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Inorganic Perchlorates and Pericyclic Reactions. IV.[1] Rate Enhancement by Specific Cation-Substrate Interaction or by Increased Internal Pressure?

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Abstract. The kinetic behaviour of Diels-Alder and ene reactions was investigated in several inorganic perchlorate-organic solvent solutions. The observed rate accelerations are the result either of specific solute-cation interactions or of the increased internal pressure of the media, depending on substrates, solvents, and metal cations.
Small rate accelerations (up to 10 times) are observed in those reactions where the solute does not give specific interactions with the cation (reactions of nitrosoarenes) or when the solvent strongly solvate the metal perchlorate. This small rate increase is largely due to the increasing of the medium internal pressure.
Large rate enhancements (from 10^2 to 10^5 times depending on substrate, solvent, and salt) are observed in Diels-Alder and ene reactions showing electrophilic solvent effects and are consistent with a catalysis of the metal cation behaving as a Lewis acid.

INTRODUCTION

The use of inorganic perchlorates in organic solvents has been found very useful in organic syntheses.[1-3] The rationalization of the kinetic acceleration observed in such reaction media is a matter of an extensive debate. The first interpretation[2] considered the kinetic effect observed in lithium perchlorate (LP) 5 M in diethyl ether (DEE) as the result of the increased solvent internal pressure.[4] An alternative[5,6] was based on the ability of the lithium cation to act as a Lewis acid with its acidity considerably influenced by solvation effects.[6,7]

The interpretation in terms of specific solute-cation interaction gave also a satisfactory rationalization of the differing sensitivities observed in Diels-Alder (DA)[8] and ene reactions[9] with sodium (SP), magnesium (MP), barium (BP), and LP in acetone (AC) solutions. Only those pericyclic reactions characterised by electrophilic solvent effects (rate increasing with the increase of the solvent electrophilicity)[10] were strongly accelerated by inorganic perchlorates.

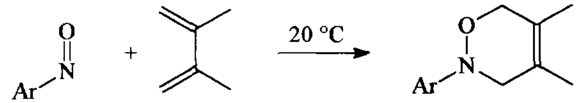
A recent report by Kumar[11] rationalized the different sensitivity of the DA reactions to inorganic perchlorates in terms of two properties of the systems: the effective internal pressure ($P_{i,eff}$) of the perchlorate solution,[12] and the activation volumes ($\Delta V^{\neq}$) of the reaction.[13] Reactions with more negative values of activation volume will be more sensitive to the increase of the internal pressure of the medium.

In order to discriminate between the mechanism involving specific solute-cation interactions and that considering the increase of the internal pressure of the reaction medium, an investigation of the kinetic effect of solutions with similar values of internal pressure on various pericyclic reactions was undertaken.

RESULTS AND DISCUSSION.

A reaction whose small solvent[10] and salt[8] effects were assigned to the increasing cohesive pressure of the media was used to test the $P_{i,eff}$ values proposed by Kumar[11] for the different solutions of inorganic perchlorates in acetone. When the kinetic data of the four salt-acetone systems for the reaction of 4-bromonitrosobenzene (**1**) with 2,3-dimethylbutadiene (DMB - **2**) (Scheme 1) were plotted *vs* their respective $P_{i,eff}$ values, a good linear relationship was obtained (Figure 1; intercept, 0.07; slope, 7.29 x 10^{-5}; r, 0.985).

Scheme 1



1 **2** **3**

Ar = 4-Br-C_6H_4

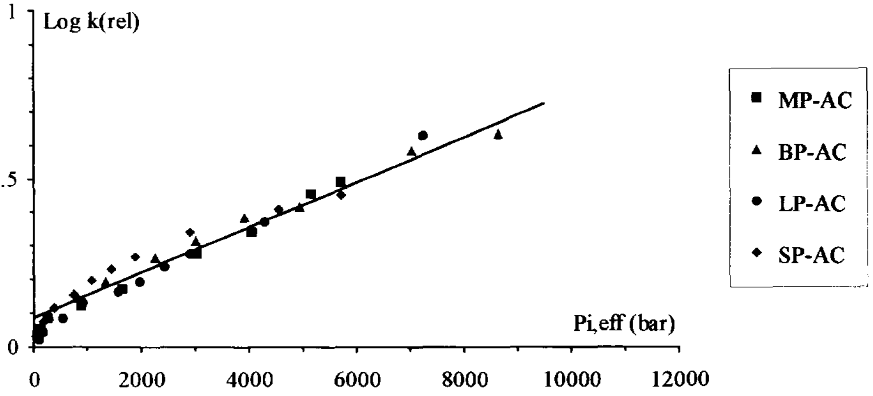


Figure 1. Plot of log k_{rel} of the DA reaction **1** + **2** *vs* Pi,eff. of solutions with varying concentrations of the different perchlorates in acetone.

