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Volume of Concert and Heavy Atom Effects in Diels-Alder Reaction Mechanisms

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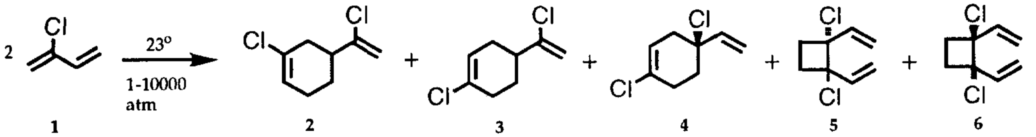
Abstract: The role of heavy atom effects (HAE) in Diels-Alder (DA) reactions is proposed in support of a stepwise-diradical mechanism. The presence of heavy atoms in diene or dienophile causes cycloadditions that are normally stereospecific in the dienophile to become nonstereospecific, because the initially-formed singlet diradical undergoes ISC to the triplet which can rotate but cannot ring close until a second ISC back to singlet. A concerted mechanism cannot accommodate these HAE. The dimerization of chloroprene, which had been analyzed via a dual mechanism based on activation-volume differences among the products, is now seen as unified in mechanism.

INTRODUCTION

Stepwise-diradical mechanisms are always possible for thermal pericyclic reactions. For those that are symmetry-allowed such as the Diels-Alder (DA), a concerted pathway is also available. The latter is expected to be favored when not forbidden because " a chemical reaction will proceed the more readily, the more *bonding* may be maintained throughout the transformation."[1] The difference in activation energy (E_a) between the two mechanisms is known as the Energy of Concert[2], and it should be large since it is equal to that of one sigma-bond, multiplied by its fractional progress down the Reaction Coordinate (RC). When the energy of concert, which can be estimated in various ways, is large, the reaction is considered to be concerted, and when it is small, a diradical mechanism is indicated.[3,4]

In addition to the energy of concert, the terms Entropy of Concert and Volume of Concert, although not heretofore explicitly used in connection with the DA, are meaningful. The concept Entropy of Concert arises because formation of concerted transition states (TSs), in which two new bonds are forming, is believed in some quarters[5] to require more restriction of the position of the reaction partners than formation of a diradical, in which only one new bond is forming. The concept Volume of Concert (without the nomenclature) was first introduced in 1972[6], and is the subject of this paper. The others will be dealt with in a subsequent article.

Stewart (following Billingham[7]) reported that chloroprene dimerized when heated to form three DA (i.e. [2 + 4], symmetry-allowed) cycloadducts and two [2 + 2] (symmetry-forbidden) cycloadducts (eq. 1)[8]. Although all three DA cycloadditions could have been concerted, he assigned only two of them to this category, with the third arising via diradicals, because the first two exhibited large negative volumes of activation (V_a) (-31 and -29 cc/mol), but the third had a smaller negative V_a (-22 cc/mol), comparable in magnitude to those of the two [2 + 2] cycloadditions (both -22 cc/mol) which are symmetry-forbidden.[6] The logic was that the diradical TSs are "considerably less compact". Thus the volume of concert is 7-9 cc/mol for the two DA cases said to be concerted, and zero for the nonconcerted DA and the two [2 + 2] cycloadditions.



(1)

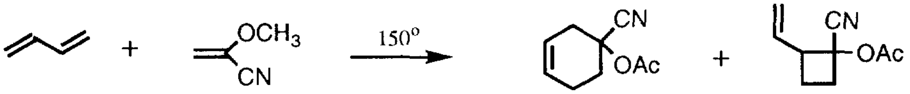
	2	3	4	5	6
Va, cc/mol:	-31	-29	-22	-22	-22
V of concert:	9	7	0	0	0
% yield, 1 atm:	20.5	15.4	21.6	23.6	18.9

