The 20 kHz sonochemical degradation of trace cyanide and dye stuffs in aqueous media

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Cyanide in alkaline aqueous solution is reported to be destroyed by a facile sonochemical process. In the presence of power ultrasound emitted from a horn probe with a frequency of 20 kHz and up to 60 W cm^{-2} intensity a decay in the concentration with first order kinetics is monitored by ion selective electrode techniques. Characteristic features of the process are (i) a rate constant inversely proportional to the solution volume, (ii) a decrease in rate upon changing the gas phase in the reactor from air to argon, and (iii) an increase in rate in the presence of higher intensity ultrasound. With these characteristic features the process is interpreted in terms of a sonochemical degradation initiated by a high energy intermediate such as $OH^\cdot$ produced in violent cavitation events. Further evidence for this mechanistic conclusion comes from complementary experiments employing low concentrations of dyes (alizarin and Procion Blue) in aqueous solutions. The sonochemical degradation of these dye solutions with 20 kHz power ultrasound is monitored by following the UV–VIS absorption. Characteristic features for the dye degradation process are in agreement with those observed for the cyanide sonolysis and therefore attributed to the same kind of sonochemical mechanism. The sonochemical degradation of cyanide proceeds with a rate an order of magnitude faster than that of the dye bleaching, possibly due in part to the faster rate of diffusion of cyanide compared to the larger organic dye molecules.

Introduction

Over the last decade sonochemistry[1] has been developed into a powerful technique with important applications in synthesis,[2] electrochemistry[3] and waste treatment.[4] In particular the sonochemical degradation of chlorinated compounds such as chlorophenols[5] and chlorohydrocarbons[6,7] have been the focus of several studies aimed at the development of new methods for the elimination of traces of toxic materials. The mechanism proposed for these sonochemical processes is usually based on the formation of short lived radical species [eqn. (1)] generated in violent cavitation events.

$$H_2O \rightarrow OH^\cdot + H^\cdot \qquad (1)$$

The $OH^\cdot$ radical has been shown to be responsible for many of the chemical effects and elegant spin trapping work by Riesz and coworkers[8] comparing pulse radiolysis and sonolysis provided firm evidence for the proposed intermediates. However, other reaction pathways can be important, as shown for example in the direct pyrolysis of thermally unstable compounds such as nitrophenol[9] and direct oxidation induced by supercritical water.[4b,10]

There are many experimental parameters which affect the sonochemical process,[11] such as the ultrasound frequency,[12] the average temperature,[13] the presence of salts[14] and the nature of the gas phase species present.[15] Pulsed ultrasound has been shown to give improved chemical yields[16] and a reactor system employing more than one frequency applied in an orthogonal direction has been proposed.[17]

In the present study sonochemical processes which lead to the degradation of cyanide and dye bleaching in aqueous solution are reported for a 20 kHz horn transducer system. In conjunction with sonoelectrochemical studies,[18] in which hydrogen peroxide was generated electrochemically and used *in situ* to induce chemical transformations, the question emerged whether sonochemistry on its own may cause beneficial processes fast enough to compete with other conventional chemical processes. Therefore in this study an attempt is made to (i) understand the parameters responsible for sonochemical processes in a 20 kHz sonoreactor system and (ii) to quantify the sonochemical reactions so that direct comparisons of kinetic parameters are possible.

Experimental

Reagents

For sonochemical experiments and analytical reactions KCN, KOCN, KI (all Aldrich), NaOH (BDH), alizarin (Aldrich), Procion Blue (donated by Zeneca Fine Chemicals, Manchester), $Cu(NO_3)_2$ (BDH), pyridine (Aldrich), chloroform, H_2SO_4, and Na_2CO_3 (all BDH) have been used in analytical or the purest commercially available grade. High purity water was taken from an Elgastat filter system (Elga, High Wycombe, UK) with a resistivity of not less than 18 MΩ cm. Argon (Pureshield, BOC) was used for solution degassing where indicated.

