Electronic Overlap Population as Reactivity Measure
IV. Bond Cleavage and Bond Formation Processes

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Electronic overlap population is explored as a reactivity measure for several bond cleavage and bond formation processes. The reactions considered include: I. decarboxylation of carboxylic acids and of their anions; II. carbon-hydrogen bond cleavage in γ-radiolysis of glutaric, methylmalonic and 3-hexendioic acids; and, III. hydrogen atom addition to butadiene and to sorbic acid.

In the previous publications [1–3] on this subject Mulliken electronic overlap population [4] was applied as a measure of reactivity for a wide range of electrocyclic [5] processes. Complete and rather satisfactory analyses of reactivity were obtained for the following cases:

a) ground and excited state cyclizations of butadiene, of hexatriene and of tetraphenyl-o-quinodimethane [2];

b) cis-stilbene like photo cyclizations of a wide range of 1,2-diarylethylenes, including various nitrogen, oxygen and sulfur heterocyclic derivatives [1, 2];

c) photocyclizations of various sulfur heterocyclic 1,4-diphenylbutadiene derivatives [2];

d) photocyclizations of pentahelicene and several of its benzo annelated derivatives [3a];

e) photodimerizations of anthracene, 2-methoxynaphthalene, sorbic acid, trans-stilbene and acenaphthylene [2, 3b].

In particular these studies show that electronic overlap population is a generally valid reactivity measure for systems where a given molecule can react in more than one way. As a rule the reactivity estimates obtained are in agreement with the experimental data.

Whereas the centers undergoing reaction in these examples are not bonded initially, the two first cases treated in the present work involve bond cleavage between bonded centers. These include decarboxylation and homolytic carbon-hydrogen bond cleavage. Some preliminary results in this direction were obtained during studies of the thermal and photochemical ring opening processes of 4a,4b-dihydrophenanthrene [6] and of its dibenzo derivatives [7].

An additional aspect of reactivity considered in the present work (Section III) is the addition of hydrogen atoms to dienes.

The electronic overlap populations in this, as well as in the previous work, were calculated from Extended Hückel (EH) [8] wavefunctions, and were found to be of sufficient accuracy for the present purposes. In some cases STO-3G [9] (ab-initio) wave functions were used in Part II and led to very similar reactivity estimates [2].

I. Decarboxylation

The kinetics of the thermal decarboxylation of carboxylic acids in solution have been widely investigated [10]. It seems nevertheless that definitive conclusions about the mechanism of this reaction are hard to reach from such studies. The present work was undertaken with the purpose of obtaining new data on one aspect of this subject, namely on the comparative reactivity of undissociated acids *vs.* the reactivity of anions. The experimental data indicate two reactivity groups.

i. In the general case the decarboxylation of the unionized acid is much slower (by ca. 10^2) than decarboxylation either of the anions or of the acid dissolved in various aromatic amines in which dissociation is assumed [10].

ii. α and β keto acids and the derived dicarboxylic acids are an exception to this reactivity pattern. In this group the anion is more resistant than the undissociated acid [10]. The experimental data seem to indicate cyclic transition states in this group, especially in the presence of aromatic amines.

The calculated electronic overlap populations $n(k,l)$ are listed in Table 1 *. The atom pairs are denoted as in I. The unionized molecule and the anion are respectively denoted as M and M^-.

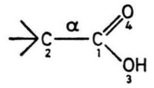
(I)

Table 1. Electronic overlap populations $n(1,2)$ for α bond of carboxylic acids (M) and their anions (M^-).

Group	Compound	M	M^-	$\Delta n(1,2)$
i	Trichloroacetic acid	0.8157	0.8073	0.0084
	nitroacetic acid	0.7980	0.7892	0.0088
	2,4-dihydroxy benzoic acid	0.9539	0.9394	0.0145
	pyridine 2-carboxylic acid	0.9139	0.9013	0.0126
	acetic acid	0.8051	0.7928	0.0123
ii	malonic acid	0.7918 (II)	0.8036 (III)	−0.0118
		0.7920 (IV)	0.7792 (V)	0.0128
	oxalic acid	0.7887 (VI)	0.8077 (VII)	−0.0190
		0.7863 (VIII)	0.7838 (IX)	0.0025

The first five molecules of Table 1 belong to class i as described before. The calculated electronic overlap populations are in complete agreement with the experimental reactivity data. The $n(1,2)$ values for M, $n^M(1,2)$ are larger than $n^{M^-}(1,2)$, indicating stronger bonds and smaller reactivity for M than for M^-. The differences $\Delta n(1,2) = n^M(1,2) - n^{M^-}(1,2)$, of about 0.01, correspond to significant energy differences [1, 2].

Noncyclic structures (e. g., IV, V, VIII and IX) of the two last molecules of Table 1 show the same trend of the $n(1,2)$ values. However this situation is reversed when cyclic structures are considered. Thus a pronounced effect is seen in the two anions III and VII. In these species the $n(1,2)$ values are considerably larger than in the unionized molecules again in agreement with the experimental observations.

