ON THE MECHANISM OF POTASSIUM IODIDE SONOLYTIC OXIDATION IN DEOXYGENATED AQUEOUS SOLUTIONS [I] NOYES SCAVENGING KINETICS

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The oxidation mechanism of sonicated KI argonated aqueous solution has been studied at 25 ºC in the range of concentration 10^{-5} - 10^{-1} M, under 1 MHz and different intensities of the ultrasonic activation. The kinetic results concerning iodine generation (I_2, I_3^-) converged to: (i) Confirmation of our main previous results and reaction mechanism concerning the role of OH-radicals as the most important active intermediate species in the sonolysis of both oxygenated and deoxygenated KI aqueous solutions. (ii) The definite evidence of the geminate-recombination diffusional kinetics of the scavenging of the OH-radicals by the reducing I^- anions.

Introduction

There are now in use two main theories that explain the "true" intimate mechanism of the activation in the frequency range of the mechanical waves, i. e. infrasound: $\nu < 16$ Hz, sound: $16 Hz < \nu < 16 kHz$ and ultrasound: $\nu > 16$ kHz upon organic and mainly inorganic aqueous solutions [1,2]. These theories focus either on the electrical hypothesis of the polarized non-imploding cavitation bubbles [1] or on the hypothesis of the implosion with or without fragmentation [2]. The last theory takes into account the derived electrical interferences and establishes very interesting parallels between sonochemistry and coronachemistry. Though not completely banished, the elder explanations of the sonochemical effects on the basis of the adiabatic heating of the gas bubbles, the shockwaves, etc. are by now considered as rather inadequate ones [3÷5].

Despite any theoretical consideration it is generally recognized the fact of the OH-radicals generation is an effect of cavitation: no cavitation - no sonochemical activation.

Moreover the OH-radicals generation by the sonication of the aqueous solutions was undoubtedly experimentally proved by the fluorescence emission of the OH species, due to the transition:

$$A^2 \textstyle\sum^+ \to X^2 \Pi + h\nu \ (309 \div 310 \text{ nm}) \tag{1}$$
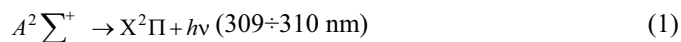
both in the case of sonoluminiscence [6,7] and coronaluminiscence [8] .

Our previous kinetic studies on the sonolysis both of inorganic aqueous solutions [9-11] and biphasic aqueous-organic systems [12] respectively, furnished kinetic proofs and kinetic models of these sonochemical reactions. These stand on OH-radicals generation

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under sonolysis as the main active intermediate species. The matter of fact is the OH/OH⁻ couple has a high standard oxidizing potential, $E_1^0 = +2.8V$ [13], considering for instance the corresponding $E_2^0 = +2.85V$ of the couple $\frac{1}{2}F_2/F^-$. Moreover the charge transfer is but diffusionally controlled, $k_d = (5\pm1) \times 10^9 \, M^{-1}s^{-1}$ [13a]. These kinetic and electrochemical arguments exclude the role of H_2O_2 as the main intermediate species in the sonolytic redox reactions as described by Weisler [14] and Lindstrom [15].

The aims of the present work are the followings:

(i)   A more accurate verification of the main experimental kinetic evidences of OH-radicals generation during the sonolysis of inorganic aqueous solutions, particularly the KI ones.

(ii)   A detailed examination of the influence of the KI concentration in the scavenging processes of OH-radicals generated by sonolysis. A special attention was paid to evidence as accurate as possible the geminate-recombination diffusionally scavenging domain. This obeys to Noyes' non-conventional kinetic equations [16÷18] that we partially proved to be independent on the type of activation: photochemical [19], thermal [20] or even sonochemical [10] one.

