THE CONCEPT OF SHIFT AMINOIMINE OF EQUILIBRIUM IN SOLUTION AMINOAZOLES AND THEIR DERIVANTS

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Aminoimine equilibrium aminoazoles and their derivants in a solution is investigated with a different set of solvents, without dependence from a structure of connections and with various substituents in a cycle.
Besides by us it has been assumed, that equilibrium should be displaced aside imino-form aminoazola and increasing fragrance quasi-aromatic systems to rise{elevate;improve;raise} antifungal activity.
Results of researches Aminoimine are submitted to dynamic isomerism æ-amino-1,2,4-triazoles (ATP), 5-AT and БАЛ in a crystal kind and in solutions, and new results in of this area received{obtained} by us.

1.1. C-amino-1,2,4-triazoles

Significant interest to chemistry aminoazoles results from opportunities of their use in chemistry of high-molecular compounds, in medicine, biology, an agriculture [1], [2].
However for the successful decision of questions of synthesis research of theoretical problems is necessary. One of main and inextricably related with the others is Aminoimine dynamic isomerism. Importance of her{it} grows in connection with use amino 1,2,4-azimides and tetrazoles as mother compounds in reactions of alkylation dihaloalkans in the environment of dipolar aprotic solvents [3] – [10], at acylation in conditions of low-temperature polyfunctional condensation dihloranhydrides dicarboxylic acids [11] – [20] salt formations under certain conditions excretions from solutions of salts aminoazoles and an encore – 3,3'-(5-amino-1,2,4-triazole-1-ил) alkanes (BATH) as ligands [21] – [29].
On a background of the big number of publications there are no works on research Aminoimine dynamic isomerism in solutions of dipolar aprotic solvents actually 5-AT, 5-amino-1,2,4-triazol (5-ATP) and 3,5-diamino-1,2,4-triazol (3,5-date) and an encore (amino-1,2,4-triazole-1-ил and tetrazole – N-ил) alkanes.
Works on an establishment of structure 5-ATP have quality character and specify presence of amino group [30], [31]. The chemical data on a structure 3,5-diamino-2-phenyl-1,2,4-triazol in the beginning have been interpreted for the benefit of diiminestructures (I) [32], but the data of ultraviolet spectroscopy received{obtained} later have been interpreted for the benefit of structures (II) or (III) [33], [34].

I II III

Analysis ИК of spectrums 3,5-diamino-1,2,4-triazol before deuteration has allowed to draw a conclusion on his{its} structure as diaminoderivative [35], however a choice between *2H-*, *4H*-forms appeared impossible.
On basis ИК of spectrums deuterized 5-ATP and his{its} salts the assumption that this connection is in amino (IV-VI), and his{its} salt in imino (VII, VIII) the form [31] is confirmed. Earlier with help ИК of spectroscopy to the same conclusion there came authors [30].

IV V
VI VII VIII IX X
XI XII

Results of X-ray crystal analysis testify to existence crystal 5-ATP in the form of amine (V) [36] – [37]. For 3,4,5-triamine-1,2,4-triazol in a crystalline state, also it is more preferable aminoform [38].

1.2. *5-amino-1H-1,2,3,4-тетразол*

In 1951 in the literature the message has appeared, that 5-aminotetrazoles exist in iminoform (XIII), instead of in aminoform (XIV) in witness whereof rather unpersuasive chemical data [39.] have been given{reduced} was originally reported, that at alkylation 1-R-5-aminotetrazoles the products described by the greater basicity, than mother compounds and consequently they have been referred to structure such as (XV) are formed. The structure of these products of alkylation has been submitted as (XVI) [40] later, and the opinion has been stated, that the difference in basicity factor specifies that mother compounds exist in aminoform (XIV). Correctness of this last conclusion proves to be true that fact, that the ultraviolet spectrum of connections of structure (XV) (R-H) differs from a corresponding spectrum of connections of structure (XVI) (R-CH3) [41].

XIII XIV XV

Similarly, aminoform 5-AT, apparently, it will be coordinated to his{its} infra-red spectrum [41], [42], and the

data of x-ray crystallography will be coordinated to structure 2-methyl-5-aminotetrazole [43].

XVI XVII XVIII XIX

Data on a question Aminoimine dynamic isomerism 5-aminotetrazol are not numerous and inconsistent. Марфи and Пиккард have shown [41], that 5-AT in a crystal kind exists in aminoform, but in ИК a spectrum of a crystal strips and imino-form are displaid{developed}. By means of comparison ИК of a spectrum 5-AT before deuteration the structure of a crystal product as amino amino-substituted [44] is proved. In work of [45] researches of monohydrate 5-AT were carried out{spent} by method КР of spectroscopy. Authors believe, that recrystallized from water 5-AT exists mainly in aminoform, and dilution of a solution favours iminoform. In opinion of authors of this work, in solutions 5-AT aminoimine equilibrium has no place.

