2514 *Russian Chemical Bulletin, International Edition, Vol. 64, No. 10, pp. 2514—2516, October, 2015*

Enthalpies of the Diels—Alder reactions of a series of dienes with tetracyanoethylene and 4-phenyl-1,2,4-triazoline-3,5-dione

V. D. Kiselev,[a]* E. A. Kashaeva,[a] L. N. Potapova,[a] D. A. Kornilov,[a] and A. I. Konovalov[b]

[a]A. M. Butlerov Chemical Institute, Kazan (Volga Region) Federal University,
18 ul. Kremlevskaya, 420008 Kazan, Russian Federation.
Fax: +7 (843) 292 7278. E-mail: vkiselev.ksu@gmail.com
[b]A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Scientific Center of the Russian Academy of Sciences,
8 ul. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843) 273 1872

The enthalpies of the Diels—Alder reactions of twenty dienes with two active dienophiles, tetracyanoethylene and 4-phenyl-1,2,4-triazoline-3,5-dione, are compared, and the corresponding relationship between them was obtained. The values of enthalpies of very slow and/or equilibrium reactions were calculated from the obtained relationship. These data obtained make it possible to optimize the conditions for such reactions.

Key words: Diels—Alder reaction, enthalpy of reaction, tetracyanoethylene, 4-phenyl-1,2,4-triazoline-3,5-dione.

The values of enthalpies of reactions in solution can be used for planning experimental conditions and, in some cases, for explaining an unusual kinetic behavior. For example, it was shown[1,2] for many reactions of [4+2] cycloaddition of the "diene-donor, dienophile-acceptor" type involving C=C bonds that the rate of the process can be predicted taking into account three main parameters:

— energies of frontier orbitals of diene and dienophile;

— balance of energies of bond dissociation and formation;

— changes in the coefficients of orbital overlapping mainly determined by the difference in the distance between the reacting atoms C(1)—C(4) in diene (R_{1-4}).

When the three factors were taken into account, the following empirical relationship was found[1,2] for the whole set of reactions (correlation coefficient $r = 0.972$, number of reactions $n = 92$):

$$\log k_2 = -28.81 + 316.3/(IP_D - E_A) - 69.9R_{1-4}/(IP_D - E_A) - 0.054\Delta H_{r-n}, \quad (1)$$

where k_2 is expressed in L mol^{-1} s^{-1}, IP_D is the ionization potential of diene (eV), E_A is the energy of electron affinity of the dienophile (eV), R_{1-4} is the distance between the atoms C(1) and C(4) (Å), and ΔH_{r-n} is the enthalpy of the reaction (kJ mol^{-1}). It was noted[1,2] that the influence of the difference in enthalpies of the reactions on their rate is comparable with the contribution of the change in the overlapping coefficients of the reacting orbitals of the reactants and that each contribution is halved over the contribution of differences to the value of $(IP_D - E_A)^{-1}$. The data obtained make it possible to explain reasons for the manifestation of the usual and "anomalous" relationship between the reactivity and selectivity and diversity in the ratio of kinetic activity and thermodynamic stability. This, in turn, makes it possible to purposefully choose reagents for the preparation of necessary products, especially in competitive processes, and to predict rates of yet unstudied Diels—Alder reactions with normal electron requirements. Many works[3,4] were devoted to the study of the influence of the balance of energies of bond dissociation and formation on the reaction rates. It should be emphasized that this balance of energies, which is manifested quantitatively as a reaction enthalpy, does not always determine the order of changing the reaction rate in a series of reactants but always affects the rates of these reactions.[3] Note that the enthalpy of the reaction in solution reflects both the balance of bond dissociation and formation energies as well as possible differences in solvation and structural strain of the addends. For a known entropy of the process, the equilibrium constants can be estimated and the reaction conditions can be planned. However, for slow and/or equilibrium cycloaddition reactions, it is difficult or even impossible to determine the enthalpy of the reaction by calorimetry with a sufficient accuracy.

