

Azo dye degradation by high-energy irradiation: kinetics and mechanism of destruction

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Abstract. The kinetics and mechanism of dye destruction is discussed on the example of Apollofix Red (AR-28) and Reactive Black 5 (RB-5) radiolysis in dilute aqueous solution. The dose dependence of colour disappearance is linear when the reactive intermediate reacts with the colour bearing part of the molecule causing destruction of the conjugation here with nearly 100% efficiency. In this case, spectrophotometry can be used to follow-up dye decomposition. Such a linear dependence was observed when hydrated electrons or hydrogen atoms reacted with the dye. However, in the case of hydroxyl radical reactions some coloured products form with absorption spectra very similar to those of the starting dye molecules. For that reason, spectrophotometric measurements give false results about the concentration of intact dye molecules. Analysis made by the HPLC (high-pressure liquid chromatography) method reveals logarithmic time dependence in agreement with a theoretical model developed.

Key words: azo dyes • decolouration • reaction mechanism • kinetics • Apollofix Red • Reactive Black 5

Introduction

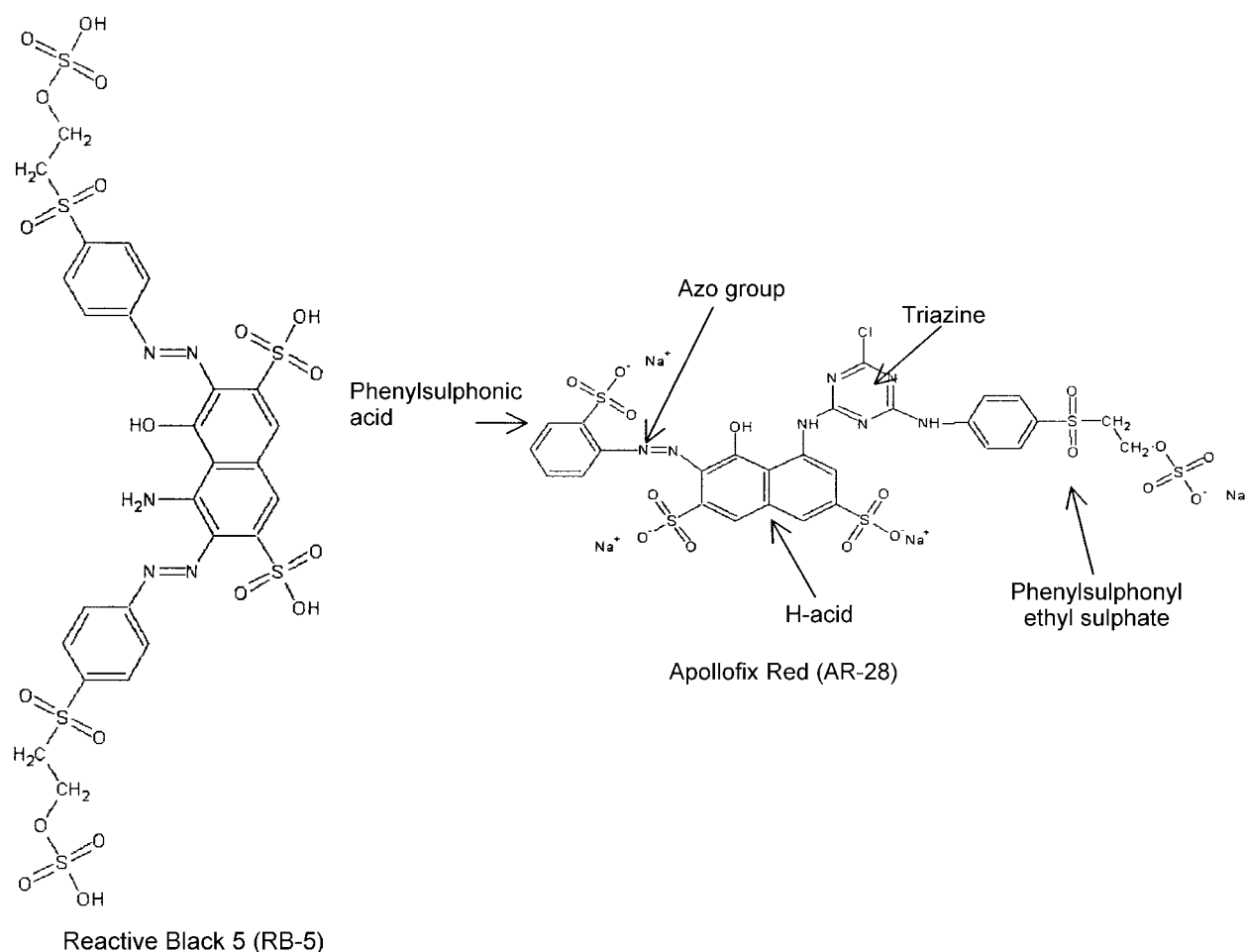
Azo dyes are produced in very large quantities and used as reactive dyes by the cotton industry. They are very stable and resistant to chemical processes. Therefore, their removal from industrial effluents by conventional methods (mechanical screening, sedimentation, biological treatment, biofilters) alone is usually not very effective. This problem can be solved by combining the conventional techniques with other methods. Radiation chemistry is one of the most promising advanced oxidation processes (AOP's) [3, 8, 9] for environmental remediation. In AOP's hydroxyl radicals are the main oxidants for the degradation of organic pollutants [13]. The disappearance of the dye is generally followed by spectrophotometry at the absorbance maximum between 450 and 600 nm.

