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The Nature of Lithium Perchlorate and Gallium Chloride Salt Effect in Cycloaddition Reactions.

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Abstract: *Comparing the acceleration effects of (4+2)-, (3+2)- and (2+2)-cycloaddition reactions in the presence of the salts of two types: gallium chloride in inert solvents and lithium perchlorate (LP) in diethyl ether (DE) it was observed that in the presence of $GaCl_3$ the acceleration effect is approximately the same (10^4 times) for the studied reactions, while in LPDE medium for the same reactions strong increase (up to 10^4 times), weak increase or even decrease of the rate and equilibrium constants take place even with the common dienophile depending on the nature of the second reagent. It was suggested that the acceleration effect of cycloaddition reactions in the presence of such Lewis acids as aluminum, gallium or boron halides is due to the sharp increase of π-acceptor properties of dienophiles and therefore increasing energy of orbital interaction, whereas LPDE medium demonstrates strong stabilization of static and/or dynamic polar forms and favors reactions with charge control.*

INTRODUCTION

The special interest to the investigation of organic reactions in salt solutions[1-8] is determined by the considerable increase of the rate of even those processes which have traditionally been considered to be low sensitive to the effects of the medium[9,10] as well as by the possible change of the direction of the reactions.[4,11,12] Current literature describes a number of examples with the easier course of reactions in LPDE medium. In the presence of LP under mild conditions and with high yield were obtained new cyclobutane adducts[11,12] which are sometimes hard to reach in common solvents.

The considerable acceleration of the Diels-Alder reaction is observed when water is used instead of organic solvents.[2,3] An even greater acceleration effect of cycloaddition reactions is observed when these reactions are performed in inert solvents in the presence of such Lewis acids as $AlHal_3$, $GaHal_3$ and $BHal_3$ where the rate of reaction increases up to 10^6 times.[10] The formation of stable *n,v*-complexes between of dienophiles and these salts was shown.[10,13,14] The sharp increase of the electrone affinity energy of activated dienophiles was concluded from the comparison of the changes of the charge transfer band energy of their π,π-complexes with hexamethylbenzene: 0.7-1.1 eV and 1.0-1.25 eV for maleimides activated by $GaCl_3$ and by $AlCl_3$ respectively.[14]

Some physical properties of LPDE solutions (electric conductivity, viscosity, density, partial molar volumes, vapor pressure and the composition of complexes) have been studied in the broad range of the salt

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concentration.[15,16] The catalytic effect of metal halides (MX_3) is usually studied in the solvents, which are not able to form *n,v*-complexes. On the contrary, the acceleration effect of reactions in the presence of $LiClO_4$ is usually studied in diethyl ether, which itself forms strong *n,v*-complexes (DN 19.2 ,Ref. 17).

Several explanations of the acceleration effect of reactions in the LPDE medium have been offered, including solvophobic interaction of the reagents, just as observed in going from usual organic solvents to water or to salting-out water-salt solutions[2,3,18], internal pressure in the LPDE medium[4] and the possible catalysis by the Li^+ cation as a Lewis acid.[6,7,19]

RESULTS AND DISCUSSION

Diels-Alder reaction. The results of kinetic measurements of the Diels-Alder (D-A) reactions in LPDE medium are given in Table 1. These data show that depending on the nature of the reagents and the solvent these effects may differ greatly. The enhanced acceleration of the rate is observed in the cases of reactions involving such dienophiles as dimethyl maleate, anhydride or imide of maleic acid, naphthoquinone and such dienes as cyclopentadiene and furan (reactions 2, 3, 5, 6, 11, 14, Table 1). For studied dienes the weak acceleration effect in the LPDE medium is observed in the reactions with substituted anthracenes and 1,3-diphenylisobenzofuran (reactions 7, 8, 9, 15, Table 1). In the case of dienophiles the low acceleration effect is observed in the reactions involving acrylonitrile (reactions 1, 8, Table 1).

Table 1. Rate constants (k, l $mol^{-1}s^{-1}$) of some cycloaddition reactions in $LiClO_4$ solutions (C_S, mol l^{-1}) at 25 °C and values of the slopes (K_S, eg-n 3).

