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Degradation of aqueous solution of potassium iodide and sodium cyanide in the presence of carbon tetrachloride

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Abstract

The degradation of potassium iodide, carbon tetrachloride and sodium cyanide has been studied using an ultrasounic probe of 20 kHz frequency. In the case of potassium iodide and sodium cyanide, the rate of degradation was much higher in presence of CCl_4. The location of the ultrasonic horn showed a significant effect in the degradation of CCl_4. © 1997 Elsevier Science B.V.

Keywords: Degradation; Sonication; Carbon tetrachloride

1. Introduction

Ever since the first paper published by Richard and Loomis [1] on the effects of ultrasound on chemical reactions, the scientific community has shown a greater interest in the application of ultrasound to chemical reactions. This application to the chemical reactions has been either to induce a chemical reaction which is not possible by other conventional methods, or to enhance the rates of reaction. A large number of reviews [2,3] have appeared which give in-depth knowledge of the wider application of ultrasound in chemical reactions. This is largely attributed to the ability of ultrasound to generate high temperatures and pressures at ambient conditions by cavitation. Like any other sound waves, ultrasound posses rarefaction and compression phases. The rarefaction phase generates cavities, while the compression phase causes the collapse of these cavities. Collapse of these cavities produces conditions of high temperatures of 5000°C and pressures of up to 1000 atm in or around the collapsing cavities. These 'hot spots' [4] are the principle factor for any sonochemical reactions.

Treatment of industrial hazardous waste has always been a major problem. Many techniques are available to recover or eliminate the toxic chemicals, and include adsorption, wet air oxidation, etc. Ultrasound, with its simple methodology and apparatus requirements, has been used as a tool for eliminating CFCs [5], hydrogen sulfide [6] and refractory waste [7]. In this article we report studies on the decomposition of aqueous solutions of potassium iodide, carbon tetrachloride and sodium cyanide in the presence and absence of carbon tetrachloride.

2. Experimental

An ultrasonic horn of 22.7 kHz frequency and operating at a rated power output of 240 W was used as a source of ultrasonic energy. A known concentration of KI (50 ml) and a known volume of carbon tetrachloride were taken in a 100 ml beaker. To this, a few drops of freshly prepared saturated starch solution was added. The reaction mixture was placed in a water bath mounted on a magnetic stirrer and then irradiated with ultrasound. As the density of CCl_4 is than water, it settles down in the aqueous phase, and hence no CCl_4 could escape into the atmosphere. In addition, preliminary results have shown that the material balance was satisfied in terms of the amount used up for the decomposition and the amount left in the system. The experimental setup is shown in Fig. 1. The iodine liberated was estimated by titrating with standard sodium thiosulphate. In the absence of CCl_4, the iodine liberated was analysed on a UV–VIS spectrophotometer at 354 nm, since the amount of iodine liberated was too low to be titrated against sodium thiosulphate.

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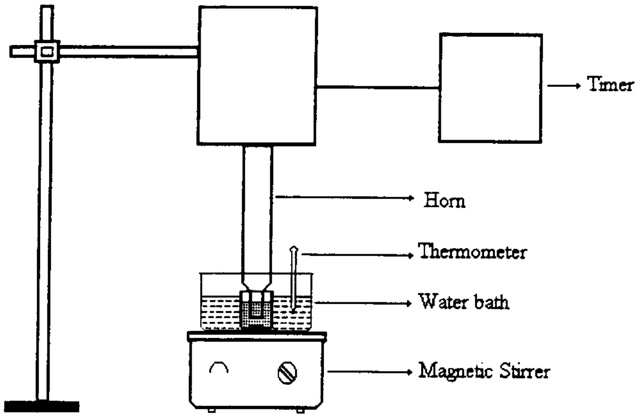

Fig. 1. Experimental setup.

The degradation of carbon tetrachloride alone (in absence of KI) in aqueous silver nitrate was monitored by determining the residual concentration of silver nitrate after filtering the white precipitate of silver chloride obtained through a sintered glass crucible. The formation of silver chloride precipitate could be as a result of chlorine free radicals [8]. The filtrate concentration, i.e. the residual silver nitrate concentration, was determined by titration with standard sodium chloride using potassium chromate as an indicator [9]. The amount of carbon tetrachloride degraded was estimated as a function of the normality of the unreacted silver nitrate. The residual concentration of cyanide was measured with standard silver nitrate solution with dimethylamine rhodanine as an indicator [10].

3. Results and discussion

3.1. Degradation of aqueous KI

The oxidation of potassium iodide has been widely used as a model reaction to study the various cavitational parameters [8,11,12]. The effect of various parameters, such as absence and presence of carbon tetrachloride, amount of carbon tetrachloride, temperature, volume and concentration of the KI solution, were studied.

The effect of temperature was studied at KI concentrations of 0.06 and 0.301 mol l^{-1}. Plots of ln[KI]$_0$/[KI] versus time gave a straight line (Fig. 2). From the figure it is seen that with an increase in temperature, the relative rate decreases, which complies with the theoretical concepts of ultrasound [13], which states that the rise in temperature would reduce the

