High-energy irradiation treatment of aqueous solutions of C.I. Reactive Black 5 azo dye: pulse radiolysis experiments

K. Dajkaa,*, E. Takácsa, D. Solpanb, L. Wojnárovitsa, O. Güvenb

a Institute of Isotope and Surface Chemistry, CRC, Hungarian Academy of Sciences. P.O. Box 77, H-1525 Budapest, Hungary
b Hacettepe University, Department of Chemistry, 06532, Beytepe/Ankara, Turkey

Abstract

The reactions of the C.I. Reactive Black 5 with short lived eaq, OH radical and H atom intermediates of water radiolysis in aqueous solution were investigated by pulse radiolysis with kinetic spectroscopic detection. The transients formed with the three intermediates have absorption maxima at ~360, ~410 and ~470 nm. The eaq adds to the azo group and the adduct radical anion rapidly protonates forming hydrazil radical. Based on the similar spectra similar intermediates are produced in H atom and hydrated electron reaction. The OH radical most probably adds to the azo group, however, it attacks also the aromatic rings. The strong absorbance found is attributed to the high conjugation of the radical site with the aromatic rings.

Keywords: Reactive Black 5; Azo-reactive dyes; Pulse radiolysis

1. Introduction

For decades the chemical reactions of the aromatic azo dyes, such as naphtol based dyes (1- and 2-arylazo-naphthols and (phenylazo) naphthalene dyes) have been in the center of interest, their photoreactions were studied in several laboratories. In photolysis singlet excited molecules, radicals and radical anions were detected as intermediates of the transformations. The reactions generally showed a strong dependence on molecular structure, solvent and in aqueous solution on the pH (Bortolus et al., 1989; Nasr et al., 1997; Vinodgopal and Kamat, 1994; Haag and Mill, 1987; Reeves and Kaiser, 1970).

Similar to the photolysis, the pulse radiolysis method is also capable to study the reactions producing reduced and oxidized intermediates of azo dyes. Besides high-energy irradiation techniques combined with conventional treatment methods can be applied in treating wastewater of textile factories. We have started to study the mechanism of the reduction and the oxidation of azo type of dyes induced by the water radiolysis intermediates by pulse radiolysis. The present paper deals with a reactive azo dye C.I. Reactive Black 5 (the structure and some of its unimolecular transformations are shown later). In alkaline solutions the sulphatoethyl sulphone group of this dye dissociates and it can form covalent type bond with the cellulose-based textiles in contrast to other types of dyes. The dye exists in its naphthoquinone hydrazone tautomeric forms in aqueous solution (Fabian and Hartmann, 1980).

2. Experimental

The C.I. Reactive Black 5, a commercial reactive bisazo dye was purchased from Aldrich (its purity was ~99%) and was used without further purification. 0.1 mmol dm⁻³ concentration solutions were applied and low doses were used to avoid a serious bleaching of the solution.

The other reagents used were of a reagent grade. The pH was set by perchloric acid or sodium hydroxide. The concentration of the additives was kept as low as possible in order to reduce the ionic strength effect. The
solutions were freshly prepared before the measurements using triple distilled water.

Pulse radiolysis measurements were carried out with 800 ns pulses of the 4 MeV electrons of a linear accelerator. Dose/pulse values were varied between 9 and 13 Gy. The changes in absorbance were followed with UV–VIS kinetic spectrophotometer in 2 cm cells. For further details concerning the setup see Földiák et al. (1988). The temperature of the solutions was 25 ± 3 °C.

Chemical additives were added into the solutions to separate the reactions of the short-lived intermediates of water radiolysis. The deoxygenation of the solutions was carried out by bubbling with the appropriate gases for 25 min before irradiation and continued during the experiments. The reactions of the hydrated electrons (e\textsubscript{aq}) were studied in Ar saturated solution in the presence of 5 V/V% tert-butanol in order to convert the OH radicals to less reactive 2-hydroxyl 2,2-dimethyl ethyl radicals. For the study of the reactions of H atoms acidic pH was used in order to convert the hydrated electrons to H atoms. These solutions also contained tert-butanol. The reactions of the OH radical with the solute were studied in N\textsubscript{2}O saturated solutions to convert the e\textsubscript{aq} to OH radicals (Swallow, 1982).

