

KINETICS OF THE THERMAL DECOMPOSITION OF AZOISOPROPANE

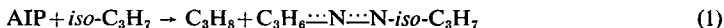
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The gas-phase pyrolysis of azoisopropane (*iso*-C₃H₇-N=N-*iso*-C₃H₇; AIP) was studied at 494–546 K in a static system. Arrhenius equations were suggested for the following reactions:



$$\log(k_1/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) = (6.7 \pm 0.2) - (27 \pm 2 \text{ kJ mol}^{-1})/2.3 \text{ RT}$$



$$\log(k_i/\text{s}^{-1}) = (14.6 \pm 0.4) - (178 \pm 4 \text{ kJ mol}^{-1})/2.3 \text{ RT}$$

The disproportionation and combination rate constant ratio for the isopropyl radical was found to be $k_d/k_c = 0.8 \pm 0.1$. Results are discussed and compared with literature data.

Introduction

Azo compounds are good sources of radicals in gas reactions and their decompositions have been the subject of kinetic studies [1–4].

There have been several studies on the thermal decomposition of azoisopropane (hereafter AIP) [1, 5–7], although the quantitative results available so far differ somewhat.

Recent thermochemical data on AIP [8] suggest new investigations for the pyrolysis of AIP. The present work was undertaken for two purposes:

- (a) measuring the kinetics of the hydrogen-abstraction reaction of *iso*-C₃H₇ from AIP; and
- (b) measuring the kinetics of the unimolecular decomposition of AIP.

Experimental

The static reaction system and the analytical methods applied on the gas-chromatograph were described earlier [9, 10].

Azoisopropane was prepared by the RENAUD—LEITCH method [11] and purified by extensive washing with water and low-temperature distillation. It was 99.8% pure, containing acetone and diethyl ether as impurities.

Results and Discussion

The thermal decomposition of AIP was studied in a static reaction system in the range 494—546 K at pressures of about 6 kN m⁻². The following products were identified by gas-chromatography: nitrogen, propane, propylene, 2,3-dimethyl-butane (DMB), 4-methyl-pentene-1 (4 MPI), as well as C₂H₄ and CH₄ at higher temperatures.

A typical product composition is shown in Table I. Some polymer formation was also observed in the reactions.

Table I

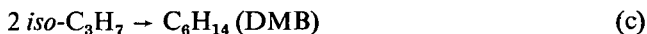
Products of AIP decomposition
T = 500 K; [AIP]₀ = 4.53 · 10⁻⁴ mol dm⁻³;
 Conversion 10%

Products	%
N ₂	40.6
C ₃ H ₈	23.6
DMB	21.7
C ₃ H ₆	14.0
4 MPI	0.1

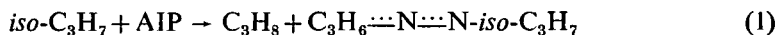
The formation of the products can be understood from the reaction shown below:



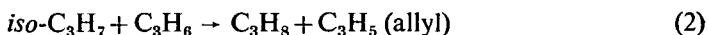
Reaction (i) is the source of N₂ and *iso*-C₃H₇ radicals, which latter can react with each other in combination and disproportionation reactions:



It can be seen in Table II that the rate of formation of C₃H₈ (R_{C₃H₈}) is higher than that of propylene (R_{C₃H₆}). This means that, besides reaction (d), another source of propane formation should exist. This may be the hydrogen-abstraction reaction of *iso*-C₃H₇:



4-Methyl-pentene-1 can be formed by the following reactions:



Reactions (2) and (3) were proved by decomposition of AIP in an excess of C₃H₆. It was observed that the rate of formation of 4MPI was proportional to the concentration of propylene.

In this study the rate constants of reactions (i) and (1) were determined. The procedure for the determinations is discussed below.

(a) *Rate Constant of Reaction (1)*

The rate of reaction (1) can be given by Eqn. (I):

$$R_{C_3H_8} - R_{C_3H_6} = k_1 [iso-C_3H_7][AIP]_0 \quad (I)$$

$R_{C_3H_8}$ and $R_{C_3H_6}$ are the initial rates of formation of C_3H_8 and C_3H_6 , respectively; $[AIP]_0$ and k_1 are the initial concentration of AIP and the rate constant of reaction (1), respectively.

