ON THE MECHANISM OF THERMAL 2+2 CYCLOADDITION REACTIONS INVOLVING FLUORO-OLEFINS

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Abstract – A concerted $2_s + 2_a$ mechanism is proposed for cycloaddition reactions of fluoro-olefins to give substituted cyclobutanes. Published data on relative rates, orientation and stereochemical course of these reactions are reconsidered and it is concluded that the concerted $2_s + 2_a$ mechanism provides a more satisfactory rationale than the commonly accepted diradical mechanism.

INTRODUCTION

Fluoro-olefins of type (1) undergo thermal 2+2 cyclodimerisation reactions and mixed cyclo-addition reactions with other olefins (2) to give substituted cyclobutanes[1,2]:
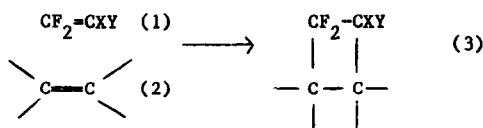
In most cases reported, at least one of the groups X and Y in (1) is fluorine, but (1, X=Y=Cl) (1, X=Y=Br) are also known to undergo 2+2 cyclodimerisation and cycloaddition reactions.

The role of (2) may be played by fluoro-olefins, simple olefins such as ethylene and by substituted olefins such as acrylonitrile. In reactions of fluoro-olefins (1) with conjugated dienes, the 2+2 cycloaddition usually predominates over the 2+4 Diels Alder reaction.

This 2+2 cycloaddition is usually assumed to proceed <u>via</u> a stepwise mechanism involving a singlet diradical intermediate (4)[2–4]
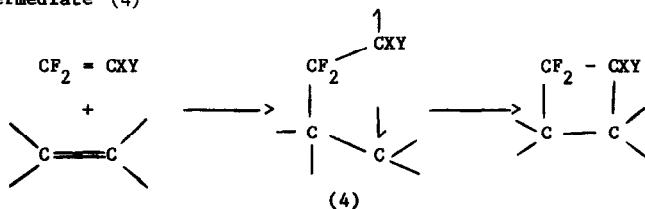
This mechanism can account for:

a) Non-stereospecificity, observed in reactions when (2) can exist in two geometrically isomeric forms.

b) The orientation of addition, which is found to be consistent with the most stable structure for (4). Thus, 1,1-dichlorodifluoroethylene dimerises to give 1,1,2,2-tetrachlorotetrafluorocyclobutane, and reacts with butadiene to give 1,1-dichloro-2,2-difluoro-4-vinyl cyclobutane.

c) The observed insensitivity of the rate to polarity of the reaction medium.

However, the stepwise diradical mechanism does have major deficiencies. In this paper it is argued that a concerted 2_s+2_a mechanism is also tenable, and is more consistent with the data on thermal 2+2 cycloaddition reactions of fluoro-olefins.

DEFICIENCIES OF THE DIRADICAL MECHANISM

The stepwise diradical mechanism has two major weaknesses:

1. It provides no answer as to why fluorine substitution is necessary. There seems no obvious reason why simple olefins such as ethylene, propylene, isobutene etc should not undergo cyclodimerisation reactions by the same mechanism.

2. The intermediacy of the diradical species (4) seems a reasonable assumption for cases such as the cyclodimerisation or addition to conjugated dienes of 1,1-dichlorodifluoroethylene, where both of the free radical centres in (4) bear free radical stabilising substituents. However, it seems less plausible when this is not the case. For example, tetrafluoroethylene reacts with ethylene and with itself to give 1,1,2,2,-tetrafluorocyclobutane and octafluorocyclobutane respectively, although the F and H substituents are poor at stabilising free radicals. Furthermore, in reactions with tetrafluoro-ethylene, ethylene is reported to be ten times as reactive as 2-butene[5], although the latter would be expected to give the more stable diradical intermediate. Kinetic data[6,7,8] on the cyclodimerisa-tion and mixed cycloaddition reactions of tetrafluoroethylene and chlorotrifluoroethylene (Table 1) seem completely at variance with the diradical mechanism. On the basis of the stabilising effects of the substituents on the free radical centres in the diradical intermediate (4), the activation energies would be expected to differ significantly, but the reported values are in fact very similar. It has been pointed out by Haszeldine et al[9] that the pre-exponential factors for these reactions are of similar magnitude to those observed in Diels-Alder reactions.

Table 1. Kinetic data for cycloaddition reactions of tetrafluoroethylene (A) and chlorotrifluoroethylene (B)

Reaction	E_{Act} (Kcal.mole^{-1})		A (1 mole^{-1}s^{-1})	Ref.
	Predicted for diradical mechanism	Observed		
2A $\longrightarrow$ C$_4$F$_8$	Highest	26.3	16.5×10^7	6
		25.4	10.3×10^7	7
A+B $\longrightarrow$ C$_4$ClF$_7$	Intermediate	26.3	8.54×10^7	6
2B $\longrightarrow$ C$_4$Cl$_2$F$_6$	Lowest	26.3	3.53×10^7	6
		26.6	4.3×10^7	8

Other data which are difficult to reconcile with the diradical mechanism are:

a) In cycloaddition reactions with styrene, the observed order of fluoro-olefin reactivities[10] is

$CF_2 = CF_2 > CF_2 = CFCl > CF_2 = CFCN > CF_2 = CFBr > CF_2 = CFI$,

with $CF_2 = CFCF_3$ and $CF_2 = CFH$ found to be inert. This conflicts with the order predicted on the basis of the relative abilities of the halogens to stabilise free radicals, which would give

$CF_2 = CFI > CF_2 = CFBr > CF_2 = CFCl > CF_2 = CF_2$.

b)   An experiment in which approximately equimolar quantities of tetrafluoroethylene and 1,1-dichloro-difluoroethylene were heated together at 200°C for 20 hr, with an initial pressure of 50 atm., gave the following results [11].

