A Study of the Electronic Structures of BF_3 Complexes with Carbonyl Compounds by ab Initio MO methods

Benjamin W. Gung* and Mark A. Wolf

Department of Chemistry, Miami University, Oxford, Ohio 45056

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The *syn*-$CH_3CHO{\cdot}BF_3$ complex is only 1.22 kcal mol^{-1} less stable than the corresponding *anti*-$CH_3CHO{\cdot}BF_3$ complex at the MP2/6-31G* level of theory. The corresponding difference in *syn*- and *anti*-$PhCHO{\cdot}BF_3$ complexes is 5.31 kcal mol^{-1}. The calculated C—C=O (129°) and C—O—B (156°) angles for *syn*-$PhCHO{\cdot}BF_3$ complexes have a much greater deviation from the standard geometries of a sp2 orbital than that (123.9° and 125.4°) calculated for *syn*-$CH_3CHO{\cdot}BF_3$ complexes. A hydrogen-bonding type of attractive interaction between F and H is identified in the syn complexs of acetaldehyde and acetone.

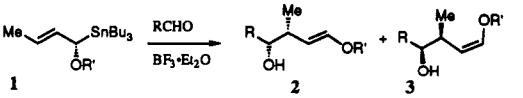
Introduction

Lewis acid catalyzed reactions have become an indispensable part of modern synthetic chemistry, especially in the art of acyclic stereocontrol.[1] The properties of Lewis acid complexes with carbonyl compounds play a major role in the outcome of the carbon–carbon bond forming process and sometimes dictate the stereochemistry of the products.[2] For example, it has been shown that by employing either BF_3 or $MgBr_2$, one can produce homoallylic alcohols with either erythro or threo stereochemistry, respectively.[3] Therefore, it is imperative to understand the properties of Lewis acid complexes with carbonyl compounds.

It has been shown by low-temperature NMR that the complexes of titanium tetrachloride with β-alkoxy aldehydes have a rigid six-membered-ring structure.[4] Stable complexes of BF_3·ketone have been studied extensively by NMR.[5] A slow interconversion between the syn and anti configurations has been observed by the variable-temperature NMR technique. Single crystals have also been obtained for a few Lewis acid complexes, and X-ray crystallography has been used to identify structural details. It is known that the complex of (*p-tert*-butylbenzaldehyde)$_2$·$SnCl_4$ has a cis arrangement of the two ligands,[6] and the complex of $PhCHO{\cdot}BF_3$ has the phenyl group anti to the BF_3.[7]

Due to rapid developments in computational chemistry, theoretical studies of relatively large organic species have now become practical for laboratory practitioners.[8] Theoretical studies of Lewis acid (LA) complexes of carbonyl compounds are in general agreement with regard to the geometries of these species.[9] For uncharged complexes, the preferred C–O–LA bond angles are bent (≈ 120°), and for charged species, linear (≈180°) structures are more stable.[9] Wiberg and LePage have studied the rotational barriers in aldehyde- and ketone-coordinated neutral Lewis acid.[9b] The C–O–LA angles in these complexes varied from 122° to 135° in boron complexes. Steric effects at α-carbons can be relieved by opening the C–O–LA angle at small energetic cost. It has been shown that the HOMO and LUMO of the carbonyl compounds have significantly decreased energies when complexed with Lewis acid, which accounts for the increased reactivity of the carbonyl compounds.[10]

However, despite the broad range of information available, until now, no difference between the BF_3 complexes of aromatic aldehydes and that of aliphatic aldehydes has been identified. To study these complexes experimentally has been problematic. Recent NMR studies[6] have shown that under conditions at which aromatic aldehydes form stable complexes with BF_3, aliphatic aldehydes either remain free or form trimers, which apparently prevents further study of these species. Theoretical study by Wiberg et al. has shown that a few percent of syn complexes of propanal·BF_3 is possible in solution. Indeed, our recent study of the reactions with chiral allylstannanes and aldehydes catalyzed by $BF_3{\cdot}Et_2O$ indicated the possibility that aliphatic aldehydes–BF_3 may exist in both anti and syn configurations, or as a rapid equilibrium mixture.[11] Our results show a dramatic reversal of diastereofacial selectivity when the starting substrates were changed from aliphatic aldehydes to aromatic aldehydes, eq 1.[11]



(1)

1		2	3
R'= (methyloxy)bzl		syn-(E)	syn-(Z)
R = Aryl (C_6H_5, p-Cl-C_6H_4, etc.)		<5	>95
= Alkyl (cyclohexyl, n-hexyl, etc.)		80	20

