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Catalysis with Inorganic Cations. VII.[1] The Catalytic Process of the Diels-Alder Reaction with Magnesium Perchlorate in CH_2Cl_2: Kinetic Investigation and Spectroscopic Detection of the Complexed Intermediate.#

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Abstract. The 2-arylidene-malonic acid dimethyl ester is a dienophile suitable to be coordinated by Mg(II). The formation of the dienophile/cation complex in a ratio 2:1 in a non-coordinating solvent has been demonstrated by NMR spectroscopy. Kinetic determinations performed in dichloromethane evidenced the high reactivity of the system. The high affinity for Mg(II) of the reacting dienophile allows the reaction to be performed under catalytic conditions, whose single steps have been clarified by both spectroscopic and kinetic methods. © 1997 Elsevier Science Ltd.

INTRODUCTION

In the previous papers of this series,[2-6] the influence of inorganic perchlorate-organic solvent solutions on both reactivity and selectivity of some pericyclic processes was investigated. The main results can be summarised as follow.

a) The metal perchlorate accelerates the rate of those Diels-Alder (DA) and ene reactions characterized by electrophilic solvent effects.[7]

b) The rate acceleration of the above reactions depends upon the organic solvent, the metal cation, and the coordinable cycloaddend. Strong polar and basic solvents decrease the efficiency of the metal cation;[2,5] among inorganic perchlorates, magnesium perchlorate (MP) is the most active cation and sodium is the less active one.[3,5] Bidentate eno- and dienophile are more sensitive to the catalysis than monodentate cycloaddends, and the catalytic efficiency of MP is excellent with 1,3-dicarbonyl substrates.[8]

c) These experiments evidenced the importance of specific interactions between metal cation and substrate because the metal cation behaves as a Lewis acid.[3,5,9,10]

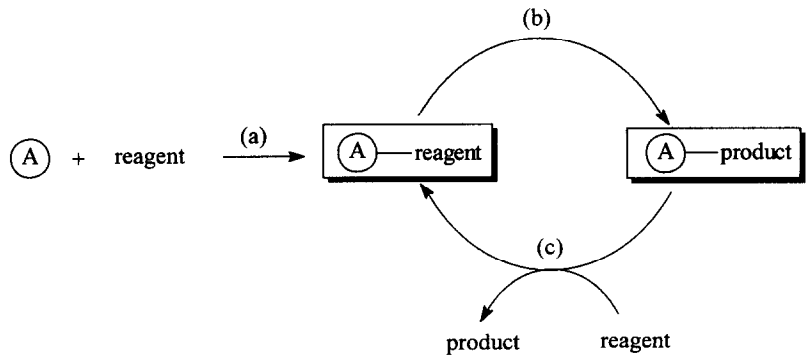
#Dedicated to Professor Gianfranco Tacconi, dear friend and colleague, on the occasion of his retirement.

All these results were obtained in the presence of large excess of inorganic salt. To our knowledge only one kinetic investigation on the DA reaction performed under catalytic conditions has been reported.[11] The rate of the $AlCl_3$-catalyzed DA between butadiene and methyl acrylate was found to be a function of the Lewis acid-acrylate complex concentration. The rate enhancement by aluminum chloride is entirely due to the lowering of the activation energy, the activation entropy (-37.7 e.u.) being very close to that of the uncatalyzed cycloaddition (-36.2 e.u.).

The MP-catalyzed DA reaction has not yet been investigated by kinetic methods. A catalyzed reaction requires the following catalytic cycle (Scheme 1): a) the cation (A) coordinates either diene or dienophile; b) the complexed reagent is more reactive than the uncomplexed one; c) the reaction product has a lower affinity for the cation than the starting reagent, so that it can be easily displaced from the complex to allow the cycle to be repeated.

In this paper we wish to report the kinetic study of the DA reaction between 2-(4-chloro-benzylidene)-malonic acid dimethyl ester (**1**) with cyclopentadiene (**2**) run in the presence of catalytic amounts of MP.

Scheme 1



RESULTS AND DISCUSSION

The starting dienophile **1** was easily prepared by Knoevenagel condensation between dimethylmalonate and 4-chloro-benzaldehyde. The thermal reaction with cyclopentadiene (benzene, 120 °C, 20 days) gave a 72% yield of *endo* and *exo* 3-(4-chloro-phenyl)-bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylic acid dimethyl ester (**3** and **4** respectively) in the ratio 1 : 2 (Scheme 2). When the reaction was run in an acetone solution of lithium perchlorate (LP) 4 M or MP 1 M, the reactivity was increased and 80-90% yield of cycloadducts was obtained at ambient temperature after 15 days and 12 hours respectively (Table 1, entries 2 and 3).