Examination of other electronic interactions, apart from the interaction between the 1 and 2 centers reveals that for the molecules of group i in Table 1 only the $2-3$ and $2-4$ interactions (see I) are of any importance. The combined effect of these interactions reinforces the effect of the $1-2$ interaction. Thus for acetic $n^M(2,3) = -0.0516$, $n^{M^-}(2,3) = -0.0677$, and $n^M(2,4) = -0.0685$, $n^{M^-}(2,4) = -0.066$. The differences $\Delta n(2,3) = -0.0161$ and $\Delta n(2,4) = 0.0019$ indicate a larger antibonding interaction in the anion which tends to weaken the $1-2$ bond. In the other molecules of this group the differences $\Delta n(2,3)$ and $\Delta n(2,4)$ are very similar to the values obtained for acetic acid.

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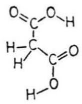

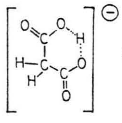
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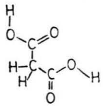

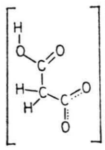
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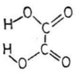

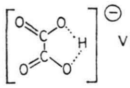
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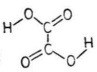

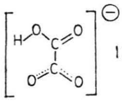
IX

II. C – H Bond Cleavage in Carboxylic Acids

Hydrogen atom abstraction is an important reaction path of γ-irradiated carboxylic acids [12]. In this section electronic overlap population will be applied to study hydrogen abstraction in γ-irradiated methyl malonic acid, glutaric acid and 3-hexendioic acid. No direct evidence is available about the path of these processes and several alternatives are possible. A) Bond cleavage can proceed from excited or ionic states of the molecules. B) The observed products may be obtained by hydrogen atom abstraction from the electronic ground state of the intact molecule by molecular fragments formed in some primary step. This last alternative will be considered here.

Methyl malonic acid (X) and glutaric acid (XI) undergo abstraction of the hydrogen atoms attached to the α-carbon atom to give free radicals $CH_3\dot{C}(COOH)_2$, X_a, and $HOOC\dot{C}HCH_2CH_2COOH$, XI_a [12].

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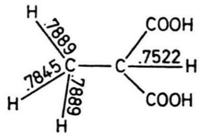
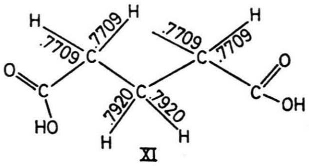
* The following bondlength values were assumed [11]:
$C-C = 1.54$ Å; $C-C$ (next to aromatic ring) $= 1.46$ Å; $C-H = 1.08$ Å; $C=O = 1.23$ Å; $C-O$ (acid) $= 1.36$ Å; $C-O$ (anion) $= 1.25$ Å; $O-H = 0.97$ Å.
The STO ls H exponent is 1.3.

The calculated $C-H$ electronic overlap populations for the ground state configuration (denoted along the bonds) are as follows,



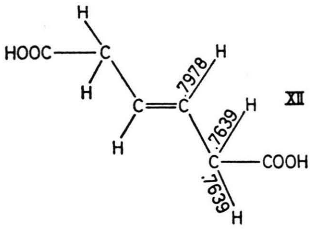
X

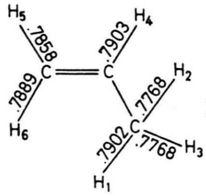


XI

The $C-H$ electronic overlap populations are thus seen to be much lower for the $C-H$ bonds nearest to the carboxyl group than for the other $C-H$ bonds. These results indicate that in the ground state α $C-H$ bonds are significantly weaker than $C-H$ bonds further removed from the COOH group. In these two cases and in that to follow the present approach seems to point to path B (i. e., formation of free radicals by H-abstraction by molecular fragments). However, one should keep in mind that a similar trend of electronic overlap populations could well be found in other electronic states.

γ-Irradiated 3-hexenedioic acid (XII) also undergoes H-abstraction at the α-position to give the allyl type free radical, $HOOC\dot{C}H-CH=CHCH_2COOH$ (XII_a)[13]. Comparison of the calculated $C-H$ electronic overlap population (see XII) with the results obtained for X, XI and for propylene, XIII gives some indication on the effects of different molecular units on the $C-H$ electronic overlap populations.





XIII

The results for propylene show that the two allylic $C-H$ bonds in the out of plane position (H_2 and H_3) have lower electronic overlap population values than the ethylenic $C-H$ bonds. The same trend, though to a larger extent, is seen for XII.

The electronic overlap populations of the methylene $C-H$ bonds in XII (0.7639) is much lower than the value for the ethylenic $C-H$ bonds (0.7978). This finding obviously indicates a significant difference in the reactivity of the two bonds with respect to the hydrogen abstraction process.