Klärner and co-workers buttressed Stewart's mechanistic scheme by showing that DA adduct **4** was indeed formed nonconcertedly, since the dienophile suffered 40% rotation during cycloaddition, which would have been impossible in a concerted cycloaddition.[9] Unfortunately, it proved experimentally too difficult to test the other two DA products for concert in this way. He subjected these and other DA cases to close and elegant mechanistic scrutiny, concluding that Stewart's dual-mechanism scheme was correct, and expanding it. Nine reactions were examined that produced both DA and [2 + 2] cycloadducts, and assuming that the latter were *bona fide* diradical-generated products their V_as were assigned volumes of concert = 0. Three of the nine reactions produced DA cycloadducts with volumes of concert large enough (7 - 14 cc/mol) to signify concerted pathways. Two of these three, and six others, produced additional DA products with volumes of concert too small (0 - 5 cc/mol) for a concerted mechanism, which were therefore assigned to the stepwise category.

Without contradicting any of Klärner's arguments or observations, it is my aim to point out that an equally comprehensive scheme for eq. 1 can be adduced that explains all the facts in a manner that is more parsimonious in that it requires not two concurrent mechanisms but only one. The only single mechanism that is possible is via diradicals.

DISCUSSION

Volume vs. Energy of Concert. In eq. 2, the volume of concert is 11.5 cc/mol, larger than any in eq. 1. This then is a prime example of the concept of volume of concert, favoring concert. Yet this is also a prime



(2)

example of *energy* of concert saying *exactly the opposite*. In three solvents - cyclohexane, acetonitrile and nitromethane - the ratio of [2 + 4] to [2 + 2] products is almost invariant with solvent or temperature, which means that the DA and the (nonconcerted) [2 + 2] cycloadditions have virtually identical E_as. Thus the energy of concert = 0, which led Little in 1965 to conclude that there was a common diradical intermediate for both cycloadducts (In toluene alone, subsequent work by Klarner did find a temperature effect indicating 5.6 Kcal/mol energy of concert).[10] Thus for the most part, Little's conclusion still stands.

Similarly, Billingham was led by the identity of activation parameters for 4- and 6- ring thermally formed dimers from chloroprene to propose that all the cycloadducts arose via diradicals.[7] Here, then, is another example (for **2** and **3**) of a clash between the volume and energy of concert criteria.

Rotation of the Dienophile in Diradicals. There are numerous examples of nonstereospecific DAs, which therefore cannot be completely concerted.[11,12] In most cases the percent of rotation is low, allowing two possibilities: either there are two different simultaneous mechanisms, concerted which allows no rotation, alongside diradical with rotation, or else there is only one mechanism, the diradical one. The first possibility is favored if the rotation in question is fast relative to ring closure, and the second if it is not. The key relationship is eq 3, which sets forth the requirements for a 100% diradical process.

$$\text{nonrotated/rotated product} = k_{\text{cycliz}}/k_{\text{rotation}} + 1 \qquad (3)$$

Taking as an example the dimerization of butadiene, where 3% rotation is observed,[9] in the limiting case - rotation very much faster than cyclization - there cannot be less than 6% diradical component. The slower rotation is, relative to cyclization, the greater the percent diradicals, and for a 100% diradical pathway cyclization must be 31.3 times faster than rotation. Although general agreement on this point is lacking, I believe 31.3 to be reasonable because (1) the products have little or no strain; (2) combination of radicals is free of intrinsic barriers, proceeding at diffusion-controlled rates for not only simple free radicals[13] but also delocalized ones such as benzyl,[13] allyl[14,15] and cyanoallyl;[16] and (3) 5- and 6-ring cyclizations go even faster than their intermolecular counterparts.[12]

