

## Fast protonation of adenosine and of its radical anion formed by hydrated electron attack; a nanosecond optical and dc-conductivity pulse radiolysis study

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The study of the reaction of the hydrated electron with adenosine by optical and dc-conductivity pulse radiolysis on nano- and microsecond timescales has been carried out in an attempt to answer the question whether the electron adduct radical becomes protonated or not. The following conclusions have been reached: (1) the reaction of the hydrated electron with adenosine is followed by a water-mediated protonation, which must be complete with 5 ns; (2) no spectral indication of a further protonation of the protonated electron adduct of adenosine of 2'-deoxyadenosine has been found between 40 and 5000 ns; (3) the equilibrium reaction between radiation produced  $H_3O^+$  and adenosine with a  $pK_a$  of 3.5 plays an important role in the kinetics of the conductivity transients.

### 1. Introduction

The question of whether or not the electron adduct (anion radical) of the purines formed on reaction with the hydrated electron becomes protonated has been studied by Moorthy and Hayon (1975) and Hissung *et al.* (1981). The answer to this question is important for the possible mechanism of the observed conversion of a purine electron adduct into a pyrimidine electron adduct in mixtures of nucleotides and in heteropolynucleotides (Visscher *et al.* to be published). Moorthy and Hayon (1975) measured the absorption spectra of adenine derivatives at 0.2  $\mu$ s after the pulse. They concluded that the reaction of adenosine with the hydrated electron results in the formation of protonated species with  $pK_a$  values of 4.6, 10.5 and 13.6 respectively. They stated that the radical formed at pH 12, which is characterized by an absorption maximum at 355 nm, is the singly protonated anion. They postulated that the species produced at pH 6-7, which is characterized by an absorption maximum at 315 nm (see figure 1A), is doubly protonated.

Hissung *et al.* (1981) measured both the optical absorption spectra and the dc-conductivity signal after pulse radiolysis of a deaerated,  $3 \times 10^{-3}$  mol dm<sup>-3</sup> solution of 2'-deoxyadenosine, containing an OH and H radical scavenger. They concluded, from an observed change in absorption with a half-life of 210 ns and the remaining conductivity in a high pH solution 10  $\mu$ s after pulse irradiation, that the electron adduct must be protonated. They associated the change in the optical spectrum with this protonation.

In the present paper we present the direct observation of the changes in both the optical absorption and the conductivity on nanosecond timescales at neutral pH. The improvement of the time resolution with respect to the dc-conductivity method used by Hissung *et al.* (1981) by at least an order of magnitude (Beck 1969) has been achieved by using the balanced detection system, developed by one of the authors (Vojnovic *et al.* 1986).

From our measurements on adenosine (optical absorption and conductivity) and 2'-deoxyadenosine (absorption alone) we draw the conclusion that indeed a fast protonation of the initial electron adduct radical occurs. However from our analysis we must conclude that the protonation is complete within 5 ns, rather than the *ca.* 200 ns suggested by Hissung *et al.* (1981).

## 2. Experimental

Adenosine and 2'-deoxyadenosine (Sigma) were used without further purification. All solutions were prepared with triply distilled water and contained, in addition to different concentrations of adenosine ( $2.5 \times 10^{-4}$  to  $5 \times 10^{-3}$  mol dm<sup>-3</sup>), 0.3 mol dm<sup>-3</sup> 2-propanol as an OH and H radical scavenger. The 2-propanol appeared to be contaminated by about  $1 \times 10^{-4}$  mol dm<sup>-3</sup> acetone. This explains the rather high reactivity of the hydrated electron towards the matrix (reaction 3, table 2). The conductivity measurements and optical absorption measurements were carried out in unbuffered, deaerated solutions, with a pH of  $6.5 \pm 0.2$ . All solutions were deaerated by bubbling with helium gas for 15 min prior to irradiation, and kept under a slight overpressure during the experiment. All measurements were carried out at ambient temperature ( $19 \pm 0.6^\circ\text{C}$ ). Solutions of adenosine in water were irradiated with 3 MeV electrons from a Van de Graaff accelerator using pulse lengths of 2 or 5 ns. The beam charge was measured by deflection of the beam onto a 50  $\Omega$  coaxial target connected to an electrometer. The dose per nanocoulomb of beam charge was approximately 2 Gy for the optical experiments and 0.25 Gy for the conductivity experiments. Both the optical (Hummel and Luthjens 1973) and the dc-conductivity technique using a balanced detection system (Vojnovic *et al.* 1986) have been fully described in previous articles. The outputs of the photomultiplier and virtual earth amplifier (Vojnovic *et al.* 1986) were fed into a Tektronix R7912 transient digitizer, which was interfaced to a LSI 11/23 microprocessor, that was used to carry out signal averaging of up to 12 traces in the case of the optical experiments (with intermediate flushing of the solution). The response time for the optical pulse radiolysis technique was 2.5 ns, the response time of the conductivity cell was 6 ns.