Tetrafluoroethylene:

    ca. 40% recovered
    ca. 30% converted to octafluorocyclobutane
    ca. 30% converted to 1,1-dichlorohexafluorocyclobutane

1,1-Dichlorodifluoroethylene:
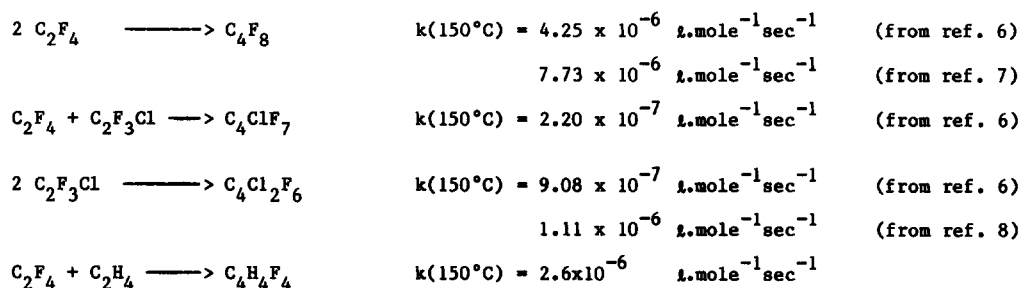
    ca. 40% recovered
    ca. 30% converted to 1,1-dichlorohexafluorocyclobutane

Since only the readily volatile products were analysed, the yield of 1,1,2,2-tetrachlorotetrafluoro-cyclobutane was not established; from the mass balance it is calculated as <u>ca.</u> 30% of the initial 1,1-dichlorodifluoroethylene. In a separate experiment [11b], 1,1-dichlorodifluoroethylene gave 43% conversion to 1,1,2,2-tetrachlorotetrafluorocyclobutane on heating at 200°C for 20 hr with an initial pressure of 100 atm.

From these data it is clear that the cyclodimerisation reactions of tetrafluoroethylene and 1,1-dichlorodifluoroethylene, and the mixed cycloaddition reaction, all have similar rate constants at 200°C.

On the basis of the diradical mechanism, the cyclodimerisation of 1,1-dichlorofluoroethylene would be expected to be much more facile than the mixed cycloaddition reaction, which in turn should be much more facile than the dimerisation of tetrafluoroethylene.

c)   Tetrafluoroethylene and ethylene react together at 150°C to give 1,1,2,2-tetrafluorocyclobutane [12] (40% yield with 8 hr reaction time and initial C_2F_4 and C_2H_4 concentrations of 0.87 and 6.7 mole ℓ^{-1} respectively). It is stated that under the reaction conditions used the dimerisation of tetrafluoroethylene does not occur as a competitive reaction [12]. From the experimental details given [12], a rough estimate of the rate constant for the C_2F_4 + C_2H_4 reaction can be made, assuming no tetrafluorocyclobutane was lost in the work up (if any was lost, the calculated rate constant would be lower than actual). This rate constant may be compared with the rate constants at the same temperature for the cycloaddition reactions involving tetrafluoroethylene and chlorotrifluoroethylene (calculated from the data shown in Table 1):

$2\ C_2F_4 \longrightarrow C_4F_8$	$k(150°C) = 4.25 \times 10^{-6}$ $\ell.\text{mole}^{-1}\text{sec}^{-1}$	(from ref. 6)
	7.73×10^{-6} $\ell.\text{mole}^{-1}\text{sec}^{-1}$	(from ref. 7)
$C_2F_4 + C_2F_3Cl \longrightarrow C_4ClF_7$	$k(150°C) = 2.20 \times 10^{-7}$ $\ell.\text{mole}^{-1}\text{sec}^{-1}$	(from ref. 6)
$2\ C_2F_3Cl \longrightarrow C_4Cl_2F_6$	$k(150°C) = 9.08 \times 10^{-7}$ $\ell.\text{mole}^{-1}\text{sec}^{-1}$	(from ref. 6)
	1.11×10^{-6} $\ell.\text{mole}^{-1}\text{sec}^{-1}$	(from ref. 8)
$C_2F_4 + C_2H_4 \longrightarrow C_4H_4F_4$	$k(150°C) = 2.6 \times 10^{-6}$ $\ell.\text{mole}^{-1}\text{sec}^{-1}$	

There is some discrepancy between these figures and the statement that competitive dimerisation of

the tetrafluoroethylene does not occur in the C_2H_4/C_2F_4 reaction, but in view of the

approximate nature of the calculations this is not serious. It is however quite clear that the

data do not support the diradical mechanism, which predicts that the $C_2F_4 + C_2H_4$ reaction

should be much the slowest of the four, since the corresponding diradical intermediate is the

least stabilised by substituents at the radical centres.

