

# ON THE MECHANISM OF POTASSIUM IODIDE SONOLYTIC OXIDATION IN DEOXYGENATED AQUEOUS SOLUTIONS.

## [II] KINETIC MODEL OF THE SATURATION EFFECT

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The oxidation kinetics of sonicated KI argonated aqueous solution differs significantly from that of the oxygenated ones whether sonolysis duration is large enough. One observed a sigmoid shape of the ( $I_2, I_3^-$ ) concentration versus the sonication time exhibiting reproducible saturation plateau.

A reaction kinetic model explaining these peculiarities was proposed, taking into account the exceptionally high oxidation power of the OH radicals, leading to  $IO^-$  and higher oxidized species.

The model was well verified by using the non-linear regression in handling the experimental data. The reaction rate  $V(\text{Ms}^{-1})$  dependence upon the concentration of sonolytic generated iodine as  $I_2$  and  $I_3^-$  verifies the equation of the kinetic model.

### Introduction

In our previous works [1,2] as well as in the note (I) [3] have been described both the essential characteristics and the general mechanism framework of KI sonolysis in the aqueous solution respectively. The main notes of this mechanism are the followings:

- (i) The generation of OH radicals during sonolysis as the major oxidizing active intermediate species in both oxygenated and argonated solution respectively.
- (ii) The important contribution of the geminate recombination scavenging processes of the OH radicals by the  $I^-$  ions, obeying the non-conventional Noyes kinetics [4, 5] at KI concentration exceeding 1.5 mM.
- (iii) The clear difference between the iodine ( $I_2, I_3^-$ ) sonolytic generation kinetics in oxygenated and the argonated KI aqueous solution. For instance at sonolysis durations below approximately 700 s, the iodine generation obeys fairly well a zero order kinetics in oxygenated solution but substantially worse in the argonated ones. For the oxygenated solutions the correlation coefficients are  $r=0.998\div 1.000$  and the rate constant errors don't exceed  $\pm 2-3\%$ . In the case of the argonated solution under exactly the same condition one obtained quite different values, e.g.  $r\sim 0.98$  and errors values of  $14\div 17\%$ .

The aim of this work was to explore in more detail the reproducibility of the saturation effects observed in the case of the argonated KI solution sonolysis and to offer a reasonable

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explanation of these effects in the terms of a simple a simple but acceptable reaction mechanism. Thence one can complete the kinetic features and the reaction mechanism of the iodine sonolytic generation in KI aqueous solutions.

## Experimental

The reagents, the analytical and the sonicated procedures as well as the sonolysis set-up have been presented in some details in the previous works [2,3]. More information about the sonolysis set-up can be found in N. Popa's Dissertation [6].

## Results and discussions

The sonolysis of argonated KI aqueous solutions for durations exceeding substantially 700s, revealed a sigmoidal shape of the kinetic curve of the iodine ( $I_2, I_3^-$ ) generation, as can be easily seen in Fig. 1.

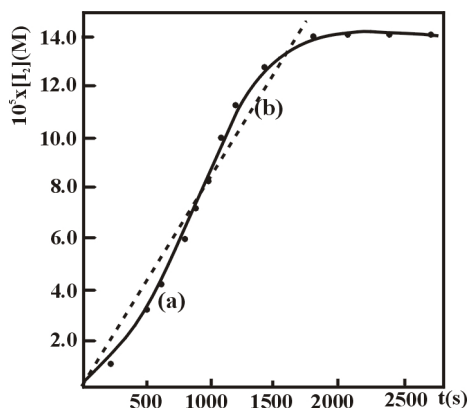


Fig. 1: The kinetic curve of iodine sonolytic generation in KI argonated aqueous solutions at large time of sonication.  $t = 25\text{ }^{\circ}\text{C}$ ;  $\nu = 1\text{ MHz}$ ;  $P_o = 588\text{ W}$ ;  $[\text{KI}] = 1\text{ mM}$ ;  $t_{\text{max}} \cong 90\text{ minutes}$ ;  $X_{\text{max}} \cong 28\%$ ; sonicated solution volume, 150 mL.

- a) solid curve - experimental dependence of  $[\text{I}_2]$  (M) versus the sonication time,  $t$ (s);  
 b) dotted curve - the supposed linear relationship between the experimental values:  $r = 0.998$ ; slope error =  $\pm 26\%$ .

It is obviously inadequate to consider the iodine generation to be first order though the correlation coefficient for 11 experimental points including the origin is  $r = 0.988$ . There are two reasons to reject such a linear relationship:

- (i) The slope error of  $\pm 26\%$  exceeds largely any error associated to both the tested analytical procedure and the reproducibility of the sonication conditions respectively ( $< 1\div 3\%$ ).
- (ii) At sonication times exceeding 30 minutes the iodine concentration as  $I_2$  and  $I_3^-$ , reaches a plateau that maintains for at least an hour. This result is very reproducible and clearly indicates that a saturation steady state establishes.