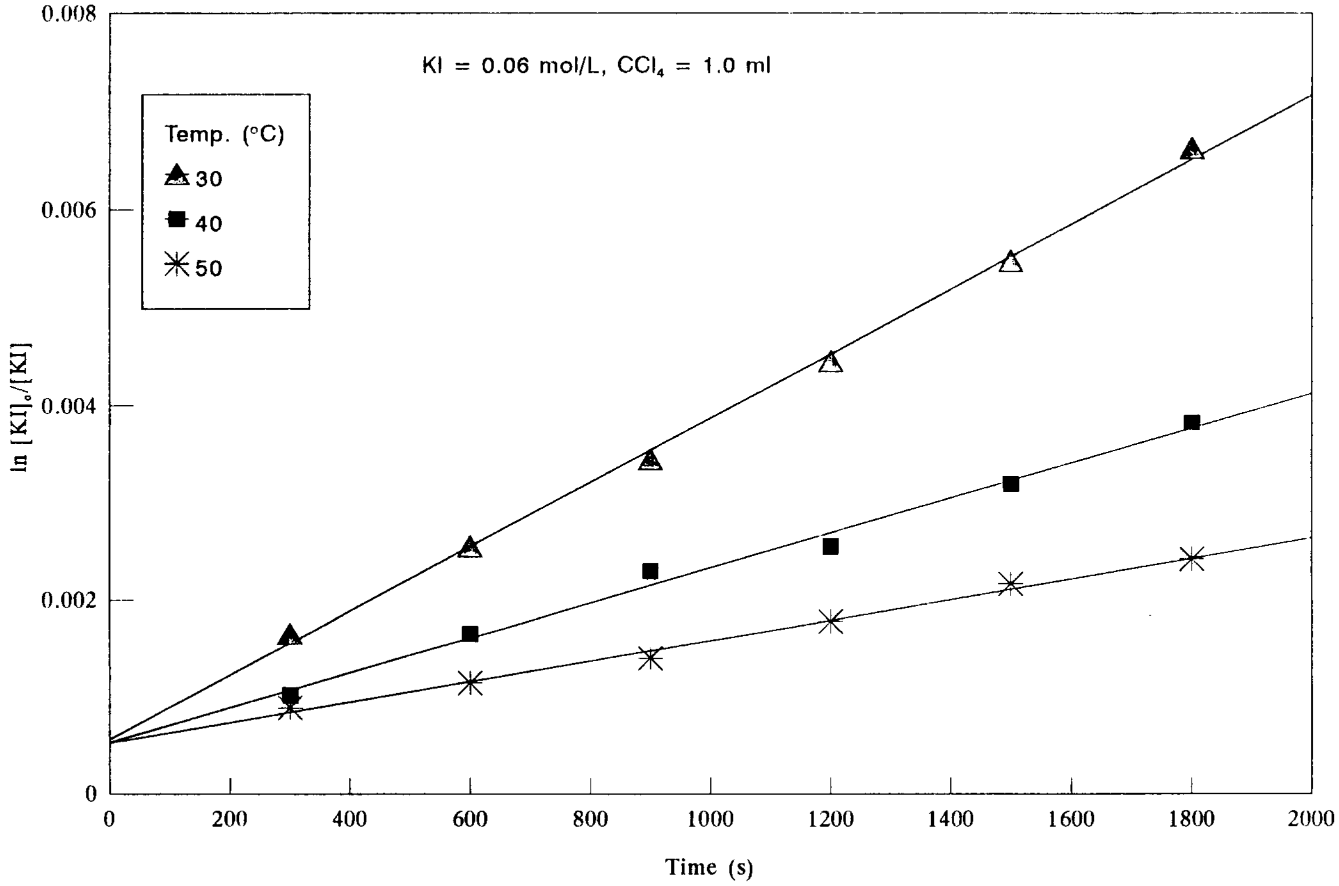

Fig. 2. Plot of ln[KI]$_0$/[KI] at different temperatures.

