Solid-State Reaction between Iodine and Mercurous Halides

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Abstract: The stoichiometry and kinetics of reactions, between (i) iodine and mercurous chloride, (ii) iodine and mercurous bromide, and (iii) iodine and mercurous iodide have been studied. HgClI is formed in reaction i and dissociates after some time into mercuric chloride and mercuric iodide. HgBrI and HgI_2 are formed in reactions ii and iii, respectively. The stoichiometry is confirmed by gravimetric studies, chemical analysis, reflectance spectra, and thermal studies. The mechanism of lateral diffusion has been established by kinetic studies (a) when the reactants are kept in contact, and (b) when they are separated by an air gap of different length. The data for reaction i are best fitted by the equation $\xi^2 = 2k_ite^{-p\xi}$, where ξ is the thickness of product layer at time t, and p and k_i are constants. For the other two reactions $\xi^n = kt$ is obeyed by the data, where k and n are constants. It has been established that diffusion in the above reactions is predominantly controlled *via* vapor phase, although, in reactions ii and iii, diffusion by surface migration is also significant. The diffusion coefficient of iodine in air and the diffusion coefficient for surface migration have been experimentally determined. The inward penetration of iodine in the grains of mercurous halides has been investigated by gravimetric studies. In order to have an idea about the magnitude of energy changes, thermochemical studies in the solid state have been made.

Mechanisms of solid-state reactions differ from the corresponding reactions in liquid and gaseous phase in many respects. The kinetics in the solid state is mainly controlled by diffusion of reactants. The nature of the interaction also has characteristic features. The solid-state reactivity of picric acid has recently been studied by Rastogi and co-workers.[1-3] The present research was undertaken to investigate the mechanism of reactions between iodine and mercurous halides as a part of general program of study of the reactivity of inorganic compounds in the solid state, including kinetics and mechanism. The present investigation shows that HgClI and HgBrI are formed in the solid state. Marcus[4] has estimated the equilibrium constants of such mercury(II) halide mixed complexes in aqueous solution and in benzene. However, these do not appear to have been isolated in the solid state in the past.

Table I

Temp, °C	Reaction i		Reaction ii		Reaction iii	
	k_i, cm²/hr	p, cm/hr	k, cm/hr	n	k, cm/hr	n
25	$(12.5 \pm 0.5) \times 10^{-3}$	31.4 ± 2.6	93.8×10^{-5}	1.90	50.5×10^{-5}	3.03
35	$(21.8 \pm 1.8) \times 10^{-3}$	31.2 ± 1.8	180.7×10^{-5}		90.2×10^{-5}	
45	$(49.8 \pm 1.7) \times 10^{-3}$	31.2 ± 2.0	343.8×10^{-5}		145.1×10^{-5}	
55	$(82.0 \pm 3.6) \times 10^{-3}$	25.6 ± 1.05	758.0×10^{-5}		236.9×10^{-5}	

Experimental Section

Material. Mercurous chloride, mercurous iodide (both G. R. E. Merck), and iodine (Judactan analytical reagent) were used without further purification. Mercurous bromide was prepared by adding potassium bromide (AR) to a solution of mercurous nitrate (E. Merck) in 1% nitric acid.

Study of the Kinetics of the Reactions in the Solid State. The kinetics of the three reactions in the solid state was studied by the technique described in earlier communications.[1,2] Iodine and mercurous halides (particle size above 300 mesh) were kept in contact in a capillary which was placed in an air thermostat whose temperature was maintained constant to ±1°. The kinetic data may be expected to depend on powder packing. This did not vitiate our experiments as the capillary was filled by taking successively very small amount of halides followed by gentle tapping for a period of 5 min. Iodine was subsequently filled in similar manner. This ensured homogeneous and identical conditions of packing in each case. This was confirmed by the reproducibility of the parameters in Table I. ξ was measured at various intervals with the help of a vernier microscope. The kinetics of the reactions was also studied when the reactants were separated by an air gap of different length. Studies were made at different temperatures. The results are given in Table I and Figures 1–3.

Gravimetric Studies. The procedure adopted was the same as that described in an earlier communication.[2] Known amounts of iodine and mercurous halides were taken in two bulbs connected with a tube, and the assembly was placed in a thermostat. The increase in weight of mercurous halides, which corresponds to the amount of iodine consumed in the reactions, was noted at different intervals at 55 and 65°. The amount of iodine consumed in the complete reaction was also measured by weighing. The results are given in Figure 4.

Chemical Analysis. The amount of mercury in the three reaction products was estimated quantitatively as mercuric sulfide and was found to be 58.1 (calculated value 54.99% for HgClI and 68.6% if the product were a mixture of $HgCl_2$ and Hg_2I_2), 51.2 (calculated value 49.2% for HgBrI), and 46.6% (calculated value 44.1% for HgI_2) for reactions i, ii, and iii, respectively.

Spectroscopic Studies. (a) **Ultraviolet Spectra of Aqueous Solution.** The spectra were investigated to check whether HgClI could be stable in aqueous solution. The spectra of aqueous solution of mercurous chloride, iodine, and a mixture of mercurous chloride and iodine were taken with the help of a Carl Zeiss spectrophotometer. No new band corresponding to HgClI could be obtained, showing thereby that HgClI does not exist as a stable species in solution.

(b) Ultraviolet Spectra of Solid Transparent Pellets. The spectra of transparent pellets of mercurous chloride, iodine,

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(1) R. P. Rastogi, P. S. Bassi, and S. L. Chaddha, *J. Phys. Chem.*, **66**, 2707 (1962).

(2) R. P. Rastogi, P. S. Bassi, and S. L. Chaddha, *ibid.*, **67**, 2569 (1963).

(3) R. P. Rastogi and N. B. Singh, *ibid.*, 70, 3315 (1966).

(4) Y. Marcus, *Acta Chem. Scand.*, 11, 610 (1957).