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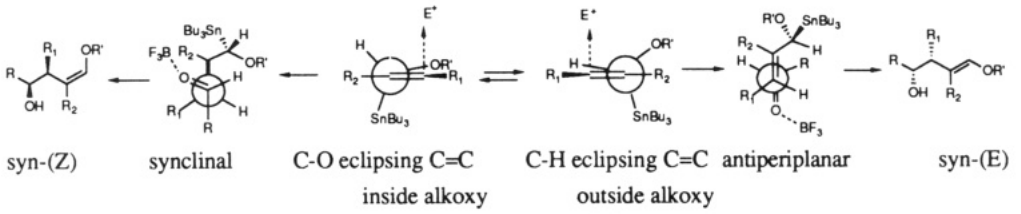

Figure 1. Attack of the electrophile on C–H eclipsed (outside alkoxy) and C–O eclipsed (inside alkoxy) conformers leads to (*E*)– and (*Z*)–enol ethers, respectively.

To rationalize our results, certain structural effects other than steric have to be operating in order to produce the dramatic reversal in π facial selectivity for the two types of aldehydes. Based solely on steric interactions suggested by Yamamoto,[12] both aliphatic and aromatic aldehydes should prefer the antiperiplanar arrangement (right-hand side of Figure 1). However, the steric bulkiness of a phenyl group is comparable to that of a cyclohexyl group, yet they gave totally different stereochemical consequences. Since steric effects cannot explain the difference, we have attributed the reversal of π facial selection to the strength of the aldehyde–BF_3 complexes, Figure 1.[11b] In particular, the strong anti complexation of aromatic aldehydes with BF_3 renders the synclinal transition state more favorable (this is true only when R_2 = H) (Figure 1, left-hand side of the equilibrium). It would be sterically unfavorable if an anti complex approaches the allylstannane through the antiperiplanar arrangement, because the BF_3 would be directly over R_1. This, combined with the "inside alkoxy" effect,[13] produces the highly selective process favoring the (Z) enol ether product. We reasoned that, like reactive intermediates, the elusive aliphatic aldehydes–BF_3 complexes would be best studied by the modern computational chemistry. Our preliminary theoretical study[11c] has corroborated the results from the reactions; i.e., there is a difference in the strength of complexation between these two types of aldehydes.

In this report, we describe the full details of the ab initio study of the BF_3 complexes of acetaldehdye and benzaldehyde at a higher level of theory (MP2/6-31G*/3-21G). In addition, acetone–BF_3 complexes have also been studied and compared with the results of the aldehydes. All possible stable conformations of each complex have been considered. The structural features of each complex, including the differences in complexation energies, bond lengths, and bond angles, are presented and discussed in terms of molecular orbital theory.

Computational Methods

Ab initio calculations are carried out by the GAUSSIAN88 and -90 programs[14] implemented on the Cray Y-MP/8 supercomputer.

