

Kurze Mitteilung

Kinetics of Reaction between Hydrazine and Iodine Solution

With 4 figures

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Abstract

The kinetics of the reaction between hydrazine and iodine has been studied. The order of the reaction is found to be one with respect to iodine concentration. Both H^+ and I' retard the rate of reaction. The values of E_{act} , $\log_{10}PZ$ and $-\Delta S$ have been calculated and are found to be 11.5 ± 0.5 k.cal/mole, 7.4 ± 0.4 (sec^{-1}) and 25.5 ± 1.0 (e.u.) respectively.

CURTIVS and SCHULZ¹ have shown that hydrazine reacts with iodine slowly in acid medium. The same reaction has been studied by STOLLE² in the bicarbonate solution with a view to developing the new method of estimation. The results of kinetics studies of the same reaction have been reported in this communication.

The materials employed are of the highest possible purity. Both hydrazine sulphate and iodine are of E. MERCK's grade. The solution of iodine is made by dissolving it in known concentration of potassium iodide solution and it has been standardized by a thiosulphate solution. The pH adjustments are made by the addition of dilute H_2SO_4 to the reaction mixture and all the measurements are carried out in a photovolt pH meter.

Iodine and hydrazine solutions are taken to two 250 ccm pyrex conical flasks and allowed to stand in the thermostat for some hours. After a certain period, both are rapidly mixed and aliquot parts are withdrawn at suitable intervals of time and analysed for residual iodine by the standard thiosulphate solution. The reaction is found to

¹ T. CURTIUS and H. SCHULZ, J. prakt. Chem. (2) **42** (1890) 539.

² R. STOLLE, J. prakt. Chem. (2) **66** (1902) 332.

be of first order with respect to iodine solution, the values of which have been calculated from the slopes of $\log \frac{a}{a-x}$ vs 't' plots which always includes 7 to 8 experimental points. Fig.1 represents a typical first order plot at different temperatures.

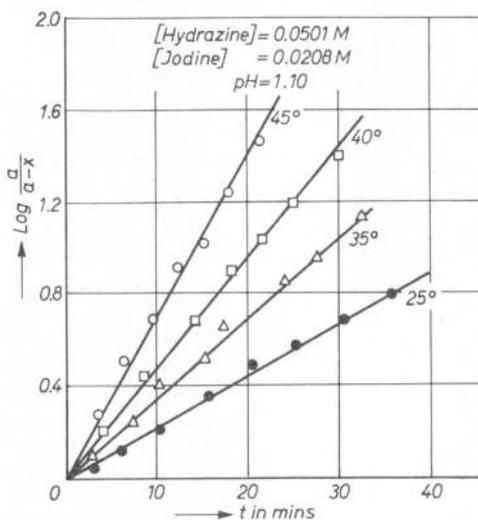


Fig. 1

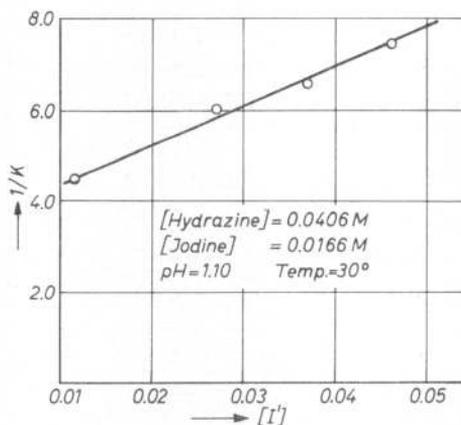


Fig. 2

Effect of iodide ions on the rate

The reaction has been studied in different iodide ion concentrations. All the experiments are performed at identical conditions of

reactants, pH and temperature. The rate constant decreases with the increase of iodide ion concentration and the plot $1/K$ against [iodide] gives a straight line (Fig. 2).

