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CATALYTIC DEHYDROGENATION OF TETRAHYDROTHIOPHENE TO THIOPHENE

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The thermodynamic conditions of the dehydrogenation of tetrahydrothiophene were studied. Experiments were carried out with various types of metal, metal oxide and metal sulphide catalysts in order to increase the rate of the equilibrium reaction,under standardized conditions.

Experiments were carried out using a suitable catalyst to determine the kinetics of the reaction. According to the calculations, the rate-determining partial process is the surface reaction.

Crude oils of high sulphur content contain various organic sulphur compounds in amounts comparable to that of the hydrocarbons. These sulphur compounds may be important raw materials in the production of a number of organic compounds. In the petroleum refining industry, as a result of corrosion hazards, endeavours are made to remove sulphur from the products. However, sulphur removal processes yield sulphur compounds which are inadequate for further processing. Accordingly, any research dealing with the recovery and further processing of organic sulphur compounds found in crude oils is of considerable interest.

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*Pét Nitrogen Works

The present work deals with the dehydrogenation of a monocyclic sulphide, tetrahydrothiophene, that is also found in crude oils.

The tetrahydrothiophene plant built within the Pét Nitrogen Works primarily serves the demand for gas-scenting agents. However, production on an industrial scale opens up the possibility for the production of other materials based on tetrahydrothiophene. These include two very important products: sulpholane and thiophene. Sulpholane is an important solvent that is used for the recovery of aromatic hydrocarbons present in aromatized petrols. The method is known as the Shell extraction technique.

Thiophene - which can also be produced by the dehydrogenation of tetrahydrothiophene - is another important compound, which is used as a raw material in the pharmaceutical, paint, pesticide and plastics industries [1, 2, 3, 4].

Properties of Thiophene and Tetrahydrothiophene

Physical Properties

The molecular weight of tetrahydrothiophene is 88.174, while that of thiophene is 84.142. There is no major difference between their densities; the density of tetrahydrothiophene at 20°C is almost equal to that of water, its value being 0.9998 g/cm^3, whereas the density of thiophene is 1.0648 g/cm^3. Their boiling points at atmospheric pressure show a rather large difference: tetrahydrothiophene boils at 121.12°C, while thiophene at 84.16°C.

Chemical Properties

Tetrahydrothiophene was first discovered in Persian crude oils. Its odour is poignant. It is miscible with a number of fluids but not with water. It can be oxidized with potassium permanga-

nate; in this reaction sulphone (known commercially as sulpholane) is produced which finds an application as a solvent. It provides crystalline compounds with mercury halides. The latter reaction, on account of the characteristic melting point, is used for identification.

Its stability is higher than that of mercaptans and consequently it can be used for gas scenting. Its sulphides are used to improve the ignition characteristics of Diesel oil. Chlorinated tetrahydrothiophene can be used as a pesticide.

In a similar manner to tetrahydrothiophene, thiophene is a colourless liquid with a slight odour resembling of garlic. Although it is insoluble in water, it is readily soluble in alcohol and ether. It is a reactive compound and its chemical properties are in the main similar to those of benzene: it can be nitrated with nitric acid and sulphonated with sulphuric acid. It forms organic metal compounds with mercury salts, and tends to form complex compounds with various metals.

Its vapours irritate the mucuous membranes. If inhaled for a longer period of time, it causes spasms, and also has an adverse effect on blood cell production. Accordingly it must be handled with care.

Dehydrogenation of Tetrahydrothiophene

YURIEV and BORISOV [5] were the first to produce thiophene from tetrahydrothiophene by dehydrogenation on a platinum-alumina and nickel sulphide-alumina catalyst. After a long interval, YURIEV and TRONOVA [6] reported in another paper on the effect of chromium oxide-alumina catalysts in the transformation of various heterocyclic compounds, including tetrahydrothiophene.

HIRAO and HATTA mentioned in their paper [7] that tetrahydrothiophene can be dehydrogenated to thiophene in the presence of a chromium oxide-alumina catalyst at 500°C.

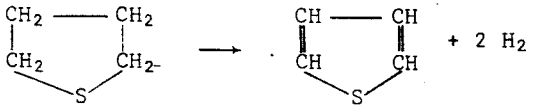
According to FRIEDMANN [8], tetrahydrothophene is dehydrogenated mostly to thiophene in the presence of elemental sulphur at a pressure of 3 atm and within a period of 10 hours at 160°C with the simultaneous production of a number of other organic sulphur compounds.

OBOLENTSEV and associates [9] studied the dehydrogenation of tetrahydrothiophene in the presence of various industrial catalysts. These authors applied benzene as a diluting component in the dehydrogenation. Their experiments were also supplemented by equilibrium calculations. According to the latter, a temperature of at least 450 to 500°C is necessary for the dehydrogenation to proceed. Decreasing the pressure or dilution with an indifferent component favourably influences the reaction.

MASHKINA and associates [10] studied the dehydrogenating action of the oxides and sulphides of metals of the third to sixth column of the periodic system upon diethyl sulphide and tetrahydrothiophene. Chromium oxide, copper chromite, cobalt molybdate and platinum were found to be the most effective.

Thermodynamics of the Reaction

Dehydrogenation of tetrahydrothiophene to thiophene proceeds according to the following equation:



The reaction heats were calculated on the basis of the Franklin-increments [11]. The calculated values are summarized in Table 1. The change in free energy of formation for the reaction was calculated with the FRANKLIN's method [11] as well as with that of van KREVELEN [13]. On the basis of these, the lowest theoretical temperature, at which the reaction is possible, can be determined. The calculated values are shown in Table 2.

