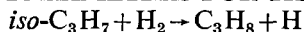


ARRHENIUS PARAMETERS FOR THE REACTION



By

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(Received 29th September, 1982)

The kinetics of decomposition of 2,2-azobispropane was studied in the presence of excess molecular hydrogen at temperatures from 473 to 559 K. The initial rates of formation of the products were determined. The results are explained in terms of the proposed mechanism by evaluation of k_4 for the reaction:



Introduction

Hydropyrolysis is an industrial method in which hydrocarbons are pyrolyzed in the presence of molecular hydrogen. This method can be applied to modify the composition of the products in the pyrolysis of hydrocarbons. The basis of the influence of molecular hydrogen in the hydropyrolysis is a competition between two elementary reactions [1]: the abstraction of hydrogen by alkyl radicals from hydrocarbons, and the abstraction of hydrogen by alkyl radicals from molecular hydrogen.

In this work the aim was to provide kinetic parameters for the reaction of isopropyl radical with molecular hydrogen. For this reaction experimental and estimated kinetic data are available. BALDWIN and coworkers [2] suggested the rate constant shown below, obtained from results on the oxidation of isobutyraldehyde:

$$\log(k_4/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 9.5 - 66.5 \text{ kJmol}^{-1}/2.3 \text{ RT}$$

For the activation energy of the title reaction Le Roy suggested 52.3 kJmol^{-1} [3].

Arrhenius parameters were estimated by means of thermochemical calculations, the following data being taken from the literature:

- a, The thermochemical data shown in Table I.
- b,

$$\log(k_{-4}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 10.8 \pm 0.4 - 32.6 \pm 3.3 \text{ kJmol}^{-1}/2.3 \text{ RT}$$

suggested by BALDWIN [4] for the reverse reaction.

The following equations were used [5]:

$$\ln \frac{A_4}{A_{-4}} = \frac{\Delta S^0}{R} \quad \text{and} \quad E_4 - E_{-4} = \Delta H^0$$

Table I

Thermochemical data [4, 6] for the reaction $iso-C_3H_7 + H_2 \xrightleftharpoons[k_4]{k_3} C_3H_8 + H$

	<i>iso-C₃H₇</i>	H ₂	C ₃ H ₈	H
$\frac{\Delta H^0}{kJmol^{-1}}$	73.6	0	-103.8	218
$\frac{S^0}{JK^{-1}mol^{-1}}$	279	130.5	269.9	114.6

where A and E are the Arrhenius A factor and activation energy, respectively; ΔS^0 and ΔH^0 are the standard entropy and enthalpy change of the reaction, respectively. The result of the estimation can be given as follows:

$$\log(k_4/dm^3 mol^{-1} s^{-1}) = 9.5 - 73.2 \text{ kmol}^{-1}/2.3 RT$$

As there are some differences between the calculated and estimated data, it seemed worth redetermining the Arrhenius parameters of the title reaction in a new system.

Experimental

The isopropyl radical was produced by thermal decomposition of 2,2-azobispropane (hereafter AIP) in the presence of excess molecular hydrogen. The ratio of the concentration of H₂ to the concentration of AIP was varied between 50 and 200 at 473–559 K. Experiments were carried out in a conventional static vacuum apparatus equipped with greaseless taps. Reactions were performed in a 108 cm³ cylindrical Pyrex vessel installed in an electric furnace. The reactions were started by measuring the pressure of the reactant in a 72 cm³ closed part of the vacuum line, thereafter shared with the reaction vessel. Reactions were quenched by admitting the products into an evacuated sampling bulb connected to the vacuum line by a high-vacuum joint. Products were analyzed by G. C. on a Perkin—Elmer F 11 gas chromatograph equipped with FID. Analyses were performed on the following columns: a 3 m column filled with 20 w% didecyl phthalate on Chromosorb PS at 343 K, and a 2 m column filled with 40/100 mesh alumina at programmed temperatures. Leads and analytical system, where necessary, were heated to 320 K by heating tape to avoid condensation and adsorption.

Reactions were performed under atmospheric pressure. Measurable reactions occurred only at high [H₂]/[AIP] ratios. To ensure high [H₂]/[AIP] ratios, the concentration of AIP in the reaction mixture was kept low. To increase the accuracy of the analyses of the products, an internal standard was used. Perfluoromethylcyclohexane (PFMCH) was selected as internal standard, as the peak of this compound did not interfere with those of the products of the reaction or the starting material. PFMCH proved to be stable under the conditions applied. In the experiments the concentration of AIP was seven times higher than that of PFMCH.