The rate of reaction (c) is given by Eqn. (II):

$$R_{DMB} = k_c [iso-C_3H_7]^2 \quad (II)$$

where R_{DMB} and k_c are the initial rate of formation of DMB and the rate constant of isopropyl combination, respectively. Equation (III) can be obtained by substituting $[iso-C_3H_7]$ in Eqn. (I) by $R_{DMB}/k_c^{1/2}$ (originating from Eqn. (II)) and dividing by R_{DMB} :

$$\frac{R_{C_3H_8} - R_{C_3H_6}}{R_{DMB}} = \frac{k_1}{k_c^{1/2}} \frac{[AIP]_0}{R_{DMB}^{1/2}} \quad (III)$$

If the reaction mechanism is correct, the ratio $(R_{C_3H_8} - R_{C_3H_6})/R_{DMB}$ should be linear as a function of $[AIP]_0/R_{DMB}^{1/2}$. The slope of the straight line is $k_1/k_c^{1/2}$.

The experimental results calculated with Eqn. (III) are shown in Fig. 1. Experimental data are collected in Table II. Ratios of k_d/k_c , together with $k_1/k_c^{1/2}$, are also shown in Table II. The ratios of $k_1/k_c^{1/2}$ were calculated with Eqn. (IV):

$$\frac{k_1}{k_c^{1/2}} = \frac{R_{C_3H_8} - R_{C_3H_6}}{R_{DMB}^{1/2} [AIP]_0} \quad (IV)$$

The experimental results shown in Fig. 1 support reaction steps (c), (d) and (1).

From the temperature-dependence of $k_1/k_c^{1/2}$ shown in Table II, Arrhenius parameters can be calculated. The temperature-dependence of $k_1/k_c^{1/2}$ is shown in Fig. 2.

Figure 2 also depicts results of DURHAM AND STEACIE [12] and RIEM AND KUTSCHKE [13], measured in the photolysis of AIP. Recent results are in agreement with the literature data. The combination of the recent results and the literature data leads to the following equation:

$$\log(k_1/k_c^{1/2} \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}) = (1.9 \pm 0.2) - (27 \pm 2 \text{ kJ mol}^{-1})/2.3 \text{ RT}$$

Taking the value of $k_c = 10^{9.5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from the paper of GOLDEN *et al.* [14], k_1 can be given as follows:

$$\log(k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (6.7 \pm 0.2) - (27 \pm 2 \text{ kJ mol}^{-1})/2.3 \text{ RT.}$$

This value is compared with the literature data in Table III.

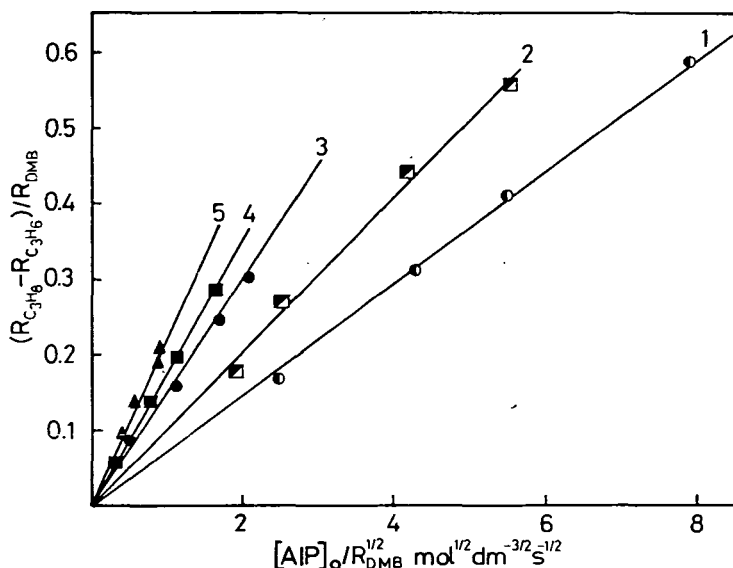


Fig. 1. $(R_{C_3H_8} - R_{C_3H_6})/R_{DMB}$ as a function of $[AIP]_0/R_{DMB}^{1/2}$. 1. 494; 2. 500; 3. 523; 4. 531; 5. 546 K