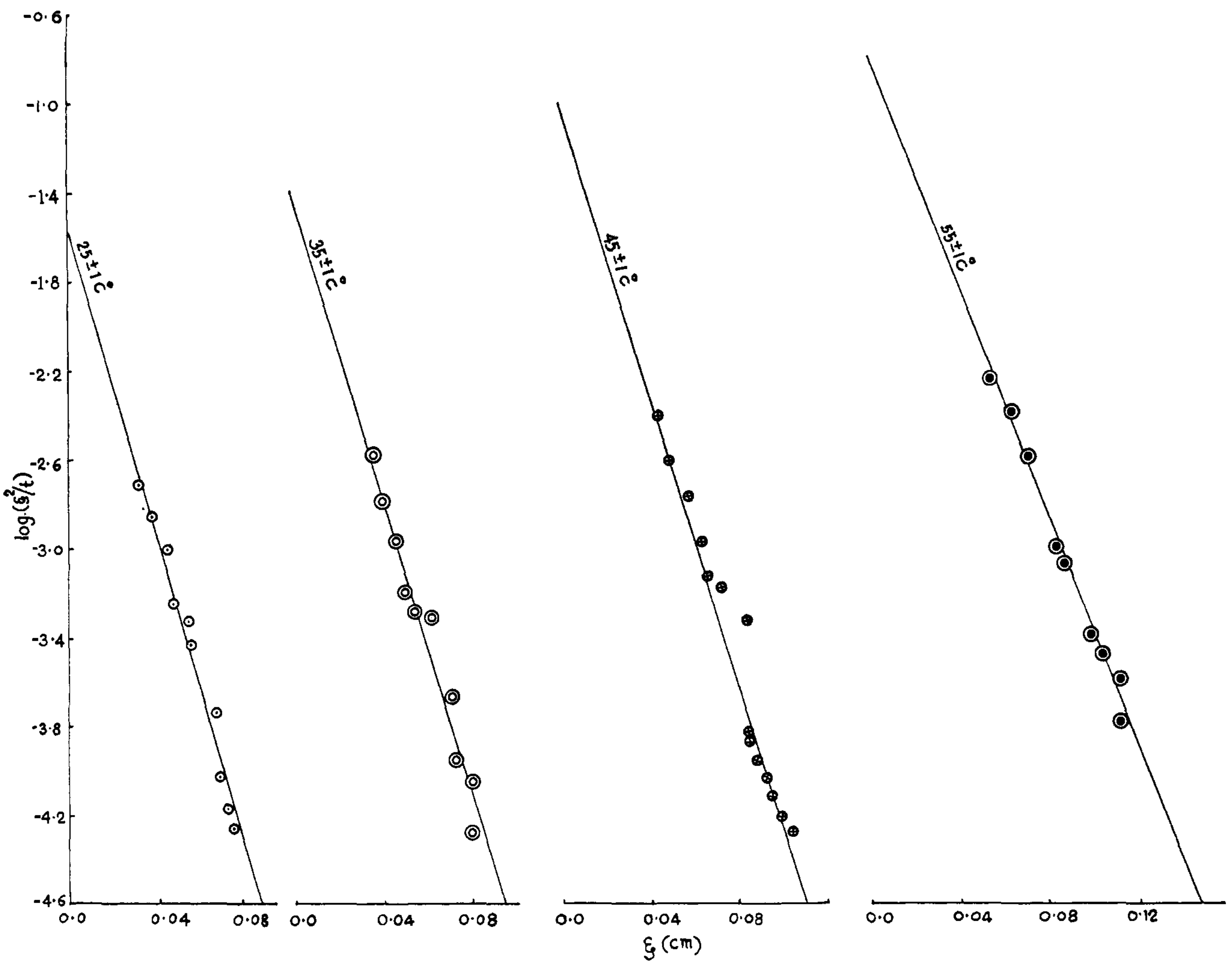

Figure 1. Kinetic data for the lateral reaction and the test of eq 2 for the reaction between iodine and mercurous chloride.

mercurous iodide, mercuric iodide, and the product of reaction i was studied with the help of a Cary 14-R spectrophotometer, using potassium bromide as the matrix material. No new peak was obtained for the product of reaction i. A peak corresponding to mercuric iodide only appeared. This was expected since during the processes of the pellet formation HgClI dissociates into mercuric chloride and mercuric iodide, which could be observed visually.

(c) **Reflectance Spectra.** The reflectance spectra of iodine, mercurous chloride, mercurous bromide, mercurous iodide, mercuric chloride, mercuric iodide, and the product of the three reactions were studied with the help of a Beckman DU spectrophotometer having a reflectance attachment. Magnesium carbonate was used as the reference material. The spectra are shown in Figures 5–7.

Thermal Studies. A weighed amount of mercurous halide was taken in a double-walled calorimeter which was placed in a thermostat at 30 ± 0.2°. A known amount of iodine was added. The mixture was stirred thoroughly, and the temperature rise was measured with the help of a precision thermometer at different time intervals. The results are given in Figures 8–10.

Experiment on Diffusion[5] of Iodine. A weighed amount of iodine was taken in a tube of known diameter. The distance of the iodine surface from the open end of the tube was known beforehand. The tube was kept in a thermostat at 65 ± 1 °. The weight of iodine diffusing away was determined at different intervals by weighing. 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 and Discussion

For a comprehensive study, the following aspects of the reactions should be considered: (i) mechanism of chemical interaction in the solid state; (ii) mechanism of inward penetration of iodine in the grains of mercurous halides; (iii) mechanism of lateral diffusion when the reactants are kept in contact and when they are separated by air gaps of different lengths. All these aspects have been found important in the solid-state reaction between picric acid and hydrocarbons investigated earlier.

Mechanism of Chemical Interactions. The stoichiometry of the reaction has been established by gravimetric studies. Two mechanisms may be postulated for reaction between iodine and mercurous chloride (reaction i), *viz.*

$$\mathrm{Hg_2Cl_2 + I_2 \longrightarrow 2HgClI} \qquad \text{(I)}$$
$$\mathrm{2HgClI \longrightarrow HgCl_2 + HgI_2}$$
$$\mathrm{2Hg_2Cl_2 + I_2 \longrightarrow 2HgCl_2 + Hg_2I_2} \qquad \text{(II)}$$
$$\mathrm{Hg_2I_2 + I_2 \longrightarrow 2HgI_2}$$

Reactions ii and iii may take place in the following manner.

$$\mathrm{Hg_2Br_2 + I_2 = 2HgBrI}$$
$$\mathrm{Hg_2I_2 + I_2 = 2HgI_2}$$

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(5) W. Jost, "Diffusion in Solids, Liquids, and Gases," Academic Press Inc., New York, N. Y., 1960, pp 8–9.

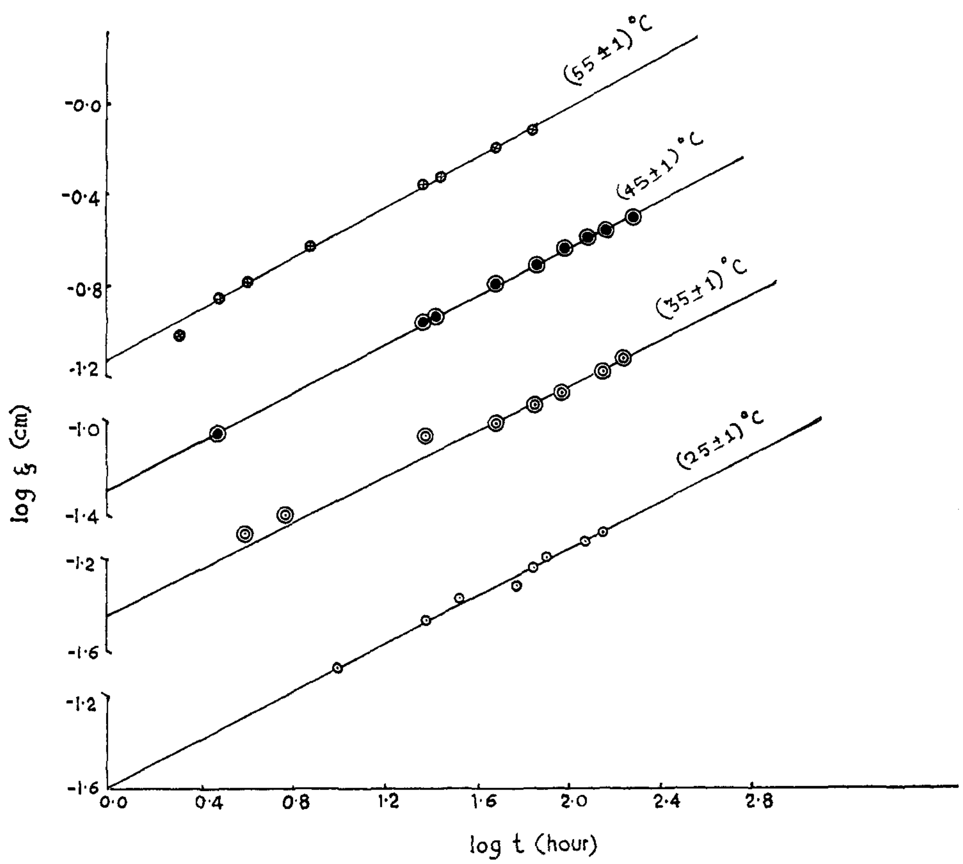

Figure 2. Kinetic data for the lateral reaction and the test of eq 3 for the reaction between iodine and mercurous bromide.