From the slope of the linear regression in Figure 1 a $\Delta V^{\neq}$ value of -4.5 cm^3 mol^{-1} can be calculated. This result contrasts the experimental $\Delta V^{\neq}$ determined for the reaction of nitrosoarenes and **2** in several solvents, *under the influence of the external pressure*, that ranges from -22 to -30 cm^3 mol^{-1}.[14] This seems an intrinsic discrepancy since a statistical analysis of the available data[13,15] evidenced that the 94% of the investigated DA reactions under external pressure have $\Delta V^{\neq}$ values ranging from -26 to -50 cm^3 mol^{-1}, whereas those calculated from the internal pressure data[11] are in the range -1/-26 cm^3 mol^{-1}.

Thus internal and external pressure act in the same direction,[11,12] but give different kinetic results on the reaction of nitrosoarenes with DMB. Table 1 reports the k_{rel} data obtained by changing the $P_{i,eff}$ of perchlorate acetone solutions for the reaction in Scheme 1 or by increasing the external pressure for the reaction of 4-chloronitrosobenzene and **2** in seven differing solvents.[14] It cannot be ignored that an increase of the rate of 2.87 is obtained either with an external pressure of 1013 bar or with a $P_{i,eff}$ of 5144 bar.

Table 1. Comparison of the P_{ext} (bar) and $P_{i,eff}$ (bar) required to obtaine similar values of k_{rel}.

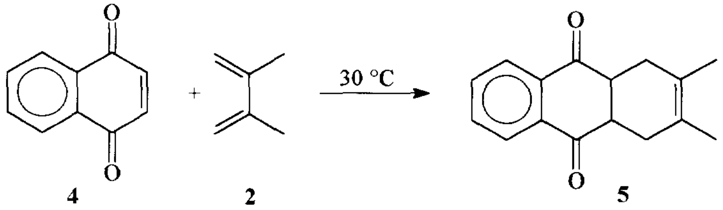
External Pressure[a]		Internal Pressure	
k_{rel}[b]	P_{ext} (bar)	k_{rel}	$P_{i,eff}$ (bar)
1	1	1	1
1.15	101	1.14	121
1.28	202	1.31	377
1.45	304	1.46	1571
1.77	507	1.72	2430
2.31	760	2.35	4290
2.87	1013	2.86	5144

[a] Ref. 14. [b]Average of k_{rel} in toluene, ethanol, dichloromethane, 1,2-dichloroethane, carbon tetrachloride, chloro and nitrobenzene.

From the graph reported in Figure 1 it can be assumed that the reaction between **1** and **2** is a suitable reference model to determine the $P_{i,eff}$ of perchlorate-organic solvent solutions and the log k_{rel} values of such reaction will be considered as an indirect measure of the increased internal pressure of the medium.

When all the available kinetic data[8] of the reaction between naphthoquinone (**4**) and **2**, Scheme 2, were plotted *vs* the corresponding $P_{i,eff}$ of inorganic perchlorates in acetone solutions,[11] the graphs reported in Figure 2 were obtained.

Schema 2



The k_{rel} values are no more linearly correlated with the $P_{i,eff}$ data and the observed trend for each single cation deeply differs from that of the reaction of 4-bromonitrosobenzene, represented by the straight line reported in the Figure 2. The reactivity in MP-AC is higher than that in BP-AC or LP-AC or SP-AC as clearly evidenced by the comparison of the relative rate in the the four systems at a $P_{i,eff}$ of 6000 bar: 282 (MP-AC), 132 (BP-AC), 105 (LP-AC), and 25 (SP-AC) and this can be considered the result of more (MP-AC) or less strong (SP-AC) specific interactions between the cation and **4**.