Cyclopentadiene + acrylonitrile (r-n 1)

LPDE, K_S=0·25

C_S	0	1·0	2·0	3·1	4·0	4·6
10^6 k	8.8	53	97	180	350	386

Ethanol-LP, K_S=0·25

C_S	0	1·24	2·44	3·38	3·56	4·20	4·40
10^5 k	2·90	5·84	12·1	19·8	23·0	24·2	25·0

Cyclopentadiene + N-phenylmaleimide (r-n 2)

LPDE, K_S=0.32

C_S	0	0·038	0·075	0·15	0·38	0·77	1·53	2·77	3·46	4·60
10^2 k	2·52	15·6	42·9	85·7	370	507	1020	2410	5300	7900

Ethanol-LP, K_S=0.23

C_S	0	0.50	0.98	1.92	3.85
k	0.59	0.78	1.10	1.62	4.63

Tetrahydrofuran-LP

C_S	0	0.095	0.38	0.57	0.76	0.87	0.95
10^2k	5.45	6.85	9.30	10.7	13.0	14.3	17.0

Ethyl acetate-LP

C_S	0	0.097	0.386	0.773
10^2 k	6.32	9.25	14.8	23.9

Cyclopentadiene + dimethyl maleate (r-n 3)

LPDE, K_S= 0.21

C_S	0	0.10	0.20	0.50	1.0	2.0	3.1
10^4 k	0.14	9.85	17.3	29.7	39.5	69.8	101

Cyclopentadiene + dimethyl fumarate (r-n 4)

LPDE, K_S=0.21

C_S	0	0.10	0.20	0.49	1.0	2.0	3.1	4.0
10^4 k	7.2	16.9	29.8	60.0	104	164	281	428

Furan + N-phenylmaleimide (r-n 5)

LPDE, K_S=0.22

C_S	0	0.05	0.10	0.18	0.25	0.50	1.0	2.0	3.1	4.0
10^6k	6.6	55	108	229	378	850	1280	1970	3220	5300

Acetone-LP

C_S	0	0.50	0.99	1.97	2.8
10^5k	1.34	2.02	3.11	6.37	14.3

Cyclopentadiene + 3-buten-2-one (r-n 6)

LPDE

Cs	0	4.6
10^5k	3.3	1400

9,10-Dimethylanthracene + maleic anhydride (r-n 7)

LPDE, Ks=0.24

C_S	0	0.83	1.92	2.74	3.62
10^3k	9.4	20.6	38.6	65.5	93.9

Acetone-LP, K_S=0.26

Cs	0	1.01	1.74	2.78	3.75	4.15	4.54
10^3 k	8.78	15.2	16.7	32.9	68.3	96.9	150

9,10-Dimethylanthracene + acrylonitrile (r-n 8)

LPDE, K_S=0.26

C_S	0	0.7	2.03	3.83
10^6 k	1.9	3.2	9.0	20

LPDE[a]

Cs	0	1.20	1.82	2.99	3.88	4.55
10^6 k	1.28	4.34	5.37	8.11	9.85	11.4

Anthracene + tetracyanoethylene (r-n 9)

LPDE

C_S	0	4.20
k	0.24	4.4

3,6-Dicarbomethoxytetrazine + hexene-1 (r-n 10)

LPDE, K_S=0.24

C_S	0	0.59	1.0	2.0	2.8	3.6
10^2 k	5.25	10.5	15.0	22.9	39.4	54.7

Cyclopentadiene + maleic anhydride (r-n 11)

LPDE

C_S	0	4.6
10^2 k	2.3	3800

trans,trans-1,4-Diphenylbutadiene + 4-phenyl-1,2,4-triazoline-3,5-dione (r-n 12)[b]

acetone-LP, K_S=0.27

C_S	0	0.31	0.50	0.80	0.99	1.2	1.4	2.0	2.5	3.0
k	0.85	0.94	1.03	1.09	1.20	1.32	1.51	2.08	2.97	3.26

2,3-Dimethylbutadiene + 1-bromo-4-nitrosobenzene (r-n 13)[b]

acetone-LP, K_s =0.20

C_S	0	0.06	0.10	0.31	0.50	0.82	1.0	1.94	3.0
10^3 k	3.7	3.9	4.1	4.5	5.0	5.4	5.8	8.7	15.8

2,3-Dimethylbutadiene + naphthoquinone-1,4 (r-n 14)[b]

acetone-LP, K_S=0.72

C_S	0	0.10	0.32	0.80	1.2	2.0	2.5	3.0	3.5	4.0
10^5 k	1.0	1.5	2.2	5.9	11.1	38.3	84	196	443	814

1,3-Diphenylisobenzofuran + N-phenylmaleimide (r-n 15)

LPDE, $K_s \approx 0$

C_S	0	0.24	0.50	1.63	3.0
k	4.92	6.67	7.47	7.46	7.42

Diphenyldiazomethane + acrylonitrile (r-n 16)

LPDE, K_S=0.23

C_S	0	0.50	1.0	2.0	3.0
10^4 k	6.26	22.5	35	54	86

C,N-Diphenylnitrone + N-phenylmaleimide (r-n 17)

LPDE, K_S= -0.23

C_S	0	1.0	3.1	4.0
10^3 k	5.30	3.34	1.17	0.59

C,N-Diphenylnitrone + N(*p*-bromophenyl)maleimide (r-n 18)

acetone-LP, K_S= -0.20

C_S	0	1.0	2.0	3.0
10^3 k	2.41	1.47	1.07	0.58

Vinylethyl ether + tetracyanoethylene (r-n 19)

LPDE, K_S=0.46

C_S	0	0.025	0.062	0.123	0.202	0.45	0.78	0.94	1.41	2.0
10^3 k	1.61	5.94	8.96	15.6	22.5	34.9	69.5	80.8	136	252

α-Methylstyrene + tetracyanoethylene (r-n 20)

LPDE, K_S=0.49

C_S	0	0.20	0.50	1.0	1.5	2.0	3.0	4.0
10^6 k	0.4	22.4	78.6	251	520	809	3040	7530

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[a] At 28 °C from Ref.6. [b] Data for reactions (12,13) at 20 °C and for r-n (14) at 30 °C is taken from Ref. 8.