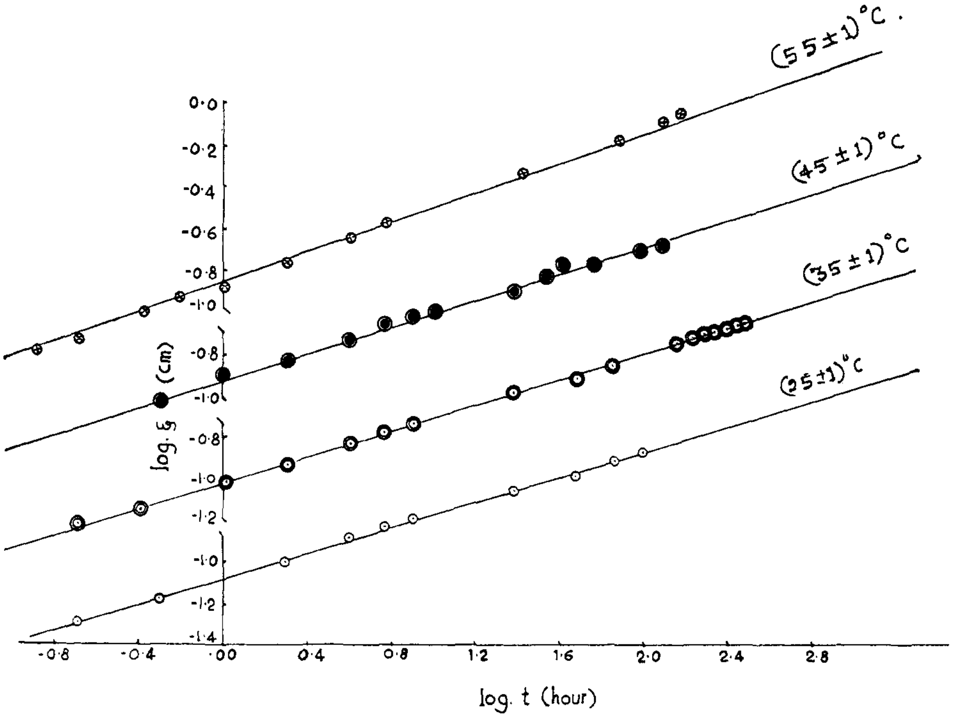

Figure 3. Kinetic data for the lateral reaction and the test of eq 3 for the reaction between iodine and mercurous iodide.

Mechanism I for reaction i postulates the formation of HgClI as intermediate product and its subsequent dissociation into a mixture of mercuric chloride and mercuric iodide. Mechanism II postulates the formation of Hg_2I_2 (yellow product) in the first stage of the reaction and subsequent reaction of iodine to form mercuric iodide. The intermediate yellow product is HgClI and not a mixture of mercuric chloride and mercurous iodide. This conclusion is supported by gravimetric studies. The total amount of iodine con-

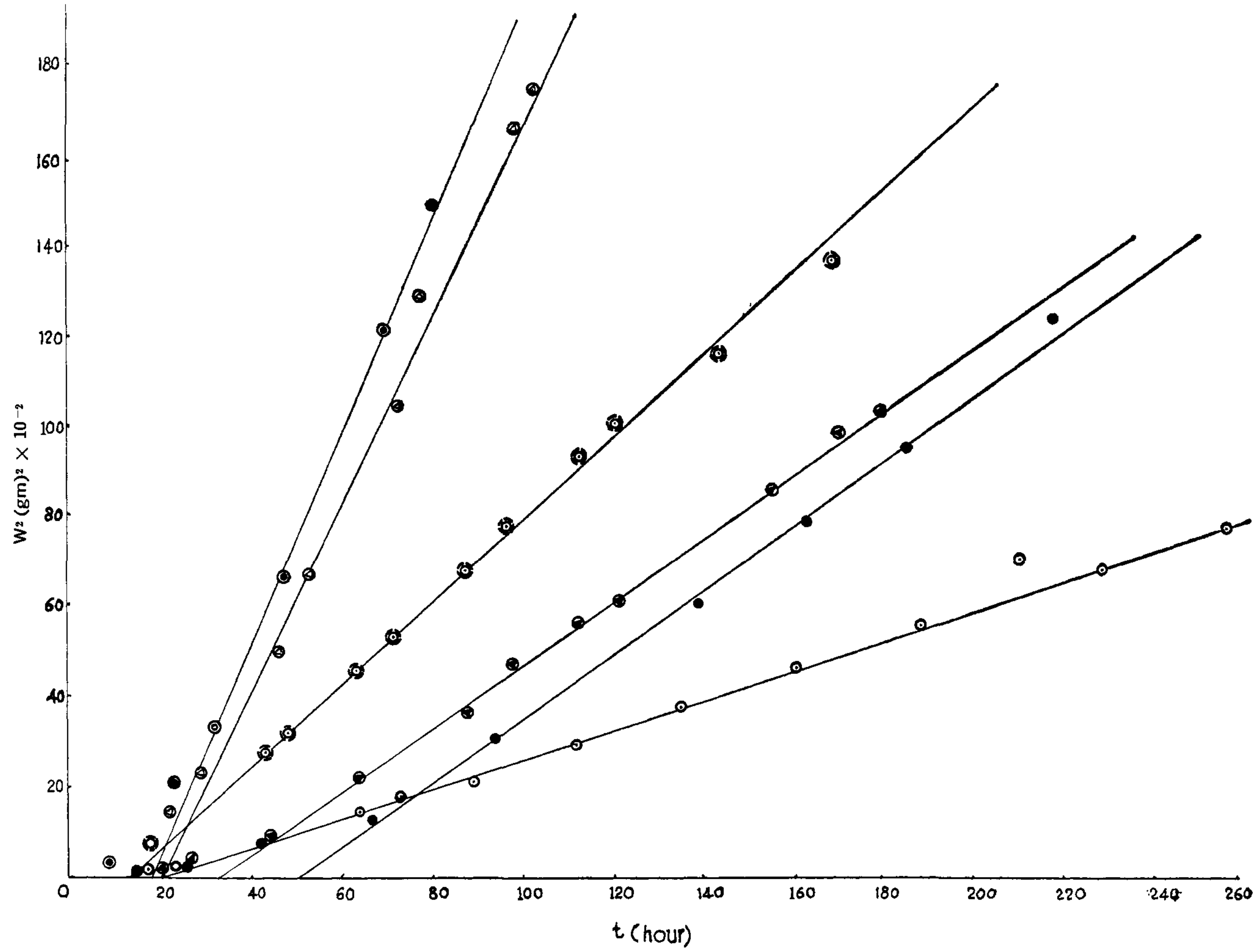

Figure 4. Kinetic data for the inward penetration of iodine in: mercurous chloride grains (-⊙-) at 55 ± 1°, (-◎-) at 65 ± 1°; mercurous bromide grains (-⊛-) at 55 ± 1°, (-◉-) at 65 ± 1°; mercurous iodide grains (-●-) at 55 ± 1°, (◎) at 65 ± 1°; and the test of eq 1.