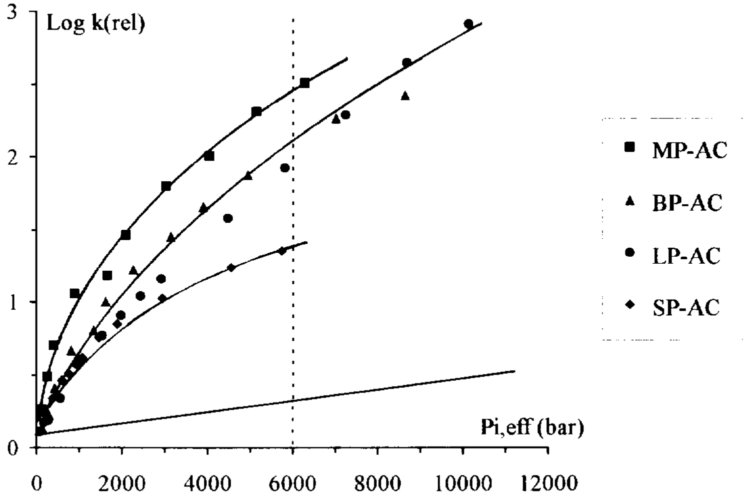


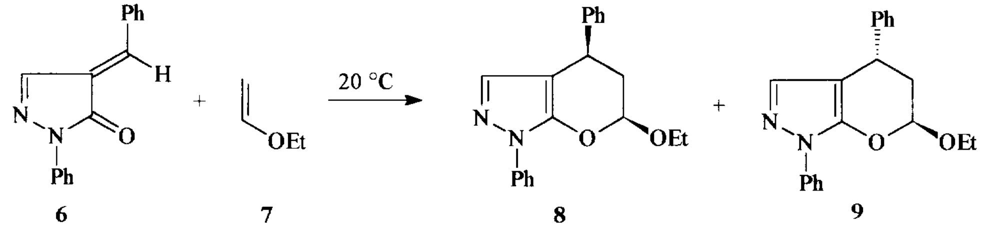
Figure 2. Plot of log k_{rel} of the DA reaction **4** + **2** *vs* Pi,eff. of solutions with varying concentrations of the different perchlorates in acetone.

In order to obtain more detailled informations on the mechanism of action of perchlorate-organic solvent solutions, the influence on differing pericyclic reactions of LP dissolved in several organic solvents [DEE, acetonitrile (AN), AC, DMSO and methanol (MEOH)] or the effect of various perchlorates [MP, BP, LP, SP, potassium (PP), and cesium (CP)] was tested.

Effect of LP in differing solvents on reactivity.

The effect of the solvent on the activity of LP was investigated on the DA reactions of **1** and **4** with **2** and of 1-phenyl-4-benzylidene-5-pyrazolone (**6**) with ethyl vinyl ether (**7**)^6 (Scheme 3).

Scheme 3



The kinetic data not already published^{6,8} were determined by u.v.-vis. spectroscopic analysis of the disappearing chromophores under pseudo-first order conditions (see experimental for details). The rate constants, average of at least three independent kinetic runs, are reported in Table 2.

The values of $P_{i,eff}$ are not available for all LP-solvent systems but the relative rate of the DA reaction of **1** and **2** can be used as a reference to discuss the kinetic results in terms of internal pressure. When the log k_{rel} values of the above DA reactions in LP-solvent solutions were plotted *vs* those of 4-bromonitrosobenzene the graphs reported in Figure 3 were obtained.

From the plots in Figure 3 it is evident the differing rate enhancements of solutions having the same value of k_{rel} for the reaction of **1** and **2** (hence the same $P_{i,eff}$ values for the above assumption) on both the reactions: **6** with **7** and **2** with **4**.

At a k_{rel} value of 1.3-1.35 for the reference reaction of **1** (whose $P_{i,eff}$ is about 800 bar), the k_{rel} values of the reaction of **6** in the differing solvents are: 176 (DEE), 43.8 (AN), 11.4 (AC), 1.6 (MEOH), and 1.7 (DMSO), and those of the reaction of **4** are: 82.6 (DEE), 12.4 (AN), 3.8 (AC), and 1.6 (DMSO).

As these values approach 1 (hence come close to the straight line of the reference with slope = 1 in the graph) the kinetic effect can be assigned to the internal pressure of the medium. This occours with strong polar and basic solvents (MEOH and DMSO) strongly solvating the lithium cation and making it less free to interact with the substrate.[6,7]

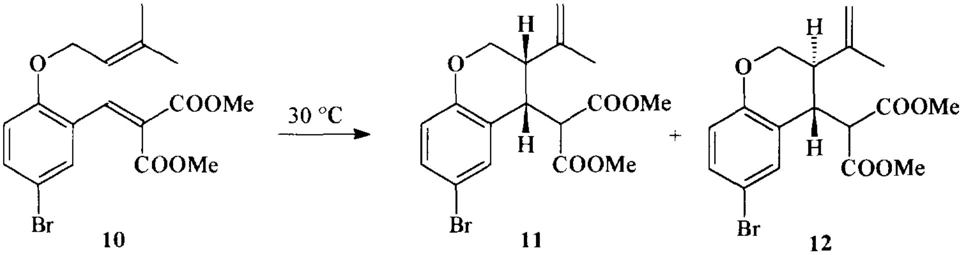
For rates increased by a factor of 10-10^2, the specific coordination between the lithium cation and substrate has to be admitted and diethyl ether is the best solvent to exalt the catalytic effect of Li^+, followed by acetonitrile and acetone.