Instrumentation

For experiments employing power ultrasound a Sonics and Materials VCX400 horn transducer system with a 1.3 cm diameter titanium alloy horn tip was used. The power output of this system was determined calorimetrically.[19,20] The sonoreactor used in this study (Fig. 1) was configured from a 400 ml volume jacketed Pyrex cell with lid and gas inlet connected to a thermostatted water bath.

The concentration of cyanide was monitored with an Orion model 9606 sure-flow combination cyanide ion selective electrode connected to a Jenway 3030 pH/mV meter (Jencons,

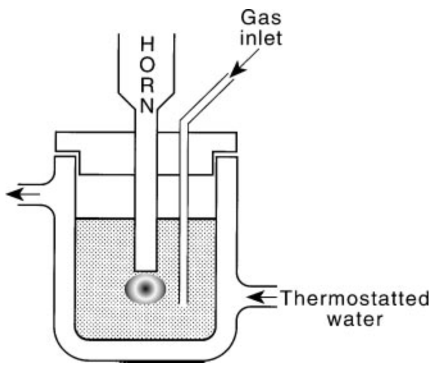


Fig. 1 Schematic representation of the 20 kHz sonoreactor employed in sonolysis experiments with a horn type ultrasound emitter immersed from the top.

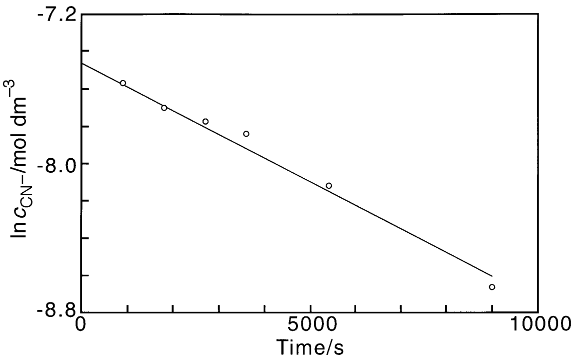


Fig. 3 Plot of the change in CN^- concentration *vs.* time observed during sonication (horn emitter, 20 kHz, 60 W cm^{-2}) of a solution in 200 ml aqueous 0.1 M NaOH.

UK). UV–VIS spectra were measured using a Unicam UV–VIS spectrometer (Unicam, Cambridge, UK). If not otherwise stated experiments were conducted at 20 ± 3 °C.

Results and discussion

The degradation of cyanide in aqueous media

Sonochemical procedures have been recognised to offer promising new approaches for the activation of heterogeneous as well as homogeneous chemical processes. However, apart from activation also completely new reaction pathways may be observed initiated by the formation of high energy intermediates in cavitation events. The sonochemical formation of $OH^{\bullet}$ and $H^{\bullet}$ in water, for example, has been well documented and experimentally verified by spin trapping methods[8] and comparison to pulse radiolysis studies. In the absence of reactive organic compounds, the sonochemical formation of $OH^{\bullet}$ radicals is followed by recombination processes, which lead to the formation of hydrogen peroxide.[21] The production of hydrogen peroxide therefore indicates indirectly the presence of high energy intermediates and allows the measurement of a relative sonochemical activity index.

In Fig. 2 the formation of hydrogen peroxide is verified and monitored by UV–VIS detection employing the iodine formation in acidified aqueous KI.[22] The plot in Fig. 2 shows data for a sample of 50 ml pure water exposed to 60 W cm^{-2} 20 kHz ultrasound in the reaction vessel shown in Fig. 1. Over a period of 6 min the concentration of hydrogen peroxide steadily increases. Under these conditions a rate constant for the formation of H_2O_2 of $k = (7.0 \pm 2.0) \times 10^{-7}$ dm^{-3} mol^{1} s^{-1} can be calculated from the experimental data. This value is in agreement with literature data for 20 kHz ultrasound.[9] For longer reaction times the decomposition of hydrogen peroxide in the absence of stabilising reagents is expected to decrease the rate of formation. It is also important to stress that the apparent rate of sonochemical hydrogen peroxide formation under the experimental conditions employed here is dependent on parameters such as the solution volume (*vide infra*). Strictly, these data may be used for comparison with other processes only if experiments have been carried out under similar experimental conditions.

