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CYCLOADDITION REACTION BETWEEN TETRACYANOETHYLENE AND N-BUTYL VINYL ETHER: THE SOLVENT DEPENDENCE OF THE VOLUME OF ACTIVATION

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There are several possibilities to strengthen the concept of the mechanistic course of a reaction by kinetic measurements. In case of cycloaddition reactions between tetracyanoethylene and a selection of enol ethers, Huisgen and Steiner used: the steric course of the reaction [1,2]; the dependence of the rate on the solvent polarity [3]; the structural variation of the enol ether [4]; and the determination of the enthalpies and entropies of activation [5] to elucidate the mechanism. Thus, evidence has been accumulated for a two-step mechanism involving a zwitterionic intermediate which would undergo a more or less strong solvation and as a result have a variable life time depending on the solvent

In our opinion the remaining activation parameter, i.e. the volume of activation, offers very useful criteria for the interpretation of the mechanism of this type of cyclisation reaction For the reaction between tetracyanoethylene and n-butyl vinyl ether we determined the pressure dependence of the rate in five different solvents at 30° C and over a range of pressure up to 2000 atm. The rate constants, which were determined spectrophotometrically [6] under pseudo-first order conditions, are listed in table 1 as the overall second order rate constants. Each constant has a reproducibility within at least 5 %.

According to the known kinetic equations the volume of activation, $\Delta V^{\neq}_{exp.}$, of a reaction is given by

$$d(\ln k)/dP = -\Delta V^{\neq}_{exp} / (RT) + \Delta\gamma \varkappa RT \qquad (1)$$

with $\varkappa$ being the compressibility of the solvent The correction term is to be applied when molar concentrations of the solutions are used

Table 1: Pressure Dependence of the Rate Constants $10^4 \cdot k$ (1/mole sec.) at 30,0° C for the Cycloaddition Reaction between Tetracyanoethylene and n-Butyl Vinyl Ether.

Solvent	Pressure (atm) 1	250	500	750	1000	1500	2000
Carbon Tetrachloride [7]	1,24	1,66	3,15	4,93	8,37	-	-
Benzene [7]	9,1	13,4	20,1	30,1	-	-	-
Dichloromethane	605	854	1250	1760	2490	4360	7330
Acetone	882	1306	1799	2367	3077	4839	7294
Acetonitrile	4527	6265	8280	10321	12988	21400	30551

By analogy to the quasi-thermodynamic form of the equation for the rate constant of a bimolecular reaction between the reactants A and B forming the transition state X

$$RT \ln k = RT \ln (k_B T/h) - \Delta G^{\neq} = RT \ln (k_B T/h) - \bar{G}_X + (\bar{G}_A + \bar{G}_B) \quad (2)$$

one can derive an equation on the basis of the partial molar volumes rather than the partial molar Gibbs free enthalpies by simply differentiating equation (2) with respect to pressure:

$$\Delta V^{\neq} = \bar{V}_X - (\bar{V}_A + \bar{V}_B) \quad (3)$$

In this form the term $\Delta V^{\neq}$ is equivalent to the experimentally obtainable $\Delta V^{\neq}_{exp.}$ which is described above. As the partial molar free enthalpy values $\bar{G}_i$ the partial molar volumes $\bar{V}_i$ can be split into a standard and an excess contribution, i.e. $(\bar{V}_i = V_i^o + V_i^e)$. Thus equation (3) rearranges to:

$$\Delta V^{\neq} = V_X^o - (V_A^o + V_B^o) + V_X^e - (V_A^e + V_B^e) \quad (4)$$

If one assumes that the standard molar volumes V_i^o are the molar volumes occupied by the species i in a solution where no interactions between solute and solvent molecules are present i.e. no solvation takes place, the first bracketed term in equation (4) represents the change in internal volume in going from the educts to the transition state In general this contribution to the overall volume of activation, often symbolized $\Delta V_I^{\neq}$, should be negative when a bond is formed and positive when a bond is broken during the rate determining step of the reaction Furthermore, the absolute value of $\Delta V_I^{\neq}$ should give an indication whether one or two bonds are simultaneously involved in the crucial step of the reaction. The second

bracketed term in equation (4) describes the change in solvation during the formation of the transition state. This contribution is symbolized as $\Delta V_2^{\neq}$ and depends on the solvent used

