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A Common Feature in the 2+2 Cycloadditions of Benzyne and $^1\Delta_g$ Molecular Oxygen to Ethylene Derivatives

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The abnormal behavior of $^1\Delta_g$ molecular oxygen in the cycloaddition reaction previously stimulated our interest in a well-established, close connection between orbital interaction and stereoselection,[1] since the singlet oxygen gives 2+2 and 4+2 cycloadducts, both retaining the configuration of the substrate olefins.[2] A consideration of the orbital interaction scheme[1] was previously found to suggest that the singlet oxygen may approach ethylene, as is represented by Model I.[3] This sort of reaction path for 2+2 cycloaddition was novel and is clearly different from the symmetry-allowed 2_s+2_a process generally proposed for concerted cycloaddition by Woodward and Hoffmann.[4] The preference for this nuclear configuration has been attributed to the fact that the interaction between the highest occupied (HO) molecular orbital (MO) of ethylene as an electron-donor and the lowest unoccupied (LU) MO of the oxygen molecule as an electron-acceptor is most favored in this nuclear configuration. The prediction of the addition mechanism

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[1] The essence of this concept may be briefly said as follows; a majority of chemical reactions should take place at the position and in the direction where the particular interaction between the frontier orbitals is most favored.

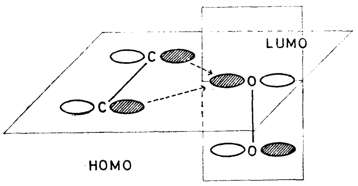
For further particulars on the HOMO-LUMO interaction scheme, see the following articles; K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971); K. Fukui and H. Fujimoto, "Mechanisms of Molecular Migrations," Vol. 2, ed. by B. S. Thyagarajan, Interscience, New York, N. Y. (1969), p. 118; K. Fukui, "Theory of Orientation and Stereoselection," Springer-Verlag, Heidelberg, (1970).

[2] For stereospecific *cis*-[2+2] cycloaddition, P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970) and for 4+2 cycloaddition with the stereochemical integrity of retention, see the following review; D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971).

[3] S. Inagaki, S. Yamabe, H. Fujimoto, and K. Fukui, This Bulletin, **45**, 3510 (1972).

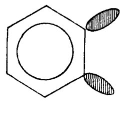
[4] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Academic Press, N. Y. (1970).

tempts us to seek the most favorable path of the reaction between olefinic C=C double bonds and benzyne, which exhibits a similar behavior toward unsaturated hydrocarbons.[5] Here, this problem will also be probed by means of the HOMO–LUMO interaction scheme.[1]

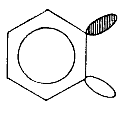


I

The electronic state of benzyne has been presented in several papers,[6] and it has been shown that the HOMO (II) and the LUMO (III) have the same symmetry property as normal mono-olefins.[6a] Accordingly, it can readily be found that the simple symmetry arguments of the Woodward-Hoffmann method[3] predict that suprafacial-suprafacial[3] cycloaddition is symmetry-forbidden and that the other mode of suprafacial-antarafacial process is not probable for the following reasons. No antarafacial mode on benzyne is conceivable since the particular MO's of benzyne extend their lobes exclusively outward from the benzene nucleus[6a] (see II and III). On the other hand, the antarafacial interaction is possible on the side of ethylene, but this $2\pi_s+2\pi_a$ process ends in the inversion of the ethylene derivative configuration, which is inconsistent with the experimental observations.[5] It follows that the simple application of the Woodward-Hoffmann dichotomy of symmetry-allowed 2_s+2_a and symmetry-forbidden 2_s+2_s processes cannot produce fruitful information on the reaction between benzyne and ethylene.


HOMO

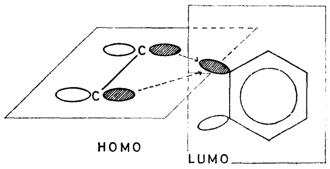
II


LUMO

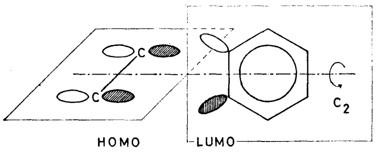
III

Here, the electronic structure of benzyne, particularly the LUMO with an abnormally low energy or with a negative eigenvalue (the result of *ab initio* calculation),[6b] should be noted; this suggests the strong electrophilicity of benzyne.[7] This characteristic is markedly different from normal olefins, but is similar to the ${}^1\Delta_g$ oxygen molecule.[4] It may, therefore, be considered that benzyne may also provide the LUMO for the critical orbital interaction with ethylene.