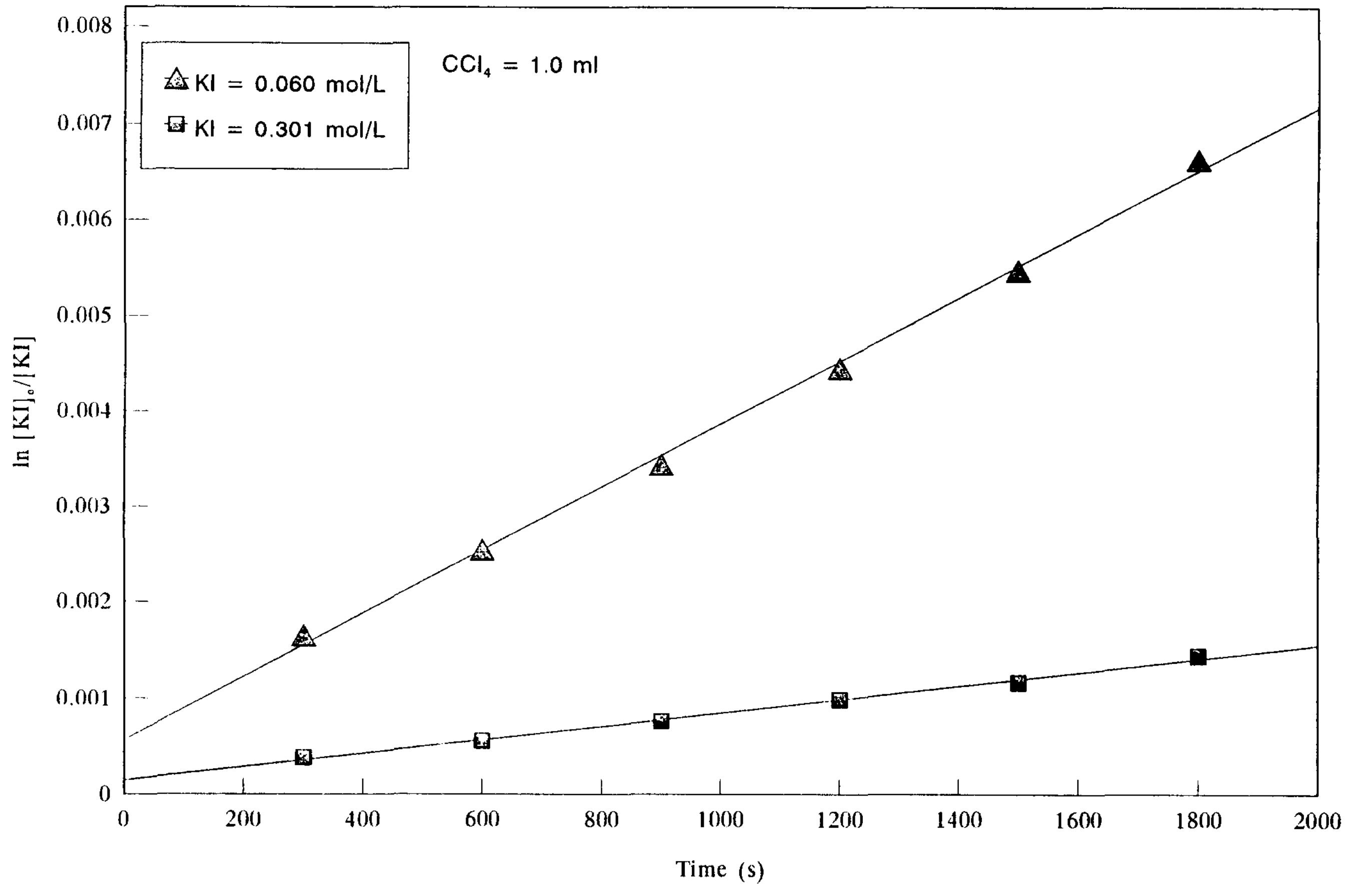

Fig. 3. Effect of concentration of KI on the rate of degradation.

temperature and pressure generated in the cavity, thereby reducing the intensity of the cavity collapse. This observation is also noticed when the concentration of KI was 0.301 mol l^{-1}. It can be seen from Fig. 3 that at a constant temperature the rate of iodine liberation for 0.301 mol l^{-1} KI solution is only marginally higher (though the relative rate is lower) than that for 0.06 mol l^{-1} KI. Gutierrez et al. [14] (ultrasonic frequency 1 MHz) have also observed that the yield of iodine is independent of the solute concentration. Naidu et al. [12] (ultrasonic bath, 25 kHz), on the other hand, have observed that the relative rate of iodine liberation increases with an increase in KI concentration. They attributed this increase to two factors: (i) the amount of hydroxyl radicals contained in the collapsing bubbles, which increase with KI concentration, but are present to a lesser extent in the liquid phase for recombination; and (ii) as the concentration of iodide is increased, the consumption of hydroxyl radicals by iodide ions becomes more effective than by the recombination of radicals for higher concentration of KI. This discrepancy in both the cases could be attributed to the frequency of the ultrasonic source used as frequency is known to affect the life of a cavity.

The presence of carbon tetrachloride had a significant effect on the oxidation reaction. In the absence of carbon tetrachloride the relative rates were much less than that in the presence of carbon tetrachloride, as shown in Fig. 4. The relative rates were higher by three orders of magnitude in the presence of carbon tetrachloride than in its absence for 0.06 mol l^{-1} KI solution, whereas they were higher only by two orders of magnitude in the case of 0.301 mol l^{-1} KI solution, which is consistent with the observation of rate being practically independent of KI concentration. This large difference is due to the formation of two oxidants, i.e. hydrogen peroxide and free chlorine, which are responsible for the higher rates in the presence of CCl_4, while only hydrogen peroxide is formed in the absence of CCl_4. In this case also, the rates decreased with an increase in the temperature.

It is interesting to note that when the volume of carbon tetrachloride is varied, there is no significant change in the relative rates of the decompostion once CCl_4 concentration was above a certain value (Fig. 5). This could be due to the fact that considering the higher concentration of KI solution in comparison with amount of CCl_4, the concentration of chlorine formed from the degradation of CCl_4 was only proportional to the CCl_4 present in the aqueous phase. Independent studies of sonicating pure CCl_4 resulted in no degradation due