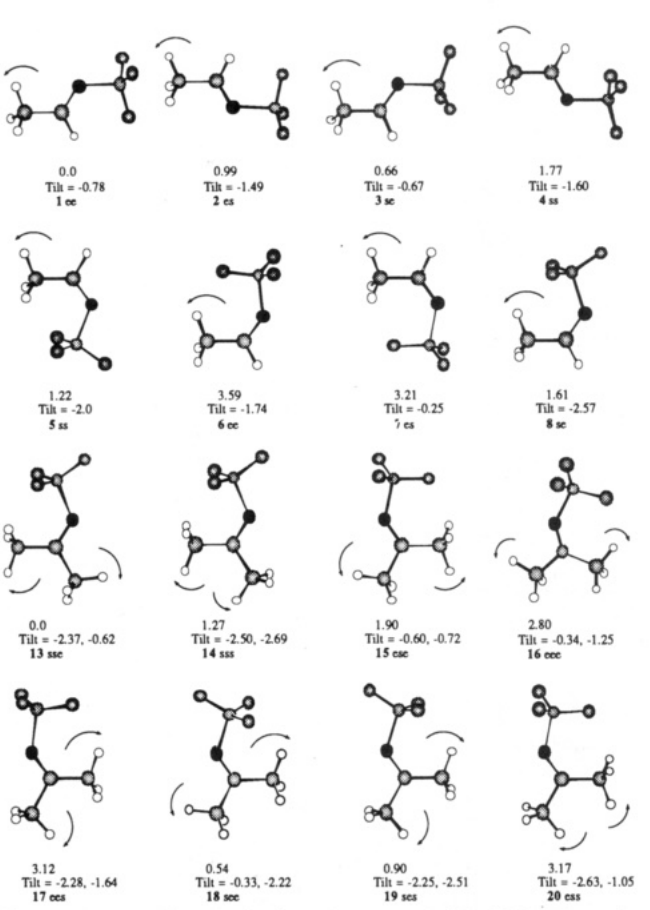

Figure 2. 3-21G optimized conformers of $CH_3CHO{\cdot}BF_3$ and $(CH_3)_2C{=}O{\cdot}BF_3$. Relative energy (kcal mol^{-1}, MP2/6-31G*/3-21G) is given below the structure. Methyl tilt angle is also shown. Tilt direction is indicated by the arrow at the methyl. The tilt angle is calculated from the data in Table II according to the equation 3 cos (α_1 + 2α) = 4 cos α_2–cos α_1 where the definition of α_1, α_2, and the tilt angle α can be found in ref 18. A methyl tilt of –0.15 is reported for the eclipsed CH_3CHO.[19a]

Structural optimizations using the 3-21G split-valence basis set were found to give reasonable B–O bond lengths. For the complexes of acetone/BF_3 and $CH_3CHO{\cdot}BF_3$, all parameters were fully optimized. For the complexes of $PhCHO{\cdot}BF_3$, the phenyl ring was constrained as planar, and the carbon–carbon bonds within the phenyl ring were constrained to equal length but not fixed length. This approximation was required to achieve reasonable computational efficiency, but may reduce the accuracy of the calculated structural parameters. However, since both syn and anti $PhCHO{\cdot}BF_3$ complexes are subjected to the same restriction, the error should cancel out to a certain extent. The readers are urged to view the results with caution since this is the first time that the GAUSSIAN programs are applied to such a large structure (12 heavy atoms). Harmonic features are calculated for each conformer. The lowest energy conformations have all possible frequencies, which is an indication of a true minimum on the 3-21G potential surface. Single-point calculations are performed for all complexes with the 6-31G* polarization basis set using the 3-21G-optimized structures. Moller–Plesset electron correlations (MP2/6-31G*) are performed for the complexes of $PhCHO{\cdot}BF_3$

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Table I. GAUSSIAN88 Computed Energies for RCHO·BF_3 Complexes

entry	conformer[a]	abs energy (rel energy)[b] 3-21G			complex energy[c]	
		3-21G	6-31G*	MP2/6-31G*	HF/6-31G*	MP2/6-31G*
	anti-$CH_3CHO·BF_3$					
1	1 ee	−473.568 045 8 (0.0)	−476.122 979 6 (0.0)	−477.143 585 8 (0.0)	−9.35	−11.91
2	2 es	−473.566 880 2 (0.73)	−476.121 485 6 (0.94)	−477.142 001 9 (0.99)	−8.42	−10.91
3	3 se	−473.563 556 0 (2.82)	−476.122 430 6 (0.35)	−477.142 534 4 (0.66)	−9.00	−11.25
4	4 ss	−473.562 222 0 (3.65)	−476.120 827 8 (1.35)	−477.140 762 5 (1.77)	−8.00	−10.13
	syn-$CH_3CHO·BF_3$					
5	5 ss	−473.566 441 4 (1.01)	−476.119 650 3 (2.09)	−477.141 640 5 (1.22)	−7.26	−10.69
6	6 ee	−473.564 753 0 (2.07)	−476.116 869 6 (3.83)	−477.137 872 1 (3.59)	−5.52	−8.32
7	7 es	−473.564 506 9 (2.22)	−476.117 188 3 (3.63)	−477.138 469 7 (3.21)	−5.72	−8.70
8	8 se	−473.563 810 6 (2.66)	−476.119 955 6 (1.90)	−477.141 015 5 (1.61)	−7.45	−10.29
	anti-$PhCHO·BF_3$					
9	9 e	−663.026 771 6 (0.0)	−666.642 710 0 (0.0)	−668.282 847 5 (0.0)	−10.85	−13.02
10	10 s	−663.022 472 2 (3.29)	−666.642 139 6 (0.36)	−668.281 539 0 (0.82)	−10.49	−12.20
	syn-$PhCHO·BF_3$					
11	11 e	−663.109 751 4 (4.41)	−666.629 125 7 (8.52)	−668.269 813 6 (8.18)	−2.33	−4.85
12	12 s	−663.018 918 7 (4.93)	−666.633 654 9 (5.68)	−668.274 382 3 (5.31)	−5.17	−7.71
	$(CH_3)_2CO·BF_3$					
13	13 sse	−512.403 777 5 (0.0)	−515.170 819 7 (0.0)		−10.29	
14	14 sss	−512.402 097 2 (1.05)	−515.168 795 4 (1.27)		−9.02	
15	15 ese	−512.401 168 8 (1.64)	−515.167 788 2 (1.90)		8.39	
16	16 eee	−512.400 885 8 (1.81)	−515.166 352 5 (2.80)		−7.49	
17	17 ees	−512.400 447 8 (2.09)	−515.165 849 8 (3.12)		−7.17	
18	18 see	−512.400 168 7 (2.26)	−515.169 963 8 (0.54)		−9.75	
19	19 ses	−512.399 638 7 (2.60)	−515.169 388 8 (0.90)		−9.39	
20	20 ess	−512.399 535 7 (2.66)	−515.165 763 7 (3.17)		−7.12	
21	CH_3CHO e	−152.055 248 6	−152.915 036 6	−153.346 026 8		
22	PhCHO e	−341.511 314 2	−343.432 381 2	−344.483 505 6		
23	CH_3COCH_3 ee	−190.877 221 2	−191.961 387 1			
24	BF_3	−321.465 844 9	−323.193 035 6	−323.788 585 8		