There are two possible explanations for such a kinetic curve shape:

- a. The solution becomes steadily degassed and the cavitation as well as sonolytic iodine generation decrease correspondingly. It is rather doubtfully to take into account this explanation. On the one part at large ultrasound frequency (1MHz) the cavitation is an unstable one, the gas bubbles are too small to aggregate and redissolve in bulk solution. On the other part the presumably evolved argon gas accumulates at the solution surface with increased pressure and redissolves according to Henry's law, especially for large durations of 30-90 minutes. In the worst case the  $[I_2]$  should increase slowly but not reaching a plateau. Moreover we did not observe  $pH$  variations subsequent to such a model.
- b. There is some chemistry involved in pure chemical or in the mixt sonochemical and chemical consumption of the generated iodine during the sonolysis of KI. Due to the almost highest oxidizing potential of the OH radicals ( $E_1^0 = +2.8$  V), the probability that I and  $I_2$  species to be oxidized at  $IO^-$  and thereafter at  $IO_3^-$  stable ions is large enough [7]. Thence one can explain the plateau in Fig. 1 as a result of the equal reaction rates of the sonolytic generation and the consumption of iodine. By considering the explanation b) we proposed a possible kinetic model as follows:



Though apparently complicated this kinetic model is quite well justified. The steps (1)-(5), were established in the previous works [1,3], the steps (7), (9) and (10) are obvious and one has to justify the steps (6) and (8). These ones are electrochemically allowed because even for the oxidizing  $I^*$  species the standard redox potential is  $E_2^0 = +1.42$  V [7] to say nothing

about  $I_2$ , by comparison to that of OH radicals  $E_1^0 = +2.8V$  [7]. For the step (3) one attributed a second order rate constant  $k_2$  because the concentration of KI substrate is 1mM. This concentration is definitely below the lowest limit of the Noyes' domain and the process is diffusionally controlled in bulk solution. The only objection that can be arose consists in the fact the  $IO^-$  species are unstable. They lead by secondary reactions to the more stable  $IO_3^-$  ions that can distort the overall kinetics resulted from the model we proposed. To anticipate, the model verification did not put in evidence such distortions. Simple mathematical treatment of the proposed kinetic model in the assumption of the steady-state approximation validity led to the overall reaction rate equation:

$$v = a \times ((b + c[I_2])^{1/2} - 1)^2 - d[I_2] \quad (11)$$

where:  $a = (k_1 P_0 / 4k_3)(k_4 + k_5)^2 \quad (12)$

$$b = (k_2[I^-] + k_4 + k_5)/(k_4 + k_5) \quad (13)$$

$$c = k_6/(k_4 + k_5) \quad (14)$$

$$d = (k_1/k_3)^{1/2} k_6 P_0^{1/2} \quad (15)$$

In order to verify the proposed kinetic model, at least qualitatively, we used a nonlinear regression test of the equation (11) based on the Newton - Raphson method. In this respect we approximated the integral kinetic curve data illustrated in Fig. 1 by using two third order polynomials with the following characteristics:

- First polynomial: correlation coefficient,  $r = 0.999$ ; determination coefficient, c. det. = 0.997; estimation error =  $\pm 5.7\%$ .
- Second polynomial: correlation coefficient,  $r = 0.999$ ; determination coefficient, c. det. = 0.997; estimation error =  $\pm 1.3\%$ .

The reaction rate,  $v$  ( $M \cdot s^{-1}$ ), values at precise iodine concentrations,  $[I_2]$  were calculated by derivation of the polynomials. We used 51 interpolated values in the non-linear regression calculation. The shape of  $v$  versus  $[I_2]$  dependence is presented in Fig. 2 for 35 interpolated values only.

As expected the reaction rate curve is asymmetrical, with a maximum located at a conversion of about 18% and with no inflection points. The results of the non-linear regression calculation were the followings:

$$a = 2.66 \times 10^{-6} (\pm 1\%) M \cdot s^{-1}; b = 1.88 (\pm 0.1\%);$$

$$c = 2203 (\pm 0.1\%) M^{-1}; d = 4.25 \times 10^{-3} (\pm 1\%) s^{-1};$$

estimation error =  $\pm 3\%$ .

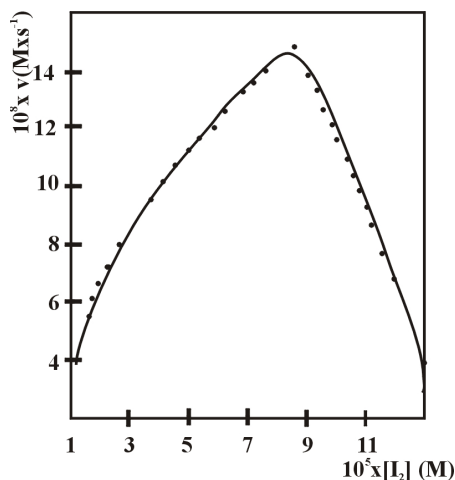


Fig. 2: The reaction rate  $v$  ( $M \cdot s^{-1}$ ) dependence versus iodine concentration,  $[I_2]$  ( $M$ ) in the sonolysis of KI argonated aqueous solutions:  $t = 25^\circ C$ ;  $\nu = 1$  MHz;  $P_o = 588$  W;  $[KI] = 1$  mM;  $t_{max} \cong 90$  minutes;  $X_{max} \cong 28\%$ ; sonicated solution volume, 150 mL; 35 interpolated couples of values.

## Conclusions

- (i) Though considered as a starting approximation, the kinetic model we proposed was unexpectedly well verified. Taking into account the parameters' error values that they seem to be not a result of a convenient compensation of experimental and computation deviations.
- (ii) For the time being it is hazardous to make kinetic parameters' evaluations. One needs more work to propose alternate kinetic models in order to be compared with that proposed in this work. Moreover one needs proofs of the oxidized iodine compounds involved and their kinetics.
- (iii) The present work explains and completes our previous studies concerning the KI sonolysis of both oxygenated and argonated aqueous solutions of this substrate.

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