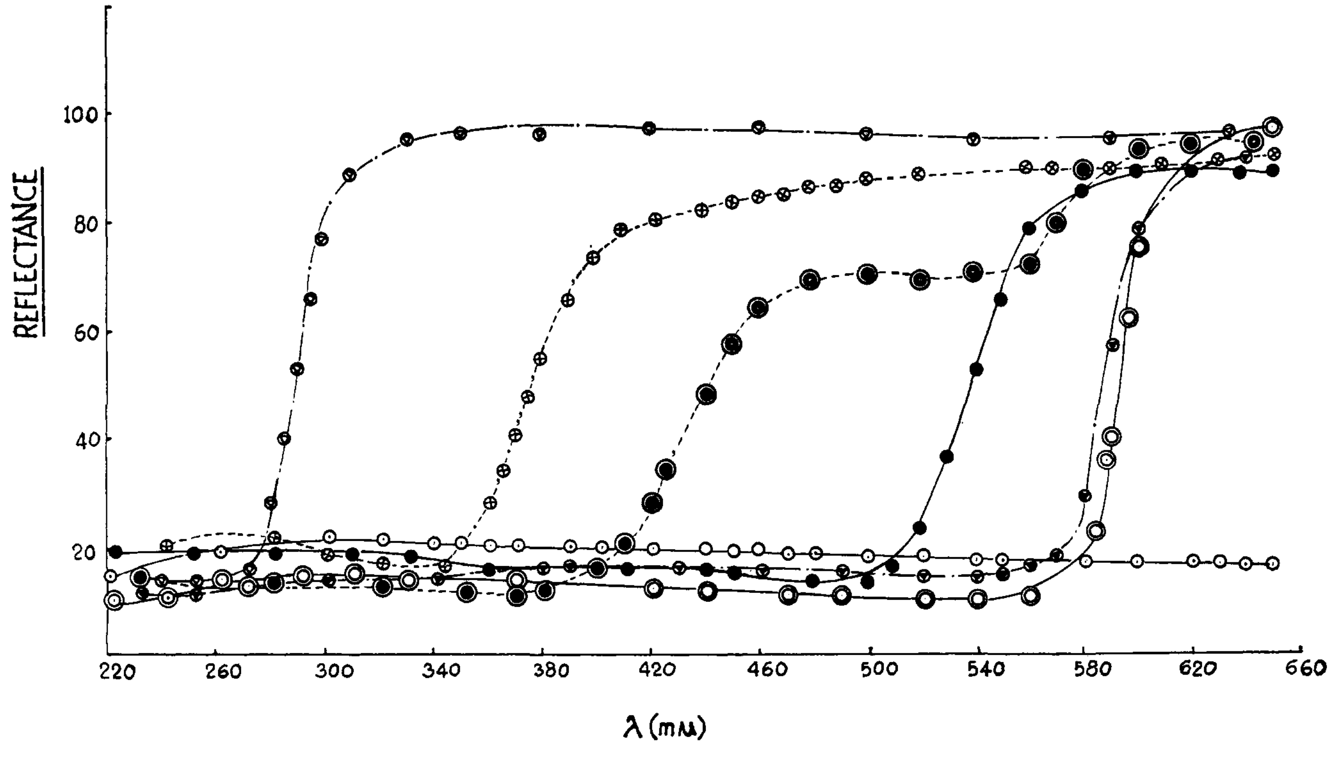

Figure 5. Proof of the formation of HgClI in the solid state by reflectance spectra: —◎—◎— $HgCl_2$, -⊗-⊗- Hg_2Cl_2, -●-●- Hg_2I_2, -⊙-⊙-HgI_2, -⊙-⊙- I_2, ---◉--◉--- yellow product HgClI, ⊛—⊛ final reaction product ($HgCl_2$ + HgI_2).

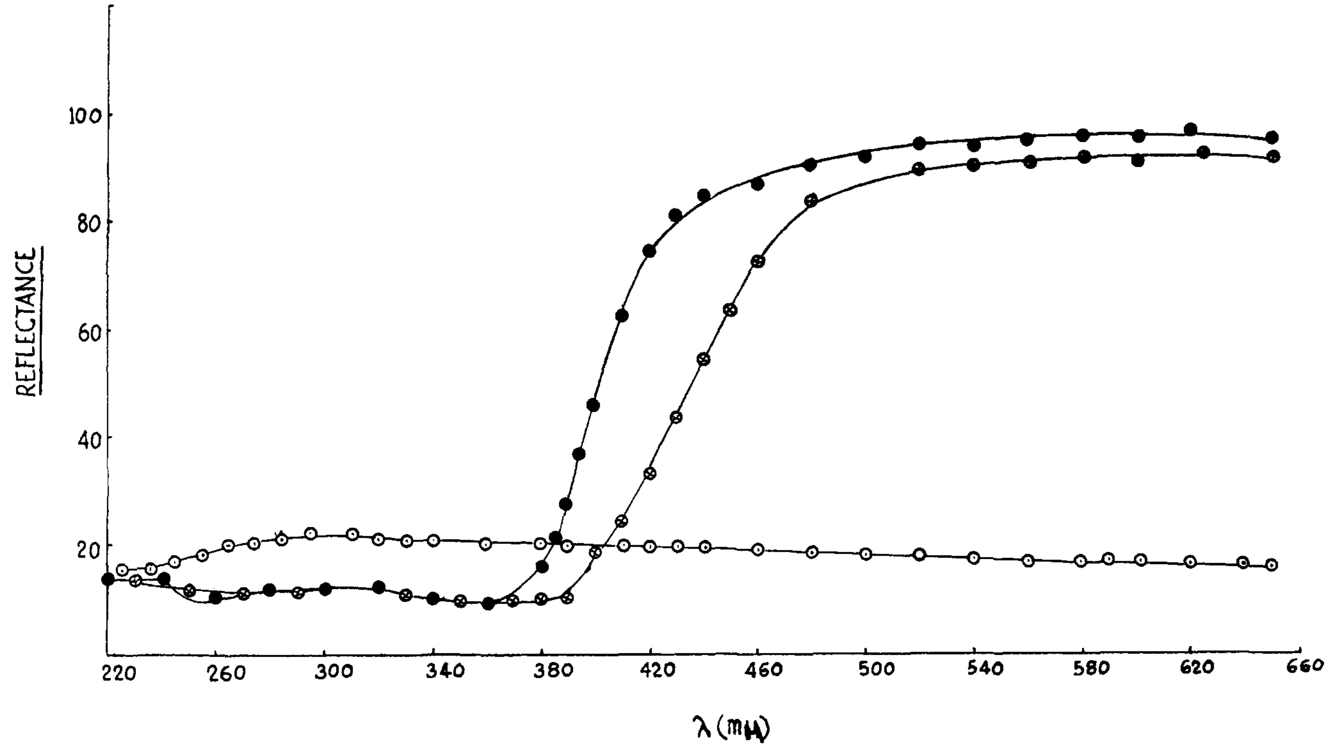

Figure 6. Proof of the formation of HgBrI in the solid state by reflectance spectra: -●-●- Hg_2Br_2, -○-○- I_2, -⊗-⊗- HgBrI (yellow product).