The effect of 20 kHz ultrasound on the concentration of cyanide in aqueous 0.1 M NaOH is shown in Fig. 3. In this experiment the volume is 400 ml and 60 W cm^{-2} ultrasound emitted from a horn probe was used. A typical first order decay in the cyanide concentration is observed over a period of 2.5 h and the rate constant can be determined to be $k = (1.3 \pm 0.2) \times 10^{-4}$ s^{-1}. However, changing the solution volume, which undergoes sonication in the reactor, dramatically changes this rate constant as shown in Fig. 4. A decrease in volume causes an approximately inversely proportional increase in the rate constant for cyanide destruction. Obviously, the sonochemical reaction does not proceed homogeneously throughout the reactor volume but is presumably localised in a volume close the ultrasound emitting horn tip (see Fig. 1). From the geometry and size of the horn tip the reaction volume may be estimated to be $V_{\text{reaction}} \approx (3 \times 10^{-6}$ m^3 and a simple extrapolation of data given in Fig. 4 allows the rate constant in this volume to be estimated as $k \approx 2 \times 10^{-2}$ s^{-1}. Compared to rate constants of chemical processes, which are observed in sonoelectrochemical experiments[23] with a rate constant of 10 to 1000 s^{-1}, this is a very slow process. However, a comparison with other sonochemical processes reveals that the cyanide degradation is indeed comparatively fast and efficient (see Table 1).

Reducing the power output of the horn causes a proportional decrease of the observed rate constant for the cyanide destruction process. In Fig. 5 the dependence is demonstrated for the sonication of a solution of 0.5 mM KCN

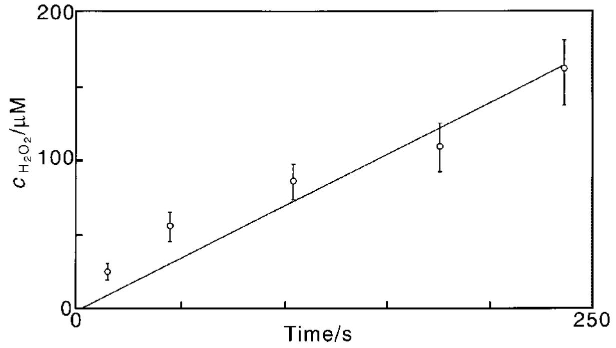


Fig. 2 Plot of the change in hydrogen peroxide concentration *vs.* time for a sonolysis experiment with 50 ml pure aerated water in the presence of 60 W cm^{-2} 20 kHz ultrasound.

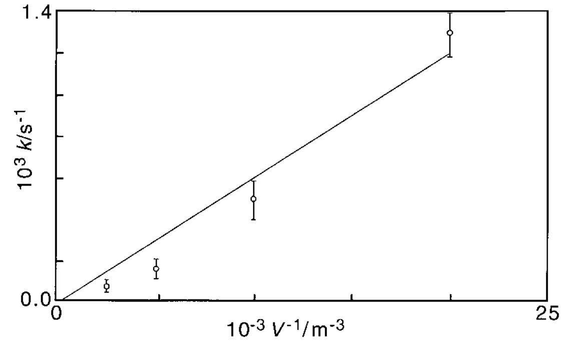


Fig. 4 Plot of the first order rate constant for the degradation of cyanide in aqueous 0.1 M NaOH (horn emitter, 20 kHz, 60 W cm^{-2}) *vs.* the inverse of the total solution volume.