Effect of different perchlorates in acetone or DMSO solutions on reactivity.

The effect of differing perchlorates was tested on the DA reactions between **2** and **1** or **4**,[8] and on the intramolecular ene reaction (IER) of 5-bromo-2(3-methyl-2-bunenyloxy)benzylidene malonic acid dimethyl ester (**10**),[16] (Scheme 4). Acetone or DMSO were the solvents for solubility reasons.

The kinetic data, some of them published in a previous paper,[8] are reported in Table 3.

Scheme 4



The kinetic effect of the differing perchlorates on the DA reaction of **1** and **2**, always small in both solvents, is in full accordance with the model involving only a change of the internal pressure of the medium.

Table 2. Rate constants[a] for DA reactions in LP/organic solvent solutions.

System	[M]	**1** + **2** (20 °C)		**6** + **7** (20 °C)		**2** + **4** (30 °C)	
		$10^3 \times k$ ($M^{-1} s^{-1}$)	k_{rel}	$10^4 \times k$ ($M^{-1} s^{-1}$)	k_{rel}	$10^5 \times k$ ($M^{-1} s^{-1}$)	k_{rel}
LP-DEE	0	1.7	1	0.35[b]	1	0.2	1
	0.1	1.8	1.05	28.5[b]	81.4	2.7	14
	0.25	2.0	1.2	48.5[b]	139	10.9	55
	0.5	2.2	1.3	61.5[b]	176	43.8	219
	0.75	2.7	1.6	68.5[b]	196	72	360
	1.0	2.9	1.7	79.0[b]	226	102	510
	1.33	3.2	1.9	87.0[b]	249	152	760
	2.0	4.9	2.9	104[b]	297	262	1310
LP-AN	0	5.5	1	0.71[b]	1	1.87	1
	0.1	5.7	1.04	6.96[b]	9.8	3.10	1.7
	0.3	6.2	1.1	10.9[b]	15.4	7.53	4.0
	0.5	6.7	1.2	16.2[c]	22.8	12.5	6.7
	0.79	7.2	1.3	31.1[b]	43.8	23.1	12.4
	1.0	8.0	1.45	35.9[b]	50.6	31.8	17.0
LP-AC	0	3.7[d]	1	0.59[b]	1	1.0[d]	1
	0.1	4.1[d]	1.1	1.58[b]	2.7	1.5[d]	1.5
	0.3	4.5[d]	1.2	4.37[b]	7.4	2.2[d]	2.2
	0.5	5.0[d]	1.35	6.7[b]	11.4	3.8[d]	3.8
	1.0	5.8[d]	1.6	12.5[b]	21.2	8.1[d]	8.1
	1.4	7.0[d]	1.8	21.9[b]	37.1	14.6[d]	14.6
	2.0	9.0[d]	2.4	43.0[b]	72.9	38.3[d]	38.3
LP-MEOH	0	5.4	1	8.0[b]	1	---	---
	0.5	7.35	1.4	12.6[b]	1.6	e	---
	1.0	9.2	1.7	25.6[b]	3.2	e	---
	2.0	13.1	2.4	56.0[b]	7	e	---
LP-DMSO	0	14.3	1	1.38	1	5.7	1
	0.5	15.7	1.1	1.66	1.2	7.8	1.4
	0.8	18.3	1.3	2.29	1.7	9.1	1.6
	1.0	21.5	1.5	2.69	2.0	10.4	1.8
	2.0	30.5	2.1	5.05	3.7	20.1	3.5

[a] The experimental error was in the limit ±3%. [b] Value taken from Ref. 6. [c] Value interpolated from the kinetic data reported in Ref. 6. [d] Value taken from Ref. 8. [e] The kinetic determinations cannot be performed due to the instability of **4** in such reaction media.