Rotational barriers for radicals, while low, are not insignificant. Even for the simplest free radical that could arise from addition to an olefin, n-Pr·, the barrier is somewhere between 0.4 - 3.1 Kcal/mole[17], and each methyl group added to the rotor raises the barrier significantly[18]. Numerous free radicals with significant rotation barriers have been compiled[11]. For our present purpose, what really matters is the *competition* between rotation and closure or cleavage. For 1,4-dimethyl-1,4-diethyl butane-1,4-diyl, cyclization (and reversion) are 50x faster than rotation[19]. Even the primary-secondary diradical 3-methylpentane-1,4-diyl closes 3.1-4.9x faster than rotation, and cleaves 7.5-14.6x faster than rotation, at 120° in octane[20]. This diradical might actually rotate even less, since some of the rotation could have occurred prior to breaking the second bond to nitrogen[20]. Inasmuch as closure of these diradicals to strained four-membered rings is inhibited by 4 Kcal/mole[21], closure/rotation ratios must be much higher than 3.1-4.9 for cyclization to relatively unstrained 6-membered rings, as in DA reactions. Another good example is Gassman's diradical, from maleonitrile and housane, which cyclizes to a quite strained bicycloheptane 9x faster than it rotates[22]. Taking further into account that the radical center of interest from chloroprene dimerization bears on its rotor substituents of mw 89.5 and 61.5, closure (and cleavage)/rotation ratios ≥ 31.5 are reasonable. This matter has been discussed with many more examples[11].

There are a few DA reactions where rotation in the dienophile is very large, and in these cases a completely diradical mechanism cannot be doubted. In addition to eq. 1 there is a group of DA reactions reported in 1974 by Mark,[23] summarized in eq. 4 and Table 1.

$$\text{Cyclopentadiene-Cl}_6 + \text{trans-X-CH=CH-Y} \xrightarrow{164°} \text{DA cycloadduct} \quad (4)$$

Table 1. Rotation of the Dienophile in DA Reactions, eq. 4

X	Y	% Dienophile Rotation in Cycloadduct
CN	CN	43
E	E	27
Ph	Ph	29
Ph	Cl	81
Me	Me	0
Me	Cl	57
Cl	Cl	95

Starting materials and products were stable to heat, with or without catalytic HCl. There was no rotation with any dienophile when the diene was cyclopentadiene itself.

It is clear in Mark's reactions that a congregation of heavy atoms (chlorine) in the vicinity of the radical centers of the diradical intermediate is closely associated with rotation. Exactly the same is true for eq. 1.

In another example, reported by Meier and co-workers in 1987, Z-dienophiles PhCH=CHOMe, MeCH=CHE and ECH=CHE underwent massive rotation during cycloaddition to 2-methylene-cyclohexa-3,5-diene-1-thione.[24] In this case a radical center is right on the heavy atom.

I proposed in 1987[12] that the Heavy Atom Effect (HAE) is responsible for Mark's results, and now extend that proposal to Meier's case, and to Stewart's observations with chloroprene.

Heavy Atom Effect (HAE). Singlet-triplet interconversion within diradicals can be catalyzed by the presence of heavy atoms, i.e. atoms below the first row of the periodic table. The effect, first observed by McClure in 1949,[25] is mediated by spin-orbit coupling (SOC)[26] and is very distance-dependent.[27] Both external[27] and internal[28] HAE are known. It is a means for magnifying the visibility of otherwise fleeting diradicals in chemistry.

Normally, in a thermal reaction such as the DA, only singlet diradicals exist because they are formed directly from closed-shell molecules. Ring closure of cyclo diradicals, or cleavage of extended diradicals back to reactants, is exceedingly fast because both steps are exothermic and virtually barrier-free.[11] That's why diradicals in thermal pericyclic reactions are so ephemeral. However, the HAE provides a route for diversion of singlet (i.e., spin-paired) diradicals to triplets (with spins parallel) which are now trapped, unable to either ring-close or revert to reactants. Of course, this situation doesn't last long, since the HAE also catalyzes spin inversion back to singlet diradicals, which then go on as before. However, during the short period when they are triplets, the diradicals do not lose their ability to perform other things radicals do easily, such as rotate. Thus rotation within thermally produced diradicals, normally difficult to observe because it must compete with other very fast reactions, is greatly increased thanks to the HAE.