The dye disappearance curves are very often described by applying some kinetic equations [4, 6, 7, 10, 15, 17–19] in order to describe the dependence of the destruction on such parameters as dose, dose rate, additives, etc. in radiolysis experiments, illumination intensity, illumination time, etc. in photo oxidation experiments [15].

For the present mechanistic and kinetic studies, the experimental results obtained during radiolysis of Apollofix Red (AR-28) and Reactive Black 5 (RB-5) are discussed. Some of the experimental results were already published [16, 20, 21].

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Scheme 1. Structures of Reactive Black 5 (RB-5) and Apollofix Red (AR-28) dyes.

The colours of these dyes are determined by the conjugated phenylsulphonic acid-azo group-H-acid parts of the molecules [1] (see Scheme 1). Any change in these parts leads to change of colour, i.e. change of the absorption spectrum in the visible range. Destruction of the extensive conjugation leads to loss of colour, i.e. disappearance of absorption in the visible range.

Experimental

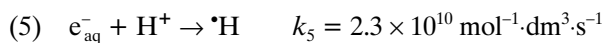
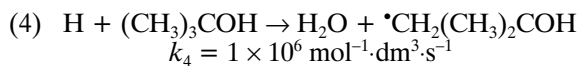
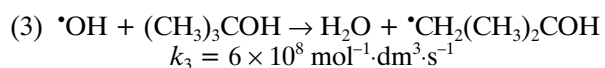
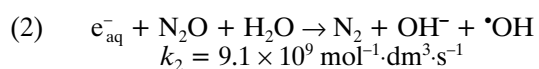
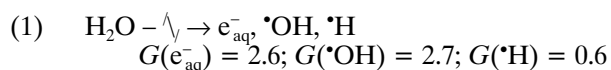
AR-28 was obtained from Taiheung Corporation (Kyunggido, South Korea), RB-5 was purchased from Aldrich, the dyes were purified by recrystallization from methanol/ethanol mixtures. Perchloric acid was used to set pH of the solutions when the $\cdot\text{H}$ atom reactions were studied. Methanol (HPLC grade) and tetrabutylammonium-hydrogen sulphate (TBAHS) were obtained from Sigma-Aldrich, *tert*-butanol from Spektrum-3D.