Since the solubility of LP in inert solvents (e.g., benzene) is very low, it is useful to compare the effect of the competive formation of complexes with two donors - dienophile and DE, on the acceleration of reactions in the presence of gallium chloride and lithium perchlorate . Gallium chloride is chosen because of its high solubility even in alkanes.[10,14] Data on the effect of the additives (diethyl ether and acetonitrile) on the reaction rate of 9,10-dimethylanthracene with the acrylonitrile and ethyl acrylate in the presence of $GaCl_3$ are given in Table 2.

Table 2. First order rate constants of the Diels-Alder reactions of 9,10-dimethylanthracene with acrylonitrile (reaction 1) and ethyl acrylate (reaction 2), and cyclopentadiene with acrylonitrile (reaction 3) in the media of dienophiles, diethyl ether, acetonitrile and there mixtures in addition of $GaCl_3$ or $LiClO_4$ at 25 °C.

Reaction 1

$C_{\text{acrylonitrile}}$ (mol l^{-1})	$C_{\text{diethyl ether}}$ (mol l^{-1})	C_{CaCl_3} (mol l^{-1})	10^4 k_{obs} (s^{-1})	K_7/K_2 [a]
15.02	0	0	0.244	-
14.40	0	0.43	133.1	-
11.27	2.41	0.39	19.3	26.2
7.77	4.64	0.32	6.20	27.2
3.92	7.28	0.33	2.39	24.1
1.49	8.67	0.34	0.79	23.9

$C_{\text{acrylonitrile}}$	$C_{\text{diethyl ether}}$	C_{LiClO_4}	k_2, (l mol^{-1} s^{-1})
0.1	9.50	0	1.9×10^{-6}
0.1	9.1	0.7	3.0×10^{-6}
15.2	0	0	1.6×10^{-6}
14.6	0	0.7	3.4×10^{-6}

$C_{\text{acrylonitrile}}$	$C_{\text{acetonitrile}}$	C_{CaCl_3}	10^4 k_{obs} (s^{-1})	K_7/K_2
11.63	4.78	0.37	17.4	15.5
9.53	7.24	0.35	9.15	16.1
7.51	9.53	0.32	5.57	14.9
5.77	11.94	0.31	3.43	14.5
3.85	14.61	0.29	1.41	18.6

Reaction 2

$C_{\text{ethyl acrylate}}$	$C_{\text{diethyl ether}}$	C_{CaCl_3}	10^4 k_{obs} (s^{-1})	K_7/K_2
9.24	0	0	0.051	-
8.90	0	0.36	61.5	-
6.92	2.41	0.34	17.7	6.2
4.62	4.86	0.33	6.00	7.2
2.31	7.22	0.36	3.53	5.9
1.15	8.42	0.35	1.64	7.8

Reaction 3

$C_{\text{acrylonitrile}}$	$C_{\text{diethyl ether}}$	C_{LiClO_4}	k_2, (l mol^{-1} s^{-1})
0.1	9.50	0	8.8×10^{-6}
0.1	9.0	1.0	5.3×10^{-5}
15.2	0	0	1.5×10^{-5}
14.4	0	1.0	4.9×10^{-5}

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[a] K_7 and K_2 are the equilibrium constants for cosolvent and dienophile with $GaCl_3$ respectively. Initial concentrations of dienes are about 10^{-3} mol l^{-1}.