Table II

Kinetic data for the determination of $k_1/k_c^{1/2}$ and k_d/k_c

T/K	$R_{C_3H_8}$	$R_{C_3H_6}$	R_{DMB}	$10^4 [AIP]_0$ mol dm ⁻³	$k_1/k_c^{1/2}$	k_d/k_c
	$10^3 R/\text{mol dm}^{-3} \text{s}^{-1}$					
494	0.217	0.179	0.218	1.12	0.071	0.82
494	0.478	0.363	0.462	3.31	0.073	0.78
494	1.27	0.822	1.19	6.02	0.068	0.69
494	3.05	1.62	2.42	12.3	0.074	0.71
500	0.382	0.321	0.361	1.06	0.097	0.78
500	0.789	0.586	0.781	2.26	0.10	0.75
500	2.11	1.26	1.94	5.67	0.11	0.65
500	5.30	2.86	4.05	12.0	0.10	0.70
523	2.83	2.44	3.54	1.26	0.16	0.84
523	7.86	6.56	7.91	3.14	0.15	0.89
523	18.5	15.1	18.7	7.45	0.14	0.80
523	29.1	20.4	28.2	11.2	0.15	0.60
531	4.84	4.48	4.04	1.01	0.16	0.69
531	15.2	13.3	12.5	2.91	0.18	0.81
531	28.4	23.3	25.3	5.52	0.18	0.92
531	64.7	48.1	57.3	12.2	0.18	0.84
546	45.4	40.8	45.9	3.01	0.22	0.89
546	86.3	74.2	80.5	5.45	0.25	0.92
546	16.9	140	163	10.8	0.22	0.86
546	182	144	180	11.8	0.23	0.80

Dimensions of $k_1/k_c^{1/2}$ are $\text{dm}^{3/2} \text{mol}^{-1/2} \text{s}^{-1/2}$.

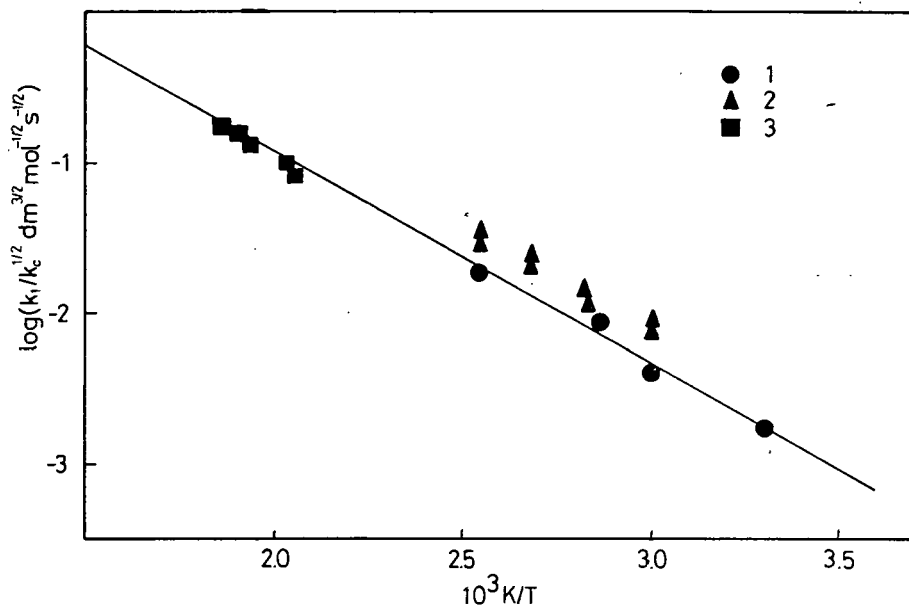


Fig. 2. Temperature-dependence of $k_1/k_c^{1/2}$. (1) Data of DURHAM and STEACIE [12]; (2) data of RIEM and KUTSCHKE [13]; (3) this work

Table III

Arrhenius parameters for $\text{AIP} + \text{iso-C}_3\text{H}_7 \rightarrow \text{C}_3\text{H}_8 + \text{C}_3\text{H}_6 + \text{N} \cdots \text{N-iso-C}_3\text{H}_7$ (1)

