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NOTE

Influence of $Th(NO_3)_4$, KCl and pH on the Reduction of $HgCl_2$ Under X- and UV-Radiations

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The yield of Hg_2Cl_2 is maximum at relatively high pH, diminished progressively with decrease of pH and is completely inhibited beyond a critical pH. In the presence of $Th(NO_3)_4$, slight reduction is observed. The results are explicable by assuming the existence of hydrated molecular ion H_2^+, (hydr.).

It has been reported[1] that the optical sensitizers like fluorescein dyes and uranyl salts, in the photo-chemical Eder's reaction in the visible, have a strong inhibiting effect when the reaction is excited by X-rays. It has been shown[2] that the oxidation rate of AsO_2^- increases with pH and reduction of methylene blue[3] increases with acidity in the absence of oxygen. As suggested by the results of Stein, Weiss and Watt[4], a study was carried out on the influence of pH, KCl and addition of small amounts of $Th(NO_3)_4$ on the reduction of $HgCl_2$.

The pH values were altered by the addition of KCl and determined by the Hellig's comparator method. The solutions of different pH were exposed to radiations for 20 min at 35 and 50°C and the yield of Hg_2Cl_2 formed was calculated. In the experiments with KCl, various weighed quantities of KCl were added to Hg_2Cl_2 and $Na_2C_2O_4$ solutions and exposed for 20 min. Experiments were also carried out with $HgCl_2$ to which different quantities of $Th(NO_3)_4$ were added.

The data (Table-1) have indicated that the yields of Hg_2Cl_2 formed diminished with increasing pH and at pH = 1.8, the reduction is completely inhibited under X-rays and at pH = 1.7, under UV radiations. This inhibiting action of pH is more marked at 50°C. The marked inhibition of the reduction by the addition of KCl is evident from Table-2. It is significant that in presence of $Th(NO_3)_4$, slight reduction is observed after 12 h.

The above experimental facts are in agreement with the assumption that H atoms can also exert an oxidising effect which increases with H-ion concentration. The oxidising effect of H atoms is well known. The possibility of this considering the earlier work[5, 6] to the present system can be shown if one assumes that in

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aqueous solution, in the presence of H^+ one obtains $H + H^+$ (hydr.) = H_2^+ (hydr.) which leads to the formation of hydrated molecular ion, capable of oxidising ferrous ion. Evidence relating to the existence of H_2^+ molecular ion in solution is available.[7] Thus:

$$Hg^+ + H_2^+ \text{ (hydr.)} \longrightarrow Hg^{2+} + H_2$$

TABLE-1
INFLUENCE OF pH ON THE REDUCTION OF $HgCl_2 + Na_2C_2O_4$ UNDER X AND UV RADIATIONS

Exposure time: 20 minutes

	Hg_2Cl_2 formed (mg/L)				
	35°C		50°C		
	X	UV	Blank	X	UV
3.60	40.9	56.9	256.3	304.2	326.2
2.80	34.6	50.3	124.2	164.3	174.5
2.60	24.2	46.4	29.1	69.9	76.2
2.30	11.0	33.8	–	37.6	50.3
2.10	4.7	28.3	14.9	15.7	42.4
1.85	2.4	19.3	5.5	6.3	20.4
1.80	–	9.4	2.4	2.4	8.7
1.75	1.2	6.3	0.8	–	6.3
1.70	–	3.9	–	–	3.9
1.65	–	–	–	–	1.6

TABLE-2
INFLUENCE OF KCL AND $Th(NO_3)_4$ ON THE REDUCTION OF $HgCl_2$ UNDER X AND UV RADIATIONS

Exposure time: 20 minutes

KCl (conc.) N	Hg_2Cl_2 formed (mg/L)		Exposure time t (min)	Hg_2Cl_2 formed (mg/L)	
	X	UV		0.1 N $Th(NO_3)_4$	0.2 N $Th(NO_3)_4$
0.1	39.3	52.4	2	–	–
0.2	35.6	47.8	8	0.19	1.18
0.4	30.8	43.9	16	1.18	3.15
0.6	26.8	38.7	24	3.15	3.84
0.8	21.9	33.1	36	4.32	5.13
1.0	18.3	29.3	48	5.13	5.94
1.5	16.3	27.4	72	5.94	6.32
2.0	15.7	26.3	–	–	–

On the other hand, in the presence of molecular oxygen (which will be formed even in de-aerated solutions), H atoms can be removed by the reaction $H + O_2 \longrightarrow HO_2$ and this process is quite fast; and at high acid concentrations, the presence of oxygen (O_2) formed by the primary process $2OH \longrightarrow H_2O + O$ and $2O \longrightarrow O_2$ completely inhibits the reduction process due to OH and O_2 radicals present.

The inhibitory influence of KCl on the reaction is mainly due to the formation of $Hg_2Cl_2 \cdot KCl$ complexes in solution. Thus, the formation of photo-chemically active component, *viz.*, $HgCl_2 \cdot Na_2C_2O_4$ complex in the reaction and the primary act of direct decomposition of this is inhibited, and hence, the small yields of Hg_2Cl_2. The reduction in the presence of $Th(NO_3)_4$ is attributed to the radiation activity of the solution.

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ERRATA

Paper entitled "In-vitro Inhibition of Mineralisation of Urinary Stone Forming Minerals by Some Dry-Fruits Extracts" by T.V.R.K. RAO *et al.*, *Asian Journal of Chemistry*, **12**(2) 467–470 (2000).

(i) In the title of paper the word "Mineral" is missing.
(ii) On page 469 (Table-3) please read Na_2CO_3 in place of Na_2PO_3.