An Unrestricted Hartree–Fock Study of the Lowest Triplet State of Methylglyoxal and Other Carbonyls

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Abstract: The unrestricted Hartree–Fock method is used to investigate the vertical excitation energies to the first triplet state ($n \to \pi^*$ type), $\Delta E_{g \to t}$ (UHF), for methylglyoxal in relation to glyoxal, dimethyglyoxal, formaldehyde, and acetaldehyde. The excitation in methylglyoxal is shown to occur mainly in the ketonic group, which acquires a much larger amount of unpaired spin in the triplet state than the aldehydic group. The similar charge redistribution upon excitation in the ketonic group of methylglyoxal to that in formaldehyde and acetaldehyde is compatible with the comparable magnitudes of the correlation energy corrections to $\Delta E_{g \to t}$ (UHF) in the three molecules. The variation of the triplet state energy with the out of plane angle, θ, of the methylene group in formaldehyde is also investigated in double ζ basis.

Introduction

Methylglyoxal (MGl) and dicarbonyls in general play a special role as acceptors in Szent-Györgyi's theory of cancer.[1] In a previous investigation[2] using the semiempirical INDO technique, we calculated MGl to possess a much lower vertical excitation energy to the first triplet state ($n \to \pi^*$ type) than that of glyoxal (Gl) and dimethylglyoxal (DMGl). In this paper we investigate further this problem using the unrestricted Hartree–Fock technique (UHF).

Method

The calculations are performed using the ab initio Gaussian-70 series of programs.[3] The basis sets chosen are the minimal STO-3G and STO-6G, as well as the double ζ one of Dunning-contracted Gaussian functions,[4] C (9s 5p/4s 2p), O (9s 5p/4s 2p), and H (4s/2s). This double ζ basis set is the same one used by Dykstra and Schaefer[5,6] in their restricted Hartree–Fock (RHF) study of the ground and excited states of Gl. The triplet state values reported here are for the lowest triplet states ($n \to \pi^*$ type) of the various molecules. For the methyl-substituted carbonyls, the calculations are done assuming one hydrogen of the methyl group to be in a cis position relative to the C=O bond of the same carbonyl group, based on Radom et al.'s study of acetaldehyde.[7,8]

Results

Table I gives the ground-state energies, E_g, and the difference in energies between the ground state and the first triplet excited state, $\Delta E_{g \to t}$ (UHF), assuming vertical excitation, for Gl, MGl, and DMGl using the above basis sets. These $\Delta E_{g \to t}$ (UHF) values are seen to be only slightly affected by the choice of the basis set or by minor variations in the geometry. The results of the UHF method are seen to agree with our previous INDO finding that the calculated vertical $\Delta E_{g \to t}$ for MGl is much lower than that for Gl and DMGl.

This lowering of the $\Delta E_{g \to t}$ (UHF) observed in MGl compared to Gl is not apparent if one compares the $\Delta E_{g \to t}$ (UHF) for the simplest analogous molecules containing a single carbonyl group, formaldehyde (F) and acetaldehyde (Ac). For standard geometries the E_g and the vertical $\Delta E_{g \to t}$ (UHF) values (in au) are respectively (STO-3G basis) -112.3525, 0.0650 (F); -150.9437, 0.0713 (Ac).

It is interesting to note that the above calculated $\Delta E_{g \to t}$ (UHF) values for F and Ac are considerably lower than the experimental value of 0.1378 au found by Staley et al. for

both.[15] This has also been found by the RHF method in the case of F by Dykstra and Schaefer[6] using the present double ζ basis and the minimal experimental geometry of F in the ground state,[11] and by Garrison et al.[12] using more extended basis. Using the present UHF method and double ζ basis we have investigated the dependence of $\Delta E_{g \to t}$ (UHF) on the geometry of F in the first triplet state, particularly with regard to the out of plane angle θ of the methylene group, holding all other coordinates fixed. The results are shown in Figure 1.