Researches Aminoimine dynamic isomerism 5-AT in solutions of dipolar aprotic solvents in the literature are absent.

The decision of a question on primary existence 5-AT in amino-or iminoform in a solution dimetilacetamide (ДМАА) will help finding-out of the schema{circuit} of interaction 5-AT with dihloranhydrides dicarboxylic acids (ДХА ДКК) with conditions of the low-temperature polyfunctional condensation, considered by us for the first time [11] – [20].

Therefore with the purpose of studying Aminoimine dynamic isomerism have been removed{have been taken off} spectrums of NMR 1H 5-AT in solution ДМАА. For comparison the spectrum in a solution of dimethyl formamide (dimethylformamide) is removed{taken off} also.

The spectrum of NMR 1H a solution 5-AT in ДМАА environment has single peak with the center at δ =6.69 м.д., which can be attributed{related} to a resonance of a proton миногруппы aromatic system, and at comparison of value of chemical shift of aniline (6.5 м.д.) [46] in system considered{examined} by us there is a shift aside weaker field on 0.19 м.д.

Comparison ИК of spectrums of solutions 5-AT in acetone, toluene, dimethylformamide, ДМАА in the field of 1640-1650 sm^{-1} (absorption the imino-group) has allowed to reveal law: the above polarity of solvent, the more equilibrium is moved aside imino-form [28], [29].

Signal with chemical shift δ =6.57 м.д. (the NMR 1H in dimethylformamide) can be attributed{related} a spectrum, similarly above described, to a resonance the imino-group in aromatic system.

At the same time we had been investigated infra-red spectrums crystal 5-AT and a solution 5-AT in ДМАА and in completely deuterized solvent. In ИК spectrums crystal 5-AT, removed{taken off} as suspension in liquid petrolatum and as the solid films prepared from solvents (CCl_4, toluene, acetone), in the field of 3500-3100 $^{sm-1}$ are observed three legible absorption bands of center{average;medium} intensity with maxima at 3420, 3363 and 3190 sm^{-1} which can be referred to the valent asymmetric and symmetric fluctuations of communications{connections} NH of amino group and to valence vibration of fragment NH тетразольного rings, accordingly. These references will well be coordinated to the data of work [47], in which calculations of frequencies and forms of normal fluctuations of tetrazole and his{its} derivants, including 5-AT have been lead{have been carried out;have been spent} ($_{\nu NH}$ 3470 and 3338; $_{\nu NH\ rings}$ of 3190 sm-1).

In spectrums of a solution 5-AT in ДМАА in the field of 3500-3100 sm^{-1} two absorption bands are displaid{developed}: center{average;medium} intensity with a maximum at 3320 sm^{-1} which can be referred to valence vibration $_{\nu NH}$ the imino-group [48], and the second strip at 3187 sm^{-1}, corresponding to fluctuation $_{\nu NH}$ a fragment тетразольного rings, and the form, intensity and position of last strip coincide with similar – crystal 5-AT.

As to area of 1550-1700 sm^{-1} in spectrums crystal 5-AT absorption bands with maxima are observed at 1672, 1648 and 1600 sm^{-1} which communications{connections} C=N the imino-group and to valence vibration of communication{connection} C=N тетразольного rings can be referred, accordingly, to валентно-straining fluctuations of amino group, and the intensive absorption band corresponding to a strip amide I ДМАА to compensate which appeared impossible. It speaks that in the field of strong absorption of solvent sensitivity of receivers of radiation of spectrophotometers is sharply depressed [49].

By consideration of area of 1100-1000 sm^{-1} in spectrums crystal 5-AT 1072 and 1050 sm^{-1} are easy to bleed three absorption bands with frequencies 1095. As have shown calculations [47] and as appears from work [50], **frequency with a maximum of 1072 sm^{-1} corresponds{meets} to valence vibration of a ring and straining – amino groups. Strips with a maximum at 1095 and 1050 sm^{-1} should be attributed{related} to straining fluctuations of communications{connections} N=N and C=N imino-form researched connection [36].**

In a spectrum of a solution 5-AT in ДМАА in this area two strips of center{average;medium} intensity with maxima are observed at 1056 and 1018 sm^{-1}. These strips correspond{meet} to strips with maxima

of 1095 and 1050 sm^{-1} in spectrums crystal 5-AT. It is possible to explain shift of frequencies influence of such strong polar solvent, as ДМАА. Similar shift of signals is observed and in spectrums of NMR 1H.

