The (2 + 2) Cycloaddition Reaction between Vinyl Alcohol and Tetracyanoethylene. A Theoretical Study of Solvent and Catalytic Effects

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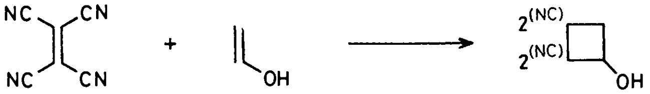
The cycloaddition reaction between tetracyanoethylene and vinyl alcohol has been studied by means of the MNDO method with CI. Catalytic and solvent effects have been simulated. It has been found that in the gas phase the mechanism is non-concerted with a biradical intermediate. In protic solvents, the intermediate has zwitterionic character and leads to the formation of an acetal.

Over the last few years, the mechanism of (2 + 2) cycloadditions has been studied extensively, both experimentally and theoretically. Based on experimental results, Huisgen[1–5] proposed a two-step mechanism involving a zwitterionic intermediate; Epiotis[6–10] concluded on theoretical grounds that the reaction takes place in two steps, with a biradical intermediate. Other theoretical studies[11–15] either support Epiotis' conclusions or find that a one-step concerted mechanism better describes (2 + 2) cycloadditions involving polar reagents.

Most theoretical studies concentrate on the dimerisation of ethylene and neglect the influence of the solvent. The comparison with experiment is, therefore, rather tenuous.

We are currently involved in an experimental study of solvent effects on reaction rates.[16] This has prompted us to envisage a supersystem containing species more closely resembling those investigated by Huisgen[17–19] and by ourselves. Accordingly, this work is devoted to the theoretical study of the reaction between tetracyanoethylene (TCNE) and vinyl alcohol (Scheme 1), the hydroxy group being taken as a model for the alkoxy group in enol ethers. Solvent effects are treated by means of Jano's model[20] and acid catalysis is simulated by gas-phase protonation.

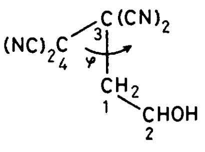


Scheme 1.

Methods

Given the size of the problem, which can hardly be treated by *ab initio* techniques, we have chosen the MNDO[21] formalism. This method leads to reasonable heats of formation and makes some allowance for non-specific correlation effects through its parameterisation. Specific correlation effects were taken into account within the half-electron[22] formalism followed by a configuration interaction (CI) based on the complete subset of the crossing orbitals encountered along the reaction path. Thus the wavefunction describing the singlet ground state smoothly evolves between the various minima and transition states and allows closed shell, biradical, or zwitterionic forms along the reaction path to be distinguished.

Each stationary point has been optimised at this level of computation. The structure of the minima was found *via* the D–F–P algorithm.[23,24] Saddle points were determined either by means of the CHAIN algorithm[25] or the reaction co-ordinate method. In the latter case, the correct choice of reaction co-ordinate is essential for the method to be successful. In the case of a concerted process the distance between the two C=C bonds is sufficient, but in the case of a non-concerted mechanism the choice is difficult because of the eventual formation of an intermediate. By its nature, the problem irreducibly depends on at least two degrees of freedom, which can be chosen as the distance *r* between the carbon atoms 1 and 3 and the dihedral angle φ between carbon atoms 2, 1, 3, and 4, as indicated in Scheme 2. If the mechanism is concerted, *r* is sufficient to describe the reaction path. In a non-concerted process, however, the reaction path evolves from *r* to φ on going from the initial approach of the reagents to the final cyclisation. If both mechanisms co-exist on the energy surface, none of the co-ordinates can unequivocally describe the reaction path (because there are two). Faced with this problem we believe it is preferable to use either a method involving a two-dimensional grid or a selective algorithm such as CHAIN.



Scheme 2.

Results and Discussion

Reaction Mechanism in the Gas Phase.—When the wavefunction is of the closed shell RHF type, the following results are obtained.

(1) The potential energy surface shows two minima, corresponding to reactants and products.

(2) Crossing of the two surfaces exist everywhere between these minima, leading the SCF method to randomly converge either on the ground state or on the closed-shell excited singlet state.

