Proton Pulse Radiolysis

H.C. Christensen, G. Nilsson, T. Reitberger
and K.-Å. Thuomas

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PROTON PULSE RADIOLYSIS

H G Christensen^x), G Nilsson^x), T Reitberger^xx)

and

K-Å Thuomas^x)

^x) AB Atomenergi, Studsvik, Nyköping, Sweden.

ABSTRACT

A 5 MeV proton accelerator (Van de Graaff) has been used for pulse radiolysis of a number of organic gases and the transient spectra obtained from the alkanes methane, ethane, propane, n-butane and neopentane have tentatively been assigned to alkyl radicals. Some methodological aspects of this new technique are discussed.

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INTRODUCTION

One objection to the use of protons in connection with pulse radiolysis has been their comparatively short range unless the energy is made very high. High energy protons require expensive accelerators and there is also a risk that radioactivity is induced in cells and equipment [1]. In certain cases, however, protons with an energy of only a few MeV can be used to advantage, viz.

(i): Investigations of radiation chemical reactions in the surface phase of liquids and solids. It is obvious that protons are more suitable than electrons for producing radicals close to the surface in such studies. In principle the experimental set up can be made quite simple, i.e. one can irradiate the free surface under controlled atmosphere in an open vessel.

(ii): Investigations of samples which have considerable light absorption or light scattering properties, such as polymers and polycrystalline solids. These can be studied in the form of thin films.

(iii): Investigations of gases at atmospheric or subatmospheric pressure where a very efficient use of the radiation energy is possible due to the well defined range of the protons and the small spread of the proton beam. In this connection it may be mentioned that the electron accelerators normally used for gas studies deposit only about 1% of the pulse energy in the gas of a normal sized gas cell [2].

In this paper we report - to our knowledge - the first pulse radiolysis study carried out with protons. Examples of items (ii) and (iii) above are given with emphasis on methodological aspects.
EXPERIMENTAL

The 5 MeV proton accelerator (Van de Graaff) in Studsvik, which normally operates with a mean current of 8-10 µA and pulses of 1-100 ns length at a frequency of 1 MHz, was modified for this experiment to give 12 µs single pulses with 0.5 mA peak current. The proton energy after passage through the exit window was 4.6 MeV. The pulse shape is shown in Fig 1, which is a registration of the Čerenkov light from protons hitting a glass surface. The energy per pulse delivered by the accelerator was $1.7 \times 10^{17}$ eV or 0.03 J. This is much less than that generally accepted in normal pulse work with electrons. However, since the range of 4.6 MeV protons is only about 45 mg/cm^2 ($Z \approx 10$) and the beam diameter is about 1 cm^2 the dose absorbed will be quite high, i.e. about 60 krad. The range of 4.6 MeV protons in water is about 0.03 cm while the range in a gas is about $10^3$ times longer. Pulse radiolysis experiments on gases are therefore more feasible and were chosen as a starting point.

Since the proton beam does not spread very much in a gas the proton energy is most efficiently utilized if the proton and light beams are collinear. The experimental set-up was arranged accordingly. If we then assume that the proton energy is homogeneously deposited the optical density $D$ of a radiation-produced species can be calculated from:

$$D = 1.5 \times 10^{-7} \frac{eEItG}{\pi r^2}$$

(1)

where $e$ is the extinction coefficient (M^{-1}cm^{-1}), $E$ the proton energy (MeV), $I$ the beam current (mA), $t$ the pulse length (µs), $G$ the yield and $r$ the beam radius (cm).
The experimental set-up for gas-phase studies is shown in Fig 2. The gas cell was open towards the proton beam and the gas under investigation was continuously flushed through the cell. The optical alignment was quite critical since the protons irradiate a narrow volume in the centre of the cell and only the light which passes this volume should be analyzed. In our first attempts we tried to irradiate through a mirror made from a thin aluminized foil placed in the same position as the plane mirror in Fig 2. However, this caused difficulties due to vibrations induced in the foil by the proton pulse. Instead we used a surface aluminized glass mirror with a 6 mm diameter central hole for the passage of the proton beam (Fig 2). The arrangement is far from ideal since about 40% of the useful light beam is lost through the hole in the mirror. After passage through the cell, the light reflected by the plane mirror was focused by a front surface aluminized spherical mirror onto the entrance slit of a Bausch and Lomb high-intensity grating monochromator. The slit chosen corresponded to an optical bandwidth of 5 nm. An EMI 9558 Q photomultiplier tube served as the light detector and its amplification was adjustable by changing the dynode current, as described by Keene [3]. The signal from the tube was amplified and displayed on a Tektronix 549 storage oscilloscope after automatic subtraction of the DC-level, which in turn was read on a digital voltmeter.

