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Solvent Effect in Pericyclic Reactions. IX.⁽¹⁾ The Ene Reaction.

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Abstract - The solvent effect on the ene reactions of diethylazodicarboxylate and triazolindione was determined in 18 and 16 solvents respectively. The first enophile gives a solvent effect that depends on solvent acidity (*type a* solvent effect), while in the second reaction the significant solvent effect is the result of the nucleophilic character of the solvent (*type b* solvent effect). These are the same solvent behaviours observed in the analogous Diels-Alder cycloadditions, and evidence of the close parallel between these two pericyclic reactions was produced by determining the effect of inorganic perchlorates on their rates.

INTRODUCTION

Pericyclic reactions are not expected to exhibit large solvent effects.(2) In some cases, the solvent acts through non-specific solute-solvent interactions as in 1,3-dipolar cycloadditions,(3) in [3,3] sigmatropic Claisen(4-6) and retro-Claisen(1) rearrangements. The change in charge separations from reagents to transition state in the concerted process gives rise to solvent effects that depend on the solvent polarity.

In many Diels-Alder (D.A.)(7) and retro-D.A.(8) reactions, solvent acts through specific interactions behaving as electrophile (*type a* solvent effect, rate increasing with the increase of the medium electrophilic power) or as nucleophile (*type b* solvent effect, rate decreasing with the increase of the medium nucleophilic power).

Very small solvent effects were experienced in some D.A. reactions like cyclopentadiene dimerization(9) and *p*.bromonitrosobenzene-dimethylbutadiene cycloaddition.(7) These were the result of non-specific solvent-solvent interactions (*type c* solvent effect) with the rate slightly increasing with the increase of the internal pressure of the medium.

The next step to infer the solvent effect on pericyclic reactions was the study of ene reaction that, in the last few years, has shown a rapid growing of synthetic applications and mechanistic investigations.(10) For a useful comparison, enophiles were suitably chosen to compare their solvent effects in ene and D.A. reactions.

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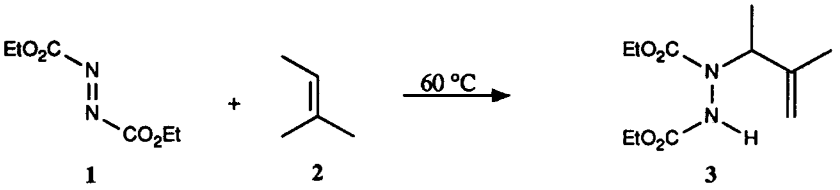
RESULTS AND DISCUSSION

Type a solvent effect

The ene reaction of diethylazodicarboxylate (DEAD, 1) is one of the the few examples involving a reagent characterized by *type a* D.A. solvent effect. Experimental evidences(11-13) confirmed the nature of concerted process for such a reaction whose solvent effect, studied by Huisgen in five aprotic solvents,(14) showed a small rate increase ($k_{nitrobenzene}/k_{cyclohexane} \approx 4$).

The reaction between DEAD and 2-methyl-2-butene (MB-2)(11) (Scheme 1) was kinetically investigated by u.v.-vis. spectroscopic analysis of the disappearing **1** at 60 °C and 410 nm, following the reaction to about 70% completion. In all solvents the monoadduct **3** was always obtained in nearly quantitative yield (all reaction mixtures were checked by n.m.r. analysis). In the presence of a 20-60 fold excess of MB, pseudo-first order rate constants were determined, and the second order were then calculated. The kinetic data reported in Table 1 are the average of at least five kinetic runs, each with varying reagent ratios.