Thus, the lead{carried out;spent} consideration of infra-red spectrums allows to conclude, that in a crystalline state 5-AT exists in amino, in a solution mainly in iminoform, that will be coordinated and to the data of work [44]. At research of the phenomenon in a number of solvents ($_{CCl4}$, toluene, acetone, ДМАА, dimethylformamide) it is established, that the quantity{amount} иминотаутомера increases on a measure of propagation of electrical dipole moment of solvent.

Thus, **criteria imino-form are absence of strips of valence vibrations of amino group of 3430-3350 sm^{-1}, presence of absorption bands of strong intensity in the field of 1280-1250 and presence of one strip at 1144-1155 sm^{-1}. aminoform there correspond{meet} presence of an intensive strip of 1390-1340 sm^{-1}, absence of absorption in the field of 1280-1250 and two strips of high intensity of 1190-1158 sm^{-1} [40]. As have shown calculations [47] and as [50] strip with a maximum of 1072 sm^{-1} appears from work corresponds{meets} to valence vibration of a ring and straining fluctuation of amino group.**

In УФ a spectrum of a saturated solution 5-AT in dimethylformamide the maximum of absorption at 293-296 nanometers is referred to иминогруппе at квазиароматического rings [41].

Decoding of the peaks registered at influence of electronic impact [51], [52] allows to confirm аминоформу crystal 5-AT (table 1).

Table 1

The mass spectrum *5-amino-1H-1,2,3,4-tetrazol*

№ peak	Weight, м/е	Width	The area absolute	The area in %
1	2	3	4	5
1.	14.0	8	920	0.890
2.	15.0	9	1034	1.000
3.	16.0	27	2967	2.870
4.	17.0	25	2026	1.960
5.	18.0	11	1406	1.360
6.	26.0	30	2316	2.240
7.	27.0	73	23208	22.450
8.	28.0	53	2636	2.550
9.	28.0	71	53891	52.130
10.	28.0	79	103378	100.00
11.	29.0	73	13853	13.400
12.	30.0	53	4518	4.370
13.	32.0	62	4187	4.050
14.	41.0	40	2719	2.630
15.	42.0	72	4724	4.570
16.	43.0	4	558	0.540
17.	43.0	9	920	0.890
18.	57.0	119	43016	41.610
19.	85.0	129	21089	20.400

Schemas{Circuits} of disintegration under influence of electronic impact BATH (26, 29, 32) are submitted on fig. 1-3.

Fig. 1. The schema{circuit} of disintegration an encore – 3,3'-(5-amino-1,2,4-triazole-1-ил) methane (26)

Fig. 2. The schema{circuit} of disintegration an encore – 3,3'-(5-amino-1,2,4-triazole-1-ил) butane (29)

Fig. 3. The schema{circuit} of disintegration an encore – 3,3'-(5-amino-1,2,4-triazole-1-ил) octane (32)

1.3. An encore – 3,3'-(5-amino-1,2,4-triazole-1-ил) alkanes

Data about Aminoimine dynamic isomerism (BATH) are limited to work of the big collective of authors [52]. It is established, that acylate'-(5-amino-1,2,4-triazoleил) octane has an encore – 3,3 иминостроение. As the basis to this absence of absorption in ИК spectrums (removed{taken off} in a solution) loose amino group (3300-3400 cm^{-1}) has served at presence of a wide strip of associated groups NH (2600-3200 cm^{-1}). Besides in the field of 1630-1670 cm^{-1} there are two strips (or one intensive), which authors fall into connections C=N aminotautomer. Further result{bring} the new data obtained both physical and chemical, and theoretical methods with use of methods of quantum chemistry and molecular mechanics.

1.4. An encore (aminoazole-N-il) alkanes

Let's result all over again the detailed interpretation IR of spectrums BAT [25-33] described earlier [38], but insufficiently studied.

In the field of 3120-3460 sm^{-1} two well resolved{allowed} absorption bands of center{average;medium} intensity which fall into to symmetric and asymmetric valence vibrations of fragment NH of amino group are observed. Frequencies ножничных straining fluctuations $_{NH2}$.of group make 1580-1665 sm^{-1}, and wide absorption bands are in an interval of 650-900 sm^{-1}, frequency and which form are various depending on a degree of formation{education} of hydrogen bridges, are caused oscillating by straining fluctuations of amino group [17].

In a result on the basis of results ИК of spectroscopy it is possible to believe aminостроение BATH [25-33] in a crystal kind unsubstituted on N (1).