Table 1. Heats of Reaction of the Dehydrogenation of Tetrahydrothiophene at Different Temperatures

Temperature °K	ΔH°, Heat of Reaction (kcal/mole)
300	32.910
400	33.252
500	33.540
600	33.752
800	33.844

Table 2. Changes in Free Energy of Formation

Temperature °K	ΔG° (reaction) [11] (kcal/mole)	ΔG° (reaction) [13] (kcal/mole)
300	11.17	11.14
400	4.08	3.87
500	-3.20	-3.44
600	-10.59	-10.70
800	-25.34	-25.56

The values calculated with the two different methods showed good agreement. It can be concluded from the above data that the reaction does not occur at 400°K, whereas it is possible at 500°K. Thiophene can also be hydrogenated an account of the equilibrium reaction. The degree of hydrogenation is negligible at atmospheric or lower pressures.

In the case of a reaction in the gaseous phase, the chemical transformation involves an increase in volume, and accordingly the decrease of pressure or the application of an indifferent diluting component - on account of its partial pressure-decreasing action - promote conversion.

EXPERIMENTS

The aim of the experiments was to study the efficiency of the various catalysts of the metal and metal-oxide-type, in order to find the most preferable to be applied in more detailed studies. The catalysts studied were different industrial products.

A tubular reactor of 11 mm I.D., made of stainless steel, was used for these experiments. The temperature of the reactor was maintained by an electrically heated mercury bath. Reactor temperature could be adjusted by varying the pressure of nitrogen gas conducted over the bath. 20 cm^3 catalyst was placed into the reactor for each experiment.The grain size of the catalyst was brought to 1 to 2 mm by crushing and sieving. The raw material was forwarded into the reactor or into the evaporator connected before the reactor by means of a piston-type pump. The product was recovered in a water-cooled condenser. Uncondensed gases and vapours were collected in a gasometer. Samples were taken from both the condensed product and the gaseous products and the samples were analyzed.

The condensed products were analyzed with a chromatograph, produced by Becker-Delft, type 2040 C-2, equipped with a flame-ionization detector.

The packing material used in the separating column was Celite (C-22) wetted with 25 per cent poly(propylene glycol). The length of the column was 1 m, the rate of the carrier gas stream 3 liters per hour, the temperature was 120°C.

Tetrahydrothiophene produced by the Pét Nitrogen Works was used. The product contained 2.5 per cent tetrahydrofurane as impurity. The diluting material was analytical-grade benzene.

A mixture containing 2 moles of benzene and 1 mole of tetrahydrothiophene was used to compare the catalysts. Experiments were carried out with each catalyst at three temperatures (450, 500 and 550°C) and at three different residence times (0.5, 1.0 and

1.5 sec). The residence time was varied by controlling the pumping rate of the feeding pump and the volumetric rate was varied accordingly. The experiments were carried out at atmospheric pressure.

The effect of the catalysts at a benzene-tetrahydrothiophene molar ratio of 2/1 and a residence time of 1 second is illustrated with the conversion and yield data summarized in Table 3.

Table 3. Effect of Different Types of Catalysts

No.	Catalyst type	THT* conversion %			Thiophene yield %		
		450	500	550	450	500	550
		°C					
1	Cobalt-molybdenum oxide	55.4	60.7	63.0	35.5	40.8	48.3
2	Nickel-tungsten sulphide	15.7	16.9	18.4	9.6	10.0	10.8
3	Platinum-alumina	11.0	27.2	44.0	6.4	16.8	33.1
4	Chromium-alumina	17.6	57.6	81.4	5.6	21.9	40.9
5	Nickel-molybdenum oxide	8.7	10.7	18.7	1.3	3.3	10.1
6	Nickel-alumina	27.6	55.5	84.0	18.7	27.6	54.0
7	Copper chromite	11.1	17.5	41.5	3.6	6.6	25.0

1. Ketjefine 124-1.5
2. Leuna-3076
3. Engelhardt product; 1.6 per cent Pt + Al_2O_3 carrier
4. Leuna-6301
5. Leuna-8199/s
6. Leuna-6524
7. Product of Pét Nitrogen Works; copper(II)-chromium(III)-oxide of the Adkins type

*Generally used abbreviation for tetrahydrothiophene

It is apparent from the data shown in Table 3. that thiophene was formed with all the catalysts used. However, in addition to dehydrogenation to thiophene, other decomposition reactions were also occurring, and this explains the fact that in every case the conversion of THT was higher than the thiophene yield. In addition

to hydrogen, hydrogen sulphide, ethane, propane and butane were detected in the product gases. In addition to the diluent benzene, there was generally mainly tetrahydrothiophene and thiophene in the liquid condensate. Traces of mercaptanes were also found.

On the basis of experiments carried out at 550°C, catalysts of the nickel-alumina, chromium-alumina and cobalt-molybdenum oxide types were found to be most active.

The platinum-alumina catalyst deserves special attention because at a relatively moderate activity it shows a higher selectivity, i.e. the difference between THT conversion and thiophene yield was smaller than in the case of other catalysts. On the other hand, the chromium-alumina catalyst seems to be inadequate for further tests, because - despite the high degree of conversion - its selectivity is poor.

On the basis of the experiments, nickel-alumina, platinum--alumina and cobalt-molybdenum-oxide catalysts were found to be adequate for further detailed studies aimed at finding the parameters of industrial production.