The gamma radiolytic experiments were carried out using a ^{60}Co irradiation facility with a dose rate of $3.0 \text{ kGy}\cdot\text{h}^{-1}$ as determined by Fricke dosimetry ($G(\text{Fe}^{2+}) = 15.6 (100 \text{ eV})^{-1}$). The solutions were bubbled with N_2 or N_2O for 5 min prior to irradiation in 5 ml Pyrex glass ampoules. 1 cm Suprasil quartz optical cells were used for taking the UV-VIS absorption spectra before and after the reaction by using a Jasco 550 UV-VIS spectrophotometer.

The chromatographic system consisted of a Jasco PU-2089Plus quaternary gradient pump, a Jasco MD-2015Plus diode-array Multiwavelength Detector and a Nucleosil 100 C18 column (Teknokroma®) (pore size $5 \mu\text{m}$, length 15 cm, diameter 0.4 cm). Separations were made using $50 \text{ mmol}\cdot\text{dm}^{-3}$ aqueous solution of TBAHS at pH 6.1 and methanol. All mobile phases were filtered using a Millipore $0.45 \mu\text{m}$ filter and were degassed by ultrasonication before use. The separations were made at room temperature using injection volume of $10 \mu\text{l}$, and flow-rate of $0.8 \text{ ml}/\text{min}$.

Standard radiation chemical techniques were applied to separate the water radiolysis intermediates and follow their reactions with the dye. The radiolysis of water supplies hydrated electron (e_{aq}^-), hydroxyl radical ($\cdot\text{OH}$) and hydrogen atom ($\cdot\text{H}$) reactive intermediates with G values (species $(100 \text{ eV})^{-1}$) shown in Eq. (1). In order to reduce the number of reactive intermediates, the reactions of $\cdot\text{OH}$ radicals were studied in N_2O saturated solutions (pH 5–6), in such solutions the hydrated electrons are converted to $\cdot\text{OH}$ radicals (Eq. (2)). When the e_{aq}^- reactions were investigated the solutions were bubbled with N_2 for deoxygenation and contained $0.5 \text{ mol}\cdot\text{dm}^{-3}$ *tert*-butanol in order to transform the $\cdot\text{OH}$ radicals to less reactive $\cdot\text{CH}_2(\text{CH}_3)_2\text{COH}$ radicals (Eq. (3)) (pH 5–6). H^\cdot atoms react with a low rate coefficient with *tert*-butanol (Eq. (4)). The H^\cdot reactions were studied in *t*-butanol

containing N_2 purged pH 1.1 solutions, where e^-_{aq} was converted to H^\bullet atom (Eq. (5)) [2].



Results and discussion

Degradation of AR-28 and RB-5

Figure 1 shows the comparison of the decolouration of AR-28 and RB-5 in the reaction with $\bullet OH$ (1A, 1B)

