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Solid State Reaction between Mercury(I) Dicarboxylates & Halogens: Part I—Reaction between Mercury(I) Oxalate & Iodine

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Reaction of iodine with solid mercury(I) oxalate has been studied. An yellow coloured intermediate is first formed which immediately changes into a red coloured final product. The red product has been identified as HgI_2. The kinetics of the bulk diffusion of iodine into solid mercury(I) oxalate has been studied, and the mechanism of propagation of the reaction has been established.

THE essential features of solid state reactions are : the destruction of the crystal lattices of the reactants, the breaking and redistribution of chemical bonds, the formation of the crystal lattices of the reaction products, formation of product layer between the reactants and lastly the diffusion of one component or the other through the product layer for further propagation of the reaction. In previous investigations[1,2] from our laboratory several reactions of the type $A(s) + B(s) \longrightarrow C(s)$ have been studied. The present work relates to an exchange reaction of the type $A(s) + B(g) \longrightarrow C(s) + D(g)$ involving mercury (I) oxalate (solid) and iodine (vapour). The interesting feature of this reaction is that iodine causes evolution of carbon dioxide from the oxalate at a temperature much lower than the decomposition temperature (140°C) of mercury(I) oxalate.

Materials and Methods

Mercury(I) nitrate (S. Merck, GR), oxalic acid (E. Merck, AR), nitric acid (AR), iodine (S. Merck, GR) were used without further purification. Mercury (I) oxalate was prepared by adding oxalic acid solution to mercury(I) nitrate solution.

The stoichiometry of the reaction was established by a method reported earlier[2]. The mercury(I) oxalate and iodine of particle size > 140 mesh were used and the experiment was carried out at temperature 48 ± 1°C [mass gain : obs. 84.4 ± 0.6; calc. for HgI_2 : 85.7%].

Chemical analysis of reaction products : *Gaseous products* — Mercury(I) oxalate was intimately mixed with iodine in 1:2 molar ratio and the mixture was taken in a pyrex tube which was connected with another tube by a standard joint. The system was kept at 60 ± 1°C for 24 hr and the gas collected in empty tube was tested with lime water and found to be carbon dioxide.

Solid products — The qualitative chemical analysis of the solid reaction product showed presence of Hg(II) and complete absence of Hg(I). Mercury was estimated as HgS[3] [Found : Hg, 43.2 ± 0.5, calc. for HgI_2 44.1%].

Powder X-ray diffraction pattern of the crystalline reaction product was taken with an X-ray diffractometer using Cu $K\alpha$ radiation (wavelength 1.5418 Å).

Kinetic studies — Kinetic studies were performed using a set-up identical to that used for stoichiometric studies. Increase in the mass of the tube containing mercury(I) oxalate was noted at different time intervals. The experiments were performed at 33°, 42°, 48° and 59° ± 1°C using tubes of equal diameter (0.7 cm). Results are shown in Fig. 1.

Study of mode of diffusion of iodine — The experiment for stoichiometric studies was repeated at temperature 31 ± 1°C. The distance between the iodine surface and mercury(I) oxalate was known beforehand. The mass of iodine diffused in mercury(I) oxalate was determined by measuring the increase in mass of mercury(I) oxalate at different time intervals. The experiment was repeated with tubes of different diameters to investigate the dependence of the diffusion coefficient of iodine on the diameter of the tube. Results are plotted in Fig. 2.

Results and Discussion

The results of the stoichiometric studies show that mercury(I) oxalate and iodine react in 1:2 molar ratio.

The stoichiometric data and qualitative and quantitative analyses of the reaction product indicate that the solid reaction product is mercury(II) iodide. This was corroborated by the powder X-ray diffraction pattern of the reaction product also. The d_{hkl} values of the reaction product were in good agreement with the d_{hkl} values for mercury(II) iodide as reported in ASTM file.