KINETIC ANALYSIS OF THE REACTION

Nickel-alumina was chosen from among the catalysts that were found to be adequate and the kinetics of the reaction were studied in the presence of this catalyst.

The aim of our studies was to obtain data on the relative rates of the elementary processes, on the details of processes occurring on the catalyst and to determine the most preferable parameters in connection with the use of the catalyst.

The experiments were carried out at 550°C and at a molar ratio 10 moles benzene/mole tetrahydrothiophene at different feeding rates. Accordingly, different residence times were obtained for the reactants. The calculations were carried out on the basis of the analytical results obtained for the starting materials and

products. The results of these experiments are given in Table 4. During the calculations, a procedure proposed by NAGY [12] was adopted. This can be summarized as follows: the rate and kinetic equations conforming to the supposed mechanism, pertaining to the stoichiometric equation, were taken from a Table. The partial pressure values were substituted into these equations, and by adopting the sign

$$x = \frac{p_i}{p}$$

the equations were linearized.

The rate values found in the equations can be calculated from the measured data.

Table 4. Dehydrogenation of Tetrahydrothiophene at Various Feeding Rates

Amount of catalyst: 20 g
Temperature: 550 °C
Pressure: 68 mm Hg

Measured data	No. of experiments					
	1.	2.	3.	4.	5.	6.
Feeding rate $B' \cdot 10^2$ (cm^3/sec)	1.815	1.957	2.50	3.15	4.78	6.25
THT concentration in the vapour mixture feed (vol.%)	9.1	9.1	9.1	9.1	9.1	9.1
THT concentration in product vapour (vol.%)	0.66	0.97	1.85	3.44	6.3	8.6
Thiophene concentration in product vapour (vol.%)	8.3	8.0	7.2	5.6	2.8	0.5

If the transformed experimental data, which are in agreement with the equations, are plotted in a diagram, it will be true that from among the rate (kinetic) equations the correct one is that

which yields corresponding pairs of values which lie on a straight line.

The stoichiometric equation of the dehydrogenation of tetrahydrothiophene is the following:

$$C_4H_8S \longrightarrow C_4H_4S + 2\ H_2$$

and the type of the equation is

$$A \longrightarrow B_1 + B_2 \qquad (1)$$

The amount of tetrahydrothiophene brought to evaporation ensures a stream of constant mass rate in the reactor. The amounts of liquid and gaseous products leaving the reactor were measured, together with the composition of the liquid. The diluting component did not take part in the reaction and in order to simplify the calculations it was not taken into account. Compression of the gases after the reactor was given by the difference of the external pressure and the partial pressure of the diluting component, which was 68.0 mm Hg. Taking the stoichiometric Equation (1) into consideration, the rate equation of the reaction is the following:

$$\frac{1}{S} = -\int_{(y_A)_0}^{(y_A)_t} \frac{dy_A}{w} = \int_{(y_{B_1})_0}^{(y_{B_1})_t} \frac{dy_{B_1}}{w} = \frac{1}{2}\int_{(y_{B_2})_0}^{(y_{B_2})_t} \frac{dy_{B_2}}{w} \qquad (2)$$

The factor 1/2 in the third expression of the rate equation originates from the stoichiometric constant.

The density of the raw material fed into the system was 0.889 g/cm^3. From the data given in Table 4., with the mass rate of feed (B), if the mass of the catalyst (m_s) is known, the volumetric rate (S) can be calculated.

$$B = B' \cdot d; \qquad S = \frac{B}{m_s} \qquad (3)$$

Tetrahydrothiophene was fed into the reactor, and thus:

$$(y_A)_0 = \frac{1}{M} ; \quad (y_{B_1})_0 = 0; \quad (y_{B_2})_0 = 0 \tag{4}$$

Taking the equation of the reaction into consideration, for the material balance the following holds:

$$(y_A)_0 - (y_A)_t = (y_{B_1})_t = \frac{1}{2} (y_{B_2})_t \tag{5}$$

The results of the calculations are summarized in Table 5.

Table 5. Values Calculated from the Experimental Data

Calculated values	No. of experiments					
	1.	2.	3.	4.	5.	6.
$B \cdot 10^2$ (g/sec)	1.615	1.740	2.220	2.800	4.250	5.560
$S \cdot 10^3$ (g/g sec)	0.807	0.870	1.110	1.400	2.125	2.780
$(y_A)_0 \cdot 10^2$ (moles/g)	1.135	1.135	1.135	1.135	1.135	1.135
$(y_A)_t \cdot 10^2$ (moles/g)	0.078	0.116	0.222	0.415	0.700	1.060
$1/S \cdot 10^{-3}$ (g sec/g)	1.240	1.150	0.900	0.715	0.470	0.360

It was not possible unequivocally to determine, on the basis of the experimental series, which of the product components influences the reaction rate in addition to the starting material.

Consequently, of the rate equations pertaining to the reaction $A \rightarrow B_1 + B_2$ found in literature all those had to be studied in which the reaction rate is dependent on the partial pressure of the starting material and of a product (Equations 6a to 6e), or on the partial pressure of all the three possible components (Equations 6f and 6g).