Scheme 1



For primary and secondary alcohols, the well known oxidation to aldehydes or ketones(15) was observed under the kinetic conditions. *The rate values of the ene reaction for these alcohols were therefore obtained as a difference between the total rate and the oxidation determined by parallel experiments.*

The solvent effect was 40 in the range n.hexane-benzyl alcohol. Table 1 reports both AN(16) and E_T(17) solvent parameters and, in spite of some deviations, the rate tends to follow more the order of increase of AN than that of E_T. The linear relationship between the kinetic data and E_T parameter has a positive slope (ρ = 0.059) and a poor regression coefficient (r = 0.835). When the same kinetic data were plotted *vs.* the AN solvent parameter, the hyperbolic graph reported in Figure 1 was obtained [see Fig.1 for coefficients of hyperbola $\log k = (1 - h\,AN)/(j - k\,AN)$, r value was 0.924]. This hyperbolic correlation can be interpreted(18) in terms of coordination of the solvent (acting as electrophile) with the enophile. This interaction lowers the LUMO of DEAD, and the reaction rate increases with the increase of AN. This is the same solvent behaviour observed in *type a* D.A. solvent effect, and to compare solvent effect of DEAD in ene and D.A. reactions, their respective kinetic data were plotted in Figure 2 giving a linear relationship with the slope lower than 1 (the D.A. cycloaddition is slightly more sensitive to the solvent electrophilicity than the ene reaction).

Moreover, the range of the activation entropies (44 ± 2 e.u.), determined in five selected solvents (Table 2), is very similar to that found for the D.A. reaction of DEAD (40 ± 2 e.u.),(7) while the activation enthalpies reflect the lower reactivity of DEAD in the ene reaction.

Table 1: Rate constants of the ene reaction between 1 and 2 at 60 °C in differing solvents with AN and E_T parameters of the solvent.

n	Solvent	AN	E_T	$10^5 \times k$ (L mol^{-1}sec^{-1})
1	n-Hexane	0	31.2	1.76 ± 0.05
2	Cyclohexane	0	30.9	2.18 ± 0.03
3	Benzene	8.2	34.3	2.99 ± 0.04
4	Ethyl acetate	9.3	38.1	1.92 ± 0.02
5	1,4-Dioxane	10.8	36.0	3.27 ± 0.02
6	Acetone	12.5	42.2	2.52 ± 0.03
7	Nitrobenzene	14.8	41.2	13.4 ± 0.5
8	DMF	16.0	43.8	6.1 ± 0.1
9	1,2-Dichloroethane	16.7	41.3	9.15 ± 0.05
10	Acetonitrile	18.9	45.6	7.6 ± 0.3
11	DMSO	19.3	45.1	14.2 ± 0.6
12	Nitromethane	20.5	46.3	13.9 ± 0.5
13	Chloroform	23.1	39.1	15.3 ± 0.5
14	t-Butanol	27.1	43.3	7.6 ± 0.2
15	2-Propanol	33.8	48.4	13.8 ± 0.2(a)
16	Ethanol	37.9	50.9	16.5 ± 0.5(a)
17	Methanol	41.3	55.5	26 ± 1(a)
18	Benzyl alcohol	50.0	50.4	70 ± 2(a)

(a)Value obtained from the total rate less the oxidation rate (see text).

Table 2. Rates and activation parameters of the ene reaction of 1 and 2 in differing solvents

T/°C	$10^5 \times k$ (l mol^{-1} s^{-1})				
	cyclohexane	benzene	acetone	t.butanol	methanol
35	------	------	------	-----	6.3 ± 0.4
50	------	------	------	4.4 ± 0.2	11.5 ± 1
60	2.18 ± 0.03	2.99 ± 0.05	2.52 ± 0.03	7.6 ± 0.2	26 ± 1
70	3.75 ± 0.02	5.5 ± 0.3	4.48 ± 0.03	12.1 ± 0.4	53 ± 2
80	6.6 ± 0.15	9.4 ± 0.1	7.8 ± 0.1	19.7 ± 0.4	------
90	11.5 ± 0.3	15.7 ± 0.3	12.8 ± 0.1	------	------
$\Delta H^{\neq a}$	12.7 ± 0.5	12.6 ± 0.4	12.4 ± 0.2	10.6 ± 0.6	12 ± 1
$-\Delta S^{\neq b}$	42 ± 1.5	42 ± 1	42.5 ± 0.5	46 ± 2	39 ± 3

a) kcal mol^{-1}; b) cal K^{-1} mol^{-1}.