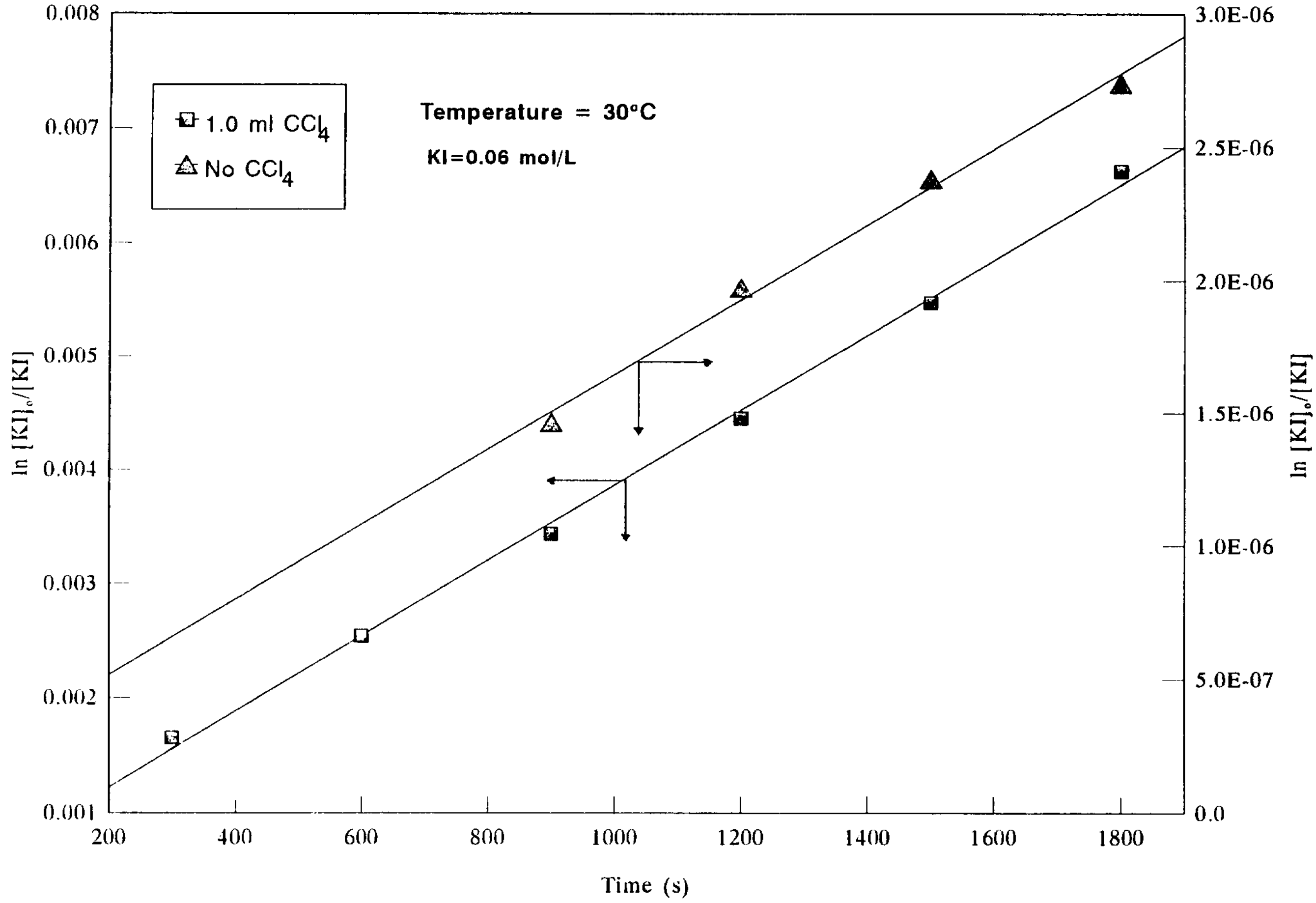

Fig. 4. Effect of CCl_4 on KI degradation.

to the difference in vapour pressure and its effect on the cavitational intensity.

The change in the volume of KI solution also showed a change in the relative rates of reaction. This was studied by varying the volume of KI solution in the range 20–50 ml while the amount of carbon tetrachloride and concentration of KI used was same in all the cases, and was subjected to 10 and 20 min of sonication. The results are shown in Table 1. It can be seen from the table that with an increase in time, for a particular volume of KI, the rate constant increases, and also with an increase in volume of KI solution, the relative rate of decomposition decreases. This rate dependence on time may be due to the limiting quantity of CCl_4 available to decompose KI, or due to the reduction in the leftover KI concentration. A correlation between the rate constant (k) and P/V (where V is the volume in m^3 and P is the power in W) for 10 min of sonication was obtained as:

$$k=4.77\times10^{-22}(P/V)^{2.33} \quad (r^2=0.83). \tag{1}$$

The correlation obtained for 20 min of sonication is as follows:

$$k=5.82\times10^{-17}(P/V)^{1.61} \quad (r^2=0.89). \tag{2}$$

The average correlation over the entire period was obtained as:

$$k=5.17\times10^{-19}(P/V)^{1.87} \quad (r^2=0.87). \tag{3}$$

It can be seen from the above equations that the exponent over (P/V) for 10 and 20 min, and overall are 2.33, 1.61 and 1.87, respectively. This indicates that the fraction of the total power utilized is higher in the early period of decomposition compared to that over the longer duration.

The Arrhenius equation, $k=Ae^{-E/RT}$, was used to determine the activation energy (E) from the slope of the plot of $-\log k$ against $1/T$ (slope$=E/2.303R$) (Table 2). From the table, it can be seen that the activation energies were 38.35 and 16.57 kJ mol^{-1} for KI concentrations of 0.06 and 0.301 mol l^{-1}, respectively, in the presence of carbon tetrachloride, while in the absence of carbon tetrachloride the activation energies for 0.06 and 0.301 mol l^{-1} KI solutions were comparable, i.e. 18.49 and 20.77 kJ mol^{-1}, respectively. Activation energy is a function of temperature. A higher value of activation energy (38.35 kJ mol^{-1}) for 0.06 mol l^{-1} KI in the presence of CCl_4 indicates the larger dependence of the reaction on temperature.