Considering two pairs of reactions of dienophiles (A_1, A_2) with dienes (D_1) and (D_2), we assumed that the difference in enthalpies of reactions of two dienophiles with a common diene is mainly determined by the difference in energies of the reacting bonds of the dienophiles

$$\Delta H_{r-n}(D_1 + A_1) - \Delta H_{r-n}(D_1 + A_2) = K_1[\Delta H_{r-n}(D_2 + A_1) - \Delta H_{r-n}(D_2 + A_2)]. \quad (2)$$

Correspondingly, for the pairs of reactions of two dienes with a common dienophile, it should be expected that the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2514—2516, October, 2015.

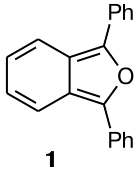
difference in enthalpies of these reactions would mainly be determined by the difference in energies of the reacting bonds of the dienes

$$\Delta H_{r-n}(D_1 + A_1) - \Delta H_{r-n}(D_2 + A_1) = \\ = K_2[\Delta H_{r-n}(D_1 + A_2) - \Delta H_{r-n}(D_2 + A_2)]. \quad (3)$$

It can be expected that the proportionality coefficients K_1 and K_2 would be close to unity. This makes it possible to calculate the enthalpy of a reaction difficult for measuring, for example, $\Delta H_{r-n}(D_1 + A_1)$, from the data obtained for three reactions convenient for measurements.

We considered the relationship between the enthalpies of the Diels—Alder reactions in solutions of twenty dienes (**1—20**) with two active dienophiles, tetracyanoethylene (**21**) and 4-phenyl-1,2,4-triazoline-3,5-dione (**22**).

The enthalpies of reactions **17** + **21**, **17** + **22**, and **18** + **22** obtained in this work and literature data are presented in Table 1.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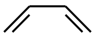
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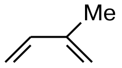
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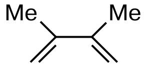
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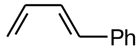
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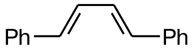
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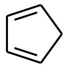
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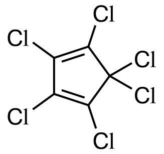
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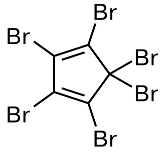
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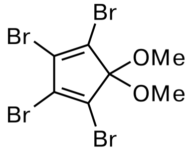
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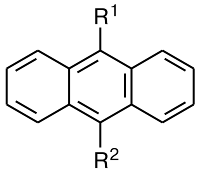
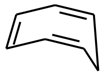

11—16

$R^1 = R^2 = H$ (**11**); $R^1 = H$, $R^2 = Cl$ (**12**), Me (**13**), OMe (**14**); $R^1 = R^2 = Me$ (**15**), OMe (**16**)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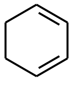
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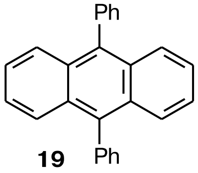
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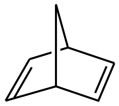
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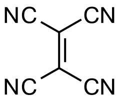
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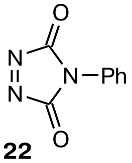
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Table 1. Enthalpies of the Diels—Alder reactions of dienes **1—20** with dienophiles **21** and **22** in solution at 25 °C

Diene	21		22	
	$-\Delta H^{21}_{r-n}$ /kJ mol^{-1}	Reference	$-\Delta H^{22}_{r-n}$ /kJ mol^{-1}	Reference
2,5-Diphenylisobenzofuran (**1**)	69[a]	5	104[b]	6
Buta-1,3-diene (**2**)	154[c]	6	201[b]	6
2-Methylbuta-1,3-diene (**3**)	166[c]	7	217[b]	6
2,3-Dimethylbuta-1,3-diene (**4**)	176[c]	8	218[b]	6
trans-1-Phenylbuta-1,3-diene (**5**)	142[c]	6	186[b]	6
trans,*trans*-1,4-Diphenylbuta-1,3-diene (**6**)	97[c]	6	142[b]	6
Cyclopentadiene (**7**)	113[c]	8	134[b]	10
Hexachlorocyclopentadiene (**8**)	47[c,d]	—	77[b]	11
Hexabromocyclopentadiene (**9**)	35[c,d]	—	64[b]	11
5,5-Dimethoxytetrabromocyclopentadiene (**10**)	65[c]	6	97[b]	11
Anthracene (**11**)	77[a]	9	105[a]	6
9-Chloroanthracene (**12**)	66[a]	9	101[a]	6
9-Methylanthracene (**13**)	85[a]	9	109[a]	6
9-Methoxyanthracene (**14**)	61[e]	9	101[a]	6
9,10-Dimethylanthracene (**15**)	88[a]	9	118[a]	6
9,10-Dimethoxyanthracene (**16**)	52[e]	9	92[a]	6
Cyclohepta-1,3,5-triene (**17**)	90[a,f]	—	110[f,g]	—
Cyclohexa-1,3-diene (**18**)	130[c]	8	160[f,g]	—
9,10-Diphenylanthracene (**19**)	23[d,g]	—	50[g]	12
Norbornadiene (**20**)	174[a,d]	–	218[g]	10