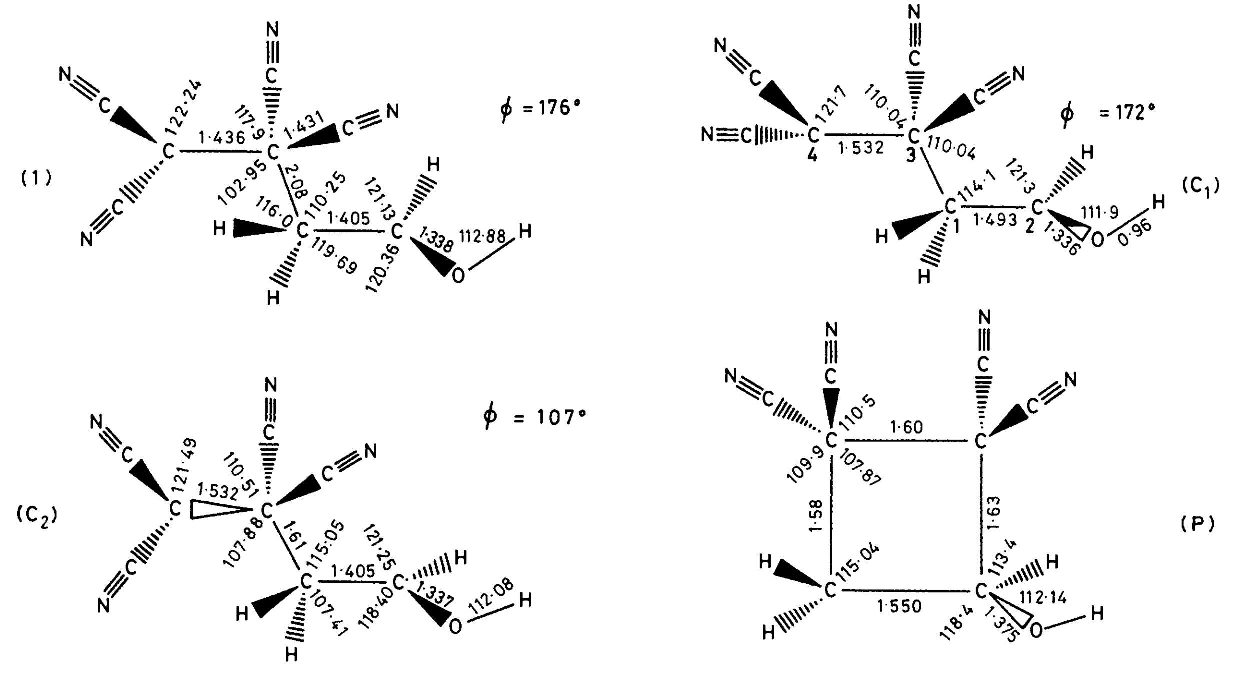
(3) Molecular orbital analysis shows that the crossing originates on the frontier orbitals only.

Therefore the subset of crossing orbitals along the reaction path is of dimension two (HOMO, LUMO). At the SCF level, the half-electron method can be implemented with two open shells for the molecular orbitals to evolve smoothly from

Table 1. Relevant features of the species involved in Scheme 1 in the gas phase

Species	Energy (kJ mol^{-1})	φ^e (°)	r^e (Å)	d(C-2–C-4) (Å)	% Open shell	Dipole moment (D)^f
(R)^a	0				0.11	
(C$_1$)^b	188	178	2.00	3.97	0.48	6.59
(I)^c	100	172	1.60	3.89	93	4.57
(C$_2$)^b	125	107	1.61	3.62	93	4.45
(P)^d	12	4	1.58	1.63	0.12	3.91

[a] Reagents. [b] Transition states. [c] Intermediate. [d] Products. [e] Defined in Scheme 2. [f] Full Tables of the components of the various dipole moments are available, on request, from the authors.



Scheme 3.

reactants to products. At the CI level, the interaction between the first three singlet states must be taken into account. Table 1 shows the characteristics of the stationary points pertaining to the singlet ground state determined at this computational level. There are two minima, essentially of closed shell character, respectively associated with reactants and products. A third minimum is observed, corresponding to an intermediate described by a system with two open shells, whose charges and dipole moment confirm its biradical character. Two transition states with either closed or open shell character connect these minima. A two-dimensional grid analysis confirms the absence of other stationary points, except for a summit lying between reactants and products. Scheme 3 shows the structures of the transition states.

Figure 1 shows the topology of the surface as a function of the fundamental co-ordinates r and φ. The saddle point C$_1$, located 188 kJ mol^{-1} above the reactants, represents the limiting step of the reaction and leads to a stable intermediate. The saddle point C$_2$, lying 25 kJ mol^{-1} above the intermediate, determines the cyclisation path leading to the products. The reaction appears as a thermodynamic equilibrium with a heat of reaction of 12.5 kJ mol^{-1}. These results are somewhat at variance with those of Durán and Bertrán,[26] in their MINDO/3 study of the reaction between vinyl alcohol and acrylaldehyde. These workers found that the second transition state is kinetically determinant and the intermediate has a *gauche* conformation.