The result is confirmed with us and a method of weight – spectroscopy [51]. As there are no the peaks, allowing to assume disintegration imino-form, and the schema{circuit} of disintegration is characteristic for aminостроения it is one more acknowledgement{confirmation} aminостроения BATH in a crystal kind.

(5-aminотетразол-N-ил) alkanes (БАТЭТР) for the first time described by us [3] have an encore in the field of 3200-3400 sm^{-1} two well resolved{allowed} strips of center{average;medium} and strong intensity which can be identified as valence vibrations of amino groups. For straining fluctuations of amino group it is observable two areas of 1590-1650 sm^{-1} and 650-900 sm^{-1}. The strip in the field of 1650 sm^{-1} is easily identified. Its{her} intensity from center{average;medium} up to very strong. She{it} is not overlaped{bridged;blocked} by other strips, as тетразольное the ring starts to capture{absorb;imbibe;occlude} about 1604 sm^{-1} [53].

The amino group connected with тетразольным by a cycle, should have two strips of nonplanar fluctuations of communications{connections} C-N and NH (at a flat structure of molecules). First of them is about 700 sm^{-1}, the second approximately{low fidelity} in the same area, as nonplanar fluctuations of communication{connection} CH (1000-1200 sm^{-1}). In spectrums БАТЭТР in these areas there are strips of small and center{average;medium} intensity which have been referred to corresponding nonplanar fluctuations.

Thus, with help ИК of spectrums it is established, that БАТЭТР in a crystal kind are in aminoform. NMR 1H spectrums confirm with the form, an arrangement and splitting of signals this assumption [3].

ИК spectrums of complexes and salts on a basis aminoazoles and BATH [29] also have one absorption band of strong or very strong intensity which is referred by us to absorption of amino group [29].Таким in the image in the field of 1620-1680 sm^{-1}, set of physical and chemical methods specifies on aminoформу an encore (aminoazol-N-ил) alkanes and their derivativ [7] – [9] in a crystal kind. Presence of absorption bands in the field of 1280 – 1250 sm^{-1} and strips 1150см-1 at all БАЛ in a solution testifies about them iminoform.

It is possible to assume, that iminoform in a solution results in redistribution of electronic density of a molecule and thus reduction of fragrance of system, and, hence, increase of antifungal activity aminoazoles and their derivants.

2. NUCLEOPHILIC SUBSTITUTION aminoazoles ДИБРОМАЛКАНАМИ (2:1) IN N ENVIRONMENT; N' – DIMETHYL FORMAMIDE

Dependence of antifungal activity on a structure in a number{line}: aminoazolы – an encore (aminoazol-N-ил) alkanes –oligoamides with aminoazolами in a stem nucleus of a macromolecule, that is with increase in quantity{amount} aminoazoles fragments, it is not investigated.
With the purpose of reception of new connections with two cycles in a molecule it is possible with the greater, than the monoreplaced azoles activity, utilised as initial{starting} amino-1,2,4-triazoles and *5-amino-1H-1,2,3,4-тетразол*.
Alkylation aminoazoles dihaloalkans in the environment of dimethylformamide (2:1) is investigated insufficiently. Therefore for specification of the schema{circuit} of interaction, the factors influencing reaction rate and drawing up of model of alkylation on an example 4-ATP research of its{her} kinetics is lead{carried out;spent}.

2.1. Kinetics of alkylation 4-amino-1,2,4-triazol

1-brombutan and 1,2-dibromoethane in aqueous dimethyl formamide

In partition 1 are considered monoaminoazoles. To establish dependence of antifungal activity on a structure (quantities{amounts} aminoazoles fragments), are taken over{accepted;assumed} attempts to synthesize new connections with two cycles in a molecule.
Such connections on a basis aminoazoles, it is especial in the salt form, in the literature are not described.
For definition of a kind of the kinetic equation describing reaction, the method of initial velocities had been determined orders of reaction on each of reagents. Initial velocity was defined{determined} graphically on tangent of angle of lean of tangent to the kinetic curve of an expenditure of reagents during the initial moment of time. At a variation of numerical values of initial concentration the linear relation of the logarithm of speeds from logarithmic function of initial concentration with tangent of angle close to unit was observed. The first order{sequence} on each of reagents is observed, to what calculations of a kinetic constant on the kinetic second-order equation which conserve{store;preserve} the constancy within the limits of an experimental error up to 70-80 % of transformation testify.
In table 2 results of calculation of values of a second-order kinetic constant are submitted at different molar parities{ratio} of reagents (100°C). On fig. 4 kinetic curves of accumulation of a bromide – ion are given{reduced} during alkylation 4-ATP 1-brombutan in dimethylformamide at 100°C.

