Relationes

The Electronic Structure and Energy of Acyloxy and Dioxacyclopropyl Cations

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The electronic structure and heats of formation of several acyloxy cations and the isomeric dioxacyclopropyl cations have been determined by MINDO/2 calculations. The potential energy surface shows the cyclic isomer to represent the least energy species. The stabilizing effect of alkyl substituents in the latter has been traced to strong hyperconjugative interaction.

Key words: Hyperconjugation – Antiaromaticity

1. Introduction

In contrast to carbonium ions, little experimental or theoretical work has been reported on organic cations in which atoms other than carbon bear the positive charge [1]. Such electron deficient species are expected to be much more reactive than carbonium ions, particularly if the positively charged hetero atom is more electronegative than carbon (e.g., nitrogen or oxygen). As part of our study of cations in which the positively charged hetero atom is incorporated in a cyclic or acyclic π-system, we were interested in the energetics and electronic structure of acyloxy cations I. These ions have been discussed occasionally as possible reactive intermediates in such processes as the Kolbe electrolysis [2] and lead tetra-acetate oxidation [3]. Interestingly, in these studies the possible role of the isomeric dioxacyclopropyl cations II in the potential energy surface of these species was not mentioned. In this communication we wish to report the results of some semiempirical SCF-MO calculations at the MINDO/2 level [4] of I and II [1].

I   II
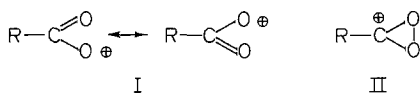
2. Results and Discussion

Our initial efforts were directed toward exploring the potential energy surface of the simplest ions I and II in which the substituent R represents hydrogen. All calculations were carried out for the singlet ground state (S_0). A portion of the

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[1] Linnett [5] has previously calculated the π-electron energies of formyloxy cation, radical and anion with neglect of σ and n orbitals of oxygen.
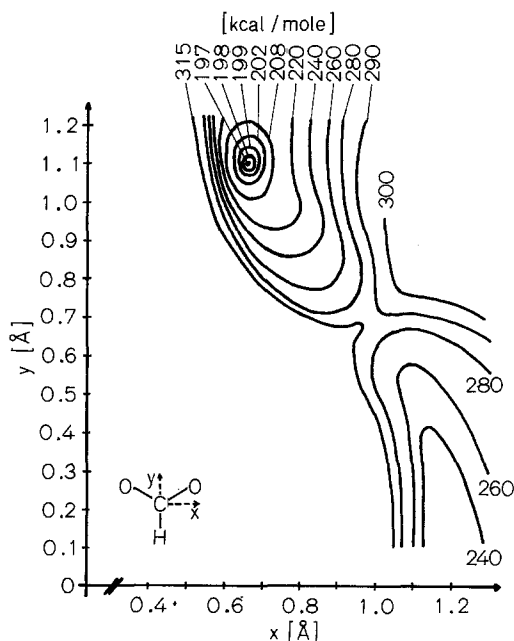
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Fig. 1. Potential energy surface of acyloxy and dioxacyclopropyl cations (I and II, R = H). The coordinates refer to the symmetrically disposed oxygen atoms, carbon being at $x = y = 0$

potential energy surface was determined by calculating the heats of formation (ΔH_f) of some 90 geometric variations. In doing so, a planar geometry was assumed[2] and a bond length of 1.1 Å assigned to the C–H bond. Thus, the C–O bond length and the O–C–O bond angle were systematically varied, giving rise to Fig. 1. The result is somewhat surprising in that no true potential energy minimum could be found for the acyclic form I. Instead, the computations show that the cyclic structure II (dioxacyclopropyl cation) represents the minimum. Application of the Simplex [6] minimization procedure fully substantiated this result[3]. Form II with optimized geometry has an O–O bond length of 1.33 Å, an O–C–O bond angle of 63° and a calculated ΔH_f value of 196.5 kcal/mole. Figure 1 shows that any increase in O–C–O bond angle (i.e., increase in O–O bond length) causes the energy to rise sharply. Thus, at an O–C–O bond angle of 120° (which has been found for many acyloxy *anions* [7]) ΔH_f is always higher than 265 kcal/mole.

As in any semiempirical calculation, the result may be an artifact of the method of computation. Thus, the MINDO/2 method is known to underestimate strain energies of small ring compounds by as much as 15 kcal/mole [8]. The method also neglects one-center differential overlap, so that the dipolar field of lone electrons in hybrid atomic orbitals is not accounted for [8]. However, the general shape of the potential energy surface shown in Fig. 1 clearly points

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[2] Non-planar forms of I and II were also tested; in all cases deviation from planarity resulted in higher ΔH_f values.

[3] Thanks are due to Dr. W. W. Schoeller for carrying out the Simplex calculations.
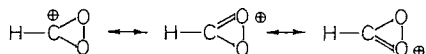
to the cyclic form II as representing the least energy species. It is noteworthy that II is actually a carbonium ion, in contrast to I, in which the oxygen atoms formally represent the electron deficient centers. In summary, any attempted generation of I may in fact lead to II[4].

