

THE KINETICS OF THE OLEFINE-BROMINE REACTION

Part IV. The Rate Equation of the Homogeneous Catalysed Thermal Reaction

BY S. V. ANANTAKRISHNAN

(Department of Chemistry, Madras Christian College, Tambaram)

AND

R. VENKATRAMAN

(Annamalai University)*

Received March 7, 1946

A TENTATIVE mechanism for this reaction was proposed by the author¹ and this was subsequently modified² so as to bring the thermal mechanism in line with the photochemical change. Since then, further work has shown that an examination of the results with a suitable reaction rate equation based on the mechanism is necessary and this constitutes the subject of the present communication.

A homogeneous catalysed reaction such as the ones under consideration can involve activation of one or both of the reactants by the catalyst. Any derivation of the kinetic equation has to consider both alternatives. The process of activation may involve the communication of the activation energy effectively to the molecules that would otherwise acquire it only very slowly and the molecules thus activated may react only after some interval during which they are liable to deactivation. As postulated in the tentative mechanism, the catalyst may remain associated with the reactant as a complex which undergoes the reaction. The various processes taking place and the concentrations involved are collected in Table I.

TABLE I

Process	Concentration	Rate Constant
Activation of reactant 1	μ_1	k_1
Deactivation of activated reactant 1	a_1	k_2
Activation of reactant 2	μ_2	k_3
Deactivation of activated reactant 2	a_2	k_4
Reaction between the activated reactants	a_1, a_2	k_5

* Now at Lingaraj College, Belgaum.

If the concentration of the catalyst is c , we get for the stationary concentration of the activated molecules the relation:

$$\begin{aligned} k_1 n_1 c - k_5 a_1 a_2 - k_2 a_1 c &= 0 \\ k_3 n_2 c - k_5 a_1 a_2 - k_4 a_2 c &= 0. \end{aligned}$$

From these two simultaneous equations, one gets

$$a_1^2 + a_1 (k_1/k_2 \cdot n_1 - k_4/k_5) - (k_1/k_2 \cdot k_4/k_5 n_1 c) - (k_3/k_2 n_2) = 0$$

Neglecting the last term which involves neither the catalyst nor the reactant 1 and taking only the positive root of the quadratic for a_1 , the reaction velocity equation

$$dx/dt = k_5 a_1 a_2$$

becomes

$$dx/dt = k_1 k_3 k_5 n_1 n_2 c / k_2 k_4 c + k_1 k_5 n_1.$$

Applying this to the Olefine-Bromine reaction catalysed by hydrogen bromide we have

$$dx/dt = k_1 k_3 k_5 [\text{Olefine}] [\text{Bromine}] \frac{[\text{Hydrogen Bromide}]}{k_2 k_4 [\text{HBr}] + k_1 k_5 [\text{Br}_2]} \quad (1)$$

If one considers, however, that only one reactant gets activated by the catalyst, we get for the stationary state

$$k_1 n_1 c - k_2 a_1 c - k_5 a_1 n_2 = 0$$

and

$$dx/dt = k_5 a_1 n_2 + k_5 k_1 n_1 n_2 c / k_2 c + k_5 n_2.$$

This gives for the present reaction

$$dx/dt = k_5 k_1 [\text{Olefine}] [\text{Bromine}] [\text{Hydrogen Bromide}] / k_2 [\text{HBr}] + k_5 [\text{Olefine}] \quad (2)$$

Expressing the hydrogen bromide concentration as a molefraction of the bromine concentration, f , equations 1 and 2 may be rewritten

$$dx/dt = k_1 k_3 k_5 [\text{Olefine}] [\text{Bromine}] \frac{f}{k_2 k_4 f + k_1 k_5} \quad (3)$$

$$dx/dt = k_1 k_5 [\text{Olefine}] [\text{Bromine}] \frac{f}{k_2 f + k_5} [\text{Olefine}] / [\text{Bromine}] \quad (4)$$