The effect is well-documented, experimentally as well as theoretically. External heavy atoms (xenon and organohalogens, the heavier the atom the stronger the effect) accelerate the polymerization of methyl methacrylate by prolonging the lifetime of thermally formed diradical dimers (•C[CH_3][E]-CH_2-$)_2$ via (temperature-independent) intersystem crossing (ISC) to triplets which, though unable to cleave back to monomer, are as capable as singlets of initiating polymerization.[29] Thus the rate of HAE-mediated S⇔T is about as fast as cleavage of diradicals to reactants. Both internal and external HAEs were seen in photocycloaddition to a phenanthrene-fused maleimide via an initially formed singlet which undergoes ISC.[30] In caged triplet radical pairs made by photolysis of dibenzyl ketone, added p-Br causes SOC to dominate ISC.[31] Alkali metal cations also exert HAE.[32] In the spin-forbidden transformation of triplet 1,3-perinaphadiyl diradical to phenalene via H tunnelling, both internal and external HAE were observed: a 6-Br accelerated reaction 6.2x in pet ether, and the rate also increased incrementally 23x over the series of solvents pet ether, Ar, Kr, Xe.[33] Bromobenzene[34] and Xe[35] decrease fluorescence and increase triplet formation in irradiated aromatic hydrocarbons. Photochemical HAE have been reviewed[28].

Closer to our present concern are experiments by Bartlett's group dating back almost 30 years.[36,37] In [2 + 2] cycloaddition (120°) to t,t-2,4-hexadiene of $CF_2{=}CF_2$ (TFE) vs. $CF_2{=}CCl_2$ (1122), unreacted diene (18%) recovered from TFE was completely unisomerized, while that from 1122 (2.3%) was 38% isomerized to c,t, c,c and 1,3-hexadiene. It is true that the 1122 reaction, being faster, has undergone more half-lives, giving more opportunity for rotation, but the difference is too great to be due to this factor only. Furthermore, during cycloaddition there is more rotation in the first-formed diradical from unisomerized hexadiene with 1122 (25.5%) than with TFE (19.4%), showing an unequivocal preference for rotation *vs.* closure in the heavy-atom-bearing diradical, despite 1122's greater reactivity. Bartlett and Hull also described a *decrease* in stereochemical scrambling effected by Cl atoms.[38] In this case, 2-butenes, 1-chloropropenes and 1,2-dichloropropenes were cycloadded to cyclopentadiene by sensitized photoaddition, which forms an initial triplet diradical whose lifetime (before ISC to the singlet which promptly ring closes) decreases with each additional Cl atom in the molecule. In all these experiments, the HAE brings about S⇔T at rates competitive with both rotation and cleavage.

Unified Mechanism for the Dimerization of Chloroprene. The only possible single mechanism is the diradical one. To be convincing, it must account for the principal phenomena observed by Stewart[6] and Klärner:[9] Dimerization of chloroprene is accompanied by 40% rotation in the dienophile whereas dimerization of butadiene involves only 3% rotation. Chloroprene produces three regioisomeric DA cycloadducts, of which one (**4**) has been shown to arise from diradicals. This regioisomer, but none of the others, is accompanied by significant amounts of two [2 + 2] cycloadducts, also undoubtedly via diradicals. The three diradical products have the same V_a, which is significantly lower (less negative) than those of the other two regioisomers **2** and **3**. (There is no evidence apart from V_as that **2** and **3** are formed concertedly, and in fact there is strong evidence *against* concert in that the E_as for 4- and 6-ring formation are identical, and the corresponding activation entropies are similar[7] *[vide supra]*).

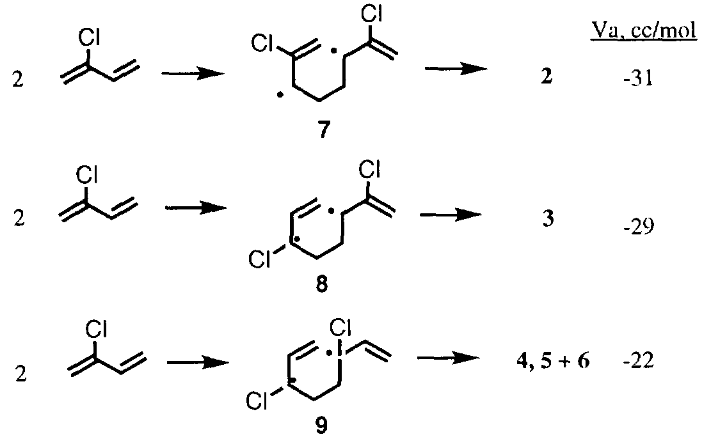
How can we account for the massive loss of stereospecificity with chloroprene *vis-a-vis* butadiene? Why should three different regioisomeric diradicals, each arising from the formation of a single carbon-carbon bond, have different V_as, and different periselectivities? The answers to these questions lie in the HAE.