Note. [a] Solvent 1,2-dichloroethane. [b] Solvent benzene. [c] Solvent dichloromethane. [d] The enthalpies of the reactions were calculated from Eq. (4). [e] Solvent 1,4-dioxane. [f] Data of the present work. [g] Solvent toluene.

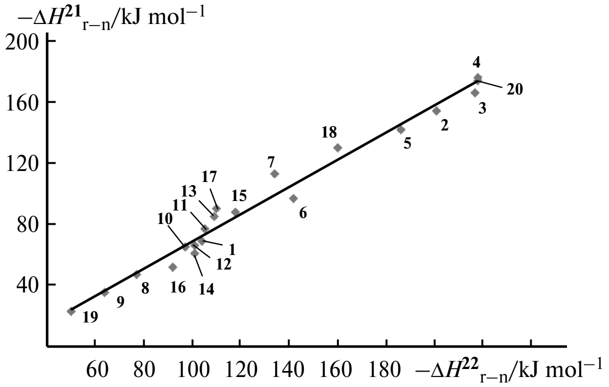

Fig. 1. Relationship between the enthalpies of the Diels—Alder reactions of dienes **1—20** with compounds **21** and **22**.

The comparison of the experimental values of enthalpies of the Diels—Alder reactions of dienes **1—20** with dienophiles **21** and **22** (Fig. 1) confirms that Eqs (2) and (3) are fulfilled

$$\Delta H^{21}{}_{r-n} = (20\pm4) + 0.887\Delta H^{22}{}_{r-n}. \qquad (4)$$

For Eq. (4), $r = 0.9896$, $SD = 6.9$, and $n = 16$.

The obtained Eq. (4) allowed us to calculate the enthalpies of reactions **8** + **21**, **9** + **21**, **19** + **21**, and **20** + **21** equal to –47, –35, –23, and –174 kJ mol^{-1}, respectively. It is difficult to measure the enthalpy of reaction **20** + **21** because of its very low rate.[10] If the entropy of Diels—Alder reaction is accepted to be –140 J mol^{-1} K^{-1} (see Refs 2 and 13), the calculated equilibrium constant for reactions **8** + **21**, **9** + **21**, and **19** + **21** at 25 °C are 8.5, $7 \cdot 10^{-2}$, and $5 \cdot 10^{-4}$ L mol^{-1}, respectively. These data clearly show that attempts to carry out slow and equilibrium processes **8** + **21**, **9** + **21**, and **19** + **21** at elevated temperatures will be unsuccessful. They can be carried out only under conditions of high hydrostatic pressure when the rate and equilibrium constant increase significantly.[14] For reaction **20** + **21**, the high value of the equilibrium constant (higher than $1 \cdot 10^{23}$ L mol^{-1}) allows it to occur at elevated temperatures.

Thus, the high reactivity of compound **22** and the enhanced exothermicity of its Diels—Alder reactions with dienes make it possible to calculate the enthalpies of slow and/or equilibrium reactions with compound **21** and to choose optimum conditions for them.