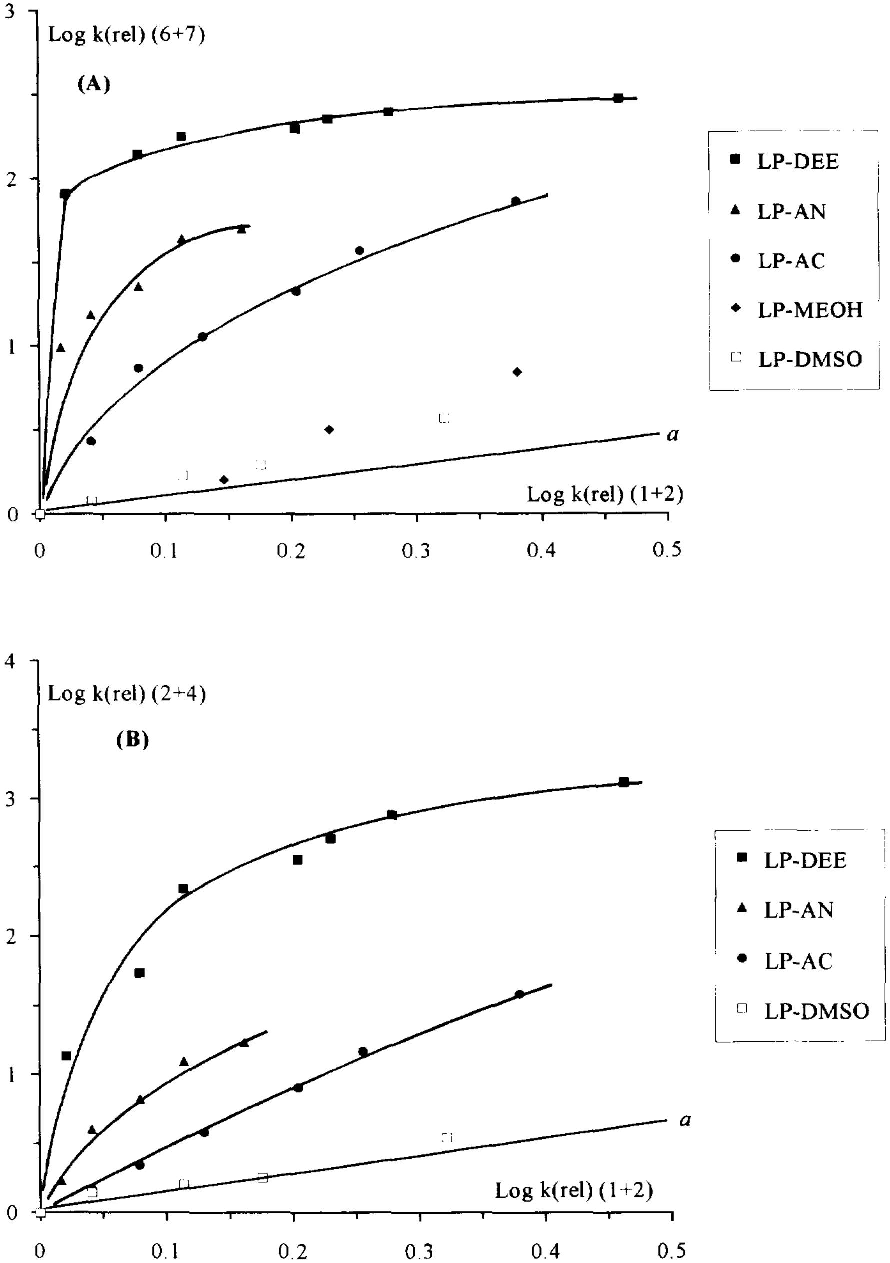


Figure 3. Plot of log k_{rel} of the DA reaction between **6** and **7** (A) and that of **4** and **2** (B) *vs* log k_{rel} of the DA reaction between **1** and **2** at varying concentrations of LP in differing solvents. The straight line (*a*) refers to log k_{rel} (**1** + **2**) on both x and y axes ($\rho = 1$).

Table 3. Rate constants[a] for DA and intramolecular ER in differing perchlorate-DMSO or AC solutions.

