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The Thermal Decomposition of Ethylene Iodide

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The homogeneous gaseous decomposition of ethylene iodide has been studied in the temperature interval 205°–230°C. It is found that two simultaneous reactions occur to give the same final products, ethylene and iodine. One is a reaction catalyzed by iodine atoms, similar to that found to occur in solutions. The other is a unimolecular decompo-

sition. The activation energies of the two reactions are 31,400 cal. and 37,500 cal., respectively. It is shown that the results for the iodine catalyzed reaction in solution and in the gas phase are in agreement indicating that the solvent has only a slight effect, if any, on the reaction rate.

THE thermal decomposition of ethylene iodide has been investigated in carbon tetrachloride solutions by Polissar.¹ Schumacher and Wiig² have studied the photochemical reaction also in carbon tetrachloride solutions. The reaction was found to be catalyzed by iodine atoms in both instances, the thermal reaction being governed by the rate expression,

$$-d[\text{C}_2\text{H}_4\text{I}_2]/dt = k[\text{C}_2\text{H}_4\text{I}_2][\text{I}_2]^{1/2},$$

while the equation

$$-d[\text{C}_2\text{H}_4\text{I}_2]/dt = k' \text{I}_{\text{abs}}^{1/2} [\text{C}_2\text{H}_4\text{I}_2]$$

represents the photochemical rate.

In a slight modification of Polissar's interpretation Schumacher³ has suggested the following mechanism for the decomposition of ethylene iodide: (1) $\text{I}_2 \rightarrow \text{I} + \text{I}$; (2) $\text{C}_2\text{H}_4\text{I}_2 + \text{I} \rightarrow \text{C}_2\text{H}_4\text{I} + \text{I}_2$; (3) $\text{C}_2\text{H}_4\text{I} \rightarrow \text{C}_2\text{H}_4 + \text{I}$.

This mechanism gives the rate expression,

$$-d[\text{C}_2\text{H}_4\text{I}_2]/dt = k_2 K_{\text{I}_2}^{1/2} [\text{C}_2\text{H}_4\text{I}_2][\text{I}_2]^{1/2}$$

when it is assumed that the equilibrium concentration of $\text{C}_2\text{H}_4\text{I}$ is very low, and that steps (1) and (3) are so fast that step (2) is the rate determining process.

In addition to the iodine catalyzed reaction Polissar found indications of an uncatalyzed decomposition of ethylene iodide, occurring simultaneously with the first reaction. This has

been entirely disregarded by Schumacher in his discussion of the reaction mechanism.

The purpose of the present investigation was to compare the rate of the gas reaction with that in solution and also to establish definitely the presence of the uncatalyzed decomposition. On account of very considerable difficulties encountered, the results obtained are not as satisfactory as could be desired. Yet we believe them of sufficient value to be worthy of a brief description.

EXPERIMENTAL METHOD

The measurements were made by the static method. The increase in pressure was followed by a mercury manometer with an intervening quartz spiral gauge, which acted as a null-point instrument. The final form of the apparatus is shown diagrammatically in Fig. 1.

The ethylene iodide was prepared by passing ethylene gas into a saturated solution of iodine in absolute alcohol.⁴ The product was washed on the filter with cold absolute alcohol and then recrystallized twice from absolute alcohol. Care was taken not to warm the alcoholic solutions above 50°C to prevent the formation of $\text{CH}_2\text{-ICH}_2\text{OC}_2\text{H}_5$.⁵ The ethylene iodide was kept in a pure form free from iodine on dry ice.

The first results obtained proved to be quite irreproducible. The final procedure, adopted after several unsuccessful modifications, was as follows: The system was thoroughly evacuated.

¹ Polissar, J. Am. Chem. Soc. **52**, 956 (1930).

² Schumacher and Wiig, Zeits. f. physik. Chemie **B11**, 45 (1930).

³ Schumacher, J. Am. Chem. Soc. **52**, 3132 (1930).

⁴ Semenov, Jahresber. Fortschritte Chem **1864**, 483.

⁵ Baumstark, Ber. **7**, 1172 (1875).