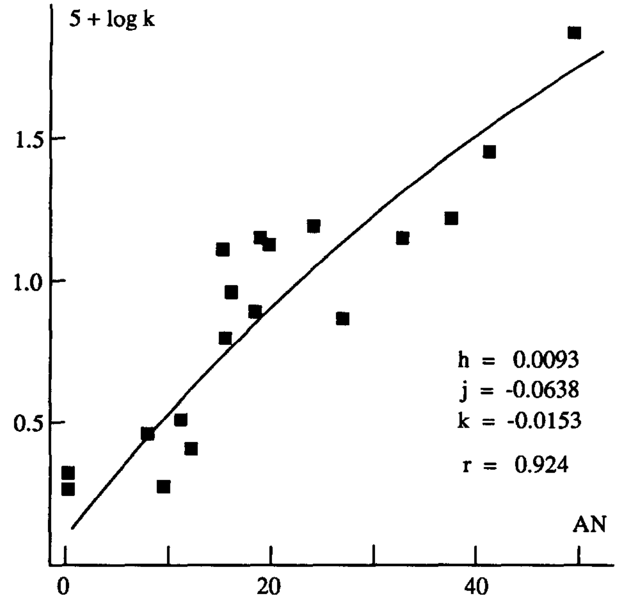


Figure 1: Rate constants of the reaction between 1 and 2 at 60 °C plotted vs the AN of the solvents.

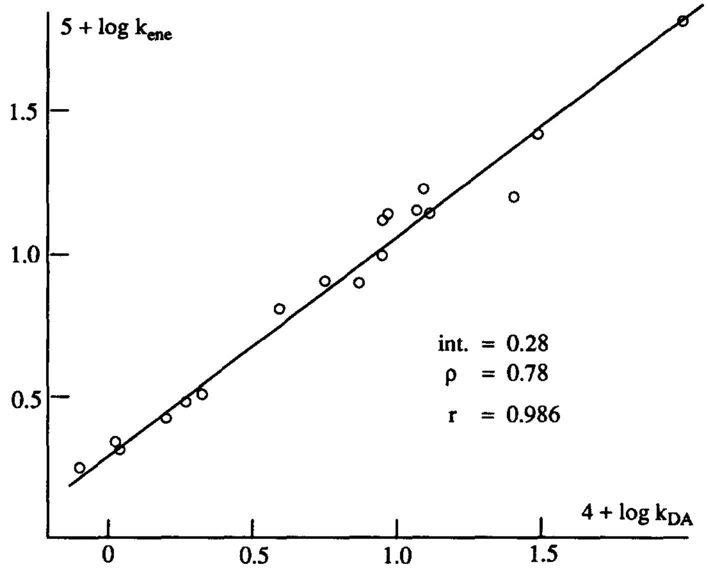
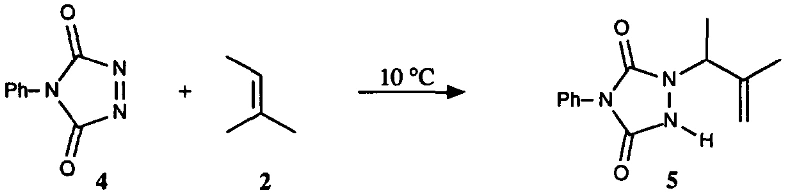


Figure 2. Plot of the rate constants of the ene of 1 and 2 (k_{ene}) vs those of the D.A. reaction of 1 and 2,3-dimethylbutadiene (k_{DA}) (Ref. 7).

Type b solvent effect

Among ene reactions with a reagent giving *type b* D.A. solvent effect, that between 1-phenyl-1,3,4-triazolin-2,5-dione (PTAD, 4) and 2 (Scheme 2) was investigated.(19)

Scheme 2



The mechanism of this reaction has been matter of a recent debate. Essentially from kinetic isotope effect, an aziridinium ion was proposed as intermediate,(20) whereas both substituent and solvent effects suggested, on the contrary, a concerted mechanism.(21) PM3 calculations evidenced similar energy profiles for both mechanisms.(22)

The above mentioned paper of Ohashi and Butler(21) studied the PTAD reaction with three olefins in six solvents, and the ratio k(CH_2Cl_2)/k(THF) was in the range 49 ± 5. This is a significant effect in the field of pericyclic reactions.

The kinetic determinations were performed in 16 solvents by u.v.-vis. spectroscopic analysis of the disappearing 4 at 10 °C and 550 nm, following the reaction to about 70% completion. The monoadduct 5 was always obtained in nearly quantitative yield (all reaction mixtures were checked by n.m.r.). The rate constants were determined under second-order conditions, and the values reported in Table 3 are the average of at least five kinetic runs (see experimental section for details).

The significant solvent effect was 238 in the range THF-chloroform. Table 3 reports both DN^N(16) and D_π(23) basicity solvent parameters and, in spite of few deviations, the rate decreased with the increasing of the solvent basicity. This trend was evident when the kinetic data were plotted *vs* the solvent parameters: with DN^N (Figure 3a) a hyperbolic correlation(7) and with D_π (Figure 3b) a linear relationship(7) were obtained.

The hyperbolic correlation with DN^N can be interpreted(7) in terms of coordination of the solvent (acting as nucleophile) with the enophile whose LUMO is therefore increased. Hence reaction rate decreased with the increase of DN^N, and this, in terms of MO interactions, is the same effect proposed by Ohashi and Butler:(21) "a strong donor-acceptor complex interaction between PTAD and the solvent seems to cause the lower reactivity of PTAD, possibly *via* an increase in the electron density of the N=N system". The analogy with *type b* D.A. solvent effect(7) was confirmed by plotting the kinetic data of the PTAD ene reaction *vs* those determined by the Konovalov group(24) for the PTAD-anthracene D.A. cycloaddition (Figure 4): a nice linear relationship ($r = 0.996$) with the slope close to 1 ($\rho = 1.08$) was obtained for the seven common solvents.

Table 3: Rate constants of the ene reaction between 4 and 2 at 10 °C in differing solvents with DN^N and D_π parameters of the solvent.

N	Solvent	D_π	DN^N	k (L mol^{-1}s^{-1})
1	Chloroform	-1.56	--	14.3 ± 0.3
2	Dichloromethane	-1.30	--	8.1 ± 0.3
3	1,2-Dichloroethane (DCE)	-1.22	0	4.9 ± 0.3
4	Chlorobenzene	-0.903	--	2.56 ± 0.02
5	Nitromethane	-0.724	0.07	1.78 ± 0.02
6	Nitrobenzene	-0.583	0.21	1.71 ± 0.04
7	Acetonitrile	-0.440	0.36	0.57 ± 0.01
8	Diethyl ether	--	0.39	0.190 ± 0.004
9	Benzene	0	--	1.26 ± 0.02
10	Acetone	0.261	0.44	0.106 ± 0.003
11	Ethyl acetate	0.289	0.44	0.109 ± 0.003
12	Dimethoxymethane	0.383	--	0.130 ± 0.004
13	Toluene	0.395	--	0.64 ± 0.03
14	1,4-Dioxane	0.590	0.38	0.150 ± 0.003
15	THF	0.639	0.52	0.060 ± 0.002
16	DMF	--	0.69	0.077 ± 0.001