Curves A and C give the variation of the total energy with θ for the ground and first triplet states, respectively, using the experimental ground-state geometry [r (C–H) = 1.102 Å, r(C=O) = 1.210 Å, $\angle$HCH = 121.1°].[11] The ground-state energy minimum, $E_g = -113.8295$ au, occurs for $\theta = 0°$ as expected, while the excited-state minimum occurs for θ between 25 and 30° (calculations made at increments of 5°). The $\Delta E_{g \to t}$ (UHF) for a vertical transition from the ground-state minimum is 0.0807 au.

Curve B corresponds to the experimental geometry of the lowest reported triplet state,[11] $^3A''[r$ (C=O) = 1.312 Å, r (C–H) = 1.09 Å, $\angle$HCH = 119°; the latter two values are assumed to be the same as in the lowest singlet $^1A''$ state]. Inclusion of these geometry variations results in a lowering of the energy of this state by $\sim$0.02 au, and a shifting of the minimum to $\theta = 32°$ (calculations made at increments of 1°) compared to the experimentally reported value of 35°.[11] The $\Delta E_{g \to t}$ (UHF) value between the ground-state minimum and the triplet-state minimum of curve B is 0.0544 au.

Discussion

The wave functions of the lowest triplet states calculated above by the UHF scheme differ from those calculated by a RHF treatment in that they incorporate spin components of higher multiplicity than the triplet, as well as including some correlation effects (see, for example, ref 13 and 14). The extent of these effects on $\Delta E_{g \to t}$ (UHF) may be estimated for the cases of Gl and F. For the vertical transition from the minimized ground-state geometry of Dykstra and Schaefer for Gl,[5] using the present double ζ basis, the RHF method yields for $\Delta E_{g \to t}$ 0.1242 au[6] while our UHF results give a value lower by 0.0208 au. Using this same basis set for the vertical transition from the experimental ground state geometry of F (curve A to curve C at $\theta = 0°$ in Figure 1), the RHF value is 0.0869 au[6] while the present UHF value is lower by 0.0062 au. If these effects are of comparable magnitude for MGl, one would expect the trends observed in Table I to appear in the RHF approximation as well.

Table I. Ground-State Energies (E_g) and Vertical Transition Energies to the First Triplet State ($\Delta E_{g\to t}$) for Gl, MGl, and DMGl (au) (1 au = 27.21 eV)

basis set		Gl			MGl	DMGl
		a	b	c	a	a
STO-3G	$E_g{}^f$	−223.5743	−223.5806	−223.5823	−262.1646	−300.7548
	$\Delta E_{g\to t}{}^g$	0.1015	0.1075	0.1097	0.0334	0.1060
STO-6G	E_g	−225.7409	−225.7470		−264.7078	
	$\Delta E_{g\to t}$	0.1008	0.1066		0.0312	
	E_g		−226.5182			
double ζ	$\Delta E_{g\to t}$		0.1034			
	$\Delta E_{g\to t}$ (exp)		0.0891^d		(0.0897–0.0905)^e	0.0930^d

^{a} Using standard geometries.[9] ^{b} Using the double ζ minimized ground-state geometry.[5] ^{c} Using the STO-3G minimized ground-state geometry.[8] ^{d} Reference 10. ^{e} Reference 16. ^{f} $E_g \equiv$ the energy of the ground state. ^{g} $\Delta E_{g\to t} \equiv$ the difference between the energies of the first triplet state and the ground state.

Table II. Distribution of Electronic Charge and Spin among the Constituent Atomic Orbitals for Ac and MGl (without $CH_3{}^-$ Groups) in Their Ground and First Triplet^a States (Standard Geometry, STO-3G Basis)^b

