maximum at 390 nm increase [Fig. 5(*b*), insets 1 and 2]. Fig. 5(*b*) shows the spectrum recorded after 70 μs.

For all quinones studied the radical cation spectra are similar to those of the corresponding radical anions. Such similarity between spectra of cations and anions occurs in the case of alternant hydrocarbons and is due to their pairing property.[16,17]

The rates at which the absorptions of $Q^{\cdot +}$ (at 620 nm) and $NZ^{\cdot +}$ (at 590 nm) increased [Fig. 4(*a*) and 5(*a*), inset 1] were

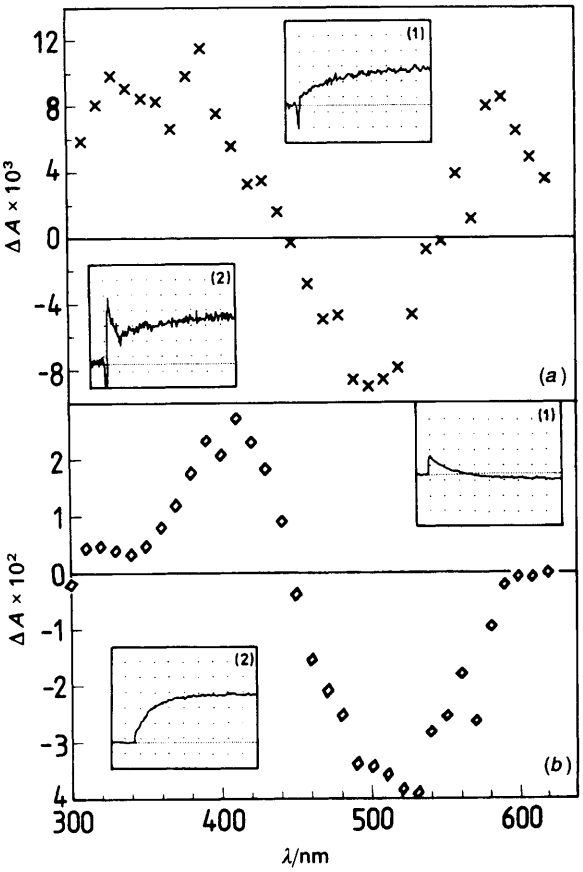

Fig. 5 Absorption spectra recorded in FR solution of NZ (1.02×10^{-4} mol dm^{-3}) at room temperature, dose 44.3 Gy: (*a*) 700 ns after the 17 ns pulse, corresponding to $NZ^{\cdot +}$. Insets: growth of absorption at 590 nm, 100 ns per division, 1.9% per division (1) and at 390 nm, 100 ns per division, 2% per division (2); (*b*) at 70 μs after the pulse. Insets: decaying absorption at 590 nm, 10 μs per division, 2.1% per division (1) and the growth at 410 nm, 10 μs per division, 1.9% per division (2)

found to be approximately pseudo-first order and led to rate constants for the reaction (1) of 3.8×10^{10} and 2.8×10^{10} dm^3 mol^{-1} s^{-1}, respectively. Owing to low signal-to-noise ratio in the case of dilute solutions of Q and NZ these rate constants were determined only for the most concentrated solutions (*ca.* 2×10^{-4} mol dm^{-3}). The yield of the radical cations formed in reaction (1) increases with quinone concentration, as expected taking into account the competition between charge transfer and geminate ion recombination (Fig. 6).

At longer times (μs timescale) $Q^{\cdot +}$ and $NZ^{\cdot +}$ take part in specific transformations, as mentioned previously. The rate of the radical cation decay is similar to the rate of the additional bleaching observed in the parent molecule absorption band [Fig. 4(*b*) and 5(*b*)]. This process seems to be first order and the calculated rate constants for Q (at 620 nm) and NZ (at 590 nm) were found to be 3.2×10^4 and 6.9×10^4 s^{-1}, respectively. The cation decay leads to permanent bleaching probably because of irreversible destruction of the chromophore. At present it is very difficult to propose a detailed mechanism for this transformation.