On the basis of stoichiometric data and characterization of the reaction product, reaction may be postulated to proceed through any of the following two chemical pathways (A and B) :

$$Hg_2C_2O_4 + I_2 \longrightarrow Hg_2I_2 + 2CO_2 \qquad \text{(i)}$$
$$Hg_2I_2 + I_2 \longrightarrow 2HgI_2 \qquad \text{(ii)}$$

(A)

$$Hg_2C_2O_4 + I_2 \longrightarrow Hg_2C_2O_4.I_2 \qquad \text{(i)}$$
$$Hg_2C_2O_4.I_2 + I_2 \longrightarrow Hg_2C_2O_4.2I_2 \qquad \text{(ii)}$$
$$Hg_2C_2O_4.2I_2 \longrightarrow 2HgI_2 + 2CO_2 \qquad \text{(iii)}$$

(B)

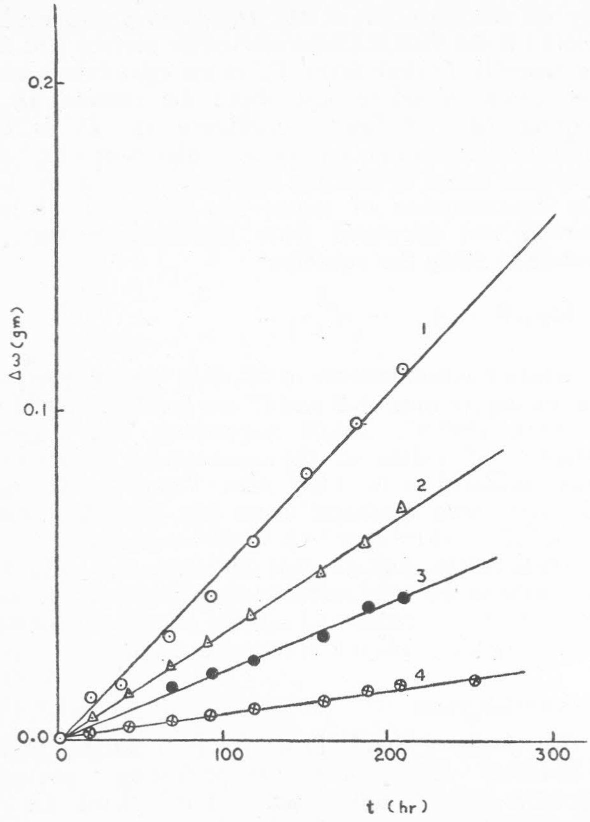


Fig. 1 — Kinetic data for the reaction between $Hg_2C_2O_4$ and I_2 [1, 59°C; 2, 48°C; 3, 42°C; 4, 33°C].

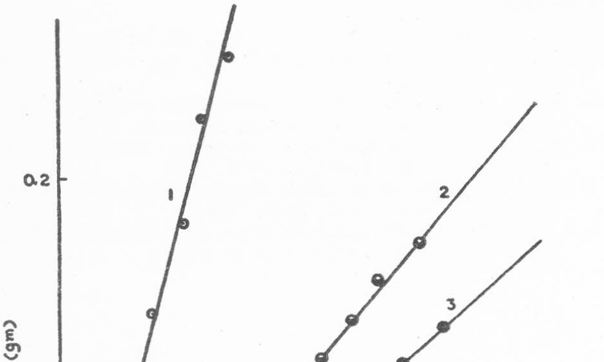
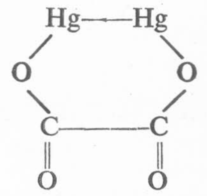


Fig. 2 — Kinetic data for the study of diffusion of iodine [1, $r = 1.2$ cm; 2, $r = 0.9$ cm; 3, $r = 0.7$ cm; 4, $r = 0.45$].

It is observed that when iodine comes in contact with the solid mercury(I) oxalate, an yellow intermediate is formed which subsequently changes to red HgI_2, the final reaction product. This yellow intermediate may be Hg_2I_2 [mechanism A(i)] or an addition complex [mechanism B]. The Hg—Hg bond in mercury(I) oxalate is weaker than Hg-O bonds. Therefore, when iodine approaches mercury(I) oxalate, Hg-Hg bond is likely to break preferentially. Thus, the probability of formation of Hg_2I_2 is ruled out and the reaction is likely to take place through mechanism B. Since the intermediate complex [mechanism B(i) or B(ii)] is very unstable and is immediately converted to the final products, the isolation and identification of the intermediate is not possible. The formation of the addition product can easily be understood if we take into consideration the structure of mercury(I) oxalate (I),



(I)

It is evident from structure (I) that the linearity of O-Hg-Hg bonds (due to the inherent *sp* hybridisation of mercury atoms) is disturbed considerably. On account of this, the molecule would be highly strained and thus possess extreme chemical reactivity. The chemical reactivity is increased due to high polarising power of mercury atoms in the molecule. When highly polarisable iodine atoms attack mercury (I) oxalate molecule the mercury atoms extend their coordination number from two to three and finally to four giving the unstable addition intermediate with mercury(I) oxalate and iodine in 1:2 molar ratio. The formation of new Hg-I bonds weakens Hg-Hg, Hg-O and I-I bonds to such an extent that the intermediate complex breaks to give the final reaction products.