If olefine and bromine concentrations are chosen to be equal and the coefficients of f be unity, both expressions lead to an identical one of the type

$$dx/dt = k' [\text{Olefine}] [\text{Bromine}] \frac{f}{f+1}. \quad (5)$$

Obviously this assumption cannot be valid in all cases but one may expect that in every instance, a range of catalyst concentration may be found where this holds good. Further, the expression will be reduced to a simple

bimolecular type if $f = \frac{k_1 k_5}{k_1 k_5 - k_2 k_4}$ in equation (3). Equation (4) will be similarly reduced to this type if the reactants are initially at the same concentration and $f = 1/1 - k_2/k_5$. It has been observed that the introduction of activating groups reduces both the period of induction and influence of the catalyst on the rate of the addition reaction (). One may expect, therefore, for each olefine three different stages in the catalysed reaction:

1. The reaction is represented by the full rate equation (3).
2. The reaction is represented by the rate equation (5).
3. The reaction gives a bimolecular constant.

Evaluation of all the constants in the full rate equation is not feasible with the existing experimental data but the general validity of the concepts may be seen by examining the figures for crotonic acid (Tables II, III and IV).

The three tables present data which correspond to the different stages mentioned in the foregoing para in the order given. The experimental work in the earlier parts of this work has shown that though the determining factor

TABLE II

Concentration of Olefine = Concentration of Bromine M/15 ; Concentration of Catalyst (HBr) : 1.05 moles % of Br

Reaction %	Rate Constant mole/min. ⁻¹ calculated using Eqn. 5	Rate Constant mole/min. ⁻¹ . Bimolecular
10	2.006	0.0168
15	2.396	0.0195
20	2.865	0.0221
25	3.115	0.0238

TABLE III

Concentration of Olefine = Concentration of Bromine M/15 ; Concentration of Catalyst (HBr) : 2.10 moles % of Br

Reaction %	Rate Constant using Equation 5 moles/min. ⁻¹	Rate Constant, Bimolecular moles/min. ⁻¹
10	1.31	0.0192
15	1.37	0.0228
20	1.38	0.0250
25	1.34	0.0269

TABLE IV
Concentration of Olefine = Concentration of Bromine M/15; Concentration of
Catalyst, (HBr) : 6.90 moles % Br

Reaction %	Rate Constant using Equation 5 moles/min. ⁻¹	Rate Constant, Bimolecular moles/min. ⁻¹
10	1.267	0.0538
15	1.340	0.0552
20	1.422	0.0552
25	1.485	0.0554

Note.—The rate constants in Tables II, III, IV refer to a temperature of 35.5° C.

in the reaction is the ratio between the catalyst and bromine, the dual activation of the double bond, *viz.*, the internal group influences and the external catalyst influence, has to be recognised and though equation 5 and the bimolecular equation can both be derived from the simpler set of reaction the more complete one is to be preferred.

Since in every case the limiting reaction is a bimolecular one,* the limiting value of the velocity constant will be proportional to $\frac{k_1 k_5}{k_1 k_5 - k_2 k_4}$. Each of these constants being specific for a reaction different catalysts may be expected to lead to different limiting values of the velocity constant. Also, the catalyst-bromine concentration ratio for each of the stages may not be the same. The following data obtained with iodine monochloride as catalyst and crotonic acid as the olefine illustrate this point.

TABLE V
Olefine and Bromine concentrations M/15

Catalyst Concentration	Reaction %	Rate Constant Eqn. 5	Rate Constant, Bimolecular
0.95 % Bromine	10	2.497	0.0109
	15	2.891	0.0228
	20	2.981	0.0252
	25	3.134	0.0296
7.80 % Bromine	10	0.8005	0.0521
	15	0.6861	0.0541
	20	0.6434	0.0552
	25	0.5659	0.0545

* Note Robertson and co-workers (*J.C.S.*, 1945, 129 &c.) at higher concentrations get the reaction as termolecular. This is considered in a later part.

The applicability of the equation to other compounds and the influence of substituent groups are considered in the next part.

SUMMARY

A kinetic equation has been derived for a homogeneous catalysed reaction in which both the reactants of a bimolecular reaction are activated by the catalyst and the equation applied to the reaction between crotonic acid and bromine catalysed by hydrogen bromide. The variation of rate with change of catalyst is also indicated.

REFERENCES

1. Anantakrishnan and Venkatraman .. *J. C. S.*, 1939, 224.
2. ————— .. *Chem. Reviews.*, 1943, 33, 52.