THE CONCERTED $2_s + 2_a$ MECHANISM

An alternative to the diradical mechanism is a concerted 2+2 cycloaddition pathway. A concerted

$2_s + 2_s$ pathway has been ruled out on the grounds that it would violate the Woodward-Hoffmann

rules [13], but a concerted thermal $2_s + 2_a$ pathway is allowed. Epiotis[14] argues for such a

mechanism in a 1972 paper, but in a subsequent paper[15] he concludes that the diradical mechanism

applies, citing the predominance of head to head orientation in cyclodimerisation of unsymmetrical

fluoro olefins such as chlorotrifluoroethylene, for which perturbation theory predicts a preference

for head to tail orientation. This point will be considered in more detail further on.

An argument often quoted against a concerted pathway is that 2+2 addition reactions involving olefins

which can exist in two geometrically isomeric forms have been found to be non-stereospecific[5,13].

However, this does not rule out the $2_s + 2_a$ pathway. In a $2_s + 2_a$ reaction the configuration of

the antarafacial component becomes inverted, so that stereospecificity (complete retention or complete

inversion of configuration) would only be expected if one of the reactant olefins exhibits a strong

preference between reacting antarafacially or suprafacially. There is such a preference in

cycloaddition reactions of ketenes to olefins, for which a strong secondary interaction involving the

antibonding orbital of the carbon-oxygen π bond causes the ketene to react as the antarafacial

component [16], but for cycloaddition reactions involving only fluoro-olefins and simple olefins this

does not apply. For 2_s+2_a reactions in general, electronic considerations lead to a preference for

the antarafacial component to be the olefin which acts as a net electron acceptor in the transition

state [17], but for non-polar cycloadditions such preferences are likely to be outweighed by steric

effects [14].

The remainder of this paper is concerned with demonstrating how the concerted $2_s + 2_a$ mechanism can

rationalise the observed features of thermal 2+2 cycloaddition reactions of fluoro-olefins.

WHY FLUORINE SUBSTITUTION IS NECESSARY

In a fluoro-olefin the olefinic carbon atoms are more electronegative than those of ethylene, due to

the electron withdrawing inductive effects of the substituents. This alone would decrease the energies

of the π and π^* orbitals relative to those of ethylene. However, there is an opposing effect due to

interaction of these orbitals with the fluorine lone pairs. Both π and π^* have antibonding character

between the carbon and fluorine atoms, and are thus raised in energy. The effect is greater for π than

for π^*, since π is the closer in energy to the fluorine 2p orbitals. Thus the energy difference

between π and π^* is lower in a fluoro-olefin than in a simple olefin. It follows that the $\pi - \pi^*$

interactions in reactions involving fluoro-olefins will be significantly stronger than the

corresponding interactions in reactions involving only simple olefins. This is illustrated by π and π^*

energies for ethylene, tetrafluoroethylene, mixed chlorofluoro-olefins and butadiene, calculated by the

Hückel method [18,19].   Orbital energies calculated by more sophisticated methods (CNDO and INDO) have

been published [20] for the olefin series $C_2H_nF_{4-n}$ (n=0 to 4), but not for the mixed chlorofluoro-

olefins, and also illustrate the trend for the $\pi-\pi^*$ energy gap to decrease with increasing fluorine

substitution. Table 2 shows the $\pi-\pi^*$ energy differences, based on the Hückel calculations, for

cyclodimerisation and mixed cycloaddition reactions involving ethylene, tetrafluoroethylene, mixed

chlorofluoro-olefins and butadiene. It is clear that the experimentally observed order of reactivities

is rationalised successfully by consideration of Hückel-based $\pi-\pi^*$ energy differences alone.

Table 2. $\pi-\pi^*$ energy differences for pairs of olefins

Olefin 1	Olefin 2	Energy difference[a] (β-units), between			Cycloaddition reaction between olefins 1 and 2
		$\pi^*(1)$ and $\pi(2)$	$\pi^*(2)$ and $\pi(1)$[b]	Mean[b]	
C_2H_4	C_2H_4	2.2	2.2	2.2	Not observed
$CF_2=CCl_2$	$CF_2=CCl_2$	2.023	2.023	2.023	Reactions proceed
C_2F_4	C_2F_4	2.005	2.005	2.005	at 150°C and above.
C_2F_4	$CF_2=CFCl$	2.044	1.974	2.009	Differences among
C_2F_4	$CF_2=CCl_2$	2.084	1.944	2.014	rate constants are
C_2F_4	C_2H_4	2.427	1.778	2.102	not large (see text).
C_2F_4	Butadiene	1.945	1.296	1.620	Proceeds at 125°C [c]
$CF_2=CCl_2$	Butadiene	2.024	1.235	1.629	Proceeds at 80°C[d]

a.   Based on published orbital energies calculated by the HMO method, using the following
parameters:

C_2H_4 and perhalo-olefins[18]: $\alpha_F = \alpha + 3\beta$, $\alpha_{Cl} = \alpha + 2\beta$, $\beta_{C-C} = 1.1\beta$

$$\beta_{C-F} = 0.7\beta, \quad \beta_{C-Cl} = 0.4\ \beta$$

Butadiene[19]: $\beta_{C-C} = \beta$

b.   Note that where olefins 1 and 2 are not the same, the $\pi^*(2) - \pi(1)$ energy difference
     is smaller than that between $\pi^*(1)$ and $\pi(2)$, and will therefore predominate in determining
     the reaction rate. A value somewhere between the figures in these two columns should
     therefore be a measure of relative rate.

c.   90% yield (after work-up, based on initial C_2F_4) of 1,1,2,2-tetrafluoro-3-vinylcyclo-
     butane after heating C_2F_4 (1 mole) and butadiene (2.3 mole) at 125°C for 8 hr in a 400 ml
     autoclave [12].

d. $k \sim 9 \times 10^{-6}$ l.mole sec^{-1} [21].

A further special feature of fluoro-olefins concerns the non-bonding interactions in 2_s+2_a cycloaddition.
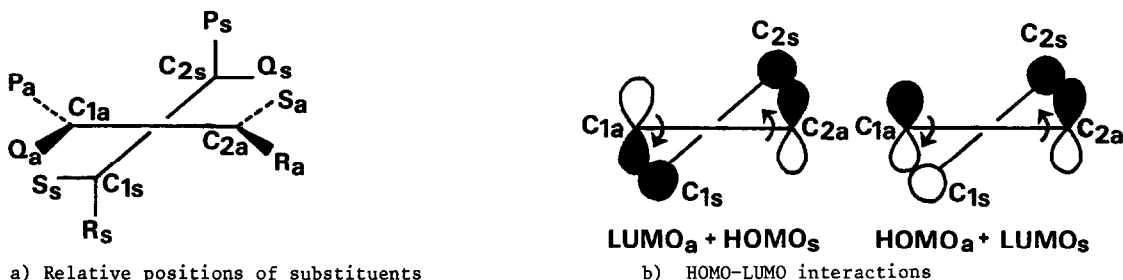
The approach geometry for a concerted 2_s+2_a cycloaddition between two olefins is shown in Figure 1a, in which the substituents on the double bonds are labelled P,Q,R,S with the suffixes s and a referring to the suprafacial and antarafacial components respectively. In this approach geometry, the major non-bonding interactions are:
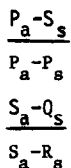
$$\underline{P_a-S_s}$$
$$P_a-P_s$$
$$\underline{S_a-Q_s}$$
$$S_a-R_s$$

Note that S_a is closer to Q_s than it is to R_s, and P_a is closer to S_s than it is to P_s, so that the interactions S_a-Q_s and P_a-S_s will be stronger than the other two. For this reason, these interactions are underlined. Two of the substituents, Q_s and R_a on the antarafacial component, are not involved in non-bonding interactions.

Figure 1 – Concerted 2_s-2_a cycloaddition

Suffixes a and s refer to the antarafacial and suprafacial components respectively

a) Relative positions of substituents (s-substituents are in the plane of the paper, a-substituents are in a plane perpendicular to that of the paper).

b) HOMO-LUMO interactions

c) Partial bonding between C_{1a} and C_{1s} corresponding to $LUMO_a$ + $HOMO_s$. View in a plane perpendicular to the $C_{1a}-C_{2a}$ bond.
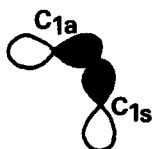
d) Reaction product
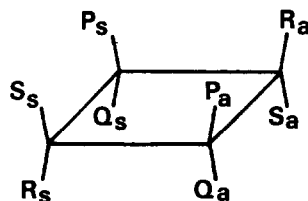
As discussed in more detail in the next section, the transition state is probably derived from this approach geometry by twisting of the double bond between C_{1a} and C_{2a}, in the direction of the curved arrows in Figure 1b. Provided the extent of twisting about $C_{1a}-C_{2a}$ is less than 90° at each end, the non-bonding interactions listed above for the approach geometry will also be the dominant ones in the transition state. Non-bonding interactions can be of major importance in determining reactivity, as shown by data on cycloaddition reactions of ketenes to olefins. For these reactions, P_a and Q_a are absent, the only major non-bonding interactions being S_a-Q_s and S_a-R_s. It is found that dimethyl and diphenyl ketenes react more readily with cis 1,2-disubstituted ethylenes, for which the transition state can have the configuration $Q_s=R_s=H$, than with the trans isomers, for which one of Q_s and R_s must be bulkier than H. Some idea of the range of magnitude of this effect is given by the data assembled in Table 3.

Table 3. Relative rate data for cycloaddition reactions of cis and trans ketenophiles with ketenes

| Ketene | Ketenophile | S_a-R_s | | k_{cis}/k_{trans} | Reference |
		Cis[a]	Trans[a]		
Dimethyl	but-2-ene	Me-H	Me-Me	At least 3[b]	22
Diphenyl	propenyl propyl ether	Ph-H	Ph-Me	ca 18.5	23
Ethoxy	but-2-ene	H-H	H-Me	15[c]	24

a. It is assumed that the most stable configuration for the transition state corresponds to $Q_s=H$ for both cis and trans isomers.

b. Isobutene reacts 8 times slower than cis-but-2-ene, whilst under the same conditions trimethylethylene and tetramethylethylene do not react[22].

c. Incorrectly quoted as 1.7 in ref. 22.

For 2_s+2_a cycloaddition reactions involving fluoro-olefins, the non-bonding interactions may be significantly weaker than they would be if the fluorine atoms were replaced by other substituents, because of the small size of the fluorine atom (van der Waals radius 1.35 Å, cf hydrogen 1.2 Å, chlorine 1.8 Å)[25]. This is a further reason why fluoro-olefins are more suitable than other olefins for participation in 2+2 cycloaddition reactions.

Thus the uniqueness of fluorine, as regards the 2+2 cycloaddition, is based on the fact that it is the smallest monovalent substituent capable of reducing the $\pi-\pi^*$ energy difference in an olefin, thereby favouring the concerted cycloaddition reaction both on steric and electronic grounds.

ORIENTATION OF ADDITION

As stated earlier, Epiotis[15] concluded that the diradical mechanism rather than the 2_s+2_a mechanism applies, on the grounds that perturbation theory predicts head to tail orientation rather than the head to head orientation which is observed, for cyclodimerisation of unsymmetrical olefins. The perturbation argument may be summarised as follows:

Consider the cyclodimerisation of an unsymmetrical olefin $C_1ab = C_2cd$ where a, b, c, d are substituents and C_1 is the more electronegative of the two olefinic carbon atoms. The coefficient of C_1 in the bonding orbital π will be larger than that of C_2, and conversely the coefficient of C_2 will be larger than that of C_1 in π^*. This is shown in exaggerated form in Figure 2a. It follows that the strongest bonding interaction between the two components in the $2_s + 2_a$ cyclodimerisation is between C_1 (π) of one olefin and $c_2(\pi^*)$ of the other in the head to tail orientation Figure 2b), and it can be shown [15] that the overall bonding interaction between the two components for this orientation is greater than for the head to head orientation (Figure 2c).

However, for relatively non-polar species such as the fluoro-olefins, this effect should be quite small, and likely to be outweighed by an opposing effect as follows. The approach geometry for the $2_s + 2_a$ concerted cycloaddition is shown in Figure 1a. As the reactants approach each other, HOMO-LUMO interactions as depicted in Figure 1b lead to bonding between C_{1a} and C_{1s} and between C_{2a} and C_{2s} (the subscripts a and s being used to label carbon atoms belonging to the antarafacial and suprafacial components respectively). This bonding is initially weak, the partial bonds being bent at right angles as shown in Figure 1c. As the reactant molecules approach each other more closely, twisting of the double bond in the antarafacial component occurs as indicated by the arrows in Figure 1b, leading to straightening and consequently strengthening of the $C_{1a}-C_{1s}$ and $C_{2a}-C_{2s}$ partial bonds. At the same time the $C_{1a}-C_{2a}$ and $C_{1s}-C_{2s}$ π bonds are weakened: in the former case by being twisted out of planarity and in the latter case by partial donation of the $\pi(s)$ electrons into $\pi^*(a)$ and the partial acceptance of $\pi(a)$ electrons into $\pi^*(s)$. It seems reasonable to assume that the transition state will correspond to a configuration in which the loss of $C_{1a}-C_{2a}$ and $C_{1s}-C_{2s}$ π bonding outweighs the gain in $C_{1a}-C_{1s}$ and $C_{2a}-C_{2s}$ bonding. Thus each of the four originally olefinic carbon atoms will have a higher free valence in the transition state than it has in the reactants or in the product.

Now consider the situation where both reactants are unsymmetrical, where the substituents on C_{2s} are better than those on C_{1s} at stabilising free radicals and those on C_{2a} are better than those on C_{1a}. The most stable transition state would be expected to correspond to C_{1s} becoming bonded to C_{1a}, with the $C_{1s}-C_{1a}$ partial bond shorter and less bent than that between C_{2s} and C_{2a}, so that the total free valence is centred mainly on C_{2s} and C_{2a} where it can best be stabilised. A very similar argument was presented by Roberts and Sharts[1] who, several years before the distinction between $2_s + 2_s$ and $2_s + 2_a$ modes of concerted cycloaddition had been recognised, suggested a concerted mechanism proceeding via a "virtual diradical" intermediate (5) as a possible alternative to the stepwise diradical mechanism:
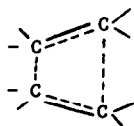
(5)

In perturbation theory terms, this orientation is favoured by increases in bonding energy, in the transition state, between C_{2s} and its substituents and between C_{2a} and its substituents. This transition state can be reached from the approach geometry shown in Figure 1, with C_{1a} twisting towards C_{1s} more than C_{2a} twists towards C_{2s}.

Thus electronic considerations for the 2_s+2_a mechanism lead to the same prediction regarding orientation of addition as does the singlet diradical mechanism. There are three important differences, however. Firstly, for the 2_s+2_a mechanism the free radical character of C_{2a} and C_{2s} need

Figure 2 - HOMO-LUMO Interactions for $2_s + 2_a$ Cyclodimerisation of Unsymmetrical Olefins

