

2+2 → 4 CYCLOADDITIONS OF TETRACYANOETHYLENE TO ENOL ETHERS ;
ACTIVATION PARAMETERS AS MECHANISTIC CRITERIA

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Activation parameters play an important role in the discussion of cycloaddition mechanisms. We have measured TCNE cycloaddition rates of three model enol ethers in 6 - 9 solvents at 4 - 8 different temperatures over a range of temperature, ΔT , of 15 - 26°. The photometry of the charge transfer complex from TCNE and an excess of enol ether was described in the preceding paper (1). The $k_1\psi$ values were reproducible within 2 - 5%; the low solubility of TCNE in cyclohexane and CCl₄ burdened the small k_2 in these solvents with an error of ±10%.


It may be emphasized that the overall constant k_2 is the rate constant of zwitterion formation multiplied with the partition coefficient of cyclization and dissociation (2). Thus, the Eyring parameters of the Table do not characterize the activation barrier of a single step, a result which, unfortunately, curtails mechanistic conclusions.

The rate constants of TCNE cycloaddition to anethole, 2,3-dihydro-4H-pyran and butyl vinyl ether are increased by factors of 29,000, 17,000 and 2,600, respectively, in going from the non-polar cyclohexane or CCl₄ to the polar acetonitrile (3). The log k_2 increase linearly with E_T , an empirical parameter of solvent polarity (4).

The Table reveals that rather small temperature coefficients are the result of moderately low activation enthalpies and large negative entropies of activation (-31 to -58 e.u.). The negative ΔS^\ddagger values exceed even those of Diels-Alder reactions (5), 1,3-dipolar cycloadditions (6) or cyclobutanone formation from ketenes and enol ethers (7); all these reactions are concerted. Although large negative activation entropies are characteristic for the highly ordered transition states of concerted cycloadditions, they are not, per se, an adequate criterion to distinguish between a one-step reaction and a two-step process which occurs via a zwitterionic intermediate. The quaternization of pyridine with methyl iodide shows sizable negative ΔS^\ddagger values (8), and

Table. Activation Parameters for TCNE Cycloadditions to Anethole, 2,3-Dihydro-4H-pyrene and Butyl Vinyl Ether in Various Solvents; ΔG^\ddagger Values at 30°C

$$\begin{array}{c} \text{H}_3\text{C} \\ | \\ \text{C}=\text{C} \\ | \quad | \\ \text{H} \quad \text{C}_6\text{H}_4\text{-OCH}_3 \end{array}$$



$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{C}=\text{C} \\ | \quad | \\ \text{H} \quad \text{OC}_4\text{H}_9 \end{array}$$

Solvent (E_T)	ΔG^\ddagger	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger	ΔH^\ddagger	ΔS^\ddagger
	(kcal/mol)	(e. u.)	(e. u.)	(kcal/mol)	(e. u.)	(e. u.)	(kcal/mol)	(e. u.)	(e. u.)
Cyclohexane (31.2)	25.4	15.9	-31				23.0	7.8	-50
Carbon tetrachloride (32.5)	24.7	8.4	-54	26.3	15.0	-37	22.6	6.5	-53
Tetrahydrofuran (37.4)	22.4	8.1	-47				20.4	6.5	-46
Ethyl acetate (38.1)	22.2	7.3	-49	23.3	8.8	-48	20.1	5.8	-47
Chloroform (39.1)	20.7	3.6	-57	22.8	7.1	-52	20.5	3.8	-55
Dichloromethane (41.1)	19.9	3.6	-54	22.7	9.2	-45	19.7	2.1	-58
Acetone (42.4)	20.6	6.2	-48				19.4	4.5	-49
Benzonitrile (42.0)	20.1	6.3	-45	21.6	7.9	-45			
Acetonitrile (46.0)	19.4	6.1	-44	20.6	5.1	-51	18.4	3.9	-48
Error Limit (\pm)		0.7	2		1.0	2.5		1.0	2.5

1-pyrrolidino-cyclopentene + CS₂ form a zwitterion with $\Delta S^\ddagger = -45$ e. u. (9).