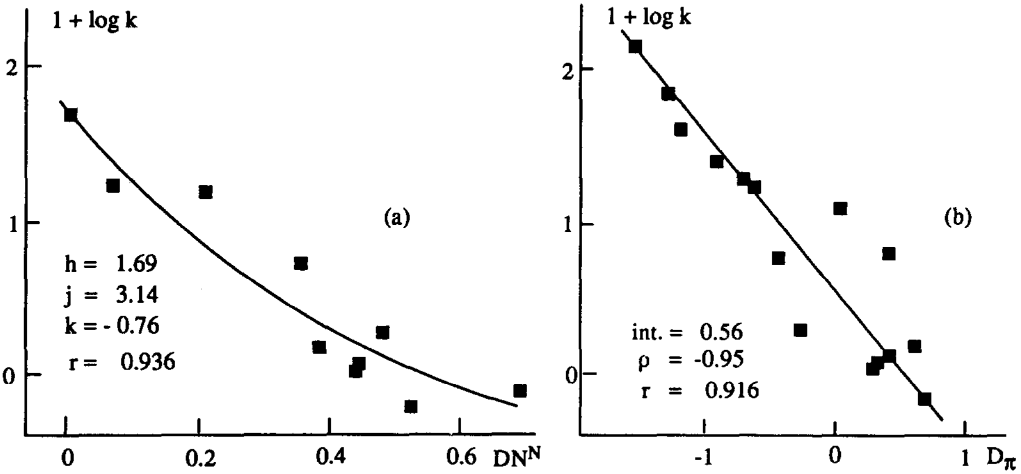


Figure 3: Rate constants of the ene reaction between 4 and 2 at 10 °C in differing solvents plotted vs either DN^N (a) or D_π (b) of the solvent.

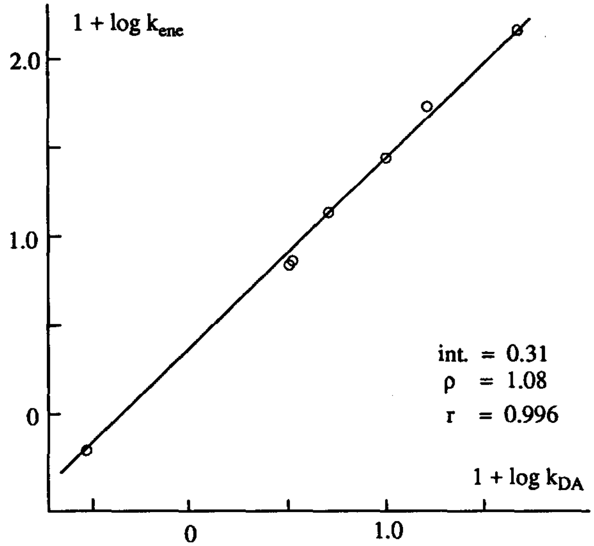


Figure 4. Plot of the rate constants of the ene reaction of 4 and 2 (k_{ene}) vs those of the D.A. reaction of 4 and anthracene (k_{DA}) (Ref. 24).

The range of the activation entropies (37 ± 4 e.u.), determined in five selected solvents (Table 4), is in accordance with a concerted reaction mechanism, while the activation enthalpies reflect the slightly higher reactivity of PTAD in the ene reaction.

Salt effect

The rate of those D.A. reactions sensitive to the solvent acidity (*type a* solvent effect) gave large salt effects which were the result of the specific interaction between the cation (acting as electrophile) and the substrate.(25,26) On the other hand, those reactions giving *type b* D.A. solvent effects were nearly insensitive to any cationic catalysis.(27)

Table 4. Rates and activation parameters of the ene reaction of 4 and 2 in differing solvents

T/°C	k (L mol^{-1} s^{-1})				
	DCE	nitrobenzene	benzene	acetone	THF
10	4.9 ± 0.3	1.71 ± 0.04	1.28 ± 0.03	0.106 ± 0.003	0.060 ± 0.002
16	6.6 ± 0.2	2.25 ± 0.06	1.43 ± 0.03	0.140 ± 0.002	0.085 ± 0.001
24	8.3 ± 0.1	2.95 ± 0.08	1.85 ± 0.03	0.208 ± 0.002	0.134 ± 0.001
30	9.9 ± 0.2	3.65 ± 0.05	2.29 ± 0.02	0.275 ± 0.005	0.180 ± 0.001
$\Delta H^{\neq a}$	5.3 ± 0.7	5.8 ± 0.4	4.5 ± 0.5	7.6 ± 0.4	8.8 ± 0.4
$-\Delta S^{\neq b}$	36.5 ± 0.5	37 ± 1	42 ± 1	36 ± 1.5	33 ± 1

$^{a)}$ kcal mol^{-1}; $^{b)}$ cal K^{-1} mol^{-1}.