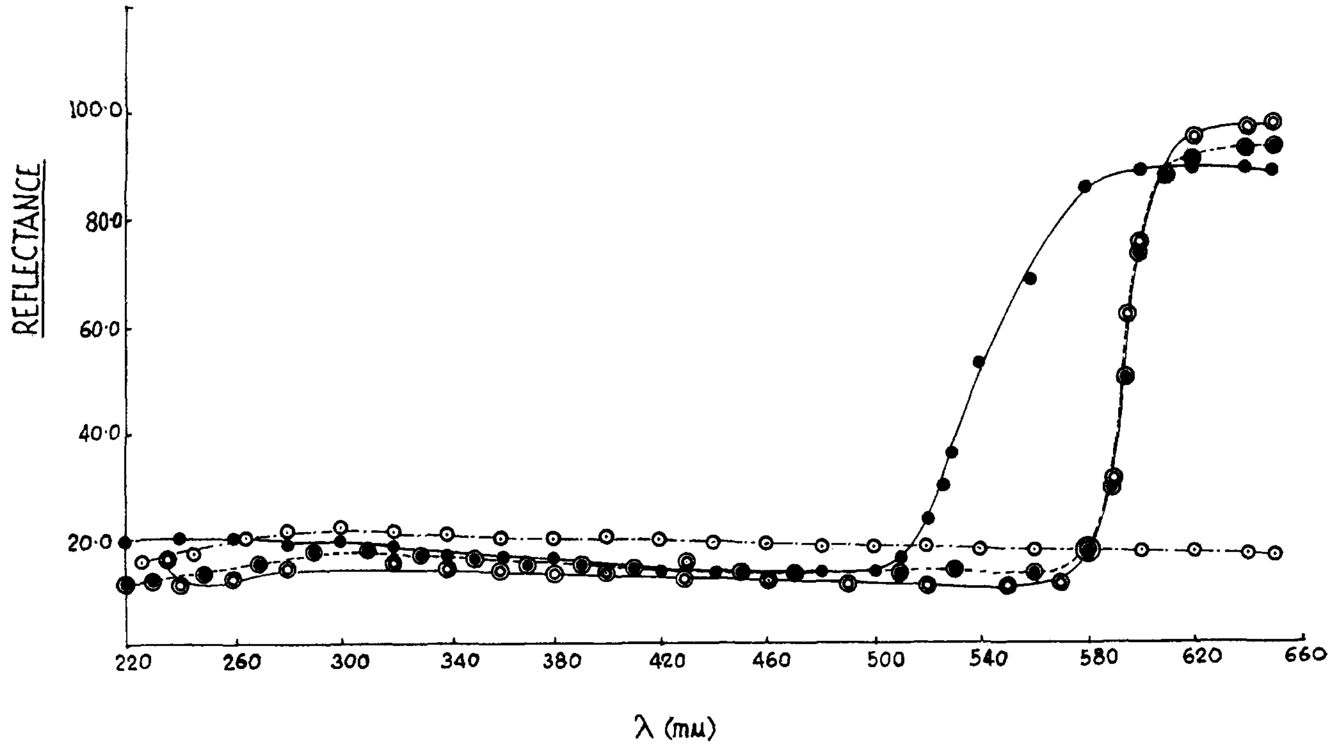

Figure 7. Proof of the formation of HgI_2 in the solid state by reflectance spectra: -●-●- Hg_2I_2, -○-○- I_2, -◎-◎- pure red HgI_2, product for reaction iii, -◉-◉-.

sumed in the over-all reaction was found to be in 1:1 molar ratio of the reactants, as is required by mechanism I. For mechanism II it ought to have been 2:1. The amount of mercury in the product was also found to correspond to mechanism I. The formation of Hg_2I_2 can be ruled out on the basis of the fact that whereas iodine immediately reacts when brought in contact with mercurous iodide to form mercuric iodide, this is not the case with the reaction product. It was observed that the yellow product was stable for some time, after which it dissociated into mercuric iodide and mercuric chloride.

In reactions ii and iii iodine and halides react in 1:1 molar ratio. This is supported by gravimetric studies

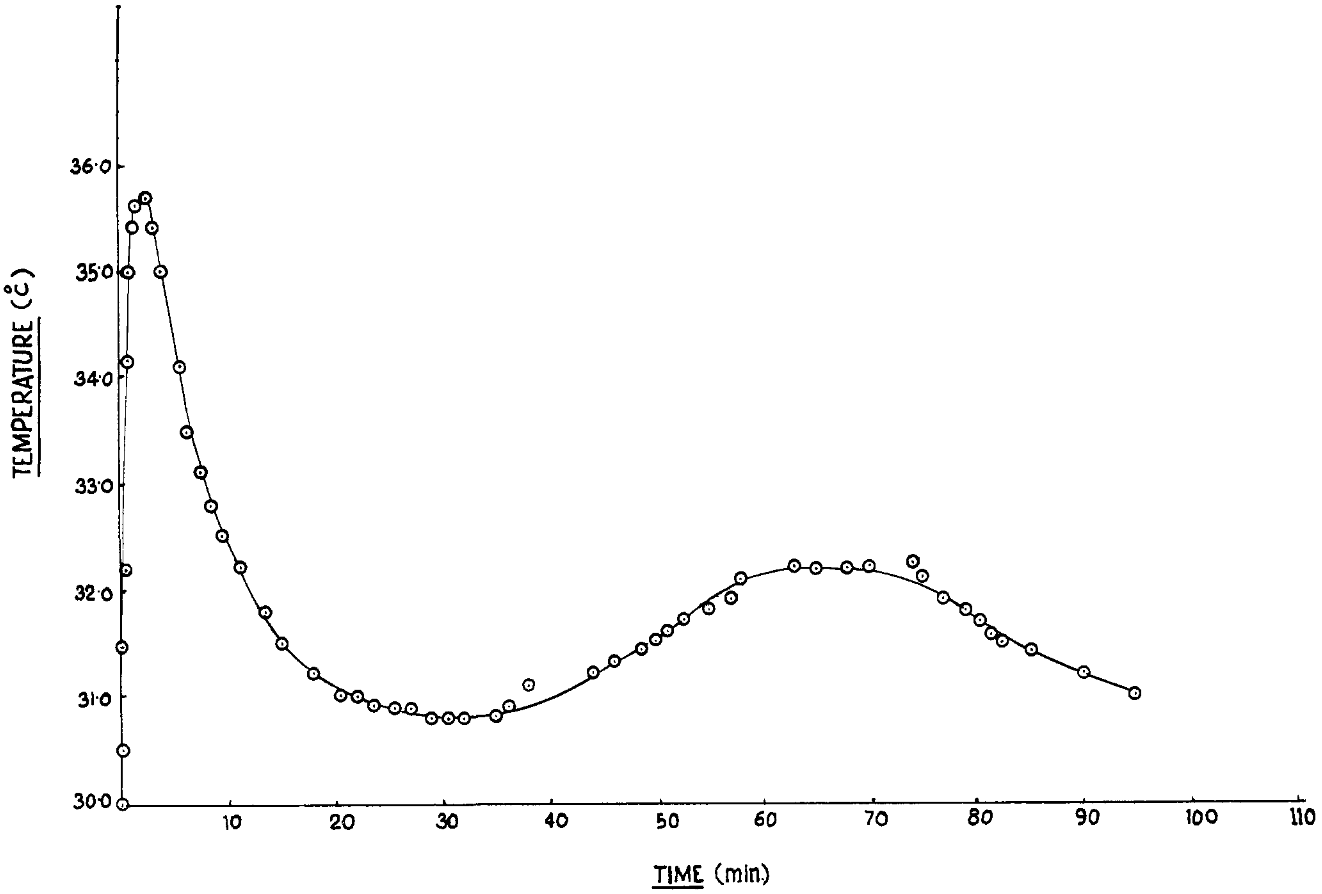

Figure 8. Temperature rise as a function of time for the reaction between iodine and mercurous chloride.

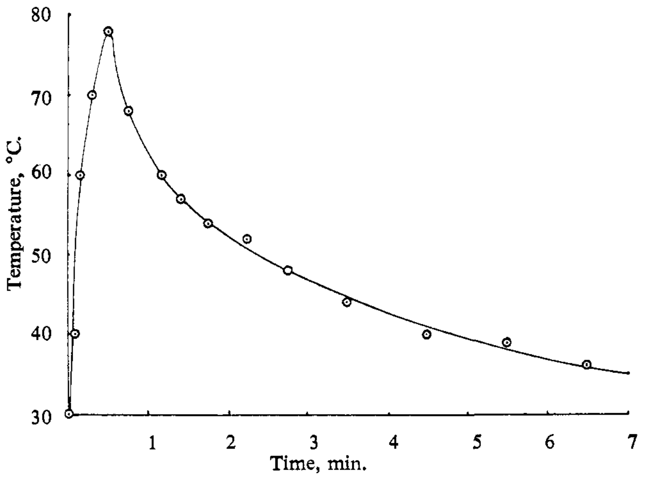

Figure 9. Temperature rise as a function of time for the reaction between iodine and mercurous bromide, reaction ii.

