On the Donor–Acceptor Relationship in Cyclic Additions

Sir:

It is well established that the Diels–Alder reaction is favored by the presence of one or more electron-attracting groups in conjugation with the carbon–carbon double bond of dienophile. Alkyl and alkoxyl groups on diene also facilitate the reaction.[1] The donor–acceptor relation between diene and dienophile was studied by Houk,[2] Sustmann,[3] and Herndon[4] from an energetical viewpoint, applying the concept of orbital interaction.[5] Sustmann's classification of the additions into the "normal" and "inverse" Diels–Alder reactions was derived on the basis of relative strength of electron transfer from diene to dienophile and that from dienophile to diene.[3] In this communication, concentrating our attention to chemical bonds, we show that the orbital interaction between antisymmetric MO's can furnish cyclic additions with concerted character. Major interaction between symmetric MO's seems to imply the possibility of another reaction mechanism. The energy is an overall quantity integrated over all the space, while chemical bonds are local in nature. Hence, examination of bond formation in chemical reactions may supply us with information which has not been reached by the usual energy criteria.

Let us consider an interaction between a donor, say A, and an acceptor, say B. For the sake of the simplicity of discussion, we assume here that the electronic structure of the interacting system composed of A and B is described by the combination of two configurational wave functions,[6]

$$\Psi = C_0\Psi_0 + C_{i\rightarrow l}\Psi_{i\rightarrow l} \qquad (1)$$

where Ψ_0 is the original configuration in which both of A and B interact with the retention of their closed-shell structures in an isolated state and $\Psi_{i\rightarrow l}$ stands for an electron transfer from the ith occupied MO, ϕ_i, of A to the lth unoccupied MO, ψ_l, of B. Then, the electron density is given by,[7,8]

$$\begin{aligned}\rho(1) = {} & \rho_{0,0}(1) + C_{i\rightarrow l}{}^2(\rho_{i\rightarrow l,i\rightarrow l}(1) - \rho_{0,0}(1)) \\ & + 2C_0C_{i\rightarrow l}(\rho_{0,i\rightarrow l}(1) - S_{0,i\rightarrow l}\rho_{0,0}(1)) \\ \cong {} & \rho_{0,0}(1) + C_{i\rightarrow l}{}^2(\psi_l(1)^2 - \phi_i(1)^2) \\ & + 2\sqrt{2}C_0C_{i\rightarrow l}(\psi_l(1)\phi_i(1) - \phi_i(1)^2 s_{il}) \qquad (2)\end{aligned}$$

in which

$$\rho_{p,q}(1) = \int\Psi_p{}^*(1,2,\ldots,N)\Psi_q(1,2,\ldots,N) \times \mathrm{d}\xi_1\mathrm{d}\tau_2\ldots\mathrm{d}\tau_N \times N$$

$$S_{0,i\rightarrow l} = \int\Psi_0{}^*\Psi_{i\rightarrow l}\mathrm{d}\tau,\ s_{il} = \int\phi_i\psi_l\,\mathrm{d}v$$

It should be noted that donor MO ϕ_i loses electrons in two distinctive ways. A fraction of the electron density is directly transferred from ϕ_i to ψ_l (sum to $C_{i\rightarrow l}{}^2$) and another fraction is consumed to create the intermolecular bonds through the orbital overlap between these MO's (sum to $2\sqrt{2}C_0C_{i\rightarrow l}s_{il}$).[9]

When the MO ϕ_i donates its electrons into the intermolecular region through an electron-transfer interaction, the nuclei of A will follow the reorganization of the electron density, pulled by the electrostatic force originating from the foregoing electrons. At the same time, the nuclei of B will also have attraction from the electron density accumulated in the intermolecular region.[10] In case of the Diels–Alder reaction, one of the termini of diene α should be bonded tightly to one of the reaction sites of dienophile β, and the other terminal of diene γ should be linked to the other reaction site of dienophile δ. In order to have the fixed framework of a six-membered ring, the interaction between α and δ and that between γ and β should be antibonding (nonbonding) or only slightly bonding. Accordingly, the electrons donated from the MO ϕ_i must be accumulated on either wings of intermolecular region where new chemical bonds will appear, connecting the reaction sites of diene and dienophile. The overlap density between two nonbonded atoms, e.g., α and δ, should be low or even negative.[11] The electron transfer interaction between the highest occupied (HO) MO of diene and the lowest unoccupied (LU) MO of dienophile obviously meets this demand, as is schematically illustrated in Figure 1a. The interaction of the HOMO of dienophile with the LUMO of diene results in an increase of electron density in the central part of the intermolecular region (Figure 1b), hence is not responsible for the formation of two apparently separated bonds between diene and dienophile (quasi)simultaneously. In case of the formation of a bridged cation, on the other hand, the incoming ion must be attracted from both of the carbons of an olefinic double bond. Thus, the electron transfer from the symmetric MO's should be predominant as shown in Figure 1c, to generate positive overlap density in the central region between the two species.

