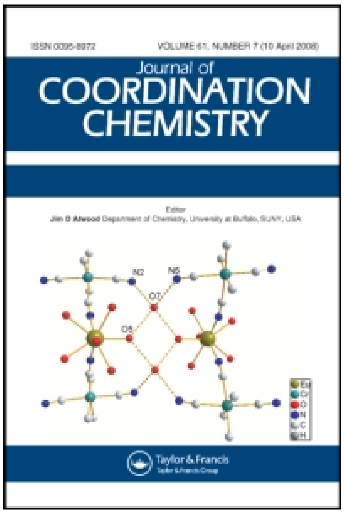

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Theoretical modeling of the isopropylium cation: Exploring nonclassical carbonyl behavior

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In the isopropylium cation, $(CH_3)_2CHO^+$, the carbonyl moiety has been shown experimentally to behave nonclassically. This work examines a variety of theoretical methods that can be used to model the structure and bonding in the isopropylium ion. Comparisons between theoretical and experimental values are made with regard to C–O and C–C bond lengths, ν(CO), and the C–C–O bond angle. The Hartree-Fock and B3LYP (DFT) methods using the 3-21G basis set provide the most accurate overall description of the structure and bonding, as compared to the experimentally derived data. These theoretical models are then used to explore the reasons for the nonclassical behavior of the isopropylium cation. It appears that, upon complexation, the ''s'' character of the C–O bond increases, resulting in a stronger bond.

Keywords: Nonclassical; Carbonyl; Isopropylium; Density functional theory; Hartree-Fock

1. Introduction

Carbon monoxide is the most common, and one of the most important ligands in transition metal chemistry. In classical metal carbonyl complexes, the metal can backbond into the empty π^* orbitals of carbon monoxide, increasing the length and decreasing the strength of the C–O bond. This interaction occurs in addition to the CO ligand using its HOMO (σ) to donate electron density to empty d orbitals on the metal center [1,2]. C–O distances (R(CO)) are longer and ν(CO) values (1.1282 Å and 2143 cm^{-1}, respectively) are lower for metal carbonyls than for the free CO molecule. The problem with using this description as a model for carbonyls is that it fails to account for over 200 metal carbonyl species with average ν(CO) values greater than 2143 cm^{-1} and C–O lengths shorter than 1.1282 Å. Such compounds are typically referred to as ''nonclassical carbonyls,'' although other terms such as ''unusual'' and ''atypical'' are also used [2].

Three types of arguments have been put forth in the literature to explain the phenomenon of nonclassical metal carbonyls: (a) the HOMO of the free CO is antibonding: complexation results in electron donation to this orbital, which weakens the C–O

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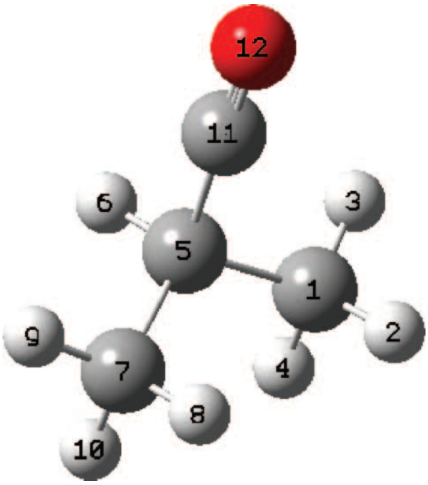

Figure 1. Structure and numbering scheme for the isopropylium cation.

bond; (b) the nonclassical properties of some carbonyls are due to electrostatic effects: when the CO ligand bonds to the rest of the complex, the approaching fragment attracts electrons from the oxygen toward the carbon end of CO. This redistributes the partial charges in the carbonyl moiety, thus making the CO bond less polar, more covalent, and therefore stronger; (c) when the CO bonds to the rest of the complex, the carbonyl carbon rehybridizes: since the new hybrid orbital that is used to bond with the oxygen atom has greater "s" character than in the free carbonyl, it leads to a shorter bond and a higher vibrational C–O frequency [3–8].

The isopropylium cation, $(CH_3)_2CHO^+$ (figure 1), is an acylium ion that is an important intermediate in a number of organic reactions. Since its carbonyl group behaves nonclassically, it has been isolated and studied experimentally [1,2,3,9]. Because of the experimental data available, the isopropylium cation provides an opportunity to use theoretical modeling to examine the phenomena that make it nonclassical. This work focuses first on choosing the most appropriate theoretical model to describe the isopropylium cation, then using it to investigate the unexpected properties of this species.

