

REDUCTION OF MERCURIC CHLORIDE BY OXALIC ACID IN THE DARK IN PRESENCE OF POTASSIUM PERMANGANATE AS INDUCTOR

By C. PRASAD AND ADANI K. BHATTACHARYA

The reaction between HgCl_2 and $\text{H}_2\text{C}_2\text{O}_4$, induced by KMnO_4 , has been studied from the viewpoint of the concentration effect of the inductor on the induction period and the extent of reduction of mercuric chloride. The induction period has been found to remain almost constant up to a certain concentration of KMnO_4 , beyond which it gradually goes on increasing till MnO_2 is precipitated when it becomes difficult to ascertain it. By increasing the concentration of the inductor, the reduction of HgCl_2 increases, but its reduction per mole of KMnO_4 at first increases rapidly and then gradually decreases. These observations suggest that the reduction of mercuric chloride is brought about through the mechanism of heterogeneous catalysis due to the activation of reacting molecules on the surface of colloidal MnO_2 , formed in the KMnO_4 - $\text{H}_2\text{C}_2\text{O}_4$ reaction.

The reduction of HgCl_2 by $\text{H}_2\text{C}_2\text{O}_4$, induced by KMnO_4 , had been studied in the past by many workers (Dhar, *Proc. K. Acad. Amsterdam*, 1920, 23, 308; Skrabal, *Z. anorg. Chem.*, 1904, 42, 1; Launer, *J. Amer. Chem. Soc.*, 1932, 54, 2597; Lidwell and Bell, *J. Chem. Soc.*, 1935, 1303). Recently Weiss ("Discussions", *Faraday Soc.*, 1947) has discussed a mechanism of this reaction based on the formation of Mn^{3+} ions and C_2O_4^- radical. Adamson (*J. Phys. Coll. Chem.*, 1951, 55, 293) has, from his studies on the kinetics of the manganous-permanganate reaction, given a very critical opinion on the mechanism suggested by Weiss and others.

Weiss observed an induction period in the reduction of HgCl_2 by oxalic acid in presence of KMnO_4 ; he referred to its importance but did not study its relation with the concentration of the inductor. We have therefore attempted to investigate this aspect of the reaction and studied the reduction of HgCl_2 with different initial concentrations of KMnO_4 .

EXPERIMENTAL

Standard solutions of mercuric chloride, oxalic acid, potassium permanganate, etc. were prepared from A. R. Chemicals, in redistilled water. The reactants were mixed together in conical flasks (same size) set up in an electrically regulated thermostat. The time interval between the mixing of the reactants and the first appearance of caenical precipitation was noted and designated as the 'induction period'.

For determining the amount of reduction of mercuric chloride in the dark, the reaction vessels, covered with black photographic paper, were similarly arranged. Total reduction of HgCl_2 was determined by pipetting out a definite volume of the reaction mixture with the help of a cotton plug into a known excess of KI solution and then back-titrating the residual KI by $M/20$ - HgCl_2 . The titre volume was further corrected by a titration error curve (Kolthoff and Stenger, "Volumetric Analysis", Vol. I, p. 156) and the reduction of HgCl_2 was calculated.

Induction Period

When KMnO_4 is added to a dilute solution containing HgCl_2 and oxalic acid, the reduction of mercuric chloride to mercurous state does not start immediately, but reduction is observed to begin after a certain time when the mixture becomes brown or colorless. This time interval is termed the 'induction period' and is connected with the mechanism of reduction of mercuric chloride.

Table I shows the relationship between the concentration of KMnO_4 in the reaction mixture containing constant concentrations of HgCl_2 and $\text{H}_2\text{C}_2\text{O}_4$, and the induction period.

TABLE I

Temp = 35°. $(\text{HgCl}_2)_0 = (\text{H}_2\text{C}_2\text{O}_4)_0 = 6.667 \times 10^{-2}$ g. mol./litre.

Conc. of KMnO_4 .	Induction period.	Colour of soln. when the Hg_2Cl_2 formation starts.
0.1667×10^{-2} equiv./litre	7.5 min.	Almost colorless
0.3333	8	Do
0.6666	8	Light brown
1.3333	8	Do
3.3330	8	Do
5.3330	9	Brown
6.6666	10	Do
10.0	18	Black due to MnO_2 ppt.
13.3333	> 24 hrs.	Do

From Table I the induction period does not appear to change appreciably by increasing the concentration of KMnO_4 up to a certain limit, beyond which it starts increasing gradually for such concentrations of the inductor as make the precipitate of MnO_2 appreciably visible. When the concentration of KMnO_4 is equivalent to that of oxalic acid, much MnO_2 is precipitated and the induction period cannot be determined within 24 hours.

It was further observed that the induction period for a reaction mixture ($\text{HgCl}_2 = \text{H}_2\text{C}_2\text{O}_4 = 6.667 \times 10^{-2}$ g. mol./litre ; $\text{KMnO}_4 = 0.3333 \times 10^{-2}$ g. equiv./litre) was 19 mins. at 25° and 8 mins. at 35°. Hence, the induction period appears to depend on the concentration of KMnO_4 as well as on the temperature of the reaction.