Results and Discussion

With regard to our earlier results [7, 8] the following reactions seemed worthy of consideration in this system:

- (1) $AIP \rightarrow N_2 + 2 iso-C_3H_7$
- (2) $2 iso-C_3H_7 \rightarrow 2,3\text{-dimethylbutane}$
- (3) $2 iso-C_3H_7 \rightarrow C_3H_8 + C_3H_6$
- (4) $iso-C_3H_7 + H_2 \rightarrow C_3H_8 + H$
- (5) $iso-C_3H_7 + AIP \rightarrow C_3H_8 + C_3H_6 \dots N \dots N\text{-}iso-C_3H_7$

In this short-form mechanism reaction (1) shows the formation of isopropyl radical, and reactions (2) and (3) its combination and disproportionation. Reaction (4) is the subject of our studies, and reaction (5) is another hydrogen-abstraction reaction in this system. Propane can be formed in reactions (4) and (5) as well as in reaction (3). From this mechanism it is to be expected that in the presence of H_2 the rate of formation of propane increases. Experiments have proved this expectation.

Kinetic data were derived from the initial rate of formation of propane by taking into account the roles of reactions (3) and (5). The concentration of isopropyl radical was calculated from the initial rate of formation of 2,3-dimethylbutane (DMB) and from the rate constant of reaction (2) taken from the literature [9].

In a closed system such as this, the rate of change of a compound ($W = \frac{dc}{dt}$) formed, transformed or decomposed by different elementary reactions can be given by vector equation I:

$$W = [v]R \quad (I)$$

where v is the stoichiometric number and R is the rate of the elementary reaction. On the basis of Eqn I, the rate of formation of any compound (W_i) can be given by

$$W_i = \sum_j v_{i,j} R_j \quad (II)$$

where $v_{i,j}$ is the stoichiometric number of component i in reaction j .

The elements of the matrix for all of the substances $i=1\dots 9$ and for all of the unidirectional reactions $j=1\dots 5$ in this system are given in Table II.

Table II

Transformed elements of $[v_{i,j}]$ matrix for substances $i = 1\dots 9$ and for reactions $j = 1\dots 5$

$j \backslash i$	1 AIP	2 N ₂	3 C ₃ H ₇ *	4 DMB	5 C ₃ H ₈ *	6 C ₃ H ₆	7 H	8 R**	9 H ₂
1	-1	1	2	0	0	0	0	0	0
2	0	0	-2	1	0	0	0	0	0
3	0	0	-2	0	1	1	0	0	0
4	0	0	-1	0	1	0	1	0	-1
5	-1	0	-1	0	1	0	0	1	0

* $C_3H_7 = iso-C_3H_7$

R** = $C_3H_6 \dots N \dots N\text{-}iso-C_3H_7$

In the experiments the initial rates of formation W_4 and W_5 were determined, *i.e.* the initial rates of formation of DMB and C_3H_8 , respectively. These are given below on the basis of the stoichiometric numbers of Table II.

$$W_4 = \frac{d[\text{DMB}]}{dt} = \sum_{j=1}^5 \nu_{4,j} R_j = \nu_{4,2} R_2 = 1 \cdot k_2 [\text{iso-C}_3\text{H}_7]^2 \quad (\text{III})$$

$$\begin{aligned} W_5 &= \frac{d[\text{C}_3\text{H}_8]}{dt} = \sum_{j=1}^5 \nu_{5,j} R_j = \nu_{5,3} R_3 + \nu_{5,4} R_4 + \\ &+ \nu_{5,5} R_5 = 1 \cdot R_3 + 1 \cdot R_4 + 1 \cdot R_5 = k_3 [\text{iso-C}_3\text{H}_7]^2 + \\ &+ k_4 [\text{iso-C}_3\text{H}_7][\text{H}_2] + k_5 [\text{iso-C}_3\text{H}_7][\text{AIP}] \end{aligned} \quad (\text{IV})$$

R_3 can be given from the ratio R_3/R_2 :

$$R_3 = \frac{k_3}{k_2} [R_2] = \frac{k_3}{k_2} \frac{d[\text{DMB}]}{dt} \quad (\text{V})$$

Taking R_3 from Eqn V and $[\text{iso-C}_3\text{H}_7] = (W_4/k_2)^{1/2}$ from Eqn III, we obtain:

$$\left(W_5 - \frac{k_3}{k_2} W_4 \right) (W_4)^{-1/2} = \frac{k_5}{k_2^{1/2}} [\text{AIP}] + \frac{k_4}{k_2^{1/2}} [\text{H}_2] \quad (\text{VI})$$

In Eqn VI, besides the measured quantities and literature data for k_2 , k_3 and k_5 , the only unknown is the value of k_4 . For the determination of k_4 , the left side of Eqn VI was plotted as a function of $[\text{H}_2]$. A straight line was found, from the slope of which $k_4/k_2^{1/2}$ was determined at seven different temperatures. Results are shown in Table III. Taking $k_2 = 10^{9.5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from the results of Golden and coworkers [9], values of k_4 were calculated.

The Arrhenius parameters of reaction (4) were determined in the usual way

Table III
Experimental data for determination of the Arrhenius parameters of reaction (4)

T/K	$10^3 k_4/k_2^{1/2} *$	$10^{-2} k_4 **$	$\log k_4$	10^3 K/T
473	0.398	5.05	2.70	2.11
493	0.972	5.46	2.74	2.03
523	4.75	26.7	3.43	1.91
543	10.5	59.0	3.77	1.84
559	10.1	56.8	3.75	1.79
563	11.0	62.0	3.79	1.78
573	13.9	78.1	3.89	1.75

$$k_4/k_2^{1/2} * = k_4/k_2^{1/2} \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$$

$$k_4 ** = k_4/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

from the temperature-dependence of k_4 . The graph of $\log k_4$ versus $1/T$ is shown in Figure 1.