Scheme 2

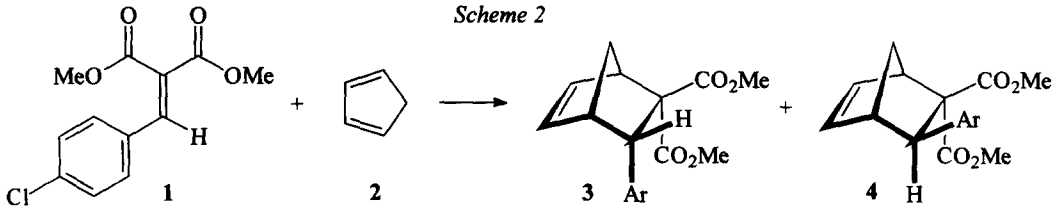
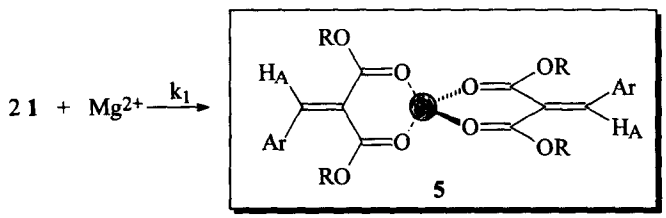


Table 1. Yields, product ratios, and rate constants at 25 °C for the reaction of **1** with **2** in differing reaction conditions.

Entry	Reaction Conditions	% Yield	[3] : [4]	$10^4 \times k_2$ (M^{-1} sec^{-1})	k_{rel}
1	Benzene, 120 °C, 20 d	72	33 : 67	---	---
2	LP-Acetone 4 M, rt, 15 d	81	78 : 22	0.1	1
3	MP-Acetone 1 M, rt, 12 h	90	83 : 17	4.5	45
4	MP (0.5 equiv)-CH_2Cl_2, rt, 30 min.	quant.	76 : 24	68.0	680

When the reaction was performed in dichloromethane with 0.5 equiv of MP, a quantitative yield of products **3** and **4** in a ratio 4 : 1 was obtained within 30 minutes (Table 1, entry 4). An evaluation of the kinetic effect was obtained by u.v.-vis. spectroscopic analysis, and these data, average of at least three kinetic runs, proved the large acceleration of the reaction run in the presence of 0.5 equiv of MP. This result can be interpreted by considering a specific coordination, not perturbed by the solvent, of the Mg^{2+} cation with the 1,3-dicarbonyl fragment to give the complex **5**, Scheme 3, whose structure was inferred by ^1H NMR spectroscopy.

Scheme 3



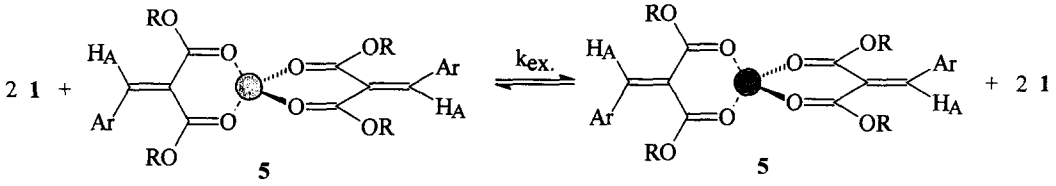
^1H NMR investigation of the complex 5. The structure of the reacting complex **5** was inferred by recording the ^{1}H-Nmr spectra of $CDCl_3$ solutions of **1** and MP in different ratios. **1** has the methoxy groups at 3.85 δ (singlet) and the benzylidenic proton (H_A) at 7.71 δ. When 0.5 equiv of MP were added, a clear solution was obtained: the methoxy signal was splitted into two singlets (4.10 and 3.89 δ) and H_A was shifted to 8.36 δ. The chemical shifts of H_A increases with the increase of complexed **1** (Table 2), and a nice linear relationship between $\Delta\delta(H_A)$ and the % of complexed **1** was observed (r = 0.989, slope = 0.0062). This trend can be rationalized assuming a rapid exchange (on the NMR time scale) of **1** on the complex **5**, and the resulting time averaged spectrum is a function of **1** bound to MP.

Table 2. Chemical shift of H_A in $CDCl_3$ at differing MP : **1** ratios.

Entry	MP : **1**	$[\mathbf{1}]_{compl}$: $[\mathbf{1}]_{free}$	$\delta(H_A)$	$\Delta\delta(H_A)$
1	0 : 1	0 : 100	7.71	0
2	1 : 10	20 : 80	7.83	0.12
3	1 : 5	60 : 40	7.89	0.18
4	1 : 4	50 : 50	8.03	0.32
5	1 : 2	100 : 0	8.36	0.65

In order to investigate this ligand exchange, VT-^{1}H-Nmr experiments on the solution of entry 4 (Table 2) were performed. At room temperature the chemical shift of H_A (8.03 δ) corresponds to a mixture of **1** unbound and bound to MP in the ratio 1:1 (Figure 1A). If the spectrum is registered at -50 °C, the ligand exchange (Scheme 4) becomes slow and the two absorptions corresponding to **1** and **5** in a ratio of about 1 : 1 are obtained (Figure 1C). The coalescence temperature was observed at -20 °C (Figure 1B).

Scheme 4



Applying the dinamic NMR theory,[12] the value of the ligand exchange constant (k_{ex}) can be calculated at a given temperature, and these values are reported in Table 3. The Eyring diagram gave a linear relationship (r = 0.999) and the activation parameters were calculated (Table 3).

Table 3. Equilibrium constants and activation parameters of the equilibrium in Scheme 4 in $CDCl_3$.

T/°C	-50	-40	-20	0	30	$\Delta H^{\neq}$ (Kcal mol^{-1})	$\Delta S^{\neq}$ (cal K^{-1} mol^{-1})
k_{ex} (sec^{-1})	72	164	484	1750	6300	7.0	-18.1

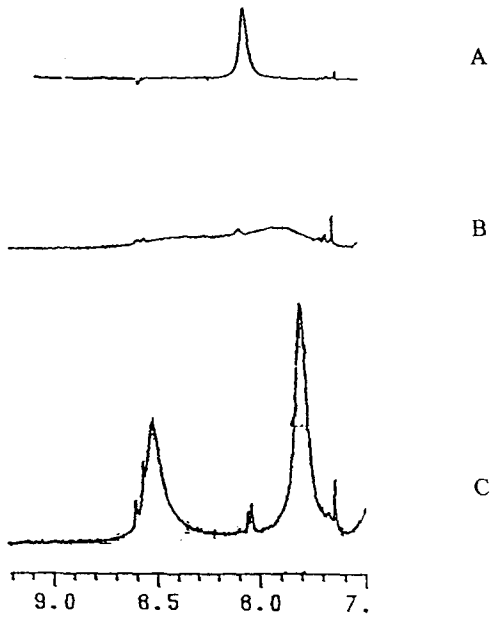


Figure 1. $CDCl_3$ ^1H-NMR spectrum of solution in Entry 4 (Table 2) at: (A) 30 °C; (B) -20 °C; (C) -50 °C.

The analogous complex prepared from cycloadduct **3** and MP in a ratio 2 : 1 in $CDCl_3$ was scarcely soluble, and accurate VT-NMR experiments could not be performed. In any case the spectrum of the solution allowed us to identify the absorptions of **3** complexed to MP. The vinylic protons of unbound **3** were at 6.28 and 6.75 δ, those of bound **3** at 6.48 and 6.60 δ, and the ratio was 1 : 1.

More interesting informations were obtained from the spectrum of a mixture of **1**, **3**, and MP in the ratio 2 : 2 : 1. The spectra of the clear solution both at -50 °C and ambient temperature showed two species largely predominant: the complex **5** and unbound **3**; only traces of unbound **1** (signal at *ca.* 7.8 δ) and bound 3

(vinylic protons between 6.4 and 6.6 δ) were detected (Figure 2). This supports the higher affinity for MP of the dienophile than the cycloadduct, what makes the catalytic process possible.

Kinetic determinations under catalytic conditions. Even if the rate acceleration obtained with an equivalent of MP in dichloromethane is impressive respect to the concentrated perchlorate acetonic solutions, the conditions of entry 4 in Table 1 does not yet represent a true catalytic system. The rate constants in solutions containing increasing amounts of **1** were determined and, as a typical example, the pseudo first order diagrams of the experiments with a ratio **1** : [MP] = 3 and with increasing concentrations of **2** are reported in Figure 3.

The starting absorbance of the solution [A(0)] did not change significantly at the beginning of the reaction. After a time dependent on the concentration of **2**, a rapid decrease of the absorbance was observed up to about 90% completion. A treatment with the classical pseudo first order kinetic equation gave good linear relationships ($r = 0.999$) and a k_2 value of $(7.0 \pm 0.3) \times 10^{-3}$ $M^{-1}sec^{-1}$ was calculated. The intercepts x(0) can be taken as a quantitative measure of the time required to observe a significative decrease of A(t), and these values (2.7, 5.8, and 11.7 minutes) increased with the decrease in cyclopentadiene concentration.