In the case of the conductivity experiments each trace was acquired from two single-shot transients taken with opposite polarizing voltage polarities and subtracted from each other. In this way any remaining signal from electron pulse interference or beam misalignment is cancelled. The polarizing voltage was applied as a pulse of 5 ms duration (Vojnovic *et al.* 1986). As can be seen from the traces of figure 4 the noise level is very low; however the trace to trace reproducibility was approximately 5 per cent, due to instability in the beam positioning of the accelerator with respect to the electrodes.

At the concentration of adenosine used, spur reactions should be negligible for the yields of secondary radicals produced (Balkas *et al.* 1970). Therefore the *G* values at 100 ns for the water radicals (see table 1) were used to fit the experimental data.

The time dependences of the concentration of the absorbing and conducting

Table 1.  $G$  values (number of species produced per 100 eV) and specific conductivity for the major species produced during the pulse.

	$H_3^+$	$OH^-$	$e_{aq}^-$	H	OH
$G$ mol/100 eV at 100 ns	3.1	0.43	2.65	0.65	2.7
$\lambda$ ( $Scm^2 mol^{-1}$ )	331	188	202		

The specific conductivity  $\lambda$  is related to the mobility of the singly charged ion by  $\lambda = eN\mu$  where  $e = 1.6 \times 10^{-19}$  C is the elementary charge,  $N = 6.02 \times 10^{23}$  is Avogadro's number and  $\mu$  is the mobility in  $cm^2 V^{-1} s^{-1}$ . The specific conductivity is given at 21°C and  $\Delta\lambda = 1.6$  per cent per °C (Anderson *et al.* 1985, Beck 1969, Fielden and Hart 1967 and Landolt-Börnstein 1960).

species were calculated by solving the rate equations, using a Hewlett-Packard 9825 calculator (Mathpac Runge Kutta program). A convolution program to mimic the time response of the experimental setup was also applied.

### 3. Results and discussion

#### 3.1. Optical pulse radiolysis

The absorption spectra of pulse irradiated solutions of adenosine and 2'-deoxyadenosine between 300 and 600 nm are shown at 40 and 800 ns following the pulse in figure 1. Two remarks can be made; firstly the spectrum of the adenosine and 2'-deoxyadenosine radicals are very similar. The former, however, has a somewhat more pronounced shoulder at 355 nm. Secondly for both compounds there are no spectral changes of any significance between 40 and 800 ns. The spectral changes as reported by Hissung *et al.* (1981), which occurred over a timescale of 200 ns and were attributed to protonation, could not be reproduced. This does not mean that protonation does not occur, but that it is either much faster than 40 ns or much slower than 800 ns, or takes place without spectral consequences.

Experiments have been carried out to study the effect of ionic strength of the solution on the kinetics of the transients on a microsecond timescale. No kinetic salt