While the partial molar volumes $\bar{V}_A$ and $\bar{V}_B$ can be determined from the concentration dependence of the apparent molar volumes ϕ_i, which in turn are accessible from density measurements, the excess volume contributions V_A^e and V_B^e cannot be obtained directly since an ideal solvent, showing no interaction with any solute, is a fiction. However, the differences between the molar volumes V_i of pure reactants and their apparent molar volumes ϕ_i should show the important variations in the solvation of reactants when changing solvent polarity. These differences $\widetilde{\Delta V}_i = V_i - \phi_i$ deviate from the exact value of V_i^e by a presumably small amount, which is, however, constant for all solvents We have determined these accessible quantities by density measurements. The results are included in table 2.

Table 2: Solvent Dependence of the Volume Contributions (ml/mole) at 30° C of Educts and Transition State for the Cycloaddition Reaction between Tetracyanoethylene and n-Butyl Vinyl Ether.

Solvent	$-\varkappa RT$	$-\Delta V^{\neq}_{exp.}$	ϕ_A	ϕ_B	$\Sigma\widetilde{\Delta V}_i$	$\bar{V}_X$	$-\Delta V_1^{\neq}$	$-\Delta V_2^{\neq}$
Carbon Tetrachloride	3	50	106	130	4	186	14	32
Benzene	3	43	110	131	9	198	14	20
Dichloromethane	2	37	107	130	5	200	14	18
Acetone	4	35	111	131	10	207	14	11
Acetonitrile	3	29	113	129	10	213	14	5

A: Tetracyanoethylene, V_A = 102 ml/mole; B. n-Butyl Vinyl Ether; V_B = 130 ml/mole

The excess volume of the transition state V_X^e can be estimated by using Kirkwoods equation

$$G_X^e = -\frac{N\mu_X^2}{r_X^3}\,\frac{\varepsilon - 1}{2\varepsilon + 1} \qquad V_X^e = -\frac{N\mu_X^2}{r_X^3}\,\frac{3}{(2\varepsilon + 1)^2}\,\frac{d\varepsilon}{dP} \qquad (5)$$

assuming that the radius r and the dipole moment are independent of pressure. The use of the Kirkwood formula appears to be justified for our model reaction because its transition state is considered to be highly polar Hence neglecting the non-electrostatic interactions should

cause only a small error Introducing all approximations into equation (4) one obtains·

$$\Delta V^{\neq}_{exp} + (V_A - \phi_A) + (V_B - \phi_B) = \Delta V^{\neq}_1 - \frac{N\mu_x^2}{r_x^3} q_p; \quad \text{with } q_p = \frac{3}{(2\varepsilon + 1)^2} \frac{d\varepsilon}{dP} \qquad (6)$$

A plot of the experimentally determined quantities of the left side versus the electrostriction parameter q_p of the corresponding solvents results in a fairly good straight line allowing an estimation of $\Delta V^{\neq}_1$ and $\Delta V^{\neq}_2$ values (see table 2). From the slope a value of (15 ± 3) D is derived for the dipole moment of the transition state. This is well in agreement with a zwitterionic structure [2]. The intercept of (14 ± 2) ml/mole for the $\Delta V^{\neq}_1$ contribution to the activation volume is a typical value for a single bond formed [8]. The solvation terms $\Delta V^{\neq}_2$ indicate a strong solvent dependence with the largest contributions for non-polar solvents, where indeed the strongest electrostriction occurs when a polar center is developed. The highly negative volues for the entropies of activation often observed for reactions with polar or zwitterionic transition states [9] are in agreement with this concept. Furthermore, the magnitudes of the $\Delta V^{\neq}_2$ values are very similar to those found for the Menschutkin reactions [9].

In summary, the pressure dependence study of the cycloaddition reaction investigated here and its interpretation support strongly the concept of a two step mechanism with a zwitterionic intermedicate as proposed by Huisgen and Steiner [1-4].

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