Experimental

a) Reagents: Merck p.a. KI further purified crystals were dissolved in dearated twice-distilled water directly in the quartz sonication vessel, at the natural pH, in order to obtain the desired substrate concentration. The solution volume was 150 mL. The solutions were subsequently deaerated by bubbling argon in the sonication vessel provided with inlet and outlet valves [21].

b) Analytical procedure: The iodine (I_2, I_3^-) amount generated by sonolysis was determined by microburette titration with freshly prepared and well-standardized $0.01N \, Na_2S_2O_3$ solution in the presence of starch indicator. Samples of 20 mL or in the case of very diluted solutions the entire 150 mL volumes were collected at precise intervals of sonolysis, titrated and I_2 amount was calculated for 150 mL volume of the solution.

c) The sonolytic set-up: We used a conventional Kovo piezoquartz ultrasonic generator, ULA-250 type and a quartz sonication cell provided with a thermostated wall, connected to an external ultrathermostat. Suitable access for the KI reactant as well as inlet and outlet valves for argonation were provided to the cell. The ultrasonic generator furnished a well-directed ultrasonic field alongside the sonication vessel, at a precise frequency of ν = 1 MHz. Well-controlled electric power could be applied to the piezoquartz, i.e., 160, 250, 350, 452 and 588 Watts, respectively.

d) Sonication procedures: Precise geometry and verified reproducible conditions of sonication were ensured. Volumes of 150 mL of KI argonated aqueous solutions were sonolyzed at 25 ºC, usually for durations of 0÷750 s from 20 to 20s, and the samples prelevated as above described **b)**. All kinetic experiments were reproduced three times for

better accuracy and precision. Tests for the influence of the applied power were made in order to compare them with our similar but less precise previous results [9÷12].

e) Data handling: consisted mainly in using linear and non-linear regression procedures by using either the experimental values only or both experimental and Lagrange interpolated values.

Results and discussion

(i) As previously observed the iodine generation by sonolysis obeys fairly well a first order kinetics for the oxygenated solutions [11] with no induction period and with correlation coefficients, $r = 0.998 \div 1.000$. The results are rather worse in the case of argonated solutions [9], with correlation coefficients $r \cong 0.98$ and rate constant errors of about $\pm 17\%$ for 8 experimental points including the origin. This discrepancy will be examined in more detail in a further note, providing that the overall sonolytic reaction of KI in argonated aqueous solutions is a rather complex one.

However in what the test of the main processes involved in the stationary generation of OH-radicals is concerned [11]:

$$H_2O \xrightarrow{\;k\,P_0\;}))) \; H^\bullet + \overset{\bullet}{O}H \tag{2}$$

$$H^\bullet + \overset{\bullet}{O}H \xrightarrow{\;k_1\;} H_2O \tag{3}$$

the conventional kinetic treatment assuming a small contribution of the scavenging reactions in OH-radicals consumption leads to the following relationship between the reaction rate v ($M\cdot s^{-1}$) and the electrical applied power, P_0 (W):]

$$v = v_0 + kP_0^{1/2} \tag{4}$$

where v_0 ($M\cdot s^{-1}$) is a limiting rate value ($M\cdot s^{-1}$) due to these scavenging reactions. Fig. 1 illustrates the validity of equation (4) and confirms and completes our previous results [9,11,12].

The equation (4) is quite well verified, e. g. 5 experimental points, correlation coefficient $r = 0.998$; $v_0 = (3.32\pm0.29)\ 10^{-9}\ M\cdot s^{-1}\ (\pm9\%)$; $k = (3.67\pm0.15)\ 10^{-9}\ M\cdot s^{-1}\ W^{-\frac{1}{2}}\ (\pm4\%)$. One can conclude the processes (2) and (3) are kinetically reconfirmed.