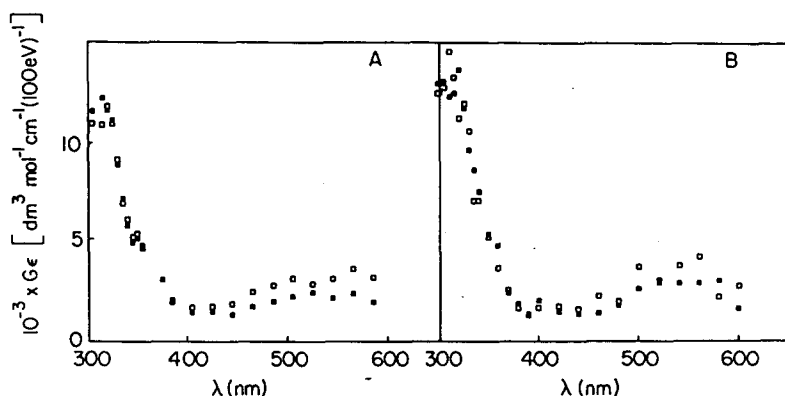


Figure 1. Optical absorption from 300 to 600 nm (in units of  $G \times \epsilon$ ) resulting from pulse radiolysis with a 5 ns 20 Gy pulse of a He-saturated aqueous solution of  $1 \text{ mol dm}^{-3}$  2-propanol containing (A)  $2 \times 10^{-2} \text{ mol dm}^{-3}$  adenosine and (B)  $5 \times 10^{-2} \text{ mol dm}^{-3}$  2'-deoxyadenosine. The figure shows spectra at  $\square$ , 40 and  $\blacksquare$ , 800 ns.

effect on the recombination rate of the radicals could be detected. The kinetic salt effect was studied using adenine instead of adenosine because the kinetic analysis in the former case was somewhat more straightforward: for both solutes the first radical formed is the species with  $\lambda_{\max} = 315$  nm; however on a microsecond timescale the adenosine radical is converted into a species with  $\lambda_{\max} = 355$  nm in competition with the radical-radical recombination, while the corresponding adenine radical reacts simply by the second order radical-radical reaction without accompanying conversions. The ionic strength were adjusted to  $\mu = 1 \times 10^{-3}$ ,  $1 \times 10^{-2}$ ,  $1 \times 10^{-1}$  and  $2 \times 10^{-1}$  mol dm $^{-3}$  using borax (pH 9.2). From the Brønsted equation it can be calculated for a reaction between singly charged species of the same sign, that e.g.  $k(\mu = 2 \times 10^{-1})/k(\mu = 1 \times 10^{-3}) = 1.9$ , which should have resulted in an almost doubling of the rate constant over the range of ionic strengths studied. However experimentally a rate constant independent of ionic strength was found  $k = 1.17 \pm 0.02 \times 10^9$  dm $^3$  mol $^{-1}$  s $^{-1}$ . Hence on a microsecond timescale at least the electron adduct of adenine (and by analogy also of adenosine) would appear to be uncharged, i.e. it must be singly protonated.

The transients have been studied on a nanosecond timescale for four adenosine concentrations ( $0.25$ ,  $0.5$ ,  $2.5$  and  $5.0 \times 10^{-3}$  mol dm $^{-3}$ ). In figure 2 the  $G \times \epsilon$  vs. time traces are shown at 315 nm (absorption maximum for the adenosine radical) and at 540 nm (to monitor the hydrated electron decay) for the highest adenosine concentration used. The decay of the solvated electron is seen to be accompanied on the same timescale by growth of the species absorbing at 315 nm. The growth is completed within 50 ns and, as pointed out above, no further spectral change is observed for times up to about a microsecond. We were unable to observe spectral changes on a timescale of a few hundred nanoseconds as suggested by previous authors, except under conditions where the primary reaction of the electron with the

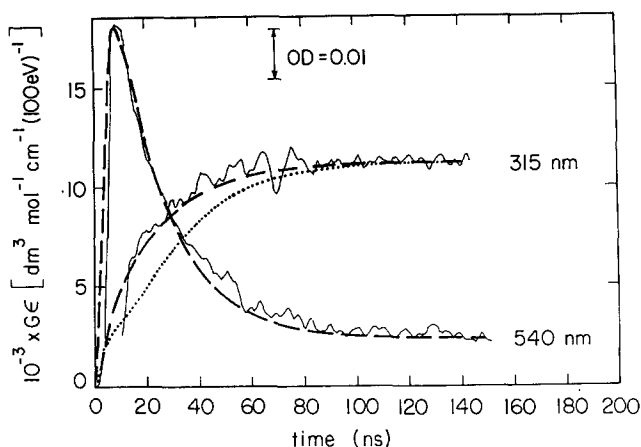


Figure 2. Time dependence of the optical absorption at 315 and 540 nm (in units of  $G \times \epsilon$ ) resulting from pulse irradiation with a 5 ns, 40 Gy pulse of a He-saturated solution aqueous containing  $5 \times 10^{-3}$  mol dm $^{-3}$  adenosine and  $0.3$  mol dm $^{-3}$  2-propanol. The dashed lines are the kinetic fits obtained using the parameters shown in table 2, and assuming the species absorbing at 315 nm to be formed 'immediately' following electron scavenging by adenosine. The dotted line was obtained by including in the calculation a 10 ns formation step subsequent to electron scavenging.

solute would be expected to occur slowly as is shown for the lower solute concentrations in figure 3.