[a] For RCHO·BF_3 complexes: ee = both B–F and C–H bonds eclipsing C=O; es = B–F eclipsing C=O and C–H staggering C=O; se = B–F staggering C=O and C–H eclipsing C=O; ss = both B–F and C–H bonds staggering C=O. For acetone/BF3 complexes: sse = B–F staggering C=O, C–H (of methyl syn to BF_3) staggering C=O, and C–H (of methyl anti to BF_3) eclipsing C=O, etc. See Figure 2 for graphics. [b] Absolute energies are in atomic units, and relative energies are in kcal mol^{-1}. The complexes of $CH_3CHO·BF_3$ and the complexes of $PhCHO·BF_3$ are compared separately. [c] Complex formation energy = E_{total} (RCHO·BF_3) − E_{total} (RCHO) − E_{total} (BF_3) without correction for zero point energy differences.

and $CH_3CHO·BF_3$. Approximately 1–2 h of CPU time is required for a single-point calculation for the $PhCHO·BF_3$ complexes at the MP2/6-31G* level.

Results and Discussion

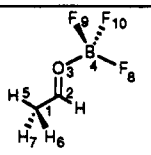
The computed energies for all possible stable conformations of each complex are shown in Table I. The es conformer signifies that the B–F bond *eclipses* C=O and the C–H *staggers* C=O, Figure 2. Despite the differences in energy predicted by different basis set, the small energy gap between syn and anti complexes of $CH_3CHO·BF_3$ is evident at all levels of theory. Remarkably, the syn complex **5** is only 1.22 kcal mol^{-1} less stable than the most stable anti complex **1** at the MP2/6-31G* level. If one assumes that the zero-point energy difference between complexes **1** and **5** is negligible, the calculated relative energy corresponds to approximately 12% of syn complex at equilibrium at room temperature.

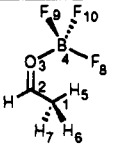
For the complexes of $PhCHO·BF_3$, there are two stable conformations for either syn or anti configuration, i.e., the B–F bond eclipsing or staggering the C=O bond. A large difference in energy between syn and anti configurations are computed at all levels of theory that were employed. At the MP2/6-31G* level of theory, the *anti*-$PhCHO·BF_3$ complex is 5.31 kcal mol^{-1} more stable than its corresponding syn isomer. This is in sharp contrast to the mere 1.22 kcal mol^{-1} difference between the most stable anti $CH_3CHO·BF_3$ and its corresponding syn isomer. Furthermore, the complex formation energies of *anti*-$PhCHO·BF_3$ are greater than that of the *anti*-$CH_3CHO·BF_3$ (entries 1–4 and 9–10, Table I). Experimentally, while *anti*-$PhCHO·BF_3$ has been prepared and isolated as a crystalline complex,[7] no direct evidence has been documented for the existence of RCHO·BF_3 (R = alkyl). In light of these facts, the differences in energy calculated for the various boron trifluoride–aldehyde complexes can be interpreted in terms of two possibilities. First, while the $PhCHO·BF_3$ produces anti complex only, the $CH_3CHO·BF_3$ could form a mixture of both syn and anti isomers. Alternatively, while PhCHO and BF_3 generate stable complexes, the CH_3CHO may yield only a dynamic equilibrium mixture with BF_3. In other words, only weak complexation occur between aliphatic aldehydes and boron trifluoride. This is consistent with Denmark's NMR investigation.[6]

