

PMO-TREATMENT OF THE STRUCTURE-REACTIVITY RELATIONSHIPS IN FREE RADICAL ADDITION REACTIONS OF CYCLOALKENES

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The effect of ring strain in molecules of C_5-C_8 cycloalkenes and that of electronegativity of the attacking radicals upon reactivity of cycloalkenes in 1,2 addition reactions was studied by using a simple perturbation approach. The trends of the experimentally determined reactivities of cycloalkenes towards CH_3 , CCl_3 , $CF_2CF_2CF_3$, CH_3CO , $NCCHCO_2H_5$, C_2H_5 , C_2H_5S and Br radicals were found to be in an acceptable agreement with the trends of the calculated Fukui's delocalisabilities D_r . The reactivity of cycloalkenes appears to be influenced by I-strain in the cycloalkene molecules as well as by electronegativity of the attacking radicals.

The effect of ring size on the reactivity of cycloalkenes in various types of addition reactions was investigated in detail over the past two decades. The trends in reactivity have been interpreted qualitatively in terms of ring strain as the dominating and common factor determining the reactivity of cycloalkenes. The quantitative approach interpreting the variations in reactivity with ring size of alicyclic compounds was most often based on the calculations of strain energies yielding satisfactory correlations with experimental data¹⁻⁷.

In the preceding work we have determined experimentally the relative reactivities of C_5-C_{12} cycloalkenes in the radical addition reaction with ethyl cyanoacetate⁸. In the meantime, analogous data have been found in the literature* for the radical 1,2 addition reactions of cycloalkenes with hydrogen bromide⁹, acetyl peroxide¹⁰, bromotrichloromethane, acetaldehyde, ethanethiol¹¹ and 1-iodoperfluoropropane¹² proceeding also with high selectivity. The aim of the present study was to interpret theoretically with the aid of quantum-chemical methods the experimentally determined order of reactivity of C_5-C_8 cycloalkenes in these reactions.

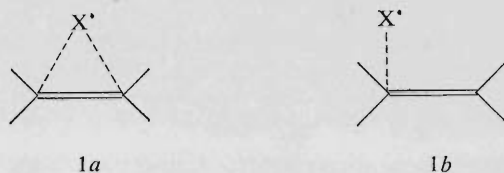
CALCULATIONS

The reactivity of cycloalkenes was estimated by using a simple perturbation approach based on the Fukui's¹³ index of delocalisability (D_r). This approach has often been utilized for interpreting the reactivities of radicals¹⁴ and has recently been applied with success by Boldt and co-

* In this context, we are correcting our statement in the previous paper, p. 1946 (ref.⁸).

workers¹⁵ to the elucidation of reactivity and regioselectivity in additions of trifluoromethyl and dicyanomethyl radicals to substituted acyclic alkenes.

Delocalisability is a static index of reactivity and its calculation does not require the knowledge of wave functions of the attacking radicals. In this approach, the structure of the transition state is assumed only indirectly in that it is necessary to locate the reaction center in the cycloalkene molecule. In the radical 1,2 addition to a C=C bond two approaches of the attacking reagent are generally possible, *i.e.*, the so-called "one-end" and "triangular" approach depicted in Scheme 1. According to the Scheme 1a, both carbon atoms of the C=C bond are simultaneously attacked in the transition state. The results summarized in a recent paper have shown this mechanism to be spin-forbidden and hence energetically unfavourable¹⁶. We have therefore chosen the "one-end" approach for the model of the transition state (Scheme 1b).



SCHEME 1

From the expression for delocalisability (Eq. (I))

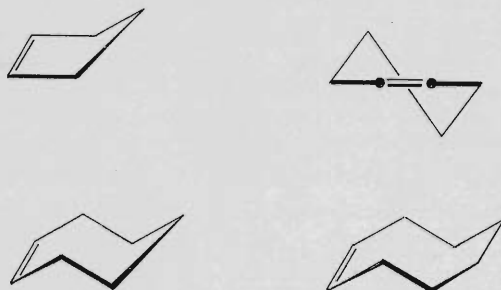
$$D_r = \sum_i^{\text{occ}} \frac{c_{ri}^2}{\alpha - \varepsilon_i} + \sum_j^{\text{unocc}} \frac{c_{rj}^2}{\varepsilon_j - \alpha} \quad (I)$$

it follows that its calculation requires the knowledge of the LCAO expansion coefficients c_{ri} , c_{rj} on the atomic orbital r (assumed to be the center of the primary attack) in the individual molecular orbitals φ_i , φ_j with pertinent energies ε_i , ε_j . In our case, the reaction center was considered to be the pure p_π orbital at the one of the C=C bond carbon atoms.