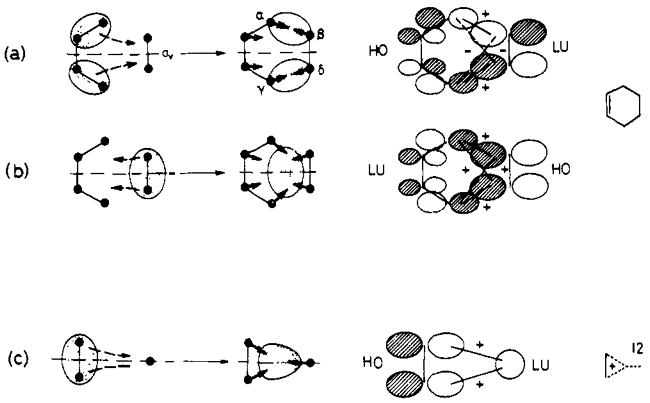

Figure 1. The modes of the electron shift associated with the orbital interactions to create intermolecular chemical bindings. The dotted areas symbolize the regions of high density changes and the arrows on black spots indicate the forces exerted on nuclei from the overlap density.

Our density analysis can locate a clearcut distinction of the consequence of the interaction between two antisymmetric MO's from that of the interaction between two symmetric MO's in cyclic additions. According to our present analysis, concerted formation of two bonds can be expected only if the dominant orbital interaction is the one between two antisymmetric MO's. Electron releasing groups on diene and electron withdrawing groups on dienophile promote the electron transfer from the HOMO of diene to the LUMO of dienophile, both being antisymmetric, in the Diels–Alder reaction. If the major interaction takes place between symmetric MO's, the cyclic addition will presumably be less concerted or experience complex formation before giving the final product. This proposition may supply us with a novel view on the mechanisms of cyclic additions and substituent effects. Further experimental study of the substituent effects on thermal cyclic additions of $4N$ and $4N + 2$ conjugated chains seems to be needed.

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References and Notes

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(6) H. Fujimoto and K. Fukui in "Chemical Reactivity and Reaction Paths", G. Klopman, Ed., Wiley-Interscience, New York, N.Y., 1974, pp 23–54.

(7) H. Fujimoto, S. Yamabe, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **44**, 2936 (1971).
(8) H. Fujimoto and R. Hoffmann, *J. Phys. Chem.*, **78**, 1874 (1974).
(9) The changes in the nuclear configurations of reactants associated with the donation and acceptance of electrons were discussed previously by the present authors. See K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **42**, 3399 (1969). Equation 2 indicates that donor MO loses electrons more rapidly than acceptor MO receives. Since the weakening of bonds between reaction sites and adjacent atoms in either reactant upon acceptance of electrons into unoccupied MO's and/or donation of electrons from occupied MO's gets smaller as the conjugation chain becomes longer, the larger conjugated system would preferably play the donor part in order to bring about harmonious displacements of nuclei in both of the reactants along a reaction path.
(10) This conclusion is derived by the application of the Hellmann-Feynman theorem to chemically interacting systems (H. Hellmann, "Einführung in Quantenchemie", Franz Deuticke 1937; R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939)). See, also, H. Nakatsuji, *J. Am. Chem. Soc.*, **95**, 345 (1973).
(11) The term "overlap density" is used here to denote the part of the interference density (K. Ruedenberg, *Rev. Mod. Phys.*, **32**, 335 (1960)) which is responsible for the intermolecular bond formation.
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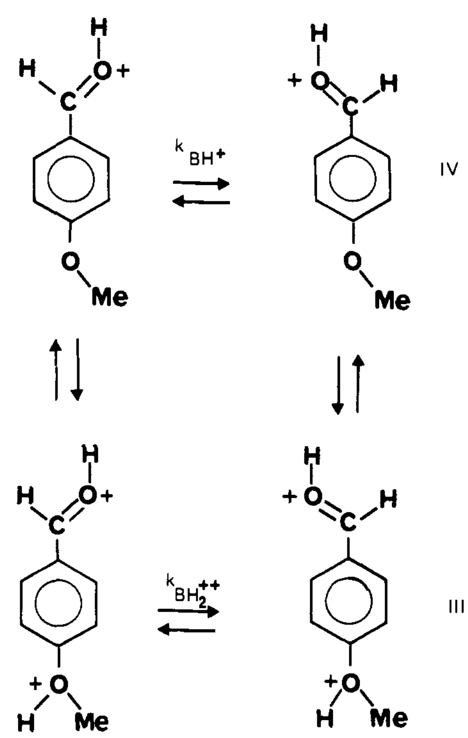
Dynamic Nuclear Magnetic Resonance. An Alternative Method for Acidity Measurements. Application to Superacids[1]