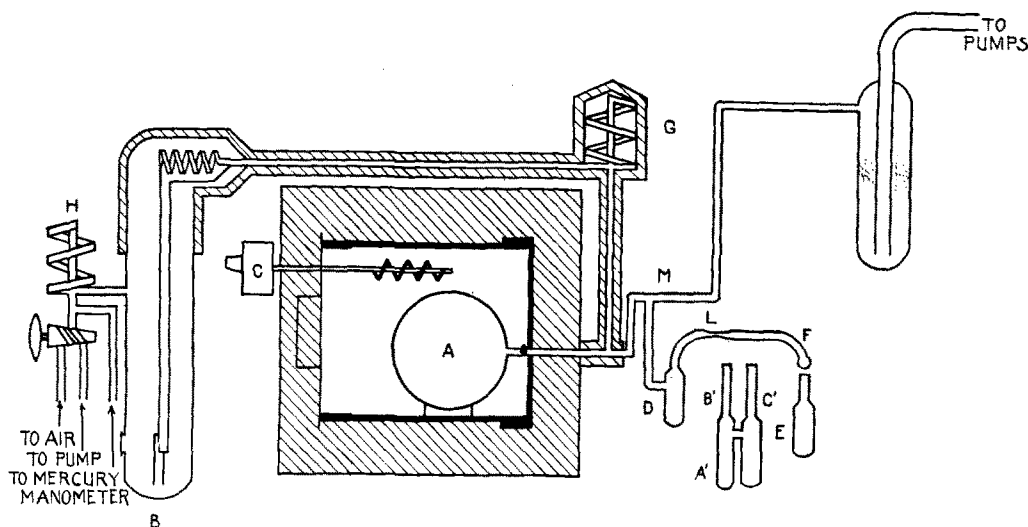


FIG. 1. The apparatus. *A*, reaction flask; *B*, quartz spiral manometer; *C*, De Khotinsky bimetallic thermoregulator; *D* and *E*, filling tubes; *G* and *H*, flexible spirals.

Air was let in through a slow leak and a large calcium chloride tube. Although the effect of moisture on the reaction was found to be negligible, its presence prevented satisfactory volatilization of the ethylene iodide at the start of a run, and thus a thorough drying of the system was essential. Tube *E*, containing ethylene iodide, was sealed on at *F*, care being taken to prevent flame products from entering the system. This precaution was found to be very essential to obtain reproducible results. After evacuation of the system the middle fraction of ethylene iodide was sublimed by gentle heating into *D*, and *E* was sealed off at *L*. Heating of ethylene iodide above the melting point was avoided, as rapid decomposition took place in the liquid phase.

The system was further evacuated while *D* was cooled with solid carbon dioxide, and was sealed off from the pump at *M*. The ethylene iodide was then volatilized into the reaction flask, and the exposed portions of the reaction system were covered with an auxiliary furnace already heated above the condensation point of the reaction mixture.

The products of the reaction were found to be completely condensable with liquid air, and the solid matter was entirely soluble in carbon tetrachloride. The final pressure remained constant within 0.3 mm over a period of several days, indicating that no polymerization of ethyl-

ene occurred. From this evidence and the doubling of the initial pressure, it was concluded that ethylene and iodine were the only reaction products.

In determining the effect of an excess of iodine on the rate it was found necessary to vaporize the ethylene iodide and the iodine separately. Otherwise iodine caused excessive decomposition of ethylene iodide. In these runs the vacuum distillation process was dispensed with the filling tube, *A'*, used. Ethylene iodide was placed in one side of it and iodine in the other. One side was sealed off and the other was attached to the system in place of the tube, *D*. The ethylene iodide was carefully vaporized first, and then the iodine.

RESULTS AND THEIR INTERPRETATION

At 195°C, on increasing the surface to volume ratio of the reaction flask four times, it was found that the reaction rate increased by a factor of about 1.8, indicating the presence of an appreciable surface reaction. At higher temperatures this heterogeneous reaction was not noticeable but even at 230°C the reaction went almost to completion in a very few minutes. These circumstances limited the accessible temperature range and made an accurate determination of the temperature coefficient impossible.

It was found that Polissar's expression for the iodine catalyzed reaction could not be fitted

to our results. They were best described by the equation,

$$-d[C_2H_4I_2]/dt = k_1[C_2H_4I_2] + k_2[C_2H_4I_2][I_2]^{1/2}.$$

This indicates the simultaneous occurrence of two reactions, namely, the iodine catalyzed reaction described by Polissar and Schumacher, and a unimolecular decomposition.