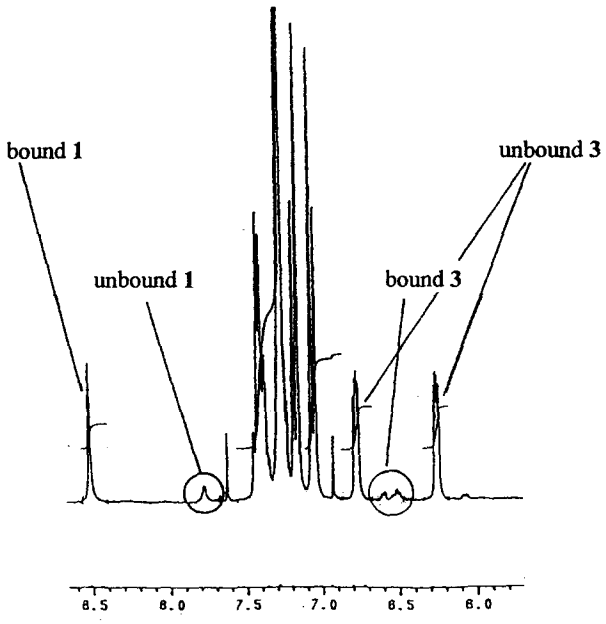


Figure 2. $CDCl_3$ ^1H-NMR spectrum of of **1**, **3**, and MP in ratio 2 : 2 : 1 at -50 °C.

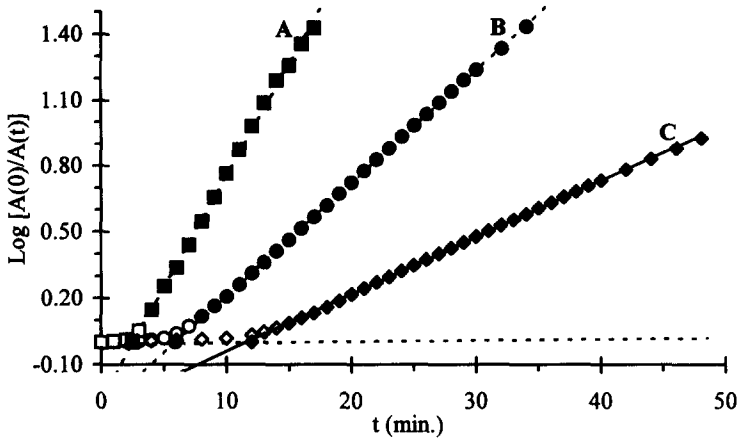


Figure 3. Plot of Log [A(0)/A(t)] *vs* t for the reaction of **1** and **2** at 25 °C for a ratio [**1**] : [MP] = 3. The diene concentration was = 0.609 (**A**), 0.304 (**B**), and 0.154 M (**C**).

The kinetic determinations were then performed with larger excess of **1**, hence under true catalytic conditions, and the results of these experiments are colleted in Table 4. The first order diagrams of the kinetic determinations run at a constant diene concentration (0.610 M) for increasing [**1**] : [MP] ratios are reported in Figure 4.

From the analysis of both data in Table 4 and graphs in Figure 4 some features can be drawn.

a) All kinetics follow, after a certain delay time, a pseudo first order behaviour and the calculated k_2 values are in reasonable accordance and independent from the [MP] : [**1**] ratio.

b) The starting absorbances at 388 nm are nearly constant for all the experiments. At this wavelength uncomplexed **1** does not absorb, the observed absorption is due to the complexed dienophile only and it is a function of the concentration of the complex **5**.

c) The delay time [x(0)] is a function of the concentration of **1** and **2**: low concentrations of **2** or large excesses of **1** give rise to longer delay times.

d) The value of x(0) can be taken as a measure of the time required to consume the excess of **1** and when it is multiplied for the concentration of **2** and divided for the number of equiv. of **1** in excess, a constant value of 1.72 ± 0.07 min is obtained that can be defined as the time required for one catalytic cycle (t_{cycle}).

Table 4. Kinetic data for the reaction of **1** and **2** at 25 °C with different [**1**] : [**2**] : [MP] ratios.