$\log \frac{A}{\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}}$	$\frac{E}{\text{kJ mol}^{-1}}$	T/K	$\log \frac{k}{\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}}_{500 \text{ K}}$	Ref.
6.7	27	303—393	3.88	[12]
6.8	28	308—400	3.87	[13]
7.3	30	300—433	4.17	[14]
6.7 ± 0.2	27 ± 2	494—546	3.88	this work

(b) Rate Constant of Reaction (i)

Rate constants of reaction (i) were calculated from the rate of consumption of AIP. Reaction (1) was taken into account by correction, as reaction (1) is also a route of AIP consumption in the decomposition.

The consumption of AIP in the decomposition reactions obeys a first-order rate equation, as shown in Fig. 3. The slopes of the lines give the rate constant of AIP consumption (k_{AIP}).

The temperature-dependence of k_{AIP} was determined and the results are shown in Fig. 4. From this dependence the value of k_{AIP} can be given in the following Arrhenius equation:

$$\log(k_{\text{AIP}}/\text{s}^{-1}) = (15.4 \pm 0.2) - (186 \pm 2 \text{ kJ mol}^{-1})/2.3 \text{ RT.}$$

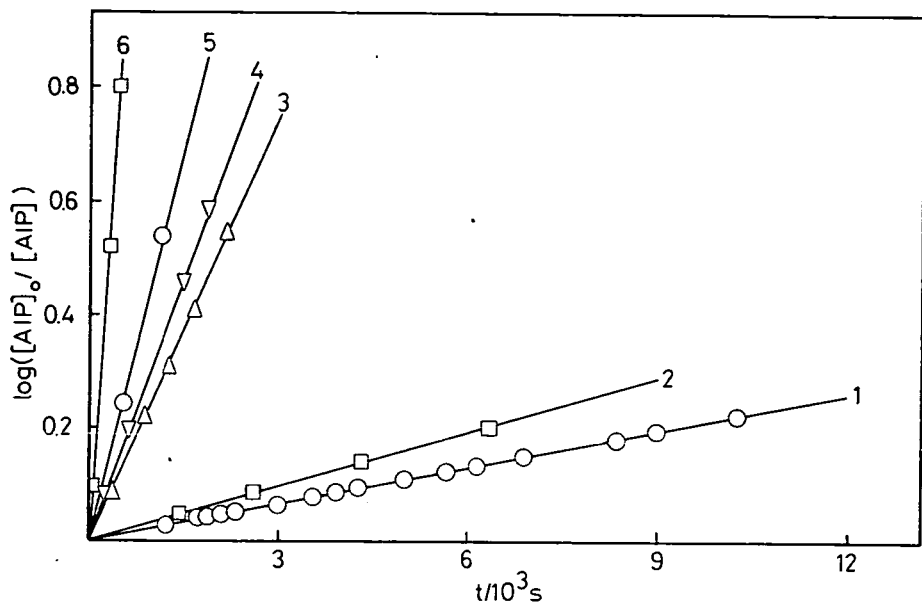


Fig. 3. Consumption of AIP in pyrolytic reactions at different temperatures. (1) 494; (2) 500; (3) 513; (4) 523; (5) 531; (6) 546 K