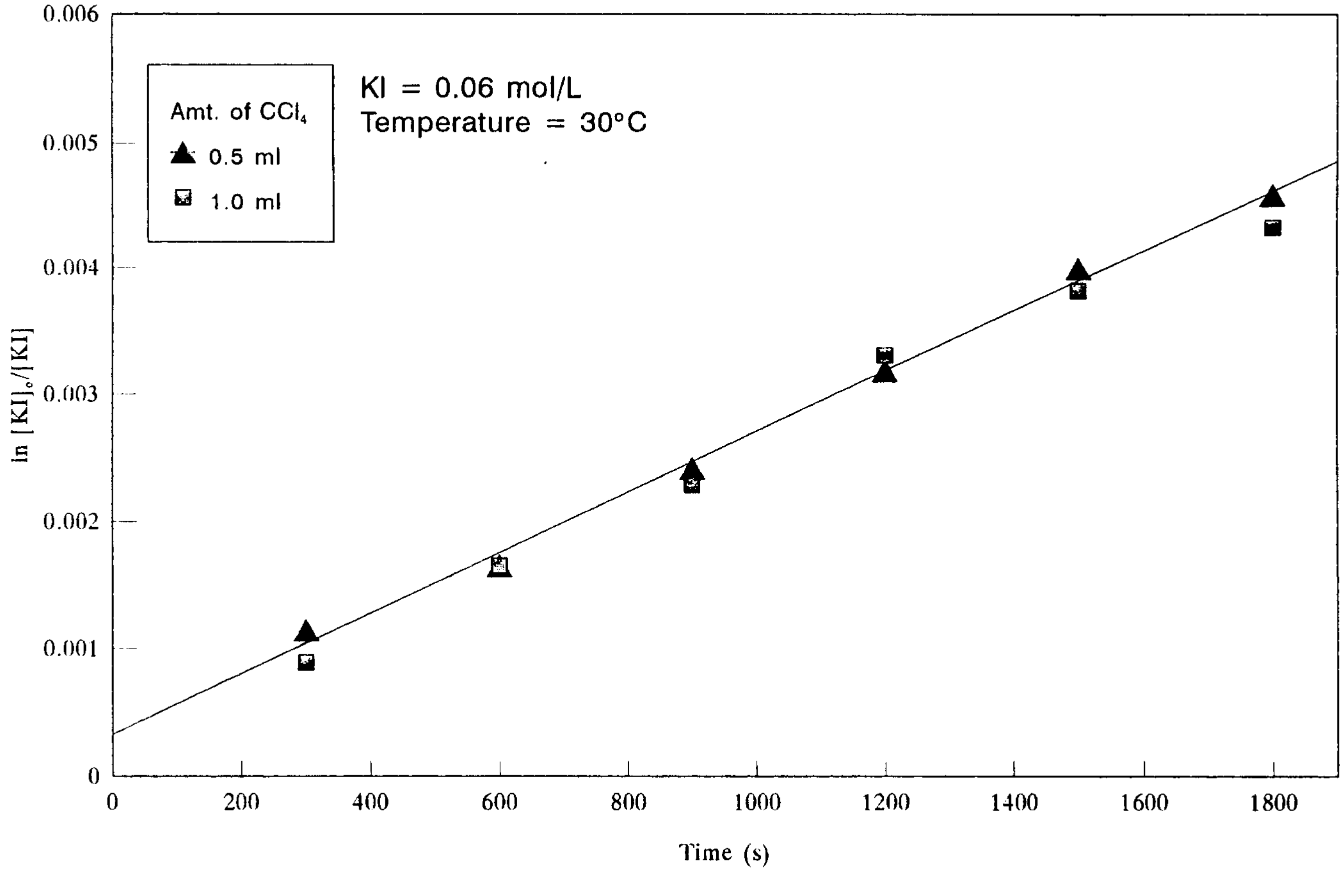

Fig. 5. Effect of volume of CCl_4 on KI degradation.

Table 1
Effect of volume of KI solution at different period of sonication, $KI = 0.06\ mol\ l^{-1}$

Volume of KI (m^3) $\times 10^{-6}$	Rate constant at different times (s^{-1})	
	10 min	20 min
2.0	10.664×10^{-6}	12.375×10^{-6}
3.0	7.230×10^{-6}	9.796×10^{-6}
4.0	4.244×10^{-6}	5.329×10^{-6}
5.0	1.052×10^{-6}	2.757×10^{-6}

Table 2
Effect of CCl_4 on activation energies

Concentration of KI	Activation energies ($kJ\ mol^{-1}$) in	
	presence of CCl_4	absence of CCl_4
0.06	38.352	18.493
0.301	16.573	20.774

The rate constants for the various parameters studied are shown in Table 3. We would like to point out that as the rate constants were found to be independent of CCl_4 concentration for $0.06\ mol\ l^{-1}$ KI, and hence no experiments were carried out for $0.301\ mol\ l^{-1}$ of KI.

Table 3
Rate constant for various parameters studied

Parameter studied	Temperature (°C)	Rate constant (s^{-1})	
		$KI = 0.06\ mol\ l^{-1}$	$KI = 0.301\ mol\ l^{-1}$
Presence of CCl_4	30	3.736×10^{-6}	8.164×10^{-7}
	40	2.204×10^{-6}	6.432×10^{-7}
	50	1.457×10^{-6}	5.436×10^{-7}
Absence of CCl_4	30	5.665×10^{-6}	1.575×10^{-7}
	40	5.121×10^{-6}	1.289×10^{-7}
	50	3.594×10^{-6}	0.944×10^{-7}
0.5 ml CCl_4	30		2.626×10^{-6}
1.0 ml CCl_4	30		2.540×10^{-6}

3.2. Degradation of aqueous CCl_4

Degradation of CCl_4 in aqueous $AgNO_3$ was carried out in a test-tube (2.2 cm i.d.). The amount of CCl_4 degraded was measured as a function of the amount of AgCl formed, which was estimated by measuring the concentration of $AgNO_3$. The effect of the amount of CCl_4 and the location of the horn on the degradation of CCl_4 was studied. Experiments were carried out to determine the rate of AgCl formation by placing the tip

Table 4
Rates of CCl_4 degradation in aqueous $AgNO_3$

Time (s)	Rate ($M\,l^{-1}\,s$) at $AgNO_3/CCl_4$ ratio of		
	1	1.67	3
600	10.729×10^{-5}	6.111×10^{-5}	4.259×10^{-5}
1200	7.279×10^{-5}	4.234×10^{-5}	3.576×10^{-5}
1800	6.121×10^{-5}	3.529×10^{-5}	3.133×10^{-5}