To gain an insight into the mode of the propagation of reaction in solid state, kinetic studies were undertaken. Kinetic data at all temperatures (Fig.1) obey an equation of the type (1),

$$\triangle\ w = kt \qquad ..(1)$$

where $\triangle w$ is the increase in mass of mercury(I) oxalate at time t and k is the rate constant. The value of k was found to increase with temperature in accordance with the Arrhenius equation,

$$k = A\ e^{-E/RT} \qquad ..(2)$$

From the Arrhenius plot energy of activation for diffusion was calculated to be 15.2 ± 0.6 kcal /mol.

Since the reaction is diffusion-controlled, it is pertinent to comment on the mode of the diffusion of iodine into the bulk of solid mercury(I) oxalate. The diffusion may be controlled either by surface migration or by vapour-phase migration. Since the energy of activation is very close to the heat of

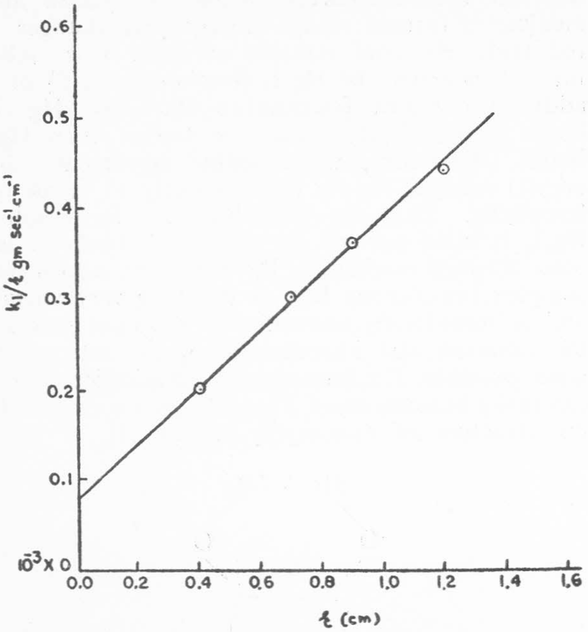


Fig. 3 — Plot of k_1/r against r.

sublimation of iodine (14.48 kcal/mol)[4], the mode of diffusion appears to be predominantly controlled by vapour phase; however, diffusion by surface migration cannot be ruled out. The relative contributions of these can be known from the diffusion experiment.

The data of the diffusion experiment obey Eq. 3,

$$S = k_1 t \qquad ..(3)$$

where S is proportional to the amount of iodine diffused in solid mercury (I) oxalate and is equal to the increase in mass of mercury(I) oxalate, t is time and k_1 is the rate constant. The value of k_1 depends on the diameter of the tube according to the following equation[5],

$$k_1/r = \alpha_{r} + \beta \qquad ..(4)$$

where r is the radius of the tube. α and β are given by the relations : $\alpha = \pi C_e D_V/l$, and $\beta = 2\pi C_e D_s$. Here l is the distance between iodine surface and the mercury(I) oxalate layer, C_e is the equilibrium concentration of iodine just above the surface, D_v is vapour-phase diffusion coefficient and D_s is the diffusion coefficient for surface migration. Eq. (4) has been tested by plotting k_1/r vs r in Fig 3. C_e, the concentration of iodine just above the iodine surface was calculated from the vapour pressure of iodine by using the equation[6].

$$\log_{10} P = A - \frac{B}{C' + t'}$$

where t′ is temperature in °C, P is vapour pressure of iodine in mm, A,B and C' are constants equal to 7.26304, 1697.87, 204.00 respectively. The vapour pressure of iodine at the experimental temperature was calculated to be 1.091 mm. Values of D_V and D_s have been evaluated from Fig. 3 and are found to be 9.76×10^{-4} and 1.12×10^{-5} respectively.

These results indicate that although the diffusion of iodine in the solid mercury (I) oxalate is controlled by both vapour phase and surface migration, vapour phase migration plays a predominant role.

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