Table 1 Kinetic data for the sonochemical degradation of trace organic compounds in aqueous solution in the presence of 20 kHz power ultrasound emitted from a horn probe

System	Volume/ml (atmosphere)	Ultrasound intensity/W cm^{-2}	Horn size diameter/cm	k/s^{-1}
Cyanide (0.1 M NaOH)	50 (air)	60	1.3	$(1.3 \pm 0.2) \times 10^{-3}$
	200 (air)	60	1.3	$(5.1 \pm 0.5) \times 10^{-4}$
	200 (argon)	60	1.3	$(2.1 \pm 0.2) \times 10^{-4}$
Alizarin (10 mM Na_2CO_3)	50 (air)	60	1.3	$(4.1 \pm 0.4) \times 10^{-5}$
	50 (argon)	60	1.3	$(3.6 \pm 0.4) \times 10^{-5}$
Procion Blue (H_2O)	50 (air)	60	1.3	$(5.1 \pm 0.5) \times 10^{-5}$
4-Chlorophenol (H_2O, 33 °C[5a])	100 (air)	50	1.1	$(5.5 \pm 0.3) \times 10^{-5}$

in 100 ml aqueous 0.1 M NaOH. The relationship between power output and rate of degradation clearly demonstrates that ultrasound causes the observed chemical transformation. The fact that the rate of the degradation process is independent of the cyanide concentration is further evidence for the process being based on a bulk solution process. First order sonochemical processes have been reported for many systems and have been explained in terms of a contribution from diffusion of reactants into the reaction centre near the cavitating bubble.[9,24] In order to rule out any contribution from a heterogeneous surface chemical process at the horn tip/solution interface an ultrasonic horn tip made out of stainless steel was used and the observed rate constants compared to those obtained with titanium alloy horn tips. Under otherwise identical reaction conditions (100 ml samples, 12 W cm^{-2}) rate constants for the cyanide destruction in aqueous 0.1 M NaOH measured with the steel tip were in good agreement with those measured with the conventional titanium alloy and therefore surface chemical effects and metal impurity effects were inferred to be negligible.

A reaction scheme consistent with the observed experimental data can be proposed based on the existing literature on ultrasound induced degradation processes. The reaction step most likely to initiate the cyanide degradation is the attack by the $OH^{\bullet}$ radical in the vicinity of a collapsing cavitation bubble. Although the products from the cyanide degradation reaction have not been identified, there is complementary information supporting this speculation available from the literature. In a pulse radiolysis study of the cyanide + $OH^{\bullet}$ reaction in pH-neutral aqueous solution the formation of cyanate as well as several other reaction products have been described.[25] A sensitive test reaction for the detection of cyanate[26] was used to quantify the amount of cyanate formed in the presence of ultrasound. The UV–VIS spectrophotometric analysis[27] of the products in the aqueous solution phase of the cyanide containing sample after a period of sonication of 1 h revealed no indication of cyanate as a major product. This finding is in contrast, for example, to the photochemical cyanide destruction at semiconductor surfaces[28] or the hydrogen peroxide method,[29] both giving predominantly OCN^-. However, cyanate anions are also known to undergo further chemical reaction steps with $OH^{\bullet}$ under pulse radiolysis conditions[30] and are known to be thermally unstable in alkaline solution.[26] Finally, the direct alkaline hydrolysis of cyanide at elevated temperatures is a known process[31] and could also contribute to the degradation process in the presence of ultrasound.

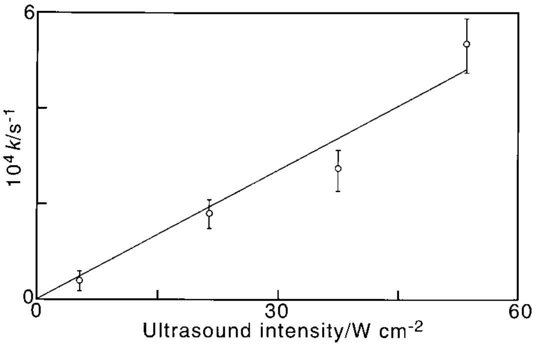


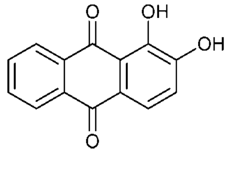
Fig. 5 Plot of the first order rate constant for the degradation of cyanide in 400 ml aqueous 0.1 M NaOH (horn emitter, 20 kHz) *vs.* ultrasound intensity.

Further experiments have been conducted to study the effect of the gas phase present in the sonochemical reactor on the rate constant for the cyanide degradation. Kinetic data are summarised in Table 1. It can be seen that a significant change in the first order rate constant occurs upon changing the gas phase from air to argon. The trend to a smaller rate in the presence of the monoatomic gas agrees well with the behaviour anticipated based on the polytropic ratio.[32] Therefore the change in the observed rate constant for the cyanide degradation upon exchanging the gas phase is further evidence for the process being sonochemically driven by cavitation.

The degradation of alizarin in aqueous media

Dye systems may be used as ideal model systems to quantify and verify the chemical effect of cavitation processes in a sonochemical reactor. This concept has, for example, been usefully employed in the sono-degradation of diphenylpicrylhydrazyl (DPPH) in organic solvents,[33] which allowed the effect of different types of solvents on the sonochemical degradation process to be studied. In this kind of bleaching process the progress of the reaction or the efficiency of the sonochemical process may conveniently be followed by direct UV–VIS spectroscopy.

The degradation of a solution of 5 μM alizarin[34] in aqueous 10 mM Na_2CO_3 in the presence of 20 kHz ultrasound followed by the characteristic UV–VIS absorption signal at 524 nm reveals a monotonous decay in concentration approximately following a first order rate law. The observed rate constant for the case of alizarin bleaching in a 50 ml solution volume is given and compared with other kinetic data in Table 1. It can be seen that the first order rate constant for the cyanide degradation process is faster by a factor of 30. An explanation for this considerable factor comes from the possibility that for low concentrations of reactants and under conditions in which first order kinetics are observed, the rate of diffusion may dominate the rate for the bimolecular reaction with $OH^{\bullet}$ radicals.[24] The tabulated value for the diffusion coefficient of cyanide in aqueous solution is 2.1×10^{-9} m^2 s^{-1}.[35] The diffusion coefficient for alizarin in water is considerably lower and may be assumed to be similar to the corresponding value for fluorescein, 0.3×10^{-9} m^2 s^{-1}.[36] This



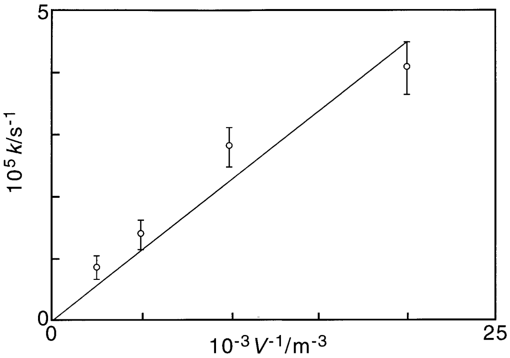


Fig. 6 Plot of the first order rate constant for the sonochemical alizarin (5 μM) bleaching process in aqueous 0.01 M Na_2CO_3 (horn emitter, 20 kHz, 60 W cm^{-2}) *vs.* the inverse of the total solution volume.

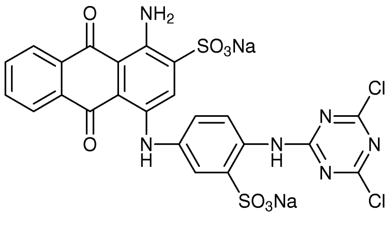
considerable difference in the rate of diffusional transport can, at least in part, explain the difference in the observed sonochemical rate constant.

The decay in the alizarin concentration monitored by UV–VIS spectroscopy revealed the anticipated first order kinetics. However, a parallel increase in the UV–VIS background signal over the 200–700 nm wavelength range had to be considered in the analysis. This increase in background was attributed to the formation of metal and metal oxide particles ejected from the horn tip during the sonication process. The characteristic features observed for the alizarin bleaching process are very similar to those detected in the cyanide degradation process. A pronounced volume effect (Fig. 6) clearly shows how the reaction is confined to a small volume near the tip of the horn probe. Further the change of the gas phase present in the sonoreactor caused a small change in the first order rate constant with a trend agreeing with the observations made for the cyanide degradation process (see Table 1).