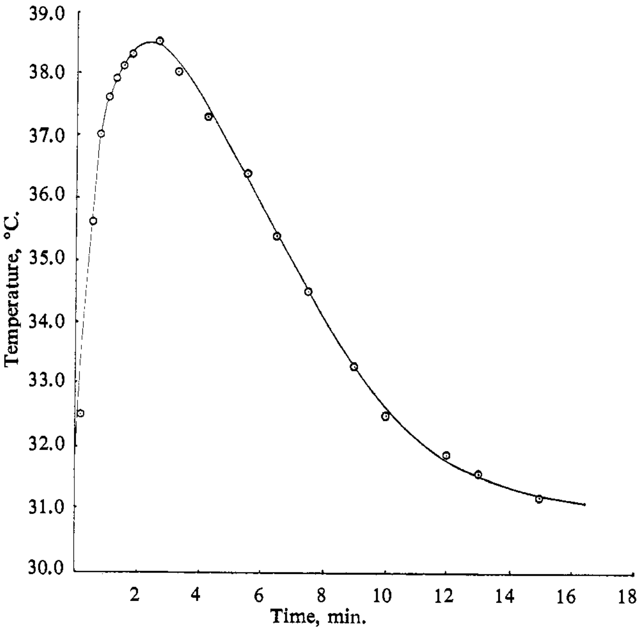

Figure 10. Temperature rise as a function of time for the reaction between iodine and mercurous iodide, reaction iii.

and chemical analysis. This suggests that the postulated mechanisms are correct.

Figure 5 shows the reflectance spectra of species involved in reaction i. A new cutoff for the product appears at 380 mμ, which supports the formation of a new species, HgClI. Another cutoff in the spectra occurs at 560 mμ, which corresponds to that of HgI_2. This happens because of conversion of HgClI into HgI_2 and $HgCl_2$ in the course of time. The cutoff at 380 mμ disappears in the spectra of the final reaction product, which is a mixture of $HgCl_2$ and HgI_2.

Figure 6 shows the spectra of mercurous bromide, iodine, and the product of reaction ii. A new cutoff appears at 370 mμ for the product. This supports the formation of a new species HgBrI.

The spectra of iodine, mercurous iodide, and the product of reaction iii are shown in Figure 7. The cutoff for the product at 560 mμ is identical with that of

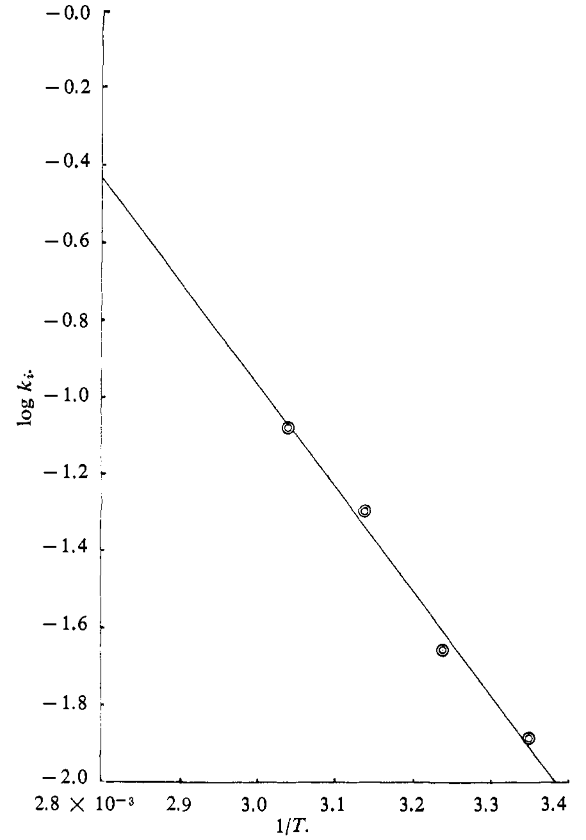

Figure 11. Dependence of k_i on temperature for the reaction between iodine and mercurous chloride.

mercuric iodide. It confirms the formation of mercuric iodide in reaction iii.

Thermal measurements further support the postulated mechanism. When reactants are mixed, heat is evolved and a rise in temperature occurs. Temperature rise has been plotted against time in Figure 8 for reaction i. The existence of two maxima shows that reaction i takes place in two steps. The first step appears to be faster than the second one. From Figures 9 and 10 it also follows that reactions ii and iii are one-step reactions.

Mechanism of Inward Penetration. Information about the mode of penetration of iodine inside the grains of mercurous halides can be obtained from gravimetric studies. Results are given in Figure 4. It may be noted that all the three reactions go to completion. The following equation is found to fit the data.

$$w^2 = k't - \text{constant} \qquad (1)$$

where w is the increase in the weight of mercurous halides, t is the time, and k' is a constant. k' is related to the diffusion coefficient. From the data at different temperature, the energy of activation is estimated to be 25.0, 26.85, and 23.8 kcal for reactions i, ii, and iii, respectively. The energy of activation is much higher than the heat of sublimation of iodine (14.03 kcal), which was estimated from known values of heat of vaporization and heat of fusion.[6] It appears that the diffusion process may involve a vacancy mechanism. Studies on semiconductivity of various reaction products may give more information about this mechanism.

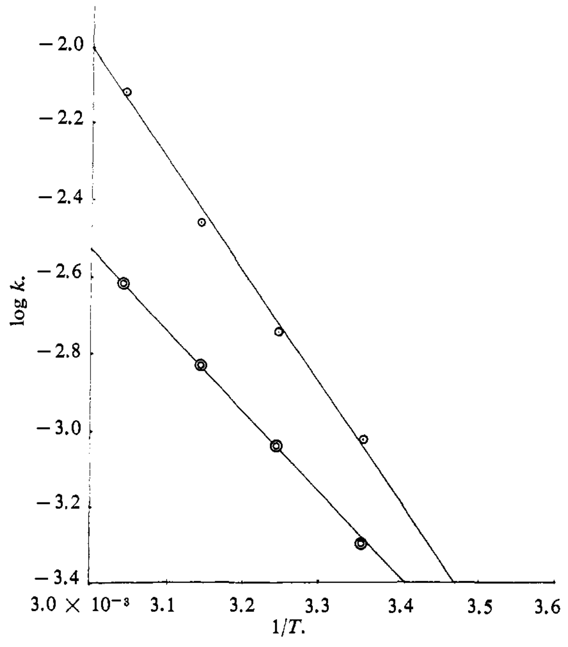

Figure 12. Dependence of k on temperature (-⊙-) for reaction ii and (-◎-) for reaction iii.

Mechanism of Lateral Diffusion. The kinetic data for reaction i are best fitted by the equation

$$\xi^2 = 2k_i t e^{-p\xi} \qquad (2)$$

Theoretical justification for eq 2 has been given in a recent communication,[3] where k_i has been shown to be related with the diffusion coefficient. In Figure 1 straight lines are obtained when log (ξ/t) is plotted against ξ; this confirms the validity of eq 2.

The kinetic data for reactons ii and iii are best fitted by the equation

$$\xi^n = kt \qquad (3)$$

The test of eq 3 was made by plotting log ξ against log t in Figures 2 and 3. The parameters of eq 2 and 3 are given in Table I.

The values in Table I are the mean values estimated from five or six measurements. Figures 11 and 12 show how k_i for reaction i and k for reactions ii and iii vary with temperature. Since k_i and k are related to the diffusion coefficient, the energy of activation for lateral diffusion would be identical with the energy of activation. The energy of activation for lateral diffusion for the three reactions has been found to be 12.7, 13.5, and 9.6 kcal, respectively.

More information about the mechanism is obtained from the study of the kinetics of reactions when the reactants are separated by an air gap of different length. Equation 2 still satisfies the data for reaction i, with different values of k_i and p. The following equation fits the data for reactions ii and iii.

$$\xi^2 = k''t \qquad (4)$$

The values of k_i' and k'' are found to depend on the length of the air gap according to

$$k_i' = ae^{q_1/(d+m)} \qquad (5)$$

$$k'' = be^{-q_2 d} \qquad (6)$$

where d is the length of the air gap and m, a, q_1, b, and

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(6) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p 419.

