Diels—Alder reaction between naphthalene and *N*-phenylmaleimide under mild conditions

V. D. Kiselev,* E. A. Kashaeva, L. N. Potapova, and G. G. Iskhakova

A. M. Butlerov Research Chemical Institute, Kazan State University,
18 ul. Kremlevskaya, 420008 Kazan, Russian Federation.
Fax: +7 (843 2) 38 7278. E-mail: vladimir.kiselev@ksu.ru

The rate and equilibrium constants for the Diels—Alder reactions between benzene or naphthalene and several dienophiles at 25 °C were calculated from the data on the ionization potentials of dienes and electron affinity energies of dienophiles, as well as the reaction enthalpies. The highest yield of the adduct was predicted for the reaction of naphthalene with *N*-phenylmaleimide. However, the time of its formation in 50% yield exceeds 30 years. The use of gallium chloride as a catalyst affords the *endo*-adduct for seven days at room temperature in 30% yield. The rate ($(2\pm0.5)\cdot10^{-6}$ L mol^{-1} s^{-1}) and equilibrium constants (5 ± 2 L mol^{-1}) of the reaction were determined.

Key words: naphthalene, *N*-phenylmaleimide, Diels—Alder reaction, kinetics, catalysis.

Many dienes, including substituted benzenes and naphthalenes, are known[1] to form molecular complexes of the π,π-type due to the interaction of the highest occupied π-orbital of a diene-donor with the lowest unoccupied π-orbital of a dienophile-acceptor. Numerous examples show that the introduction of donating substituents enhances the stability of π,π-complexes and increases the rate of the Diels—Alder reaction of dienes.[2—4]

Benzene does not react with dienophiles in the Diels—Alder reaction because of the high conjugation energy. Only UV irradiation in the presence of maleic anhydride results in the unstable [2+2] adduct, which is stabilized by the subsequent [4+2] addition of the second dienophile molecule.[4]

The Diels—Alder reaction with naphthalene does not either occur at room temperature and usual pressure. The adduct was obtained[5] in ~1% yield for 24 h with a great maleic anhydride excess at 100 °C. More drastic temperature conditions are unfavorable for the yield of the target adduct, because the process is reversible. Only elevated temperature (100 °C) and pressure (10—12 kbar) make it possible to achieve 90% yield of the product.[6,7]

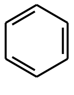
It has previously been shown[2,3] that the quantitative description of the rate of the Diels—Alder reaction between different reagents containing C=C bonds at 25 °C requires data on the ionization potential of the diene ($\mathrm{IP_D}$), electron affinity energy of the dienophile (E_A), interatomic C(1)—C(4) distance in the diene ($R_{\mathrm{C(1)-C(4)}}$), and balance of energies of the bond cleavage and formation (reaction enthalpy, ΔH_react)

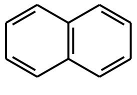
$$\lg k_2 = -28.81 + 316.3/(\mathrm{IP_D} - E_\mathrm{A}) - 69.9R_{\mathrm{C(1)-C(4)}}/(\mathrm{IP_D} - E_\mathrm{A}) - 0.054\Delta H_\mathrm{react}, \quad (1)$$

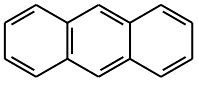
$r = 0.972$, $n = 93$, $s_0 = 0.9$,

where r is the correlation coefficient, n is the number of experimental points, and s_0 is the standard deviation from the dependence obtained. In correlation (1) the k_2 values are expressed in L mol^{-1} s^{-1}, $\mathrm{IP_D}$ and E_A are expressed in eV, $R_{\mathrm{C(1)-C(4)}}$ is in Å, and ΔH_react is kJ mol^{-1}. This allows one to predict the rates of the Diels—Alder reac-

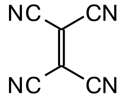
Dienes


1

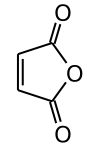

2


3

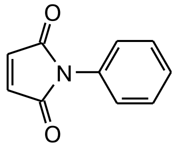
Dienophiles



4



5



6

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 51—54, January, 2004.