It is significant that it is diradical **9**, in which both Cl atoms are bonded to radical centers, that produces highly rotated cycloadducts, because it is this diradical that has the best opportunity for HAE-mediated ISC. Butadiene, of course, has no heavy atom; that's why it dimerizes with only 3% rotation. The similarity to

Mark's case[23] is obvious.

With regard to the next question, the first thing to recognize is that there is a correlation (not previously noticed) between V_a and the number of Cl atoms that are borne directly on a radical center.

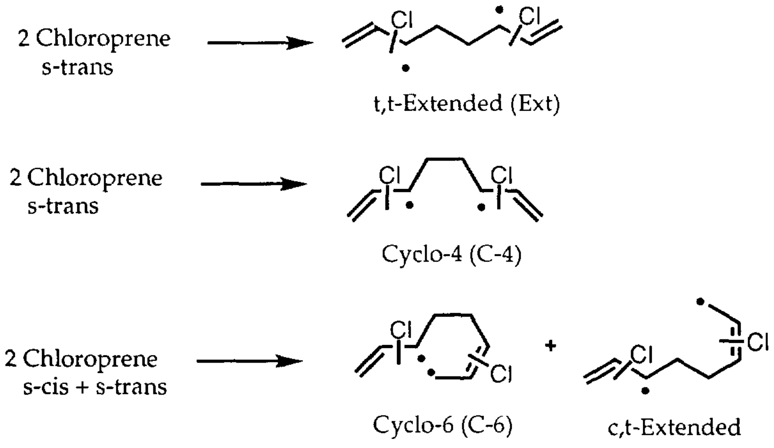
Scheme 1



The HAE-derived propensity of the diradicals to enter the triplet manifold increases in the order **7**<**8**<**9**, and the V_a decreases smoothly in the same order. The connection between triplet diradicals and V_a lies in the fact that extended diradicals, which are kinetically favored for steric reasons but cannot cyclize directly to products, have different volume requirements from cyclo diradicals, which are kinetically disfavored but can cyclize directly to products.

Let us first consider the shapes of diradicals that can be formed directly from two chloroprene molecules. Of the 22 possible shapes, the four best of their type are shown in Scheme 2.

Scheme 2



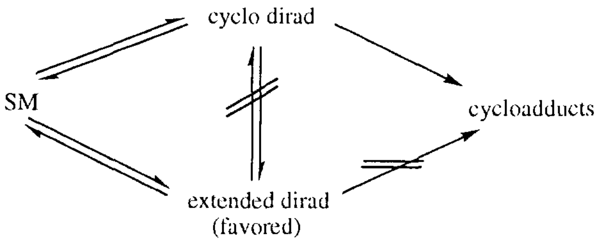
The terminology is based on what the diradicals can do (other than revert to reactants) without any significant bond rotations; thus cyclo-6 (C-6) means it can cyclize to a 6-membered ring, cyclo-4 (C-4) to a 4-membered ring, while extended forms cannot cyclize at all and therefore can only go back to chloroprene. Single-bond rotations are slower than 6-ring cyclization *(vide supra)* or reversal to reactants, but competitive with 4-ring cyclization which has a higher barrier (*ca.* 4 Kcal/mol)[21] than 6-ring cyclization owing to strain in the 4-membered rings. Therefore the diradicals cannot interconvert directly, but only via reversal to reactants.[11,12,39]

All other things being equal, since chloroprene is almost 100% s-trans[40] one expects formation of t,t-extended and C-4, which are accessible from all s-trans chloroprene, to be favored over C-6 or c,t-extended, which require one s-cis reaction partner. Steric factors favor t,t-extended >c,t-extended > C-4 > C-6. Thus most of the diradicals will be extended, which cannot cyclize and thus merely revert to chloroprene, leaving no memento other than a reduced frequency factor. Under normal circumstances (singlet diradicals only) cyclization of C-6 to comparatively unstrained 6-membered rings is strongly favored over cyclization of C-4 to highly strained 4-membered rings. That's why most DA reactions give 6-ring products in preference to 4-ring.[41]