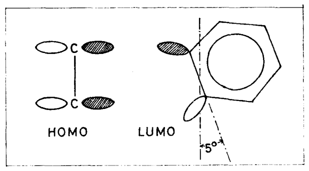
The above discussion allows us to predict the most favorable reaction path, using the degree of interaction between the HOMO of ethylene and the LUMO of benzyne as the primary measure. We will examine the same sorts of models (IV, V, and VI) as with the singlet oxygen. Here, the IV candidate corresponds to that which was predicted to be the most feasible with ${}^1\Delta_g$ oxygen,[4] in which the benzyne structure lies in the bisecting plane of the ethylenic C–C bond with one of its particular carbon atoms in the vertical plane of ethylene. The V illustration represents some models with C_2 symmetry, including a symmetry-forbidden $2\pi_s+2\pi_s$ process, where the molecular plane of benzyne intersects the plane containing the ethylene π-orbital at the angles of 0°, 30°, and 90°. The last model, VI, is intended for a step-by-step reaction, whether ionic or radical-like. The parallel relation between the C=C bond of ethylene and the C≡C bond of benzyne is broken a little (5°) in the coplane. The overlap integrals between the HOMO of ethylene and the LUMO of benzyne are calculated for each model in order to estimate the degree of orbital interaction between them.[8] The results show that the overlap integral for the IV model is the largest (0.026) among those of the models examined (*cf.* 0.000 for V's and 0.003 for VI).[9] On comparing these values, we see that the IV model is the most appropriate. The prediction made here on the basis of the HOMO–LUMO interaction is consistent with that drawn from the total energy by extended Hückel calculations (−701.501 eV for IV and higher than −701.440 eV for V's and VI).[9]



IV



V



VI

The nuclear configuration IV is also shown to have good grounds for the most probable structure of the transition state or the intermediate structure in the 2+2 cycloaddition between benzyne and ethylene. Here it is

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5) For example, see the review, I. Tabushi and H. Yamada, *Yuki Gosei Kyokai Shi*, **28**, 667 (1970).

6) a) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968), T. Yonezawa, H. Konishi, and H. Kato, This Bulletin, **42**, 933 (1969); b) D. L. Wilhite and J. L. Whitten, *J. Amer. Chem. Soc.*, **93**, 2858 (1971).

7) In fact, benzyne readly reacts with a variety of nucleophiles such as anion (alkoxide, metal amide and carbanion), sulfides, phosphorus compounds, amines, ethers, and so on; see the Ref. 5.

8) K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989 (1968).

9) These values are obtained by the calculation on each model where the distance between the relevant C=C bond of benzyne and that of ethylene is 3 Å apart from each other. For more detailed calculation, D. M. Hayes and R. Hoffmann, *J. Phys. Chem.*, **76**, 656 (1972).

noteworthy that good electron-acceptors, *e.g.*, ketenes[10] and tetracyanoethylene,[11] also afford 2+2 cycloadducts with a retention of the configuration. Whether or not these cycloadditions are intrinisically identical with those of $^1\Delta_g$ molecular oxygen and benzyne is a question requiring further study,[12] but it can be expected that this mechanism is pervasive throughout 2+2 cycloadditions between electron-donating and electron-accepting multiple bonds.

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[10] See the article cited in the Ref. 4.

[11] See; P. D. Bartlett, *Quart. Rev. Chem. Soc.*, **24**, 473 (1970).

[12] Subsequent to the submission to this manuscribt, a detailed calculation on the ketene [2+2] addition has appeared and has drawn entirely the same conclusion as is proposed here [R. Sustmann, A. Ansmann, and F. Vahrenholt, *J. Amer. Chem. Soc.*, **94**, 8099 (1972)].