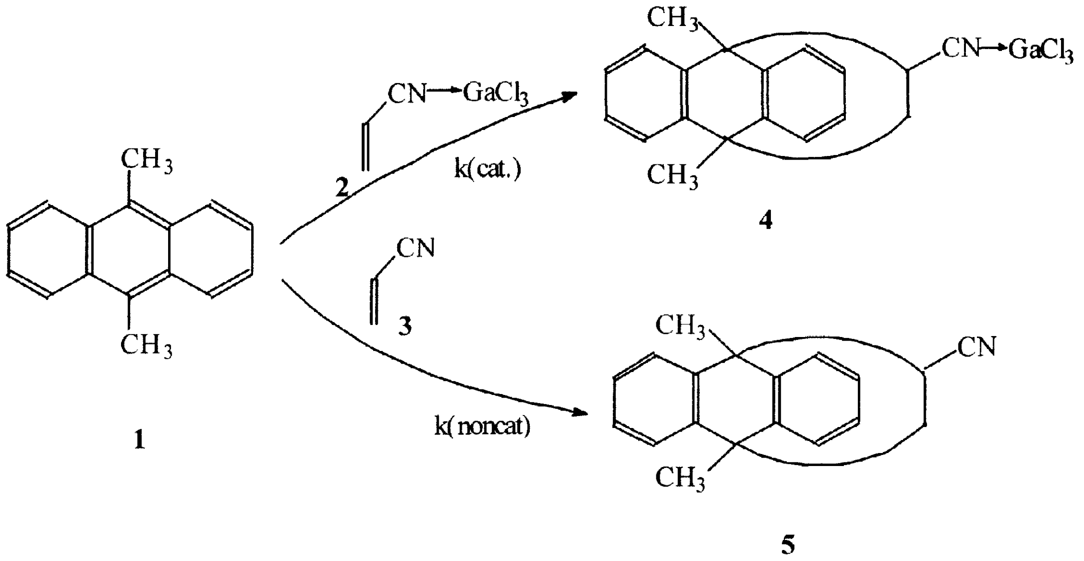
When the reaction with acrylonitrile or ethyl acrylate is carried out in the medium of the dienophile without the cosolvent all $GaCl_3$ is bound into a complex with the dienophile, and the acceleration effect equals 1.9×10^4 and 3.1×10^4 times respectively (Table 2). Near the same acceleration effect of these reactions in the presence of $GaCl_3$ (5.9×10^4 and 4.5×10^4 respectively) was obtained in benzene solution.[10] The addition of DE or acetonitrile leads to the redistribution of $GaCl_3$ because of the competing formation of *n,v*-complexes with dienophile and cosolvent (Scheme 1).

The concentration of the activated dienophile decreases with the increase of the concentration of *n*-donor cosolvent. In the medium of DE or acetonitrile the acceleration effect disappears. When concentration of the diene is considerably less than the concentration of dienophile and $GaCl_3$ the effective first order rate constant of the reaction is described by equation (1)

$$ln(C_{01}/C_1)/t = k_1 = k_{\text{cat.}} C_2 + k_{\text{noncat.}} C_3 \qquad (1)$$

The known values of the catalytic (k_{cat}), noncatalytic (k_{noncat}) and effective (k_1) rate constants allow one to calculate the equilibrium concentration of the complex (C_2) and the ratio of equilibrium constants for two complexes (K_7 / K_2) (Table 2).

When $GaCl_3$ is replaced by $LiClO_4$ the relative acceleration of the reaction of acrylonitrile with 9,10-dimethylanthracene in the medium of acrylonitrile or DE is practically the same (Table 2). For the reaction with cyclopentadiene the acceleration in LPDE is even higher than in the LP-dienophile medium. In addition, with the increase of the concentration of maleic anhydride in the LPDE medium (2.52×10^{-2} , 5.03×10^{-2}, 7.51×10^{-2}, 1.02×10^{-1} and 1.50×10^{-1} mol l^{-1}) the rate constant of the reaction with 9,10-dimethylanthracene at 25 °C decreases (0.171, 0.160, 0.142, 0.138 and 0.124 l mol^{-1} s^{-1}). If the mechanism of the activation of dienophile in the presence of LP and MX_3 is the same[6] then the acceleration effect of reaction must be higher in going from DE to acrylonitrile as a solvent. The experimental data (Table 2) do not agree with this supposition.



$$2 + \underset{6}{Et_2O} \overset{K}{\rightleftharpoons} \underset{7}{Et_2O \rightarrow GaCl_3} + 3$$

Scheme 1

The assumption about the activation of dienophiles in the presence of the LP in diethyl ether similar to the case of typical Lewis acids (MX_3) was resulted from such data.[6] The acceleration effect in the LPDE medium for the reaction of 9,10-dimethylanthracene with acrylonitrile is lower than that in the reaction with the fumaronitrile or with the dimethyl acetylenedicarboxylate where the dienophiles have two *n*-donor centers for the coordination of the salt. Besides, when going from the DE to the LPDE medium there was no change in the rate of the reaction of 1,3-diphenylisobenzofuran with styrene having no *n*-donor centers. We have repeated the measurements of the rate constant for the last reaction and obtained near the same results. But we have also found the absence of the acceleration effect in LPDE medium for reaction of 1,3-diphenylisobenzofuran with N-phenylmaleimide which has *two n-donor centers* for the coordination with the Lewis acid (r-n 15, Table 1).

