Dual One-centre Frontier-orbital Interactions in [2 + 2] Cycloadditions of Ketenes

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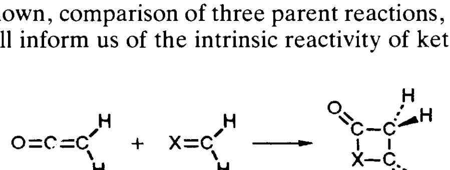
Dual one-centre frontier–orbital interactions are found to control the paths of cycloadditions of ketene to ethylene, methylenimine and formaldehyde by the analysis of the intrinsic reaction coordinates calculated with the MP2/6-31G* basis set.

Ketenes undergo cycloadditions to double bonds in the 'symmetry-forbidden' [2 + 2] way rather than in the allowed [4 + 2] way.[1] This mysterious selectivity has been attributed to a variety of orbital interactions[2] starting from the [π2s + π2a] type of Woodward–Hoffmann rule.[3] Recently, transition states (TSs) of the ketene addition to ethylene have been searched for with *ab initio* calculations.[4–6] However, these calculations have not provided the precise orbital picture for the [2 + 2] paths.

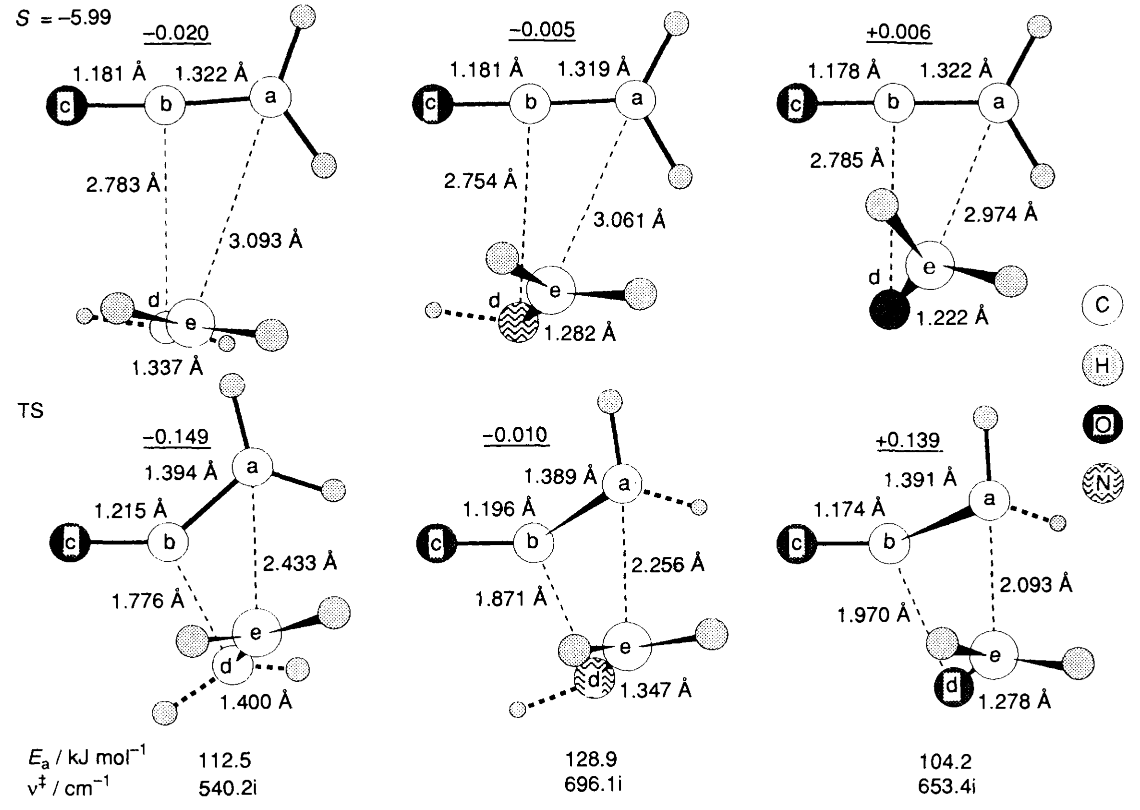
In this communication, we show the quantitative analysis of the frontier molecular orbital (FMO) interactions in the following three ketene cycloadditions. Since various [2 + 2] additions of olefin,[7] imine[8] and carbonyl[9] double bonds are known, comparison of three parent reactions, (1), (2) and (3), will inform us of the intrinsic reactivity of ketene.