1.1. *Details of calculations*

The GAUSSIAN suite of programs was used for all calculations [10]. Calculations were carried out at three levels of theory using Hartree-Fock Theory [11], Density Functional Theory (using Becke's three parameter exchange-correlation hybrid functionals [12] and the correlation functionals of Lee, Yang, and Parr [13] and Perdew and Wang [14–18]), and second order Møller-Plesset Perturbation Theory [19,20]. Eight basis sets were used with each method: STO-3G [21,22], 3-21G [23–25], 3-21+G**[26,27], 6-31G, 6-31G(d,p) [28–30], 6-311G, 6-311G(d,p) [31,32] and cc-pVQZ [33–35].

For the first set of calculations, a single input file representing the initial structure of the isopropylium cation was generated with the GaussView program [36]. This structure was then optimized and frequency calculations were performed [37,38] using each method and basis set. A stable wavefunction was obtained for the whole molecule plus the individual fragments (CO and $(CH_3)_2^+$) using the best methods. Partial charges on individual atoms were calculated using both a Mulliken [39] population analysis and a Natural Bond Orbital [40–47] analysis.

Geometry optimization calculations at the MP2 level of theory with a cc-pVQZ basis set were too large to perform either on a Pentium IV Dell PC or on EMU's Sun Sparc mainframe computer. In general, the cc-pVQZ basis set required large amounts of memory and generated results that were not better than those from other basis sets or methods. Consequently, this basis set was not used for frequency calculations.

2. Results and discussion

2.1. *Determining the best theoretical model*

With the goal of finding the closest match between theoretical modeling and experimental data for the isopropylium cation, five variables were considered: bond lengths for the C–O bond (atoms 11 and 12 in figure 1) and two C–C bonds (C_{11}–C_5 and C_5–C_1) were examined, since experimental data are available for these bonds (1.101 Å for C–O, 1.458 Å for C_{11}–C_5, and 1.538 Å for C_5–C_1) [1,2]. Experimentally, the bond length for C_5–C_7 is found to be equal to that of C_5–C_1 [1] and therefore such comparisons would be redundant. Empirical information is also available for ν(CO) (2257 cm^{-1}) and the C–C–O (C_5–C_{11}–O) bond angle (177.4°) [1,2], so these measurements were also examined. A comparison between experimental and calculated bond lengths and vibrational frequencies is shown in tables 1 and 2, respectively.

The data indicate that, when using the HF method, the 6-311G basis set produces the best C–O bond length, the 3-21G basis set produces the best C_{11}–C_5 bond length, and the cc-pVQZ basis set produces the best C_5–C_1 bond length. When utilizing B3LYP, the 6-311G basis set with polarized functions produces the best C–O bond length and cc-pVQZ the best C_5–C_1 bond length. The 6-311G basis set gives the best results for the C_{11}–C_5 bond length. The results of the B3PW91 method demonstrate that the best C–O bond length was produced by the 6-31G basis set, which also produced the best C_{11}–C_5 bond length. It was the cc-pVQZ basis set that produced the best C_5–C_1 bond length for B3PW91. Finally, when the MP2 method was employed, the 6-311G basis set produced both the best C–O bond length and the best C_5–C_1 bond length. The best C_{11}–C_5 bond length was produced by the 3-21G basis set. Of the bond lengths shown in table 1, the most important one for the purpose of this work is the C–O bond length. Based on this variable only, the best method/basis set combination is HF/6-311G. This combination also produces very good results for the other two bond lengths.

Table 2 shows that, in terms of reproducing vibrational frequencies, the 3-21G basis set gives the best results for all methods and adding polarized functions increases the accuracy. The best method is again Hartree-Fock, although B3LYP at the 3-21G level is also noteworthy. In summary, the 3-21G basis set, with either HF or B3LYP, gives the best overall results for bond lengths and frequencies when compared with experimental results. It is interesting to note that the most accurate C–O bond length (1.108 Å) is found with the 6-311G basis set, while the vibrational frequency that is

Table 1. A comparison of C–O and C–C bond lengths by method and basis set. The experimental data is based on the crystal structure of $[(CH_3)_2CHCO][SbCl_6]$ [2,3]. Smallest deviations from experiment are highlighted in bold. NC = not calculated.

