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A THEORETICAL INVESTIGATION OF α-HYDROGEN ABSTRACTION FROM SOME ORGANIC ANIONS

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Abstract—The process of α-hydrogen abstraction from methoxide, formate and isopropoxide ions has been examined, using an SCMO method, by calculating changes in electronic charge on αH and C-αH bond orders, as the C-αH bond orders, as the C—αH bond was extended with the residual moiety retaining its equilibrium geometry. In all cases negative charge accumulates on αH with increasing C—αH separation and the systems yield H^- at sufficiently large C—αH distances. Possible implications for the mechanisms of oxidation of the anions by dehydrogenation are discussed.

THERE IS considerable evidence that the oxidation of many weak organic acids in aqueous solution involves the acid-base properties of these molecules. In a number of important cases the anion (conjugate base) of the reductant undergoes oxidation more readily than does the neutral molecule; for example (a) the formate ion is oxidized to CO_2 by chlorine some 10^4 times faster than is neutral formic acid; (b) the rate of permanganate oxidation of benzhydrol exhibits first-order dependence on hydroxyl ion concentration. These, and many others,[1] may be regarded as examples of α-hydrogen abstraction processes and the manner in which the abstraction occurs determines the character of the redox reaction.

Two possibilities for abstraction are (a) a one-electron equivalent *H-atom* transfer; this implies radical intermediates in the reaction mechanism e.g.

$$R_2CHO^- + Ox \rightarrow R_2CO^- + HOx$$

(b) a two-electron equivalent *hydride ion* transfer i.e.

$$R_2CHO^- + Ox \rightarrow R_2CO + HOx^-$$

analysis of the available experimental data does not allow an unequivocal conclusion to be drawn,[1] and it is in this context that we have examined theoretically the process of α-hydrogen abstraction from isolated organic anions.

CALCULATIONAL METHODS AND RESULTS

Three systems were investigated in the present work:

(a) the formate ion, $HCOO^-$ (b) the methoxide ion, CH_3O^- and (c) the *iso* propoxide ion, $(CH_3)_2CO^-$. The geometries of all three are illustrated in Fig. 1. The effect of removing a hydrogen atom in the α position was simulated by increasing the C—αH distances along the C—αH axis, other bond lengths and angles in the species being left unchanged. The object of the calculations was then to examine the change of electronic charge on this hydrogen atom as this process was carried out.

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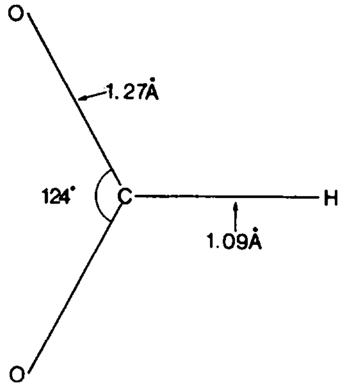

FIG. 1(a)

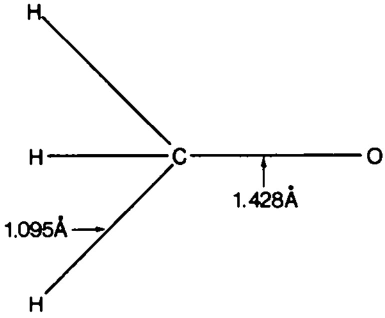

FIG. 1(b)

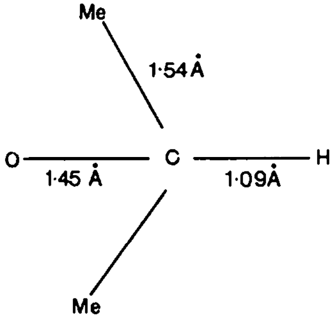

FIG. 1(c)

The Pople–Santry–Segal SCMO method[2] was used throughout. This takes account of all valence electrons in the species, and since, in each of the ions considered, there is an even number of electrons then the closed-shell SCF equations suffice. This technique requires values for the elements of a core Hamiltonian matrix. The diagonal elements of this matrix ($H_{\mu\mu}$) appropriate to the 1*s* orbital of hydrogen and the 2*s*, 2*p* orbitals of carbon and oxygen were taken from previous work.[2, 3] The off-diagonal elements ($H_{\mu\nu}$) were computed from the overlap integrals between all possible orbital pairs and the appropriate bonding parameters, B_{I}^{0}, from each atom, i.e. for orbitals μ and ν centred on Atoms A and B, we have,

$$H_{\mu\nu} = S_{\mu\nu}/2\,(\beta_A^\circ + \beta_B^\circ) = S_{\mu\nu}\beta_{AB}^\circ \tag{1}$$

Appropriate values for B_i° are H: -9 eV. C: -21 eV. O: -31 eV.

