

Kinetics of benzenesulfonates elimination by UV and UV/H₂O₂

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Abstract

The kinetics of elimination of eight benzenesulfonate derivatives (BS) have been studied in aqueous solution. Experiments were performed at 25 °C, at pH = 6.0, in a batch photochemical reactor in the absence and the presence of hydrogen peroxide. For all substrates the degradation was shown to be effective using UV alone (253.7 nm) and the coupling H₂O₂/UV (generating hydroxyl radicals). The quantum yields for direct photolysis were evaluated to be in the range of 0.03–0.05 for BS except for nitro derivatives for which values about 100 times lower were obtained. The degradation is usually faster in the presence of hydrogen peroxide, but the efficiency depends on hydrogen peroxide starting concentration. The second order rate constants of reaction between BS and HO• radicals, k_{BS} , have been determined. Values ranging between 0.7 and $12.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ according to the substituent on the benzene ring were obtained by working with different hydrogen peroxide starting concentration. Hammett-type correlation was obtained for the reaction of HO• radicals with BS $\log k_{BS} = 9.56 - 0.87 \sum \sigma$. The optimal hydrogen peroxide concentration leading to the highest rate of BS degradation was calculated. It mainly depends on the second order rate constant between HO• radicals and BS.

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Keywords: Benzenesulfonate derivatives; Hydrogen peroxide; HO• radicals; Phototransformation; UV

1. Introduction

Benzene and naphthalene sulfonates play an important role in industrial processes. They are used as intermediates in the production of chemicals such as azo dyes, optical brighteners, detergents, pharmaceuticals, tanning agents, etc. [1–3]. These compounds are very soluble in water and only very slightly absorb onto the organic material because of their low K_{OW} [4]. Because of their extensive use, some of them are detected in natural waters [5]. Recently, a study inventoried the presence of the different naphthalene and benzenesulfonates in four landfills [6]. Even if these chemicals are not reported to have any genotoxic or carcinogenic effects, their presence may lead to perturbations of the ecosystems. The presence of substituents significantly modifies the biodegradability of benzenesulfonate derivatives (BS). It has been shown that BS substituted with alkyl groups were easily biodegraded although hydroxy, nitro, amino containing-BS were difficult to eliminate [7]. To our knowledge, only one study investigates for

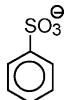
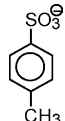
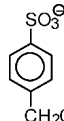
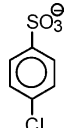
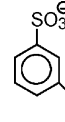
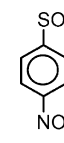
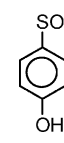
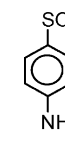
the chemical degradation of benzenesulfonate derivatives. Sangchark et al. studied the transformation of five BS by the photocatalytic system TiO₂/UV ($\lambda_{exc.} > 310 \text{ nm}$) [8]. The high efficiency of this process is due to the generation of hydroxyl radicals, very powerful oxidant, able to react with most of organic pollutants with high second order rate constant. These constants of reaction between BS and hydroxyl radicals are only known for benzenesulfonate and 4-methylbenzenesulfonate [9]. Among the well known advanced oxidation processes (AOP) and beside TiO₂/UV, the activation of hydrogen peroxide by UV has been extensively studied from analytical and kinetic points of view [10–13]. The efficiency of H₂O₂/UV is due to the generation of 2 mol of hydroxyl radicals/mol of hydrogen peroxide photolyzed. However, hydroxyl radicals also react with hydrogen peroxide that limits the efficiency of the process in terms of pollutants degradation.

The present work studies the efficiency of the UV irradiation (253.7 nm) and of the coupling of UV with H₂O₂ for the degradation of BS. Firstly, quantum yields of BS photolysis have been determined from experiments conducted in the absence of H₂O₂. Then, second order rate constants for reaction between BS and hydroxyl radicals have been evaluated and a correlation with the Hammett constants has

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Table 1
Formulas, Hammett constants and molar absorption coefficients at 253.7 nm of BS

Compound	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8
Formula								
σ (Hammett)	0	-0.17	-0.15	0.23	0.71	0.78	-0.37	-0.66
ϵ_{BS} ($M^{-1} cm^{-1}$)	300	285	375	215	7040	8090	570	12950

been shown. Optimal hydrogen peroxide concentrations exist, depending on the compound.