Method	Basis set	C–O (Å)	Difference from Exp. (Å)	C_{11}–C_5 (Å)	Difference from Exp. (Å)	C_5–C_1 (Å)	Difference from Exp. (Å)
HF	STO-3G	1.141	0.040	1.553	0.095	1.555	0.017
	3-21G	1.113	0.012	1.458	0.000	1.564	0.026
	3-21+G**	1.112	0.011	NC		NC	
	6-31G	1.113	0.012	1.473	0.015	1.553	0.015
	6-31++G(2d,2p)	1.090	0.011	NC		NC	
	6-311G	1.108	0.007	1.472	0.014	1.550	0.012
	6-311++G(2d,2p)	1.088	0.013	NC		NC	
	cc-pVQZ	1.087	−0.014	1.473	0.015	1.543	0.005
B3LYP	STO-3G	1.188	0.087	1.515	0.057	1.581	0.043
	3-21G	1.143	0.042	1.427	−0.031	1.578	0.040
	3-21+G**	1.142	0.041	NC		NC	
	6-31G	1.145	0.044	1.438	−0.020	1.572	0.034
	6-31++G(2d,2p)	1.121	0.020	NC		NC	
	6-311G	1.139	0.038	1.434	−0.024	1.569	0.031
	cc-pVQZ	1.115	0.014	1.432	−0.026	1.556	0.018
B3PW91	STO-3G	1.187	0.086	1.504	0.046	1.573	0.035
	3-21G	1.143	0.042	1.423	−0.035	1.571	0.033
	6-31G	1.114	0.013	1.433	−0.025	1.564	0.026
	6-311G	1.138	0.037	1.429	−0.029	1.561	0.023
	cc-pVQZ	1.115	0.014	1.427	−0.031	1.549	0.011
MP2	STO-3G	1.204	0.103	1.555	0.097	1.574	0.036
	3-21G	1.157	0.056	1.454	−0.004	1.574	0.036
	6-31G	1.164	0.063	1.468	0.010	1.570	0.032
	6-311G	1.158	0.057	1.463	0.005	1.564	0.026

nearest the experimental value ($2227\,cm^{-1}$ *vs* $2257\,cm^{-1}$) is achieved with the 3-21G basis set.

As indicated, C_5–C_{11}–O bond angles were also evaluated and the bond angle information is listed in table 3. The B3LYP method in combination with the STO-3G basis set produced an angle within 0.117° of the experimentally obtained angle of 177.4°. This combination, however, had comparably poor measures for the other variables. The STO-3G set also worked well in determining the bond angle when using B3PW91 (177.650°). All HF basis sets produced C_5–C_{11}–O bond angles within two degrees of experimental data. In general, both Density Functional Theory methods and second order Møller-Plesset Perturbation Theory found the best bond angles. The best C_5–C_{11}–O bond angle (179.085°, with a deviation of 1.685° from the experimental value) in the HF data is the one given when using the 3-21G basis set. Again, B3LYP does best when coupled with the 3-21G basis set. The bond angle from this method deviates only 1.016° from experiment. It would seem that amongst HF basis sets, 3-21G is the best one for all variables. Even for the C–O bond length, the loss in accuracy from the 6-311G set is negligible (0.012 Å *vs* 0.007 Å, respectively).

To select the most appropriate theoretical models for the isopropylium cation, the key variables were compared amongst methods. The Hartree-Fock method coupled with the 3-21G basis set and Density Functional Theory at the B3LYP/3-21G level provide the most accurate computational representation.

Table 2. A comparison of vibrational frequencies by method and basis set. The experimental data is based on the crystal structure of [$(CH_3)_2CHCO$][$SbCl_6$] [2,3].

	ν(CO) cm^{-1}	Difference from experimental value (cm^{-1})
HF		
STO-3G	2557	300
3-21G	2227	−30
3-21+G**	2453	−196
6-31G	2197	−60
6-31++G(2d,2p)	2582	−325
6-311G	2148	−109
6-311++G(2d,2p)	2577	−319
B3LYP		
STO-3G	2523	266
3-21G	2193	−64
3-21+G**	2216	41
6-31G	2176	−81
6-31++G(2d,2p)	2314	57
6-311G	2114	−143
B3PW91		
STO-3G	2532	275
3-21G	2198	−59
6-31G	2179	−78
6-311G	2122	−135
MP2		
STO-3G	2514	257
3-21G	2203	−54
6-31G	2202	−55
6-311G	3239	982

2.2. *Analysis of bonding in the isopropylium cation*

Having determined the best computational models, we now examine the bonding characteristics of the isopropylium cation in order to explain its nonclassical behavior. The three hypotheses detailed in the introduction were examined in order.

First, the three-dimensional surface of the Highest Occupied Molecular Orbital (HOMO) of the carbonyl ligand is produced using both methods, HF/3-21G and B3LYP/3-21G. The surface is shown in figure 2; clearly, there is no node in the internuclear region, thus leading to the conclusion that this is not an antibonding orbital.

The second possible explanation for the unexpected behavior of this molecule is electrostatic effects. Table 4 compares the partial charges on two carbons (C_{11} and C_5) and oxygen, both in the whole molecule and in the separated fragments (CO and $CH(CH_3)_2^+$). The data indicate that the charge on C_{11} (on the carbonyl ligand) is much more positive in the whole molecule than in the carbonyl fragment. When the molecule is intact, electrons from C_{11} flow to C_5 (and the rest of the alkyl group), increasing the charge of C_{11} from about 0.05 to about 1.0. Consequently, the C–O bond is found to be more polar in the whole molecule than in the CO fragment. This contradicts the hypothesis that electrostatic interactions make the CO bond less polar and more covalent upon complexation.