atom no.	orbital	G(α = β)	T(α)	T(α − β)	n(T − G)	G(α = β)	T(α)	T(α − β)	n(T − G)	G′^{c}(α = β)	T′(α)	T′(α − β)	n′(T − G)
	1s	0.999	0.999	0.000	0.000	0.999	0.999	0.000	0.000	0.999	0.999	0.000	0.000
	2s	0.934	0.957	0.033	0.013	0.935	0.957	0.033	0.011	0.935	0.948	0.024	0.002
1	2p$_x$	0.882	0.903	0.687	−0.645	0.886	0.908	0.700	−0.656	0.889	0.894	0.023	−0.013
	2p$_y$	0.737	0.767	0.233	−0.173	0.736	0.765	0.225	−0.167	0.736	0.752	0.030	0.002
	2p$_z$	0.552	0.999	0.210	0.684	0.545	0.984	0.190	0.688	0.533	0.878	0.674	0.016
	1s	0.997	0.996	0.000	−0.002	0.997	0.997	0.000	0.000	0.997	0.997	0.000	0.000
	2s	0.566	0.573	0.064	−0.050	0.556	0.569	0.051	−0.025	0.562	0.514	−0.067	−0.029
2	2p$_x$	0.481	0.461	−0.011	−0.029	0.460	0.466	0.000	0.012	0.471	0.436	0.024	−0.046
	2p$_y$	0.434	0.393	−0.013	−0.069	0.438	0.398	−0.021	−0.059	0.451	0.424	−0.043	−0.011
	2p$_z$	0.455	0.988	0.768	0.298	0.461	0.849	0.601	0.175	0.468	0.282	−0.482	0.110
3	1s	0.472	0.463	0.000	−0.018					0.464	0.494	0.042	0.018

^{a} (Number of α-spin electrons − number of β-spin electrons) = 2. ^{b} G(α = β) ≡ the number of electrons with α or β spin in a given atomic orbital in the ground state. T(α) ≡ the number of electrons with α spin in a given atomic orbital in the triplet state. T(α − β) ≡ the number of α-spin electrons in excess of the β-spin electrons in a given atomic orbital in the triplet state. n(T − G) ≡ the total number of electrons in a given atomic orbital in the triplet state less the total number of electrons in that same orbital in the ground state. ^{c} The primes in the columns refer to the primed atomic numbers.
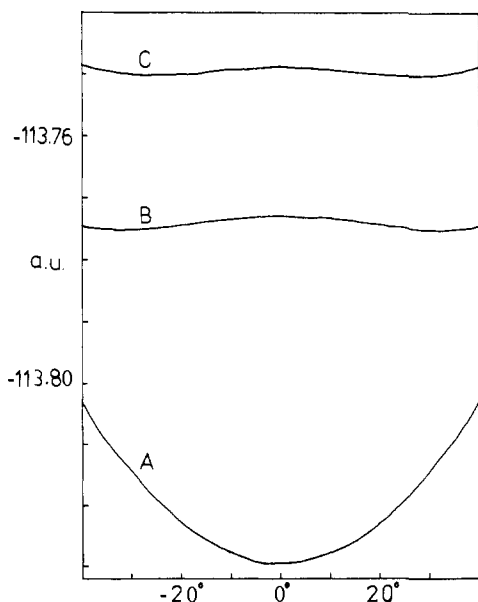

Figure 1. The variation of the total energy (au) of formaldehyde, using the double ζ basis, with the out of plane angle, θ, of the methylene group. Curves A and C are for the ground and first triplet state, respectively, using the ground-state experimental bond lengths and angles.[11] Curve B is for the triplet state using the experimental bond angles and bond lengths for that state[11] (see Results section).

Since MGl, F, and Ac all yield small $\Delta E_{g\to t}$ (UHF) values, are there any similarities in their electronic charge and spin distribution? Table II shows such a distribution among the various atomic orbitals of the carbonyl groups based on a Mulliken population analysis for Ac and MGl in their ground and first triplet excited state. The carbonyl group distribution in Ac is very similar to that in F. The distribution in the methyl groups of Ac and MGl is quite similar. For consistency of comparison the values shown in Table II are those using the STO-3G basis for the molecules in their standard geometry. The following observations may be made based on Table II.