Fig. 4. Kinetic curves of accumulation of a bromide – ion in reaction of alkylation 4-amino-1,2,4-triazol 1-brombutan. With – concentration (мг·мл-1), t – time (mines). Concentration 4-АТ (моль·л$^{-1}$): 1-0,52,2-0,54,3-0,49. Concentration 1-brominebutane (моль·л-1): 1-0,49,2-0,78, 3-1,32.

So, dependences of a second-order kinetic constant of reaction on temperature have been designed under the Arrhenius equation and Эйринга активационные parameters which are given{reduced} in table 3.

Table 2

Second-order kinetic constants of reaction of alkylation 4-amino-1,2,4-triazol 1-brombutan

№ hall marks	Concentration of a bromide-ion				Concentration of a bromide-ion				Concentration of a bromide-ion			
	т, сек	C^1	C^2	$k\cdot10^2$	t, сек	C^1	C^2	$k\cdot10^2$	т, сек	C^1	C^2	$k\cdot10^2$
	Сат=0.52 a mole / ½, Сб=0.49 a mole / ½				Сат=0.54 a mole / ½, Сб=0.78 a mole / ½				Сат=0.49 a mole / ½, Сб=1.32 a mole / ½			
1	2	3	4	5	6	7	8	9	10	11	12	13
1	0	0	0		0	0	0		0	0	0	
2	10	11.56	0.144	8.13	10	16.77	0.211	7.98	10	22.59	0.282	7.34
3	20	18.11	0.226	8.27	20	24.90	0.311	8.02	20	31.14	0.389	7.19
4	30	21.85	0.273	8.02	30	29.06	0.361	7.68	30	35.50	0.443	7.36
5	40	24.06	0.305	7.50	40	32.13	0.403	7.73	40	38.05	0.475	7.94
6	50	26.37	0.329	7.74	50	34.10	0.421	7.69	50	38.60	0.482	7.22

7	60	28.22	0.352	7.98	60	36.00	0.454	8.19	60	39.40	0.492	7.76
8	70	29.34	0.336	7.86	70	37.02	0.463	8.22	70	39.60	0.495	7.36
9	80	30.52	0.381	8.02	80	37.60	0.471	8.03	-	-	-	-
1	2	3	4	5	6	7	8	9	10	11	12	13
10	90	31.64	0.395	8.35	90	38.00	0.475	7.76	-	-	-	-
	Kcp	-	-	7.98	-	-	-	7.92	-	-	-	7.45
2	10	19.36	0.242	7.69	10	17.41	0.217	8.46	10	20.11	0.251	8.18
3	20	27.97	0.350	7.73	20	24.90	0.311	8.02	20	27.35	0.341	7.32
4	30	31.87	0.398	7.23	30	28.64	0.357	7.36	30	32.21	0.402	7.47
5	40	35.06	0.437	7.52	40	32.01	0.400	7.63	40	35,50	0.443	7.99
6	50	36.87	0.460	7.70	50	34.06	0.425	7.59	50	37.06	0.462	7.87
7	60	38.12	0.475	8.03	60	35.60	0.445	7.75	60	38.43	0.479	7.58
8	70	38.51	0.479	7.89	70	36.31	0.454	7.36	70	38.84	0.484	7.51
9	80	38.82	0.482	7.15	80	37.30	0.466	7.58	80	39.10	0.488	7.80
10	90	39.24	0.489	7.63	90	38.02	0.475	7.76	90	39.32	0.491	7.54
11	100	39.60	0.495	7.84	100	38.51	0.481	7.87	100	39.50	0.493	7.40
	Kcp	-	-	7.64	-	-	-	7.74	-	-	-	7.67

Table 3

Активационные parameters of reaction of alkylation 4-amino-1,2,4-triazol 1-brombutan

t, °C t, °C t, °C $\Delta E_{акт}$ Дж·моль-1 LgA $\Delta H°_{обр}$. Дж·моль-1 ΔS ° Дж·моль-1

Parameters	t,°C	t,°C	t,°C	$\Delta E_{акт}$ Дж·моль$^{-1}$	Lg A	$\Delta H°_{обр.}$ Дж·моль$^{-1}$	$\Delta S°$ Дж·моль$^{-1}$
Temperature	80	90	100	-	-	-	-
k, л / (a mole · сек) $\cdot 10^2$	1.92	3.36	7.62	72.08	5.69	67.84	-146.3

Thus, the first order{sequence} of researched reaction on each of reagents and the general{common} second order{sequence} and as high negative value of entropy of activation testify to passing reaction of alkylation on the mechanism of dimolecular nucleophilic substitution.