Sir:

Despite considerable work published in the field of superacid chemistry,[2] evaluation of the acidity of the superacid solvents is still in its infancy. The experimental chemistry is very much ahead of direct acidity measurements. Many kinetic and product analysis data[3,4] show that the acidity of the FSO_3H-SbF_5 system increases with increasing SbF_5 concentration at least up to the 1:1 ratio (Magic acid) and that the FH:SbF_5 system is even more acidic. However, since the pioneering work of Gillespie[5,6] on superacid acidity no progress has been reported on systems containing more than 10 mol % of SbF_5 in FSO_3H. The main reasons we suppose are the difficulties encountered in direct measurement of the BH^+/ B ratio using uv spectroscopy; besides the eventual medium dependence of the absorption maxima it is difficult to find weak enough bases with overlapping log I values in the strong acids.

We would like to present here an alternative method of determination of the BH^+/B ratio based on DNMR technique which seems to overcome some of the previously met obstacles. The principle is based on the well-known fact that the barrier to rotation around a single bond having some π character is very sensitive to all factors which enhance π electron delocalization.[7] For example, in the conjugate acid of the benzaldehydes[8] and acetophenones[9] the barriers to rotation around the phenyl-CO bond is about the double of the barrier in the free base. For this reason a very small amount of free base in strong acid solution can be detected monitoring the observed barrier to internal rotation.[10] In order to investigate the FSO_3H-SbF_5 system in a region overlapping earlier work, we choose the *p*-methoxybenzaldehyde indicator which is already monoprotonated on the carbonyl oxygen in pure FSO_3H with a barrier as determined by ^1H DNMR $\Delta G^{\ddagger}_{BH^+} = 78$ kJ mol^{-1}. From 30% SbF_5 in FSO_3H up to Magic acid, the base is diprotonated and the barrier as measured by ^1H DNMR is $\Delta G^{\ddagger}_{BH^{2+}} = 54$ kJ mol^{-1}. This is in agreement with the acidity independence of the barrier which we demonstrated in earlier work.[10]

Scheme I



In the intermediate acid region the observed line shape results from an overall exchange rate due to two competing processes (Scheme I): (a) the direct rotation in monoprotonated compound I → IV and (b) protonation-fast rotation in the diprotonated species-deprotonation: I → II → III → IV.

As the CH_3OH^+ proton cannot be observed even in Magic acid, we know that the acid-base exchange rate on this site is very fast compared to the measured intramolecular rotations. For this reason the observed rate of rotation is a function of the relative population of BH_2^{2+} and BH^+ (eq 1 and 2)

$$P_{BH_2^{2+}} + P_{BH^+} = 1 \tag{1}$$

$$k_{obsd} = k_{BH^+}(1 - P_{BH_2^{2+}}) + k_{BH_2^{2+}} P_{BH_2^{2+}} \tag{2}$$

at a given temperature k_{obsd} is measured from the ^1H line shape using the program DNMR3 due to Binsch;[11] $k_{BH_2^{2+}}$ and k_{BH^+} are known from the corresponding $\Delta G^{\ddagger}$ values. The relative population can then be used in an acidity function (see eq 3).

$$H_s = pK_{BH_2^{2+}} - \log \frac{P_{BH_2^{2+}}}{1 - P_{BH_2^{2+}}} \tag{3}$$

For a number of reasons[12,13] this acidity function measured here should not be called H_0, but as our results overlap with Gillespie's values in the 5–10% SbF_5 region, this approximation will not alter the demonstration of the applicability of the DNMR method.

The value of $pK_{BH_2^{2+}}$ has been determined by measuring k_{obsd} in a region of known acidity (6–8%). We found $pK_{BH_2^{2+}} = -19.3$.

It was then possible to calculate the relation between the observed barrier to rotation and the acidity of the medium (Figure 1; curve 1). We notice that this method enables us to cover about 4–5 H_0 units below $pK_{BH_2^{2+}}$ with the same indicator as the observed barrier to rotation changes when $10^{-6} < P_{BH_2^{2+}} < 10^{-1}$.

On the other hand, with the protonated *p*-methoxybenzaldehyde, the C=OH$^+$ proton is shifted 2 ppm downfield on second protonation, and we may use the classical NMR shift method[14] as complementary information on the BH_2^{2+}/BH^+ ratio. ($\delta_{BH^+} = 14.8$; $\delta_{BH_2^{2+}} = 12.4$ ppm.) The $pK_{BH_2^{2+}}$ can also be calculated from data obtained in the 8% SbF_5 region for known acidity and we find $pK_{BH_2^{2+}} = -19.5$. The calculated curve of δ C=OH$^+$ vs. H_0 is plotted on Figure 1 (curve 2). It