

Effect of a Competing n Donor on the Rate of AlCl_3 -Catalyzed Diels–Alder Reaction of 9,10-Dimethylantracene with Maleic Anhydride

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Abstract—The catalytic effect of AlCl_3 on the Diels–Alder reaction of 9,10-dimethylantracene with maleic anhydride is dramatically weakened on addition of a competing n donor, dibutyl ether. The n, ν complex of aluminum chloride with dibutyl ether is considerably more stable than the complex with maleic anhydride; therefore, the catalytic effect is suppressed even at comparable concentrations of these n donors.

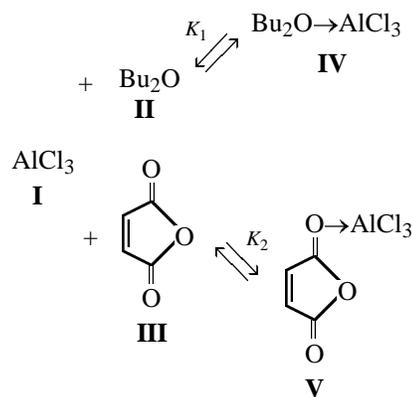
It is commonly believed today that the Diels–Alder reaction is a concerted single-stage low-polar process controlled by the energy of interaction of the molecular orbitals [1]. The reactivity of the reaction participants is satisfactorily described on the quantitative level by jointly considering the energy of interaction of the frontier orbitals, conjugation energy in the starting compounds, and the structure of the diene ($\text{C}^1\text{--C}^4$ distance) [2]. The contribution of the latter factor appeared to be proportional to the squared coefficients of overlap of the reacting orbitals; this was found [3] immediately after experimental observation of the dependence of the reaction rate on R_{1-4} in the diene [4].

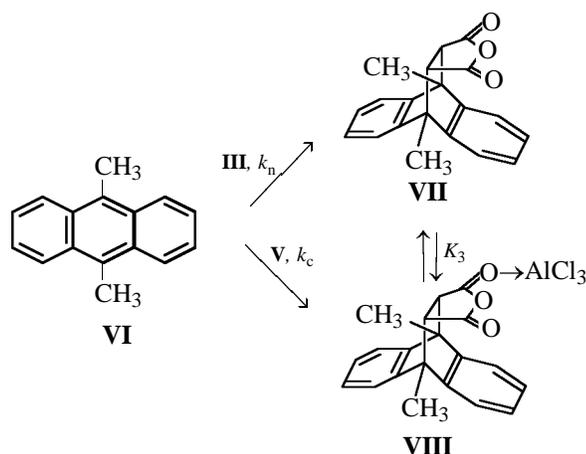
Dienophiles form fairly stable n, ν complexes with Lewis acids owing to interaction of the lone electron pair in the activating group, usually conjugated with the reaction center, and the low-lying vacant orbital in the Lewis acid [2, 5]. The electron affinity of substituted N -arylmaleinimides increases by 0.7–1.15 and 1.0–1.22 eV on formation of n, ν complexes with GaCl_3 [6] and AlCl_3 [7], respectively. The factors of acceleration of the Diels–Alder reaction involving maleinimides in the presence of GaCl_3 and AlCl_3 in inert media, calculated from these data, are nicely consistent with the experiment [6, 7]. Usually, the reaction rate increases by factors of more than 10^4 in the presence of GaCl_3 and more than 10^5 in the presence of AlCl_3 [2]. In an inert medium, the Lewis acid is completely bound in a complex with the dienophile usually present in excess. When the Lewis acid is in excess, it can form a π, ν complex with the diene, which can be followed by its transformation into the σ complex and dimerization or polymerization, depending on the structure of the diene [2, 5]. Because

of the large difference in the reactivity of free and activated (by binding in an n, ν complex) dienophile, the contribution of the reaction with the free dienophile to the overall process is negligible. Since, when performing Diels–Alder reactions, the Lewis acid is taken in small concentration, the presence of even small amounts of n donors other than the dienophile can drastically decrease the catalytic effect.