The important volume principle is this: formation of a single bond leading to an *extended* conformation involves a *small* volume change (*ca.* - 5 cc/mol), but leading to a *cyclo* conformation it involves a *large* volume change (*ca.* -30 to -40 cc/mol).[9,42] The reason for the difference is not that cyclo conformations are intrinsically smaller than extended ones, but rather that cyclic arrays have a higher packing fraction, i.e. there is less empty space in the solvent shell surrounding them.

Scheme 3 depicts the state of affairs with a normal DA, i.e. one that occurs entirely within the singlet manifold. It should be understood that rotations shown as restricted are not necessarily inhibited in the usual sense. Rather, they are slow only *in comparison* with other very fast steps, i.e. cyclization and reversion to reactants (*vide supra*).

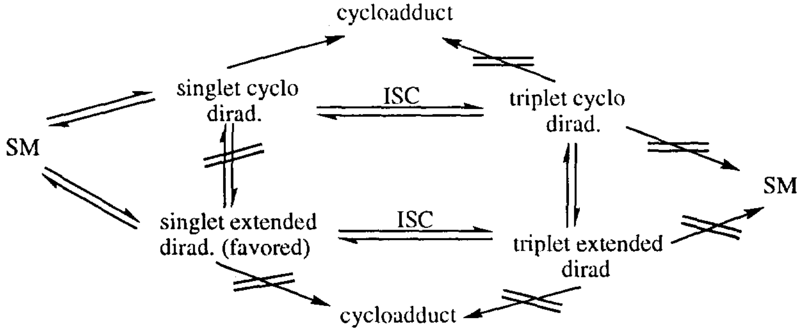
Scheme 3



Cyclo diradicals (V_a = -30 to -40 cc/mol) participate in product formation, but extended ones (V_a = - 5 cc/mol), favored though they are, do not because they cannot cyclize without first converting to the cyclo form by means of bond rotation, which is too slow to compete with reversion to reactants. Consequently, normal DAs have large negative V_as.

When the HAE is introduced, however, the picture becomes more complex (Scheme 4). Thanks to rapid ISC, the initally formed singlet diradicals can become triplets, which are unable to either cyclize or revert to reactants. They can rotate, however, so now there is a pathway for direct transformation of extended to cyclo diradicals. Triplet c,t-extended diradicals rotate to cyclo diradicals which cyclize after a second ISC back to singlets. Since extended diradicals initially form faster, the more easily ISC occurs the more extended diradicals will participate in product formation, with the result that the observed overall V_a will become less negative. That is why V_a becomes less and less negative as chlorine atoms are moved one by one onto radical centers.

Scheme 4



The next question is why significant amounts of [2 + 2] cycloadduct are formed only from diradical regioisomer **9**, in which both chlorines are on radical centers. The answer becomes apparent when one remembers that the HAE can be either internal or external, i.e. it matters only how close the heavy atom is to the radical center, not whether or not it is bonded to it.

Diradical **9** alone is peculiarly favored in this respect because when and only when it is in the C-4 conformation, each Cl atom is close to not only its own radical center but also *the other radical center.* Therefore, during its rotational peregrinations in the triplet manifold, whenever **9** passes through conformer C-4 (especially favored since it arises from the most accessible form, t,t-extended) it undergoes ISC to the singlet at a higher rate than in any other conformation (or than diradicals **7** or **8** in any possible conformation). In this way **9** has a special pipeline to the 4-ring cycloadducts **5** and **6** which compensates for the disadvantageous strain in the formation of 4-rings.

The conclusion is that all the peculiar features of this system flow naturally from heavy atom effects exerted by the chlorine atoms within diradical intermediates. Thus a single mechanism, the diradical one, explains all the facts without the necessity of invoking two different mechanisms.

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