A quantitative kinetic analysis of the optical data was carried out, based on a reaction scheme in which the product of electron attachment monitored at 315 nm is formed either directly, i.e. is the electron adduct (reaction 1)



or is the product formed in a subsequent protonation step (reaction 2).



Account was also taken in the Runge Kutta calculations of the decay of electrons via reaction with trace amounts of impurities (for instance, traces of acetone, see Experimental) in the 2-propanol used. The formation and decay of 2-propanol radicals and hydrated electrons, which have a significant extinction coefficient at 315 nm ( $200$  and  $900 \text{ dm}^{-2} \text{ mol}^{-1} \text{ cm}^{-1}$ , respectively) (Boyle *et al.* 1969, Fielden and Hart 1967) were also included in the kinetic scheme. In table 2 the reactions of the species which are used for fitting the experimental data in this paper are listed, together with literature values of the rate constants where these are available.

Since the transient at 540 nm is largely due to the solvated electron with  $\epsilon = 8700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  (Boyle *et al.* 1969, Fielden and Hart 1967) the rate constant for reaction (1) can be determined quite accurately from this decay and is found to be  $(1.0 \pm 0.05) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for adenosine, which agrees reasonably well with reported values (cf.  $9.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , Shragge *et al.* 1971 and  $1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , Moorthy and Hayon 1975). This kinetic parameter is subsequently used in the kinetic scheme for the calculation of the time development of the solute radical species formed.

The dashed lines in figures 2 and 3 were calculated on the basis of the 'immediate'

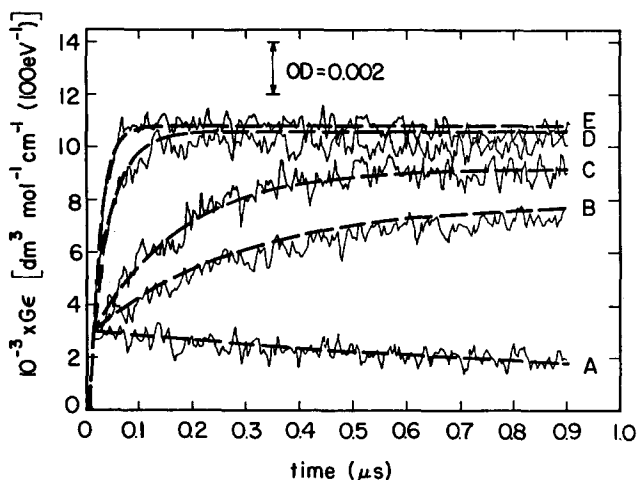


Figure 3. Time-dependence of the optical absorption at 315 nm (in units of  $G \times \epsilon$ ) resulting from pulse irradiation with a 2 ns, 10 Gy pulse of a He-saturated solution containing  $0.3 \text{ mol dm}^{-3}$  2-propanol and adenosine at a concentration of; (A) 0, (B)  $2.5 \times 10^{-4}$ , (D)  $2.5 \times 10^{-3}$ , (E)  $5 \times 10^{-3} \text{ mol dm}^{-3}$ . The dashed lines are kinetic fits using parameters shown in table 2.

Table 2. Reactions and rate constants used in this paper.

