The Reactivity of Hydrogen Atoms of Unsaturated Hydrocarbons in Metathetical Reactions

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In order to discuss quantum-mechanically the reactivity of the hydrogen atoms of unsaturated compounds in abstraction reactions, the stabilization energy due to π conjugation occurring in the structure of the final product, which is calculated by the molecular orbital method, has been employed as a measure of the reactivity.[1] However, no attention has been paid to the behavior of the σ electrons of the unsaturated compounds which must play the main part in these reactions. The present authors have previously proposed a new reactivity index—delocalizability, D_r—which has proved to be a satisfactory one for metathetical reactions of saturated hydrocarbons.[2] In the present paper, we will treat the σ electronic system in various unsaturated hydrocarbons, such as olefins, alkylbenzenes and acetylenes, by the same method as that used in our previous paper[3] in order to show the calculated values of $D_r^{(R)}$ (delocalizability for radical reaction) at each hydrogen atom in these compounds. The results display a good correlation with experience and generally explain the high reactivity of α hydrogen atoms in unsaturated hydrocarbons.

Theoretical

As has already been shown, the σ electronic structure in unsaturated compounds is investigated by the LCAO MO method, taking only σ-electrons explicitly into consideration. Accordingly, the molecular orbitals in these molecules are represented by a linear combination of hydrogen 1s orbitals and carbon hybridized orbitals.

The values of the parameters used in the present paper are summarized as follows:

Coulomb integrals

$C(sp^3)$: α $C(sp^2)$: $\alpha+0.1\beta$
$C(sp)$: $\alpha+0.2\beta$ H: $\alpha-0.2\beta$

resonance integrals

a) between adjacent carbon atoms:
$C(sp^3)$–$C(sp^3)$: β $C(sp^2)$–$C(sp^2)$: 1.2β
$C(sp)$–$C(sp)$: 1.3β $C(sp^3)$–$C(sp^2)$: β
$C(sp^3)$–$C(sp)$: 1.1β

b) between carbon and hydrogen atoms:
$C(sp^3)$–H: 1.1β $C(sp^2)$–H: 1.1β
$C(sp)$–H: 1.2β

c) between two orbitals in the same carbon atom:
$C(sp^3)$–$C(sp^3)$: 0.34β $C(sp^2)$–$C(sp^2)$: 0.40β
$C(sp)$–$C(sp)$: 0.70β

where α and β denote the Coulomb integral of an sp^3 carbon atom and the resonance integral between two sp^3 hybridized orbitals at the C–C σ bond respectively.* This parameter system is convenient for comparing the value of the $D_r^{(R)}$ of unsaturated compounds with those of saturated compounds which have already been calculated.[2]

The reactivity index referred to as the delocalizability for the radical reaction, $D_r^{(R)}$, may then be given as:

$$D_r^{(R)}=\sum_i^{occ}\frac{(C_r^i)^2}{\lambda_i}+\sum_j^{unocc}\frac{(C_r^j)^2}{-\lambda_j}$$

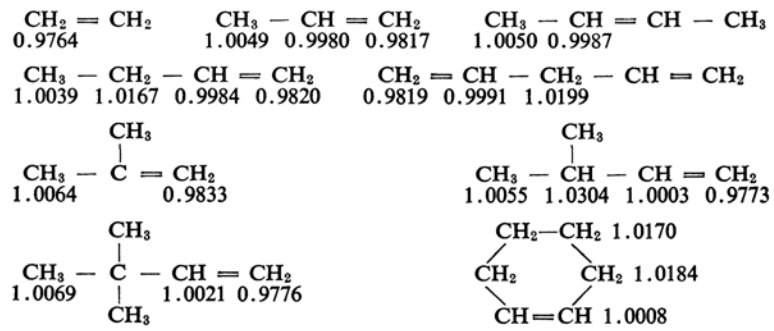
where C_r^i is the coefficient of the rth σ orbital in the ith MO and λ_i is given by $\varepsilon_i=\alpha+\lambda_i\beta$, in which ε_i is the energy of ith MO.

