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TESTING OF SOME DYNAMIC KINETIC EQUATIONS

PART III. ZERO-ORDER REACTION

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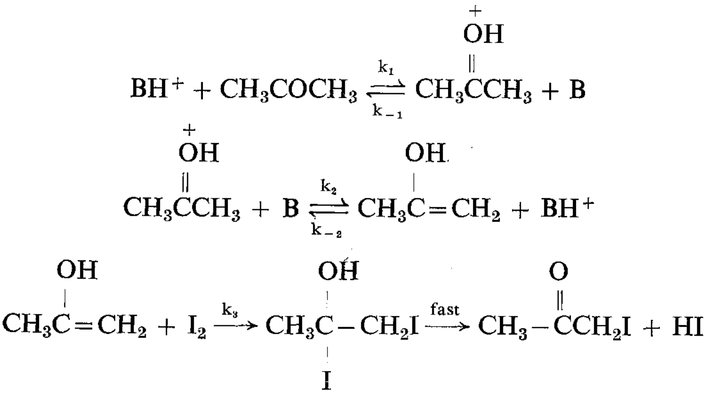
The acid-catalysed iodination of acetone in aqueous solution was used to test three dynamic kinetic equations. The Freeman and Carroll treatment yields the most satisfactory results.

In the first part of this paper [1] a first-order reaction was used to test four dynamic kinetic equations. It was concluded that the Freeman and Carroll treatment was the most satisfactory. In the second part of this paper[2] a second-order reaction was used to test three equations. The Horowitz and Metzger equation was not tested because the inflection point was difficult to determine. The same conclusion was reached. It is desirable to use a zero-order reaction to test these equations, and this has been done in the present work. The acid-catalyzed iodination of acetone was chosen for this purpose.

This reaction is one of the most fully investigated. The following prototropic general acid catalysis mechanism proposed by Bell and Jones [3] is now generally accepted:



$$\mathrm{BH^+ + CH_3COCH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3\overset{\overset{\overset{+}{OH}}{\|}}{C}CH_3 + B} \qquad (1)$$

$$\mathrm{CH_3\overset{\overset{\overset{+}{OH}}{\|}}{C}CH_3 + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_3\overset{\overset{OH}{|}}{C}{=}CH_2 + BH^+} \qquad (2)$$

$$\mathrm{CH_3\overset{\overset{OH}{|}}{C}{=}CH_2 + I_2 \xrightarrow{k_3} CH_3\underset{\underset{I}{|}}{\overset{\overset{OH}{|}}{C}}{-}CH_2I \xrightarrow{fast} CH_3{-}\overset{\overset{O}{\|}}{C}CH_2I + HI} \qquad (3)$$

Application of steady-state treatment gives rise to [4]

$$v = \frac{k_1k_2k_3[\mathrm{BH^+}][A][\mathrm{I_2}]}{k_{-1}k_{-2}[\mathrm{BH^+}] + (k_{-1} + k_2)k_3[\mathrm{I_2}]} \qquad (4)$$

When $[I_2]$ is sufficiently large, the rate is

$$v = \frac{k_1 k_2 [BH^+][A]}{k_{-1} + k_2} \tag{5}$$

The reaction is zero order to iodine. The activation energies of the forward and backward reactions were reported to be 20.4 and 16.5 kcal per mole, respectively, by Sytilin and Gorbachev [5].

Experimental

All the chemicals used were of reagent grade, without further purification.

5 ml acetone, 15 ml 2*M* H_2SO_4 and 205 ml distilled water were mixed in a 500 ml Erlenmeyer flask, which was placed in a water-bath cooled down with ice. 25 ml standard iodine solution (0.03833 *N*), which had attained the same temperature was added. The bath was then heated up at a rate of 1° per 3 minutes. The reactions were followed by extracting 10 ml samples at intervals; these were delivered into a 50 ml flask containing 5 ml 1*N* sodium acetate solution and about 20 ml ice-cold water to stop the reaction, and titrated immediately with standard 0.01026 *N* sodium thiosulfate solution, starch being used as indicator. Isothermal kinetic runs were carried out at 0.1°, 9.9°, 19.8° and 30.1° by the same procedure. For the two low-temperature runs 20 ml 2*M* H_2SO_4 and 200 ml H_2O were used in order to make the reaction faster.