1. $W = f(p_A, p_{B_1})$ 2. $W = f(p_A, p_{B_2})$

$$W = \frac{p_A}{a^I + b^I p_A + c^I p_{B_1}}; \qquad W = \frac{p_A}{a^I + b^I p_A + d^I p_{B_2}} \tag{6a}$$

$$W = \frac{p_A}{a^{II} + c^{II}\sqrt{p_{B_1}}}; \qquad W = \frac{p_A}{a^{II} + d^{II}\sqrt{p_{B_2}}} \tag{6b}$$

$$W = \frac{p_A}{(a^{III} + b^{III} p_A + c^{III} p_{B_1})^2}; \quad W = \frac{p_A}{(a^{III} + b^{III} p_A + d^{III} p_{B_2})^2} \tag{6c}$$

$$W = \frac{p_A}{(a^{IV} + b^{IV} p_A + c^{IV}\sqrt{p_{B_1}})^2}; \quad W = \frac{p_A}{(a^{IV} + b^{IV} p_A + d^{IV}\sqrt{p_{B_2}})^2} \tag{6d}$$

$$W = \frac{p_A}{a^V + c^V p_{B_1}}; \qquad W = \frac{p_A}{a^V + d^V p_{B_2}} \tag{6e}$$

3. $W = f(p_A, p_{B_1}, p_{B_2})$

$$W = \frac{p_A}{a^{VI} + c^{VI} p_{B_1} + d^{VI} p_{B_2}} \tag{6f}$$

$$W = \frac{p_A}{(a^{VII} + b^{VII} p_A + c^{VII} p_{B_1} + d^{VII} p_{B_2})^2} \tag{6g}$$

The partial pressures can be substituted by the mole fractions in the gaseous phase:

$$\frac{P_A}{P} = \frac{(y_A)_t}{3(y_A)_o - 2(y_A)_t} \tag{7a}$$

$$\frac{P_{B1}}{P} = \frac{1}{3}\left(1 - \frac{P_A}{P}\right) \tag{7b}$$

$$\frac{P_{B_2}}{P} = \frac{2}{3}\left(1 - \frac{P_A}{P}\right) \tag{7c}$$

By dividing Equations (6) by the total pressure (P), substituting the values given in Equation (7) and ntroducing

$$\frac{P_A}{P} = x$$

we have linearized rate Equation (6):

$$\frac{x}{W} = \left(\frac{a^I}{P} + \frac{2}{3}d^I\right) + \left(b^I - \frac{2}{3}d^I\right)x \quad ; \quad \frac{x}{W} = \alpha^I + \beta^I x \tag{8a}$$

$$\frac{x}{W} = \left(\frac{a^I}{P} + \frac{1}{3}c^I\right) + \left(b^I - \frac{1}{3}c^I\right)x$$

$$\frac{x}{W} = \frac{a^{II}}{P} + \sqrt{\frac{2}{3}}\,\frac{d^{II}}{\sqrt{P}}\sqrt{1-x} \quad ; \quad \frac{x}{W} = \alpha^{II} + \gamma^{II}\sqrt{1-x} \tag{8b}$$

$$\frac{x}{W} = \frac{a^{II}}{P} + \sqrt{\frac{1}{3}}\,\frac{c^{II}}{\sqrt{P}}\sqrt{1-x}$$

$$\sqrt{\frac{x}{W}} = \sqrt{P}\left[\left(\frac{a^{III}}{P} + \frac{2}{3}\,d^{III}\right) + \left(b^{III} - \frac{2}{3}\,d^{III}\right)x\right]$$

$$\sqrt{\frac{x}{W}} = \sqrt{P}\left[\left(\frac{a^{III}}{P} + \frac{1}{3}\,c^{III}\right) + \left(b^{III} - \frac{1}{3}\,c^{III}\right)x\right]$$

$$; \quad \sqrt{\frac{x}{W}} = \alpha^{III} + \beta^{III}x \qquad (8c)$$

$$\sqrt{\frac{x}{W}} = \sqrt{P}\left(\frac{a^{IV}}{P} + b^{IV}x + \sqrt{\frac{2}{3}}\,\frac{d^{IV}}{\sqrt{P}}\,\sqrt{1-x}\right)$$

$$\sqrt{\frac{x}{W}} = \sqrt{P}\left(\frac{a^{IV}}{P} + b^{IV}x + \sqrt{\frac{1}{3}}\,\frac{c^{IV}}{\sqrt{P}}\,\sqrt{1-x}\right)$$

$$; \quad \sqrt{\frac{x}{W}} = \alpha^{IV} + \beta^{IV}x + \gamma^{IV}\sqrt{1-x} \qquad (8d)$$

$$\frac{x}{W} = \frac{a^{V}}{P} + \frac{2}{3}\,d^{V}(1 - x)$$

$$\frac{x}{W} = \frac{a^{V}}{P} + \frac{1}{3}\,c^{V}(1 - x)$$

$$; \quad \frac{x}{W} = \alpha^{V} + \gamma^{V}(1 - x) \qquad (8e)$$

$$\frac{x}{W} = \left(\frac{a^{VI}}{P} + \frac{1}{3}\,c^{VI} + \frac{2}{3}\,d^{VI}\right) - \left(\frac{1}{3}\,c^{VI} + \frac{2}{3}\,d^{VI}\right)x \; ; \; \frac{x}{W} = \alpha^{VI} - \gamma^{VI}x \qquad (8f)$$

$$\sqrt{\frac{x}{W}} = \sqrt{P}\left[\left(\frac{a^{VII}}{P} + \frac{1}{3}\,c^{VII} + \frac{2}{3}\,d^{VII}\right) + \left(b^{VII} - \frac{1}{3}\,c^{VII} - \frac{2}{3}\,d^{VII}\right)x\right] ;$$

$$\sqrt{\frac{x}{W}} = \alpha^{VII} + \beta^{VII}x \qquad (8g)$$

The specific reaction rate (w) can be calculated from the following Equation:

$$w = -\frac{d(y_A)_t}{d(1/S)} \approx -\frac{\Delta(y_A)_t}{\Delta(1/S)} \qquad (9)$$

If $(y_A)_t$ is plotted against 1/S on the basis of Table 5 (Fig.1).