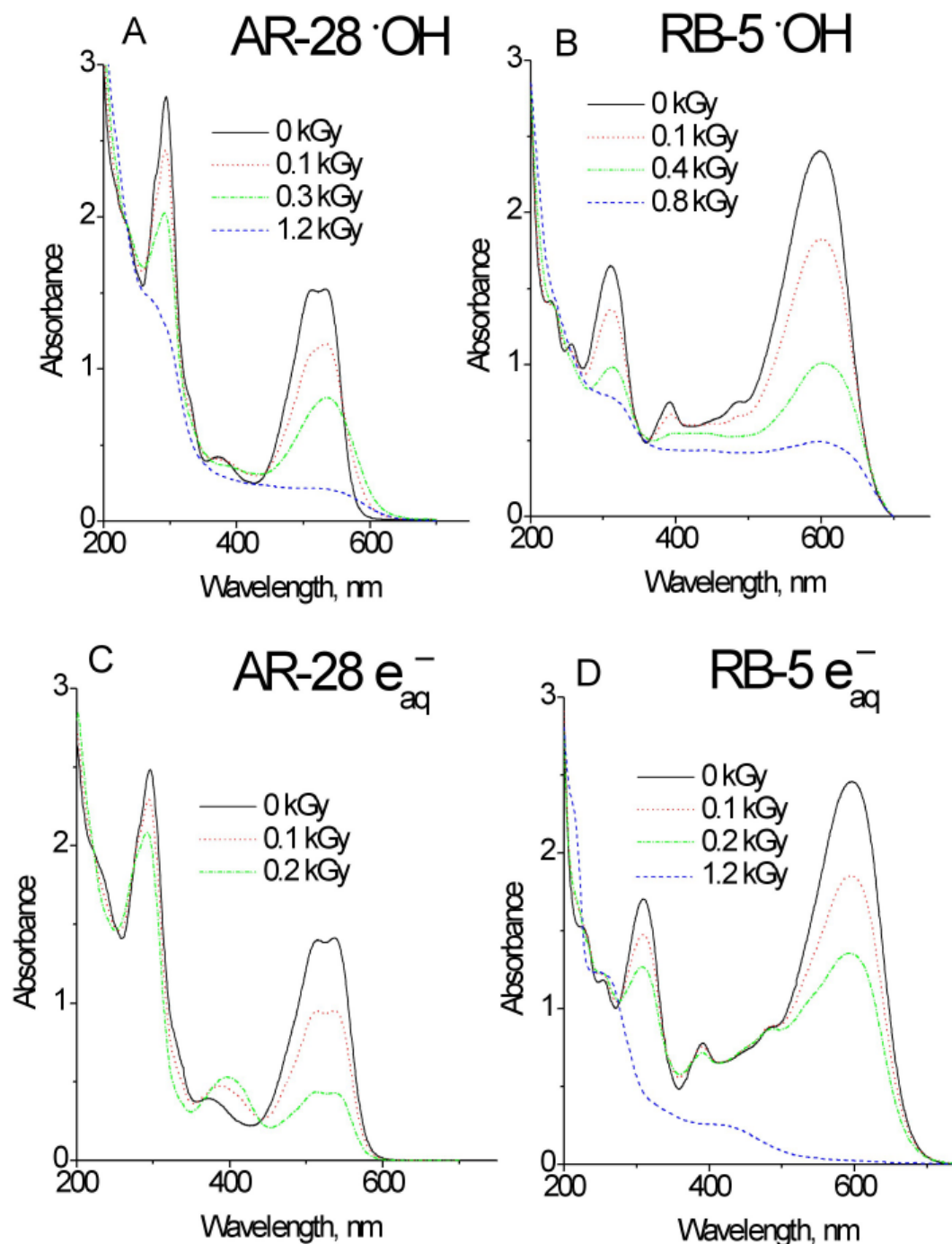


Fig. 1. Decolouration plots of AR-28 ($0.085 \text{ mmol} \cdot \text{dm}^{-3}$) and RB-5 ($0.1 \text{ mmol} \cdot \text{dm}^{-3}$) obtained when the hydroxyl radicals reacted with the dye (A, B), or when the hydrated electrons were the reaction partners (C, D).

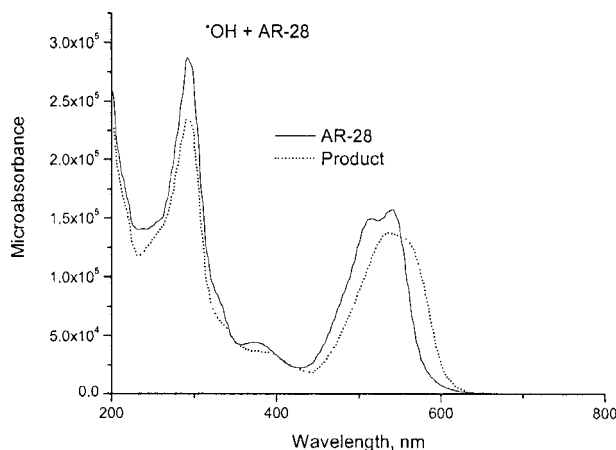


Fig. 2. Comparison of the absorption spectra of AR-28 and one of its main transformation products formed in $\bullet\text{OH}$ radical reaction. The spectra were recorded by using diode-array detection after HPLC separation.