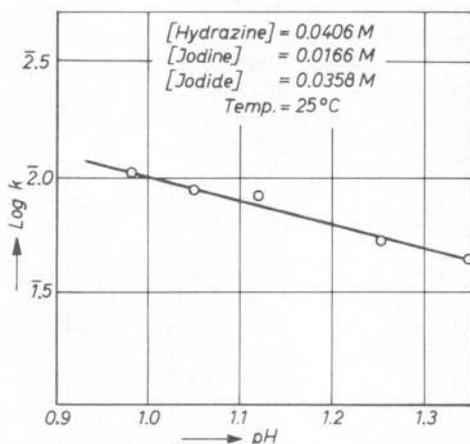


Fig. 3

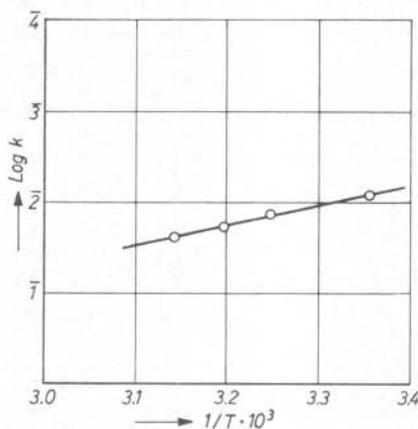


Fig. 4

Effect of pH on the rate

This reaction has been studied at different acid concentrations. The concentration of reactants and iodide ion are kept fixed in every case. It is found that with the increase of pH , the rate of reaction also increases. The pH of the solutions is varied between limits 0.98 to 1.35. A linear relationship is found to hold good when $\log K$ is plotted against pH (Fig. 3).

Influence of temperature on the reaction velocity

The reaction has also been studied at four different temperatures and all the experiments are carried out at identical conditions of reactant, pH and iodide ion concentration. The results have been recorded in the Fig. 4. From the slope of the $\log K$ vs. $1/T$ plot, the activation energy has been calculated. The values of E_{act} , $\log_{10} PZ$ and $-\Delta S$ have been found to be 11.5 ± 0.5 k. cal/mole, 7.4 ± 0.4 (sec^{-1}) and 25.5 ± 1.0 (e.u.) respectively.

Influence of solvents on the rate

The reaction velocities have been calculated in various acetic acid – water binary mixtures. It has been found that the velocity constant increases as the % of acetic acid decreases. The results have been recorded in the following Table.

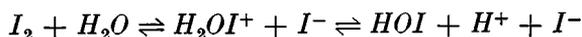
[Hydrazine] = 0.0206 M, [Iodine] = 0.0105 M
 [I⁻] = 0.0212 M, $pH = 1.15$, Temp. = 30°C

No.	% acetic acid	$K \times 10$ (min^{-1})
1	10	1.382
2	20	0.6909
3	30	0.4606
4	40	0.2303

It has already been mentioned that both iodide and hydrogen ions retard the rate of reaction. Therefore, it may be suggested that neither iodine nor its ions (+ ve or - ve) be the reacting species, since iodine exists in solution along with the ionic species I_3^- and H_2OI^+ .

As has been observed in the present case the rate of reaction decreases with the increase in iodide ion concentration and hence I_3^- cannot act as the reacting entity since in that case the reaction would have been accelerated with the increase of iodide ion concentration as suggested by the following equilibrium equation: $I_2 + I^- \rightleftharpoons I_3^-$.

The increase in the rate of reaction with decreasing iodide ion concentration on the other hand suggests that either HIO or H_2OI^+ is the reacting entity since any increase in iodide ion concentration will decrease the concentration of either of them.



Now to decide between HIO or H_2OI^+ is the reacting species the study of the effect of H^+ ion concentration has been helpful. Thus if

H_2OI^+ is the reacting entity, the rate of reaction would have increased since an increase in H^+ ion concentration would lead to an increase in the concentration of H_2OI^+ in the equilibrium mixture. But the present experiment shows that increase in concentration of H^+ ion actually leads to an overall decrease in the reaction rate. The observed decrease in reaction rate with increase in H^+ ion concentration, however, gets a ready explanation on the assumption that HIO is the reacting species, since any increase in H^+ ion concentration will lead to a decrease in the concentration of HIO .

However, the oxidation potential of iodine – iodide system, can also be altered by varying iodide and (or) iodine concentration. The potential decreases as the concentration of iodide ion is increased. Again, it is known that oxidation potential in some systems can be influenced by the H^+ ion concentration but in the case of iodine-iodide system H^+ ions are not involved and therefore the potential is not appreciably affected by the hydrogen ions. So the dependence of H^+ ion on the rate justifies that it plays a significant role during the reaction and this is formed by the hydrolysis of iodine solution. Furthermore, the observed increase of the rate constant with decrease of solvents at constant pH support that HOI is the reacting entity.

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