

^{17}O and ^{13}C NMR/*ab Initio*/IGLO/GIAO-MP2 Study of Oxonium and Carboxonium Ions (Dications) and Comparison with Experimental Data¹

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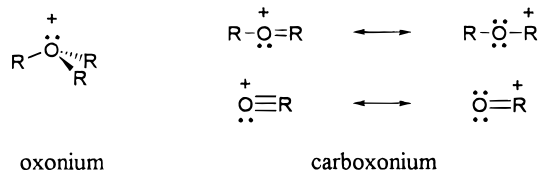
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Abstract: A series of oxonium and carboxonium ions and their corresponding protonated dications were investigated by *ab initio*/IGLO/GIAO-MP2 methods. The calculated ^{17}O and ^{13}C NMR chemical shifts were compared with the solution phase experimental data for the monocations. The structures and energies of a number of oxonium and carboxonium dications and the effect of diprotonation on the ^{17}O and ^{13}C NMR chemical shifts were also studied.

Introduction

Oxonium and carboxonium ions are important intermediates in many acid-catalyzed reactions. Considerable interest has centered on the elucidation of their structure and electronic properties by experimental and theoretical methods.^{2–6} Meer-

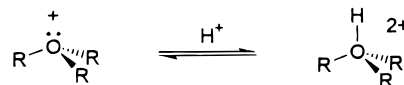


wein's pioneering studies² in the 1930s established trialkyloxonium and alkoxy-, dialkoxy-, and trialkoxycarbonium salts as versatile, widely used synthetic reagents in alkylation reactions. Acidic oxonium and carboxonium salts have been subsequently observed by NMR spectroscopy as long-lived, stable ions under superacid conditions.⁷

^{13}C NMR spectroscopy has been used extensively to study the structure of carboxonium and oxycarbonium ions,⁷ since it allows the direct monitoring of the cationic center and since the chemical shifts and coupling constants can be correlated to the geometry and hybridization of the cation. In previous studies,⁸ we have also applied ^{17}O NMR spectroscopy to investigate a series of oxonium and carboxonium ions. ^{17}O NMR spectroscopy proved to be particularly useful because of its sensitivity to changes in the carbon–oxygen π -bond order.^{9–11}

However, due to lone pair interactions at the oxygen atom, ^{17}O NMR chemical shifts are especially prone to solvent effects. In some cases, the magnitudes of solvent effects were found to be similar to or even to exceed those observed for lone pair protonation.^{12–14} These interesting experimental results⁸ called for a theoretical reinvestigation and a comparison of experimental and theoretical data. A reliable method for the calculation of ^{16}O NMR chemical shifts of oxonium and carboxonium ions has not been previously available.

Based on the greatly enhanced reactivity of oxonium and carboxonium salts in superacids, Olah¹⁵ suggested the *super-electrophilic* activation of these ions in a number of acid-catalyzed reactions. Theoretical calculations were also used to explain the enhanced reactivity of these ions.⁶ *Superelectrophiles* are electron-deficient intermediates (electrophiles) capable of further protonation (*protosolvation*) or Lewis acid coordination. The resulting doubly electron-deficient or dicationic ions are substantially more reactive than their parent oxonium or carboxonium ions. There is direct experimental evidence for the



formation of such highly reactive superelectrophiles as NO_2H^{2+} and $\text{CH}_3\text{COH}^{2+}$ in superacids.¹⁵ ^{17}O NMR spectroscopic studies of nitronium ion in superacidic $\text{HSO}_3\text{F}/\text{SbF}_5$ medium have indicated the involvement of the gtonic protonitronium dication, NO_2H^{2+} .¹⁶ This dication has also been observed in the gas phase.¹⁷ IR studies of the acetyl cation also show significant shifts of the CO frequency, depending on the acidity of the system, again indicating protolytic activation of acetyl cation leading to protoacetyl dication.¹⁸ Hydrogen/deuterium exchange experiments with H_3O^+ and H_3S^+ in superacids have indicated

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the involvement of such dications as H_4O^{2+} and H_4S^{2+} , respectively.^{19,20} Even the smallest two-electron-containing diatomic dication, He_2^{2+} , has been observed in the gas phase by charge-stripping mass spectrometry.²¹ These studies indicated that many dications, although thermodynamically unstable, have considerable kinetic barriers for decomposition.²² In superacid solutions, further stabilization of the dications is possible due to clustering (*i.e.*, charge dispersion). High-level calculations are particularly useful for probing these dications. The combination of *ab initio*-optimized geometries, theoretically computed NMR chemical shifts, and experimental NMR data affords a powerful tool for structural elucidations. *Noncorrelated* methods such as IGLO^{23–25} and LORG²⁶ allow the prediction of NMR chemical shifts and have been applied extensively to carbocation structures.²⁷ Recently, methods for *correlated* chemical shift calculations have been devised, namely GIAO-MP2²⁸ and SOPPA.^{29,30} In addition, a multiconfigurational SCF version of IGLO has been formulated and implemented for problems that require an MCSCF wave function.³¹ First applications of the GIAO-MP2 method show, in some cases, significant improvements in accuracy over the chemical shift results computed at the SCF level (*e.g.*, IGLO or LORG).^{32–34} So far, however, only limited studies have been reported on the application GIAO-MP2 to the calculation of ^{17}O NMR chemical shifts.