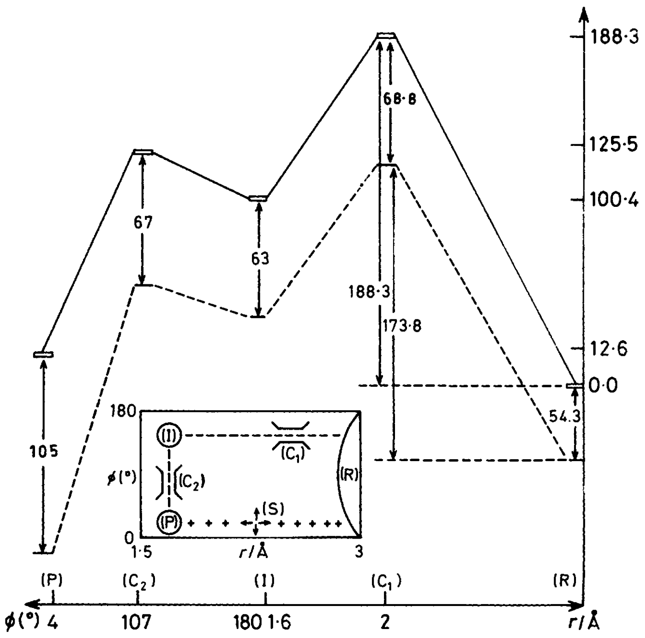


Figure 1. Energy profile for Scheme 1: (——) Gas phase. (– – –) 'Solvated' system

We also find that the reaction path avoids the ridge connecting reactants and product *via* summit S, as indicated in the insert of Figure 1. The absence of a secondary valley in this region of the surface directly illustrates how a hypothetical concerted mechanism is forbidden by the Woodward–Hoffmann rules. The optimised structures of the transition states, the intermediate, and the final product are given in Scheme 3.

Solvent Effects and Acid Catalysis.—Huisgen's hypothesis regarding the structures of the intermediate and the transition state is based on two pieces of experimental evidence.

(1) There is a large increase of the reaction rate with increasing solvent polarity (as determined by its dielectric constant). This is taken to imply the existence of a zwitterionic transition state.

(2) In alcoholic solution acetal formation competes strongly with cycloaddition. Huisgen concluded that this fact also supports the zwitterionic character of the intermediate, for such a species should be able to react rapidly with a solvated proton and thereafter with the alkoxy counterion.

Medium effects on reaction rates can be treated either by considering discrete solvent–solute interactions (crude 'molecular' approach) or by methods such as that of Jano, wherein the solvent is treated as a continuous dielectric medium. In Jano's approach, Born's electrostatic formalism[27] is extended to polyatomic systems through equation (1) where $E_{\text{solv.}}$ is the

$$E_{\text{solv.}} = (1/D - 1)(0.5 \sum_{i} Q_i^2 J_{ii} + \sum_{i<j} Q_i Q_j J_{ij}) \qquad (1)$$

solvation energy, J_{ij} is the Coulomb integral between centres i and j, Q_i and Q_j are the net charges on these centres, and D is the dielectric constant of the solvent. We have studied the limiting case of a solvent endowed with a very high dielectric constant. J_{ss} values were used in order to maintain the spherical symmetry of the core charges in the MNDO formalism.

The approach is certainly very simplistic as it ignores, for instance, the polarisation of the electronic cloud under the influence of the reaction field. These limitations notwithstanding, one finds that the activation barrier is lowered by *ca.* 12 kJ mol^{-1}: this amounts to a *ca.* 10^3 increase of the rate constant, relative to the gas-phase value.

We have also tried a 'molecular' approach using a single 'solvent' molecule. HCN was chosen because of its dipole moment (*ca.* 4 D), low acidity, and tractable size. This attempt was unsuccessful as we failed to find any stable configuration for a supersystem containing one HCN molecule in the neighbourhood of the polar sites of the intermediate or of the transition states. This result might reflect the inadequacy of the MNDO method for the description of molecular aggregates of this kind, possibly because it overestimates the core–core repulsions.[28]

In a protic solvent, protons can be fixed either on one of the ethylenic carbons of TCNE or on the hydroxy group of vinyl alcohol. The minima and saddle points corresponding to these two sites of protonation are indicated in Table 2, the level of description being analogous to that used above (SCF half-electron, CI, optimisation of the geometry). The most stable reactants correspond to the *O*-protonated form, but the order of stability of the first transition state and the intermediate is reversed. In the case of the *C*-protonation of TCNE, cyclisation is blocked upon formation of the intermediate. The first saddle point is highest in all cases, as shown in Figure 2. The nature of the wavefunction describing the reactants, the second saddle point, and the products is little affected by protonation. Open and closed shells are strongly mixed in the first saddle point and the energy varies by 33 kJ mol^{-1} depending on the site of protonation. The nature of the wavefunction of the intermediate very much depends on the site of protonation, indicating the possibility of it rearranging its electronic structure in a protic environment.