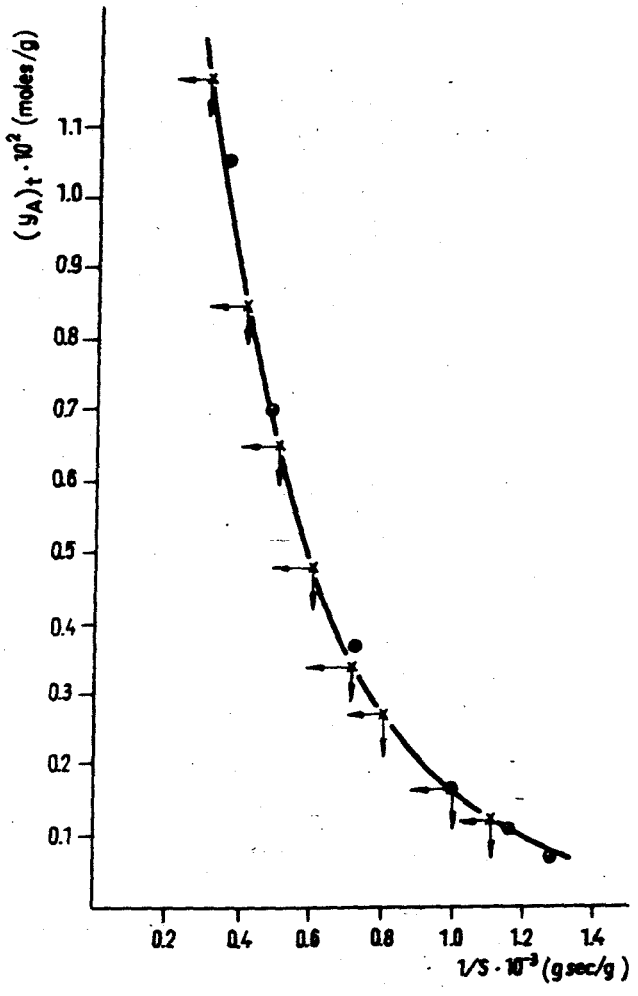


Fig.1. The alteration of THT concentration with the reaction time. ● measured values; x values used in the differentiation.

The difference quotients were calculated by taking the $\Delta(1/S)$ values and the corresponding $\Delta(y_A)_t$ values from Fig. 1. The result of

the calculations is shown in Table 6. Fig.2. was plotted on the basis of Table 6; The Figure shows the difference quotients - which, according to Equation (9), correspond to the specific reaction rates - plotted against $(y_A)_t$.

Table 6. Values of the Difference Quotients as Calculated from Measured Results

Residence time $\frac{1}{S}\cdot 10^{-3}$ (g sec/g)	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1
$(y_A)_t \cdot 10^2$ (moles/g)	1.15	0.86	0.65	0.49	0.38	0.29	0.22	0.17	0.13
$w = \frac{\Delta(y_A)_t}{\Delta(1/S)} \cdot 10^5$ (moles/g sec)	-	2.9	2.1	1.6	1.1	0.9	0.7	0.5	0.4

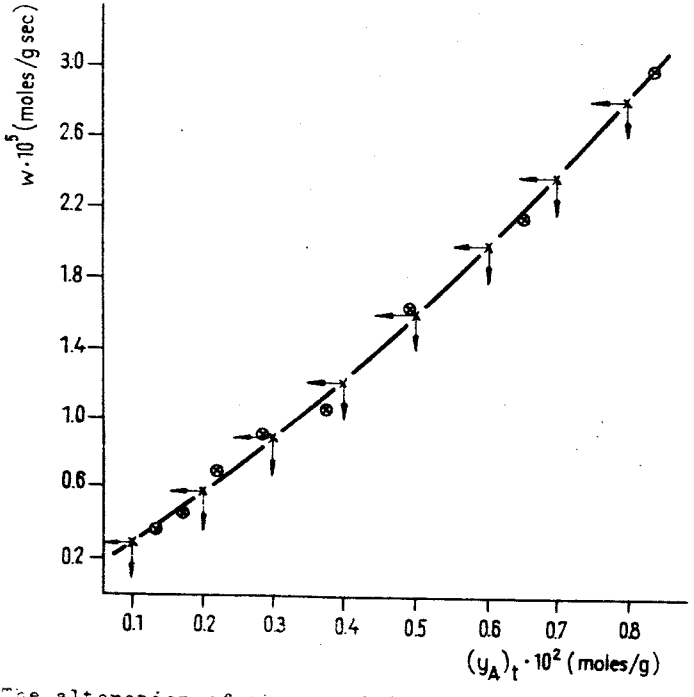


Fig. 2. The alteration of the specific reaction rate with the THT concentration. ⊗ calculated values; x the values of the curve

Knowing the specific reaction rate (w) and the mass of the catalyst, the rate of the dehydrogenation reaction can be written as follows:

$$W = w \cdot m_s \tag{10}$$

The w values, corresponding to increasing $(y_A)_t$ values and necessary for calculation of the linearized rate Equations (8a to 8g), were read from Fig.2. The detailed calculation is shown in Table 7. The linearized rate equations constructed in this manner are shown in Figs. (3a to 3e).