tion with dienophiles **4—6** for benzene (**1**) and naphthalene (**2**). The ionization potentials for benzene (9.246 eV) and naphthalene (8.14 eV)[8] and electron affinities energies of dienophiles **4—6** are known.[2,3] Using the heat of formation,[9] one can calculate the enthalpies of 1,4-addition of the hydrogen molecule to benzene (**1**) (+23±4 kJ mol^{-1}), naphthalene (**2**) (−8±4 kJ mol^{-1}), and anthracene (**3**) (−71±4 kJ mol^{-1}).

Comparison of the experimental enthalpies[2,3] of the Diels—Alder reactions for anthracene (**3**) with tetracyanoethylene (**4**) (−77 kJ mol^{-1}), maleic anhydride (**5**) (−93 kJ mol^{-1}), or *N*-phenylmaleimide (**6**) (−106 kJ mol^{-1}) makes it possible to estimate the thermal effects of interaction of these dienophiles with benzene (+17±4, +1±4, −12±4 kJ mol^{-1}) and naphthalene (−14±4, −30±4, −43±4 kJ mol^{-1}), respectively (Table 1). Additional data on the electron affinity energy[2,3] of tetracyanoethylene (2.88 eV), maleic anhydride (0.97 eV), and *N*-phenylmaleimide (0.89 eV) and interatomic distances in aromatic dienes **1—3** (2.81 Å) allow the calculation of logarithms of the rate constants ($\log k_2$) of these reactions by Eq. (1) (see Table 1). Accepting the entropies of these reactions to be the same[3] and equal to −150 J mol^{-1} K^{-1}, one can estimate the equilibrium constants (K_{eq}) (see Table 1). The half-life times were calculated for the reactions of the reactants with concentrations of 0.5 and 5 mol L^{-1} (see Table 1). Taking into account the equilibrium constants, the maximum conversion of dienophiles **4—6** in the Diels—Alder reaction with benzene is much lower than 0.001% under these conditions, while for naphthalene this parameter is ~0.001, 4, and 70% for the reactions with tetracyanoethylene, maleic anhydride, and *N*-phenylmaleimide, respectively. When the pressure is increased to 10—12 kbar, one can expect an increase in the rate and equilibrium constants by three orders of magnitude.[10]

Catalysis by Lewis acids makes it possible to increase the reaction rate by five orders of magnitude without changing the equilibrium constant.[2,3] Since the activation enthalpy is much higher than the reaction enthalpy, an increase in the reaction rate constant (k_2) with temperature is sharper than a decrease in the equilibrium constant. However, the $\log K_{eq}$ value for benzene is very low even in the reaction with *N*-phenylmaleimide (−5.6±1.0). Thus, for the Diels—Alder reactions involving benzene and *N*-phenylmaleimide in the presence of aluminum or gallium chlorides at 10—12 kbar and 25 °C, one can expect an increase in k_2 from $2 \cdot 10^{-14}$ to $2 \cdot 10^{-6}$ L mol^{-1} s^{-1} and in K_{eq} from $2.5 \cdot 10^{-6}$ to $2.5 \cdot 10^{-3}$ L mol^{-1} with the maximum conversion not higher than 1—2% for 20—30 h. When the pressure is released, the K_{eq} value again becomes equal to $2.5 \cdot 10^{-6}$ L mol^{-1} but the rate of adduct decomposition is rather low ($7 \cdot 10^{-9}$ s^{-1}), which allows one to detect its formation. It is known[2,3] that the introduction of donating groups, for example, methyl groups, into positions 1 and 4 of diene and replacement of ethylenic dienophiles by acetylenic dienophiles exert a favorable effect on the kinetic and thermodynamic parameters of the Diels—Alder reaction. This was experimentally confirmed for polymethylnaphthalenes and even polymethylbenzenes.[4] It is clear that several products of the reactions between benzene and dienophiles with the double bond can much more easily been obtained by the interaction of the corresponding cyclohexadienes with acetylenic dienophiles. However, the susceptibility of the adducts to decomposition with benzene formation accompanies both these processes.