Entry	10^3 [MP]	10^3 [**1**]	[**2**]	[**1**] : [MP]	$\varepsilon_{388\ nm}$	$10^3 \times k_2$	[**3**] : [**4**]	x(0) (min)	t_{cycle} (min)
1	5.67	11.2	0.610	2	339	6.8	76 : 24	0	0
2	6.06	18.1	0.154	3	347	7.4	:	11.7	1.80
3	6.06	18.1	0.303	3	349	6.9	:	5.8	1.77
4	6.06	18.1	0.609	3	353	6.8	:	2.7	1.65
5	5.31	26.8	0.610	5	347	6.3	73 : 27	8.2	1.65
6	5.38	37.6	0.155	7	344	6.8	:	55.0	1.7
7	5.38	37.6	0.306	7	351	7.2	:	27.1	1.65
8	5.38	37.6	0.610	7	352	6.5	:	14.0	1.71
9	5.60	55.9	0.610	10	335	6.3	79 : 21	23.9	1.83
Av.					346 ± 6	6.7 ± 0.3	76 : 24		1.72 ± 0.07

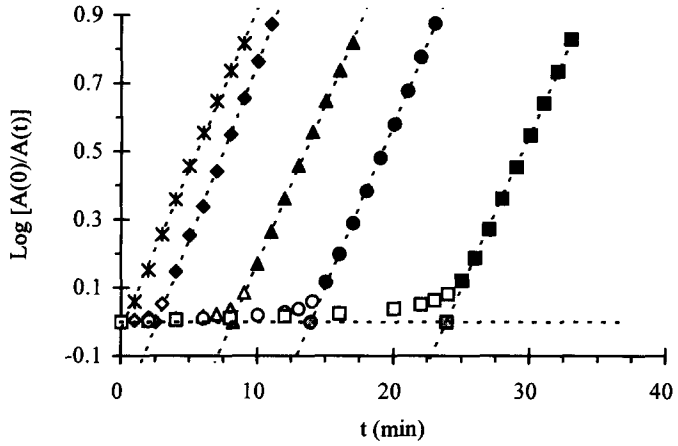
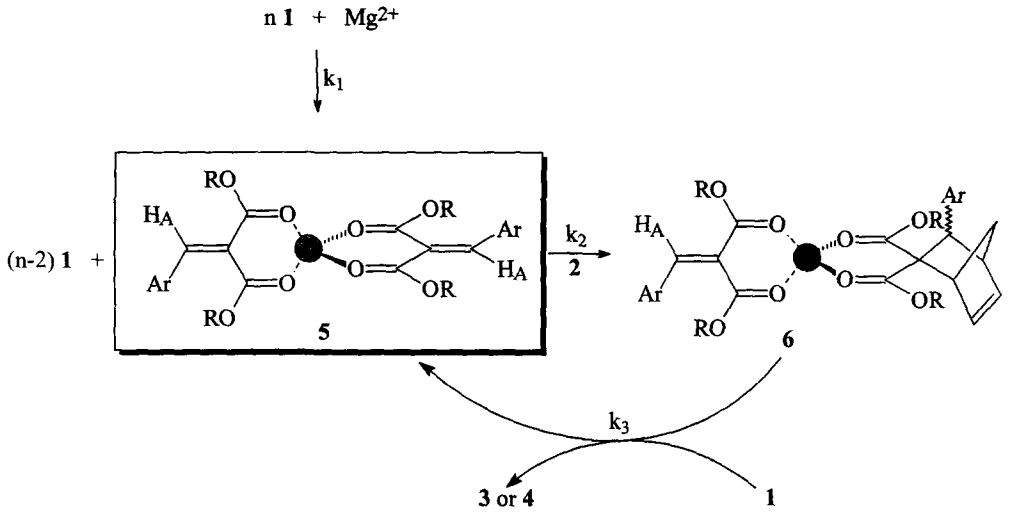


Figure 4. Plot of Log [A(0)/A(t)] *vs* t for the reaction of **1** and **2** at 25 °C at a diene concentration of 0.610 M. Ratios [**1**] : [MP] = 1 : n; n = 2 (*), n = 3 (◆), n = 5 (▲); n = 7 (●), and n = 10 (■).

From all these considerations it is possible to propose the following mechanism. a) The Mg^{2+} is coordinated by 2 equiv of **1** (a bidentate ligand) to give the tetrahedral complex **5**. b) The complex **5** react with cyclopentadiene (k_2) to give a complex **6** in which one equiv. of cycloadduct is coordinated to the cation. c) In the presence of **1**, a rapid ligand exchange (k_3) is established until **1** is present in the reaction mixture (Scheme 5).