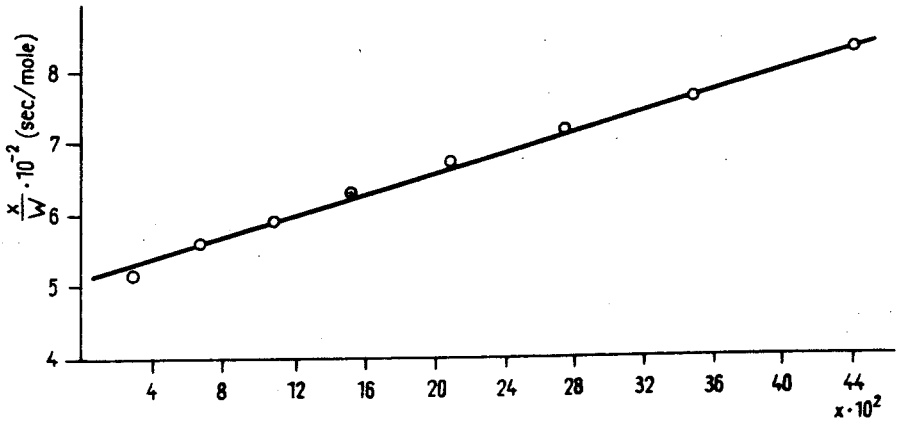


Fig. 3a. The linearized rate equation, based on Equation (8a).

It is apparent from these Figures that the calculated values appear along a straight line only in the case of Figs (3a) and (3e).

From these two the

$$\frac{x}{W} = \alpha^I + \beta^I x$$

equation was accepted which corresponds to Fig. (3a) as the one best fitting the conditions. (The slope of the straight line constructed in Fig. (3e) is negative.)

Table 7. Data of the Linearized Kinetic Equations

$(y_A)_t \cdot 10^2$ (moles/g)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
$w \cdot 10^5$ (mole/g sec)	0.30	0.60	0.90	1.22	1.58	1.92	2.28	2.66
$W \cdot 10^4$ (mole/sec)	0.60	1.20	1.80	2.44	3.16	3.84	4.56	5.32
$[3(y_A)_0 - 2(y_A)_t] \cdot 10^2$	3.2	3.0	2.8	2.6	2.4	2.2	2.0	1.8
$x = p_A/P = \frac{(y_A)_t}{3(y_A)_0 - 2(y_A)_t} \cdot 10^2$	3.12	6.67	10.70	15.40	20.85	27.30	35.0	44.1
$\frac{x}{W} \cdot 10^{-2}$ (sec/mole)	5.20	5.56	5.94	6.32	6.62	7.12	7.67	8.29
$(1 - x) \cdot 10$	9.69	9.33	8.93	8.46	7.92	7.27	6.50	5.59
$\frac{x}{W}$ ($sec^{1/2}/mole^{1/2}$)	22.8	23.6	24.4	25.15	25.75	26.65	27.65	28.75
$\sqrt{1 - x} \cdot 10$	9.83	9.66	9.45	9.19	8.90	8.52	8.06	7.46
$35.4 - \frac{x}{W}$ ($sec^{1/2}/mole^{1/2}$)	12.6	11.8	11.0	10.25	9.65	8.75	7.75	6.65
$\frac{35.4 - \frac{x}{W}}{\sqrt{1 - x}}$	12.83	12.21	11.63	11.16	10.83	10.27	9.61	8.91

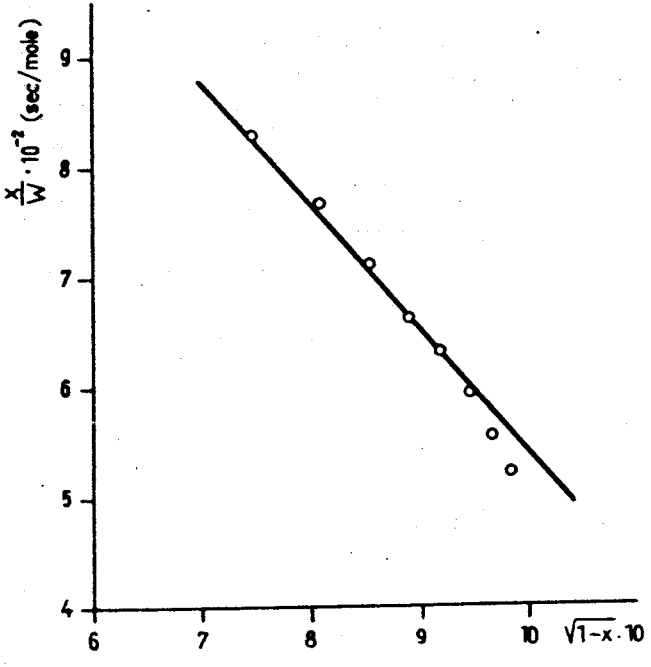


Fig. 3b. The linearized rate equation, based on Equation (8b).