1; X = CH_2
2; X = NH
3; X = O

The FMO theory is derived from the perturbation theory[10] and is concerned not with TS but with the early stages of the addition. Therefore, accurate geometries of these stages are indispensable to describe quantitatively the FMO interaction. The combination of the search for the intrinsic reaction coordinate (IRC)[11] and the configuration analysis (CA)[12] on the IRC geometry are the best tools for elucidating the orbital-level mechanism of the concerted[13] [2 + 2] cycloaddition of the ketene. In order to use this unique tool, first, the TSs of reactions (1), (2) and (3) are determined with the second-order Møller–Plesset wavefunction on the 6-31G* basis set (MP2/6-31G*) and subsequently the IRC paths[14] are traced. Computations are made using the GAUSSIAN 90 program.[15]

Fig. 1 shows the early stage and TS geometries. At TS, only one imaginary frequency ($\nu^{\ddagger}$) is calculated which shows each geometry obtained is of the true saddle point in reactions (1), (2) or (3). The rank of the activation energies, E_a, (2) > (1) > (3), is of mechanistic interest. The difference of the $C^a\cdots C^e$ distance at TS [2.433 in reaction (1), 2.256 in reaction (2) and 2.093 Å in reaction (3)] is also noteworthy, because these



(1) Ketene to ethylene (2) Ketene to methylenimine (3) Ketene to formaldehyde

Fig. 1 Geometries of reactions, (1), (2) and (3) at $S = -5.99$ u$^{1/2}$ a_0 on IRC and those of TSs ($S = 0.0$) obtained with MP2/6-31G*. The underlined numbers attached to ketene denote net charges (negative, anionic). AT TS, the computed activation energies (E_a) and imaginary harmonic frequencies (ν‡) are also exhibited.

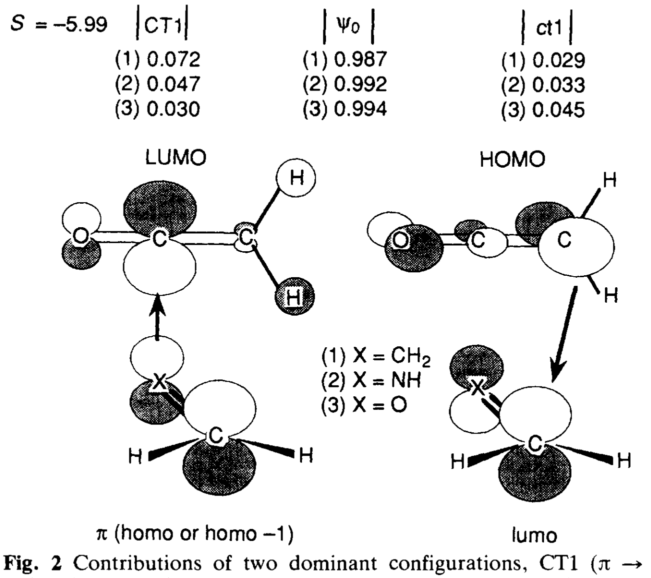
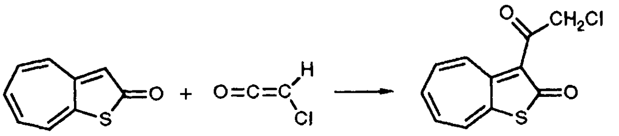


Fig. 2 Contributions of two dominant configurations, CT1 (π → LUMO) and ct1 (HOMO → lumo) except the adiabatically interacting configuration ψ_0 derived from CA. The capital letters, HOMO and LUMO, are for ketene and the small letters, homo, homo-1 and lumo, are when X = H_2C. The homos of methylenimine and formaldehyde are in-plane lone-pair orbitals which contribute to the charge-transfer interactions |CT2|s, homo → LUMO, 0.016 in (2) and 0.010 in (3) to the smaller extent than those in Fig. 2.

distances are almost equal at $S = -5.99$. This difference-equality contrast demonstrates that the $C^a\cdots C^e$ bond formation is advanced in reaction (3) and is behind in reaction (1). The progress in the other bond formation is in the rank $C^b\cdots C^d$ in (1) > $C^b\cdots N^d$ in (2) > $C^b\cdots O^d$ in (3) at S = −5.99 → TS. At S = −5.99 and TS, the ketene is an electron acceptor in reactions (1) and (2), while it is a donor in reaction (3).



To analyse those geometric characteristics, second, the CA is carried out at S = −5.99 and two dominant configurations (except ψ_0) are drawn in Fig. 2; CT and ct denote charge-transfer interactions. The dominance of CT1 and ct1 indicates that the FMO interaction does control the reaction path. The rank, (1) > (2) > (3) of |CT1| is in contrast with that, (3) > (2) > (1) of |ct1|. This donor–acceptor contrast is reflected in net charges of ketene (−0.020 of (1), −0.005 of (2) and +0.006 of (3) in $S = -5.99$ of Fig. 1). The effective $C^b\cdots C^d$ bond formation in (1) is ascribed to CT1, while the $C^a\cdots C^e$ one is to ct1. The largest E_a (128.9 kJ mol^{-1}) of (2) in Fig. 1 is attributable to the merely moderate contribution of CT1 and ct1.