Results and Discussion

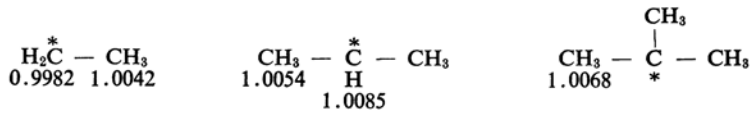
The calculated $D_r^{(R)}$ values of the hydrogen atoms in various unsaturated hydrocarbons are given in Figs. 1a, b, c and d. In Fig. 2 the calculated $D_r^{(R)}$ values of hydrogen atoms are plotted according to their grouping. A detailed discussion with regard to the variation in the $D_r^{(R)}$ in each group will be given in the following sections. As a general trend, it can be pointed out that the reactivity of a hydrogen atom bonded to an sp^3 carbon atom will be larger than that of hydrogen atoms attached to an sp^2 or sp carbon atom, and also larger than that of the same kind

1) E. g. G. W. Wheland, *J. Am. Chem. Soc.*, **63**, 2025 (1941); C. A. Coulson, *Discussions Faraday Soc.*, **2**, 9 (1947); A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley, N. Y. (1961).
2) K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34**, 1111 (1961).
3) K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura and C. Nagata, ibid., **35**, 38 (1962).

* In Ref. 3 we adopted a parameter system which was based on the sp^2 carbon atom, whereas in the present paper the system is based on the sp^3 carbon atom. No essential difference exists between these two parameter systems.

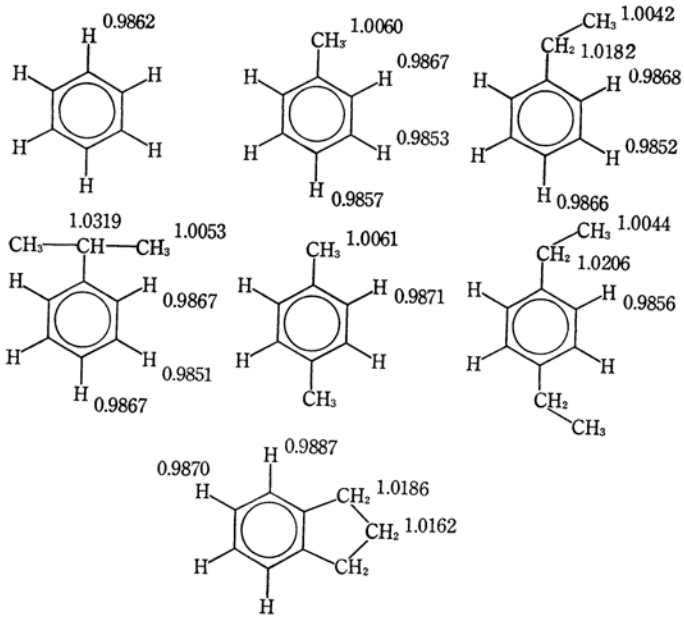


(a) Olefins

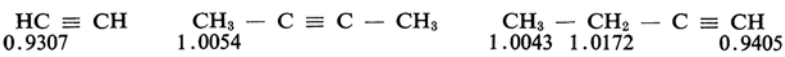


* C: sp^2 carbon atom

(b) Alkyl ions and radicals



(c) Alkylbenzenes



(d) Acetylenes

Fig. 1. The calculated values of $D_r^{(R)}$ of the H atoms in various unsaturated hydrocarbons.

(that is, primary, secondary or tertiary) in saturated hydrocarbons.

In particular, the large reactivity of hydrogen atoms in the α-methylenic group is interpreted by $D_r^{(R)}$ values, for instance, in cyclohexenene and indane molecules.

Olefins.—The calculated $D_r^{(R)}$ values of hydrogen atoms in several olefinic compounds are summarized in Fig. 1a. The value of $D_r^{(R)}$ falls in a definite range for each type of hydrogen atom; the average $D_r^{(R)}$ value of hydrogen atoms of the same type, that is, of each primary, secondary and tertiary hydrogens, is compared in Table I with the rate

