A Molecular Orbital Interpretation of the Ring-opening Polymerization

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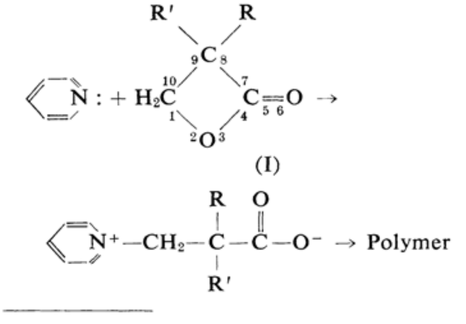
One of the most interesting problems in ring-opening polymerization is that of the fission of a particular bond in a definite catalyst. No quantum mechanical interpretation of the results, however, has yet been proposed. In this short communication, it will be shown that the reactivity indices for σ electron systems, that is, the delocalizability (D_r) and the frontier electron density (f_r) proposed in our previous paper,[1] are useful in explaining the experimental results of ring-opening polymerizations of β-propiolactone derivatives by Watanabe, Hayashi and Okamura.[2] It will be pointed out that, in β-propiolactone derivatives (I), the bond fission takes place at the β C–O bond with a basic catalyst such as pyridine:



(I)

(1)

The rate of the polymerization in these derivatives is found to decrease as follows:

α,α-bischloromethyl β-propiolactone >
α-ethyl, α-chloromethyl β-propiolactone >
α-methyl, α-chloromethyl β-propiolactone >
β-propiolactone > α,α-dimethyl
β-propiolactone

With an acid catalyst such as BF_3OEt_2, the order of the reaction rate is reversed; hence, it may be supposed that the magnitude of the σ electron density at the β-carbon atom may be correlated with the experimental results presented above.

We have tentatively treated these compounds by the C–C skeleton method[3] for the sake of simplicity. The values of the parameters used may be summarized as follows:

Coulomb integrals:

$$C(sp^3)=\alpha,\ C(sp^2)=\alpha+0.1\beta,$$

$$\text{and } O(\text{etheric})=O(\text{ketonic})=\alpha+0.3\,\beta.$$

Resonance integrals:

$$C(sp^3)\text{–}C(sp^3)=\beta,\ C(sp^3)\text{–}C(sp^2)=\beta,$$

$$C(sp^3)\text{–}O(\text{etheric})=0.6\beta,$$

$$C(sp^2)\text{–}O(\text{etheric})=0.7\beta,$$

$$C(sp^2)\text{–}O(\text{ketonic})=1.2\beta,$$

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[1] K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34**, 443, 1111 (1961).

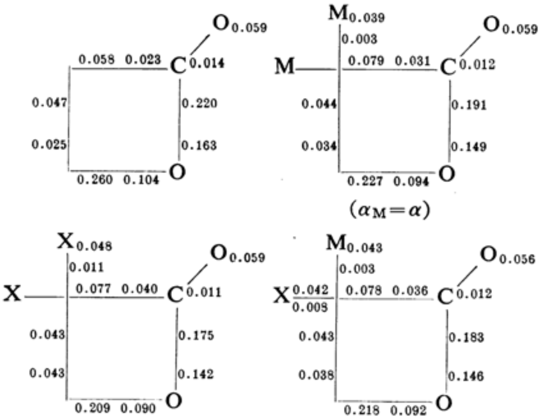
[2] H. Watanabe, K. Hayashi and S. Okamura, *Summary of the 12th Symposium on High Polymers*, Nagoya, (1963), p. 221.

[3] H. Yoshizumi, *Trans. Faraday Soc.*, **53**, 125 (1957): K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **33**, 1197 (1960).

$$\left.\begin{array}{l} \mathrm{C(sp^3)\text{–}C(sp^3)}=0.34\beta, \\ \mathrm{C(sp^2)\text{–}C(sp^2)}=0.40\beta, \\ \mathrm{O\text{–}O}=0.30\beta, \end{array}\right\}\text{ between two hybridized orbitals of the same atom.}$$

In order to characterize the electronic effect of the substituent group at the α-carbon atom in β-propiolactone, two symbols are employed. M denotes an electron-repelling group, and X, an electron-attracting group. We make use of one parameter to represent their electronic effect. The value of the Coulomb integral of M is taken tentatively to be -0.2 (for ethyl)* and to be 0 (for the methyl group), and that of X, to be $+0.2$ and $+0.4$ for the chloromethyl group. The values of the resonance integral for C–M and C–X are taken to be β.

Since it is evident from our frontier electron concept that the frontier orbital of pyridine for an electron acceptor is the highest-occupied lone-pair orbital of nitrogen, we can assume a weak interaction between the nitrogen lone-pair electrons in pyridine and the σ orbital in β-propiolactone derivative molecules at the transition state. Hence, $D_r^{(N)}$ and $f_r^{(N)}$ are employed as the reactivity indices. In Fig. 1, the calculated values of $f_r^{(N)}$ with respect to several lactones are listed. The position of the largest $f_r^{(N)}$ is common with respect to all of these compounds and is the orbital 1 (cf. Eq. (1). This finding is compatible with the experimental evidence.[2)] The calculated $D_r^{(N)}$'s of σ orbitals at the β-C atom in the C–O bond are shown in Table I. In view of this finding the more repulsive the substituent group is, the lower is the reactivity of the compound. In the case of the electron-attracting substituent, the more attracting the substituent group is, the higher is the reactivity. This theoretical results is approximately consistent with the experiment which is indicated in Reaction (1).



$(\alpha_M=\alpha)$

$(\alpha_X=\alpha+0.2\beta)$ $(\alpha_M=\alpha,\ \alpha_X=\alpha+0.2\beta)$

Fig. 1. Values of $f_r^{(N)}$ of some β-propiolactone derivatives.

TABLE I. CALCULATED VALUES OF $D_r^{(N)}$ AT σ ORBITAL (1) in various β-PROPIOLACTONE DERIVATIVES

X[a)] $=+0.4$ $X=+0.4$	1.570
$X=+0.2$ $X=+0.2$	1.538
$M=0$ $X=+0.2$	1.536
$M=0$ $X=+0.2$	1.522
$M=-0.2$ $X=+0.4$	1.519
M none X none	1.510
$M=0$ $M=0$	1.510
$M=-0.2$ $M=-0.2$	1.489

a) X and M denote the values of the Coulomb integral of X and M respectively.

Accordingly, it may be seen that $D_r^{(N)}$ and $f_r^{(N)}$ are appropriate indices for discussing the reactivity of ring-opening polymerization.

For the case of acidic catalysts, the electrophilic reactivity indices, $D_r^{(E)}$ and $f_r^{(E)}$, can be used. These results will be published in the near future.

The calculation has been carried out on a KDC-I digital computer at Kyoto University.

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* Altough this value may be too large, it is adopted just for the convenience of calculation.