The goal of this work was to study quantitatively the effect exerted by additions of an n -donor compound to an inert solvent on the rate of the catalytic reaction. We chose the following objects: catalyst, AlCl_3 **I**; neutral donor, dibutyl ether **II** (it forms a stable complex **IV** with AlCl_3); dienophile, maleic anhydride **III**; diene, 9,10-dimethylantracene **VI**; and solvent, 1,2-dichloroethane.

When the reaction is performed in the absence of **II**, with the concentration of the dienophile, c_{III} , being higher than that of the catalyst, c_{I} , and with both con-





centrations being considerably higher than that of the diene, c_{VI} , the following relationship is observed.

$$\ln(c_{\text{VI}}^0/c_{\text{VI}}) = c_{\text{V}}k_c\tau. \quad (1)$$

Here, c_{VI}^0 and c_{VI} are the initial and running (at instant τ) concentrations of the diene, respectively, and k_c is the second-order rate constant of the catalyzed reaction. In the presence of ether **II**, AlCl_3 is redistributed between **II** and **III**, forming n, ν complexes **IV** and **V**. The overall distribution of AlCl_3 between complexes **IV**, **V**, and **VIII** (with the reaction product) is given by

$$c_{\text{IV}}/c_{\text{II}}K_1 = c_{\text{V}}/c_{\text{III}}K_2 = c_{\text{VIII}}/c_{\text{V}}K_3. \quad (2)$$

Here, K_1 , K_2 , and K_3 correspond to the equilibrium constants for n, ν complexes **IV**, **V**, and **VIII**, respectively. The equilibrium constants are difficult to determine, since they exceed 10^8 l mol^{-1} [5]. According to [8], the enthalpy of formation of complex **VIII** is more negative than that of **V** by 4 kJ mol^{-1} , and the K_3/K_2 ratio is 10. The initial concentration of **III** under our conditions exceeded by a factor of ~ 100 that of diene **VI** and hence the sum of the concentrations of adducts **VII** and **VIII**. Hence,

$$c_{\text{V}}/c_{\text{VIII}} = c_{\text{III}}K_2/c_{\text{V}}K_3 > 10. \quad (3)$$

In this case, AlCl_3 from complex **VIII** will be virtually fully returned to form complex **V**. It should be noted that such a redistribution should occur at any concentrations of **V**, even if they are considerably lower than the sum of the concentrations of **VII** and **VIII**. In the absence of ether **II**, AlCl_3 is virtually fully bound with dienophile **III**, and at the concentration ratio taken the process can be considered as purely

catalytic. Since the accelerating effect (k_c/k_n) in this reaction in the presence of AlCl_3 is 10^5 [7], the contribution of the rate of the parallel noncatalyzed reaction does not exceed 1%, even at the ratio $c_{\text{III}}/c_{\text{IV}} 2 \times 10^3$. In the presence of competing n donor **II**, the concentration of **V** can decrease to such an extent that the ratio $c_{\text{III}}/c_{\text{V}}$ will become larger than 2×10^3 . In this case, the rates of the parallel reactions yielding **VII** and **VIII** will become comparable [Eqs. (4), (5)].

$$d(c_{\text{VI}})/d\tau = k_n c_{\text{VI}} c_{\text{III}} + k_c c_{\text{VI}} c_{\text{V}}, \quad (4)$$

$$\begin{aligned} d \ln(c_{\text{VI}})/d\tau &= k_n c_{\text{III}} + k_c c_{\text{V}} = k_n c_{\text{III}}^0 + c_{\text{V}}(k_c - k_n) \\ &= k_n c_{\text{III}}^0 + k_c c_{\text{V}}. \end{aligned} \quad (5)$$

Here, c_{III}^0 and c_{III} are the total concentration of **III** and the concentration of free **III**, respectively; k_n and k_c are the rate constants of the noncatalyzed and catalyzed reaction. Since the ratio k_c/k_n is high, $k_c - k_n \approx k_c$.