No.	Reactions	Product(s)	Rate	Unit
1	$e_{\text{aq}}^- + \text{A}$	$\text{A}^-$	$1.0 \times 10^{10}$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
2	$\text{A}^- + \text{H}_2\text{O}$	$\text{AH}^- + \text{OH}^-$	$> 2 \times 10^6$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
3†	$e_{\text{aq}}^- (+ \text{M})$		$1 \times 10^6$	$\text{s}^{-1}$
-4	$\text{H}^+ + \text{A}$	$\text{AH}^+$	$8 \times 10^9$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
4	$\text{AH}^+$	$\text{A} + \text{H}^+$	$2.5 \times 10^6$	$\text{s}^{-1}$
5§	$e_{\text{aq}}^- + e_{\text{aq}}^-$	$2\text{OH}^-$	$5.6 \times 10^9$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
6§	$e_{\text{aq}}^- + \text{H}_3\text{O}^+$	$\text{H}$	$2.35 \times 10^{10}$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
7†	$\text{H}_3\text{O}^+ (+ \text{M})$		$10^5$	$\text{s}^{-1}$
8§	$\text{H}_3^+ + \text{OH}^-$	$2\text{H}_2\text{O}$	$1.15 \times 10^{11}$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
9	$\text{AH}^+ + \text{OH}^-$	$\text{A} + \text{H}_2\text{O}$	$2 \times 10^{10}$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
10‡§	$2\text{-PrOH} + \text{OH}^\cdot$	$2\text{-PrOH}^\cdot$	$2.2 \times 10^9$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
11‡§	$2\text{-PrOH} + \text{H}^\cdot$	$2\text{-PrOH}^\cdot$	$7.9 \times 10^7$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
12¶	$2\text{-PrOH}^\cdot + 2\text{-PrOH}^\cdot$		$0.7 \times 10^9$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
12§	$\text{acetone} + e_{\text{aq}}^-$		$5.7 \times 10^9$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$

† First order rate constant with impurities, values are derived from the fitting procedure.

‡ 2-PrOH stands for 2-propanol.

§ Anbar *et al.* (1975).

¶ Simec *et al.* (1969).

formation of the 315 nm transient on electron attachment. The dotted line in figure 2 shows the growth which would be expected for a species formed subsequent to electron attachment with a delay time of 10 ns, i.e.  $k_2 = 2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Clearly 'immediate' formation results in a better fit to the experimental data.

From the optical data we can therefore conclude that the absorbing species formed is either the electron adduct or, if it is the protonated form of the electron adduct, that protonation must occur on a timescale of 5 ns or less. The alternative explanation, that protonation is relatively slow but results in a species with an absorption spectrum almost identical to the radical anion, is possible but considered to be rather unlikely.

From the fitting of the optical absorption measurements an extinction coefficient of  $3900 \pm 300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  is found for the product of reaction (1) or (2). This value agrees well with the extinction coefficient of  $4000 \pm 400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  for the same species as found by analysing adenosine spectra at longer times (Visscher *et al.*, in preparation).

### 3.2. Dc conductivity

Figure 4 shows the dc-conductivity traces after pulse irradiation of the same solutions as used in the optical experiments. The conductivity is seen to decrease significantly after the pulse with a rate which increases with increasing adenosine concentration, indicating the reaction of at least one of the major primary conducting species,  $e_{\text{aq}}^-$  or  $\text{H}_3\text{O}^+$ , with the solute. The observation that the conductivity was changing on the same timescale as found for the decay of the electron absorption in the optical experiments suggested initially that the phenomena were in fact directly related, and that the conductivity transients could therefore possibly be described in terms of reactions (1) and (2).

Attempts to fit the data on this basis were, however, unsuccessful due to the decrease in conductivity being much larger than could be explained even by

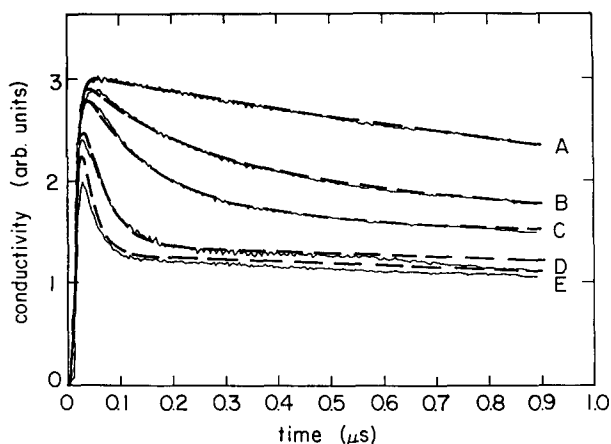


Figure 4. Time-dependence of the dc-conductivity in arbitrary units resulting from pulse irradiation with a 5 ns pulse of a He-saturated solution containing  $0.3 \text{ mol dm}^{-3}$  2-propanol and adenosine at a concentration of: (A) 0, (B)  $2.5 \times 10^{-4}$ , (D)  $2.5 \times 10^{-3}$ , (E)  $5 \times 10^{-3} \text{ mol dm}^{-3}$ . The dashed lines are kinetic fits using the parameters shown in tables 1 and 2.