From the slope and intercept of Fig. 1, the rate constant of reaction [4] is

$$\log(k_4/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (10.3 \pm 0.7) - (69.4 \pm 6.7 \text{ kJmol}^{-1})/2.3 RT$$

where the errors in brackets are the standard deviations.

To check these data, Arrhenius parameters for the reverse reaction were calculated by means of thermochemical calculations, the results of which gave:

$$\log(k_{-4}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (11.6 \pm 0.7) - (28.8 \pm 6.7 \text{ kJmol}^{-1})/2.3 RT$$

This expression is similar to that obtained experimentally [4].

The Arrhenius parameters of reaction [4] were compared with those of similar

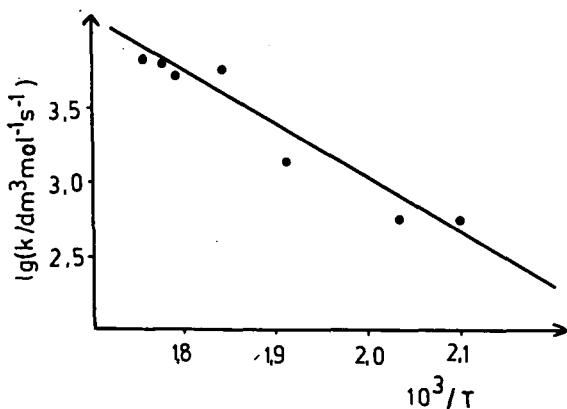


Figure 1. Temperature-dependence of k_4 .

Table IV

Arrhenius parameters of the reaction
 $R + H_2 \rightarrow RH + H$
 (from Reference [10])

Reaction	$\log A^*$	E^*	$\log k^*$	
			700 K	1000 K
$CH_3 + H_2 \rightarrow CH_4 + H$	9.2	47.3	5.7	6.7
$C_2H_6 + H_2 \rightarrow C_2H_8 + H$	9.6	58.6	5.2	6.5
$1-C_3H_7 + H_2 \rightarrow C_3H_8 + H$	9.2	64.4	4.4	5.8
$2-C_3H_7 + H_2 \rightarrow C_3H_8 + H$	10.3 ± 0.7	69.4 ± 6.7	5.1	6.7
$2-C_4H_9 + H_2 \rightarrow C_4H_{10} + H$	9.7	71.9	4.3	5.9

$\log A^* = \log A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $E^* = E/\text{kJmol}^{-1}$
 $\log k^* = \log k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

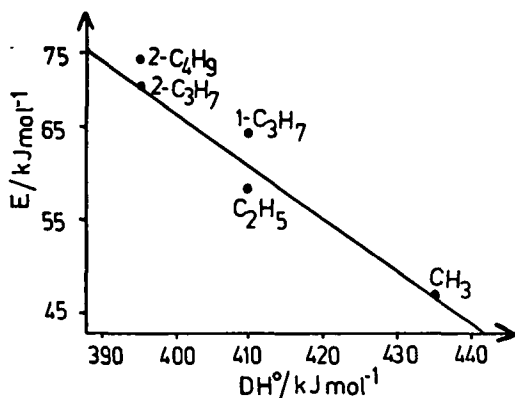


Figure 2. Application of Polanyi's rule for the reaction $R \cdot + \text{H}_2 \rightarrow \text{RH} + \text{H}$. E = activation energy, DH^0 = bond-dissociation energy.

reactions, compiled in Table IV together with rate constants at the usual temperature of hydrolysis. It can be seen from Table IV that the activation energies increase with increasing carbon number of the reacting radicals, and secondary radicals have higher activation energies than primary radicals. Such an increase in activation energies is in accordance with the Polanyi rule, as can be seen from Figure 2, where activation energies (E) are shown versus the bond-dissociation energies (DH^0) of the R-H bond. A comparison of the rate constants in Table IV proves that different hydrocarbon radicals behave similarly in their reactions with molecular hydro-

gen, especially at higher temperatures. This means that in the hydrolysis of hydrocarbons all of the radicals present need consideration.

Acknowledgement

The author is indebted to Professor T. Bérces for initiating this work.

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АРРЕНИУСОВСКИЕ ПАРАМЕТРЫ ДЛЯ РЕАКЦИИ $\text{изо-C}_3\text{H}_7 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8 + \text{H}$

Л. Сировица

Изучена кинетика распада 2,2-азобис-пропана в присутствии избытка молекулярного водорода в интервале температур от 343 до 559 К. Определены начальные скорости образования продуктов. Полученные результаты обсуждены с точки зрения предложенного механизма с расчетом k для реакции:

