Conformational Adaptation: A New Aspect of Substitutent Effects[1)]

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Synopsis. Methoxyl (CH_3O–) substituent on unsaturated molecules was suggested by ab initio molecular orbital calculation and qualitative orbital interaction theory to change from coplanar to vertical conformation on electron acceptance. The conformational adaptation can make it possible that methoxyl group is less electron-donating than methyl group.

Substituent effects of methoxyl and methyl groups on unsaturated molecules are usually understood in terms of high electron-donating capability of methoxyl vs. methyl groups. However, reversed order of donating capabilities was observed for electron affinities of benzene derivatives measured by electron transmission spectroscopy[2)] and the half-wave potentials of substituted 9,10-dihydro-9,10-*o*-benzenoanthracene-1,4-diones.[3)] These experimental findings have provoked theoretical study of prototypical substituted unsaturated compounds, i.e., propene (**1**) and methyl vinyl ether (**2**). Ab initio molecular orbital calculations have suggested that methoxyl groups could be weaker donors than methyl groups due to conformational change of methoxyl groups on electron acceptance (conformational adaptation).

The geometries of **1** and **2** and their radical anions were fully optimized by ab initio molecular orbital calculations with the 3-21G basis set. Figure 1 shows the relative energies. The results show the reversed order of the electron-donating capabilities. The methoxy-substituted molecule was found to be less destabilized on the one-electron reduction. The energy difference between the neutral molecule and the radical anion is 3.41 eV for **2**, smaller than 3.61 eV for **1**. The energies of the 3-21G optimized geometries were calculated with the 6-31G* and 6-31+G basis sets to estimate the effects of polarization and diffuse orbitals. The single point 6-31G*//3-21G and 6-31+G//3-21G calculations also give small energy differences (3.34 eV and 2.64 eV) for the methoxy derivative, relative to those (3.45 eV and 2.75 eV) for the methyl derivative, respectively.

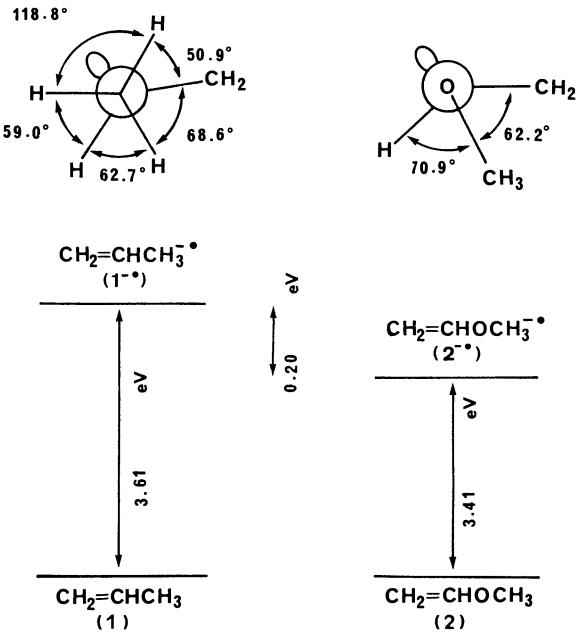

Fig. 1. Energy differences between the neutral states and the radical anions of propene and methyl vinyl ether.

The reverse ordering is attributed to the conformational adaptation to the anionization (Fig. 2). In the neutral state the CH_3–O bond lies on the molecular plane. The planar conformation is the most suitable for CH_3O– as a donor. The lone pair p-orbital on the methoxyl oxygen is allowed to interact most effectively with the unsaturated moieties. Electron acceptance changes parts of the conjugated group from an acceptor to a donor. The methoxyl groups adapt themselves to accepting electrons as much as possible. The LUMO of CH_3O– groups is the antibonding orbital of the CH_3–O bond. For the greatest overlapping with the π-orbitals of the conjugated groups, CH_3O– is required to be vertical to the molecular plane. In fact, CH_3–O bond is antiperiplanar to the SOMO on the adjacent unsaturated carbon atom (Fig. 1).

The change in electron distribution of the radical anion with the conformational adaptation supports the preceding argument. The negative charge on CH_3O– increases by 0.014 e^- with the change from the planar to fully optimized geometry.

A possible explanation of the reversed order of donating capabilities simply in terms of inductive effects cannot be supported by the present calculations. The geometries of the radical anions were optimized under the constraint of the C_s symmetry (symmetric with respect to the reflection in the molecular plane). The energy difference 4.02 eV between the neutral

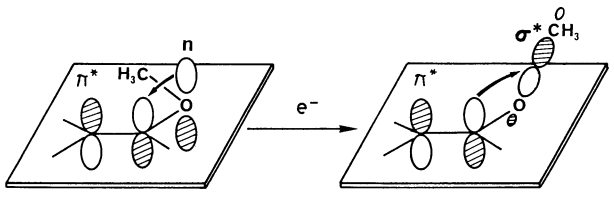

Fig. 2. Conformational adaptation.

methoxy derivative and its radical anion is greater than 3.78 eV of the methyl derivative. This does not indicate that inductive effects are predominant, since inductive effects are considered to be independent of the conformations.

Substituent effects have been discussed in terms of resonance and inductive effects. Conformational changes possible to be accompanied have not explicitly been taken into consideration. In fact, the electron transmission spectra of benzene derivatives were successfully explained in a usual manner,[2] and the half-wave potentials of substituted 9,10-dihydro-9,10-*o*-benzenoanthracene-1,4-diones can be understood similarly.[3] However, the present study suggests an interesting possibility that conformational change may play a significant role in the substituent effects. Although no convincing experimental evidence is available, the concept of the conformational adaptation proposed here remains to be substantiated by experimental observation. Very recently, a theoretical interpretation of the hyperfine structure observed in the ESR spectra of radical anions of aryl methyl ethers suggested the possibility of similar rotational isomerism.[4]

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References

1) Presented at the 19th Symposium on Structural Organic Chemistry, Sendai, October 13, 1987.

2) K. D. Jordan, J. A. Michejda, and P. D. Burrow, *J. Am. Chem. Soc.*, **98**, 7189 (1976).

3) K. Yamamura, H. Miyake, S. Himeno, S. Inagaki, K. Nakasuji, and I. Murata, *Chem. Lett.*, **1988**, 1819.

4) M. C. R. L. R. Lazana, M. L. T. M. B. Franco, and B. J. Herold, *J. Am. Chem. Soc.*, **111**, 8640 (1989).