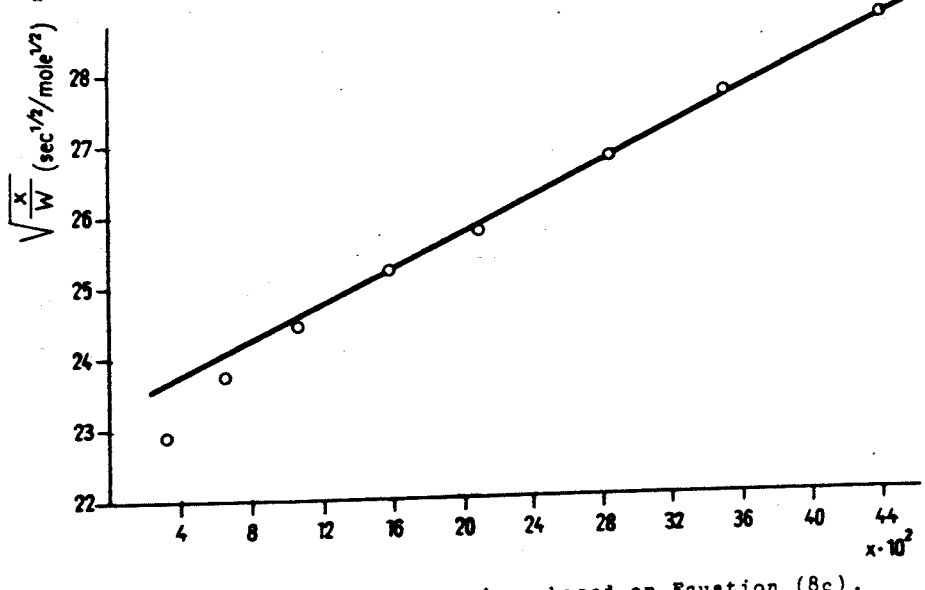


Fig. 3c. The linearized rate equation, based on Equation (8c).

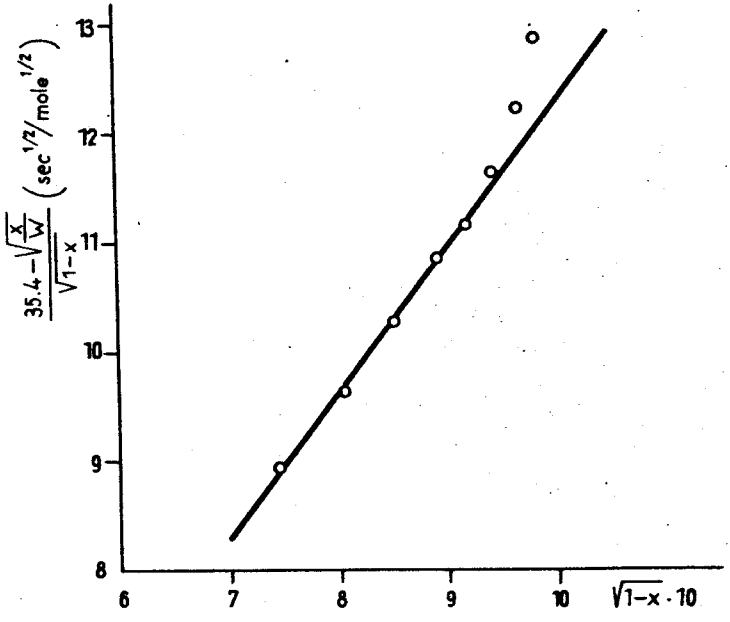


Fig. 3d. The linearized rate equation, based on Equation (8d).

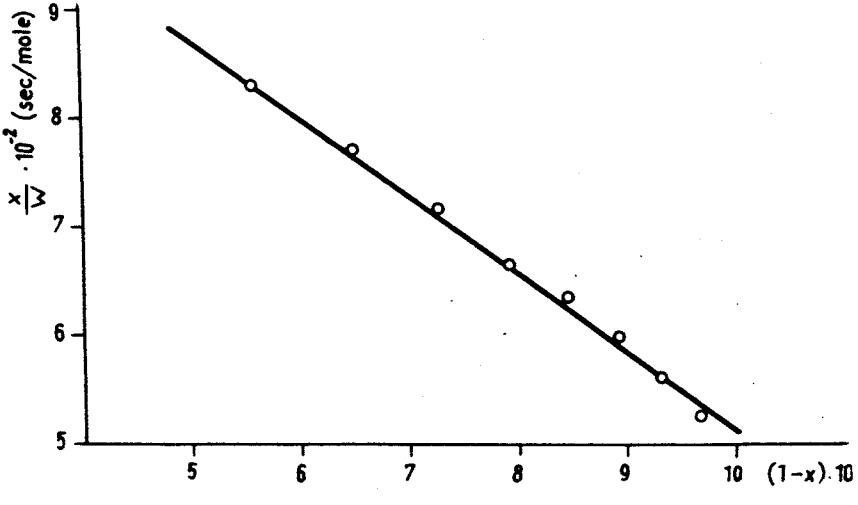


Fig. 3e. The linearized rate equation, based on Equation (8e).

The values of constants α and β can be determined on the basis of Fig. (3a):

$$\alpha^I = 5.05 \cdot 10^2 \text{ (sec/mole)}$$
$$\beta^I = 7.5 \cdot 10^2 \text{ (sec/mole)}$$

A detailed explanation of the meaning of the constants is given in the following:

$$\alpha^I = \frac{a^I}{P} + \frac{2}{3} d^I \qquad \alpha^I = \frac{a^I}{P} + \frac{1}{3} c^I$$

$$\beta^I = b^I - \frac{2}{3} d^I \qquad \beta^I = b^I - \frac{1}{3} c^I$$

$$\frac{a^I}{P} + \frac{2}{3} d^I > 0 \; ; \quad \frac{2}{3} d^I < b^I \neq 0$$

$$\frac{a^I}{P} + \frac{1}{3} c^I > 0 \; ; \quad \frac{1}{3} c^I < b^I \neq 0$$

According to the tables published in literature [11], the surface reaction is the rate-determining partial process in the case of this type of reaction. One of the products formed is adsorbed; consequently both cases of Equation (8a) were studied:

$$W = \frac{p_A}{a + bp_A + cp_{B_1}} = \frac{1}{a} \cdot \frac{p_A}{\left(1 + \frac{b}{a} p_A + \frac{c}{a} p_{B_1}\right)}$$