The mechanism for the dye bleaching process is very likely to parallel that observed for other types of organic molecules associated with the presence of OH˙ radical species generated in the violent cavitation processes. A study of the pulse radiolytic bleaching of azo dye molecules in aqueous media[37] has been published recently with evidence for the nearly diffusion controlled bimolecular reaction between the dye and OH˙. On the other hand, the presence of sonochemically generated hydrogen peroxide in the solution phase may theoretically also contribute to the process. However, the known second order rate constants for the peroxide bleaching process, $k = 4.4 \times 10^{-3}$ dm^3 mol^{-1} s^{-1},[38] together with the extremely low concentration of sonochemically generated H_2O_2 in the order of 1–2 mM (*vide supra*) make the rate for this more indirect sonochemical oxidation process too small to compete and to account for the detected change in the dye concentration.

The degradation of Procion Blue in aqueous media

Finally, a solution of the reactive dye Procion Blue[34] has been investigated in the presence of 20 kHz ultrasound in the reactor shown in Fig. 1. Procion Blue is a reactive dye, used for direct covalent binding to fabric, which slowly hydrolyses in aqueous media. For a solution of 4 μM of this dye in water again an approximately first order decay in concentration induced by sonolysis is observed by direct UV–VIS spectroscopic monitoring at a wavelength of 598 nm (Fig. 7). The rate constant for the process, $k = (5.1 \pm 0.5) \times 10^{-5}$ s^{-1} (see Table 1), is very similar to that observed for the alizarin degradation. The characteristics for the bleaching process parallel those observed for cyanide degradation and alizarin bleaching and a similar reaction scheme is assumed to be responsible.



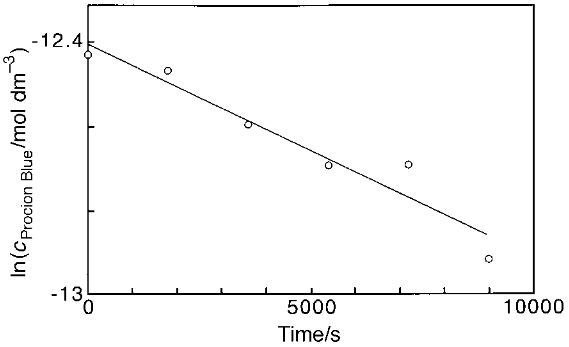


Fig. 7 Plot of the change in concentration of Procion Blue in water *vs.* sonication time in the presence of 20 kHz 60 W cm^{-2} ultrasound.

Kinetic data for the sonochemical destruction of chlorophenols in aqueous media using a very similar sonochemical reactor with 20 kHz horn probe published by Serpone *et al.*[5a] may also be compared with the results described here for cyanide and dye destruction. Although obtained in a 100 ml volume the rate constant for the reaction of 4-chlorophenol with OH˙ in the presence of ultrasound, $k = (5.5 \pm 0.3) \times 10^{-5}$ s^{-1}, is consistent with data obtained in this study.

Conclusions

It has been shown that the sonochemical degradation of cyanide anions and dye molecules in aqueous solution *via* treatment with 20 kHz ultrasound is possible. The characteristic features of the processes observed for the cyanide, alizarin and Procion Blue degradation are (i) dependence on ultrasound power, (ii) a first order rate constant approximately inversely proportional to the total solution volume, and (iii) effects induced by changing the gas atmosphere in the sonoreactor. All three processes are proposed to be initiated/dominated by a reaction with OH˙ produced locally in the vicinity of collapsing cavitation bubbles. However, direct evidence for the proposed mechanism based on the identification of products is not available. Differences in the observed first order rate constant under identical experimental conditions suggest that diffusion of the reactant into the reaction centre and/or additional thermolysis may be factors dominating the overall rate of the process.

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