and e_{aq}^- (1C, 1D), respectively. When $\bullet\text{OH}$ radicals reacted with the dye, during the decolouration the shape of the spectra in the visible range changed: the visible bands shifted to longer wavelengths. After separation of the main product formed from AR-28 by HPLC, we found that its spectrum is very similar to the spectrum of the starting dye. The only difference is the shift of the visible band to longer wavelength (Fig. 2) and this causes the change in the shape of the UV-VIS spectra (Fig. 1A). The initial G values (extrapolated to zero dose) of dye disappearance were 2.92 for RB 5 and 2.5 for AR-28.

When e_{aq}^- reacted with the dyes (Figs. 1C and 1D), the intensity of the visible absorption decreased with the radiation dose without any major change in the shape of the spectrum in the visible range for AR-28. In the case of RB-5 there is no change in the spectrum above ca. 550 nm. The initial G values (extrapolated to zero dose) of dye disappearance were 1.91 for RB 5 and 2.6 for AR-28.

Mechanism of degradation

As it was discussed in our former papers [20, 21] $\bullet\text{OH}$ radical has very high reactivity with the aromatic ring

and with the azo group subparts of the molecule [12, 14]. The addition of $\bullet\text{OH}$ radical to an aromatic ring on the conjugated part of the molecule results in a cyclohexadienyl type radical. This radical may disappear in radical-radical combination reaction where dimer molecule is produced (in this reaction the conjugation may be destroyed). Radical disproportionation leads to compounds that contain cyclohexadiene ring and another compound with extensive conjugation in the molecule characteristic of the dye. However, the latter molecule contains an extra OH group in the conjugated part of the molecule (see Scheme 2). For that reason, its absorption spectrum is slightly different from that of the starting molecule. This shift in the spectrum certainly affects the molar extinction coefficient, and, therefore, any kinetic analysis based on the absorbance measurements should be handled with a certain caution. The correct analysis should be based on chemical separation and individual compound analysis (most conveniently by the HPLC method).

The hydrated electron (and also the H^\bullet atom) is suggested to react with the azo group (with rate coefficients close to the diffusion controlled limit [5, 11]) destroying the conjugation with nearly 100% efficiency [20, 21]. The other parts of the molecule and the products formed during decay have smaller reactivity with e_{aq}^- and H^\bullet atom than the azo group.