We investigated the temperature dependence of the rate constants for formation and subsequent decay of $Q^{\cdot +}$. Owing to high melting point of freon-113 (238 K) the experiments could be done only in a very limited temperature range (240–296 K). According to the Eyring equation the activation enthalpy $\Delta H^{\neq}$ was determined from the slope and activation entropy $\Delta S^{\neq}$ from the intercept of a plot of $\ln(k/T)$ *vs.* $1/T$ (Fig. 7). The enthalpy of activation ($\Delta H^{\neq}$) of $Q^{\cdot +}$ formation (8.34 kJ mol^{-1}) was found to be slightly lower than that of $Q^{\cdot +}$ decay (10.27 kJ mol^{-1}). On the contrary the entropy of activation ($\Delta S^{\neq}$) was much more negative for the decay (-128 J mol^{-1} K^{-1}) than for the cation formation (-16.8 J mol^{-1} K^{-1}), which seems reasonable taking into account the destruction of the chromophore on the long timescale.

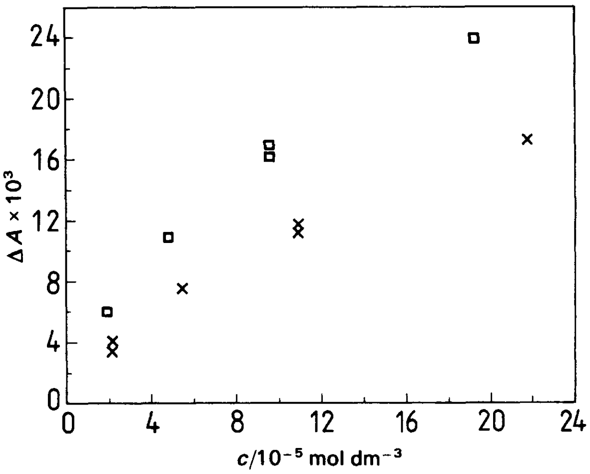

Fig. 6 Relation between the yield of the cation formation and the concentration of the parent quinone in FR solutions. Absorptions were measured in maximum at 620 nm for Q (□) and at 590 nm for NZ (×) solutions at room temperature. Dose 44.6 Gy

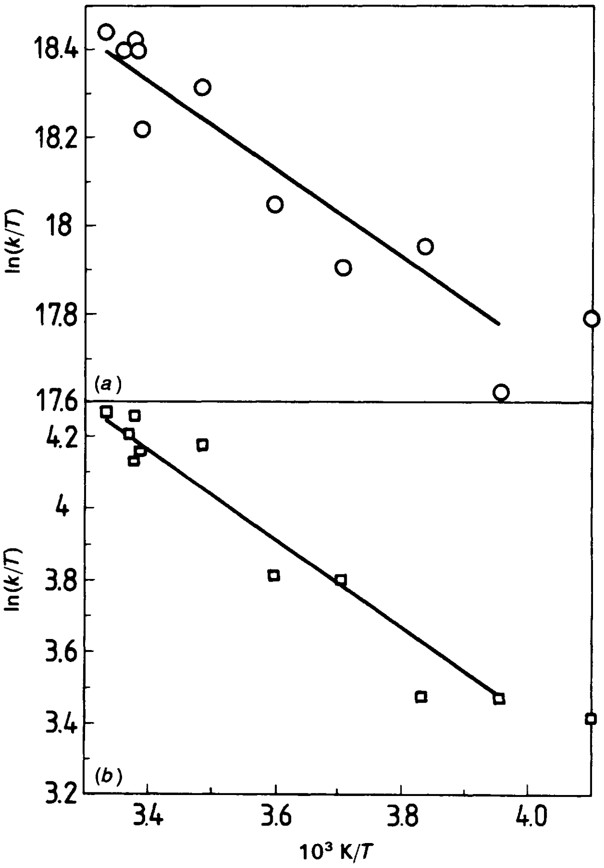

Fig. 7 Temperature dependence of the rate constants for the formation (*a*) and the decay (*b*) of $Q^{\cdot +}$ followed at 620 nm in pulse irradiated FR solution of Q (1.96×10^{-4} mol dm^{-3}). Dose 44 Gy

Recently we have begun to investigate the structure of quinone radical cations using EPR. We hope that the structure and transformation mechanism of these radical cations will be solved.

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