Fig. 2 and Fig. 3 give a plot of the quantity, $-d[C_2H_4I_2]/dt/[C_2H_4I_2]$ vs. $[I_2]^{1/2}$. Fig. 2 shows results at 478°K, 493°K and 503°K in an empty 500 cc Pyrex flask; Fig. 3 shows results at 478°K and 493°K in a similar flask filled with pieces of 10 mm Pyrex tubing which increased the total surface four times. The different runs are distinguished by characteristic markings.

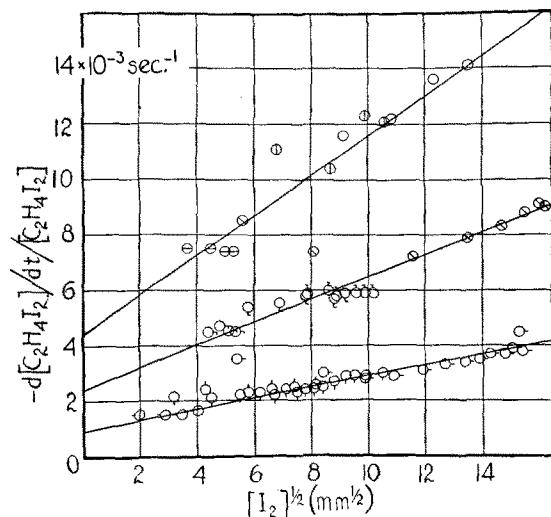


FIG. 2. A plot of $-d[C_2H_4I_2]/dt/[C_2H_4I_2]$ vs. $[I_2]^{1/2}$ for the empty reaction flask. Upper curve 503°K. Middle curve, 493°K. Lower curve, 478°K.

Some of the runs, particularly in the empty flask, show abnormally high initial velocities. This behavior was still much more pronounced in earlier runs not shown in the figures. As the technique of purifying the substance, evacuating and filling the reaction system was refined, the velocities became increasingly consistent with the rate expressions as given above. This is evidence that the deviations are due to extraneous causes, presumably some impurity eliminated by the more painstaking technique employed in the final series of experiments. In these plots the slopes of the straight lines drawn

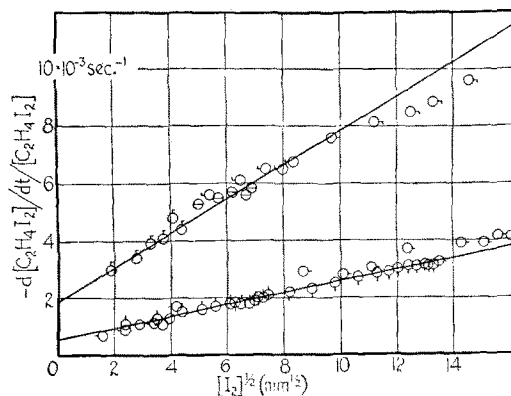


FIG. 3. A plot of $-d[C_2H_4I_2]/dt/[C_2H_4I_2]$ vs. $[I_2]^{1/2}$ for the filled reaction flask. Upper curve, 493°K. Lower curve, 478°K.

give the velocity constants of the iodine catalyzed reaction, while their intercepts with the ordinate axis are the velocity constants for the unimolecular reaction.

The values obtained in this manner are given in Table I.

The agreement of these results is not very good, but it shows without any doubt that the unimolecular reaction is existent and that both reactions are essentially homogeneous.

The activation energies obtained from the above data for the unimolecular reaction are 35,600 cal. for the unfilled flask and 37,600 cal. for the filled flask. They are 28,700 cal. and 32,800 cal., respectively, for the iodine catalyzed reaction. As our experimental results do not allow a satisfactory choice between these values, for the succeeding discussion we shall use the average values: 36,600 cal. for the unimolecular, and 30,200 cal. for the iodine catalyzed reaction. The uncertainty of these values is probably ± 3000 cal.

The information obtained in these experiments on the unimolecular reaction is rather meager. From the agreement of the experimental data

TABLE I.

Temp.	Unimolecular reaction		Iodine catalyzed reaction	
	Empty flask	Filled flask	Empty flask	Filled flask
	$(10^{-3} \text{ sec.}^{-1})$		$(10^{-4} \text{ mm}^{1/2} \text{ sec.}^{-1})$	
478°K	0.9	0.5	1.78	2.0
493°	2.4	1.8	4.24	5.95
503°	4.4		7.12	

with the first order rate expression, it may be concluded that the falling off of the unimolecular velocity constant occurs at lower pressures than those studied, i.e., 25 mm to 250 mm initial pressure of ethylene iodide. Expressing the velocity constant in the form, $k = Ae^{-E/RT}$, it is found that the constant, A , is approximately 10^{13} . This is the same order of magnitude as is found in many other unimolecular reactions. The usual computation⁶ shows that ethylene iodide has a sufficient number of degrees of freedom to maintain the necessary rate of activation.