Experimental

Commercial reagents (Sigma-Aldrich) were used. Prior to use, dienes **17** and **18** were distilled, and dienophiles **21** and **22** were purified by sublimation (100 °C, 100 Pa). Solvents were purified using known methods.[15] The order of measuring the heat effects was described earlier.[16] In reaction **17** + **21**, a weighed sample (30—50 mg) of sublimed tetracyanoethylene was added to a solution of cycloheptatriene in 1,2-dichloroethane (150 mL) placed in the Dewar flask of a differential calorimeter. The enthalpy of the reaction in solution was calculated taking into account the heat of dissolution of **21** (21.3 kJ mol^{-1}). The following values were obtained: –91.5, –89.4, –91.0, –89.0, –90.0, and –90.2 kJ mol^{-1}. The average value of the enthalpy of reaction **17** + **21** is –90.2±0.7 kJ mol^{-1}. The following values were obtained for the reaction of diene **17** with compound **22** in toluene (the heat of dissolution of **22** is 18.3 kJ mol^{-1}): –110.2, –110.4, –110.9, and –109.2 kJ mol^{-1}. The average value of the enthalpy of reaction **17** + **22** is –110.2±0.2 kJ mol^{-1}. The following values were obtained for reaction **18** + **22** in toluene: –158.5, –158.1, –162.5, –160.2, and –159.3 kJ mol^{-1}. The average value of the enthalpy of reaction **18** + **22** is –159.7±1.3 kJ mol^{-1}.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 12-03-00029a).

References

1. V. D. Kiselev, I. I. Shakirova, A. I. Konovalov, *Russ. Chem. Bull.* (*Int. Ed.*), 2013, **63**, 290 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2013, 290].
2. V. D. Kiselev, A. I. Konovalov, *J. Phys. Org. Chem.*, 2009, **22**, 466.
3. N. N. Semenov, *O nekotorykh problemakh khimicheskoi kinetiki i reaktsionnoi sposobnosti* [*On Some Problems of Chemical Kinetics and Reactivity*], Izd-vo AN SSSR, Moscow, 1958, 686 pp. (in Russian).
4. G. S. Hammond, *J. Am. Chem. Soc.*, 1955, **77**, 334.
5. V. D. Kiselev, A. N. Ustyugov, I. P. Breus, A. I. Konovalov, *Dokl. Akad. Nauk SSSR*, 1977, **234**, 1089 (in Russian).
6. V. D. Kiselev, A. I. Konovalov, *Zh. Org. Khim.*, 1986, **22**, 1133 [*J. Org. Chem. USSR*, 1986, **22**].
7. F. E. Rogers, *J. Phys. Chem.*, 1971, **75**, 1734.
8. F. E. Rogers, *J. Phys. Chem.*, 1972, **76**, 106.
9. V. D. Kiselev, A. I. Konovalov, E. A. Veisman, A. N. Ustyugov, *Zh. Org. Khim.*, 1978, **14**, 128 [*J. Org. Chem. USSR*, 1978, **14**].
10. V. D. Kiselev, I. I. Shakirova, D. A. Kornilov, H. A. Kashaeva, L. N. Potapova, A. I. Konovalov, *J. Phys. Org. Chem.*, 2013, **26**, 47.
11. A. M. Mustafaev, N. R. Adigezalov, V. D. Kiselev, A. I. Konovalov, M. M. Guseinov, *Zh. Org. Khim.*, 1980, **16**, 2549 [*J. Org. Chem. USSR*, 1980, **16**].
12. V. D. Kiselev, D. A. Kornilov, E. A. Kashaeva, L. N. Potapova, D. B. Krivolapov, I. A. Litvinov, A. I. Konovalov, *Zh. Fiz. Khim.*, 2014, **88**, 1914 [*Russ. J. Rhys. Chem.* (*Engl. Transl.*), 2014, **88**].
13. A. Mielert, C. Braig, J. Sauer, J. Martelli, R. Sustmann, *Liebigs Ann. Chem.*, 1980, **1980**, 954.
14. F. Wurche, F.-G. Klärner, in *High Pressure Chemistry*, Eds R. van Eldik and F.-G. Klärner, Wiley-VCH, Weinheim, 2002, 458 pp.
15. J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvents*, John Wiley, New York—Chichester—Brisbane—Toronto—Singapore, 1986, 1325 pp.
16. V. D. Kiselev, E. A. Kashaeva, N. A. Luzanova, A. I. Konovalov, *Thermochim. Acta*, 1997, **303**, 225.

Received November 27, 2014;
in revised form April 7, 2015