For acetone·BF_3 complex, there are no syn/anti isomers, but there are eight possible conformations with regard to the rotational isomers of BF_3 and two CH_3 groups. In general, the $(CH_3)_2C=O·BF_3$ complexes also have a larger complex formation energy than the complexes of $CH_3CHO·BF_3$. By different energy gaps, both basis sets predict that the sse conformation is the most stable isomer among the eight conformations, and the ess is the least stable form (entries 13–20, Table I). As will be discussed later, these subtle energy differences among conformers reveal a coulombic attractive interaction between F and H in the doubly staggered forms.

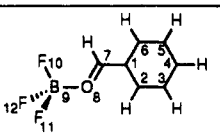
By the examination of the calculated structures, it becomes clear why such a difference exists between the BF_3 complexes of aromatic and aliphatic aldehydes. In the next a few paragraphs, the more obvious effects, such as resonance and steric repulsion, which accounts for major part of the difference, will be discussed first. It will then be followed by a discussion of the less obvious electronic effects, such as hyperconjugation and hydrogen bonding which, we think, are partially responsible for the energy differences observed.

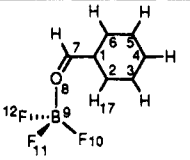
Table II. Selected Structural Parameters in BF_3 Complexes (3-21G)



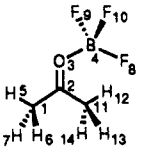


	conformation				conformation			
unit	1 ee	2 es	3 se	4 ss	5 ss	6 ee	7 es	8 se
r_{O-B}	1.652	1.649	1.662	1.660	1.646	1.658	1.648	1.655
$r_{5,8}$					2.37	2.07	2.43	2.45
∠1,2,3	122.16	121.06	122.46	121.35	123.91	126.99	126.10	126.17
∠2,3,4	123.51	123.47	120.92	121.05	125.36	136.08	132.35	126.95





	conformation				conformation	
unit	9 e	10 s	BF_3	PhCHO	11 e	12 s
r_{O-B}	1.626	1.635			1.647	1.628
$r_{C=O}$	1.242	1.240		1.211	1.235	1.239
$r_{7,1}$	1.437	1.439		1.475	1.444	1.445
$r_{10,17}$	4.411	4.73			1.952	2.259
$r_{6,1}$	1.387	1.387		1.384	1.387	1.386
∠9,8,7	123.16	121.02			154.39	139.45



	conformation							
unit	13 sse	14 sss	15 ese	16[a] ese	17 ees	18 see	19 ses	12 ess
r_{O-B}	1.626	1.622	1.630	1.639	1.635	1.636	1.633	1.26

[a] The dihedral angle H–C–C–O was constrained. Otherwise it collapses to conformer 15.

The average calculated B–O bond length of the acetaldehyde complexes is about 1.65 Å, Table II. On the other hand, the average calculated B–O bond length of the acetone complexes is about 1.63 Å, i.e., 0.02 Å shorter. The *anti*-PhCHO·BF_3 is the only aldehyde complex whose B–O distance is comparable to those of the acetone complexes. This difference in B–O bond lengths is closely related to the ability of the substituent at the carbonyl carbon to stabilize the developing positive charge. The complexes of PhCHO·BF_3 are stabilized by resonance effect, and the complexes of $(Me)_2C{=}O{\cdot}BF_3$ are stabilized by hyperconjugation. The α C—C(=O) bond of these complexes all decreased in length with the PhCHO·BF_3 changing most (*anti*-PhCHO·BF_3, −0.038 Å; *syn*-PhCHO·BF_3, −0.031 Å), Table II. The dramatic shortening of the α bond of the benzaldehyde complexes is consistent with a substantial π bonding between the carbonyl carbon and the phenyl ring. The shortening of the α C—C(=O) bond(s) in acetone complexes can be explained by the hyperconjugation of the π(Me) and the $\pi^*_{C=O}$ orbitals. The complexes of $CH_3CHO{\cdot}BF_3$ do not enjoy the same degree of stabilization. Analogy can be made by comparing the stabilities of the BF_3 complexes to that of the carbocations. For BF_3 complexes, the order of stability is: aromatic aldehyde > acetone > aliphatic aldehyde, which parallels the order of stability for the carbocations: benzylic > tertiary > secondary.