a)   HOMO and LUMO

b)   Head to tail
dimerisation –
$HOMO_a$ + $LUMO_s$ and
$LUMO_a$ + $HOMO_s$

c)   Head to tail
dimerisation –
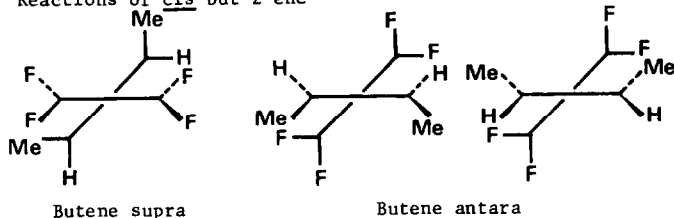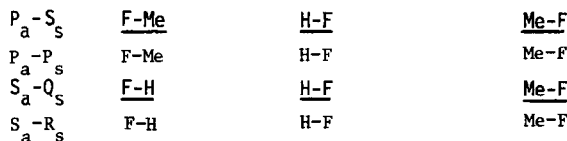$HOMO_a$ + $LUMO_s$ and
$LUMO_a$ + $HOMO_s$
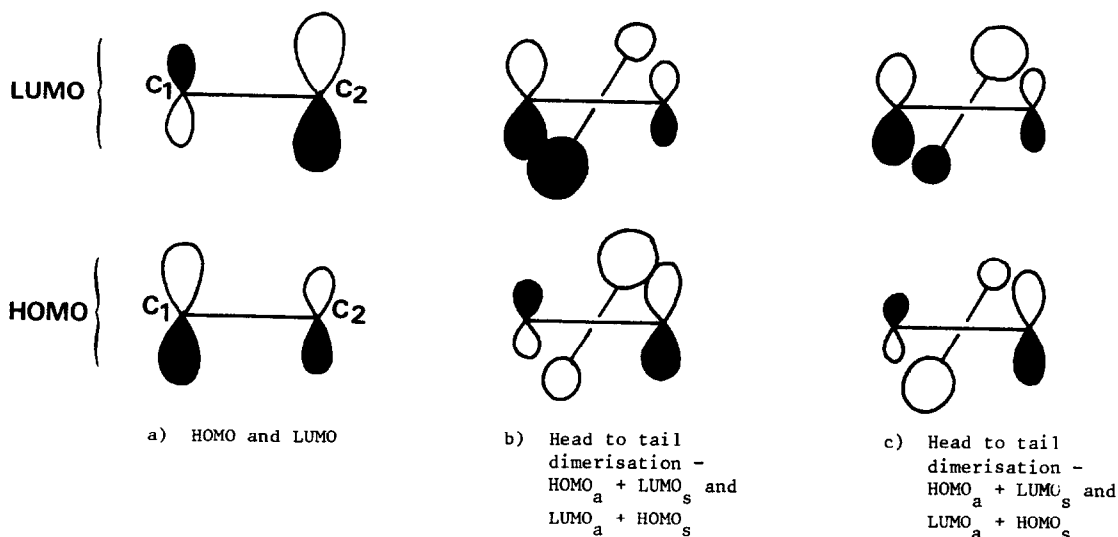
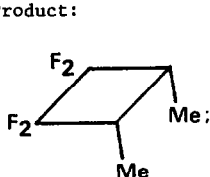Figure 3 - Non-bonding interactions for concerted $2_s + 2_a$ cycloadditions of tetrafluoroethylene to but-2-enes
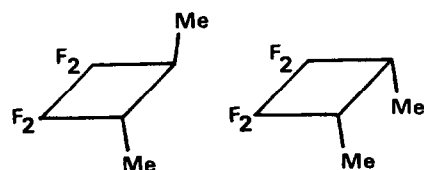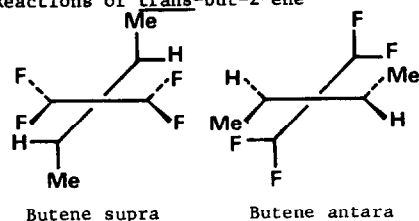
Reactions of cis-but-2-ene

Reactions of trans-but-2-ene

	Butene supra	Butene antara		Butene supra	Butene antara
Major interactions:					
P_a-S_s	F-Me	H-F	Me-F	F-H	H-F
P_a-P_s	F-Me	H-F	Me-F	F-Me	H-F
S_a-Q_s	F-H	H-F	Me-F	F-H	Me-F
S_a-R_s	F-H	H-F	Me-F	F-Me	Me-F

Product:

not be large at any stage in the reaction. Secondly, in the 2_s+2_a mechanism free rotation about $C_{1a}-C_{2a}$ and about $C_{1s}-C_{2s}$ is not possible at any stage in the reaction. Thirdly, for the 2_s+2_a mechanism free rotation about $C_{1s}-C_{1a}$ is not possible.

STEREOCHEMISTRY OF ADDITION

The stereochemical course of 2+2 cycloadditions involving fluoro-olefins can be rationalised in terms of the non-bonding interactions in the 2_s+2_a transition state. As discussed earlier, these interactions may be taken as being qualitatively the same as those for the approach geometry shown in Figure 1a. The following examples illustrate how the 2_s+2_a mechanism can account for the published findings.

$\underline{CF_2 = CF_2 + CHD = CHD}$
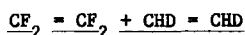
The substituents on both reactants are all small, so that non-bonding interactions will be weak. There are no electronic factors which would cause either reactant to exhibit a strong preference between reacting antarafacially or suprafacially. Thus for either the cis or the trans isomer of 1,2-dideuteroethylene, there will be two competitive reactions with tetrafluoroethylene – one where the dideuteroethylene reacts antarafacially with inversion of configuration in the product, the other where the dideuteroethylene reacts suprafacially with retention of configuration in the product, e.g.
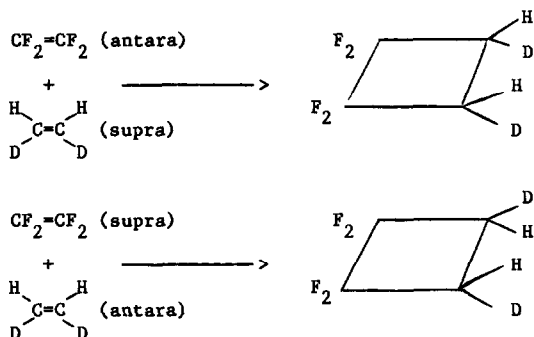
It is not possible to predict which of these two reactions will be faster, but it seems unlikely that one will predominate to the exclusion of the other.