The off-diagonal elements of the Fock matrix may then be obtained from[2]

$$F_{\mu\nu} = \beta_{AB}^\circ S_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{AB} \tag{2}$$

The two-centre electron repulsion integrals γ_{AB} are atomic parameters and can be computed theoretically from Roothaan's expressions;[4] P is the orbital charge density matrix wherein the diagonal terms $P_{\mu\mu}$, are atomic orbital charge densities and the off-diagonals $P_{\mu\nu}$ are orbital-orbital bond orders. The total charge on a particular atom A is then,

$$P_{AA} = \sum_{\mu}^{A} P_{\mu\mu}$$

The diagonal elements of the Fock matrix, $F_{\mu\mu}$, are given by,

$$F_{\mu\mu} = H_{\mu\mu} - \tfrac{1}{2}P_{\mu\mu}\gamma_{AA} + P_{AA}\gamma_{AA} + \sum_{B(\neq A)} P_{BB}\gamma_{AB} \tag{3}$$

Using the quantities specified in this way, the SCF equations were solved using a fully automatic SCMO programme. The self-consistent eigenvalues, orbital density matrix and F-matrix obtained thus enable the total energy of the system to be calculated.

$$E_{\text{total}} = \tfrac{1}{2}\sum_{\mu,\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) + \sum_{A<B}\sum Z_A Z_B/R_{AB}$$

Of particular interest to us in these calculations is the total charge on the α-hydrogen atom P_{HH}: since we suppose that only the 1s orbital of hydrogen participates to any extent in bonding then $P_{HH} = P_{\mu\mu}$ for this atom.

The formate ion $HCOO^-$

The ion, (Fig. 1(a).) is planar and symmetrical about the C—H internuclear axis. The bond angles and lengths are those of its sodium salt.

If the 1s^2 cores of carbon and oxygen are neglected the system possesses eighteen electrons of which twelve originate from the oxygen atoms, four from the carbon and one from the hydrogen. The remaining electron cannot be allotted to any particular atom and so was supposed initially to be smeared out evenly over the four centres. The results of calculations on this system in which the "extra" electron was neglected (except for inclusion in the electron density computation) did not differ significantly from these in which it was initially smeared out evenly. In all, thirteen orbitals were considered i.e. 1 on hydrogen and 4 on each of the other three atoms. Calculations were performed to determine the change of electronic charge on the hydrogen atom on increasing the C—H distance gradually from a point just less than its equilibrium value (1·09 Å). The geometry of the residual moiety was assumed to remain fixed although a detailed study of the *energetics* of the abstraction would require this also to be considered variable. The results are shown on Fig. 2. The charge on this atom increases steadily to ~1·5 e when the C—H distance is ~2·9 Å. The curve then rises steeply and at ~3·4 Å the charge becomes equal to two electrons.

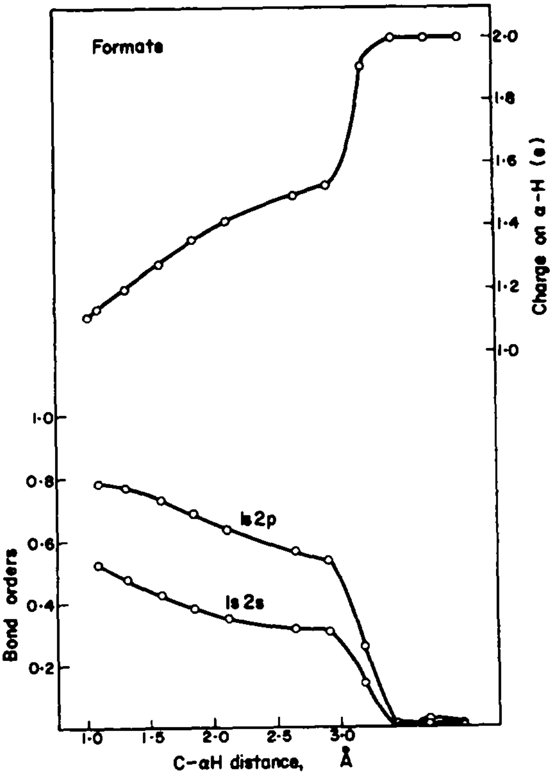
Formate
2·0
1·8
1·6
1·4
1·2
1·0
Charge on α-H (e)
1·0
0·8
0·6
0·4
0·2
Bond orders
ls2p
ls 2s
1·0
1·5
2·0
2·5
3·0
C–αH distance, Å