of the horn in (i) the aqueous layer, and (ii) the organic layer (CCl_4). It was observed that when sonication was carried out by placing the horn in the aqueous layer, the rate of AgCl formation was higher than when the horn was placed in the organic layer. It was further observed that when sonication of the same amount of CCl_4 and $AgNO_3$ was carried out in a beaker, no precipitation of AgCl was observed when the horn was placed in CCl_4. This is probably due to the fact that when sonication is carried out in a test tube, the small bubbles formed in the organic layer (CCl_4) coalesce at the interface of the aqueous layer and the organic layer to form a larger bubble which then floats to the surface of the aqueous layer without collapsing. This bubble, when carried to the surface, contains some CCl_4 which is not able to escape freely due to the lesser space available between the horn (1.9 cm o.d.) and the wall of the test tube (2.4 cm o.d). Owing to this, the bubble collapses into the aqueous layer and the contents (amount of CCl_4 carried by the bubble) then disperse into the aqueous layer due to ultrasonic wave motions or acoustic streaming caused by the horn. This supplies a certain quantity of CCl_4 to the aqueous layer for decomposition. This was not observed in the case of a beaker or in a test tube of larger i.d. (2.6 cm) where there is a larger space available for the bubble to escape freely without supplying CCl_4 to the aqueous layer for decompostion. As a result of which, no CCl_4 decomposition and AgCl precipitation was observed in the beaker when the horn was placed in CCl_4. In addition, at the interface of aqueous and the organic layer, a vigorous stirring takes place (due to the smaller distance from the horn tip to the test tube wall) which removes CCl_4 as fine droplets which disperse into the aqueous layer. As pointed out by Chivate and Pandit [15] the cavitation effects of the ultrasonic horn are restricted in the vicinity of the horn, and thus the geometry of the reactor can play a vital role in deciding the overall rates of the reaction.

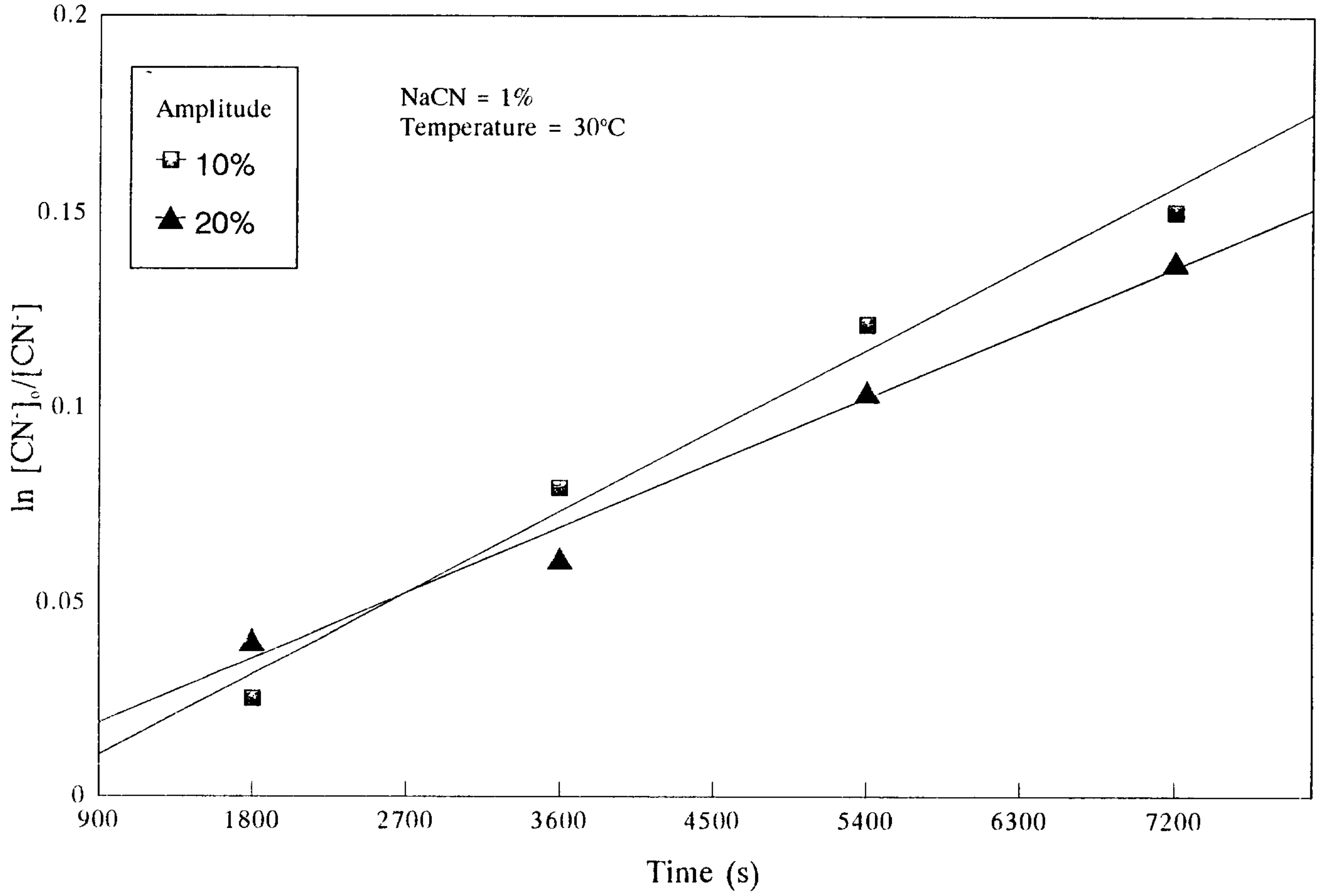

Fig. 6. Effect of amplitude (intensity) on rate of cyanide degradation.