The higher temperature coefficient of the unimolecular reaction explains why Polissar found only indications of an uncatalyzed reaction, while it is found to be quite prominent in the higher temperature range covered in this investigation.

As has been pointed out by Polissar and by Schumacher, the activation energy of the iodine catalyzed reaction is equal to one-half the heat of dissociation of the iodine molecule plus the heat of activation of the reaction between iodine atoms and the ethylene iodide molecules. The former is equal to 18,300 cal.⁷ and the latter therefore is equal to 11,900 cal. ± 3000 cal. This value agrees within experimental error with those values found for the reaction in solution.^{1, 2}

It is possible to calculate the number of collisions between iodine atoms and ethylene iodide molecules since the concentration of the iodine atoms is that of the thermal equilibrium and the latter is accurately known. At 478°K the dissociation constant of iodine is 3.75×10^{-9} mm Hg as calculated from the equation of Gibson and Heitler.⁸ Assuming diameters of 4×10^{-8} and 3×10^{-8} cm for the ethylene iodide molecule and the iodine atom respectively, the total number of collisions at unit pressure between ethylene iodide and iodine molecules is 1.7×10^{18} cc⁻¹ sec.⁻¹. The number of ethylene iodide molecules decomposing under the same conditions is 4.1×10^{13} cc⁻¹ sec.⁻¹. The ratio of the two is 2.4×10^{-5} . This corresponds to an activation energy of 12,300 cal. if it is assumed that the entire activation energy is contained

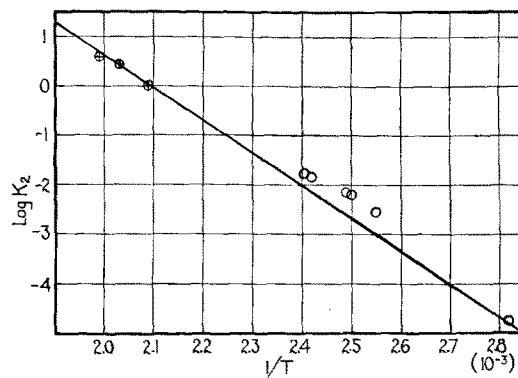


FIG. 4. A plot of $\log k$ vs. $1/T$. Circles, Polissar; circles with crosses, Arnold and Kistiakowsky.

in only two degrees of freedom and that the steric factor is unity.

It is of some interest to compare the absolute reaction rates in solution and in the gas phase. Fig. 4 shows a plot of the logarithms of the constants (mols^{-1/2} cc^{1/2} sec.⁻¹) for the iodine catalyzed reaction determined by Polissar and those (average) from this investigation plotted against the inverse temperature. The straight line drawn through our points corresponds to an activation energy of 31,400 cal. It will be seen that Polissar's values differ from our extrapolation only by about a factor of two. Considering the uncertainties of the extrapolation, one may conclude that the reaction velocity in solution and in the gas phase are essentially the same and that the solvent has very little influence, not only on the activation energy, but also on the collision frequency between the reacting molecules.

In conclusion it may be pointed out that the gaseous decomposition of ethylene iodide is one of the very few reactions in which two entirely independent reaction mechanisms occur with essentially equal rates in the same temperature range to give the same final products. In this respect ethylene iodide occupies a position intermediate between hydrogen iodide and hydrogen bromide. The second of these, as is well known, decomposes exclusively through atomic chains, while the other decomposes bimolecularly. The latter, and not a unimolecular reaction, is to be expected, of course, because the hydrogen iodide molecule contains only one atom of iodine and, furthermore, has only a few degrees of freedom.

⁶ Kassel, *Kinetics of Homogeneous Gas Reactions*, New York, Chemical Catalog Company, 1932.

⁷ Bodenstein and Stark, *Zeits. f. Elektrochemie* **16**, 961 (1910).

⁸ Gibson and Heitler, *Zeits. f. Physik* **49**, 465 (1928).