It follows that a mixture of $\underline{cis}$ and $\underline{trans}$ 1,2-dideutero-3,3,4,4-tetrafluorocyclobutanes should result from reaction of tetrafluoroethylene with either isomer of 1,2-dideuteroethylene. This is in agreement with what is reported [13] : both reactions give products shown by their infrared spectra to be mixtures of the two cyclobutanes. Close inspection of the spectra reproduced in the original reference does reveal some differences. This would be expected on the basis of the concerted 2_s+2_a mechanism, since it would be unreasonable to expect absolutely no preference as to whether the tetrafluoroethylene or the dideuteroethylene reacts suprafacially.

$\underline{CF_2=CF_2 + CH_3.CH:CH.CH_3}$
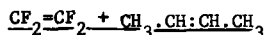
There are no obvious electronic factors which would lead to a strong preference as to which component should react antarafacially and which suprafacially. The non-bonding interactions for the various possible configurations are shown in Figure 3. It can be seen that for the reaction of $\underline{cis}$-butene

with tetrafluoroethylene, there is a steric preference for the butene to react antarafacially, since in

this configuration the only significant non-bonding interactions are between H and F. For the reaction

of trans-butene with tetrafluoroethylene the steric preference is for the trans-butene to react

suprafacially. Irrespective of whether the trans-butene reacts suprafacially or antarafacially there

are two Me-F and two H-F non-bonding interactions, but for the former case the more important pair of

interactions P_a-P_s and S_a-Q_s are both F-H whereas for the latter case the S_a-Q_s interaction is Me-F.

Thus, of the two butenes, the cis isomer should exhibit the stronger preference for reacting

antarafacially, resulting in a greater degree of inversion of configuration in the cyclobutane

produced. The reported findings[5] are in agreement with this analysis: cis-butene reacts with

tetrafluoroethylene at 175° to give 1,1,2,2-tetrafluorodimethyl cyclobutanes in the proportion 41.8 cis

to 58.2 trans, i.e. 58.2% inversion, whereas trans-butene gives the cyclobutanes in the proportions

72 trans to 28 cis, i.e. 28% inversion.

$CF_2=CFCl$ and $CF_2=CFBr$ dimerisation

Electronic considerations lead to a preference for the formation of 1,2-dihalohexafluorocyclobutanes

rather than the 1,3 isomers. For the 2_s+2_a pathway there are four possible approach geometries leading

to 1,2-dihalohexafluorocyclobutanes, as shown in Figure 4. Approach geometries (a) and (b) are clearly

disfavoured on steric grounds; for (a) there are three F-X or X-F interactions and for (b) there are

one X-F and one X-X interaction. Approach geometries (c) and (d) each exhibit only one F-X interaction

and no X-X interactions. The F-X interaction corresponding to geometry (d) would be expected to be

larger than that corresponding to geometry (c) in the transition state, so that considerations of the

Figure 4 – Non-bonding interactions for concerted 2_s + 2_a cyclodimerisation of
           trifluorohaloethylenes

X = Cl or Br, all other substituents F

| | (a) | (b) | (c) | (d) |
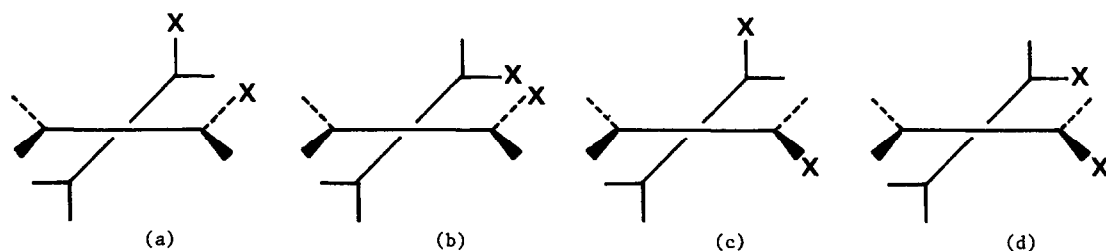
Major interactions:

P_a-S_s	F-F	F-F	F-F	F-F
P_a-P_s	F-X	F-F	F-X	F-F
S_a-Q_s	X-F	X-X	F-F	F-X
S_a-R_s	X-F	X-F	F-F	F-F
Orientation of X groups in product	trans	cis	cis	trans

non-bonding interactions leads to an overall preference for formation of the cis product. The
magnitude of this preference cannot be estimated simply: it will depend on the relative magnitudes of
F-X interactions of types P_a-P_s and S_a-Q_s. However, it is clear that there should be no
preference for formation of the trans 1,2-dihalohexafluorocyclobutane, which would be predicted to be
the major product from the diradical pathway. The reported findings are consistent with this analysis.
Dimerisation of chlorotrifluoroethylene at 304.5-509.1°C was reported in 1952 [6] to give
1,2-dichlorohexafluorocyclobutane exclusively, with a cis:trans ratio of 5-10:1, but in a 1960 paper
from the same group [26] it is stated that the cis and trans isomer are produced in approximately
equal amounts over a temperature range from 130 to 225°C. A cis:trans ratio of about 1:1 has
subsequently been reported by another group[8], who found that the equilibrium ratio was 1:1.67.
Dimerisation of bromotrifluoroethylene gives 1,2-dibromohexafluorocyclobutanes with a cis:trans ratio
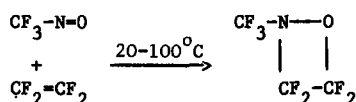of 60:40[27].

CONCLUSIONS

The concerted 2_s+2_a mechanism can account satisfactorily for the observed data concerning 2+2
cycloaddition reactions of fluoro-olefins.