Results and Discussion

The isothermal kinetics for the acid-catalysed iodination of acetone are shown in Fig. 1, in which the concentration of iodine is plotted against time. All the points fall on straight lines, indicating that the reaction is zero order to iodine

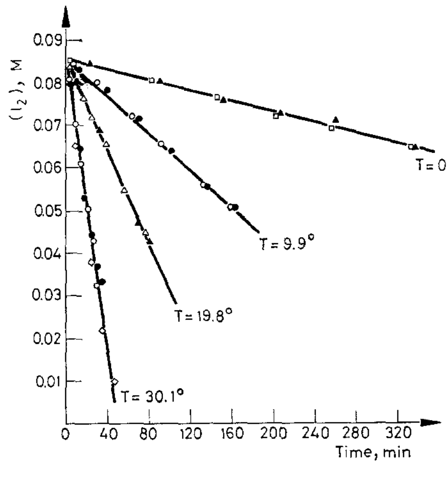


Fig. 1. Isothermal kinetics of the acid catalysed iodination of acetone

under the experimental conditions up to 90% conversion. The pseudo-zero-order rate constants determined from the slopes of the straight lines are 0.02978, 0.1028, 0.2556 and 0.7879 mole · liter^{-1} · min^{-1} for 0.1°, 9.9°, 19.8° and 30.1°, respectively. Since 20 ml 2*M* H_2SO_4 was used in the 0.1° and 9.9° runs, compared with

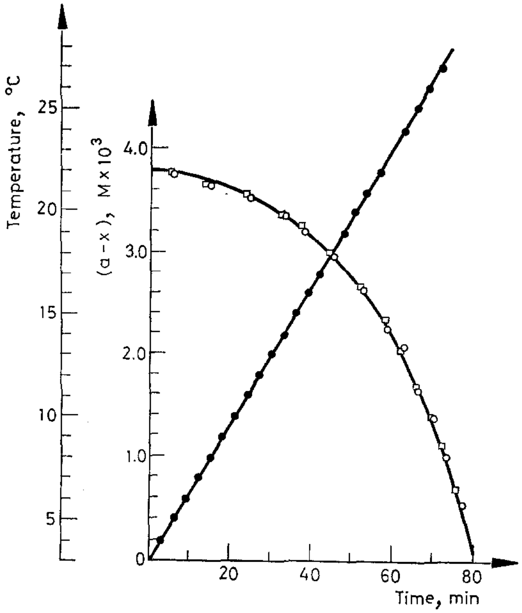


Fig. 2. Dynamic kinetic runs for iodination of acetone

Table 1

Dynamic kinetic run of iodination of acetone

Time (min)	0.01026 N $Na_2S_2O_3$ added (ml)	$[I_2]M \times 10^3$
5.18	7.38	3.805
13.90	7.17	3.677
23.95	6.98	3.619
32.55	6.61	3.405
37.45	6.36	3.274
44.77	5.88	3.024
52.05	5.21	2.663
57.95	4.59	2.370
62.28	4.01	2.081
66.04	3.29	1.650
69.72	2.72	1.410
72.52	2.16	1.128
76.00	1.35	0.702

15 ml in the other isothermal runs and dynamic runs, it is necessary to convert the rate constants at these two temperatures to the same basis as in other runs, by multiplying by a factor of $\frac{15}{20}$; the rate constants at 0.1° and 9.9° then become 0.02234 and 0.07710 mole · liter^{-1} · min^{-1}, respectively. The Arrhenius plot is linear. From the slope of the straight line, the activation energy was calculated to be 82.0 kJ (19.6 kcal) per mole.