For naphthalene the highest rate is expected in the reaction with tetracyanoethylene (**4**) but the conversion under standard conditions is so low that adduct formation cannot be detected (see Table 1). The experimental data at elevated temperatures indicate a much higher yield of

Table 1. Calculated parameters of the Diels—Alder reaction for benzene (**1**), naphthalene (**2**), and anthracene (**3**) with tetracyanoethylene (**4**), maleic anhydride (**5**), and *N*-phenylmaleimide (**6**): enthalpies of reactions (ΔH_{react}/kJ mol^{-1}), rate constants ($\log(k_2$/L mol^{-1} s^{-1})), equilibrium constants ($\log(K_{eq}$/L mol^{-1})), half-period of the reaction ($\tau_{0.5}$/s) at the initial concentrations of the reactants 0.5 and 5 mol L^{-1}, and equilibrium conversion (α_{eq} (%)) at 25 °C

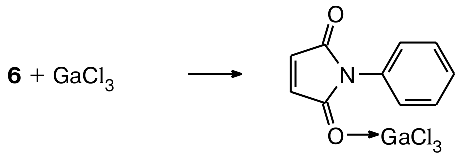
Diene	Dienophile	ΔH_{react}	$\log k_2$	$\tau_{0.5}$	$\log K_{eq}$	α_{eq}
1	**4**	+17±4	−10.8±0.9	$9 \cdot 10^{9}$	−10.6±1.0	$1 \cdot 10^{-(8\pm1)}$
1	**5**	+1±4	−13.9±0.9	$1 \cdot 10^{13}$	−7.9±1.0	$6 \cdot 10^{-(6\pm0.5)}$
1	**6**	−12±4	−13.7±0.9	$7 \cdot 10^{12}$	−5.6±1.0	$(1—3) \cdot 10^{-3}$
2	**4**	−14±4	−5.2±0.9	$2 \cdot 10^{4}$	−5.3±1.0	$2 \cdot 10^{-(3\pm0.5)}$
2	**5**	−30±4	−10.4±0.9	$3.5 \cdot 10^{9}$	−2.5±1.0	4±2
2	**6**	−43±4	−9.9±0.9	$1 \cdot 10^{9}$	−0.3±1.0	70±20
3	**4**	−77*	0.48*	—	5.5±1.0	—
3	**5**	−93*	−5.22*	—	8.3±1.0	—
3	**6**	−106*	−5.14*	—	10.5±1.0	—

* Published data.[2,3]

the products in the reaction of naphthalene with *N*-phenylmaleimide[11] than that with maleic anhydride,[5] which agrees with the results of calculations (see Table 1). However, all these reactions do not occur at standard temperature because of very low rates.

In this work, we studied the reaction of naphthalene (**2**) with *N*-phenylmaleimide (**6**) at room temperature. According to the presented calculations (see Table 1), the half-life (more than 30 years) is too long for experiment. An extensive material on the kinetic data indicates that the Diels—Alder reaction is accelerated in the presence of Lewis acid.[2,3] Gallium chloride, which is easily soluble in inert organic solvents, forms a stable *n*,*v*-complex with many dienophiles, including maleimides.[2,3] The electron affinity energy of *N*-phenylmaleimide (**6**) for its transformation into the *n*,*v*-complex (**7**) with gallium chloride (Scheme 1) increases from 0.89 to 1.93 eV.[12] The rate of the Diels—Alder reaction between substituted anthracenes and activated dienophile (**7**) increases by $5 \cdot 10^4$ times.[13] It follows from these data that the rate constant of the reaction of naphthalene with *N*-phenylmaleimide can increase from $1.2 \cdot 10^{-10}$ to $6 \cdot 10^{-6}$ L mol^{-1} s^{-1}.