Since HOMO and LUMO of ketene expand orthogonally, their FMO interaction take place independently. The independence is regarded as two one-centre FMO interactions (left side of Fig. 3) and is entirely different from the in-plane orbital overlapping required in 1,3-dipolar (right side of Fig. 3) and Diels–Alder cycloadditions. That is, two one-centre MO overlaps are not concerned with orbital symmetries, [2 + 2] and [4 + 2]. In some cases, one of two becomes extremely important leading to the zwitterionic intermediate. In fact, the one-centre adduct of chloroketene to 1-thia-2-azulenone has been reported recently.[16] The combination of the low-lying (inactive) HOMO and small lumo lobe on the C^e of aromatic compounds will make the ketene a one-centre electrophilic reagent like NO_2^+.

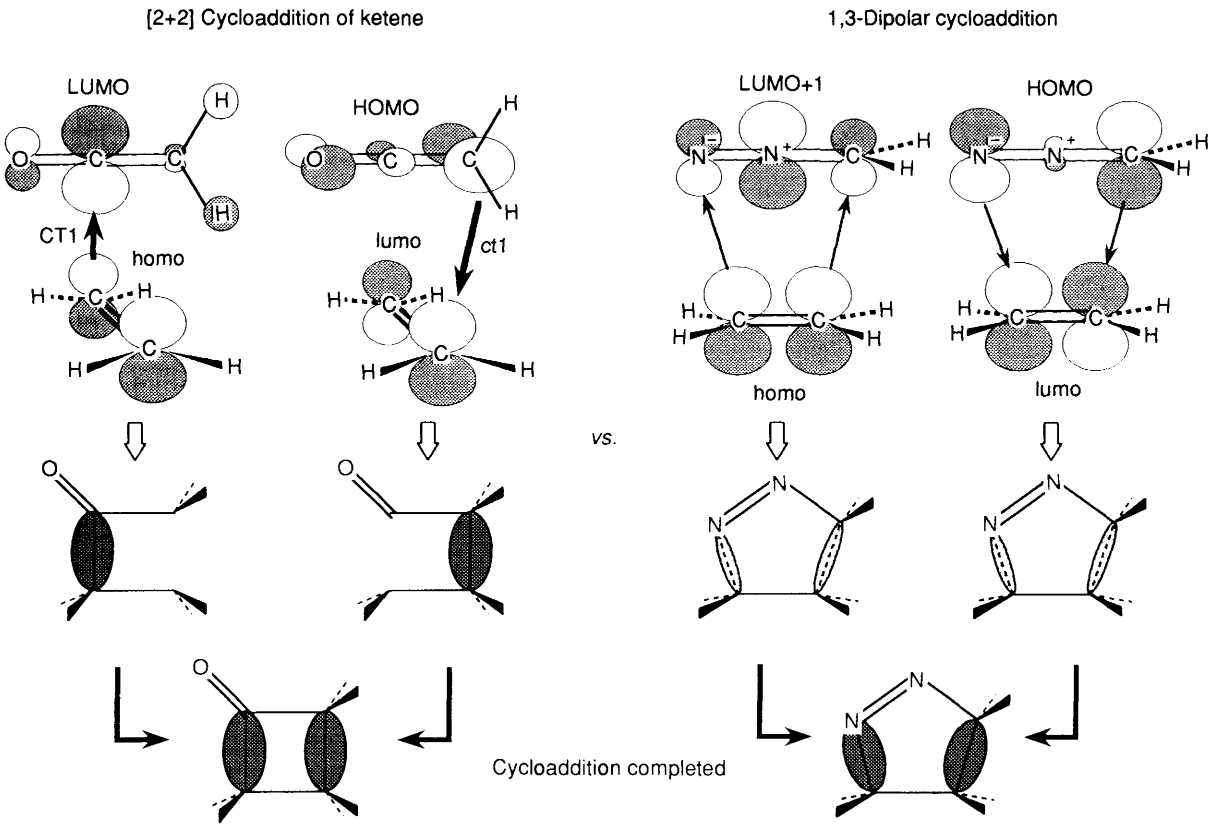


Fig. 3 Schematic presentation of dual one-centre frontier–orbital interactions. The different FMO interactions lead to different cycloadducts. While ketene reacts with ethylene in two one-centre MO overlaps, diazomethane does in symmetric and antisymmetric (in-plane) MO overlaps.

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