Improvement of a technique of kinetic experiment has shown essential lacks of use of dimethyl formamide which are caused by low solubility of products of alkylation in clear solvent and impossibility of carrying out of reaction in homogeneous conditions at fixed concentration of salt during all experiment.

It is established, that the optimal on physical and chemical properties is composition of solvent of dimethylformamide: H_2O in a volumetric parity{ratio} 4:1 in which solubility of reagents is high enough, reaction proceeds{runs} in homogeneous conditions in a wide interval of concentration of reactants and during experiment of time acceptable to carrying out.

Research of influence of this composition of solvent on passing of reaction of alkylation has shown, that increase in a volumetric parity{ratio} of dimethylformamide: H_2O results in some increase in speed. In table 2 and 4 value of a kinetic constant of alkylation 4-ATP in a mix of dimethylformamide is given{reduced}: water (4:1) at 100°C.

Table 4

Specific reaction rates of alkylation 4-amino-1,2,4-triazol in a mix of dimethylformamide: water (4:1) at 100°C

№ about	Concentration of a bromide-ion				№ about	Concentration of a bromide-ion			
	τ, сек	C^1	C^2	$k \cdot 10^2$		τ, сек	C^1	C^2	$k \cdot 10^2$
	Сат.0.58 a mole/l, Сб=0.56 A mole/l					Сат.58 a mole/l, Сб=0.56 A mole/l			
1	2	3	4	5	6	7	8	9	10
1	8	11.18	0.139	9.67	8	36	25.06	0.313	9.28
2	12	14.08	0.176	9.03	9	40	25.92	0.324	9.16
3	16	16.54	0.208	8.87	10	44	26.80	0.335	9.19
4	20	19.04	0.238	9.05	11	48	27.68	0.346	9.32
5	24	20.70	0.258	8.91	12	60	29.50	0.368	9.32
6	28	22.54	0.281	9.19					
7	32	23.94	0.299	9.28	kcp				9.19

Use of aqueous dimethylformamide and high temperatures insignificantly complicated reaction of alkylation by an opportunity of passing of hydrolysis 1-brominebutane. Hydrolysis 1-brominebutane considerably affected at high molar parities{ratio}; the alkylating agent: 4-ATP at degrees of transformation more than 60 %, therefore in water- dimethyl formamide a solution carried out{spent} reaction up to 50-60 % of a degree of transformation.
In simulated condition kinetic curves of accumulation of a bromide – ion have been received{obtained} at alkylation 4-ATP by 1,2-dibromoethane. Proceeding from earlier received{obtained} data, the general{common} kinetic process flow diagram of alkylation 4-ATP 1,2-dibromoethane can be presented as system of series-parallel second-order reactions (A), (B), thus it is necessary to include collateral reaction in the schema{circuit} of formation{education} of a bromide – ion (C).

$$BrCH_2CHBr + H_2O \xrightarrow{k_0} Br + \text{hydrolysates} \qquad (C)$$

As received{obtained} experimental data included only kinetic curves of accumulation of a finished product – a bromide – ion for calculation of constants of speeds of separate stages k_1 and k_2 it was necessary to use mathematical methods of processing of results for system of two series-parallel reactions. In this connection we had been lead{had been carried out;had been spent} the analysis of mathematical methods and schemas{circuits} of calculation of systems of series-parallel reactions.
The mathematical analysis of system n the linear – independent differential equations for the typical schema{circuit} of series-parallel process is considered earlier. The decision of system of the differential equations demands introduction of the dimensionless variables which results in complex{difficult} enough mathematical expression of dependence of a second-order kinetic constant from concentration of initial{starting} reagents and time.
In work [57] mathematical methods of the analysis of experimental kinetic constants of second-order speeds of two series-parallel reactions given for calculation are considered. The schema{circuit} of the chemical equations of series-parallel process and the equations of speeds is described by the following equations:

$$A + B \xrightarrow{k_1} C$$

$$A + B \xrightarrow{k_2} C$$

KINETIC CONSTANTS k_1 and k_2 can be calculated from the experimental kinetic data under the following formulas:

Where *and*, *b* – initial концентарции initial{starting} reagents (моль·л-1),
Õ – the current concentration of reagent And (моль·л-1)
Thus, precomputation is necessary for a method of numerical differentiation from experimental kinetic curves corresponding integral ξi differential, a numerical or graphic method. Routinely even slight errors in definition of these sizes, in particular differential , result in the big mistakes in definition of constants of speeds.
The method of graphic integration can be utilised at stoichiometric relationships of reagents. Series-parallel process in the schema{circuit} of graphic integration is described by the following set of equations [58]:

Variable

Variable.