FIG. 2

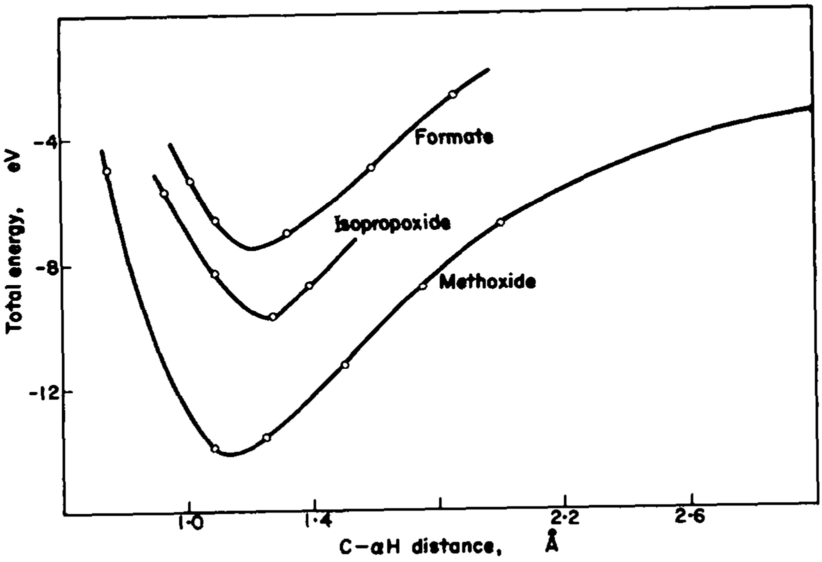
-4
-8
-12
Total energy, eV
Formate
Isopropoxide
Methoxide
1·0
1·4
2·2
2·6
C–αH distance, Å

FIG. 3

We conclude therefore that, at C—H distances greater than 3·4 Å, the system decomposes into a hydride ion and CO_2.

A plot of the total energy of the system (from equation 4) is shown in Fig. 3. For convenience the energy curves for all three ions (*vide infra*) have been plotted on the same diagram, although it must be stressed that their *absolute* energies are not in the same region; for the formate ion the energy zero is −1226 eV. This ion has minimum energy when the Sp. C—H distance lies between 1·15 and 1·25 Å. This is in acceptable agreement with the experimental value which is 1·09 Å.

The methoxide ion, CH_3O^-

In considering this ion [Fig. 1(b)] it was assumed for simplicity that the arrangement of the hydrogen and oxygen atoms around the carbon was exactly tetrahedral. The unique C_3 axis (i.e. the C—O bond) was labelled as z. The bond lengths were taken from Ref. 5.

If the $1s^2$ cores of carbon and oxygen are neglected the system has fourteen valence electrons and eleven orbitals. As in the formate system, one of these electrons must be initially spread out over the five centres. A series of calculations of P_{HH} were then made with different C—H bond lengths and the resultant variation in charged plotted (Fig. 4). The charge on hydrogen increases from one electron when the C—H

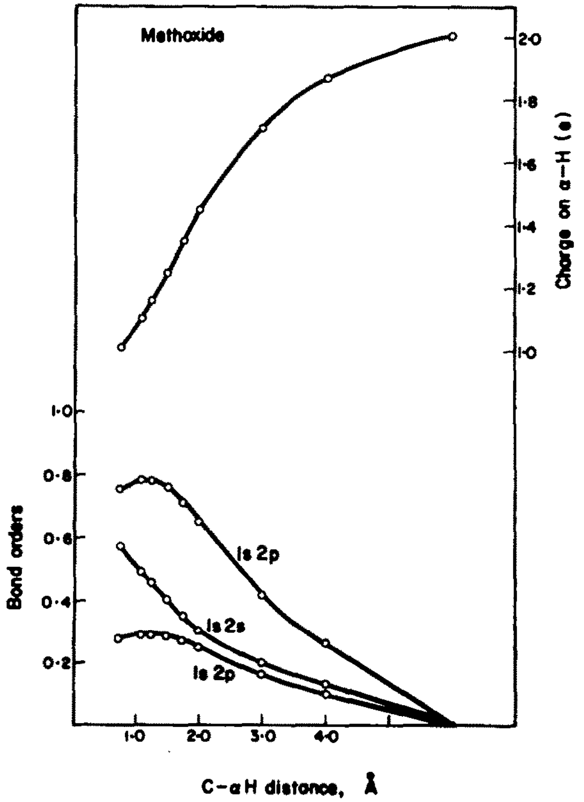

FIG. 4

bond length is 0·75 Å (somewhat below the equilibrium distance) to two electrons at a C—H distance of ~6 Å. This indicates that when the hydrogen atom is more than 6 Å distance from the carbon atom it goes over to a hydride ion. Fig. 3 illustrates the changes in total energy of the methoxide anion as the C—H length increases. The zero for this system corresponds to an energy of −685 eV. The minimum of the plot occurs between 1·0 and 1·2 Å which corresponds closely to the equilibrium value of 1·095 Å.