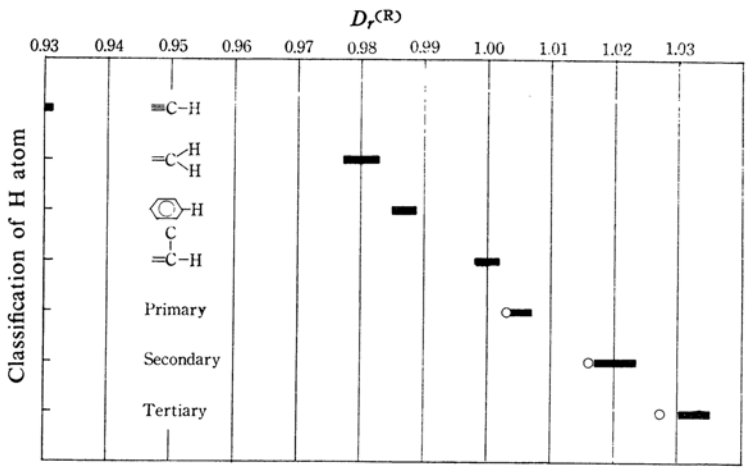


Fig. 2. The value of $D_r^{(R)}$ and the kind of hydrogen atoms.
■: in unsaturated compounds
○: in saturated compounds (average)

TABLE I. CHANGE OF AVERAGE OF $D_r^{(R)}$ AND OBSERVED RATE CONSTANTS ACCORDING TO THE TYPE OF THE HYDROGEN ATOM IN HYDROCARBONS

Type of H atom	$D_r^{(R)}$		$k\times10^{-6}$ per atom at 182°C toward CH_3 radical[4] mol^{-1} cc. sec^{-1}	
	Olefins	Paraffins[2]	Olefins	Paraffins
Primary hydrogen	1.006	1.003	5	0.3
Secondary hydrogen	1.017	1.016	17	2.1
Tertiary hydrogen	1.030	1.027	53	15

TABLE II. THE CALCULATED $D_r^{(R)}$ VALUES AND THE EXPERIMENTAL ACTIVATION ENERGIES AND REACTIVITIES IN α HYDROGEN ATOMS IN OLEFINIC HYDROCARBONS

Compound	$D_r^{(R)}$	Activation energy[a] kcal./mol.		Reactivity per α-hydrogen atom
		Ref. 4	Ref. 5*	Ref. 4
$CH_2:CH_2$	0.9764	10.0	—	1.4
$CH_3CH:CH_2$	1.0049	7.7	13.5[a]	8
$CH_3CH:CHCH_3$	1.0050	7.7	—	10
$(CH_3)_2C:CH_2$	1.0064	7.3	—	8
$(CH_3)_3CCH:CH_2$	1.0069	—	—	—
$CH_3CH_2CH:CH_2$	1.0167	7.6	11.5[a]	33
	1.0184	—	9.5[a]	—
$(CH_3)_2CHCH:CH_2$	1.0304	7.4	8.1[b]	102

* These values correspond to the average of the hydrogen atom with similar circumstances.
a) The attacking reagent is the CH_3 radical in Ref. 4 and olefinic peroxy radicals in Ref. 5.

constants characteristic of various types of hydrogen atoms in metathetical reaction by means of the methyl radical.[4] A parallelism is observed between these two and the calculated values of olefins are on an average larger than those of corresponding paraffins, although the differences between them are rather smaller than expected and the calculated orders of reactivity between the different types of hydrogen atoms in unsaturated and saturated hydrocarbons are inconsistent with the observed values. These discrepancies may result from the neglect of π conjugation energies.

In Fig. 1a, the $D_r^{(R)}$ values of α methylenes in 1-butene, 1, 4-pentadiene and cyclohexene are large, obviously corresponding to the large reactivities. That is, in cyclohexene the $D_r^{(R)}$

4) A. F. Trotman-Dickenson, *Quart. Revs.*, **7**, 198 (1953); A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

of the α-hydrogen atom is 1.0184, while at the β-hydrogen atom it is 1.0170. In 1, 4-pentadiene, the hydrogen atom of the methylene has a value of 1.0199, which is larger than that of the average of methylenes in paraffins (ca. 1.016).

These $D_r^{(R)}$ values of hydrogen atoms on α carbon atoms in several olefinic molecules are listed in Table II, together with the observed activation energies[4,5] and experimental reactivities[4] in hydrogen abstraction reactions. (In Ref. 4, the values were obtained in the reactions with the methyl radical, and in Ref. 5, the values in the autoxidation reactions with benzoyl peroxide as an initiator were estimated by assuming frequency factors to be constant for all reactants). We can remark with a certain reservation that there is an apparent parallelism between calculated and observed values, since Trotman-Dickenson has pointed out that the rate in these type reactions does not depend on the magnitudes of the activation energy, but on that of frequency factor.[4] This point should be reinvestigated by future calculations and experiments.