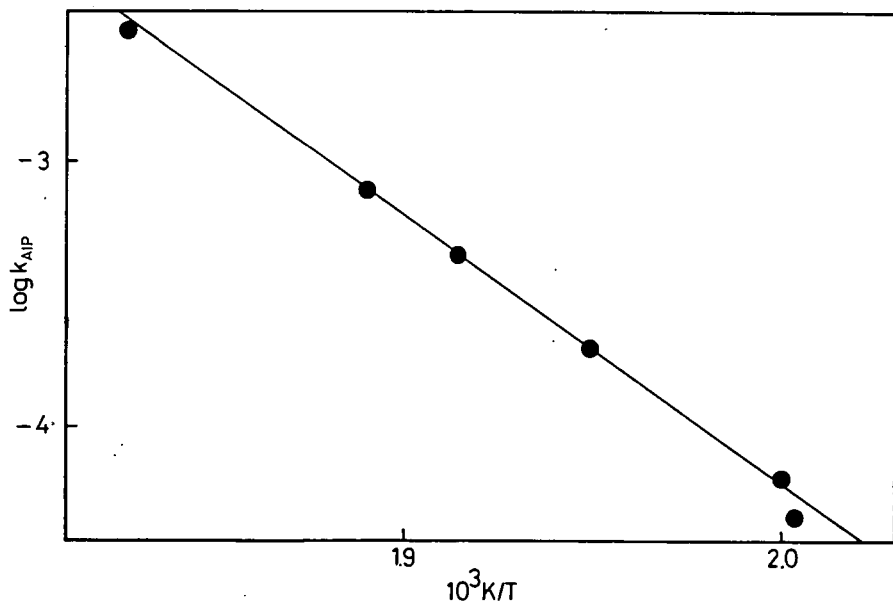


Fig. 4. Temperature-dependence of k_{AIP}

This rate constant is characteristic for the consumption of AIP in the decomposition reaction, which consists of two main processes, reactions (i) and (1).

The evaluation of the rate constant of reaction (i) is based on considerations in which the role of reaction (1) is estimated. From the experimental data the role of reaction (1) in the consumption of AIP can be given by the following formula:

$$x\% = \left(\frac{100 R_1}{R_{\text{AIP}}} \right)_{t=0} \quad (\text{V})$$

The results of calculations are shown in Table IV.

Table IV

The role of the reaction $\text{AIP} + \text{iso-C}_3\text{H}_7 \rightarrow \text{C}_3\text{H}_8 + \text{C}_3\text{H}_6 + \text{N}=\text{N-iso-C}_3\text{H}_7$ (1) in AIP decomposition

T/K	$\frac{10^4 [\text{AIP}]_0}{\text{mol dm}^{-3}}$	$10^8 R_{\text{DMB}}$	$10^8 R_{\text{AIP}}$	$10^9 R_1$	x %
		R/mol dm ⁻³ s ⁻¹			
494	3.24	0.61	1.29	2.94	22.8
500	3.20	1.02	2.21	4.07	18.4
523	3.06	7.58	15.3	14.1	9.2
531	3.01	12.5	28.9	18.9	6.5
546	2.93	44.0	90.2	42.0	4.6

From the known role of reaction (1), the value of k_i can be calculated with the following expression:

$$k_i = \frac{2.3}{t} \log \frac{[\text{AIP}]_0}{[\text{AIP}] + ([\text{AIP}]_0 - [\text{AIP}]) (R_1)_0 / (R_{\text{AIP}})_0}, \quad (\text{VI})$$

where $[\text{AIP}]_0$ and $[\text{AIP}]$ are concentrations at zero time and time t , respectively; $(R_1)_0$ is the initial rate of reaction (1); and $(R_{\text{AIP}})_0$ is the initial rate of consumption of AIP.

The temperature-dependence of k_i can be given by the following Arrhenius equation:

$$\log(k_i/\text{s}^{-1}) = (14.6 \pm 0.4) - (178 \pm 4 \text{ kJ mol}^{-1})/2.3 \text{ RT}. \quad (\text{VI})$$

These Arrhenius parameters are compared with the literature data in Table V.

The Arrhenius parameters reported here are very different from those of BENSON and O'NEAL [1] and GOLDEN et al. [7].

BENSON and O'NEAL suggested an activation energy from thermochemical calculations. Their A factor was calculated from the experimental rate constant of RAMSPERGER [5] with their estimated activation energy. Heats of formation necessary for the calculation of the activation energy are shown in Table VI. BENSON and O'NEAL used thermochemical data of AIP calculated from the heat of combustion of AIP [15].

Recent data of ENGEL et al. [8] for the heat of combustion of AIP suggest that earlier data are probably erroneous. Thermochemical data on AIP were re-

Table V
Arrhenius parameters of reaction (i); $AIP \rightarrow N_2 + 2 \text{ iso-C}_3\text{H}_7$ (i)

$\log (A/s^{-1})$	$\frac{E}{\text{kJ mol}^{-1}}$	$-\log (k/s^{-1})$ $T=494 \text{ K}$	T/K	Ref.
13.75	171	4.34	523—563	[5]
13.68	171	4.41	503—673	[6]
16.4	198	4.54	—	[1]
16.6*	200*	4.55*	625—854	[7]
18.1	213	4.43		
13.7	170	4.28		
14.6 ± 0.4	178 ± 4	4.33	494—546	this work

* Preferred by the authors.