Crucial for the detection of a transient signal is the signal to noise ratio (S/N). If only shot noise at the photocathode is considered we have [4]

\[ S/N = 2.3D(I_k)^{1/2}(2e\Delta f)^{-1/2} \]  

(2)

where D is the optical density, I_k the photocathode current, e the electronic charge, and \( \Delta f \) the electrical band width. Due to the slow decay of the observed transients a rise time of \( \sim 10 \mu s \) was found to
be adequate. This corresponds to $\Delta f \sim 40$ kHz. Since the EMI 9558 tube should be operated with $I_k \leq 5$ $\mu$A the limiting value for the optical density ($S/N = 1$) becomes $\sim 10^{-5}$. However, in practice variations in the analyzing light intensity (Xe-lamp) and vibrations in the optical system were found to reduce the $S/N$-ratio considerably. An estimate of the real detection limit for the optical density of the entire system is $\sim 5 \times 10^{-4}$.

RESULTS

A quantitative test of the equipment was obtained by irradiating pure oxygen gas since the $G$-value (12.8) [5] and extinction coefficient ($3180$ M$^{-1}$ cm$^{-1}$) [6] of ozone which is formed during irradiation are known. These values are also high, which facilitates the experiment. The experimental result is shown in Fig 3. The peak position is at 252 nm which agrees well with the reported value of 255 nm [5]. The optical density at the peak is $1.2 \times 10^{-2}$ and from eq (1) we would expect $D = 3.5 \times 10^{-2}$. The optical density is thus about 30% of the expected value, which is a good result considering the primitive gas cell used in the experiment.

We have also irradiated methane, ethane, propane, $n$-butane, neopentane, ethylene, propylene, butadiene and isobutylene. For all these gases in the range 200 to 700 nm we found a transient absorption only below 300 nm, (Figs 4 - 12). For the alkanes the transient absorption is located in the range where one would expect the corresponding alkyl radical to absorb. We therefore tentatively assign the transient spectra obtained in alkanes to alkyl radicals. If we use the ozone system as a dosimeter, $\varepsilon G$-values can be estimated for the peak of the transient absorptions. These values and the peak positions are given in Table 1.
Table 1

<table>
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<th>Species</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon G$ (M$^{-1}$ cm$^{-1}$ species/100 eV $\times 10^3$)</th>
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<tbody>
<tr>
<td>Methane</td>
<td>217</td>
<td>13</td>
</tr>
<tr>
<td>Ethane</td>
<td>225</td>
<td>27</td>
</tr>
<tr>
<td>Propane</td>
<td>225</td>
<td>23</td>
</tr>
<tr>
<td>n-butane</td>
<td>232</td>
<td>19</td>
</tr>
<tr>
<td>Neopentane</td>
<td>245</td>
<td>22</td>
</tr>
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The absorption of the methyl radical is known and the position of the peak as given by Herzberg [7] is located at 216 nm which agrees very well with the peak position in Fig 4. In flames of ethyl ether and ethane Gaydon et al. [8] have observed absorptions at about 224 nm which they provisionally assigned to the ethyl radical. This absorption band is close to our peak position in ethane, Fig 5. Recently Stevens et al. [9] have presented spectra of the methyl and ethyl radicals obtained after pulse radiolysis of methane and ethane in aqueous solutions. Our methyl radical spectrum is in fairly good agreement whereas our ethyl radical spectrum disagrees with their published spectra. Stevens et al. did not find any maximum in the wavelength range 210 - 270 nm for the ethyl radical spectrum. The rapid rise in the 200 nm region of the ethyl radical spectrum in water may, however, be due to a charge transfer interaction of a similar type to that described for the hydrogen atom in water [10], since the electron affinities of these two radicals are about the same [11].

Fig 13 shows the result of an irradiation of cyclohexane vapour with argon as the carrier gas. The observed transient shows a marked shoulder at about 245 nm where the cyclohexyl radical is reported to absorb in liquid cyclohexane [12 - 14]. In this case we observed aerosol formation after each pulse and this probably caused some light scattering.
For the olefins the transient absorptions obtained are more difficult to interpret since at short wavelengths these compounds also possess intrinsic absorptions. On the basis of the present data we are therefore not in a position to assign the spectra to particular species.

Finally, Fig 14 shows the transient absorption observed in a sample of commercial polyethylene foil, (0.3 mm thick). This irradiation was carried out in an argon atmosphere.

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Fig 6. " " " " " " " propane.
Fig 7. " " " " " " " n-butane.
Fig 8. " " " " " " " neopentane.
Fig 9. " " " " " " " ethylene.
Fig 10. " " " " " " " propylene.
Fig 11. " " " " " " " butadiene.
Fig 12. " " " " " " " isobutylene.
Fig 13. " " " " " " " cyclohexane vapor.
Fig 14. " " " " " " a pulse irradiated polyethylene-foil.
Fig 1. The proton pulse. 10 μs/div.
Proton beam

Preamplifier

Photo-multiplier

Monochromator

Amplifier

Oscilloscope

Digital voltmeter

Plane mirror

Gas inlet

Xe-lamp

Supracil window

Spherical mirror

Fig. 2. The experimental set up.
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