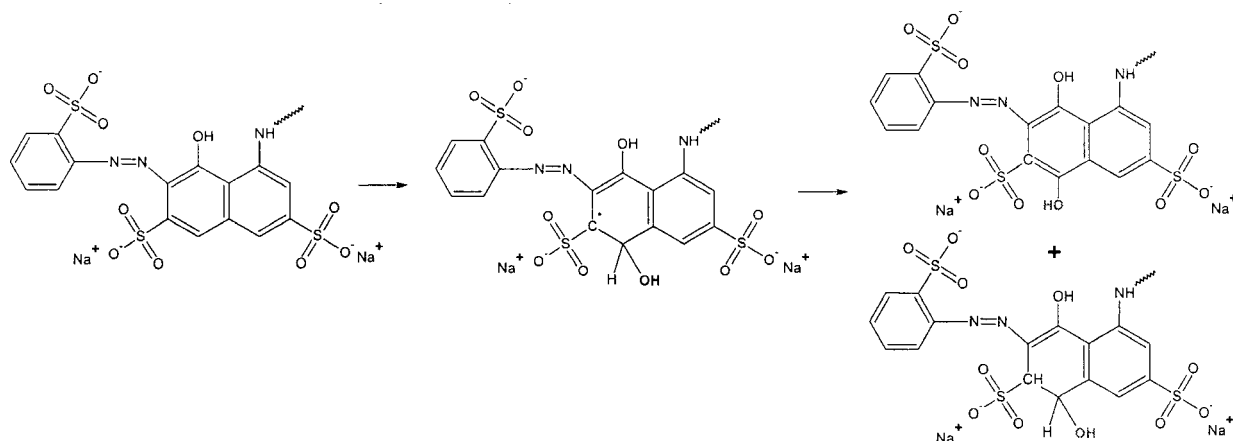
Kinetic analysis

Under steady state conditions, the $\bullet\text{OH}$, H^\bullet , e_{aq}^- intermediates that destroy the dye molecules may react practically exclusively with the intact dye molecules decolourizing them. The time dependence of dye disappearance can be described by the differential equation:

$$(6) \quad -\frac{d[\text{Dye}]}{dt} = k[\text{I}][\text{Dye}]$$

In the equation $[\text{Dye}]$ represents the dye concentration, $[\text{I}]$ is the intermediate radical concentration, and k is the second order rate coefficient.

During steady-state radiolysis, the intermediate radicals form with a constant rate (r_1) and they decay with the same rate ($k[\text{I}][\text{Dye}]$):



Scheme 2. Degradation of AR-28 by $\bullet\text{OH}$ radical.

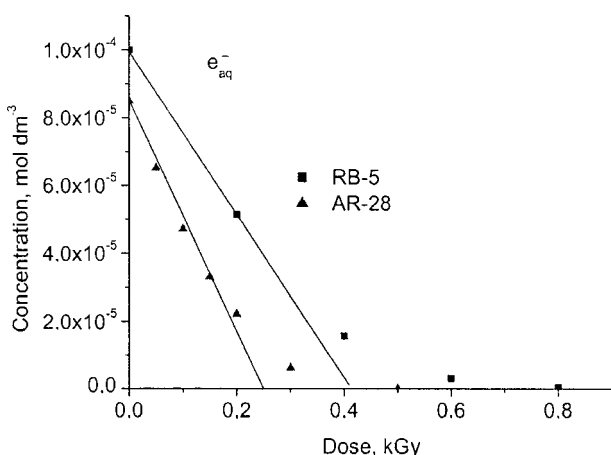


Fig. 3. Dose dependence of decolouration of AR-28 and RB-5 caused by hydrated electron.

$$(7) \quad \frac{d[I]}{dt} = r_1 - k[I][Dye] \approx 0$$

At the beginning of the process, when the dye concentration is high, the intermediate radicals quickly react with the solute molecules, and therefore, the intermediate radical concentration is low. At the end of the process, [Dye] is low and $k[I]$ is high. Substituting $[I] \approx r_1/k [Dye]$ into Eq. (6), after integration, we obtain linear time dependence (since the irradiation is usually carried with a constant dose rate, there is linear dose dependence):

$$(8) \quad \frac{[Dye]}{[Dye]_0} = 1 - \frac{r_1}{[Dye]_0} t = 1 - k_{obs} t$$

Such a linear dependence was observed several times during decolouration at the beginning part of the process. We found linear initial dose dependence, when in radiolysis the hydrated electrons or the hydrogen atoms reacted with the dyes (Figs. 3 and 4). As we mentioned before, these intermediates were found to react principally with the azo group causing destruction of the intensive conjugation in the molecule through the azo bond. In AR-28 there is only one azo group with high reactivity, and here the linearity is maintained till about 80% destruction. In the RB-5 there are two azo groups. When e_{aq}^- or $\cdot H$ destroys one of them, due to the decreased conjugation, the longest wavelength absorption disappears. However, the other azo group may also react with high rate coefficient with e_{aq}^- or $\cdot H$ and, therefore, the linear range is shorter. The formation rates of reactive intermediates at a dose rate of $3 \text{ kGy} \cdot \text{h}^{-1}$, calculated from the slopes of the straight lines are $r_{I, \text{measured}} \approx (2.0\text{--}2.5) \times 10^{-7} \text{ mol} \cdot \text{s}^{-1}$ for both e_{aq}^- and $\cdot H$. The value is just slightly lower than the value calculated based on the radiation chemical yield of the intermediates: $r_{I, \text{calculated}} \approx 2.8 \times 10^{-7} \text{ mol} \cdot \text{s}^{-1}$.