In the D-A reactions of the type "diene-donor, dienophile-acceptor" in benzene solution in the presence of BCl_3, $GaCl_3$ and $AlCl_3$ the relatively stable acceleration effect (10^3, 10^4 and 10^5 times, respectively)[10] was observed. On the other hand, in the LPDE medium the acceleration effect differs greatly even for the reactions with the common dienophile (Table 1).

From near the same values of enthalpy of the complexes formation of the dienophiles and the adducts with the $GaCl_3$ follows that enthalpy of D-A reactions and the equilibrium constants both in the presence and in the absence of $GaCl_3$ are almost the same.[10] We observed in the LPDE medium (Table 3) that the rate constant of forward reaction of furan with maleimides (k_2) and the equilibrium constant (K_{eq}) increase with the increase of the concentration of LP in DE. This favorable combination of the effects of LPDE on the rate and equilibrium may be especially useful for carrying out slow and/or equilibrium processes.

Table 3. The rate and equilibrium constants of the reactions of furan with N-phenylmaleimide (reaction 1), and C,N-diphenylnitrone with N-(*p*-bromophenyl)maleimide (reaction 2) and with N-phenylmaleimide (reaction 3) in $LiClO_4$ solutions at 25 °C.

Reaction	Solvent	C_{LiClO_4} (mol l^{-1})	k_2 (l mol^{-1} s^{-1})	K_{eq} (l mol^{-1})
1	Diethyl ether	0	$(6.6\pm0.3)\times10^{-6}$	3.6±0.2
1	Diethyl ether	0.05	$(5.5\pm0.20)\times10^{-5}$ [a]	25±1.0
1	Diethyl ether	4.0	$(5.3\pm0.11)\times10^{-3}$	1180±30
2	Diethyl ether	0	$(6.12\pm0.30)\times10^{-3}$	4500±200
2	Diethyl ether	3.0	-	100±3
2	Acetone	0	$(2.41\pm0.10)\times10^{-3}$	2200±160
2	Acetone	1.0	$(1.47\pm0.10)\times10^{-3}$	530±13
2	Acetone	3.0	$(5.80\pm0.25)\times10^{-4}$	310±18
3	Diethyl ether	0	$(5.30\pm0.30)\times10^{-3}$	913±13
3	Diethyl ether	4.0	$(5.90\pm0.25)\times10^{-4}$	303±6

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[a] Experimental value of the rate constant of the adduct decomposition is $(2.30\pm0.30)\times10^{-6}$ s^{-1}.

As it was noted above, the acceleration effect of the D-A reaction with acrylonitrile or ethyl acrylate in the presence of the $GaCl_3$ in benzene is near the same as in the dienophile medium. The acceleration effect of the D-A reactions in the presence of the LP depends to a large extent on the polarity of the solvent (Table 1). The strongest acceleration effect is observed in the medium of the low polar DE. At low concentrations (0-0.3 *M* $LiClO_4$) the normal salt effect[20] usually takes place:

$$k_s = k_0(1 + B_s C_s) \qquad (2)$$

At high concentrations (0.5-5 *M* $LiClO_4$) the relation (3) is usually realized.

$$logk_s = D + K_sC_s \qquad (3)$$

Here k_s and k_o are the reaction rate constants in the salt solution and pure solvent, C_s is the molar concentration of the salt, and other values are the experimental constants. Equation (3) corresponds to the effects of the medium induced by the metal salts.[21]

The relation (2) formally corresponds to the catalytic process which has been studied in detail in solvolytic reactions in the presence of LP, where the observed strong acceleration effect is explained by the stabilization of the polar transition state by the salt solution.[20]. In the solvolytic reactions the value of the factor B_s (equation 2) decreases sharply with the increase of the dielectric constant of the solvent.[1,22] Similar dependence of factor B_s is observed and in the D-A reaction of cyclopentadiene with N-phenylmaleimide (Table 4).

Table 4. The effect of low concentration of $LiClO_4$ solutions in polar solvents on the rate acceleration (B_s, equation 2) in the Diels-Alder reaction of cyclopentadiene with N-phenylmaleimide (B_1) and solvolysis of 4-methoxyneophyle tosylate (B_2)

Solvent	Dielectric constant, ε	B_1	B_2[a]
Diethyl ether	4.2	147	298 000
Ethyl acetate	6.0	3.5	553
Tetrahydrofuran	7.4	2.0	482
Ethanol	24.3	1.0	-