(a) The ground-state populations of various orbitals given in the columns G(α = β), for the same type of atom (e.g., carbonyl O or C) are almost independent of the particular molecule. (b) The α- and (α − β)-spin orbital populations for the corresponding type of atoms in the triplet state, shown in the columns T(α) and T(α − β), are quite similar in F, Ac, and the keto group of MGl. (c) The net electronic charge redistribution among the orbitals upon excitation is shown in the column n(T − G). In F and Ac, the main charge redistribution involves a loss of ~0.7 and ~0.2 e from the O 2p$_x$ and 2p$_y$ orbitals, respectively, and a gain of ~0.7 and ~0.3 e in the 2p$_z$ orbitals of O and the carbonyl C, respectively. In MGl, the redistribution in the keto group is very similar to that in F and Ac. However, the largest rearrangement in its aldyhdic group is an increase of ~0.1 e in the population of the 2p$_z$ orbital of the carbonyl C. The main rearrangement, and hence $^3n\pi^*$
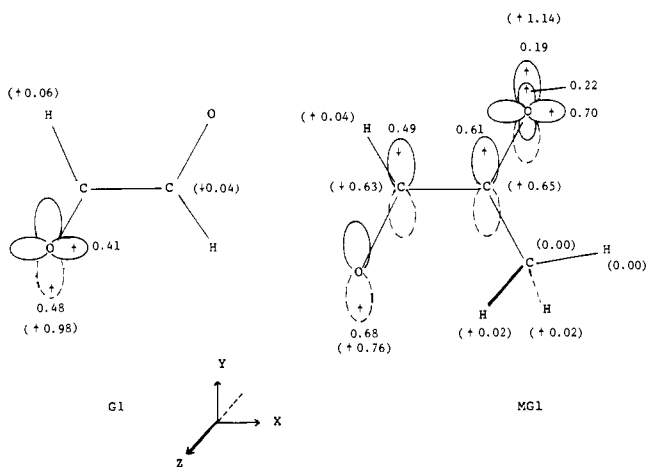
Figure 2. The triplet state net electron spin population of the atomic orbitals in Gl and DMGl using the STO-6G basis and standard geometries. ↑ and ↓ refer to α and β spin, respectively. Orbital populations less than 0.1 are not shown. The total electron spin for the atom is given in parentheses.

excitation, is thus seen to be localized on the ketonic carbonyl group in MGl.

Although the above observations are drawn from an STO-3G basis calculation, they are independent of the basis set. The STO-6G calculation for MGl in its standard geometry yielded almost identical numbers with those in Table II. The double ζ basis results for F using its experimental ground-state geometry[11] yielded the same trends in its various columns as in Table II. In this latter case, the values of $T(\alpha)$, $T(\alpha - \beta)$, and hence $n(T - G)$ of F are affected only very slightly if one uses for the excited-state geometry the experimental one[11] corresponding to the minimum of curve B at $\theta = 32°$ in Figure 1.

Figure 2 depicts the main net orbital spins in the triplet state, $T(\alpha - \beta)$, for MGl as compared to Gl in their standard ground-state geometry using the STO-6G basis. In contrast to Gl, the ketonic O shows an increase of net α-spin density while the aldehydic O shows a decrease. Most of the net unpaired α spin in MGl, 1.83 e, is on the ketonic group leaving the aldehydic group with only 0.17 e. It is interesting to note that the methyl group, whose introduction is responsible for these large differences in spin density between the two carbonyl groups, has itself almost negligible net spin density.

Because of the similarity of the charge redistribution among the various atomic orbitals upon excitation in F, Ac, and the ketonic group of MGl [together with observation (a)] it is reasonable to expect the correlation energy corrections to

$\Delta E_{g \to t}$ (UHF), $\Delta E_{g \to t}$ (corr) [defined as: $\Delta E_{g \to t}$ (exp) $-$ $\Delta E_{g \to t}$ (UHF)], to be of comparable magnitude in them. This is illustrated in STO-3G basis for standard geometries, where the $\Delta E_{g \to t}$ (corr) values (au) are 0.0728, 0.0665, and (0.0563–0.0571) for F, Ac, and MGl, respectively.

Nitzche and Davidson have recently found a broken symmetry SCF solution for the lowest triplet state of Gl which is $\sim$1.5 eV (0.0551 au) lower than the symmetric solution given in Table I (private communication, work in progress),[17] which yields a low $\Delta E_{g \to t}$ (UHF) value similar to that of MGl in Table I. A correlation energy correction comparable to that for MGl above could then bring it into reasonable agreement with experiment.

References and Notes

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