The constant α appearing in Eq. (I) has the meaning of energy of the single-occupied molecular orbital of a radical (SOMO). Because there a relationship exists between the energy α and the electronegativity of a radical it is possible, by using different values of α for the calculation of D_r , to model to a certain extent the effect of electronegativity of various attacking radicals upon the reactivity of cycloalkenes. The large negative values of α refer to additions of electronegative radicals such as fluorine atom or trifluoromethyl.

From the conclusions of the preceding studies it follows that the ring strain in the molecules of cycloalkenes is to be considered as the dominating factor determining the rate of the addition reaction¹⁻⁷. An attempt to elucidate theoretically the difference in reactivity of cycloalkenes requires therefore to use such quantum-chemical methods which reflect reasonably the changes in the ring strain with the variation of the ring size. Bearing this in mind and in the interest of obtaining the most reliable wave functions, we have performed a full geometry optimization for all the individual members in the series of C₅-C₈ cycloalkenes. The size of the molecules studied permitted us to carry out the calculations only at the level of semiempirical methods of which we used the standard CNDO/2 procedure implemented by variable metric optimization program DERIVAL written by Pancir¹⁷. Nevertheless, the high demand on the computing time forced us to limit the optimization for each cycloalkene only to one conformer that has been assigned either experimentally or with the aid of molecular mechanics⁵ as the most stable one.

Accordingly, the calculations were performed by utilizing the envelope conformation for cyclopentene, the half-chair conformation for cyclohexene and the chair conformation for *cis*-cycloheptene and *cis*-cyclooctene (Scheme 2).



SCHEME 2

RESULTS AND DISCUSSION

The calculated values of delocalisabilities D_r and the experimentally determined relative reactivities of C_5 — C_8 cycloalkenes are summarized in Table I. The relative reactivities expressed in the form of relative rate constants (k_n/k_6) refer to the radical addition reactions with acetyl peroxide (I), bromotrichloromethane (II), acetaldehyde (III), 1-iodoperfluoropropane (IV), ethyl cyano acetate (V), ethanethiol (VI) and hydrogen bromide (VII). The addition reactions under question can be divided into two groups. In the first group the addends I—V form a new C—C bond in the radical addition step and the addition reaction is irreversible. When for this group of addends the values $(k_n/k_6)_V$ were plotted against $(k_n/k_6)_I$ (correlation coefficient $r = 0.9910$), $(k_n/k_6)_{II}$ ($r = 0.9911$), $(k_n/k_6)_{III}$ ($r = 0.9890$) and $(k_n/k_6)_{IV}$ ($r = 0.9459$), in all cases satisfactory linear correlations were obtained. The differences in the relative reactivity of cycloalkenes varied within one order of magnitude and the values of (k_n/k_6) decreased in the sequence *cis*-cyclooctene > cyclopentene > *cis*-cycloheptene > cyclohexene.

As to the second group of addends, ethanethiol and hydrogen bromide form the C—S and C—Br bond, respectively, in the radical addition step, the addition is a reversible reaction^{18,19}, the differences in the relative reactivities of cycloalkenes toward these addends are more pronounced and the values of (k_n/k_6) show a reverse trend. These results suggest that the magnitude of the ring strain is most probably not the only factor affecting the reactivity of cycloalkenes. The difference in the trends of cycloalkene reactivities in reactions with the first and the second group of addends was attributed by Gale¹¹ to the reversibility of the radical addition step in the case of hydrogen bromide and ethanethiol. Not excluding this phenomenon, we rather believe that also the proper structure of the radical applies in these reactions. In the

TABLE I
 Calculated values of the Fukui's delocalisabilities ($-D_i$) and relative reactivities (k_n/k_6) of C_5 — C_8 cycloalkenes (C_n) in the 1,2-addition reactions with various radicals

C_n	$-D_i(\gamma^2/eV)$				k_n/k_6						
	$\alpha_1 = -10 \text{ eV}$	$\alpha_2 = -5 \text{ eV}$	$\alpha_3 = 0 \text{ eV}$		$CH_3CO\cdot$	$CCl_3\cdot$	$\dot{C}F_2CF_2CF_3$	$CH_3\cdot$	$NC\dot{C}HCO_2C_2H_5$	$Br\cdot$	$C_2H_5S\cdot$
C_5	0.1637	0.0986	0.1019		2.6	5.6	2.2	6.44	3.72	0.73	—
C_6	0.1577	0.0982	0.1315		1.0	1.0	1.0	1.0	1.0	1.0	1.0
<i>cis</i> - C_7	0.1680	0.0980	0.1278		2.2	3.0	1.4	4.67	3.02	0.37	—
<i>cis</i> - C_8	0.1709	0.0990	0.1250		2.9	8.0	2.7	7.44	4.8	~0.01	~0.05