TABLE II

Relationship between the amount of KMnO_4 added and the extent of reduction of mercuric chloride.

Temp. = 35°. $(\text{HgCl}_2)_0 = (\text{H}_2\text{C}_2\text{O}_4)_0 = 6.667 \times 10^{-2}$ g. mol./litre.

$(\text{KMnO}_4)_0$.	HgCl_2 (reduced).	$\frac{\text{HgCl}_2 \text{ (reduced)}}{(\text{KMnO}_4)}$	$(\text{KMnO}_4)_0$.	HgCl_2 (reduced).	$\frac{\text{HgCl}_2 \text{ (reduced)}}{(\text{KMnO}_4)}$
$0.1667 \text{ mol./litre} \times 10^{-3}$	$1.333 \text{ mol./litre} \times 10^{-3}$	18.0	$3.333 \text{ mol./litre} \times 10^3$	$15.33 \text{ mol./litre} \times 10^3$	4.6
0.25	3.333	13.3	5.0	15.83	3.17
0.3333	5.1	15.3	6.667	17.17	2.575
0.5	7.333	14.67	8.333	18.0	2.16
0.6667	8.5	12.75	10.0	19.83	1.98
1.667	12.33	7.4			

From Table II the total reduction of HgCl_2 appears to increase with increasing concentration of KMnO_4 . It is further observed that the reduction of HgCl_2 per mole of KMnO_4 rapidly increases in the beginning but slows down afterwards. This suggests that some KMnO_4 becomes ineffective in inducing the reduction of mercuric chloride in the later stages.

Probable Mechanism

In view of the observations recorded in Table I, we are of the opinion that the first stage of the reduction starts in the formation of highly dispersed MnO_2 sol. The reduction of HgCl_2 is then brought about by the activation of the molecules on the surface of colloidal MnO_2 . In other words, the induction takes place through the energy of surface catalysis, and hence, the primary stage of activation and the subsequent reduction of HgCl_2 appear to be governed by a heterogeneous mechanism. The heterogeneous character of this reaction (in its initial stage) is supported by the observations on the period of induction in Table I. It has been observed that there is very little increase in the induction period within the concentrations of KMnO_4 0.1667–6.6666 equiv./litre $\times 10^{-2}$. But on adding more of permanganate, MnO_2 is precipitated and the induction period also increases appreciably. This suggests a sudden decrease in the surface due to the precipitation of the MnO_2 sol at higher concentrations of KMnO_4 . Under such condition longer time would be required by the oxalic acid to bring the precipitated MnO_2 to the optimum stage of dispersion at which the activation of HgCl_2 or $\text{H}_2\text{C}_2\text{O}_4$ or of both takes place. The induction period is therefore bound to increase according to this heterogeneous mechanism of activation.

The temperature effect on the induction period also supports the theory of heterogeneous mechanism in the primary stage of the reaction. If it is assumed that molecules are activated by thermal effects, it is obvious that the rate of activation of molecules due to surface catalysis will be greater at 35° than that at 25° , and this has actually been observed.

This view is further supported by the fact that when different amounts of colloidal MnO_2 are added to a mixture of HgCl_2 and $\text{H}_2\text{C}_2\text{O}_4$, the induction period is almost the same, and very much less (hardly 2-3 minutes) while the extent of reduction of HgCl_2 increases with higher concentrations of colloidal MnO_2 , as observed with KMnO_4 an inductor.

In the quantitative study of the total reduction of HgCl_2 , it has been observed that the reduction continues for a pretty long time even when the brown colour of the solution has been completely discharged. At the colorless stage, it appears that the highly dispersed MnO_2 has been dissolved by oxalic acid, releasing Mn^{2+} ions which act as catalyst in this reaction (vide Dhar, *J. Chem. Soc.*, 1917, 111, 695). Hence, the whole mechanism of this reaction, in all probability, is a phenomenon of heterogeneous cum homogeneous catalysis, the primary stage being the surface activation of the reactant molecules followed by the catalytic influence of Mn^{2+} ions during the later stages.

Previous workers (Weiss and others, *loc.cit.*) have explained this reaction by chain mechanism initiated through the formation of Mn^{3+} and C_2O_4^- . While we do not argue against their mechanism, the fact remains that the formation of Mn^{3+} and C_2O_4^- at tem-

peratures of 25° and 35° is more hypothetical than the mechanism of surface activation and catalytic influence of Mn^{2+} ion, suggested by us. It may further be stated that there is hardly any reference in the literature regarding the temperature at which Mn^{2+} ion can remain stable. It appears from the behaviour of manganic salts that they are very unstable at ordinary temperatures, and hence, any mechanism based on the formation of Mn^{3+} ion and $C_2O_4^-$ radical seems to be conflicting with the stability of these ions.

In view of many other factors, which are known to play their role in this reaction, it may prove a helpful guide to study its kinetics in the catalysed state and determine the apparent order, temperature coefficient and activation energy.

CHEMICAL LABORATORIES,
AGRA COLLEGE, AGRA.

Received January 30, 1950.