2. Experimental

Benzenesulfonate, 4-methylbenzenesulfonate, 4-ethylbenzenesulfonate, 4-chlorobenzenesulfonate, 4-hydroxybenzenesulfonate, 4-aminobenzenesulfonate, 3-nitrobenzenesulfonate and 4-nitrobenzenesulfonate, hydrogen peroxide, sodium hydroxide, tetrabutylammonium bromide, methanol were commercial products of the purest grade available. The chemical formula of 8 BS studied are shown in Table 1.

All solutions were prepared with purified water (resistivity $18 M\Omega cm$ —DOC $<0.1 mg C l^{-1}$) obtained using a Millipore device (Milli-Q). All the experiments have been performed at pH 6.0. The ionic strength was not controlled.

The irradiation set-up was a batch photoreactor (volume of irradiated solution = 3.7 l, optical reactor pathlength = 6.75 cm). The lamp (Vuilbert et Lourmat low pressure Hg lamp T6C) was located at the center of the reactor, in a quartz sleeve. The number of photons was evaluated with hydrogen peroxide actinometry as described elsewhere [14]. Actinometries were performed weekly. The value obtained was $0.84 \pm 0.06 \times 10^{-6} \text{ einstein } l^{-1} s^{-1}$ during the period of experiments. Hydrogen peroxide was measured by the Ti-complexometry method described by Eisenberg [15]. UV-Vis spectra were recorded on a Safas double-beam spectrometer, using either 1 or 5 cm cell. The disappearance of benzenesulfonate derivatives was quantified by HPLC using a Waters system equipped with a Waters Delta Pak column (150 mm \times 35 mm). A UV absorbance detector was used; the wavelength was adjusted for each BS. The eluant was a MeOH–water mixture acidified with H_3PO_4 , or in which tetrabutylammonium bromide was added as an ion pair-reagent. The reproducibility was within $\pm 3\%$.

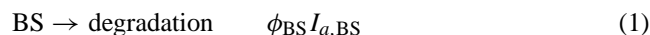
3. UV-Vis characterization of benzenesulfonate derivatives

The UV-Vis spectra of benzenesulfonate derivatives (BS) were recorded to determine their molar absorption

coefficients at 253.7 nm. The results are gathered in Table 1. Very good accuracy was observed for this determination (R.S.D. lowest than 1%).

4. Direct photolysis at 253.7 nm

Aqueous solutions of BS were irradiated at 253.7 nm. A disappearance of the organic compounds is observed according to:



Working concentrations were such as $A_{253.7 \text{ nm}}$ (absorbance at 253.7 nm) = $\epsilon_{BS} \ell [BS]$ will be lower than 0.02. Thus, the rate of photolysis of BS can be simplified from (I) to (II):

$$-\frac{d[BS]}{dt} = \phi_{BS} I_{a,BS} = \phi_{BS} I_0 (1 - 10^{-\epsilon_{BS}[BS]\ell}) \quad (I)$$

$$-\frac{d[BS]}{dt} = 2.303 \phi_{BS} I_0 \epsilon_{BS} [BS] \ell \quad (II)$$

where ϕ_{BS} and I_a are the quantum yield (mol einstein^{-1}) and the rate of light absorption ($\text{einstein } l^{-1} s^{-1}$), respectively, I_0 is the photon fluence rate ($\text{einstein } l^{-1} s^{-1}$), ϵ_{BS} the molar absorption coefficient, $[BS]$ and ℓ are the concentration and the reactor optical pathlength, respectively. Eq. (II) indicates that the photolysis of BS should obey an apparent first order kinetics law (see Fig. 1).