Table VI
Heats of formation for the calculation of the activation energy of reaction (i)

	AIP	<i>iso-C</i> ₃ H ₇	<i>iso-C</i> ₃ H ₇ —N=N
ΔH_f° 298 kJ mol ⁻¹	87.5*	73.3	212.2*
	36.0**	73.3	140.7**

* Calculated from the data of Coates and Sutton [15].

** Calculated from the data of Engel *et al.* [8].

calculated in this work from the heat of combustion of AIP determined by ENGEL *et al.* [8].

Estimation of the activation energy of reaction (i) using the new thermochemical data results in 178 kJ mol⁻¹, in good agreement with the experimental data reported here.

Rate constants for reaction (i) determined in different laboratories are very similar. This means that the thermochemical calculations also make the recent value of the A factor probably correct.

References

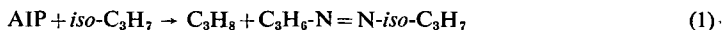
- [1] Benson, S. W., H. E. O'Neal: Kinetic Data on Gas Phase Unimolecular Reaction NSRDS-NBS 21, 31 1970.
- [2] Strausz, O. P., J. W. Lown, H. E. Gunning: Comprehensive Chemical Kinetics, 5. eds. C. H. Bamford and C. F. H. Tipper, Elsevier, New York, 1972.
- [3] Ramsperger, H. C.: J. Amer. Chem. Soc. **51**, 2134 (1929).
- [4] Crawford, R. J., K. Tagaki: J. Amer. Chem. Soc. **94**, 7406 (1972).
- [5] Ramsperger, H. C.: J. Amer. Chem. Soc. **50**, 714 (1928).
- [6] Geiseler, G., J. Hoffman: Z. Phys. Chem. N. F. **57**, 3 (1968).
- [7] Perona, M. J., P. C. Beadle, D. M. Golden: Int. J. Chem. Kinet. **5**, 495 (1973).
- [8] Engel, P. S., J. L. Wood, J. P. Sweet, J. L. Margrave: J. Amer. Chem. Soc. **96**, 2381 (1974).
- [9] Szirovicza, L., F. Márta: Int. J. Chem. Kinet. **8**, 897 (1976).
- [10] Szirovicza, L., F. Márta: React. Kinet. Catal. Lett. **2**, 383 (1975).

- [11] *Renaud, R., L. C. Leitch*: *Canad. J. Chem.* **32**, 545 (1954).
 [12] *Durham, R. W., E. W. R. Steacie*: *Canad. J. Chem.* **31**, 377 (1953).
 [13] *Riem, R. H., K. O. Kutschke*: *Canad. J. Chem.* **38**, 2332 (1960).
 [14] *Berkley, R. E., G. N. C. Woodall, O. P. Strausz, H. E. Gunning*: *Canad. J. Chem.* **47**, 3305 (1969).
 [15] *Coates, G. E., L. E. Sutton*: *J. Chem. Soc.* 1187 (1948).

КИНЕТИКА ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ АЗОИЗОПРОПАНА

Л. Сировица

Изучен пиролиз в газовой фазе азоизопропана (изо- $C_3H_7N=N$ -изо- C_3H_7 , AIP) в статических условиях при температурах 494 и 546 К. Предложены уравнения Аррениуса для следующих реакций:



$$\log(k_1/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}) = (6.7 \pm 0.2) - (27.2 \text{ kJ mol}^{-1})/2.3 \text{ RT}$$



$$\log(k_i/\text{s}^{-1}) = (14.6 \pm 0.4) - (178 \pm 4 \text{ kJ mol}^{-1})/2.3 \text{ RT}$$

Найдено соотношение скоростей диспропорционирования и рекомбинации для изопропильного радикала равное $k_d/k_c = 0,80 \pm 0,1$. Обсуждены полученные результаты и сопоставлены с литературными данными.