The corresponding kinetic-equation is:

$$W = k \frac{p_A}{1 + K_A p_A + K_{B_1} p_{B_1}}$$

By comparison of the two equations:

$$k = \frac{1}{a} \; ; \quad K_A = \frac{b}{a} \; ; \quad K_{B_1} = \frac{c}{a} \quad \text{or}$$

$$a = \frac{1}{k} \; ; \quad b = \frac{K_A}{k} \; ; \quad c = \frac{K_{B_1}}{k}$$

When the constants α and β are expressed with rate and equilibrium constants:

$$\alpha = \frac{a}{P} + \frac{1}{3} c = \frac{1}{kP} + \frac{1}{3} \frac{K_{B_1}}{k} = \frac{1}{k} \left(\frac{1}{P} + \frac{1}{3} K_{B_1} \right)$$

$$\beta = b - \frac{1}{3} c = \frac{K_A}{k} - \frac{1}{3} \frac{K_{B_1}}{k} = \frac{1}{k} \left(K_A - \frac{1}{3} K_{B_1} \right)$$

If $K_{B_1} \approx 0$:

$$\alpha = \frac{1}{kP} \rightarrow k = \frac{1}{\alpha P}$$

$$\beta = \frac{K_A}{k} \rightarrow K_A = \beta k = \frac{\beta}{\alpha} \cdot \frac{1}{P}$$

In this case:

$$k = \frac{1}{5.05 \cdot 10^2 \cdot 68} = 2.92 \cdot 10^{-5} \text{ moles/mm Hg sec}$$

$$K_A = 7.5 \cdot 10^2 \cdot 2.92 \cdot 10^{-5} = 2.19 \cdot 10^{-2} \text{ 1/mm Hg}$$

If $K_{B_1} \neq 0$, the values of k, K_A and K_{B_1} cannot be calculated separately.

If component B_2 (hydrogen) is adsorbed, the rate equation is the following:

$$W = \frac{p_A}{a + bp_A + dp_{B_2}}$$

The corresponding kinetic equation is:

$$W = k \frac{p_A}{1 + K_A p_A + K_{B_2} p_{B_2}}$$

In a similar manner to the foregoing:

$$a = \frac{1}{k} \qquad b = \frac{K_A}{k} \qquad d = \frac{K_{B_2}}{k}$$

further

$$\alpha = \frac{a}{P} + \frac{2}{3} d = \frac{1}{k} \left(\frac{1}{P} + \frac{2}{3} K_{B_2}\right)$$

$$\beta = b - \frac{2}{3} d = \frac{1}{k} \left(K_A - \frac{2}{3} K_{B_2}\right)$$

If K_{B_2} 0, the values of k and K_A are identical to those calculated in the foregoing; the values of the physical constants cannot be calculated in the opposite case.

Accordingly, on the basis of the kinetic studies it can be concluded that the dehydrogenation proceeds through the following stages:

1. Adsorption on the catalyst.
2. Chemical reaction on the surface.
3. Desorption.

An analysis of the kinetic equation obtained leads to the following conclusions:

1. The global reaction rate is, through the rate constant, propotional to the surface of the catalyst ($k = F(S_o)\vec{k} K_A$). Accordingly it is preferable to use a dehydrogenating catalyst of as high a specific surface as possible.

2. At low tetrahydrothiophene partial pressures the kinetic equation becomes simpler (the value of $K_A p_A$ may be neglected) and the reaction rate is proportional to the partial pressure of tetrahydrothiophene:

$$W = k \cdot p_A$$

Industrial realization of this condition is uneconomic.

3. Side reactions are negligible at lower temperatures. At the same time, desorption of the products may be accelerated by elevation of the temperature.

The experimental results make it possible to determine the data necessary for reactor design in further experiments carried out on a pilot plant scale.

LIST OF SYMBOLS

A_i	starting components of the reaction
B_i	components of the reaction product
B	mass rate of gas stream (g/sec)
d	density (g/cm^3)
K_{A_i}, K_{B_i}	adsorption equilibrium constants of the components (1/mm Hg)
M	molecular weight
m_s	mass of catalyst (g)
P_{A_i}, P_{B_i}	partial pressures of the components (mm Hg)
P	gas area pressure (mm Hg)
S	volumetric rate of gas stream (g/g sec)
t	time of reaction (sec)
V	catalyst volume (cm^3)
w	specific reaction rate (moles/g sec)

W	reaction rate (moles/sec)
x	conversion (dimensionless)
y_{A_i}, y_{B_i}	concentration of components (moles/g)

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РЕЗЮМЕ

Авторами были изучены термодинамические условия дегидрогенизации тетрагидротиофена. При стандартных условиях реакции были выполнены опыты с применением катализаторов из металла, окиси металла или сульфида металла различного типа, произведенных и в промышленном масштабе, с целью повышения скорости равновесной реакции.

При использовании соответственно выбранного катализатора проводились измерения для определения кинетики реакции. Согласно расчетам авторов, частным процессом определяющим скорость является поверхностная реакция.