The ene reaction of DEAD and PTAD are characterized by *type a* and *type b* solvent effect respectively. It should be expected for the former reaction a large, whereas for the latter one a small salt effect.

To test this hypothesis, the rate constants of the reactions in scheme 1 and 2 were determined in the presence of increasing amount of lithium (LP), sodium (SP), barium (BP), and magnesium perchlorate (MP) in acetone solutions.

The DEAD ene reaction in MP - acetone solutions was not performed due to the instability of **1** under the experimental conditions. For all the reported concentrations of LP, SP, and BP, the reaction was checked by n.m.r. analysis (see experimental section for details), and in each case only the monoadduct **3** was observed.

For lower salt concentrations of LP and BP, and for all MP and SP concentrations, the ene reaction of PTAD gave only the adduct **5**. When the concentrations of LP are higher than 3.0 M, and BP higher than 1.4 M, two new products, in addition to **5**, were evidenced in the reaction mixture by n.m.r.. One of these side products was isolated, characterized by elemental analysis and spectral data (see experimental section for details), and found to be the triazo [1,2-c] oxadiazine **6**. The second side-product during work-up of the reaction mixture was converted into **5**. The formation of **6** requires the presence of a zwitterionic intermediate **7** and therefore the rate constants in such polar media were too inaccurate to be considered.

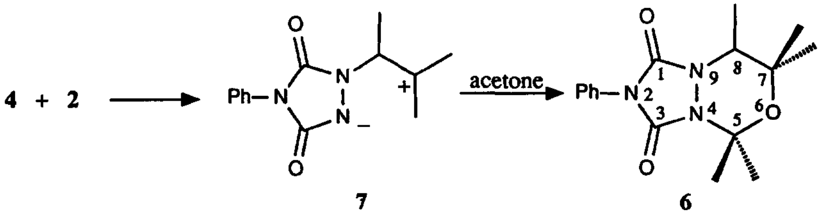
Table 5. Rate constants for the ene reaction of ***1*** *and* ***2*** *at 25 °C in differing concentrations of metal perchlorates-acetone solutions.*

Salt	[M]	$10^5 \times k$ ($l\,mol^{-1}sec^{-1}$)	k_{rel}	Salt	[M]	$10^5 \times k$ ($l\,mol^{-1}sec^{-1}$)	k_{rel}
----	---	0.25 ± 0.01[(a)]	1	BP	1.00	9.17 ± 0.02	36.7
					1.75	94 ± 1	376
LP	1.00	0.88 ± 0.04	3.52		2.00	240 ± 4	960
	2.00	3.60 ± 0.06	14.4	SP	1.00	1.25 ± 0.01	5.0
	3.00	21.1 ± 0.1	84.4		1.80	3.63 ± 0.02	14.5
	4.00	264 ± 8	1056		2.40	7.55 ± 0.03	30.2

(a) Rate constant extrapolated from the Arrhenius diagramm (see experimental section for details).

Table 6. Rate constants for the ene reaction of ***4*** *and* ***2*** *at 10 °C in differing concentrations of metal perchlorates-acetone solutions.*

Salt	[M]	k ($l\,mol^{-1}sec^{-1}$)	k_{rel}	Salt	[M]	k ($l\,mol^{-1}sec^{-1}$)	k_{rel}
----	---	0.106 ± 0.003	1	LP	1.00	0.166 ± 0.002	1.6
MP	1.00	0.182 ± 0.005	1.7		2.50	0.374 ± 0.004	3.5
	1.20	0.184 ± 0.004	1.7	SP	1.00	0.180 ± 0.001	1.7
BP	1.00	0.255 ± 0.002	2.4		2.20	0.395 ± 0.005	3.7



From the comparison of the kinetic data in Table 5 and 6 (average of five independent kinetic runs) the different response of the two ene reactions to the cationic catalysis appears evident. The salt effect in the DEAD reaction is large, while that of PTAD is very small. This result parallels that obtained for D.A. reaction and confirms the hypothesis that only those reaction giving *type a* solvent effect will be characterized by a cationic catalysis. In a recent paper of Gill and co-workers,(28) the ene reaction of indan-1,2,3-trione (*type b* solvent effect) was insensitive to the catalysis with Lewis acids.