Data for duplicate dynamic kinetic runs are shown in Tables 1 and 2 and are plotted in Fig. 2. Freeman and Carroll treatment is shown in Table 3, and the

Table 2

Another dynamic kinetic run of iodination of acetone

Time (min)	0.01026 N $Na_2S_2O_3$ added (ml)	$[I_2]M\times10^3$
5.78	7.31	3.739
14.80	7.09	3.606
24.78	6.87	3.519
33.30	6.52	3.331
38.14	6.27	3.202
45.53	5.79	2.962
52.78	5.13	2.619
58.70	4.43	2.225
63.15	3.88	2.015
66.80	3.22	1.646
70.52	2.52	1.285
73.30	1.94	0.989
76.74	1.12	0.558

Table 3

Freeman and Carroll's treatment of iodination of acetone

Time (min)	Temp. (K)	$(a-x)\times10^3$M	$\frac{dx}{dt}\times10^6$	$\frac{\Delta\log\frac{dx}{dt}}{\Delta\log(a-x)}$	$\frac{\Delta\frac{1}{T}\times10^4}{\Delta\log(a-x)}$
30	286.2	3.44	2.20		
35	287.8	3.32	2.83	−7.092	13.12
40	289.5	3.17	3.37	−5.217	11.34
45	291.2	2.99	4.05	−4.353	9.86
50	292.8	2.77	4.78	−3.582	8.46
55	294.5	2.52	5.65	−3.031	7.32
60	296.2	2.25	7.06	−2.746	6.40
65	297.8	1.83	8.19	−2.083	5.00
70	299.5	1.37	10.00	−1.645	3.89

data are plotted in Fig. 3. It is seen from Fig. 2 that the two points at the beginning of the run do not seem to be very accurate. The slope drawn at 30 min on the curve is taken as the reference for Freeman and Carroll treatment. From Fig. 3 it is seen that, with the exception of the initial three points, the points can be fitted into a straight line; the intercept on the *Y* axis indicates the order of reaction, zero. From the slope of the straight line an activation energy of 81.6 kJ per mole was obtained, which agrees perfectly well with that obtained from isothermal kinetics.

Treatment of the data by the method of Achar et al. is shown in Table 4 and the results are plotted in Fig. 4. It is seen that the points for $n = 0$ fit a straight

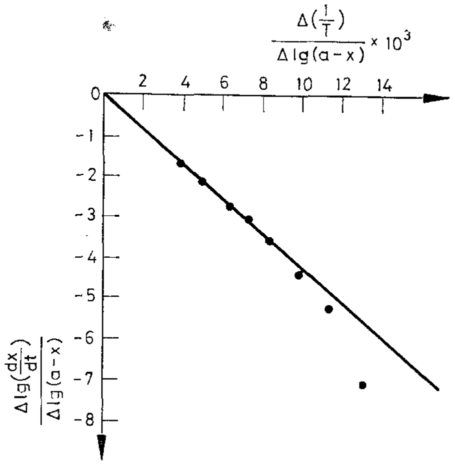


Fig. 3. Freeman and Carroll treatment for iodination of acetone

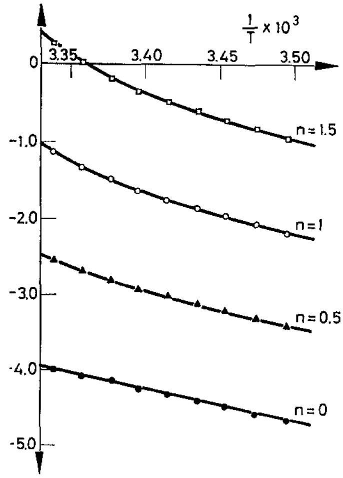


Fig. 4. Achar, Brindley and Sharp treatment for iodination of acetone

Table 4

Treatment of data on iodination of acetone by the method of Achar et al.

Time (min)	$\frac{1}{T} \times 10^3$	$\log \frac{dx/dt}{(a-x)^{0.0}}$ n = 0	$\log \frac{dx/dt}{(a-x)^{0.5}}$ n = 0.5	$\log \frac{dx/dt}{(a-x)^{1.0}}$ n = 1.0	$\log \frac{dx/dt}{(a-x)^{1.5}}$ n = 1.5
30	3.495	−4.655	−3.422	−2.194	−0.962
35	3.474	−4.546	−3.308	−2.069	−0.830
40	3.454	−4.472	−3.222	−1.973	−0.724
45	3.435	−4.390	−3.130	−1.868	−0.606
50	3.415	−4.320	−3.041	−1.763	−0.484
55	3.396	−4.247	−2.948	−1.649	−0.350
60	3.377	−4.150	−2.827	−1.503	−0.179
65	3.358	−4.086	−2.717	−1.349	0.020
70	3.339	−3.999	−2.568	−1.136	0.295

line with an activation energy of 79.1 kJ per mole. With other orders, the plots are all curved. Further, they do not intersect.