Reactions like zwitterion formation which are accompanied by a strong increase of solvation due to charge separation display large negative ΔS^\ddagger values as a consequence of the electrostriction of solvent molecules by the incipient charge centers. Should one not expect greater negative ΔS^\ddagger values for highly polar than for non-polar solvents because the polar solvent molecules ought to become attached to the charge centers of the activated complex more firmly? The data of the Table do not fulfil this expectation. The highest negative ΔS^\ddagger values were found for chlorinated methanes as solvents.

The activation parameters of one of the three model reactions are singled out in the Figure. The straight lines for O- and N-containing solvents show slopes of the same sign, i.e., decreasing ΔH^\ddagger and smaller negative ΔS^\ddagger values both contribute to an acceleration of rate. Cyclohexane and the chlorinated methanes reveal a non-linear relation of the compensation type.

Several examples of ionizations in which also negative ΔS^\ddagger values increase with decreasing solvent

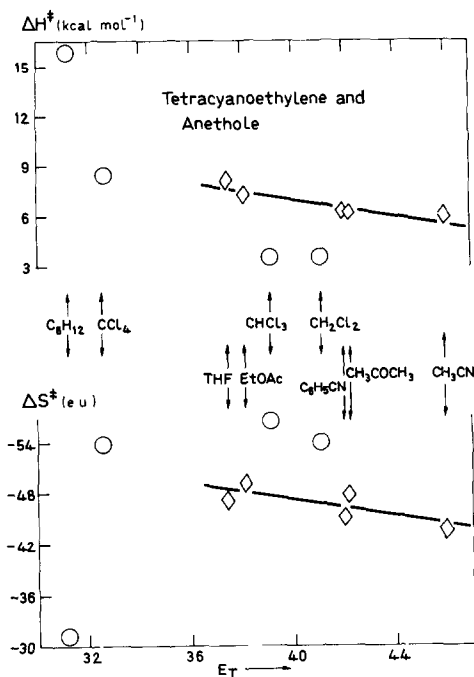
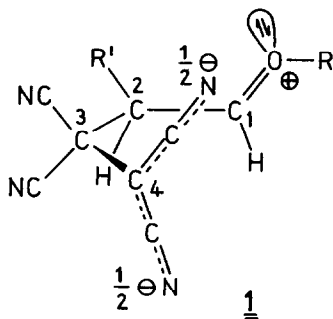


Figure. Eyring parameters of the cycloadditions of TCNE to anethole in various solvents as a function of the empirical solvent parameter E_T

polarity have been described (10). The phenomenon was attributed to the partially frozen state of highly polar solvents such as water or alcohols as a consequence of hydrogen bonding and other intermolecular forces. Becoming attached to ionic centers, these molecules suffer less additional entropy decrease. *E.g.*, Hartmann, Kelm, and Rinck (8) measured $\Delta S^\ddagger = -22$ and -37 e.u. for the reaction of pyridine with methyl iodide in methanol and in CCl_4 , respectively.

In our case the strongly ordered hydroxylic solvents have not been used. Thus, other reasons must contribute to the large spread of negative activation entropies. We comment on the intriguing phenomenon without offering a final answer.

1. The formation of the zwitterion in the conformation 1 having the smallest distance between charge centers demands a strict orientation of the two reactants in the transition state. The requirement of low Coulomb potential becomes less stringent in more polar solvents as testified by the lessening degree of stereospecificity (11,12).



This growing flexibility of the transition state with increasing solvent polarity leads to smaller negative ΔS^\ddagger values.

2. The incipient zwitterionic charge centers induce polarization of CCl_4 molecules or increase that of CHCl_3 and CH_2Cl_2 . Also the chlorinated methanes lose their translatory and rotatory degrees of freedom when frozen around the ionic centers though their solvation enthalpy is inferior to that of the O- and N-containing solvents.

3. The three enol ethers of the Table possess dipole moments of 1.76, 1.33 and 1.25 D, respectively, with values of 14.0, 10.7 and 10.3 D the corresponding transition states of zwitterion formation (3) reveal a substantially larger polarity. It is conceivable that highly polar solvents solvate the reactants while the transition states of zwitterion formation also enforce the freezing of less polar solvent molecules to the polar centers.

4. The assumption that the solvent dependence of ΔH^\ddagger and ΔS^\ddagger in the Table reflects that of k_i for zwitterion formation alone, is oversimplified. Also the partition coefficient, $k_c / (k_c + k_{-1})$, may depend on solvent and temperature and will influence the data of the Table.

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