For the *syn*-PhCHO·BF_3 complexes, although the resonance stabilization ability of the phenyl group delocalizes the developing positive charge, the steric repulsion between the F atoms and the *o*-phenyl H have caused the overall complexation process to be less favorable. The interatomic distances between the F and the ortho phenyl H are 1.95 and 2.26 Å for eclipsed and staggered forms respectively, Table II. These distances are well below the sum (2.67 Å) of the empirical van der Waals radius for F and H.[23] As a result, the C–O–B angles (139° and 156° in the staggered and eclipsed *syn*-PhCHO·BF_3 complex, respectively) seriously deviate from the configuration (120°) of a sp2 orbital. Consequently, the complex is destabilized. On the other hand, the C–O–B angles for *syn*-$CH_3CHO{\cdot}BF_3$ are 127° and 136° in the staggered and eclipsed forms, respectively, which only slightly deviate from the normals. These differences certainly account for major part of the energy differences calculated.

The more subtle stereochemical effects can be found from the differences in the relative energies among each series. There is a preference for the B–F and C–H bonds eclipsing C=O as indicated by the stability order of the *anti*-$CH_3CHO{\cdot}BF_3$ complexes (ee > se > se > ss) where no steric effects or dipole-induced dipole interactions (such effects affect the syn isomers) are involved. This preference is about 0.7 kcal mol^{-1} for B–F and 1.0 kcal mol^{-1} for C–H bonds as computed by the MP2/6-31G* for the differences between ee and se, es and ss conformers of *anti*-$CH_3CHO{\cdot}BF_3$ (entries 1–4, Table I) and between e and s conformers of *anti*-PhCHO·BF_3 (entries 9–10, Table I).

The preference for B–F eclipsing C=O is controlled by two electronic effects. Torsional strain and dipole–dipole repulsion are present in conformations where C–F linkage is eclipsed with the lone pair on oxygen. On the other

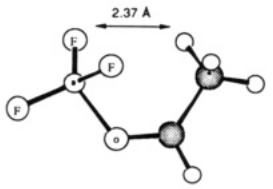


Figure 3. Optimized structure of the ss conformer for the *syn*-$CH_3CHO{\cdot}BF_3$.

hand, an attractive two electron interaction between the lone pair of the oxygen atom and the B–F σ^* orbital is present in the conformer where C–F bond is eclipsed with the C=O bond. The latter electronic effect is known as the "negative hyperconjugation" (anomeric effect),[14] and is sensitive to the relative geometry of the interacting molecular orbitals. Maximum stabilization is reached when the dihedral angle of C–O–B–F is zero. The negative hyperconjugation has been demonstrated theoretically for many molecular systems, both for anions and for neutral molecules.[15-17] Recent NMR experiments have confirmed that a high energy barrier exists in the inversion–rotation in compounds, such as FCH_2–NR_2.[18a] However, as far as we know, this is the first study describing such an electronic effect in an Lewis acid complex. Understanding of the negative hyperconjugation effect is important to the understanding of why *syn*-$PhCHO{\cdot}BF_3$ is unstable. As described above, maximum stabilization of a $RCHO{\cdot}BF_3$ complex is reached when the dihedral angle of C–O–B–F is zero. However, this is also the most sterically unfavorable conformation for the *syn*-$PhCHO{\cdot}BF_3$ complex. Thus, the advantage of negative hyperconjugation is more than offset by the steric repulsion.

A hydrogen-bonding type of attractive interaction is another electronic effect that can be considered for causing the difference between the BF_3 complexes of aromatic and aliphatic aldehydes. The greater stabilities of the ss conformer **5** among *syn*-$CH_3CHO{\cdot}BF_3$ and the sse and sss conformers **13** and **14** among $(Me)_2C{=}O{\cdot}BF_3$ cannot be rationalized by steric effects. These results are also in contrast to the analyses of torsional strain and hyperconjugative effects.[13] Wiberg and LePage were the first to report such an observation for the complex of acetone·BH_3.[9b] Currently, we believe that this surprising outcome is not an artefact; but this is rather an attractive interaction between the F and the H atoms, Figure 3.