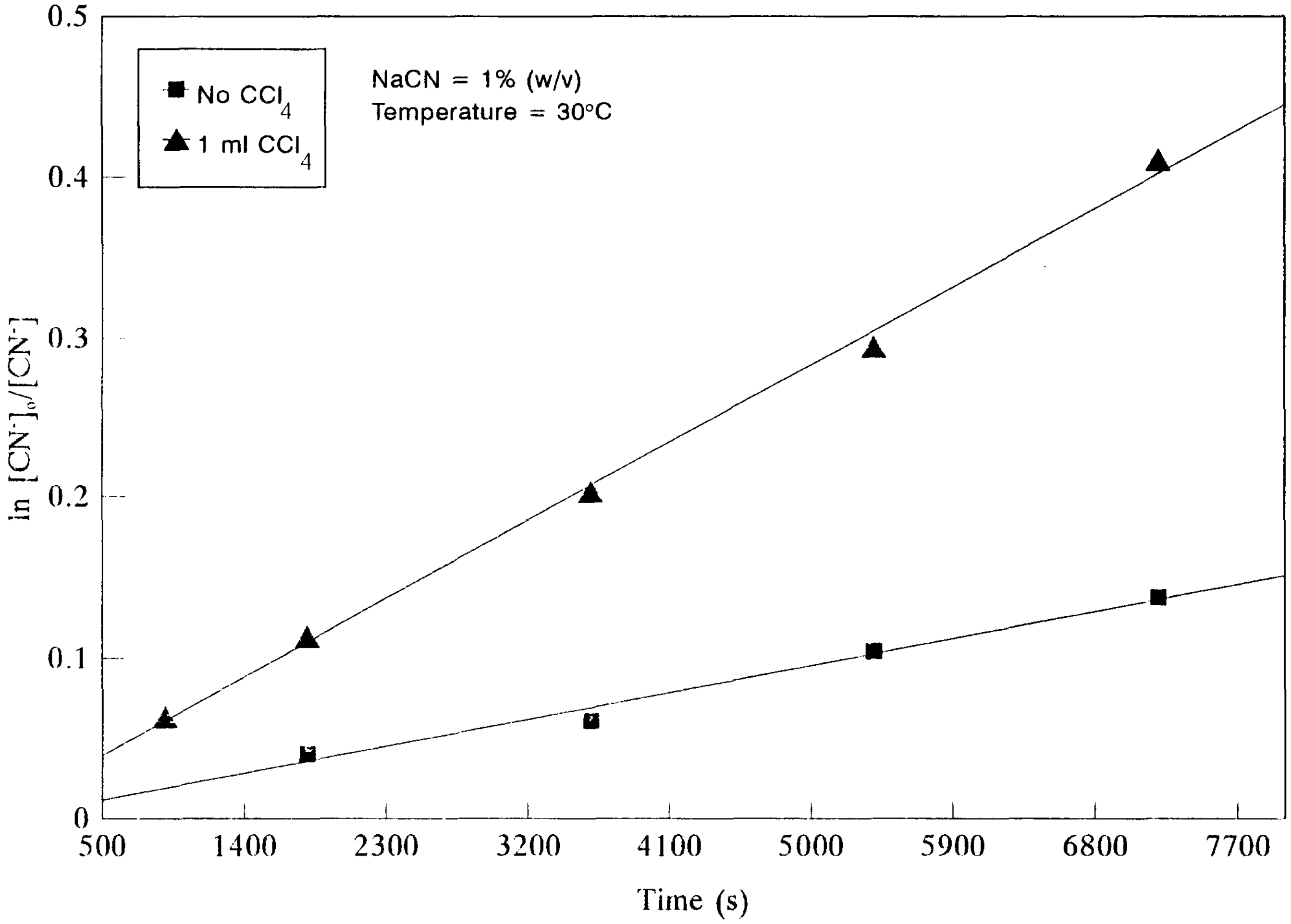

Fig. 7. Effect of CCl_4 on cyanide degradation.

The rate of CCl_4 decomposition is shown in Table 4. It can be seen from the table that the rate decreases with an increase in time, which is similar to the observatin made during the decomposition of aqueous KI solution. In addition, it can be observed from the table that with an increase in the ratio of AgCl to CCl_4, the rate also decreases. As in the case of decomposition of KI, correlations of average rate versus P/V were obtained as:

$$\text{Rate} = 3.85 \times 10^{-20}(P/V)^{2.16}. \quad (4)$$

Comparing this correlation with the correlation for KI decomposition Eq. (3), it can be seen that the exponent over the term P/V is approximately the same. This further indicates that the rate of degradation is independent of the system studied and is solely dependent on the type of ultrasonic equipment. Irradiating pure CCl_4 did not result in any degradation, as stated earlier. This may be due to less severe cavitating conditions in CCl_4 due to its higher vapour pressure. Thus, water as a cavitation medium is a must for such degradation within the limitations of the equipment used [16].

3.3. Degradation of aqueous sodium cyanide

Sodium cyanide and other cyanides are widely known as some of the most toxic compounds. Industries such as photographic processing, electroplating, petroleum refineries, etc. are major sources of cyanide wastes; the destruction of such waste has always been a challenge to the chemical industries. Many techniques are available for the destruction of cyanides including biological treatment, chemical oxidation, adsorption and catalytic oxidation, ion-exchange, precipitation and wet air oxidation. Chemical oxidation is generally performed by either alkaline chlorination [17], ozonation [18], hydrogen peroxide [19] or permanganate oxidants [20].

The degradation of sodium cyanide was studied at varying amplitude (intensity) at a fixed frequency, in the presence of varying volumes of carbon tetrachloride. It can be seen from Fig. 6 that the rate of cyanide degradation has a weak dependence on the intensity. The concentration of the cyanide was found to decrease by 13.96% when the amplitude used was 10%, whereas the reduction was 12.87% at an amplitude of 20% at