Scheme 5



Activation Parameters. The rates of the catalyzed DA reactions under the conditions reported in Table 4 (entries 1 and 5) were determined at four different temperatures and the activation parameters were calculated (Table 5). The activation entropies are in accordance with the data reported for the $AlCl_3$[13] or $GaCl_3$[14] catalyzed DA reactions of monodentate dienophiles ($\Delta S^{\neq}$ = -37.7 and -34.2 e.u. respectively). Moreover these values are fully consistent with a concerted process, allowing to exclude any mechanistic change. Even if the activation parameters for the uncatalyzed cycloaddition cannot be determined, the typical value of $\Delta S^{\neq}$ found in the catalyzed reaction, allows to conclude that the observed large rate acceleration has to be entirely due to the lowering of the activation enthalpy.

Table 5. Rates and activation parameters of the catalyzed DA reaction of **1** with different MP : **1** ratio.

	[MP] : [1] = 1 : 2		[MP] : [1] = 1 : 5	
T/°C	$10^3 \times k_2$ (M^{-1} sec^{-1})	t_{cycle} (min)	$10^3 \times k_2$ (M^{-1} sec^{-1})	t_{cycle} (min)
15	4.10 ± 0.03	---	3.90 ± 0.1	2.54
20	5.05 ± 0.05	---	4.85 ± 0.1	2.35
25	6.80 ± 0.10	---	6.30 ± 0.1	1.65
30	9.20 ± 0.05	---	8.05 ± 0.1	1.40
$\Delta H^{\neq}$ (Kcal mol^{-1})	8.8 ± 0.3		7.9 ± 0.5	
$\Delta S^{\neq}$ (cal K^{-1} mol^{-1})	-39 ± 1		-42 ± 1.5	

To clarify the mechanism reported in Scheme 5 and to find the rate determining step of the process, some further informations about k_1 and k_3 are required. The first step of the catalytic cycle is the complexation of **1** and MP and this does not seem to be the rate-determining step since an evaluation of k_1 was obtained with the following experiment.

The required amount of MP (2.2 mg) was weighed in a cuvette and thermostatted at 25 °C. A solution of **1** in dichloromethane (2 mL) was added in order to have a ratio of **1** : MP equal to 5, and the increase of absorbance at 388 nm was monitored under stirring (Figure 5A). An exponential increase in the absorbance was observed and after about 80 minutes a plateau was reached. A pseudo first order treatment of the data gave a good linear relationship (r = 0.998, Figure 5B) from whose slope a k_1 value of 6.1 x 10^{-2} $M^{-1}sec^{-1}$ was calculated. This value is 10 times higher than k_2 and hence the complexation is not the rate determining step. In any case all solutions were prepared from 4 to 16 hours before the kinetic runs.

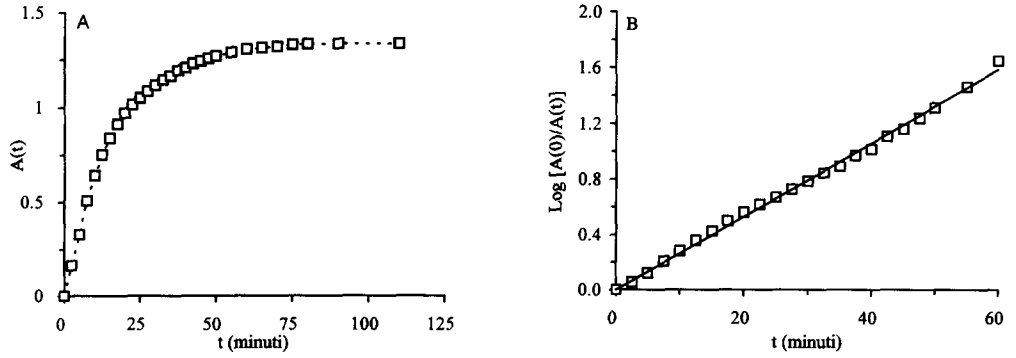
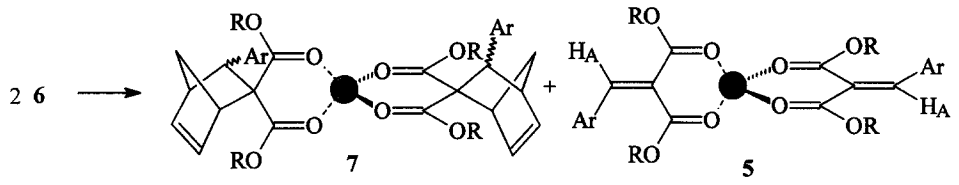


Figure 5. Plot of A(t) (A) and Log[A(0)/A/t)] (B) *vs* t for the complexation of **1** with MP at 25 °C.