Besides the energy minimum corresponding to II, Fig. 1 also shows the beginnings of a second energy minimum. Hoping to find in this valley a species more stable than II, the Simplex procedure was applied once more. The minimum was found to be a symmetrically protonated form of carbon dioxide, having a planar, non-classical form III with an O–C–O bond angle of 154°. The calculated ΔH_f value of 219 kcal/mole indicates a very unstable species

$$C \overset{\displaystyle O}{\underset{\displaystyle O}{\lessgtr}} {\cdots} \overset{\displaystyle \oplus}{H}$$

III

The present computations all refer to closed shell species and do not guarantee that the lowest triplet state might not actually represent the ground state. However, we do not believe this to be the case, since the calculated energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the S_0 state of II (R = H) has the extremely high value of 10 eV. This enormous energy difference makes it quite unlikely that, inspite of possible electron correlation effects, the lowest triplet could actually be of lower energy than the S_0 state. Similar results were found for the acyclic form I (R = H) at various geometries.

Having established that II (R = H) in its S_0 state is the most stable form, we investigated its electronic structure. Figure 2 shows the thirteen MO's of II, along with those of I (O–C–O bond angle of 120°). The fact that several MO's of the cyclic form display striking similarities to the well known Walsh orbitals of cyclopropane is not surprising. It is interesting to note that the HOMO of II (a_2) is antibonding in nature. This is consistent with the resonance forms shown below, which indicate some degree of antiaromatic character due to the delocalization of four π-electrons in a cyclic system.

$$H-C \overset{\oplus O}{\underset{O}{\lessgtr}} \longleftrightarrow H-C \overset{O}{\underset{O}{\lessgtr}} \oplus \longleftrightarrow H-C \overset{O}{\underset{O \oplus}{\lessgtr}}$$

We next probed the possibility of stabilizing II by replacing the H-atom by various substituents. In doing so, the optimized geometry of II was employed, to which the substituents with fixed geometry were attached. Although various conformations were tested, small geometric changes within the substituent which might occur upon interaction with the cationic center were not considered. In this manner ΔH_f values corresponding to the optimized conformation were calculated for several substituted cations (Table 1). The results demonstrate that replacing hydrogen by such substituents as methyl has a dramatic influence on the heat of formation. Methyl substitution results in a change in ΔH_f from 196.5 to 152.2 kcal/mole. The difference of 44 kcal/mole indicates strong interaction between the positive carbon atom and the methyl group. Mere attachment

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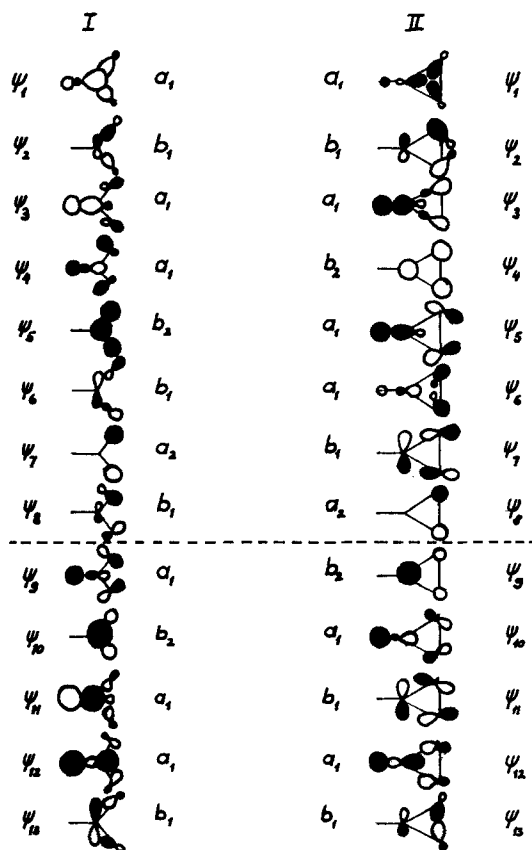[4] Dioxacyclopropyl cations II have not been detected experimentally to date.

Fig. 2. Molecular orbitals of acyloxy and dioxacyclopropyl cations (I and II, R = H). All p_z orbitals of carbon and oxygen are shown as circles. The MO's above the dashed line are doubly occupied

of a methyl group to a cationic carbon center without interaction ("localized C–C bond") has been shown to lower the heat of formation by only 8–10 kcal/mole [9]. Thus, the greater part of the 44 kcal/mole must be attributed to hyperconjugative stabilization. Consistent with this interpretation is the distribution of formal charges computed for methyl substituted II, which demonstrates the pronounced difference in formal charge between configurationally different hydrogen atoms,

Table 1. Calculated heats of formation (ΔH_f) of substituted dioxacyclopropyl cations II

Substituent	ΔH_f (kcal/mole)
Hydrogen	196.5
Methyl	152.2
Ethyl	141.4
Cyclopropyl	168.0
Phenyl	173.8
Vinyl	167.8

Table 2. Calculated distribution of formal charges of methyl dioxacyclopropyl cation
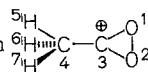
Atom	Formal charge
1	-0.103
2	$+0.825$
3	-0.103
4	-0.011
5	$+0.142$
6	$+0.125$
7	$+0.125$

as well as the electron donor properties of the alkyl group (Table 2). The important information to be gained from these calculations is not the precise numbers, but rather the qualitative conclusion regarding the stability of substituted ions II (Table 1). Alkyl substitution should greatly enhance the feasibility of generating the ions experimentally.

Our calculations demonstrate that the ions discussed here (II) are potentially capable of existence. Thermodynamically they are comparable to many carbonium ions which in fact have been prepared. Thus, ΔH_f values of 130 to 180 kcal/mole for stable carbonium ions in solution are not uncommon [10]. However, the present calculations do not consider kinetic stability. It is conceivable that the ions are quite reactive, stabilizing themselves via rearrangement, cycloaddition with proper substrates or decomposition into carbon dioxide and carbonium ions.

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