System	[M]	**1 + 2** (20 °C)		**2 + 4** (30 °C)		**10** (30 °C)	
		10^3 x k (M^{-1} s^{-1})	k_{rel}	10^5 x k (M^{-1} s^{-1})	k_{rel}	10^7 x k (s^{-1})	k_{rel}
AC	0	3.7[b]	1	1.0[b]	1	0.019[d]	1
MP-AC	0.05	4.2[b]	1.1	1.84[b]	1.8	115	6100
	0.1	4.5[b]	1.2	3.1[b]	3.1	509	26800
	0.5	5.5[b]	1.5	15.4[b]	15.4	4400	230000
	1.0	8.1[b]	2.2	102[b]	102	17500[d]	910000
	1.4	12.5[b,c]	3.4	324[b]	324	49400	2600000
BP-AC	0.1	4.6[b]	1.2	1.70[b]	1.7	---	---
	0.5	5.8[b]	1.6	6.43[b]	6.4	---	---
	0.8	6.82[b]	1.8	16.9[b]	16.9	10.2[e]	540
	2.0	16.0[b]	4.3	267[b]	267	54.0[d]	2,800
LP-AC	0.5	5.0[b]	1.35	3.8[b]	3.8	---	---
	1.0	5.77[b]	1.6	8.1[b]	8.1	3.5	180
	2.0	8.7[b]	2.35	38.3[b]	38.3	13.7	720
	3.0	15.8[b]	4.3	196[b]	196	46.1	2,400
	4.0	22.6[b]	6.1	814[b]	814	160[d]	8,400
SP-AC	0.5	4.85[b]	1.3	2.20[b]	2.2	f	---
	1.0	5.84[b]	1.6	4.19[b]	4.2	f	---
	1.8	8.1[b]	2.2	10.7[b]	10.7	f	---
	2.6	10.5[b]	2.8	22.7[b]	22.7	f	---
DMSO	0	14.3	1	5.7	1	f	---
MP-DMSO	0.5	26.1	1.8	10.4	1.8	f	---
BP-DMSO	0.5	22.7	1.6	10.35	1.8	f	---
	0.8	28.4	2.0	15.0	2.6	f	---
LP-DMSO	0.5	15.7	1.1	7.8	1.4	f	---
	1.0	21.5	1.5	10.1	1.8	f	---
	2.0	30.5	2.1	20.1	3.5	f	---
SP-DMSO	0.5	16.3	1.1	7.85	1.4	f	---
	1.0	20.6	1.4	10.4	1.8	f	---
PP-DMSO	0.5	16.0	1.1	8.15	1.4	f	---
	1.0	21.7	1.5	10.4	1.8	f	---
	2.0	27.2	1.9	16.6	2.9	f	---
CP-DMSO	0.5	16.3	1.1	7.75	1.35	f	---
	1.0	21.1	1.5	10.2	1.8	f	---

[a])The experimental error was in the limit ±3%. [b])Value taken from Ref. 8. [c])Value at 1.3 M. [d])Value taken from Ref. 16. [e])Value at 1.0 M. [f])No reaction was observed in such media.

The reaction of naphthoquinone **4** have the solvent dependent effect shown by the plots reported in Figure 4A. If DMSO is the solvent, the kinetic data approach the reference line (a): the solvation of the cations prevents any their ability to behave as electrophiles and the resulting small effect can be considered largely due to the increase of the internal pressure. When acetone is the solvent large kinetic effects in the range $10\text{-}10^2$ are observed. Magnesium perchlorate is the most active catalyst followed by BP, LP, and SP in the order.

If this effect is a signe of the cation catalysis, the rate enhancement shown by the IER of **10** cast any doubt on the role of the inorganic perchlorates. The uncatalyzed reaction of **10** is not easy and requires heating at 130 °C, hence it is not surprising that no reaction is observed at 30 °C in DMSO with all perchlorates. In acetone SP is again inactive, but LP, BP, and MP have the very large kinetic effect shown by Figure 4B. The first two cations give k_{rel} increase up to an order of 10^3; MP-AC is a specific catalyst of the reaction and a 1.4 M solution increase the rate of the IER 8×10^5 times more than the DA reaction of **1** and **2**.

Furthermore the greater rate enhancements observed for the IER of **10** than those of the DA reaction of **4**, are not compatible with the dependence on $P_{i,eff}$ and $\Delta V^{\neq}$ since an intramolecular pericyclic process is expected to have $\Delta V^{\neq}$ less negative than an intermolecular one and hence also a lower rate enhancement with the increase of the internal pressure of the medium.

CONCLUSION

The data reported in this paper support the observation that strong rate enhancement of DA and ene reactions are evidenced when the metal perchlorate behaves as a Lewis acid giving rise to specific solute-cation interactions. The comparison of the k_{rel} in the four perchlorate-acetone solutions with very similar values of $P_{i,eff}$ (Table 4) reveals that SP-AC 2.3 M (4550 bar) is a little more active than MP-AC 1.0 M (4053 bar) for the reaction of **1** and **2**, but is about 5 times less active in the reaction of **4** and **2**. This difference become dramatic for the IER of **10**, where no reaction was observed in SP-AC, while the reaction in MP-AC is completed within few minutes.