Treatment of the data by Coats and Redfern method is shown in Table 5 with the corresponding plot in Fig. 5. The points for $n = 0$ and $n = 0.5$ lie on straight lines. The activation energies calculated from the slopes are 93.3 and 105.4 kJ per mole, respectively.

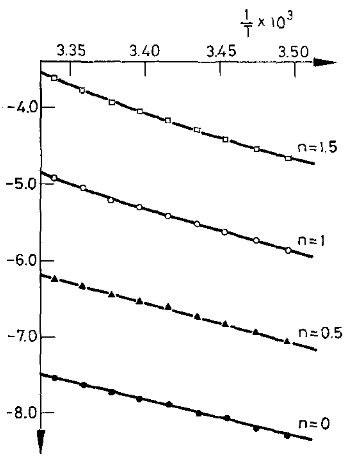


Fig. 5. Coats and Redfern treatment for iodination of acetone

Conclusion

The above results show that Freeman and Carroll treatment yields the correct reaction order. The energy of activation obtained by the method agrees excellently with that derived from isothermal kinetics, which agrees very well with the litera-

Table 5

Coats and Redfern treatment of data on iodination of acetone

Time (min)	$\log \frac{a - (a - x)}{T^2}$ n = 0	$\log \frac{a^{0.5} - (a - x)^{0.5}}{0.5 \cdot T^2}$ n = 0.5	$\log \frac{-\ln\left(\frac{(a - x)}{a}\right)}{T^2}$ n = 1.0	$\log \frac{a^{-0.5} - (a - x)^{-0.5}}{(-0.5) \cdot T^2}$ n = 1.5
30	−8.315	−7.099	−5.879	−4.659
35	−8.207	−6.982	−5.758	−4.538
40	−8.103	−6.874	−5.645	−4.416
45	−8.003	−6.765	−5.532	−4.299
50	−7.907	−6.665	−5.419	−4.177
55	−7.820	−6.565	−5.315	−4.060
60	−7.742	−6.479	−5.215	−3.947
65	−7.647	−6.366	−5.080	−3.786
70	−7.560	−6.253	−4.941	−3.617

$a = 3.833 \times 10^{-3}$ M.

ture value. Such good agreement could only be attributed to coincidence, because there are several steps involved in obtaining the final results, and each step could give rise to some error, for instance, error in carrying out the experiment, error in curve fitting and error in slope measurement. Unless some errors happen to cancel each other by chance, it would be impossible to obtain such a good result. The treatment by Achar et al. also gives the right reaction order. The energy of activation obtained by this method differs from the isothermal value by about 3.5%; this could also be considered good agreement. Coats and Redfern treatment gives an activation energy which is 10% higher than the isothermal value, for $n = 0$. For $n = 0.5$, the activation energy obtained by this method is 25% too high. Besides predicting an incorrect activation energy, this method could not give the right order of reaction, because points for $n = 0$ and $n = 0.5$ can be fitted into two straight lines.

From this series of tests it is seen that Coats and Redfern method fails completely in all cases. Treatment according to Achar et al. did not give the right order of reaction in the case of the ammonium cyanate–urea conversion. This treatment also fails in the case of the catalytic decomposition of H_2O_2. In the iodination of acetone, however, this treatment gives a satisfactory result: the correct reaction order and an activation energy within allowable error (less than 10%). Freeman and Carroll treatment yields satisfactory results in all cases.

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RÉSUMÉ — Trois méthodes ont été utilisées pour étudier la cinétique de l'ioduration catalytique de l'acétone en solution aqueuse. Celle de Freeman et Caroll donne les résultats les plus satisfaisants.

ZUSAMMENFASSUNG — Die katalytische Jodierung des Acetons in wäßriger Lösung wurde zur Untersuchung von dynamischen kinetischen Gleichungen herangezogen. Die Freeman-Caroll'sche Behandlung gab die entsprechendsten Ergebnisse.

Резюме — На примере реакции иодирования ацетона в водном растворе, катализируемой кислотой, были проверены три динамические кинетические уравнения. Обработка по методу Фримена и Кэррола дает наиболее приемлемые результаты.