The rate k_3 of the ligand exchange between complexes **5** and **6** cannot be determined. In any case an idea of its value can be obtained by assuming it to be not so far from k_{ex} of the ligand exchange equilibrium in Scheme 4. A value of 5.8 x 10^3 sec^{-1} is 10^6 times higher than the cycloaddition rate and hence it can be concluded that rate determing step of the overall catalytic process is the DA cycloaddition.

A last point has to be clarified. When the excess **1** has been consumed, the intermediate complex **6** cannot exchange the ligand to give **5**, and it still has bound 1 equiv of unreacted **1**. From kinetic evidences (the linearity is observed up to more than 90% reaction completion) and from the high MP-affinity of **1**, it seems reasonable to propose a dismutation of complex **6** into complexes **7** and **5**, with the latter one suitable to bring the reaction to completion, Scheme 6.

Scheme 6



CONCLUSION

The data reported in this paper allow to clarify the mechanism of the DA cycloaddition catalyzed by MP. The rate acceleration observed in dichlorometane in the presence of 0.5 or less than 0.5 equiv. of MP is larger than that observed in concentrated solutions of LP or MP in acetone. The activation parameters point out an activation entropy in accordance with a concerted mechanism, and the rate acceleration is entirely due to a lowering in the activation enthalpy. This strong increase in the reactivity is a consequence of the formation of a complex between the substrate and MP, demonstrated by the ^{1}H-NMR spectroscopy, and the observed kinetic behaviour for the true catalytic reaction can be rationalized with the following cycle. The magnesium cation coordinates the 1,3-dicarbonyl fragment of **1** to give the complex **5**. This reacts with cyclopentadiene to give the complex **6** that, if excess **1** is present in solution, gives, by a ligand exchange, again complex **5**. When the excess of **1** is consumed, **6** gives a disproportion to complexes **7** and **5**, with this latter again reacting with cyclopentadiene, until the reaction comes to the end.

Among all these steps, the rate determining one is the cycloaddition. From the average k_2 value reported in Table 4, a half-life time of 1.72 min can be calculated. This value is in nice accordance with the time required for one catalytic cycle.

EXPERIMENTAL SECTION

Melting points were determined by the capillary method and are uncorrected. Elemental analyses were made on C. Erba CHN analyzer mod. 1106. ^{1}H-Nmr (TMS as standard) were recorded on a Bruker AC 300 spectrometer, ir spectra (nujol mulls) on a Perkin Elmer 881 spectrophotometer. Column chromatography: silica gel 230-400 mesh.

Materials. Used 4-chloro-benzaldehyde was a commercial product. Cyclopentadiene (**2**) was freshly distilled from commercial dicyclopentadiene. Dichloromethane (stabilized with amylene) for the kinetic runs was distilled anhydrous HPLC grade reagent. The metal perchlorates were grade reagent; lithium perchlorate was dried under vacuum at 140°C for 8 hours (caution: all perchlorates are potenzial explosives and must be handled with care).[15]

4-Chloro-2-benzylidene malonic acid dimethyl ester (**1**). It was prepared by Knoevenagel condensation of dimethylmalonate and 4- chloro-benzaldehyde using piperidine and benzoic acid as catalyst following the procedure reported in the literature.[16] **1** was obtained as white crystals by chromathographic separation over silica gel (eluant: cyclohexane-ethyl acetate 90:10), m.p. 39-41°C (from methanol) (lit. 55-56 °C[16a] and 69-72 °C[16b]). Ir: 1725 cm^{-1}. ^{1}H-Nmr ($CDCl_3$), δ: 7.70 (1H, s, vinylic proton), 7.37 (4H, aromatic protons), 3.86 (6H, s, -OCH_3). Elem. anal.: Calc. for $C_{12}H_{11}O_4Cl$: C, 56.6; H, 4.3%. Found: C, 56.8; H, 4.2%.

Thermal DA reaction between 1 and 2 (Entry 1 - Table1). A solution of **1** (0.382 g - 1.5 mmol) and **2** (0.800 g - 12.1 mmol) in benzene was heated for 20 days at 120°C in a Paar bomb. The solution was evaporated and the residue was column chromatographed (eluant: cyclohexane-ethyl acetate 85:15). The first fraction (0.345 g - 72% yield) was a mixture of **3** and **4** in a ratio of 33:67 (^{1}H-Nmr analyses). The second fraction was unreacted **1** (0.106 g - 28% yield). By addition of petroleum ether to the first fraction, pure **3** was obtained as white needles, m.p. 76-78°C (from petroleum ether). Ir: 1728 and 1754 cm^{-1}. ^{1}H-Nmr, δ: 7.03 (2H, aromatic protons), 7.17 (2H, aromatic protons), 6.74 (1H, dd, J = 3.0 and 5.5 Hz, vinylic proton), 6.28 (1H, dd, J = 3.0 and 5.5 Hz, vinylic proton), 4.43 (1H, d, J = 3.2 Hz, H_3), 3.78 (3H, s, OCH_3), 3.17 (3H, s, OCH_3), 3.45 (1H, m, H_1), 3.05 (1H, bs, H_4), 1.58 (1H, dt, J = 9.0 and 1.5 Hz, $H_{7'}$), 1.49 (1H, dt, J = 9.0 and 1.75 Hz, H_7). Elem. anal.; Calcd. for $C_{17}H_{17}O_4Cl$: C, 63.7; H, 5.3%. Found: C, 63.8; H, 5.3%.