The distortion of a methyl group from the standard C_{3v} group symmetry, i.e., the methyl tilt, has been used as an experimentally accessible parameter as an indication of certain electronic effects.[19-21] Boggs has studied the methyl tilt effect and suggested that overlap repulsion between C–H bonds was the main cause.[19] Radom et al.[20] have shown that methyl tilt can be rationalized by attractive force (hyperconjugation) alone. The preference for C–H bond eclipsing C=O has been discussed for a number of compounds, such as acetaldehyde and acetone by Wiberg et al.[21] It was concluded that the overlap repulsion between the methyl C–H (Me) and the aldehydic C–H (CHO) was the cause for the rotational barrier in acetaldehyde, rather than the effect of hyperconjugation.

Rather large methyl tilt was calculated for complexes where intramolecular hydrogen bonding is possible, Figure 2. When the B–F and C–H of the complexes are in the same plane, such as those in ss (**5**), sse (**13**), and sss (**14**), an attractive interaction makes the complexes more stable. In fact, a recent theoretical study by Reynolds[22b] has shown that carbon can be a good hydrogen bond donor if it is activated by an electron-withdrawing group. In the $CH_3CHO{\cdot}BF_3$ and acetone·BF_3 complexes, the methyl carbon is activated by the $C{=}O{\cdot}BF_3$, a strong electron-withdrawing group.[5e] Therefore, a large methyl tilt is computed for **5**, **13**, and **14** as the result of combined effects of overlap repulsion and coulombic attraction. The interatomic distances between the staggered F atoms of the OBF_3 moiety and the methyl hydrogens are 2.37 Å in the ss confomer of *syn*-$CH_3CHO{\cdot}BF_3$, **5**, Figure 3. While this distance is shorter than the sum (2.67 Å) of the empirical van der Waals radius for F and H,[23] it is almost identical to the C–H···O type of hydrogen bonding.[22] The distances between the methyl hydrogen atoms and the BF_3 fluorine atoms are 2.36 Å in the sse and sss conformers of $(CH_3)_2CO{\cdot}BF_3$ complexes. Again, it is an indication of intramolecular hydrogen bonding. On the other hand, no such structural feature is available for the *syn*-$PhCHO{\cdot}BF_3$ complexes.

Conclusions

Ab initio MO study at the MP2/6-31G*//3-21G level has revealed only a small difference in the strength of the syn and anti aliphatic aldehyde BF_3 complexes, while the energy difference between the *syn*- and the *anti*-$PhCHO{\cdot}BF_3$ is large at all levels of theory. The BF_3 complexes have the following order of stability: *anti*-$PhCHO{\cdot}BF_3$ > *anti*-$CH_3CHO{\cdot}BF_3$ > *syn*-$CH_3CHO{\cdot}BF_3$ > *syn*-$PhCHO{\cdot}BF_3$. The strong anti complexation of PhCHO is rationalized by considering the ability of the phenyl ring to stabilize the developing positive charge by resonance, which is evidenced by the shortening of the α-C–C(=O) bond in the calculated structure. Steric effect is accountable for the instability of the *syn*-$PhCHO{\cdot}BF_3$ complex. The order of the relative stability of the *syn*-$CH_3CHO{\cdot}BF_3$ and the $(CH_3)_2CO{\cdot}BF_3$ complexes is consistent with a hydrogen-bonding type of attractive interaction in the doubly staggered forms. Significant "methyl tilt" angles were found for these BF_3 complexes where intramolecular hydrogen bondings are possible. Hyperconjugation (both positive and negative) and torsional strain are identified as the origin for the relatively greater stability of the eclipsed conformations in the *anti*-$RCHO{\cdot}BF_3$ complexes.

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Registry No. $CH_3CHO{\cdot}BF_3$, 306-73-0; $PhCHO{\cdot}BF_3$, 456-30-4; $(CH_3)_2CO{\cdot}BF_3$, 661-27-8; CH_3CHO, 75-07-0; PhCHO, 100-52-7; CH_3COCH_3, 67-64-1; BF_3, 7637-07-2.