At higher doses, however, the dye is depleted; therefore, the e_{aq}^- and $\cdot H$ intermediates of water radiolysis react mainly with the products of radiolysis and only a small part of the intermediates reacts with the azo moiety causing decolouration. For that reason,

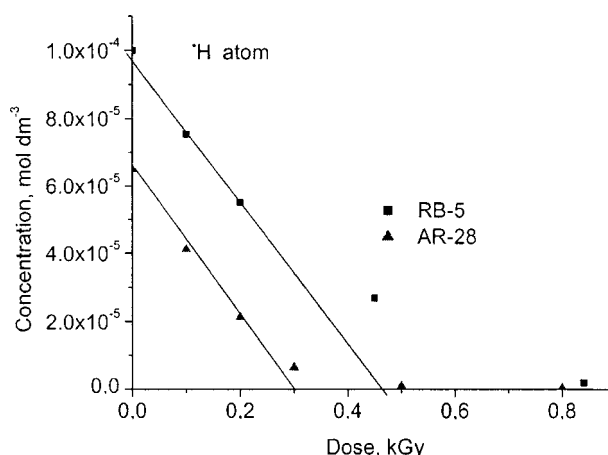


Fig. 4. Dose dependence of decolouration of AR-28 and RB-5 caused by $\cdot H$ atom.

the time dependence curve at higher depletion deviates from linearity.

The reaction of $\cdot OH$ radical with the dye is different from the reactions of e_{aq}^- and $\cdot H$. The $\cdot OH$ radical reacts with practically diffusion limited rate coefficient ($k \approx 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$) with the aromatic rings and probably also with the $-N=N-$ double bond. The dye molecules generally have several places for the attack, e.g. AR-28 has five aromatic rings and one $-N=N-$ double bond. The reaction with the $-N=N-$ double bond or with the rings involved in the extensive conjugation leads to the destruction of the conjugation, so may decolourize the molecule. However, the new products have also high, practically the same reactivity towards the $\cdot OH$ radicals as the starting compound. That is probably true for the product of the product, i.e. for the secondary product, tertiary product, etc. For that reason, the rate equations should be written in the following form:

$$(9) \quad -\frac{d[Dye]}{dt} = k[\cdot OH][Dye]$$

$$(10) \quad \frac{d[\cdot OH]}{dt} = r_{OH} - k[Dye][\cdot OH] - k[Product][\cdot OH] \approx 0$$

Since – as it was mentioned before – the reaction of $\cdot OH$ with both the dye and the products is practically diffusion limited; we use for both reactions the same k rate coefficient. Applying the simplification:

$$(11) \quad [Product] \approx [Dye]_0 - [Dye]$$

also taking $[\cdot OH] \approx r_{OH}/k[Dye]_0$ expressed from formulae (6) and (7) ($I = \cdot OH$), the differential equation has the form:

$$(12) \quad -\frac{d[Dye]}{dt} = \frac{[Dye]r_{OH}}{[Dye]_0}$$

After integration, we obtain logarithmic time dependence (Eq. (13)) with rate parameter of $k_{obs} = r_{OH}/[Dye]_0$.

$$(13) \quad \ln \frac{[Dye]}{[Dye]_0} = -\frac{r_{OH}}{[Dye]_0} t = -k_{obs} t$$