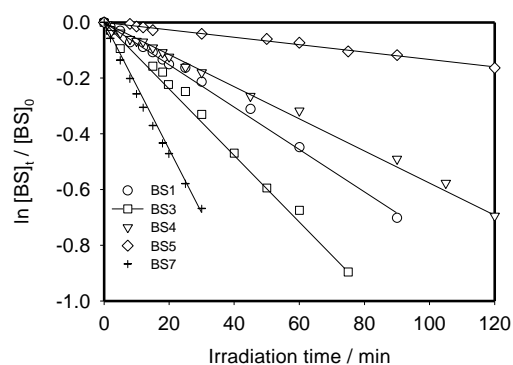


Fig. 1. Examples of semi-logarithmic plot of the disappearance of BS upon irradiation at 253.7 nm in aqueous solution at pH = 6.0, $[BS] = 1$ or $0.4 \mu M$. Straight lines represent linear regressions.

Table 2
Quantum yield of BS photolysis at 253.7 nm in aqueous solution

Compound	Quantum yield ϕ_{BS} (R^2)
BS1	0.033 (0.998)
BS2	0.050 (0.998)
BS3	0.042 (0.998)
BS4	0.037 (0.997)
BS5	0.0005 (0.996)
BS6	0.0004 (0.998)
BS7	0.050 (0.995)
BS8	0.038 (0.998)

Standard deviations estimated with three measurements are <1%.

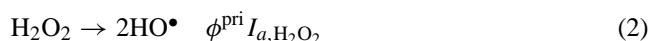
Eq. (II) can be written for the benzenesulfonate derivatives and also for hydrogen peroxide used as an actinometer. After division, Eq. (III) is obtained:

$$\phi_{\text{BS}} = \frac{\phi_{\text{H}_2\text{O}_2} \times \varepsilon_{\text{H}_2\text{O}_2}}{\varepsilon_{\text{BS}}} \times \frac{\Delta \ln([\text{BS}]_0/[\text{BS}]_t)/\Delta t}{\Delta \ln([\text{H}_2\text{O}_2]_0/[\text{H}_2\text{O}_2]_t)/\Delta t} \quad (\text{III})$$

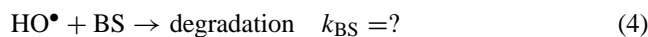
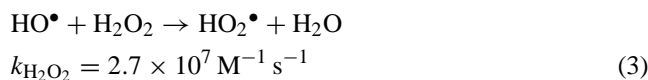
The quantum yields of BS direct photolysis were calculated according to Eq. (III). The results are gathered in Table 2. A quite similar photochemical efficiency is observed for the different BS, except for nitro-substituted BS that present a quantum yield about 100 times lower in agreement with the well-known strong inactivating effect of the nitro substituent.

5. Degradation induced by HO• radicals generated by H₂O₂/UV

It is well known that the irradiation ($\lambda_{\text{exc.}} = 253.7$ nm) of hydrogen peroxide in aqueous solution leads to the production of HO• radicals.



In the presence of BS, hydroxyl radicals react either with H₂O₂ or BS:



The steady-state concentration of hydroxyl radicals at a given time t is:

$$[\text{HO}\bullet]_{\text{ss}} = \frac{2\phi^{\text{pri}} \times I_{a,\text{H}_2\text{O}_2}}{k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] + k_{\text{BS}}[\text{BS}]} \quad (\text{IV})$$

where ϕ^{pri} is the initial quantum yield of hydrogen peroxide disappearance, equal to 0.5 [14], $I_{a,\text{H}_2\text{O}_2}$, the rate of light absorption by H₂O₂. The reaction of HO₂• (or O₂•⁻) with BS was not considered because reactivity of these species is much lower than that of HO• radicals [16].

If hydrogen peroxide concentration is high enough to consider that:

1. the incident light is completely absorbed by hydrogen peroxide;
2. the decrease in H₂O₂ concentration is low (<5%) in the time scale of the experiments;
3. $k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]_0 \gg k_{\text{BS}}[\text{BS}]_0$.