Relative rate data, which in several cases are inconsistent with the diradical mechanism, may be
interpreted in terms of the differences in energy between the HOMO of one reactant and the LUMO of the
other. The 2_s+2_a mechanism allows the orientation of 2+2 cycloaddition reactions to be interpreted
in terms of the free-radical stabilising power of the olefinic substituents, but without requiring a
high degree of free radical character to develop at any point along the reaction profile. The stereo-
chemical course of 2+2 cycloaddition reactions can be interpreted in terms of the non-bonding
interactions in the transition state for the 2_s+2_a cycloaddition.

It is therefore concluded that the concerted 2_s+2_a mechanism rather than the diradical mechanism
applies in many cases of 2+2 cycloaddition reactions involving fluoro-olefins, especially those
reactions for which the intermediate corresponding to the diradical mechanism would not have strongly
stabilising substitutents at both free radical centres. The arguments presented here do not preclude
the possibility that the diradical mechanism might apply for reactions where the intermediate would
be particularly stabilised, such as the cycloaddition reactions between 1,1-dichlorodifluoroethylene
and conjugated dienes, but even for these cases the 2_s+2_a mechanism is equally tenable and, as
Epiotis has shown by arguments analogous to those presented here, correctly predicts the
stereochemical course of reaction[14].

It also seems possible that the concerted 2_s+2_a mechanism applies for the thermal cycloaddition
reactions between trifluoronitrosomethane and fluoro-olefins, forming oxazetidines[28], e.g.

$$CF_3-N=O \qquad\qquad CF_3-N{-\!\!-}O$$
$$\xrightarrow{20-100°C} \qquad |\quad\;|$$
$$+ \qquad\qquad\qquad\qquad$$
$$CF_2=CF_2 \qquad\qquad CF_2-CF_2$$

Trifluoronitrosomethane seems particularly suited to participate in 2_s+2_a reactions, since if it reacts as the antarafacial component with $R_a=CF_3$ (Figure 1a) the non-bonding interactions are minimal.

Haszeldine et al have previously suggested[9] that the above reaction is concerted, on the basis of a kinetic study in which the pre-exponential factor was found to be in the same range as the pre-exponential factors for Diels-Alder reactions and dimerisation and mixed cycloaddition reactions of tetrafluoroethylene and chlorotrifluoroethylene.

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ADDENDUM

After this paper had been accepted an investigation by Dolbier and Wicks into the stereo-
chemistry of 2+2 cycloaddition of 1,1-difluoroallene to (Z)-β-deuterostyrene was published[29].
The allene reacts about 80-85% at the CF_2 = C bond and about 15-20% at the CH_2 = C bond. The
degree to which the Z configuration of the styrene is retained in the product is greater when the
allene reacts at the CH_2 = C bond than when it reacts at the CF_2 = C bond:
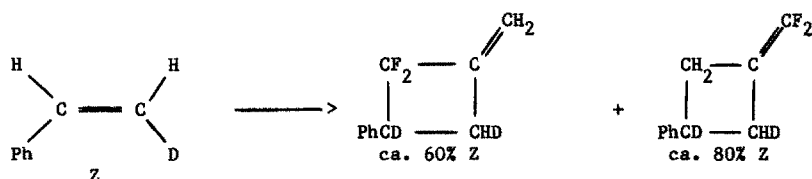
Dolbier and Wicks present a mechanistic rationâle, based on the diradical mechanism, for this
difference in stereospecificity. However, a simple explanation can be given in terms of the
concerted $2_s + 2_a$ mechanism, as follows.

There are no steric factors which would lead to a strong preference as to which compound should
react as the antarafacial component. The extent to which the allene will tend to react
antarafacially will be influenced by the extent to which π^* of the non-reacting allenic double bond
can interact with the occupied olefinic π orbital (cf. the strong secondary interaction in ketene
cycloadditions) in the configuration allene (antara)-olefin (supra). This will depend on the extent
to which this π^* orbital tends to be located on the central carbon atom, and, inversely, on the
energy difference between these two orbitals.

When 1,1-difluoroallene reacts at CF_2 = C, the non-reacting double bond is C = CH_2. Since
the central carbon atom is sp hybridised, and hence more electronegative than the CH_2 carbon
atom, $\pi^*(C = CH_2)$ will be located more at the terminal carbon atom than at the central atom. Also,
its energy will be much higher than that of π(olefin). For these two reasons, interaction between
$\pi^*(C = CH_2)$ and π(olefin) will be relatively weak.

When the allene reacts at CH_2 = C, the non-reacting double bond is C = CF_2. Since the
terminal carbon atom bears electronegative fluorine substituents, $\pi^*(C = CF_2)$ will be located at
the central carbon atom to a greater extent than is $\pi^*(C = CH_2)$. Also, because of the high
electronegativity of the F-substituents, π^* $(C = CF_2)$ will be lower in energy than π^* $(C = CH_2)$.
For these two reasons, π^* $(C = CF_2)$ can interact more strongly than $\pi^*(C = CH_2)$ with π (olefin)
when the allene reacts antarafacially. Thus there is a greater tendency for the allene to react
antarafacially, corresponding to retention of stereochemistry in the styrene moiety, when it
reacts at C = CH_2.

In effect, when 1,1-difluoroallene reacts at CF_2 = C it tends to behave like a fluoro-olefin, and
when it reacts at CH_2 = C it tends to behave like a ketene.

ADDITIONAL REFERENCE

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