The isopropoxide ion. $(CH_3)_2CHO^-$

Fig. 1(c) shows the ion with appropriate bond lengths. It is convenient to define the C—H(α) bond as the central *z* axis since it lies on the molecular reflection plane.

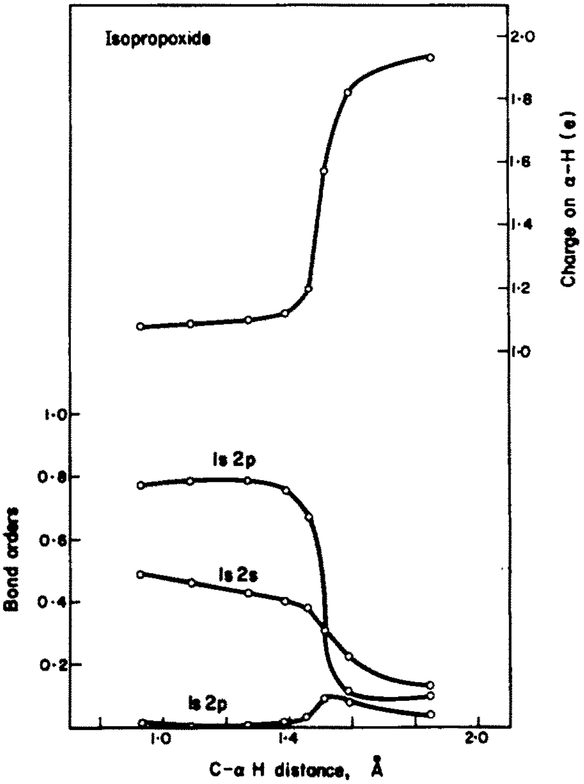

FIG. 5

For the purpose of all calculations the model assumed a central carbon atom tetrahedral surrounded by a hydrogen, an oxygen and two methyl groups. The valence electrons and orbitals were designated as before, hence there are 23 orbitals and 26 electrons.

The charge on the α hydrogen atom is plotted against the C—H dlstance in Fig. 5. It increases slowly to 1·2 electrons when the C—H length is 1·45 Å after which it rises rapidly to 1·8 electrons over a sp. dlstance of 0·15 Å and then rises more gradually to 2 electrons. Thus the hydrogen goes over to hydride at a considerably smaller C—αH distance than it does for either the formate or methanolate ions. The energy plot for the isopropoxide ion is shown in Fig. 3: the energy zero corresponds to −1034 eV. The lowest point of the curve occurs between 1·1 and 1·3 Å which may be compared with an experimental equilibrium internuclear distance of 1·09 Å.

DISCUSSION

For the three species considered the charge carried by the α—H nucleus is near to 1 electron in the neighbourhood of the equilibrium C—αH internuclear separation and, in all cases, stretching of the C—αH bond results in increases in charge on α—H, with parallel decreases in bond order, and ultimately to the generation of hydride ion. Our calculations describe α-hydrogen abstraction for the isolated ions and the results suggest that hydride-ion abstraction may properly be regarded as the norm dehydrogenation behaviour of these species.

The key question, when real oxidations are considered, is to what extent is charge generation on α-hydrogen developed in the transition states for the reactions? Interaction of the anions with the electrophilic centre of an oxidant might be expected to enhance the electron displacement leading to hydride-ion generation, suggesting that hydride-ion abstraction is a particularly favoured pathway in these processes. For hydrogen atom transfer to occur the oxidant must possess properties which could suppress change development on α-hydrogen as the C—αH bond is extended. Such an effect could perhaps arise with an oxidant which carried an overall negative charge. Alternatively, repulsive interactions involving the ligand environment of an oxidant centre might effectively inhibit charge development on α—H and lead to H-atom transfer. Effects of this type are clearly possible with oxy-anion oxidants such as permanganate ion.

The development of more general statements concerning the process of α—H abstraction requires an examination of a much wider range of anion species; the present work was limited by the available computer facilities. Extension of the work to neutral molecules is clearly desirable, as is an examination of the possibility that coupled proton and hydride ion transfer may be a facile type of α—H abstraction processes under suitable conditions.

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