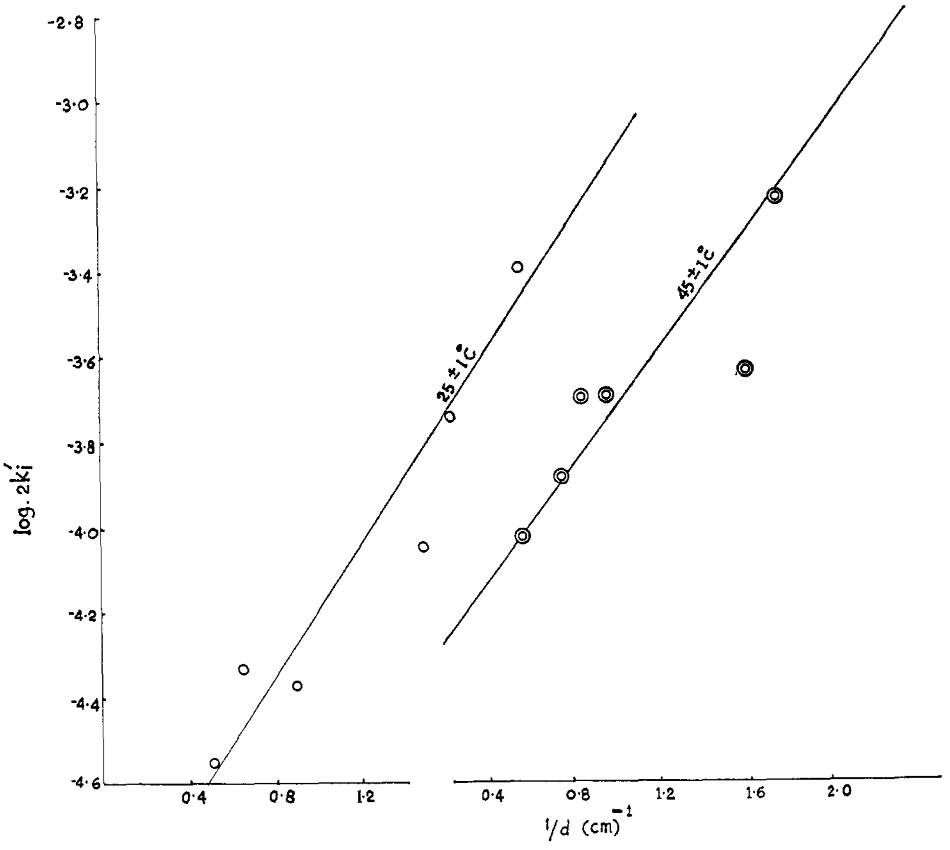

Figure 13. Dependence of k_i' on the length of the air gap and test of eq 5.

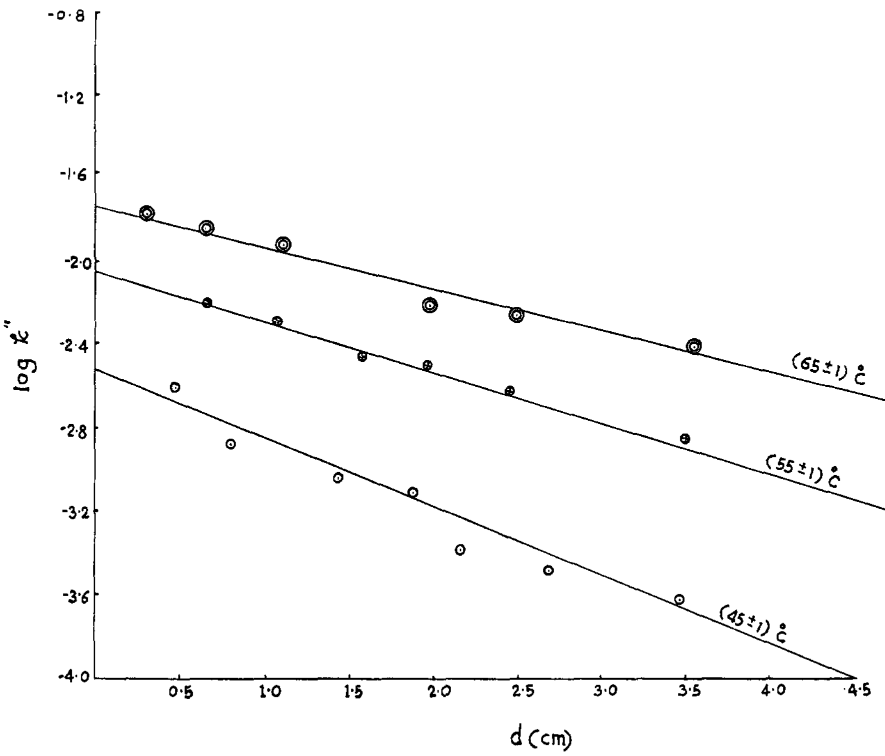

Figure 14. Dependence of k'' on the length of the air gap and test of eq 6 for the reaction between iodine and mercurous bromide.

q_2 are constants. In Figure 13 log $2k_i'$ is plotted against $1/d$ and in Figures 14 and 15 log k'' has been plotted against d.

The form of eq 5 supports the vapor-phase mechanism for reaction i since, when $d = 0$, k_i' attains the value obtained when the reactants are kept in contact. However, eq 6 shows that the diffusion partially occurs by surface migration since, when $d \rightarrow 0$, $k \rightarrow 0$.

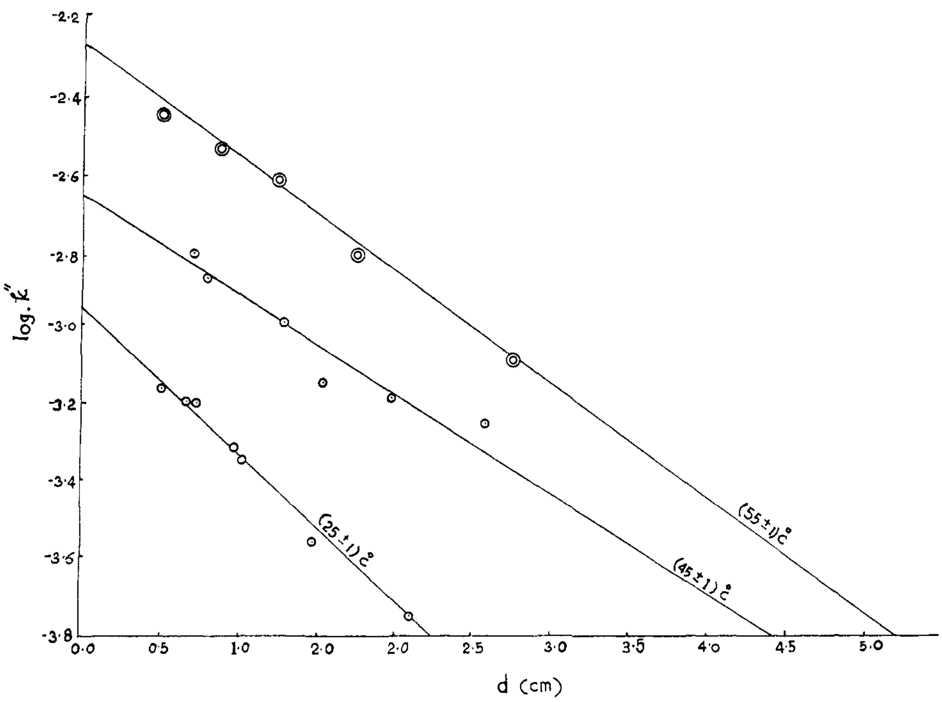

Figure 15. Dependence of k'' on the length of the air gap and test of eq 6 for the reaction between iodine and mercurous iodide.