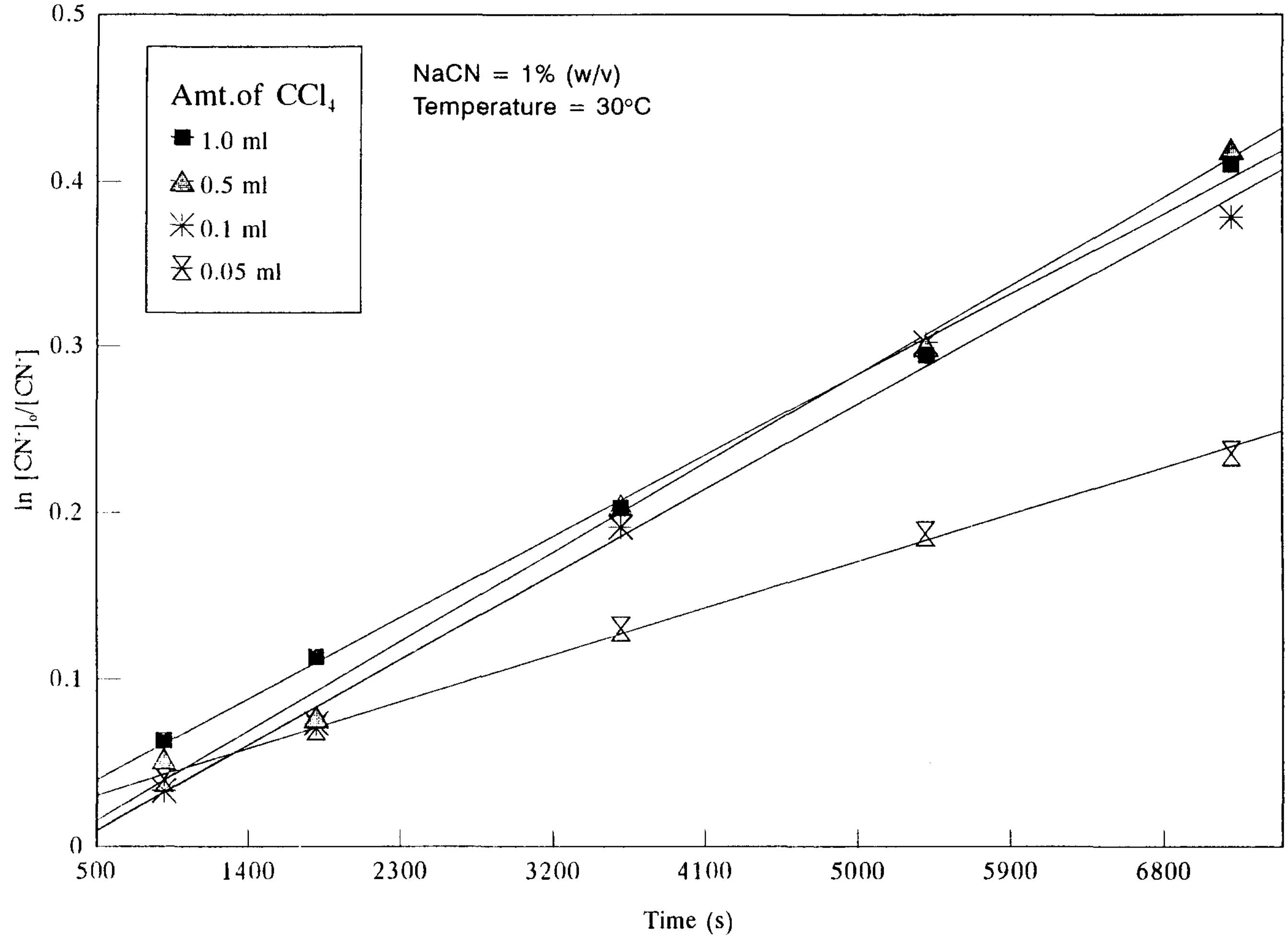

Fig. 8. Effect of amount of CCl_4 on cyanide degradation.

30 min of sonication. This variation is within the accuracy of the analytical method, and thus it can be concluded that the degradation rate was independent of the intensity of sonication used in this study.

The degradation was also studied in the presence of carbon tetrachloride, since it is well known that sonication of aqueous solutions of carbon tetrachloride results in the formation of free chlorine [8], and it has been reported that cyanide can be degraded by alkaline chlorination [17]. In the presence of carbon tetrachloride the rate of sodium cyanide degradation was found to be much faster than that in the absence of carbon tetrachloride (Fig. 7). This could be attributed to the formation of hydrogen peroxide as the only oxidant in the absence of carbon tetrachloride, while in the presence of carbon tetrachloride there is a combined effect of two oxidizing agents, free chlorine and hydrogen peroxide. A reduction of up to 40% in the concentration of cyanide in the presence of carbon tetrachloride is achieved compared to only 13% in the absence of carbon tetrachloride in a 30 min sonication period.

The effect of the amount of CCl_4 was studied in the range 1–0.05 ml (Fig. 8). With increasing CCl_4 volume there is an increase in the rate of degradation of cyanide. A lower reduction of cyanide was observed (25%) with 0.05 ml of CCl_4 compared to a 40% reduction with 1 ml of CCl_4. It was observed that at lower volumes of CCl_4 (0.05 and 0.1 ml), there was complete disappearance of CCl_4 within 10 min of sonication. This may be responsible for the lower rates observed at 30 min sonication period. From this figure it is observed that the rate of degradation of NaCN is again similar to that observed for the aqueous KI solutions or for the degrdation of CCl_4 in an aqueous medium, which confirms the earlier hypothesis of degradation being nearly independent of the system used and depends only on the type of equipment used.

4. Conclusions

The decomposition of KI was studied in the presence and absence of CCl_4. The relative rates of reaction were higher in the presence of CCl_4 than in the absence of

CCl_4. With an increase in the temperature, the rate of KI degradation decreases. No change in the rates were observed when the volume of CCl_4 was varied over the range specified in this work. The location of the ultrasonic horn showed a significant effect on the decomposition of CCl_4 in an aqueous solution of silver nitrate, and no degradation of CCl_4 was observed when the horn was placed in the organic phase (CCl_4).

Degradation of sodium cyanide was much higher in the presence of CCl_4 than in absence of CCl_4 as was the case for the degradation of aqueous KI solutions. The degradation rate of the added CCl_4 was the deciding factor for the degradation rate of NaCN and KI solutions in water. This could be important in terms of waste water treatment, which could be achieved at ambient conditions by mixing wastes having different organic compounds. The rates of degradation as observed for all the above systems, were of a similar order of magnitude, showing independence with respect to the chemical system and being dependent on the equipment alone.

Acknowledgements

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