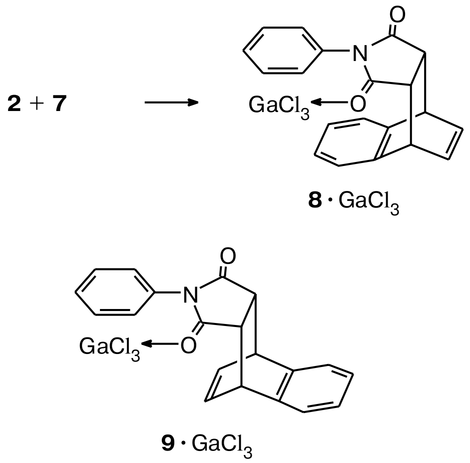
Scheme 1



7

The *endo*- (m.p. 161 °C, with decomp.) and *exo*-adducts (m.p. 172 °C, with decomp.) have recently[7] been isolated in the reaction of naphthalene with maleic anhydride at 100 °C and 12 kbar in $CHCl_3$. The chemical shifts in the ^1H and ^{13}C NMR spectra differ significantly for the *endo*- and *exo*-adducts.[7] However, the NMR spectra of the adduct obtained in the catalyzed reaction **2** + **7** (Scheme 2) indicate the presence of only one isomer (**8** or **9**). Taking into account the increased energy of interaction in the adduct between the fragments of the π-releasing benzene and π-withdrawing maleimide rings in the complex with $GaCl_3$, one should expect the kinetic preference of formation of *endo*-adduct **8**. The reaction at room temperature and crystallization of the adduct from a solution prevent the accumulation of thermodynamically more stable *exo*-adduct **9**. *Exo*-isomer **9** with m.p. 206 °C was obtained[11] as the main product in the reaction **2** + **6** in boiling xylene (140 °C), whereas the adduct obtained in our work had m.p. 194—195 °C (with decomp.). Comparison of these data agrees with the *endo*-form of the resulting adduct **8**.

Scheme 2



The experimental value of the rate constant of the catalyzed reaction at 22±2 °C is equal to $(2.0\pm0.5) \cdot 10^{-6}$ L mol^{-1} s^{-1}, which corresponds satisfactorily to the calculated value ($6 \cdot 10^{-6}$ L mol^{-1} s^{-1}). The change in the absorption of the π,π-complex for 24 days (from 0.954 to 0.320) made it possible to estimate the equilibrium constant of the catalyzed reaction (5±2 L mol^{-1}).

Experimental

^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian Unity-300 instrument in a $CDCl_3$ solution using the signal of the proton of $CHCl_3$, whose traces were in the solution, as an internal standard. The δ values were calculated relatively to Me_4Si. Commercial *N*-phenylmaleimide (Aldrich), benzene (reagent grade), and naphthalene (reagent grade) were used.

***endo*-*N*-Phenyl-2,3-benzobicyclo[2.2.2]octa-2,5-diene-7,8-dicarboximide (8).** Gallium chloride (1.01 g, 5.7 mmol) was dissolved in anhydrous benzene (reagent grade) containing *N*-phenylmaleimide (1.15 g, 6.6 mmol), and then naphthalene (12.8 g, 0.1 mol) was added.* Argon was passed through the resulting solution, and the reactor was tightly corked and left for 7 days at 22 °C. Already two days after, a precipitate of the adduct complex with gallium chloride ($\mathbf{8} \cdot GaCl_3$) began to form. After 7 days, the precipitate was filtered off, powdered, washed with benzene and hexane, and dissolved in CH_2Cl_2. Gallium chloride was removed from adduct $\mathbf{8} \cdot GaCl_3$ with aqueous ammonia, and the solution was washed with water and dried with $MgSO_4$. The volume of the solution was brought to 20 mL, and the adduct was precipitated with hexane and dried *in vacuo*. The yield of pure adduct **8** was 0.6 g (30% calculated per taken imide **6**), m.p. 194—195 °C (with decomp.). Found (%): C, 79.97; H, 4.95; N, 4.80. $C_{20}H_{15}NO_2$. Calculated (%): C, 79.72; H, 5.02; N, 4.65. ^1H NMR, δ: 3.16 (m, 2 H, H(7),

---

* A solution of naphthalene with $GaCl_3$ in benzene darkens in the absence of dienophile **6**, and its subsequent addition does not regenerate diene **2**.