framework of our perturbation approach, the value of α in Eq. (1) for the calculation of delocalisability implies the difference in the radical structures. The magnitude of α is determined first of all by the electronegativity of the radical. Generally, it can be stated that the electronegativity of a radical increases with the decreasing value of α . In an attempt to express the difference in electronegativity of the individual radicals we have calculated D_r for three various model values of α ($\alpha_1 = -10$ eV; $\alpha_2 = -5$ eV; $\alpha_3 = 0$ eV) covering a quite wide range of electronegativities. The dependence of the calculated values of D_r upon size for the all three model values of α is demonstrated in Fig. 1. As Fig. 1 shows, the trends in the D_r values significantly depend not only on the size of the cycloalkene ring but also on the electronegativity of the attacking radical. It can roughly be stated that the trend in the relative reactivities of cycloalkenes toward the most electronegative radicals ($\alpha_1 = -10$ eV) is nearly a mirror image to that found for the least electronegative radicals ($\alpha_3 = 0$ eV). From the results listed in Table I it follows that the trends in the relative reactivities of cycloalkenes toward the more electronegative radicals such as CH_3CO , CH_3 , CCl_3 , $\text{CF}_2\text{CF}_2\text{CF}_3$ and $\text{NCCHCO}_2\text{C}_2\text{H}_5$ are correctly reflected in D_r values corresponding to $\alpha_1 = -10$ eV. Taking into account that this value is only a model one and that it need not hence correspond the SOMO energy of any of the

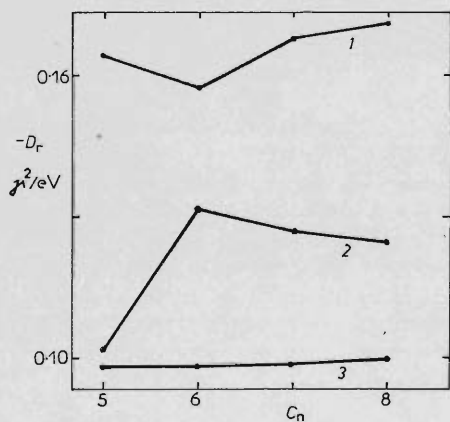


FIG. 1

Dependence of the Fukui's delocalisabilities ($-D_r$) calculated for values $\alpha_1 = -10$ eV 1, $\alpha_3 = 0$ eV 2 and $\alpha_2 = -5$ eV 3 upon the ring size (C_n) of C_5 – C_8 cycloalkenes

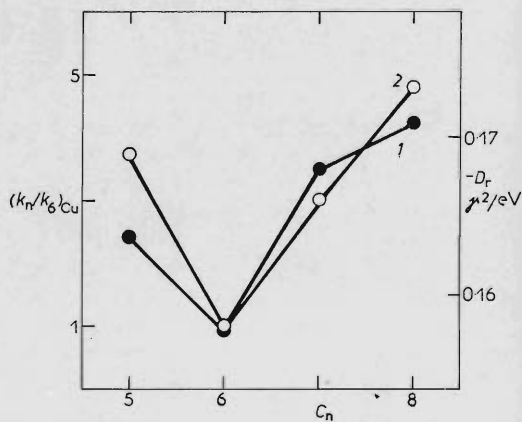


FIG. 2

Calculated values of delocalisabilities ($-D_r$) (●) and experimentally determined relative reactivities (k_n/k_6) (○) of C_5 – C_8 cycloalkenes as a function of ring size (C_n) in the radical addition reaction with ethyl cyano acetate catalysed by copper(II) oxide

radicals under question, we find here a quite satisfactory agreement between the theory and experiment. An analogous accordance is clearly demonstrated in Fig. 2. The calculated values of delocalisabilities D_r for cyclopentene and cyclohexene are consistent with the results of Kharash and coworkers^{20,21} indicating the rate of addition of the trichloromethyl radical to cyclopentene to be 3.2 times as high as that to cyclohexene. Moreover, the delocalisabilities D_r for the addition of the substantially less electronegative ethylthiyl and bromine radicals actually show, again in agreement with the experiment, an inverse trend of reactivity; cyclohexene is here the most reactive and *cis*-cyclooctene the least reactive member of the cycloalkene series. Comparing all the calculated and experimental data, we meet with one exception: whereas the calculated values of D_r indicate a lower reactivity for cyclopentene when compared with cycloheptene, an inverse trend results for both hydrocarbons from the comparison of experimental values of (k_5/k_6) and (k_7/k_6) .

Therefore, it can be concluded that, except for the above inconsistency, the simple PMO approach allows to interpret successfully the expected effect of the ring strain as well as the effect of the relative electronegativity of the attacking radical upon the reactivity of C_5 — C_8 cycloalkenes in the radical addition reactions. We believe that a more general validity of this conclusion could be attained by availability of further experimental data concerning the relative reactivities of cycloalkenes toward the more electropositive radicals in this type of reactions. These data are only scarce at present.

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