### 3. Results and discussion

After the pulse of the accelerated electrons the buildup of the transient absorbance was measured in the μs time scale. The decay was followed in the ms time range. All of the intermediates of the reactions between the dye and the water radiolysis transients have absorption maxima at ~ 360, ~ 410 and ~ 470 nm, but the absolute values and also the ratios of the maximum absorbances depended on the reaction partner. With all the three intermediates the initial rise of the absorbance was very fast and it was completed within a few μs. The decay was very slow and a considerable absorbance remained even 5 ms after the pulse.

There were differences in the spectra of the product of the e\textsubscript{aq} reaction depending on the pH of the dye solution. The differences are probably due to the different forms of the dye. In alkaline solutions the sulphatoethyl sulphone group is converted into vinyl sulphone group (Fig. 1), and also the two SO\textsubscript{3} groups connected to the central naphthol ring are protonated in acidic solution. During the pulse radiolysis of the azobenzene (Flamigni and Monti, 1985) the e\textsubscript{aq} was suggested to react with the azo group: the electron adduct radical anion formed in the reaction quickly protonate to hydrazil radical. These radicals had very long lifetime. In the case of azobenzene there were two intensive absorption bands in the spectra one at around 370 nm and the other around 540 nm. These bands also appear in our spectra in Fig. 1. However, in our case there is also an absorption band at about 420 nm. Since this band is very strong when the OH radicals react with the dye the band may belong to some radical addition product formed by radical attack on the aromatic rings.

The absorption maxima of the intermediates in acidic solutions are similar in the cases of e\textsubscript{aq} and the H atom.
reactions (Fig. 2), suggesting similar intermediates for both reactions. Therefore, the H atom addition probably preferably occurs also on the azo group.

OH radical is supposed to attack also the azo group (Krapfenbauer et al., 2000), besides it may add to the aromatic ring system of the dye (Fig. 3). In the
absorbance–time profiles after the first fast rise, which is due to the reaction of OH with the dye the absorbance continues to increase more slowly and completed in about 100 µs. The absorbance disappears very slowly in the millisecond time range. The slow increase after the first fast rise is probably due to a rearrangement of the initially formed radical to a more conjugated system. Similar phenomenon was also observed in the reactions of H atoms.

The absorption spectra obtained in reaction with eaq, OH radical and H atom are rather complicated. This can be due to the several reactive sites of this large molecule, which can be attacked by the water radicals, forming several radical species from the dye. The complicated spectra are the superposition of the spectra of the different intermediates. Moreover, the tautomerism mentioned in the Introduction and shown in Fig. 3 may also complicate this spectrum. The appearance of azo and naphthoquinone hydrazone tautomeric forms in the same time causes double peaks in the spectra of the dye solutions.

4. Conclusion

The intermediates of water radiolysis, eaq, H and OH react with the dye molecules in very fast reactions with rate constants in the \(10^{10} \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}\) range. Partly similar absorption spectra were found in the three reactions indicating similar intermediates. Under most conditions investigated hydrazyl type radicals form with high yield. Therefore, the decoloration reactions well detected in the gamma radiolysis experiments (Solpan et al., 2003) partly take place in similar reactions with all the three intermediates of water radiolysis.

Acknowledgements

We gratefully acknowledge the generous financial support from the International Atomic Energy Agency and the Hungarian Research Found (OTKA No. T037 363, T 25403 and T 037294). The authors wish to thank for the support given by the Scientific and Technical Research Council of Turkey (TUBITAK) and Hungarian Academy of Sciences (HAS).

References