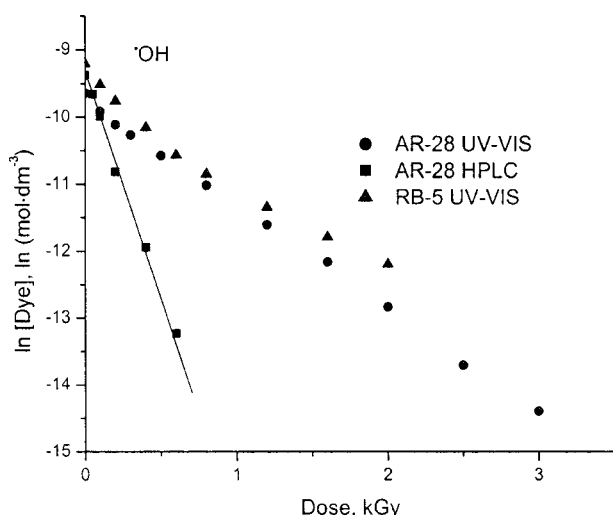


Fig. 5. Dose dependence of decolouration caused by hydroxyl radicals, as measured by spectrophotometric evaluation, or by HPLC separation and evaluation.

By expanding the logarithmic term in series and keeping only the first part Eq. (13) is transformed into Eq. (8) which means that at low conversion the dose dependence is again linear.

Figure 5 shows the $\ln[\text{Dye}]/[\text{Dye}]_0$ vs. dose plot obtained when the dyes were degraded by $\cdot\text{OH}$ radicals (N_2O saturated solution). Good linear logarithmic plot was obtained when the dye concentrations in the irradiated solutions were determined by the HPLC method. The figure also shows the dose dependences obtained by spectrophotometric evaluation at the absorbance maximum in AR-28 and RB-5 solutions. The strong positive deviations from the linearity, as it was mentioned before, may be attributed to reformation of the somewhat modified dye molecules.

In Eq. (13) $k_{\text{obs}} = r_{\text{OH}}/[\text{Dye}]_0$, i.e. it is the ratio of the intermediate formation rate and the initial dye concentration. The slope of the curve obtained by HPLC in Fig. 5 is $k_{\text{obs}} = 6.4 \text{ kGy}^{-1}$, or using the dose rate applied (3 $\text{kGy}\cdot\text{h}^{-1}$), $5.4 \times 10^{-2} \text{ s}^{-1}$. Then, the formation rate of $\cdot\text{OH}$ radicals based on the dye disappearance is $r_{\text{OH,measured}} = 4.6 \times 10^{-7} \text{ mol}\cdot\text{s}^{-1}$, the value agrees well with the one calculated from the dose rate and the known radiation chemical yield $\cdot\text{OH}$ radicals, $r_{\text{OH,calculated}} \approx 4.7 \times 10^{-7} \text{ mol}\cdot\text{s}^{-1}$. The high value of $r_{\text{OH,measured}}$ indicates that the $\cdot\text{OH}$ radicals react with practically 100% efficiency with the dye molecules transforming them to new, coloured, or non-coloured products.

Conclusions

AR-28 and RB-5 can be effectively decomposed by $\cdot\text{OH}$ and e_{aq}^- intermediates of water radiolysis. $\cdot\text{OH}$ radicals add to the aromatic rings and as products of this reaction hydroxylated dyes and probably quinine type molecules and dimers are formed. These products have also high reactivity towards $\cdot\text{OH}$ radicals. e_{aq}^- and $\cdot\text{H}$ atom attacks the azo group, instantly destroying the electron conjugation in the dye molecules and the

products formed are less reactive towards e_{aq}^- and $\cdot\text{H}$ atom. The dose dependence of colour disappearance is linear when e_{aq}^- or $\cdot\text{H}$ atom reacts with the dye molecules. In case of $\cdot\text{OH}$ reactions there is logarithmic dose dependence of dye disappearance. In the paper a kinetic model was proposed which described the experimental results.

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