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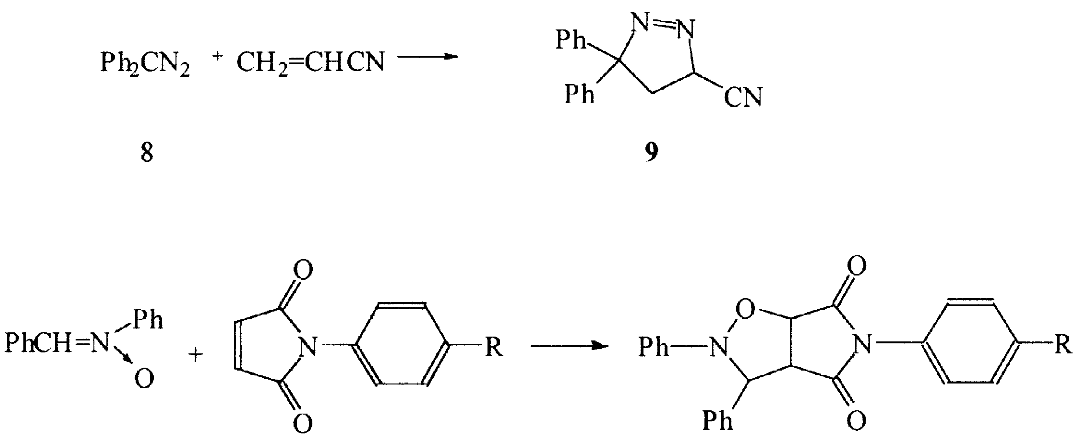
[a] The values of B_2 taken from Ref. 1.

In the reactions with the large acceleration effect in LPDE medium (reactions 2,3,5, Table 1) the main part of this effect takes place at low concentrations of LP (up to 0.3 *M* of the salt). At high concentrations of LP (0.5-5 *M*) most reactions display almost the same slope (K_s, Table 1).

Reactions of 1,3-dipolar cycloaddition. We have studied the reactions of the diphenyldiazomethane (**8**) with the acrylonitrile and C,N-diphenylnitrone (**10**) with maleimides (**11a,b**) (Scheme 2).

The LPDE effect in reaction of diphenyldiazomethane (reaction 16, Table 1) is similar to the effects in the studied Diels-Alder reactions. The LPDE effect in the reaction with dipolar nitrone (**10**) was unexpected (reactions 17, 18, Table 1). Here the values of the rate and equilibrium constants of the reactions (Tables 1, 3) *decrease* with the increase of the concentration of LP in DE and in acetone. The UV spectrum of the nitrone (**10**) in the LPDE medium does not have a new charge transfer band, but displays a slight hypsochromic shift of the n,π^*- absorption band (321.5 *nm* in diethyl ether). This is similar to the change of the low-energy absorption band of Reichardt' dye in polar solvents.[23] The effect of LPDE medium on E_T values of nitrone (**10**) correlates with Sauer' data[5] of LPDE effect on endo/exo ratio of adducts in the reaction of cyclopentadiene with methyl acrylate: E_T **(10)** = (9.64 ± 0.21) Ω + (84.40 ± 0.34) with r=0.995. In contrast to the case of the dienes, the solubility of nitrone (**10**) *does not decrease but increases* when the LPDE solution is used instead of DE.



8 9

10 11a,b 12a,b

R = H (**a**); R = Br (**b**)

Scheme 2

It is worth noting that the acceleration effect in the LPDE medium is usually greater for those Diels-

Table 5

Solvent effect on the rate constants of some cycloaddition reactions[9,10] at 25 °C : (1) - 9,10-dimethylanthracene + maleic anhydride; (2) - cyclopentadiene + N-phenylmaleimide; (3) - furane + N-phenylmaleimide; (4) - C,N-diphenylnitrone + N-(p-bromophenyl)maleimide; (5) - tetracyanoethylene + p-tolylvinylsulfide. $k_{rel.} = k_s/k_{Et_2O}$

Solvent	$E_T(30)$[a]	$k_{rel.}$ (1)	$k_{rel.}$ (2)	$k_{rel.}$ (3)	$k_{rel.}$ (4)	$k_{rel.}$ (5)
Diethyl ether	34.3	1	1	1	1	1[b]
1,4-Dioxane	36.0	1.2	2.8	2.5	0.81	-
Tetrahydrofuran	37.4	0.56	2.2	-	-	51
Ethyl acetate	38.1	0.94	2.5	-	-	67
Acetone	42.2	0.94	-	2.0	0.39	1140
Dimethylsulfoxide	45.0	1.5	16.4	-	0.36	-
Acetonitrile	46.0	1.5	-	3.0	0.33	9900

