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A comparison of the PVCILO calculated stabilization energies of the DA complexes of *N*-phenylmaleimide and 4-phenyl-1,2,4-triazoline-3,5-dione with methyl vinyl ether

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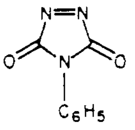
Summary

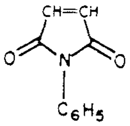
A PVCILO method has been used to compare the stabilization energies of the electron donor electron acceptor complexes between methyl vinyl ether as donor and the enophiles, 4-phenyl 1-1,2,4-triazoline-3,5-dione (1) and N-phenylmaleimide (2), respectively, as acceptor. A stabilization energy difference in favor of the more reactive **1** was obtained, which is being interpreted as an explanation for the enhanced rate of reaction of **1** vs **2**, often by factors $>10^4$.

Discussion and Results

4-Substituted triazolinediones are exceptionally strong electron acceptors and are among the most powerful enophiles and dienophiles known. They react with vinyl ethers and esters, styrenes, *B*-diketones, and alkenes. They have also been used as low-temperature modifiers of diene polymers to produce products which vary widely from thermoplastic elastomers at low conversion to rigid, amorphous polymers with high softening points at high conversion[1,2]. The modified polymers possess an acidic proton, as they contain the 1,4-disubstituted-1,2,4-triazolidine-3,5-dione function. For example, the product of the reaction of propene with **1**,



4-Phenyltriazolinedione
1



N-Phenylmaleimide
2

1-allyl-4-phenyl-1,2,4-triazolidine-3,5-dione, has $pK_a = 4.71$[3]. Cmpd. **1** is isoelectronic with **2**.

Cmpd. **1** is 1000 times more reactive in the Diels-Alder reaction with 2-chloro-1,3-butadiene than tetracyanoethylene, and 2000 times more reactive than maleic anhydride. The corresponding methyl derivative is at least 3×10^4 times more reactive than the conventional azodicarboxylates[1]. The many reactions of these powerful electron acceptors are generally rapid, often being complete within a matter of seconds within the range of 0°C to room temperature.

More recent investigations have shown that complex reactions occur with allyl silanes[4], styrenes[5,6], and electron rich aromatic compounds[7,8]. An unusual product is obtained via reaction of **1** with 2,6-dichlorostyrene in which migration of a chlorine atom from the aromatic ring to an

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** *Present address:* Department of Polymer Science and Engineering, Suncheon National University, Suncheon, Cheonnam 540, Korea aliphatic carbon of the side chain occurs[5]. Bis-triazolinediones have been used as cross-linking agents for polydienes[9] with styrenes via Diels-Alder-ene alternating sequences[10], and in modification of polymers containing electron rich aromatic groups [8].

The relationship of these compounds to maleic anhydride and **2**, both widely studied electron acceptor molecules, is apparent because of the isoelectronic nature of **2** with **1**[11-13]. Styrene initially undergoes a Diels-Alder reaction with strong electron acceptors (e.g. **1**, **2**, etc.) followed competively by (1) a second Diels-Alder reaction[11] or (2) an ene reaction[12]. Structures **1** and **2** undergo these reactions at remarkably different rates, those of **1** being several thousand times faster than those of **2**. Both the structure of the styrene and the acceptor molecule play a role in the distribution of the products between these two routes[5]. Structural factors favoring the ene over the Diels-Alder route, in the case of 2-pyridone with enophiles have been evaluated by a self-consistent perturbational molecular oribital theory (SCF-PMO) approach[13].

Alternating copolymerization of electron donor (D) and electron acceptor (A) vinyl monomers has been known for more than fifty years[14], yet there is still no complete agreement as to the details of the mechanism of these interesting systems[15]. Our interest in the cyclocopolymerization of divinyl ether (DVE) and maleic anhydride (MA) which forms an alternating cyclocopolymer of 1:2 molar ratio, and which has been widely investigated for its biological properties, prompted an investigative program designed to evaluate the role of donor-acceptor complexes (DA) in alternating copolymerization[16-18]. The effects of five experimental parameters, in accord with the Mulliken theory of charge-transfer[19], on the stereochemistry of copolymers derived from 2-chloroethyl vinyl ether and MA were predicted and these predictions tested experimentally. The results of this study were consistent with participation of the DA in the