Supplementary Material Available: Table of selected structural parameters and Z-matrix of complexes 1–12 (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Electrooxidative Cyclization of *N*-Acylhydrazones of Aldehydes and Ketones to Δ^3-1,3,4-Oxadiazolines and 1,3,4-Oxadiazoles

Toshiro Chiba* and Mitsuhiro Okimoto

Department of Applied Chemistry, Kitami Institute of Technology, Kitami, Japan 090

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The electrolytic oxidation of ketone *N*-acylhydrazones (1) in methanolic sodium acetate induced their intramolecular cyclization to the corresponding 2-methoxy-Δ^3-1,3,4-oxadiazolines **3**. The thermal stability of a given oxadiazoline and what products were formed by its thermal decomposition was found to depend on the natures of the substituents at C-2. Thus, 2-methoxy-2-phenyloxadiazolines preferentially yielded oxiranes **5**, whereas 2-alkyl-2-methoxyoxadiazolines preferentially gave enol ethers **6**. 2,2-Dimethoxyoxadiazolines decomposed to the parent ketones and many unidentified products. The electrolytic oxidation of aldehyde *N*-acylhydrazones **2** gave 2,5-disubstituted 1,3,4-oxadiazoles **4**. The oxidative cyclization of the *N*-benzoylhydrazones of aliphatic aldehydes gave especially high yields of the corresponding heterocycles.

Introduction

The oxidative cyclization of such hydrazine derivatives of aldehydes and ketones as carbohydrazones, thiocarbohydrazones, semicarbazones, and thiosemicarbazones to nitrogen-containing heterocycles can be induced by a number of oxidizing agents.[1] However, to induce such cyclizations electrolytically has certain merits. Electrochemical oxidations obviously do not require oxidizing chemicals and, furthermore, can be performed under mild conditions, e.g., at room temperature. Indeed, many reports[2] of the electrochemically induced intra- and intermolecular cyclization of hydrazine derivatives of aldehydes and ketones have appeared. Most, however, describe the electrolysis of solutions of such compounds in aprotic solvents like acetonitrile.

Previously, we reported[3] that the electrochemical oxidation of ketone *N*-acylhydrazones **1** in methanolic sodium cyanide gives nitrogen and the corresponding nitriles (R_1R_2CHCN) and methyl esters ($MeOCOR_3$). Here, we report that the electrochemical oxidation of **1** and aldehyde *N*-acylhydrazones **2** in methanolic sodium acetate affords oxadiazolines **3** and oxadiazoles **4**, respectively. We also describe the products of the thermal decomposition of compounds **3**.

Results and Discussion

Preparative-scale constant-current electrolyses were performed at room temperature in a divided cell equipped with a carbon rod anode. The results of the electrooxidation of aliphatic ketone *N*-acylhydrazones **1** are summarized in Table I. In all cases, the starting hydrazone **1** was almost wholly consumed by the time 3 F/mol of electricity had passed through the solution and was converted into the corresponding 2-methoxy-Δ^3-1,3,4-oxadiazoline **3** in a yield of between 30 and 77%. The yield of

Scheme I

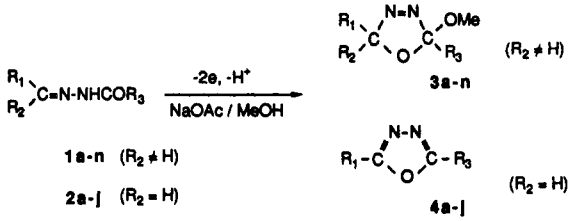

Table I. Synthesis of 2-Methoxy-Δ^3-1,3,4-oxadiazolines by the Electrooxidative Cyclization of Ketone *N*-Acylhydrazones[a]

	hydrazone 1			oxadiazoline 3 (yield, %)[b]
	R_1	R_2	R_3	
1a	Me	Me	Ph	**3a** (70)
1b	*n*-Pr	*n*-Pr	Ph	**3b** (65)
1c	*i*-Pr	*i*-Pr	Ph	**3c** (67)
1d	$-(CH_2)_5-$		Ph	**3d** (77)
1e	Me	Me	Me	**3e** (61)
1f	*n*-Pr	*n*-Pr	Me	**3f** (67)
1g	$-(CH_2)_5-$		Me	**3g** (70)
1h	$-(CH_2)_5-$		*n*-Pr	**3h** (73)
1i	$-(CH_2)_5-$		*i*-Pr	**3i** (73)
1j	$-(CH_2)_4-$		*n*-Pr	**3j** (71)
1k	*n*-Pr	*n*-Pr	*n*-Pr	**3k** (66)
1l	Me	Me	OMe	**3l** (30)
1m	*n*-Pr	*n*-Pr	OMe	**3m** (43)
1n	$-(CH_2)_5-$		OMe	**3n** (50)

[a] Analyte: hydrazone (30 mmol), NaOAc (15 mmol), and MeOH (80 mL). Strength of constant current: 0.5 A. Quantity of electricity: 3 F/mol. Temperature: ca. 15 °C. [b] Isolated yield.

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