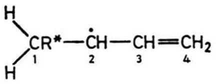
III. H-Atom Addition to Diene Systems

γ-Irradiation of carboxylic acid derivatives of butadiene was recently shown to result in H atom or alkyl radical addition to give allyl type free radicals[13]. Thus sorbic acid,

$$CH_3CH=CH-CH=CHCOOH \quad (XIV)$$

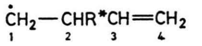
on γ-irradiation undergoes addition at the terminal C-atom of the butadiene system nearest to the methyl group, to give a substituted allyl free radical of the type $CH_3CHR\dot{C}HCH=CHCOOH$[13]. In the present section we shall apply electronic population analysis to the study of such reactions. First the reactivity of butadiene will be considered and then the method will be applied to the sorbic acid molecule itself. For sake of simplicity attack by a hydrogen atom will be assumed.

Two modes of addition of a hydrogen atom or of a molecular fragment R^* to a diene system are possible in principle, either at a terminal atom as in XV



XV

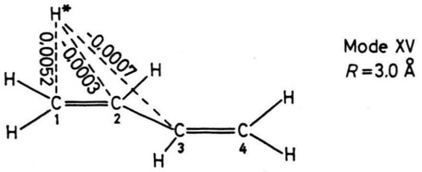
or at central atom as in XVI

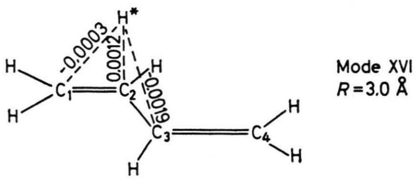


$$\underset{1}{\dot{C}H_2}-\underset{2}{CHR^*}\underset{3}{CH}=\underset{4}{CH_2}$$

XVI

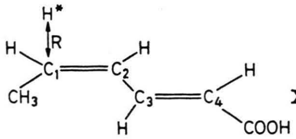
Mode XV results in formation of a substituted allyl free radical with the unpaired electron delocalized over atoms 2, 3 and 4 whereas in XVI the unpaired electron is localized essentially in a pure $2p_z$ orbital on C_1, separated from the C_3-C_4 double bond by the C_2 methylene unit. In this case both considerations of relative stability of the products and of relative reactivity of the starting species can be applied. Considerations of relative stability are best treated by an HMO approach as described elsewhere[13]. However, the relative reactivity is conveniently treated by the present Mulliken population analysis. In the model considered a hydrogen atom is placed at a distance R from the molecular plane of an s-trans butadiene molecule, either opposite a terminal C-atom or opposite a central C-atom, corresponding to addition by mode XV or XVI, respectively. For a distance of $R = 3.0$ Å the electronic overlap populations values are as follws,



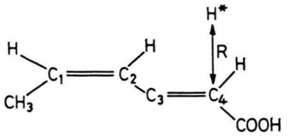


In the present context the electronic overlap populations are taken as indicative of the reactivity of the various C atoms during the initial stages of the reaction. In mode XV the interaction $H^* - C_1$ $[n(C_1 - H^*) = 0.0052]$ is considerably more bonding than the interactions $H^* - C_2$ $[n(C_2 - H^*) = 0.0012]$ in mode XVI. Similarly and going in the same direction, mode XVI shows an antibonding $H^* - C_3$ interaction $[n(C_3 - H^*) = -0.0019]$. It follows that as far as the interatomic interactions are concerned reaction through mode XV is preferred over reaction through mode XVI. The EH electronic energies ($E_A = -404.218$ eV, $E_B = -404.191$ eV), indicate that even in the early stages of reaction the product formed by mode XV is more stable than that formed by mode XVI. These arguments establish the preference for formation of an allyl radical over other species. However, they cannot predict what radical will be produced in molecules of the type $X - \underset{1}{C}H = \underset{2}{C}H - \underset{3}{C}H = \underset{4}{C}HY$ when X is widely different from Y. Thus in the case of trans,trans-sorbic acid and of trans,trans-sorbamide ($X = CH_3$ and $Y = COOH$ or $CONH_2$) the esr spectra of γ-irradiated crystals indicate that addition occurs at C_1 and not at C_4 [13].

The same method used for treating the reactivity of the different positions of butadiene was applied to this case. An H atom (H*) was brought to a distance R from the molecular plane of sorbic acid, in case XVII opposite C_1, and in case XVIII opposite C_4.



XVII



XVIII

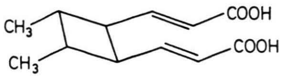
The Mulliken electronic overlap populations calculated from EH wavefunctions for the two cases are listed in Table 2.

Table 2. Electronic overlap population for modes XVII and XVIII.

R, Å	XVII $n(C_1-H^*)$	XVIII $n(C_4-H^*)$
3.0	0.0041	0.0037
2.5	0.0270	0.0235
2.0	0.1244	0.0969

For all these distances $n(C_1 - H^*)$ for mode XVII is seen to be larger than $n(C_4 - H^*)$ for mode XVIII, in agreement with the experimental data.

The present results for addition to sorbic acid are in accord with other experimental findings which confirm the greater reactivity of this molecule at C_1. Thus uv irradiation of sorbic acid results in the formation of dimers XIX and XX, the yield of XIX being ten-fold larger than that of XX [15].



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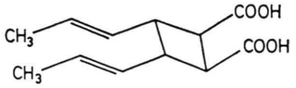

XX

This reactivity pattern was explained in Part II by the approach of the present paper [2].

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