(ii) In a previous note [10] concerning the sonolytic oxidation of Fe (II) sulphate in acid aqueous solutions we observed that Fe^{2+}_{aq} ions act as efficient scavengers for the OH radicals. By chance the scavenger concentration range we explored superimposed partially over the Noyes' domain [13b]. Consequently we put into evidence a geminate-recombination scavenging kinetics though not completely and not so clearly. Detailed kinetic measurements over a large KI concentration range in oxygenated aqueous solutions [11] did not evidence such effects. This is probably due to O_2 saturation level, acting like a nivelating Noyes' scavenger. We presumed such effects can be observed only in the absence of O_2 and explored the entire range $10^{-5} \div 10^{-1}$ M of KI concentrations in sonicated argonated solutions.

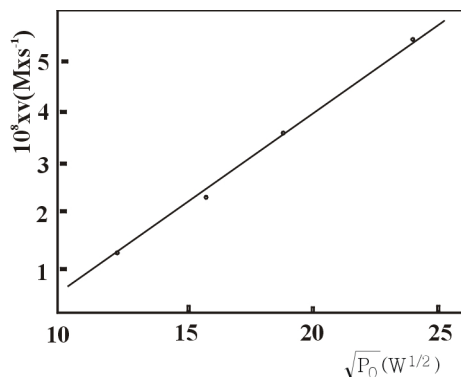Fig. 1: *The kinetic evidence of radicalar nature of steady-state generation of OH species under sonolysis:* [I⁻] = 10⁻² M; *t* = 25 ºC; ν = 1 MHz; the sonicated solution volume, 150 mL.

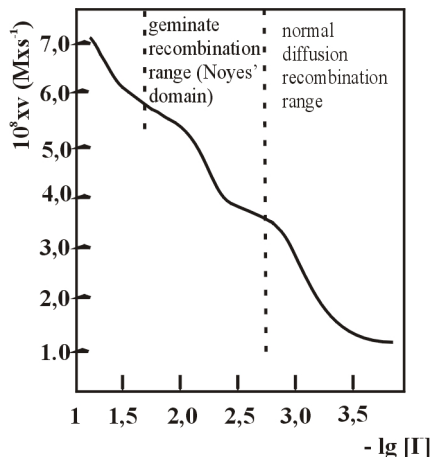Fig. 2: *The dependence v* (M⁻ s⁻¹) *versus –log[I⁻] for the scavenging effect of I⁻ ions on the sonolytic generated OH radicals:* t = 25 ⁰C; *v* = 1 MHz; P_0 = 588 W; the sonicated solution volume, 150 mL.

As established for the photochemical reactions, the relative reaction rate, v/v_1 were v_1 is the maximum reaction rate value, or the absolute and the relative quantum yields depend on the square root of the scavenger concentration in the Noyes' domain [16,17]. Moreover the scavenging process though an elementary one does not obey a conventional kinetics. Consequently no rate constant can be attribute to it. The reaction rate is best characterized under such conditions by the reaction probability that is a function of the reaction time, t, more precisely depends on $t^{-3/2}$. The scavenging process is controlled by the random motions of the active molecular fragments, in our case OH-radicals in the proximity of the solvent cage wall not by the diffusion in bulk solution. Consequently both the simplest and the more sophisticated models of such scavenging processes estimate the lifetime of the molecular fragments in the range 10÷100 ps. In Fig. 2 is shown the experimental dependence of the reaction rate, v on the –log[I⁻], surprisingly similar to the theoretical predicted one for the case of photochemical reactions [13b].

One observes the Noyes' domain is located approximately in the range $1.8^x10^{-3}÷2.2^x10^{-2}$ M of KI concentrations. The checking-out of the corresponding simplest Noyes' equation:

$$v\!\!\Big/\!\!_{v_1} = q + p[I^-]^{1/2} \tag{5}$$

were q and p are specific parameters. The most important one, p, is defined by the equation:

$$p = 2a \cdot (2\pi k_s)^{1/2} \tag{6}$$

were a ≅ 10^{-6} M$^{-1/2}$ for common solvents, e.g., H_2O, describes the random solvent molecules motion nearby the solvent cage and k_s (M^{-1}s^{-1}) is a pseudo second order rate constant of the scavenging process [16,17]. Table 1 summarizes the main experimental and derived values corresponding to the Noyes' domain.