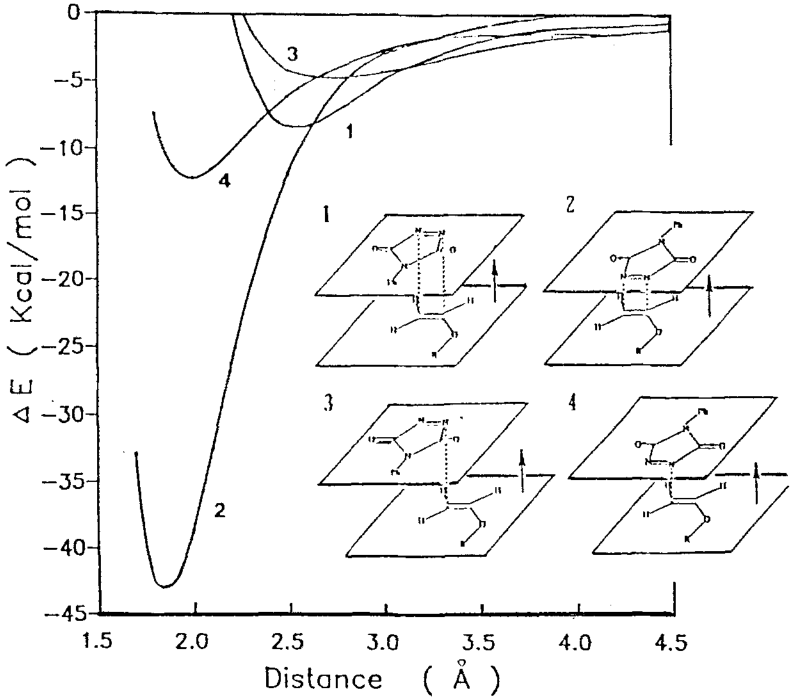


Figure 1. Geometries 1-4 for the DA complex of 1-MVE, and plots of calculated stabilization energies vs distance for each.

propagation step in all five parameters studied. Furthermore, under the most favorable conditions for DA participation, the observed stereochemistry was inconsistent with the competing "free monomer" mechanism of alternating copolymerization. The Mulliken theory also predicts head-to-head (H-H) monomer orientation in the copolymer via DA participation whereas head-to-tail (H-T) orientation is predicted via the "free monomer" mechanism. The presence of H-H structures in a suitably selected comonomer pair was confirmed[17]. These findings are supported by a later similar study[20]. Evidence for steric control via DA participation had been presented earlier in the case of copolymerization of 1,3-butadiene with MA. The microstructure of the alternating copolymer was found to be rich in the cis-1.4-diene unit whereas the trans-1,4-diene unit predominates in the butadiene homopolymer[21].

We have recently conducted both experiments[22] and theoretical calculations[23,24] in further attempts to provide a better understanding of these reactions. It is the purpose of this paper to justify the remarkably different rates of these reactions of compounds such as **1** and **2**. As a comparison, the relative rates of the reactions of chlorine and bromine atoms with methane may be cited. The energy of activation, E_a, of the chlorine-methane reaction = 4 kcal, whereas that for the corresponding bromine reaction = 18 kcal. The chlorine atom reaction has been found to be 25 x 10^4 times as fast as the corresponding bromine reaction.

In order to obtain some quantitive data for comparison, we have continued our study of Localized Bond (PVCILO) Calculations on suitable pairs of electron donors and acceptors[24]. The PVCILO method is a modified PCILO (pertubation configuartion interaction using localized

Table 1. Summary of calculated stabilization energies of Geometries 1-12 for the DA complex of 1-MVE and Geometries 13-14 for the DA complex of 2-MVE.

Geometry Number	MVE Complex with	Optimum Distance, A	Maximum Stabilization Energy Kcal/mol
1	1	2.5	- 8.5
2	1	1.9	- 43.0
3	1	2.6	- 5.0
4	1	2.0	- 12.0
5	1	1.8	- 36.4
6	1	1.9	- 11.0
7	1	2.0	- 6.5
8	1	-	not calculated
9	1	2.1	- 15.0
10	1	2.1	- 10.5
11	1	2.5	- 8.0
12	1	2.0	- 10.0
13	2	2.7	- 5.0
14	2	2.0	- 28.8

orbitals) method and is applied to predict the ability of DA formation and the most stable geometric structures of the DA. The geometric parameters of **1** and **2** were obtained by AM1[25]. Methyl vinyl ether (MVE) was used as D in all cases. The geometric parameters of cis-MVE used were the same as used before[24].

We considered four geometries of DA between **1** and MVE from each of the following three groups: (1) the planes of the A and D molecules are parallel to each other (Geometries 1-4, Figure 1 and Table 1). (2) the double bonds of the A and D molecules are parallel but the planes are vertical to each other (Geometries 5-8, Figure 2 and Table 1); and (3) the planes area parallel but the double bonds are perpendicular to each other (Geometries 9-12, Figure 2 and Table 1). (Geometry No. 8 was not calculated since No. 6 showed lower energy than No. 5.)

Of these 12 geometries, No. 2 possesses the highest stabilization energy, -43.0 Kcal/mol when the molecules are separated by 1.9 Å (Figure 1). This value when compared to a value of -35.7 Kcal/mol for the tetracyanoethylene-MVE system[24] is consistent with the much enhanced reactivity of **1** with donors.

complexes with **1** were examined and the results of two of these geometries (Geometries 13-14) are shown in Figure 3. The methoxy group of MVE appears to hinder approach of the acceptor molecule, as the differences between Geometries 13 and 14 indicate.