Values of constants of speeds of separate stages k_1 and k_2 can be calculated on the equations:

Where
Routinely values of the corresponding integrals which are included in the equation, are defined{determined} by a method of graphic integration.
Methods of numerical differentiation and graphic integration in work [60] have been a little bit modified. By authors at carrying out of the mathematical analysis of kinetic curves of accumulation of a chloride – ion for process of alkylation of dimethylhydrazine by 1,2-ethylene dichloride it has been shown, that experimental data well апроксимируются powermode function of a kind, where *and* and *b* – constant{stationary} [54,55].
Using a parity{ratio}, authors of calculations of differentials and the integrals which are included in the equations, apply the following analytical expressions:

The analysis of system of the differential equations describing kinetics of series-parallel reactions:

Has shown, that the system has the exact decision only at fixed discrete values $k_1 : k_2 = 2,3,4, \ldots$
By these authors it has been established, that the attitude{relation} of times of passing of reaction up to two fixed degrees of transformation depends only from k_1 / k_2.
The kinetic constant k_1 is unequivocally connected to auxiliary size t the following equation:

Where $_{In}$ – initial concentration of substance In; $k = k_2 / k_1$; $b = [In] / _{[In]}$.
Frost and Shwemer have theoretically calculated [59] sizes of the attitude{relation} of times for values k_1 / k_2 in an interval from 2 up to 0, and also sizes t.
Mathematical обрабтка results of kinetic experiments it has been lead{it has been carried out;it has been spent} on IBM-PC-486 DX4-120 with use of the programs written by us for a method of numerical differentiation and a method of graphic integration.
The set of experimental data as kinetic curves has been received{obtained} with a fixed error, therefore at mathematical processing experimental results have lead{have carried out;have spent} апроксимирующую the curve which smooths possible{probable} exhausts due to an error of experiment. For this purpose least square method (МНК) which is based on construction approximating function y (x) of a condition of a minimum of size Q – the sums of squares of deviations{rejections} utilised

In our case апроксимацию experimental kinetic dependence it was manufactured{made} by a powermode polynom which allows to calculate easily the first and the second derivativ analyzed function in any point of the curve.
We also utilis the program of calculation of constants of second-order speeds by a method of numerical integration of system of the differential equations describing the kinetic schema{circuit} of alkylation 4-ATP by 1,2-dibromoethane (A), (B), (C). In a basis of the program the condition is necessary, that the integral from the experimental kinetic curve of accumulation of a bromide – ion within the limits of integration from 0 up to t is function of two variables ($_{k1}$ and $_{k2}$).

In this connection the algorithm of calculation has consisten in the following: the program calculated the integrated area under the experimental kinetic curve of accumulation of a bromide – ion, expected a file of values of sizes $_{It}$ a method of numerical integration of system of the differential equations at various values $_{k1}$ and $_{k2}$ and defined{determined} value $_{k1}$ and $_{k2}$ which in the best way describe kinetics of accumulation of a bromide – ion. For criterion of an estimation the size of the sum of standard deviation of settlement and experimental values C_i (Óáßþ) was accepted. And $_{Ci}$ (Ýß»)..
On fig. 5 kinetic curves of an expenditure initial{starting} (1,2), accumulation of a bromide – ion (3), the intermediate (4) products designed by a method of numerical integration in comparison with the experimental curve of accumulation of a bromide – ion are shown.

Fig. 5. Kinetic curves of an expenditure initial{starting}, intermediate and termination products and accumulation of a bromide – ion (initial Concentration calculation) Cam=0.56 a mole / ½-1, Cэб=0.27.

In table 5 results of calculations of constants of speeds $_{k1}$ and $_{k2}$ for reaction of alkylation 4-amino-1,2,4-triazol, the different mathematical schemas{circuits} executed with the help are given{reduced}. Results of calculations of constants of speeds $_{k1}$ and $_{k2}$ are received{obtained} as average value at calculation of 5-6 kinetic curves which have been removed{which have been taken off} at a various molar parity{ratio} amine / alkylating the agent.
Sufficient convergence of the experimental and settlement data testifies to correctness of the chosen kinetic schema{circuit} of reaction of alkylation 4-amino-1,2,4-azimide 1,2-dibromoethane. Mathematical processing is lead{carried out;spent} for constants of speeds at different temperatures and received{obtained} values utilised for calculation активационных parameters (table 5, 7).