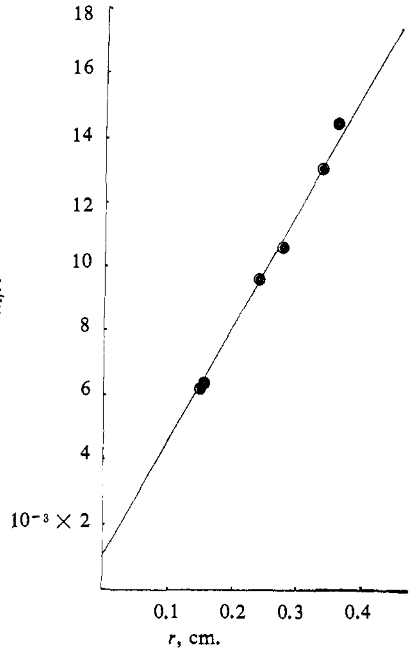

Figure 16. Estimation of the diffusion coefficient of iodine in air and the coefficient for surface migration, and test of eq 8.

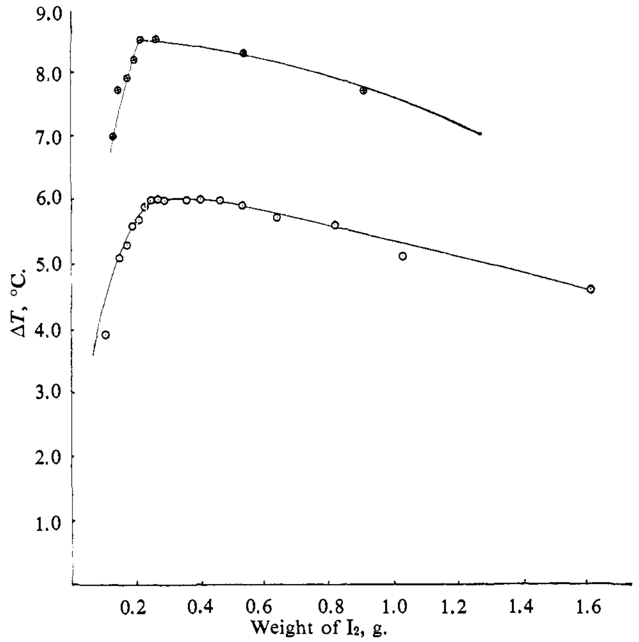

Figure 17. Temperature rise as a function of the amount of iodine added to a fixed amount of mercurous chloride (-⊙-⊙-) and mercurous iodide (-⊗-⊗-).

The surface migration of iodine is not an uncommon feature. The experiment on diffusion of iodine in air supports this fact. The data are fitted by

$$s = k_1 t \tag{7}$$

where s is the amount of iodine diffused in air, t is the time, and k_1 is a constant. The value of k_1 depends on the diameter of the tube according to

$$k_1/r = \alpha r + \beta \tag{8}$$

α and β are given by $\alpha = \pi c_e D_v/l$ and $\beta = 2\pi c_e D_s$, where r is radius of the tube, l is the distance of iodine surface from open end of the tube, c_e is the equilibrium concentration of iodine just above the surface, D_v is the vapor-phase diffusion coefficient, and D_s is the diffusion coefficient for surface migration. The test of eq 8 has been made by plotting k_1/r against r in Figure 16.

The values of D_v and D_s has been evaluated from Figure 16 and are found to be 0.0647 and 4.0×10^{-4} cm^2/sec at 65°.

In order to understand the nature of bond rearrangement, it is worthwhile to discuss the thermochemical data. A sudden rise in temperature occurs on mixing iodine and mercurous halides, leading to the formation of HgClI, HgBrI, and HgI_2 as reaction products. The maximum rise in temperature does not take more than 2-3 min in all cases. It would be noted that very small amounts of iodine would be consumed in such a short time interval. This indicates that the reaction of iodine, at least on the surface of mercurous halide grains, is very fast. In order to have an idea about the exact amount of iodine needed to react with mercurous halides during this period, different amounts of iodine were added to a known amount of mercurous chloride and mercurous iodide and the rise in temperature was noted. The results are given in Figure 17.

The amount of iodine which reacts instantaneously with mercurous chloride and mercurous iodide can be approximately estimated from Figure 17. Knowing the amount of reactants consumed and the temperature rise, an approximate estimate of heat of reaction can be made. For the first step of reaction i, it is found to be 2.0 kcal/mole. It was found that when 0.6485 g of iodine was added to 6.0707 g of mercurous chloride, no iodine was left unreacted. The approximate value of the heat of dissociation of HgClI into mercuric chloride and mercuric iodide is estimated to be 0.2 kcal/mole. In a similar manner the approximate value of the heat of reaction for reactions ii and iii were estimated to be 3.9 and 1.23 kcal/mole, respectively.

At this stage it is pertinent to make a few remarks about the physics of the reactions. It is quite clear that electron transfer is not involved in the reactions in the solid state, since E° for the following reaction would be -0.37 v.

$$Hg_2^{2+} + I_2 = 2Hg^{2+} + 2I^-$$

The above reaction would not be thermodynamically favored. Experiments show that above reaction does not occur in aqueous medium. The magnitude of energy changes in the reactions as estimated above show that some sort of weak interaction is involved. It may either be charge-transfer interaction or dipole-induced dipole interaction. The latter has recently been shown to be involved in the formation of picrates of naphthols.[3] Subsequent lattice rearrangement may lead to the formation of reaction products. The break of HgClI seems to involve the displacement of interpenetrating lattices of mercuric chloride and mercuric iodide, since the energy change in the process is very small.

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Protonation of Aromatic Hydrocarbon Dinegative Ions. A Thermodynamical Study of the Carbanions MH^-

N. H. Velthorst and G. J. Hoijtink

Contribution from the Laboratory for Physical Chemistry of the Free University and the Laboratory for Physical Chemistry, University of Amsterdam, Amsterdam, The Netherlands. *Received July 12, 1966*

Abstract: The disproportionation of the carbanions MH^- derived from anthracene, tetracene, pentacene, pyrene, perylene, and phenanthrene has been investigated. The experimental results point to the occurrence of the following disproportionation equilibria: $2MH^- \rightleftarrows MH_2 + M^{2-}$, for tetracene and pentacene; $2MH^- \rightleftarrows MH_2^- + M^-$, for phenanthrene; and $2MH^- \rightleftarrows MH_2^{2-} + M$, for pyrene and perylene. For the carbanion derived from anthracene no observable disproportionation was found. Except for the carbanion from phenanthrene the tendency toward disproportionation could be explained from a thermodynamical study based on experimental and semiempirical data.

In a previous paper[1] a study has been made of the protonation of the dinegative ions of some aromatic hydrocarbons. The primary reaction products formed are the carbanions MH^- (eq 1) as has been established

$$M^{2-} + H^+ \rightleftarrows MH^- \tag{1}$$

for naphthalene, anthracene, tetracene, and pyrene by a comparison of their absorption spectra with those of the corresponding carbonium ions MH^+. The present paper deals with the disproportionation of some carbanions MH^- into their dihydro product MH_2 and the dinegative ion M^{2-} (eq 2). Such a disproportionation

$$2MH^- \rightleftarrows MH_2 + M^{2-} \tag{2}$$

reaction may be followed by an electron transfer according to eq 3 provided the reduction potential of the

$$MH_2 + M^{2-} \rightleftarrows MH_2^- + M^- \tag{3}$$

mononegative ion M^- is lower than that of the dihydro product MH_2. When the first reduction potential of MH_2 and the second reduction potential of M differ sufficiently, even two electrons may be transferred.

$$M^{2-} + MH_2 \rightleftarrows M + MH_2^{2-} \tag{4}$$

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[1] N. H. Velthorst and G. J. Hoijtink, *J. Am. Chem. Soc.*, **87**, 4529 1965).