The ^{1}H-Nmr signals of **4** were detected by recording the spectrum of the mother liquor; δ: 7.03 (2H, aromatic protons), 7.17 (2H, aromatic protons), 6.51 (1H, dd, J = 3.0 and 5.5 Hz, vinylic proton), 6.07 (1H, dd, J = 3.0 and 5.5 Hz, vinylic proton), 3.74 (1H, d, J = 2.1 Hz, H_3), 3.73 (3H, s, OCH_3), 3.13 (3H, s, OCH_3), 3.42 (1H, m, H_1), 3.05 (1H, m, H_4), 2.58 (1H, dt, J = 9 and 2 Hz, $H_{7'}$), 1.80 (1H, dq, J = 9 and 2 Hz, H_7).

Catalyzed reaction between 1 and 2 in LP/acetone 4M. (Entry 2 - Table1). 0.800 g of **2** were added to a stirred solution of **1** (0.382 g - 1.5 mmol) in 5 mL of a 4M lithium perchlorate-acetone solution. After 15 days at room temperature, the reaction mixture was poured in water, extracted with CH_2Cl_2 (3×20 mL), dried on Na_2SO_4 and evaporated to dryness. The residue was column chromatographed as previously described obtaining 0.390 g (81% yield) of a mixture of **3** and **4** and 0.073 g of unreacted **1** (19% yield).

Catalyzed reaction between 1 and 2 in MP/acetone 1M. (Entry 3 - Table 1). 0.800 g of **2** were added to a stirred solution of **1** (0.382 g- 1.5 mmol) in 1M MP-acetone solution. The reaction was complete after 3 hours at room temperature. After usual work-up, 0.435 g (90% yield) of cycloadduct mixture were obtained.

Reaction between 1 and 2 catalyzed by MP (0.5 eqv) in CH_2Cl_2. (Entry 4). A solution of **1** (0.636 g - 0.25 mmol) and MP (0.028 g - 0.125 mmol) in anhydrous CH_2Cl_2 was stirred at room temperature until complete dissolution. Cyclopentadiene was then added and the stirring continued at room temperature for 30 minutes. After usual work-up, a quantitative yield of **3** and **4** in the ratio of 76 : 24 was obtained.

^{1}H-Nmr investigation of the complex between 1 and MP. The solutions of **1** and MP in several ratios (Table 2) were prepared dissolving about 5 mg of MP and the required amount of **1** in 1 mL of $CDCl_3$ at room temperature. The ^{1}H-Nmr spectra of these solutions were then recorded at the reported temperature.

Kinetic determinations under catalytic conditions. The overall reaction rates were measured by following the disappereance of the complex **5** on a Perkin Elmer Lambda 16 spectrophotometer provided with a thermostatted cell transport assembly and a automatic multicell programmer. The solutions were measured in 1.00 cm OS Hellma couvettes with 3 ml capacity; measurements were taken at 25°C at wavelength 388 nm. The rate constants were determined as follow. The needed amounts of MP (15 mg - 0.067 mmol) and **1** (0.04-0.18 g) were weighed in a 10 mL volumetric flask that was filled with anhydrous CH_2Cl_2 and the solution was stirred until complete dissolution of the salt. About 0.5 - 1 g of cyclopentadiene were weighed in a 5 mL volumetric flask that was filled with the solvent. At least three samples of the solution containing the chromophore (2 ml measured with a calibrate syringe) were placed in three couvettes thermostatted at the required temperature and constants amounts of cyclopentadiene solution (0.25 - 0.5 ml) were added. After vigorous mixing, the kinetic determinations were initiated.

Determination of the 3/4 ratio. This was determined by ^{1}H-Nmr. The solutions of the kinetic runs were quenced in water, extracted with CH_2Cl_2, dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in $CDCl_3$ and the ^{1}H-Nmr spectrum was recorded. The data reported are the average of at least three indipendent experiments and the error was ± 1%.

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