It follows from (2) and (3) that the concentration of the complex, c_{V} , should remain constant throughout the reaction, even if $c_{\text{VI}} \geq c_{\text{V}}$. If all these assumptions are valid, then Eq. (5) can be integrated:

$$\ln(c_{\text{VI}}^0/c_{\text{VI}}) = \ln(D_{\text{VI}}^0/D_{\text{VI}}) = (k_n c_{\text{III}}^0 + k_c c_{\text{V}})\tau = A\tau. \quad (6)$$

Here, c_{VI}^0 and c_{VI} are the initial and running concentrations of diene **VI**, respectively; D_{VI}^0 and D_{VI} are the initial and running optical densities related to **VI**; and A is a constant equal to $k_n c_{\text{III}}^0 + k_c c_{\text{V}}$. Relationship (6) was checked experimentally (see figure). The linear correlation ($r = 0.9998$) is observed even at high conversions of **VI**, which confirms our assumptions.

The experimental data on the effect of **II** on the reaction rate are listed in the table. The rate constants of the noncatalyzed reaction, k_n , in 1,2-dichloroethane and dibutyl ether at 23°C are $(3.08 \pm 0.05) \times 10^{-2}$ and $(1.33 \pm 0.04) \times 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$, respectively. The linear correlation (see figure) is observed for all the experimental series (no. 1–6, see table). The experimental data (see table) allow calculation of the concentration of the activated dienophile: $c_{\text{V}} = (A - k_n c_{\text{III}}^0)/k_c$. In experimental series nos. 1–4 (see table), the content of ether **II** in 1,2-dichloroethane was less than 0.5 vol %; therefore, the contribution of the noncatalyzed process was calculated taking into account the rate constant (k_n) in 1,2-dichloroethane. In experimental series nos. 5 and 6 (see table), we used the weighted average rate constants of the noncatalyzed reaction in a mixture of these solvents, although these corrections do not noticeably affect the conclusions. Comparison of the A and $k_n c_{\text{III}}^0$ values obtained shows that the contribution of the catalytic process is

Initial concentrations (M) of AlCl_3 (c_{I}^0), Bu_2O (c_{II}^0), and maleic anhydride (c_{III}^0), coefficient *A* of Eq. (6), contribution to *A* from the noncatalyzed reaction ($k_n c_{\text{III}}^0$), calculated concentration of activated dienophile (c_{V}), and volume fraction of Bu_2O **II** in solution (V_{II}/V , %)

Run no.	$c_{\text{I}}^0 \times 10^3$	$c_{\text{II}}^0 \times 10^2$	$c_{\text{III}}^0 \times 10^2$	$c_{\text{II}}^0/c_{\text{III}}^0$	$A \times 10^3$	$A \times 10^2/c_{\text{III}}^0$	$k_n \times 10^2$	$k_n \times 10^3 c_{\text{III}}^0$	$c_{\text{V}} \times 10^8$	V_{II}/V
1	2.60	1.14	5.20	0.22	8.4	16.2	3.08	1.60	335 ± 23	0.12
2	3.64	1.54	5.83	0.26	6.7	11.5	3.08	1.80	242 ± 18	0.16
3	3.26	3.63	4.12	0.88	1.8	4.37	3.08	1.27	26 ± 7	0.38
4	3.28	3.92	3.62	1.08	1.7	4.70	3.08	1.11	29 ± 7	0.41
5	11.2	60	4.10	14.6	1.1	2.73	2.96	1.21	-5 ± 6	6.80
6	8.41	111	4.42	25.1	1.2	2.71	2.84	1.26	-3 ± 6	13.5

noticeable only at low ratios $c_{\text{II}}/c_{\text{III}}$ (run nos. 1–4, see table). At the dibutyl ether content exceeding 0.5%, the catalytic effect of AlCl_3 is fully suppressed (run nos. 5, 6; see table).