H(8)); 4.60 (m, 2 H, H(1), H(4)); 6.65 (m, 2 H, H(5), H(6)); 7.15—7.52 (m, 9 H, H arom.). ^{13}C NMR, δ: 42.76 (C(1), C(4)); 47.04 (C(7), C(8)); 124.42, 126.93, 127.09, 129.40, 129.81, 132.46, 134.79, 142.61 (C(5), C(6), and 12 C arom.); 177.01 (2 C=O).

Measurement of the reaction rate. A benzene solution of reactants **6** (0.0458 mol L^{-1}), $GaCl_3$ (0.040 mol L^{-1}), and **2** (0.416 mol L^{-1}) was prepared. The solution was placed in a quartz cell (l = 1 cm), whose upper part was welded (through transient alloys) to a molybdenum glass tube. Dry argon was passed through the cell, and the tube was sealed. At these concentrations and temperature of 22±2 °C, crystals of the adduct are not precipitated even for 24 days. At an excessive naphthalene concentration (C_2), the current concentration of the π,π-complex (C_c) between reactants **2** and **7** is proportional to the current concentration of activated dienophile **7** (C_7)

$$C_c = C_7K_cC_2/(1 + K_cC_2),$$

where K_c is the equilibrium constant of the π,π-complex between reactants **2** and **7**. The change in the absorption of the π,π-complex (A_c) for 24 days (from 0.954 to 0.320) made it possible to determine the rate constant ($(2.0\pm0.5)\cdot10^{-6}$ L mol^{-1} s^{-1}) from the initial part of the $\ln A_c$—t plot, and then the equilibrium constant of the catalyzed reaction (5±2 L mol^{-1}) was calculated.

References

1. R. Foster, *Organic Charge-Transfer-Complexes*, Academic Press, London—New York, 1960, 33.
2. V. D. Kiselev and A. I. Konovalov, *Usp. Khim.*, 1989, **58**, 383 [*Russ. Chem. Rev.*, 1989, **58** (Engl. Transl.)].
3. A. I. Konovalov and V. D. Kiselev, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 279 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 293].
4. A. S. Onishchenko, *Dienovyi sintez* [*Diene Synthesis*], Izd-vo AN SSSR, Moscow, 1963, 650 pp. (in Russian).
5. M. C. Kloetzel and H. L. Herzog, *J. Am. Chem. Soc.*, 1950, **72**, 1991.
6. W. H. Jones, D. Mangold, and H. Plieninger, *Tetrahedron*, 1962, **18**, 267.
7. F.-G. Klarner and V. Breitkopf, *Eur. J. Org. Chem.*, 1999, 2757.
8. *Handbook of Chemistry and Physics*, 75th ed., Eds. D. R. Lide and H. P. R. Frederikse, CRC Press: Boca Raton, Ann Arbor—London—Tokyo, 1994—1995.
9. J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London—New York, 1970, 643 pp.
10. A. Drljaca, C. D. Hubbard, R. Van Eldik, T. Asano, M. A. Basilevsky, and W. J. le Noble, *Chem. Rev.*, 1998, **98**, 2167.
11. I. G. Dinulescu, M. Avram, and C. D. Nenitzescu, *Chem. Ber.*, 1960, **93**, 1795.
12. V. D. Kiselev, I. M. Shakirov, and A. I. Konovalov, *Zh. Org. Khim.*, 1984, **20**, 1454 [*J. Org. Chem. USSR*, 1984, **20** (Engl. Transl.)].
13. V. D. Kiselev, D. G. Khuzyasheva, and A. I. Konovalov, *Zh. Org. Khim.*, 1983, **19**, 1268 [*J. Org. Chem. USSR*, 1983, **19** (Engl. Transl.)].

Received May 5, 2003