Our findings regarding the continuously *O*-protonated path are somewhat different from those reported by Durán and Bertrán,[26] regarding both the structure of the intermediate and the position of the highest saddle point. Moreover, we do not observe any acid catalysis in this case. Along the *C*-protonated

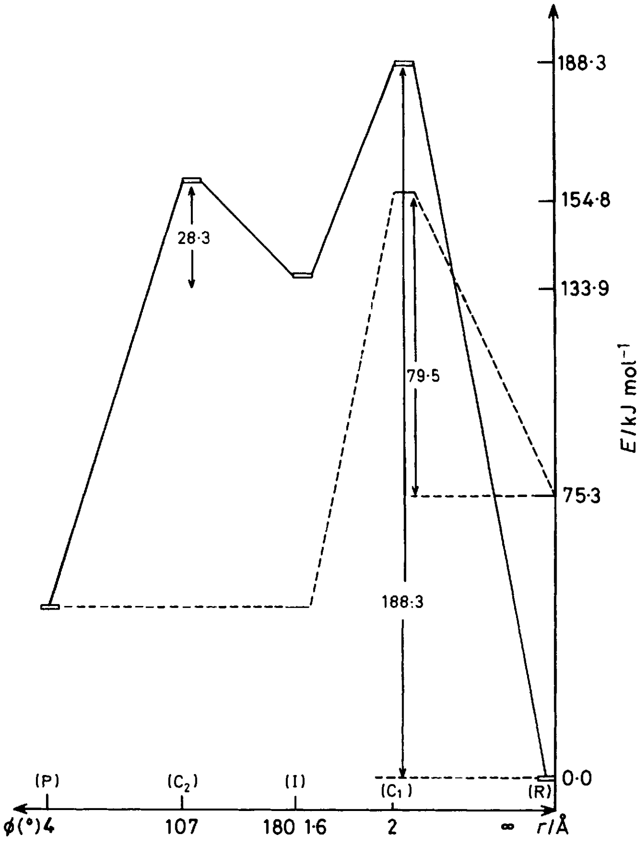


Figure 2. Energy profile for Scheme 1 for acid catalysis conditions in the gas phase. (——) *O*-Protonation path. (– – –) *C*-Protonation path

Table 2. Relevant features of the species involved in Scheme 1 under acid catalysis conditions

	Reagents		F.t.s.[a]		(I)[b]		S.t.s.[c]		P^d
Total energy	O-p[h]	C-p[i]	O-p	C-p	O-p	C-p	O-p	C-p	O-p
(OP)[e] (kJ mol^{-1})	0	75	188	156	134	50	159		46
% (OP)[f]	0.002	0.002	36	34	87	0.003	88		0.005
% (CL)[g]	96	97	54	62	0.09	99	0.08		98

[a] First transition state. [b] Intermediate. [c] Second transition state. [d] Products. [e] Open shell wavefunction. [f] Percentage open-shell character. [g] Percentage closed-shell character. [h] Oxygen protonation. [i] Carbon protonation.

path, on the other hand, the activation barrier is only 84 kJ mol^{-1} high. In the presence of an alkoxide counterion, the intermediate can undergo a fast reaction leading to the acetal. In the absence of a counterion the intermediate has to rearrange itself into the *O*-protonated form, in order to reach the second saddle point, the one leading to the products. Our model cannot show this migration, which obviously requires solvent assistance.

This kinetic analysis along the various reaction paths is not contradicted by the thermodynamic study of the surface. Thus, the activation energy is given by the energy difference between the most stable reactants and the most favourable saddle point leading to a protonated intermediate: this indicates that in a protic environment, the activation barrier is lowered by 33 kJ mol^{-1} with respect to the gas-phase value.

Conclusions.—This semiempirical study shows that the mechanism of (2 + 2) cycloaddition between vinyl alcohol and TCNE is a non-concerted one, as suggested by the Woodward–Hoffmann rules. The kinetics of the reaction are determined by the first step, the outcome of which is an intermediate having a *trans*-conformation and an essentially biradical character. The calculated gas-phase activation energy (188 kJ mol^{-1}) can be reduced by 12 kJ mol^{-1} by the influence of a highly polar solvent. Under conditions of acid catalysis there is a specific lowering of the activation energy amounting to 33 kJ mol^{-1}.

Although the intermediate is a biradical, it can undergo an electronic rearrangement in the presence of a proton. If an alkoxide counterion is available, the acetal can be formed in a process competing favourably with cyclisation.

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