The activation parameters (Table 7 and 8), determined for each ene reaction, do not support dramatic changes of mechanism in the presence of perchlorates and the changes in $\Delta S^{\neq}$ are analogous to those found for other pericyclic reactions.(27,29)

*Table 7. Rates and activation parameters of the ene reaction of **1** and **2** in the presence of the three inorganic perchlorates at the concentration of 1.0 M.*

T/°C	10^5 k (L mol^{-1} s^{-1})		
	BP	LP	SP
20	7.35 ± 0.1	0.74 ± 0.01	0.90 ± 0.01
25	9.17 ± 0.02	0.88 ± 0.04	1.25 ± 0.01
30	12.6 ± 0.15	1.38 ± 0.03	1.66 ± 0.05
35	16.9 ± 0.1	1.81 ± 0.03	2.36 ± 0.04
$\Delta H^{\neq a}$	9.6 ± 0.5	10.6 ± 0.6	10.8 ± 0.5
$-\Delta S^{\neq b}$	45 ± 1	46 ± 1	45 ± 1

a) kcal mol^{-1}; b) cal K^{-1} mol^{-1}.

*Table 8. Rates and activation parameters of the ene reaction of **4** and **2** in the presence of the four inorganic perchlorates at the concentration of 1.0 M.*

T/°C	k (L mol^{-1} s^{-1})			
	MP	BP	LP	SP
10	0.182 ± 0.005	0.255 ± 0.002	0.166 ± 0.002	0.180 ± 0.001
16	0.260 ± 0.005	0.339 ± 0.005	0.228 ± 0.002	0.246 ± 0.004
24	0.407 ± 0.004	0.539 ± 0.004	0.349 ± 0.002	0.366 ± 0.005
30	0.542 ± 0.004	0.715 ± 0.005	0.507 ± 0.003	0.494 ± 0.008
$\Delta H^{\neq a}$	8.8 ± 0.4	8.4 ± 0.2	8.9 ± 0.3	8.0 ± 0.2
$-\Delta S^{\neq b}$	31 ± 1	32 ± 1	31 ± 1	33.5 ± 1.5

a) kcal mol^{-1}; b) cal K^{-1} mol^{-1}.

CONCLUSION

The solvent effect on the ene reaction has been investigated and the results closely parallel those of the D.A. cycloaddition. Both reactions are indeed characterized by significant solvent effects due to specific solute-solvent interaction. If solvent acts as an electrophile, the rate increases with the increase of the electrophilic character of the solvent (*type a* solvent effect) and the reaction exhibits large salt effect.

If solvent behaves as a nucleophile the rate decreases with the increase of the nucleophilic character of the medium (*type b* solvent effect) and the reaction is insensitive to any cationic catalylis.

EXPERIMENTAL SECTION

Materials - Diethylazodicarboxylate **1** and 2-methyl-2-butene **2** were commercial freshly distilled products. The solvents for the kinetic runs 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)(30).

4-Phenyl-1,2,4-triazolin-3,5-dione (8) - This was prepared in accordance with the literature method.(31)

Reaction of 1 and 2 - The reaction was performed as reported in the literature,(11) and (2-methyl-2-butenyl)-bicarbamic acid ethyl ester **3** was obtained in nearly quantitative yield with b.p. and n.m.r. spectra identical to those reported in the literature.(11)

Reaction of 4 and 2 - The reaction was performed as reported in the literature,(19) and 1-(3-methyl-2-butenyl)-4-phenyl-1,2,4-triazoline-3,5-dione **5** was obtained in nearly quantitative yield as whyte crystall, m.p. 147 °C (from diethylether) (lit.(19) 147-148.5 °C).