Then Eq. (IV) becomes:

$$[\text{HO}\bullet]_{\text{ss}} = \frac{2\phi^{\text{pri}} \times I_0}{k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]_0} \quad (\text{V})$$

The rate of BS disappearance can be written according to relation (VI) (the direct photolysis at 253.7 nm being negligible) and the integrated form is Eq. (VII).

$$-\frac{d[\text{BS}]}{dt} = k_{\text{BS}}[\text{BS}][\text{HO}\bullet]_{\text{ss}} \quad (\text{VI})$$

$$-\ln \frac{[\text{BS}]_t}{[\text{BS}]_0} = \frac{k_{\text{BS}} \times 2\phi^{\text{pri}} \times I_0}{k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]_0} t \quad (\text{VII})$$

Aqueous solutions of BS (≈ 0.5 μM) were irradiated in the presence of large amounts of hydrogen peroxide ($[\text{H}_2\text{O}_2]_0 = 0.038$ or 0.075 M) at 253.7 nm. No change in BS concentration was observed in the presence of such excess of hydrogen peroxide but in the absence of UV light meaning that no dark reaction occurred. In the time scale of the experiments, the concentration of hydrogen peroxide was shown to remain almost constant: $[\text{H}_2\text{O}_2]_t/[\text{H}_2\text{O}_2]_0 > 0.98$. The kinetics of elimination for three BS are shown in Fig. 2 as examples. In agreement with Eq. (VII), straight lines are obtained meaning that apparent first order kinetics law is verified. The second order rate constants can be calculated from the slopes of the straight lines. The values are shown in Table 3.

Tabulated values are $4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for BS1 and 3.7 or $6.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for BS2 [9]. The values obtained from our work are in good agreement with those of literature.

The Hammett correlation is classically used to predict the effect of substituents on reaction-rate constants between

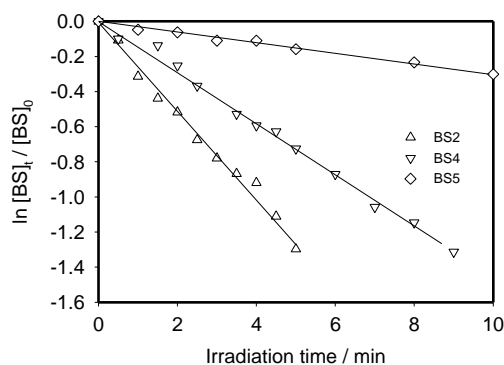


Fig. 2. Examples of kinetics of BS disappearance in the presence of high amounts of hydrogen peroxide upon irradiation at 253.7 nm at pH = 6.0. $[\text{BS}]_0 = 0.5$ μM , $[\text{H}_2\text{O}_2]_0 = 0.038$ M (semi-logarithmic plot).

Table 3
Second order rate constant of HO• reaction with BS

Compound	$k_{BS} \pm \text{S.D. (M}^{-1} \text{s}^{-1}) (R^2)$
BS1	$3.7 \pm 0.4 \times 10^9 (0.998)$
BS2	$5.3 \pm 0.3 \times 10^9 (0.998)$
BS3	$6.1 \pm 0.7 \times 10^9 (0.998)$
BS4	$2.9 \pm 0.2 \times 10^9 (0.997)$
BS5	$0.7 \pm 0.1 \times 10^9 (0.996)$
BS6	$0.7 \pm 0.1 \times 10^9 (0.998)$
BS7	$5.6 \pm 0.2 \times 10^9 (0.995)$
BS8	$12.6 \pm 0.2 \times 10^9 (0.998)$

Standard deviations estimated with at least four measurements with two different $[\text{H}_2\text{O}_2]_0$ (0.038 and 0.075 M).

organic compounds and oxidants (e.g. [8,17,18]). The Hammett constant (σ) reflects the inductive and resonance effects of substituents on the electron density of the aromatic ring. For $\sigma > 0$, substituents have an electron-withdrawing effect (e.g. $-\text{NO}_2$), whereas for $\sigma < 0$ substituents exert an electron-releasing effect (e.g. $-\text{NH}_2$). The non-substituted benzenesulfonate was used as a reference compound ($\sum \sigma_{o,m,p} = 0$). Values of σ were taken from Murov et al. [19] and they are gathered in Table 1. Fig. 3 shows the correlation between the second order rate constants and Hammett constants.