Table 5

Constants of speeds k1 and k2 alkylations 4-amino-1,2,4-azimide 1,2-dibromoethane

Design techniques of constants of speeds	TEMPERATURE 343 K	
	k1, моль/ (л·сек) ·102	k2 моль/ (л·сек)· 102
Numerical differentiation	2.75±0.30	2.60±0.35
Graphic integration	3.04±0.24	2.87±0.37
Attitudes{Relations} of time	2.68±0.37	2.65±0.28
Numerical integration	2.96±0.18	2.72±0.32

Table 6

Constants of speeds of the first and second stages Alkylations 4-amino-1,2,4-azimide 1,2-dibromoethane (a method of numerical integration)

Temperature, To	T=343		T=353		T=363		T=373	
k, a mole /l·sec ·10^2	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2
	0.50± 0.01	0.39+ 0.01	0.97± 0.07	0.83± 0.08	1.81± 0.25	1.50± 0.19	2.96± 0.18	2.72± 0.32

Table 7

Активационные parameters of reaction 4-amino-1,2,4-triazol with 1,2-dibromoethane in Aqueous dimethyl formamide

Activations parameters	1-n a stage	2-n a stage
ΔЕакт, кДж/моль	63.3	68.6

LgA	5.65	6.26
$\Delta H°_{обр}$, кДж/моль	57.1	62.4
$\Delta S^{\neq}$, Дж/(моль·К)	-148.7	-135.1

Thus, kinetic parameters of interaction 4-amino-1,2,4-triazol with have allowed to establish as the general{common} criteria, characteristic for SN2-reactions, and distinction in reactivity 1-brominebutane and 1,2-dibromoethane:
- нуклеофил participates in a stage determining reaction rate which is described under the kinetic second-order law,
- активационные parameters of interaction are characterized by high negative values of entropy of activation which testify to significant dimensional requirements to transitive активационному to a complex and the steric difficulties connected to his{its} formation{education};
- Electrophilic substituents, in general, accelerate SN2-reactions [61] a little, therefore it was possible to expect, that the kinetic constant of the first stage of alkylation 4-ATP 1,2-dibromoethane will be more second-order kinetic constants of reaction 4-ATP with 1-brombutan whereas experimental data have shown a revertive parity{ratio} of constants of speeds;
- The similar parity{ratio} could be assumed and for value of constants of speeds of the first and second stages of reaction of alkylation 4-ATP 1,2-dibromoethane as cation 4-ATP is more electrophilic substituent, than atom of bromine, however, we receive{obtain} revertive results.
Use of this principle allows to assume, that the structure of a transient state of researched reaction is closer to structure of termination products and, hence, has character of an ion карбония.

2.2.1. Alkylation 4-amino-1,2,4-azimide

Alkylation – a simple path of synthesis моно-and дизамещенных tetrazoles of a various structure which reception by other methods frequently appears impossible. In the theoretical attitude{relation} this reaction represents the big interest as can serve as convenient model at studying the heterocyclic substrates having dual reactivity [1].
Data on synthesis биспроизводных 4-ATP are small and are limited to work [62] in which the gross – formulas corresponding to products of alkylation 4-amino-of 1,2,4-azimide by 1,3-dibromopropane and 1,4-дибrombutan are resulted, however is not resulted a concrete technique of synthesis and constitutional formulas of received{obtained} substances, and identical melting point of these two individual connections does not allow to count their identification safety. As at alkylation of 1,2,4-azimide probably reception of two isomers: N (1) and N (4) with prevalence N (1) isomers, excretion of a main product from a reaction mixture is enough a laborious problem{task} [63], [64]. Reaction of alkylation 4-ATP passes региоселективно and at the subsequent deamination (1) replaced 1,2,4-azimides [63] – [65] are received{obtained} with high yield N.
At alkylation 4-amino-3,5-R-1,2,4-triazoles sixfold surplus of 1,2-dibromoethane with the subsequent deamination четвертичной salts authors [66] receive{obtain} 1-хлорэтил-1,2,4-azimides with a yield of 59-65 %.
As reaction четвертичного alkylations of derivants 4-ATP is investigated basically by the example of monoalkylation, was of interest to consider interaction 4-ATP with дигалогензамещенными connections that would expand synthetic opportunities. Besides reception an encore – 1,1'-(4-amino-1,2,4-triazoleио) alkanes in the salt form allowed to hope for amplification{strengthening} of their activity as fungicides.
Interaction 4-ATP with дибромалканами at 80-90°C us for the first time receives{obtains} bromides an encore – 1,1'-(4-amino-1,2,4-triazoleио) alkanes [5].