Table 4. Comparison at similar $P_{i,eff}$ values of k_{rel} data for the DA reactions of **4** and **2**, and the IER of **10**.

System	MPAC 1.0 M	BPAC 1.2 M	LPAC 2.0 M	SPAC 2.3 M
$P_{i,eff.}$	4053	3905	4290	4550
k_{rel} (**1** + **2**)	2.2	2.4	2.35	2.6
k_{rel} (**4** + **2**)	102	45.8	38.3	17.5
k_{rel} (**10**)	910000	≈ 600	720	no reaction

The $\Delta V^{\neq}$ of the reaction of **10** can be reasonably considered constant within the series of perchlorates, then the model based on $P_{i,eff.}$ and $\Delta V^{\neq}$ cannot give a satisfactory explanation for the observed behaviour.

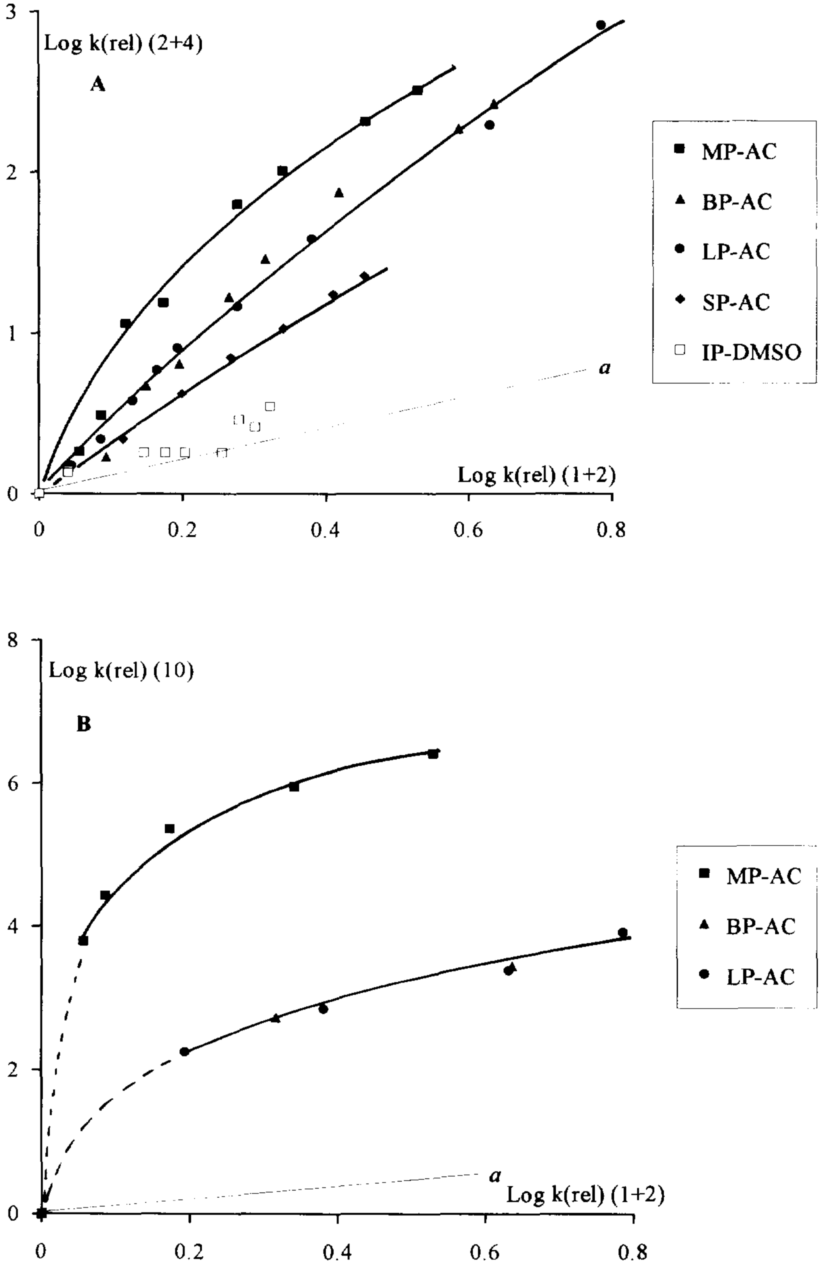


Figure 4 Plot of log k_{rel} of the DA reaction between **2** and **4** (**A**) and of log k_{rel} of the IER reaction of **10** (**B**) *vs* log k_{rel} of the DA reaction between **1** and **2** at varying concentrations of differing perchlorates in acetone and DMSO. The straight line (*a*) refers to log k_{rel} (**1** + **2**) on both x and y axes ($\rho = 1$).