A good linear plot is obtained for $\log(k_{BS}/k_H)$ versus σ . The linear regression for the reaction of hydroxyl radicals with the eight BS is $\log k_{BS} = 9.56 - 0.87\sigma$. The negative sign of the Hammett slope is typical of electrophilic reaction because decreasing the Hammett constant corresponds to increasing the activating effect of the substituents. This quite low value also agrees with the high reactivity and weak selectivity of hydroxyl radicals.

Hydrogen peroxide concentrations previously used for the determination of the rate constants are not optimal concentrations that allow the highest rate of BS elimination. Actually, hydroxyl radicals react with hydrogen peroxide. That

$$[\text{HO}\cdot]_{ss}^0 = \frac{2\phi^{pri} \times I_0 \times ((\varepsilon_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]_0)/(\varepsilon_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]_0 + \varepsilon_{\text{BS}}[\text{BS}]_0)) \times (1 - 10^{-\ell(\varepsilon_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]_0 + \varepsilon_{\text{BS}}[\text{BS}]_0)})}{k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]_0 + k_{\text{BS}}[\text{BS}]_0} \quad (\text{VIII})$$

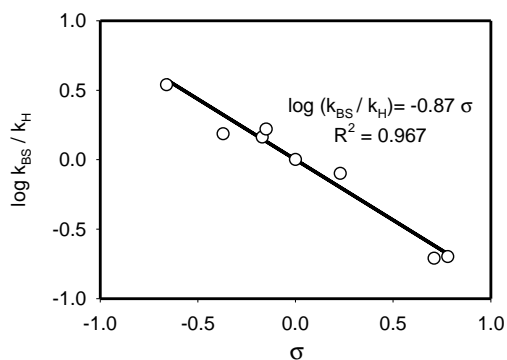


Fig. 3. Correlations between the second order rate constants and the Hammett constants.

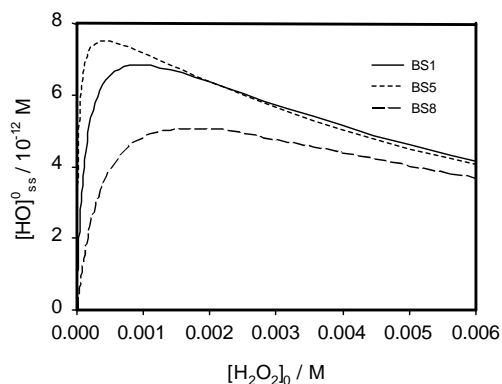


Fig. 4. Evaluation of the initial steady-state concentration of hydroxyl radicals as a function of $[\text{H}_2\text{O}_2]_0$, in the presence of $1 \mu\text{M}$ of BS. Calculations according to Eq. (VI).

means that hydrogen peroxide acts as a hydroxyl radicals scavenger in terms of BS elimination because of competition between reactions (3) and (4). This phenomenon is well known and has been extensively described (e.g. [20,21]). When the concentration of hydrogen peroxide decreases, the direct photolysis of BS is no more negligible. For a given concentration of BS, the highest initial rate of BS disappearance will be obtained when the highest initial steady-state concentration in hydroxyl radicals will be reached, beside the direct photolysis of the organic compounds. Among BS selected, three different cases can be distinguished. BS1 weakly absorbs at 253.7 nm and reacts quite efficiently with UV and hydroxyl radicals. BS6 strongly absorbs light at 253.7 nm but reaction with UV and hydroxyl radicals is less efficient. BS8 strongly absorbs light at 253.7 nm too and reacts very efficiently with UV and hydroxyl radicals. Computer calculations of the initial steady-state concentration of $\text{HO}\cdot$ [$\text{HO}\cdot]_{ss}^0$ (Eq. (III) rearranged as Eq. (VIII)) as a function of $[\text{H}_2\text{O}_2]_0$ give the curves plotted in Fig. 4. Primary by-products arising from BS transformation are not taken into account as HO radicals trap.