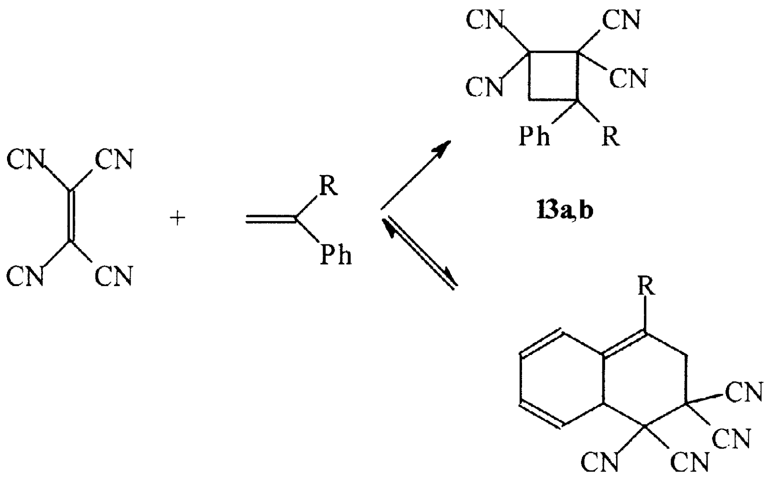
Ethanol	51.9	3.1	23.4	11.2	0.30	-
Formamide	56.6	17.9	90.5	42.4	-	-
0.5 M LPDE	52 [c]	1.7	171	129	0.6	200 [d]

[a] Ref. 23. [b] For dibutyl ether. [c] Estimated value [5]. [d] For reaction tetracyanoethylene + α-methylstyrene.

Alder reactions (Tables 1) which display greater acceleration in polar solvents (Table 5). On the contrary, the reaction rate of nitrone (**10**) with maleimide decreases in polar solvents (Table 5). Thus the LPDE medium affects the rate of the reaction like the strong polar medium.

The unusual effect of the LPDE on the rate of the reactions with the nitrone (reactions 16, 17, Table 1) differs drastically from effect of gallium chloride in benzene solution, where acceleration of this reaction is more than 5x10^4 times.[10,24]

Reactions of (2+2)-cycloaddition. For the reagents with the enhanced donor-acceptor interaction, the activation energy of of (2+2)-cycloaddition reactions usually decreases. Therefore we studied (2+2)-reactions with the high electron acceptor tetracyanoethylene (Scheme 3).



13a,b

14a,b

R = H (**a**)

R = CH_3 (**b**)

Scheme 3

Adduct (**14a**) was detected in the reaction performed under elevated pressure. When the pressure relieved this adduct breaks down quickly.[25] In 5*M* solution of LP in acetone, where the solubility of tetracyanoethylene is considerably higher than that in the LPDE, at room temperature we observed (^{1}H NMR) the quick accumulation of ~7% of the adducts (**14a,b**) whose concentrations then gradually decreased down to zero with nearly quantitative yield of the adducts (**13a,b**). We can conclude that in the salt solution the formation of (4+2) adducts (**14a,b**) is kinetically more preferable than the formation of the (2+2) adducts (**13a,b**) but here the chemoselectivity is determined by the thermodynamic control.

The acceleration effect of the reaction of α-methylstyrene with tetracyanoethylene in the LPDE medium is greater than in other studied reactions and makes $2\ 10^4$ times (r-n 20, Table 1). The enhanced sensitivity of the reaction rates of (2+2)-cycloaddition to the polarity of the solvent is well-known. It is in accord with its proved bipolar mechanism.[26] The correlation between the magnitude of the acceleration effect in the LPDE medium and the influence of the solvent polarity is also observed (Table 5). The effect of the high concentration of the LP in diethyl ether on the rate of the (2+2)-cycloaddition reactions of tetracyanoethylene with ethylvinyl ether and α-methylstyrene (Ks, Table 1) is significantly higher than in the Diels-Alder reactions.

CONCLUSION

The effects of $GaCl_3$ and $LiClO_4$ on the rate and the equilibrium of the studied reactions considered as a whole show that the mechanisms of the effect of these salts differ considerably.

All the experimental data on the effects of aluminum, gallium and boron halides on cycloaddition reactions in inert solutions are in accord with the mechanism of the coordination of these Lewis acids on *n*-donor center of the reagent with the following consequences: near the same acceleration effect in the reactions of dienophile with dienes of different structures, the weak change in the equilibrium parameters of the reactions, the sharp reduction of the acceleration effect when the *n*-donor cosolvents are added, the considerable bathochromic shift of the long-wave n-π^* absorption band of the dienophiles when n,v-complexes are formed with these salts, and the considerable decrease of the π-π^* charge transfer energy in the intermolecular π-π - complexes with hexamethylbenzene.

The cycloaddition reactions in LPDE medium are characterized by a different set of features: the variety of kinetic salt effects in the reactions even with the same dienophile, namely, from acceleration to retardation depending on the structure of another reagent; the considerable change of the equilibrium constants of the reactions; weak decrease or even increase of the rate of reactions when diethyl ether as cosolvent is added; the distinct manifestation of polar rather than donor-acceptor properties of the LPDE medium.