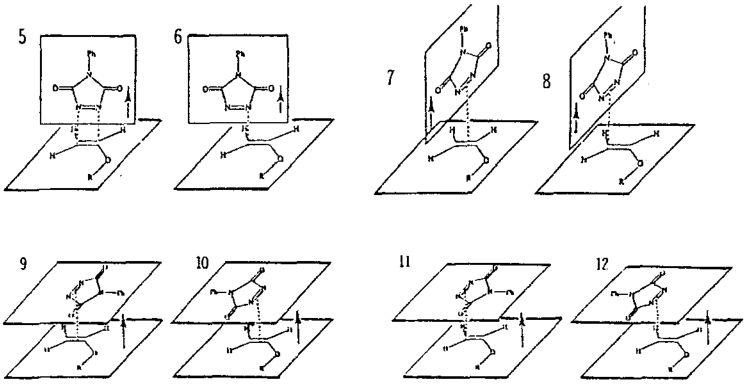


Figure 2. Geometries 5-12 for the DA complex of 1-MVE. Calculated stabilization energies are shown in Table 1.

The stabilization energy of Geometry No. 14 is -28.8 Kcal/mol; this difference, 14.2 Kcal/mol, between this geometry and Geometry No. 2 is attributal to the remarkably higher reactivity of **1** than that of **2**.

Another geometry, No. 5, where the planes of the two molecules are perpendicular to each other showed a rather high stabilization energy of -36.4 Kcal/mol at 1.8 Å separation. A shorter distance of 1.6 Å also showed a high stabilization energy. This geometry was considered on the basis of the published literature[26,27], in which it had been assumed as a necessary geometry in the case of reaction of adamantylideneadamantane 3 with methyltriazolinedone to yield the diazetidine, 5 rather than the ene reaction product (See Equation 1).

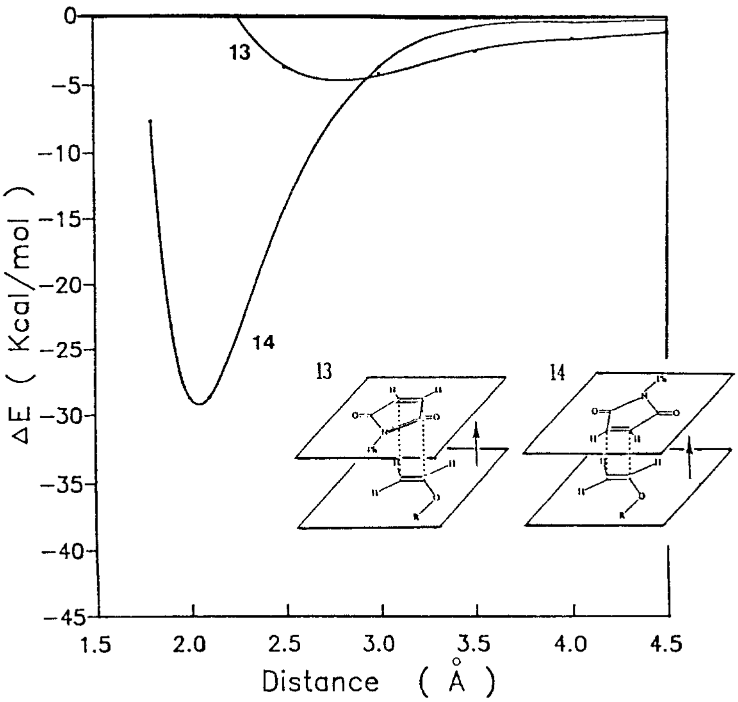
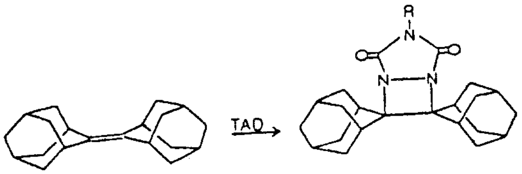
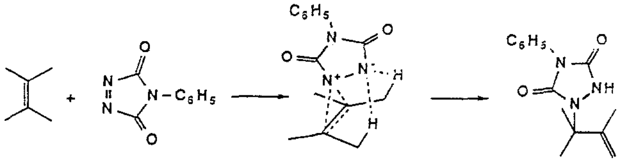


Figure 3. Geometries 13-14 for the DA complex of 2-MVE and plots of calculated stabilization energies vs distance for each.



Eq. 1

Geometries 3,4,6,8,11, and 12 (Figure 2) were considered on the basis of a published paper in which a mechanism had been proposed requiring this type of geometry[28]. (See Equation 2) Surprisingly, Geometry No.12 showed a significant stabilization energy of -16.0 Kcal/mol at a distance of 2.0 Å



Eq. 2

It can be concluded that PVCILO calculations in these systems provide reasonable values of stabilization energies based on a variety of geometries, and that these values are consistent with the known reactivities of these molecules.

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