An unexpectedly low content of activated (bound in a complex with AlCl_3) maleic anhydride in the presence of comparable amount of another *n* donor can be explained, taking into account Eq. (2), by assuming that the complex of AlCl_3 with ether **II** is considerably more stable than the complex with dienophile **III**. The low solubility of AlCl_3 does not allow direct determination of the enthalpies of formation of these complexes. In this work, we used the method based on competing formation of benzene-insoluble complex **IX** of AlCl_3 with a stronger *n* donor, triethylamine **X**. The quantity ΔH_1 is equal to the difference between the enthalpies of formation of the complexes of AlCl_3 with **X** and **III**, and the quantity ΔH_2 is the similar difference for the complexes with **X** and **II**.

$$\Delta H_1 = \Delta H_{\text{IX}} - \Delta H_{\text{V}},$$

$$\Delta H_2 = \Delta H_{\text{IX}} - \Delta H_{\text{IV}},$$

$$\Delta H_{\text{IV}} - \Delta H_{\text{V}} = \Delta H_1 - \Delta H_2.$$

The experimental values of ΔH_1 and ΔH_2 are -170 and -117 kJ mol^{-1} , respectively. Hence, the difference between the enthalpies of formation of complexes of AlCl_3 with dibutyl ether and maleic anhydride is -53 kJ mol^{-1} . Direct measurements of the enthalpy of formation of the benzene-soluble complex of GaCl_3 with dibutyl ether and maleic anhydride gave the values of -67 [9] and -41 [10] kJ mol^{-1} , respectively. These data show that these Lewis acids form with dibutyl ether considerably more stable complexes than with maleic anhydride. It is known that electron-withdrawing substituents introduced into the molecule of an *n* donor considerably reduce the stability of *n,v* complexes [7].

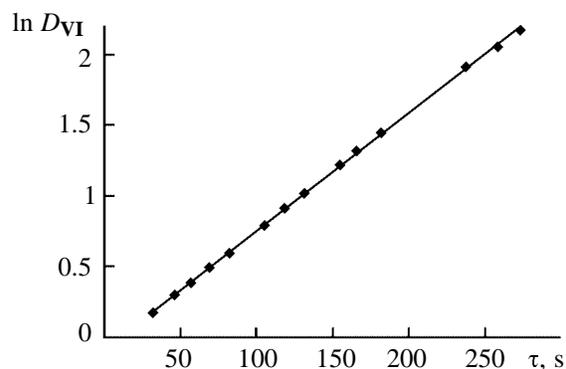
Our results show that the strong catalytic effect of

a Lewis acid can be fully suppressed even by trace amounts of competing *n* donors. To enhance the efficiency of the catalytic process, the solvent should be thoroughly purified to remove *n*-donor impurities, or Lewis acids should be taken in increased concentrations.

EXPERIMENTAL

9,10-Dimethylanthracene **VI** was purified by column chromatography (Al_2O_3 , benzene–hexane, 1 : 5); mp 182 – 183°C (published data [11]; mp 183 – 184°C). Maleic anhydride was distilled before use. Solvents were purified by common procedures [12].

The reaction was performed in a temperature-controlled quartz cell ($l = 1$ cm) with a ground-glass stopper. The reaction progress was monitored by a decrease in the absorption of **VI** in the range 380 – 385 nm. The optical purity was checked by the absence of absorption after the reaction completion. In all the cases, the initial concentration of the dienophile exceeded that of the diene [$(1$ – $3) \times 10^{-4}$ M] by a factor of ~ 100 .



Experimental check of relationship (6) by the dependence of the optical density of the diene ($\ln D_{\text{VI}}$) on time τ (c_{I}^0 2.60×10^{-3} , c_{II}^0 1.14×10^{-2} , and c_{III}^0 5.20×10^{-2} M; 1,2-dichloroethane, 23°C).

Thermochemical measurements were performed with a differential calorimeter (volume of each cell 180 cm³). The experimental procedure is described elsewhere [13].

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