These data on the effect of the LPDE at low concentrations of the salt correspond better to the mechanism of the electrostatic stabilization of the static and/or the dynamic polar states by the LPDE medium. In this case the maximum stabilization energy is realized in diethyl ether - the media with large donor number, but low dielectric constant. All salts can be considered in terms of Lewis acids with certain part of covalent and electrostatic contribution in the interaction energy of acid-base complexes.[27] For relatively soft Lewis acids as $AlHal_3$ and $GaHal_3$ the main contribution to the donor-acceptor interaction energy is covalent bonding and for $LiClO_4$ as hard Lewis acid - electrostatic bonding.[27] This is in agreement with the fact that the effect of the LP on the rate of the solvolytic and the cycloaddition reactions is determined not by the *n*-donor properties of the solvent but by its polarity (Table 4).

Houke[30] and Pagni[31] also had doubt about the same mechanism of the effects of LPDE solutions and common Lewis acids (MX_3). The mechanism of electrostatic stabilization by the LPDE medium can explain a number of peculiarities in the experiments. For example, the retardation of the reaction rate involving nitrone (reactions 17, 18, Table 1) can be due to the stabilization of this 1,3-dipole to a greater extent than to the transition state, when going from diethyl ether to the LPDE solution. The correlation between the value and direction of the effect of solvent polarity on the rates of the studied reactions and the observed LPDE effect is also understandable. Very low equilibrium constant for a complex of diethyl ether with $LiClO_4$ [15,16] in comparison with $GaCl_3$ [10,14] is in accord with this assumption.

EXPERIMENTAL

Materials and Methods. Stability of reagents, products and reaction pathway in LP solutions were analyzed by UV- and NMR-spectroscopy. No side reactions were observed.

Lithium perchlorate was dried in vacuum (~100 Pa) at 160 °C for 25-30 hours up to m.p. 240 °C (in sealed tube). Molarity of LPDE solutions (C_{LPDE} up to 5 mol l^{-1}) were calculated from correlation: $C_{LPDE} = 6.1217x10^{-2}\ P + 9.67x10^{-4}\ P^2$ (N=31, R=0.9999), where P is per cent by weight of LP in diethyl ether solution.

Purified solvents were stored under molecular sieves (4A). Furan, cyclopentadiene, 3-buten-2-one and acrylonitrile were redistilled immediately before use.

All kinetics and equilibrium measurements were performed following the change in absorbance at appropriate wavelengths in quartz cell with fine fitted stopper, that was placed in a thermostated cell compartment of a "Specord UV-VIS" spectrophotometer. For highly volatile cyclopentadiene and furan quartz cells were used with going on sealed narrow molybdenum glass tube. ^1H-spectrum were performed on spectrometer " Varian HA-100D" (100 MHz) and ^{13}C spectrum on "Bruker-WH-90" (22.63 MHz) with HMDS as standard.

All reagents and products have been described in literature except for two cyclobutanes (**13a,b**).

1,1,2,2-Tetracyano-3-phenylcyclobytane (**13a**) To a solution of styrene (0.35 g) and tetracyanoethylene (0.41 g) in 5 ml of anhydrous acetone was added dried lithium perchlorate (4.7 g). The mixture was dissolved with magnetic stirring at room temperature and after 6 h white crystal product was filtered off, washed with pentane and than diethyl ether. Yield 0.31 g (41 %), m.p. 157-158 °C. Found (%): C 72.84; H 3.44; N 23.40. $C_{14}H_8N_4$ requires C 72.41; H 3.44; N 24.14.

^1H NMR {100 MHz; $(CD_3)_2CO$} δ_A 3.85 , δ_B 3.61 , δ_X 4.95 (3 H, $^2J_{AB}$ 12.5, $^3J_{AX}$ 11 Hz, $^3J_{BX}$ 9Hz, ABX system), 7.5 (s, 5H); ^{13}C NMR (22.63 MHz, $CDCl_3:Me_2CO$, 2:1) 34.71, 36.46, 45.36, 48.22 (4C), 111.46 (4C, CN), 126.86-141.04 (6C, Ph).

1,1,2,2-Tetracyano-3-phenyl-3-methylcyclobytane **(13b)** The preparation method was the same as above. From 0.19 g of α-methylstyrene and 0.19 g of tetracyanoethylene in 3 ml acetone and 1.7 g of $LiClO_4$ was obtained 0.18 g (48%) of product **(13b)**. M.p. 182-183 °C. Found (%): C 73.33; H 4.03; N 22.66. $C_{15}H_{10}N_4$ requires C 73.17; H 4.07; N 22.76; ^{1}H NMR {100 MHz; $CDCl_3$} δ 2.0 (s,3H), δ_A 3.09,δ_B 3.67 (2 H, $^2J_{AB}$ 12 Hz), 7.04-7.48 (m, 5 H); ^{13}C NMR {22.63 MHz, $CDCl_3$:Me_2CO, 2:1} 28.92 (1C, Me), 32.89, 41.20, 47.48. 51.21 (4C) , 111.46 (4C, CN), 125.76-141.42 (6C, Ph).

According to ^{1}H NMR data of the reaction mixtures the yields of products **(13a,b)** were near to quantitative, but their preparative methods were not optimized here.

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