As expected, $[\text{HO}\cdot]_{ss}^0$ reached a maximum for an optimal initial starting hydrogen peroxide concentration $[\text{H}_2\text{O}_2]_{\text{OPT}}$. Garcia Einschlag et al. recently described similar curves for nitro aromatic derivatives [20]. In H_2O_2 solutions containing BS, $[\text{HO}\cdot]_{ss}^0$ decreases in the same order as k_{BS} increases. Simultaneously, $[\text{H}_2\text{O}_2]_{\text{OPT}}$ increases. Values of $[\text{H}_2\text{O}_2]_{\text{OPT}}$ equal to 0.40, 0.85 and 1.70 mM have been estimated for BS6, BS1 and BS8, respectively.

Simulations of pollutants degradation in $\text{H}_2\text{O}_2/\text{UV}$ process by Gepasi software [22,23] have been successfully achieved in our lab [24,25]. The values of $[\text{H}_2\text{O}_2]_{\text{OPT}}$, k_{BS} , ϕ_{BS} were introduced in the kinetic modeling software Gepasi and simulations were performed. Reactions (1)–(3) were taken into account together with recombination of radicals. The fraction of light absorbed by H_2O_2 and BS, the

concentrations of the compounds and of radical species are calculated for each irradiation time with a step of 0.2 s. The starting concentration of hydrogen peroxide was varied beside the optimum value previously determined. We observed that the highest initial rate of BS disappearance was actually obtained for $[\text{H}_2\text{O}_2]_{\text{OPT}}$. In a recent study, Garcia Einschlag et al. demonstrated that $[\text{H}_2\text{O}_2]_{\text{OPT}}$ could be evaluated according to Eq. (IX) in the $\text{H}_2\text{O}_2/\text{UV}$ (253.7 nm) process [18,20]:

$$\frac{[\text{H}_2\text{O}_2]_{\text{OPT}}}{[\text{S}]_0} = \left(\frac{\varepsilon_{\text{S}} k_{\text{S}}}{\varepsilon_{\text{H}_2\text{O}_2} k_{\text{H}_2\text{O}_2}} \right)^{0.5} \quad (\text{IX})$$

where $[\text{S}]_0$ is the starting concentration of pollutant, ε and k correspond to the molar absorption coefficient and to the second order rate constant of S or H_2O_2 , respectively.

However, Eq. (IX) was obtained after simplification due to complete absorption of the light. In our experimental conditions specially in terms of pollutants concentrations, total absorption of emitted light at 253.7 nm was not achieved, leading thus to the impossibility of using Eq. (IX). In this work, we demonstrated that $[\text{H}_2\text{O}_2]_{\text{OPT}}$ can be obtained by computer calculations when direct photolysis quantum yields, second order rate constants and parameters related to the photoreactor are known.

6. Conclusion

This work presents an investigation of UV (253.7 nm) and UV/ H_2O_2 degradation of benzenesulfonate derivatives (BS) in aqueous solution from a kinetic point of view. The quantum yields of BS photolysis have been determined to be about 0.03–0.05 for BS except nitro-substituted BS for which the phototransformation occurs about 100 times slower because of the strong deactivating effect of nitro group. In the presence of a large excess of hydrogen peroxide, no degradation of BS occurs in the absence of UV light. Upon irradiation, the degradation of BS is efficient because of the generation of hydroxyl radicals. Second order rate constants of HO^\bullet radicals reaction with BS have been determined. Values ranging from 0.7×10^9 to $12.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, very well correlated with Hammett constants, have been determined. Optimal starting concentrations of hydrogen peroxide leading to the fastest BS degradation were estimated by computer calculations.

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