5,5,7,7,8-Pentamethyl-2-phenyl-1,3-dioxo-triazo[1,2-c]oxadiazine 6 - This product was isolated by flash chromatography (cyclohexane - ethyl acetate 4:1) from the reaction between **2** and **4** in BP or LP acetone solutions with high salt concentrations. The product was crystallized by ethanol (10-30% yield depending on salt and its concentration), white crystals, m.p. 143-144 °C. Elem. anal.; calc. for $C_{16}H_{21}N_3O_3$: C, 63.4; H, 7.0; N, 13.9. Found: C, 63.3; H, 7.0; N, 13.8. I.R. (nujol mulls): 1710 and 1765 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 7.3-7.6 (5H, aromatic protons), 3.96 (q, 1H, *H*-8), 1.86 (s, 3H, *Me*-5), 1.66 (s, 3H, *Me*-5), 1.56 (s, 3H, *Me*-7), 1.31 (d, 3H, *Me*-8), 1.27 (s, 3H, *Me*-7). ^{13}C-Nmr ($CDCl_3$) δ: 151.05 and 131.15 (carbonyl carbon atoms); 128.95, 127.95, and 125.39 (aromatic carbons); 88.99 (*C*-5); 74.49 (*C*-7); 55.82 (*C*-8); 28.80, 27.85, 26.92, and 24.41 (4 CH_3 - *Me*-5 and *Me*-7), 12.14 (1 CH_3 - *Me*-8).

Kinetics - The overall reaction rates were measured by following the disappearance of the chromophores **1** and **4** on a Perkin Elmer Lambda 16 spectrophotometer provided with a thermostatted-cell transport assembly and an automatic multicell programmer. The solutions were measured in 1.00 cm OS Hellma couvettes with 3 cm^3 capacity; measuraments were taken at the wavelengths of 410 nm for **1** and 550 nm for **4**.

The rate constants for the ene reaction of **1** and **2** were determined as follow. To the half-filled volumetric flask containing **1** (about 20-30 mg) dissolved in the solvent was added about 1 cm^3 of **2**, and the flask was then filled up to 25 cm^3 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 (5-100 min, depending on solvent and temperature) the reaction was quenched, and the residual absorbance of **1** was determined.

The rate constants for the ene reaction of **4** and **2** were determined as follow. Weighed amounts of the enophile **4** (0.025-0.035 g) were added to the solvent solution in a 10 cm^3 volumetric flask. The ene solution was prepared by adding **2** (0.12-0.15 g) to an accurately weighed 5 cm^3 volumetric flask containing *ca.* 3 cm^3 of the solvent. After the ene addition, the flask was again weighed for an accurate determination of the ene amount, then filled with the solvent. Four samples of the solution containing the enophile (4 - 2.00 cm^3 measured with a calibrated syringe) were placed in the couvettes thermostatted at the required temperature, and constant amounts (from 0.25 to 0.50 cm^3, accurately measured with a microsyringe) of the ene solution were added. After vigorous mixing, the kinetic determinations were initiated.

For the determination of the rate constants in perchlorate-acetone solutions, the procedure was as follow. In a 10 cm^3 volumetric flask the salt-acetone solution was prepared by weighing the needed amount of metal perchlorate. The flask was filled with acetone and then again weighed in order to determine the salt concentration. Weighed amounts of the enophile **1** (15-20 mg) or **4** (0.025-0.035 g) were added to the salt-solvent solution. The ene solution was prepared as previously described. The kinetic runs were then performed by the usual procedure.

The pseudo-first order rate constants for the ene reactions **1** + **2** were calculated from the slope of the graph obtained by plotting log (A°/A_t) *vs* t, being A° and A_t the absorbance value at time 0 and *t* respectively. The second order rate constants for the ene reaction of **4** and **2** were calculated from the slope of the graph obtained by plotting the left side of equation 1 *vs* t:

$$\frac{1}{B^\circ - A^\circ} \log \frac{A^\circ \times B_t}{B^\circ \times A_t} = k\,t \qquad (1)$$

A° and B° being the starting concentrations of **4** and **2**, A_t and B_t the actual concentrations calculated from the residual absorbance of **4** at the time *t*. In each case good linear relationships ($r \geq 0.999$) were obtained up to 70% completion.

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