complete conversion of all electrons to low mobility molecular ions (reaction (1) only). The rapid formation of the mobile  $\text{OH}^-$  ion via reaction (2), subsequent to attachment would result in even worse agreement with experiment. This lack of agreement with the data can be seen by simply considering the fractional decrease in conductivity expected due to reaction (1) alone or followed by subsequent rapid proton abstraction i.e.

$$G(e_{\text{aq}}^-)\lambda_{e_{\text{aq}}^-} / \sum_{\text{cond.spec}} G\lambda$$

and

$$G(e_{\text{aq}}^-)[\lambda_{e_{\text{aq}}^-} - \lambda_{\text{OH}^-}] / \sum_{\text{cond.spec}} G\lambda$$

which are 0.326 and 0.023 respectively (see table 1). The eventual plateau level observed however corresponds to a much larger fractional decrease in conductivity of 0.6 at the highest concentrations. The concentration-dependent plateau values for the dc-conductivity measurements cannot be ascribed to incomplete hydrated electron scavenging due to competition between the reaction of the hydrated electron with adenosine and the other electron decay reactions (3), (5) and (6) (see table 2) because in the dc-conductivity measurements the  $e_{\text{aq}}^-$  is measured and not the adenosine radical as in the optical measurements.

Both the absolute magnitude of the decrease, and the fact that the plateau value is solute concentration-dependent, indicated that additional reactions are occurring which involve the protons initially formed. The effect of including the acid-base equilibrium



in the kinetic analysis was therefore investigated. The  $pK_a$  of adenosine has been determined to be 3.5 (CRC 1975, Bloomfield et al. 1974) from which  $k_4/k_{-4} = 3.16 \times 10^{-4}$ . The fit of the calculated transient conductivity to the data using this value of  $pK_a$  is found to be good, (see figure 4) if a reasonable value of  $8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  is taken for  $k_4$  and a rapid protonation of the adenosine radical anion occurs, i.e. reaction (1) followed by reaction (2). If, on the other hand, electron addition to adenosine is taken to yield a low mobility adenosine molecular anion through reaction (1) alone much too low plateau conductivities are calculated.

The following scheme has been proposed by Moorthy and Hayon (1975):



where  $AH_2^{\cdot+}$  and  $AH^{\cdot}$  have absorption maxima at 315 nm and 355 nm, respectively, and the  $pK_a$  for the equilibrium is 10.5. According to this the electron adduct should be present eventually almost completely in the doubly protonated form at the pH used in the present work. The lack of effect of ionic strength on the eventual decay of the electron adduct referred to previously would, however, strongly argue against a charged form, either negative or positive, of this intermediate. The present conductivity data also argue against the rapid formation (within 200 ns) of  $AH_2^{\cdot+}$  as suggested. Because of the very low concentrations of  $A^{\cdot-}$  and  $H_3O^+$  produced by the pulse a bimolecular reaction of these species could not occur rapidly enough to explain the formation of protonated  $A^{\cdot-}$  species. The process suggested by Moorthy and Hayon would therefore have to involve proton abstraction from the aqueous medium. This would, however, result in the rapid formation of two  $OH^-$  per electron and hence a net increase in the conductivity after the pulse due to attachment. Even if all radiation produced protons formed in the pulse reacted with the solute as suggested, the maximum overall decrease in the conductivity would be only 40 per cent. This is, however, in disagreement with the effects observed.

#### 4. Conclusions

The conclusion is therefore that the decay of the conductivity signal is mainly due to the reaction of radiation-produced protons with the solute resulting in the establishment of the acid-base equilibrium as given by equation (4). The expected decay of the conductivity signal via the attachment of electrons to adenosine (reaction 1) leading to a low mobility adenosine anion, is apparently cancelled by a rapid formation of the high mobility  $OH^-$  species, due to the protonation of the adenosine anion (reaction 2). So two separate protonation reactions are needed to describe the pulse radiolysis experiments on adenosine: the protonation of the parent adenosine molecule by  $H_3O^+$  formed in the pulse, and the protonation of the radical anion by  $H_2O$  following electron attachment to adenosine. If the reaction of the electron with the adenosine is the rate determining step, then the second protonation reaction must be faster than 5 ns. This implies that the rate constant for the protonation reaction of the adenosine anion radical (reaction 2) must be greater than  $2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The validity of the model is further strengthened by the fact that traces measured at a much higher pH (about 9.5) can be described by the same set of parameters.

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