Table 1 The experimental and derived values corresponding to Noyes' domain:
$t = 25\ ^oC$; $\nu = 1$ MHz; $P_0 = 588$ W; the sonicated solution volume, 150 mL.

$10^3 \cdot [I^-]$ (M)	$10^2 \cdot [I^-]^{1/2}$ ($M^{1/2}$)	$10^8 \cdot v$ ($M \cdot s^{-1}$)	v/v_1
1.0	3.162	2.862	0.519
2.5	5.000	3.468	0.628
5.0	7.071	3.872	0.701
7.5	8.660	4.444	0.805
10.0	10.000	4.983	0.902
25.0	15.811	5.522	1.000

The Noyes' equation was verified graphically and the plot is shown in Fig. 3.
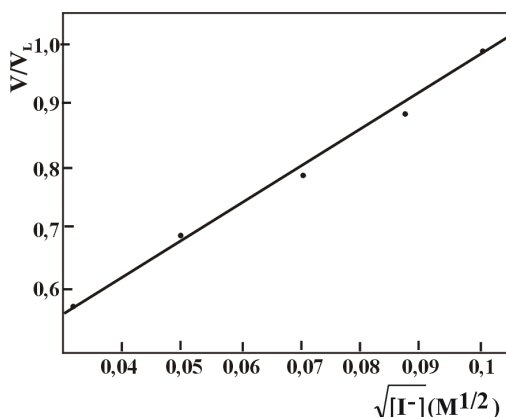

Fig. 3: *The linear dependence of v/v_1 versus $[I^-]^{1/2}$ (Noyes' equation):*
$t = 25^oC$; $\nu = 1$ MHz; $P_0 = 588$ W; the sonicated solution volume, 150 mL.

The non-linear regression of the experimental and Lagrange interpolated data taking into account equation (5) led to the following results: $q=(0.3813\pm0.0286)$ $(\pm7.5\%)$; $p=(5.9949\pm0.3977)$ $M^{-1/2}$ $(\pm6.6\%)$; estimation error $= \pm2.8\%$. By using the values of $a \cong 10^{-6}\ M^{-1/2}$, $p = 5.9949\ M^{-1/2}$ and the equation (6) one obtained for $[I^-]=0.02$ M a lifetime value of the OH-radicals, $\tau = 35$ ps, corresponding to that predicted by Noyes' theory.

Therefore the KI sonolytic oxidation in argonated aqueous solutions can be explained satisfactorily besides the processes (2) and (3) by the following ones:

$$I^- + \overset{\bullet}{O}H \xrightarrow{\ k_2\ } I^\bullet + OH^- \tag{7}$$

$$2I^\bullet \xrightarrow{\ k_3\ } I_2 \tag{8}$$

$$I_{2aq} + I^- \xleftarrow{\ K\ } I_3^- \tag{9}$$

The process (7) is a scavenging elementary one and has no rate constant. All processes are very fast and the reaction rate will depend mainly on $P_0^{1/2}$, following closely the steady state concentration of the OH-radicals. The kinetic model (2)÷(9) holds exclusively for relative short sonication intervals, less than 750 s and the $[I^-]$ within 1.5 mM÷25 mM.

Conclusions

(i)   At relatively low substrate conversions, ~ 10%, and at 1.5 mM < [I⁻] < 25 mM the OH-radicals reduction obeys the Noyes' equation (5), corresponding to the geminate-recombination scavenging processes nearby the solvent cage. Consequently at [I⁻] < 1.5 mM, the OH-radicals reduction will be governed by the diffusionally controlled processes in bulk solution. This kind of non-conventional Noyes' kinetics seems to be more common than earlier presumed, independent of the type of activation: thermal, photochemical and by now the sonochemical one.

(ii)   The kinetic model (2)÷(9) explain satisfactorily the experimental data taking into account the very high oxidizing potential of the OH radicals.

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