Finally, the character of the hybrid orbital produced during complexation is considered. The percent "s" character in the sigma bond is shown in table 5. When CO is a free ligand, the sigma bond is approximately 22–25% "s". When this is compared

Table 3. A comparison of C_5–C_{11}–O bond angles by method and basis set. The experimental data is based on the crystal structure of $[(CH_3)_2CHCO][SbCl_6]$ [2,3].

	C_5–C_{11}–O angle (°)	Difference from experimental value (°)
HF		
STO-3G	179.314	1.914
3-21G	179.085	1.685
3-21+G**	179.222	1.822
6-31G	179.189	1.789
6-31++G(2d,2p)	179.239	1.839
6-311G	179.275	1.875
6-311++G(2d,2p)	179.241	1.841
cc-pVQZ	179.328	1.928
B3LYP		
STO-3G	177.517	0.117
3-21G	178.416	1.016
3-21+G**	178.632	1.232
6-31G	179.402	2.002
6-31++G(2d,2p)	178.215	0.815
6-311G	178.214	0.814
cc-pVQZ	178.460	1.060
B3PW91		
STO-3G	177.650	0.250
3-21G	178.484	1.084
6-31G	178.227	0.827
6-311G	178.370	0.970
cc-pVQZ	178.608	1.208
MP2		
STO-3G	178.332	0.932
3-21G	178.733	1.333
6-31G	178.274	0.874
6-311G	178.292	0.892

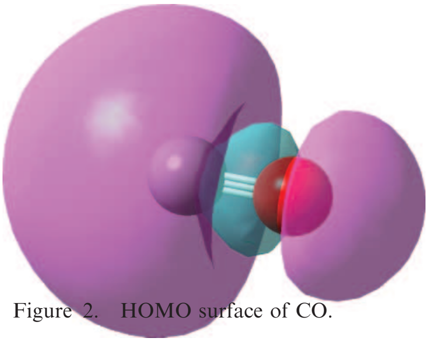

Figure 2. HOMO surface of CO.

to the 38% "s" character of the sigma bond after the CO has bonded to $CH(CH_3)_2^+$, it follows that there is significant increase of the "s" character. This then, supports the third hypothesis.

3. Conclusions

While each method reproduces experimental values well, some methods fare better than others. Ignoring the C–C bond data and weighting the ν(CO) and C–O bond length

Table 4. A comparison of partial charges on selected atoms. The fragments are CO and $CH(CH_3)_2^+$.

	Fragments		Whole molecule	
Atom (Method)	NBO	Mulliken	NBO	Mulliken
C_5 (HF/3-21G)	−0.481	−0.541	0.456	0.097
C_5 (B3LYP/3-21G)	−0.481	−0.470	0.312	0.052
C_{11} (HF/3-21G)	0.553	0.334	1.079	0.895
C_{11} (B3LYP/3-21G)	0.436	0.039	0.928	0.765
O (HF/3-21G)	−0.553	−0.334	−0.290	−0.322
O (B3LYP/3-21G)	−0.436	−0.039	−0.180	−0.228

Table 5. Percent "s" character in CO sigma bond.

Method	CO ligand	$(CH_3)_2CHO^+$
HF/3-21G	24.98	37.94
B3LYP/3-21G	21.62	37.58

Table 6. A comparison of HF and B3LYP calculations using the 3-21G basis set.

Variable	HF 3-21G	Difference from exp.	B3LYP	Difference from exp.
C–O	1.113 Å	0.012 Å	1.143 Å	0.042 Å
ν(CO)	2227 cm^{-1}	−30 cm^{-1}	2243 cm^{-1}	14 cm^{-1}
C_5–C_{11}–O	179.085°	1.685°	178.416°	1.016°

more than the C_5–C_{11}–O bond angle, Hartree-Fock and B3LYP emerge as the best methods. The C–O bond length of 1.108 Å derived with the 6-311G basis set is only slightly longer than that of the 3-21G set. Coupled with the relatively accurate ν(CO) of 2227 cm^{-1} (HF) and 2193 cm^{-1} (B3LYP) and a C_5–C_{11}–O bond angle deviation of 1.685° (HF) and 1.016° (B3LYP), the 3-21G basis set is revealed as the best choice. A summary of results from the best calculations is given in table 6.

With two acceptable theoretical models chosen, the character of the CO sigma bond is the clearest choice for explaining nonclassical characteristics. The CO HOMO is clearly bonding, not antibonding. Polarity of the CO bond actually increases, rather than decrease, as a result of bonding with the $CH(CH_3)_2^+$, negating the electrostatic effect explanation. Instead, we see that the percent "s" of the CO sigma bond significantly increases when the hybrid orbital is formed in complexation. A greater percent of "s" character (rather than "p") helps explain the increased bond strength in the CO.

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