Analogously the rate enhancement found in the reactions of **4** and **6** are again interpretable with a specific interaction of the cation acting as a Lewis acid, while the small rate increase of the reaction of 4-bromonitrosobenzene or that of the other substrates in strong polar and basic solvents (MEOH and DMSO) is conceivable with non specific interactions as the increase internal pressure of the reaction medium.

EXPERIMENTAL SECTION

Materials. Dimethyl butadiene (**2**) was a commercial, freshly distilled product; 1,4-naphthoquinone (**4**) was a commercial recrystallized product. All other product have been already described: **1** and **3**;[10] **5**;[18] **6**, **8**, and **9**;[6] **10-12**.[16] The solvents for the kinetic runs were distilled anhydrous u.v.-vis. spectroscopic grade reagents. The metal perchlorates were grade reagent; with the exclusion of MP, all other salts were dried under vacuum at 140 °C for 8 hours (caution: all perchlorates are potential explosives and must be handled with care).[17]

Kinetic determinations. The overall reaction rates were measured by following the disappearance of the chromophore **1**, **4**, **6**, and **10** on a Perkin Elmer Lambda 16 spectrophotometer provided with a thermostated cell transport assembly and an automatic multicell programmer. The solutions were measured in 1.00 cm OS Hellma couvettes with 3 ml capacity . Measuraments were taken at wavelengths of 740-760 nm for **1**, 340-360 nm for **4**, 410-440 nm for **6**, and 370-380 nm for **10** depending on the salt and on its concentration.

The needed amount of metal perchlorate was weighed in a 10 ml volumetric flask; weighed amounts of the chromophore were added to the salt-solvent solution (25-30 mg of **1**, and 2-3 mg of **4** or **6**). The solution of DMB or EVE was prepared by adding **2** or **7** (0.3-0.5 g) to an accurately weighed 5-mL volumetric flask containing *ca.* 3 mL of the required solvent. After the reagent addition, the flask was again weighed for an accurate determination of the DMB or EVE concentration and then filled with the solvent. Three samples of the solution containing the chromophore (2 mL measured with a calibrated syringe) were placed in three cuvettes thermostated at the required temperature, and constant amounts of the DMB or EVE solution (0.25-0.50 mL) were added. After vigorous mixing, the kinetic determinations were initiated. For the IER of **10**, a slightly different procedure was followed. Variable amounts of the salt solutions (*ca.* 2.5 mL), prepared as described above, were directly thermostated at 30 °C. Amounts of **10** were then added to the solution in order to obtain absorbance values in the range 0.8-1.6 A. After vigorous mixing the kinetic determinations were initiated.

The rate constants for the DA reaction of **4** in pure dee at 30 °C was determined by extrapolation of the Arrenhius diagramm. To a half-filled 25 ml volumetric flask were added about 10 mg of **4**, about 1.0 g of DMB, and the flask was then filled with the solvent. Seven samples were prepared for each run. At t=0, the samples were placed in a thermostat at the required temperature, and the initial absorbance of the solution was determined on a further sample. At appropriate time intervals the reaction was quenched and the residual absorbance of **4** was determined. The determinations were performed in the range 60-75 °C with the results: $10^5 \times k\ (M^{-1}sec^{-1}) = 2.35 \pm 0.05$ (60 °C), 3.2 ± 0.1 (65 °C), 4.5 ± 0.15 (70 °C), and 6.7 ± 0.1 (75 °C). From these data a $\Delta H^\ddagger$ of 15.4 ± 0.8 kcal mol^{-1} and a $-\Delta S^\ddagger$ of 34 ± 2 e.u. were calculated.

Determination of the [11]/[12] ratio. This was performed by ^{1}H-Nmr: 15-20 mg of **10** were allowed to react in the perchlorates solutions (5 ml - 30 °C). The reaction mixture was then quenched in water, extracted with dichloromethane, evaporated to dryness, the residue dissolved in $CDCl_3$, and the ^{1}H-Nmr was then recorded. The data reported are the average of at least three independent experiments, and the error is in the limit ± 0.5 %. MP-AC: 76:24 (0.05M), 77:23 (0.5M), 81:19 (1.0 M), and 83:17 (1.4 M); BP-AC: 82:18 (1.0 M) and 84.5:15.5 (2.0 M); LP-AC: 85:15 (2.0 M), 87:13 (3.0 M), and 89:11 (4.0 M).

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