Alkyl Ions and Radicals.—For the sake of comparison, calculated values of $D_r^{(R)}$ in some alkyl ion or radicals* are indicated in Fig. 1b. It is of interest to see that the reactivity of hydrogen atoms bonded to an sp^3 carbon atom is larger than that of the hydrogen atoms of an sp^2 carbon atom which had the same circumstances in a parent molecule. In this way, the change in the hybridization of a carbon atom from sp^3 to sp^2 causes a deactivation of the hydrogen atoms attached to this carbon atom and a simultaneous slight activation of the hydrogen atoms in other parts of the molecule.

Alkylbenzenes.—The calculation with respect to several alkylbenzenes was also made; the results are shown in Fig. 1c. The reactivity of α hydrogen atoms may be clearly recognized. For instance, in the indane molecule, the $D_r^{(R)}$ value of the α hydrogen atom is 1.0186 and that of the β hydrogen atom is 1.0162, while it is about 0.99 at the hydrogen atoms on the benzene ring. Similarly, in ethylbenzene the value at the methylene group is 1.0184. These values correspond to the largest one among those of different positions in each hydrocarbon of this sort; such an order of magnitude is larger than that of the hydrogen atoms of the corresponding class (that is, primary, secondary or tertiary) in saturated hydrocarbons.

5) a) L. Bateman, *Quart. Revs.*, **8**, 147 (1954); b) J. L. Bolland, ibid., **3**, 1 (1948).

* If we neglect the behavior of π electrons, the σ electronic states of the ion and the radical are identical for the first approximation.

TABLE III. THE VALUES OF $D_r^{(R)}$ AND THE EXPERIMENTAL REACTIVITY OF α-HYDROGEN TOWARD THE CCl_3 RADICAL IN VARIOUS ALKYLBENZENES

Compound	Type of H atom	$D_r^{(R)}$	Relative[6] rate per α-hydrogen atom k
Benzene	—	0.9862	—
Toluene	prim.	1.0060	0.080
p-Xylene	prim.	1.0061	0.090
Ethylbenzene	sec.	1.0184	0.37
Indan	sec.	1.0186	0.57
Diphenylmethane	sec.	1.0231	0.958
Isopropylbenzene	tert.	1.0319	1.00
Triphenylmethane	tert.	1.0450	4.00

In Table III the $D_r^{(R)}$ values of α hydrogen atoms in these compounds are listed, together with the relative rates per hydrogen atom as summarized by Russell[6] in the hydrogen abstraction reaction. The parallelism between the calculated theoretical indices, $D_r^{(R)}$, and the experimental indices is almost sufficient. However, Russell and Desmond[7] recently pointed out that diphenylmethane is less reactive than ethylbenzene in reaction with the chlorine atom and with the bromine atom. This result seems to be inconsistent with the result indicated in Table III. This discrepancy will be discussed in the last part of the present paper.

Acetylenic Compounds.—Figure 1d illustrates some acetylenic compounds with their $D_r^{(R)}$. The acetylene hydrogen atom is the least reactive of the common hydrocarbon molecules. The hydrogen atoms in the methyl and methylene groups of alkyl derivatives of acetylene are in general more reactive than the corresponding atoms in saturated hydrocarbons, according to our calculation. The $D_r^{(R)}$ values of α hydrogen atoms in alkyl acetylenes are given in Table IV, together with the observed activation energies and reactivities obtained by Trotman-Dickenson.[4] The calculated reactivity is not parallel with the observed activation energy with respect to ethylacetylene and

TABLE IV. THE VALUE OF $D_r^{(R)}$ AND OBSERVED ACTIVATION ENERGY AND REACTIVITY OF α-HYDROGEN ATOM IN SOME ALKYL ACETYLENES

Compound	$D_r^{(R)}$	Activation[4] energy kcal./mol.	Reactivity[4] toward CH_3 radical
$CH{\equiv}CH$	0.9307	—	—
$CH_3C{\equiv}CCH_3$	1.0054	8.6	11
$CH_3CH_2C{\equiv}CH$	1.0172	9.1	33

6) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

7) G. A. Russell and K. M. Desmond, ibid., **85**, 365 (1963).

dimethylacetylene. However, it agrees with the observed reactivity as defined by Trotman-Dickenson.[4]

As has been described in preceding sections, a good parallelism is observed, with some exceptions, between the calculated magnitude of $D_r^{(R)}$ and the experimental reactivity in hydrogen abstraction reactions. However, we should not neglect the following problems, which have to be taken into account before accepting the theoretical results mentioned above as being of significance. One of these problems is: which is the more essential index in this type of reaction, the delocalizability, derived by considering the σ type transition state, or the π conjugation energy in the radical species formed as the result of a hydrogen abstraction.

The answer of this question may be dependent upon the model for the transition state. That is, in the scheme:

$$\mathrm{R:H} + \mathrm{X}\cdot \rightarrow \mathrm{R:H\cdot X} \rightarrow \quad \text{(I)}$$

$$\mathrm{R\cdot H:X} \rightarrow \mathrm{R}\cdot + \mathrm{H:X} \quad \text{(II)}$$

if model I happens to correspond to the actual transition state, the reactivity will be represented by $D_r^{(R)}$, whereas, for the transition state represented by model II, the π conjugation energy will become a better index. Fortunately, the orders of reactivity predicted by these two indecies are almost parallel with each other in simple unsaturated hydrocarbons.[1]

The next problem is that an attacking radical which will bring about a large polarization to hydrocarbon molecules in its approach may yield a different order of reactivity from such a nonpolar radical as an alkyl radical.[6-8] This polar effect is explained by the procedure mentioned in our previous paper.[9] In deriving the index, $D_r^{(R)}$, the Coulomb energy of the orbital of an attacking reagent was assumed to be equal to that of the sp^3 hybridized orbital of the carbon atom. However, for polarizing radicals like chlorine and bromine this assumption has to be changed. We remember that in our previous paper[2] the Coulomb energies of chlorine and bromine atoms were taken as $\alpha+0.5\beta$ and $\alpha+0.45\beta$ respectively. We use these values, so that $D_r^{(R)}$ is given by the following equation:

$$D_r^{(R)}(\lambda_a) = \sum_i^{\mathrm{occ}} \frac{(C_r^i)^2}{\lambda_i-\lambda_a} + \sum_j^{\mathrm{unocc}} \frac{(C_r^j)^2}{-\lambda_j+\lambda_a}$$

$$= \frac{1}{2} D_r^{(E)}(\lambda_a) + \frac{1}{2} D_r^{(N)}(\lambda_a)$$

in which λ_a is the coefficient in the Coulomb energy of the attacking reagent orbital, $\alpha+\lambda_a$, and $D_r^{(E)}$ and $D_r^{(N)}$ denote the delocalizability for the electrophilic attack and for the nucleophilic attack, respectively. For an electronegative reagent, the sign of λ_a will be positive. In this way, with the electronegative reagent orbital, the magnitude of $D_r^{(E)}$ increases and at the same time that of $D_r^{(N)}$ decreases. That is, an electronegative reagent shows a more electrophilic character than otherwise in the reaction, thus changing the reactivity. For instance, the $D_r^{(E)}$, $D_r^{(N)}$ and $D_r^{(R)}$ values of the α hydrogen atom are 1.0288, 1.0080 and 1.0184 respectively in ethylbenzene, and 1.0178, 1.0284 and 1.0231 respectively in diphenylmethane. Hence, if the electrophilic character of the reaction is larger, the reactivity may be in the order; ethylbenzene>diphenylmethane, which was observed in the experiment of Russell and Desmond.[7],*

The numerical calculation has been carried out on the digital computer, KDC-I, of Kyoto University.

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8) J. M. Tedder, *Quart. Revs.*, **14**, 336 (1960).
9) K. Morokuma, H. Kato and K. Fukui, This Bulletin, **36**, 542 (1963).

* The orders of magnitude of $D_r^{(N)}$ and $D_r^{(E)}$ are parallel with that of $D_r^{(R)}$ in olefinic compounds, and so the reactivity orders obtained by the above treatment do not vary from the order given in Table II.