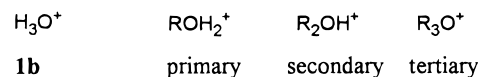
In this paper, we report the systematic study of ^{13}C and ^{17}O NMR chemical shifts of a series of oxonium and carboxonium ions using the IGLO, GIAO-SCF, and GIAO-MP2 methods. We have previously¹⁵ presented theoretical and experimental work (based, for example, on hydrogen/deuterium exchange) in support of the existence of oxonium and carboxonium dications. This paper reports the evaluation of the observed ^{13}C and ^{17}O NMR spectroscopic data in regard to the intermediacy of the superelectrophilic protoxonium dications and discusses the effect of further protonation on the ^{17}O and ^{13}C NMR chemical shifts of oxonium and carboxonium ions.

Results and Discussion

Geometries were fully optimized at the MP2/6-31G* level. Restricted Hartree–Fock calculations were performed throughout. Unless otherwise stated, MP2/6-31G* structures will be discussed in the text. IGLO (basis II) calculations were performed according to the reported method.²³ GIAO-SCF and GIAO-MP2 calculations were performed with the ACES II program employing various basis sets.²⁸ MP2/6-31G*-opti-

mized geometries have been used for the chemical shift calculations. The ^{13}C and ^{17}O NMR chemical shifts (δ values) are referenced to TMS and H_2O , respectively. Calculated and experimental ^{17}O and ^{13}C NMR chemical shifts of oxonium and carboxonium ions are given in Table 1. Computed total energies (in hartrees) at the MP2/6-31G* level are shown in Table 2.

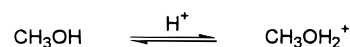
Saturated Oxonium Ions. Oxonium ions contain a positively charged, trivalent oxygen atom with an electron octet.¹ The hydronium ion, H_3O^+ (**1b**), first suggested in 1907,^{35,36} is the parent of saturated oxonium ions. By substituting one, two, or all three hydrogen atoms with alkyl groups, primary, secondary, or tertiary alkyloxonium ions, respectively, are formed.



(i) Mono- and Diprotonated Water. The hydronium ion **1b** is the parent of saturated oxonium ions. It has been studied extensively both in the gas phase and in solution.⁷ In superacid solution, it is readily observed by ^{17}O and ^1H NMR as a static, nonexchanging species. The geometries of the pyramidal **1b** and of the tetrahedral protohydronium dication, **1c**, are depicted in Figure 1 and agree with previous⁶ lower level calculations. IGLO predicts a $\delta^{17}\text{O}$ of -2.2 in **1b**, which is shielded by 12.2 ppm from the experimental value of $\delta^{17}\text{O}_{\text{exp}}$ 10.0 (Table 1). GIAO-SCF produces chemical shifts of $\delta^{17}\text{O}$ 21.7 using the tzp/dz basis set and $\delta^{17}\text{O}$ 18.2 using the qz2p/qz2p basis set. Correlated GIAO-MP2(qz2p/qz2p) predicts a chemical shift of $\delta^{17}\text{O}$ 24.4, deviating by 14.2 ppm from the experimental value. A similar deviation was also reported recently³⁷ by Sauer *et al.*, who used the correlated SOPPA method to calculate ^{17}O NMR chemical shifts of **1b**. Changes in the basis set of both GIAO-SCF and GIAO-MP2 calculations result in only small chemical shift differences (for a comparison between different basis sets, see Table 1).

Experimental evidence for the existence of the protohydronium dication, H_4O^{2+} (**1c**), came from the observation of hydrogen/deuterium exchange in isotopic hydronium ions with strong superacids.^{15,19} **1c** was subjected previously to several theoretical investigations, from which it was concluded that diprotonation of water leads to a high-lying intermediate with a considerable kinetic barrier to dissociation.⁶ In our studies, GIAO-MP2(qz2p/qz2p) calculations indicate that the oxygen atom in **1c** ($\delta^{17}\text{O}$ 39.2) is deshielded by only 15 ppm with respect to **1b** ($\delta^{17}\text{O}$ 24.4). This indicates that it might be difficult to substantiate the protohydronium ion experimentally by ^{17}O NMR, especially if it is present only in a small equilibrium concentration.

(ii) Mono- and Diprotonated Methanol. Protonation of methanol (**2a**) under superacidic stable-ion conditions gives the methyloxonium ion as a well-defined oxonium ion.⁷ Both IGLO-



and GIAO-MP2(qz2p/qz2p)-calculated $\delta^{13}\text{C}$ values for CH_3OH_2^+ (**2b**, 78.4 and 84.5, respectively) are in reasonable agreement with the experimental value of $\delta^{13}\text{C}_{\text{exp}}$ 62.9. The GIAO-MP2(qz2p/qz2p)-calculated $\delta^{17}\text{O}$ is 14.3, deshielded by 21 ppm compared to **2a** ($\delta^{17}\text{O}$ -6.8). This is, again, in excellent agreement with the experimentally observed deshielding at the oxygen atom in **2b** ($\delta^{17}\text{O}_{\text{exp}}$ -15.0) of 25 ppm relative to **2a** ($\delta^{17}\text{O}_{\text{exp}}$ -40.0). The order and magnitude of these effects are

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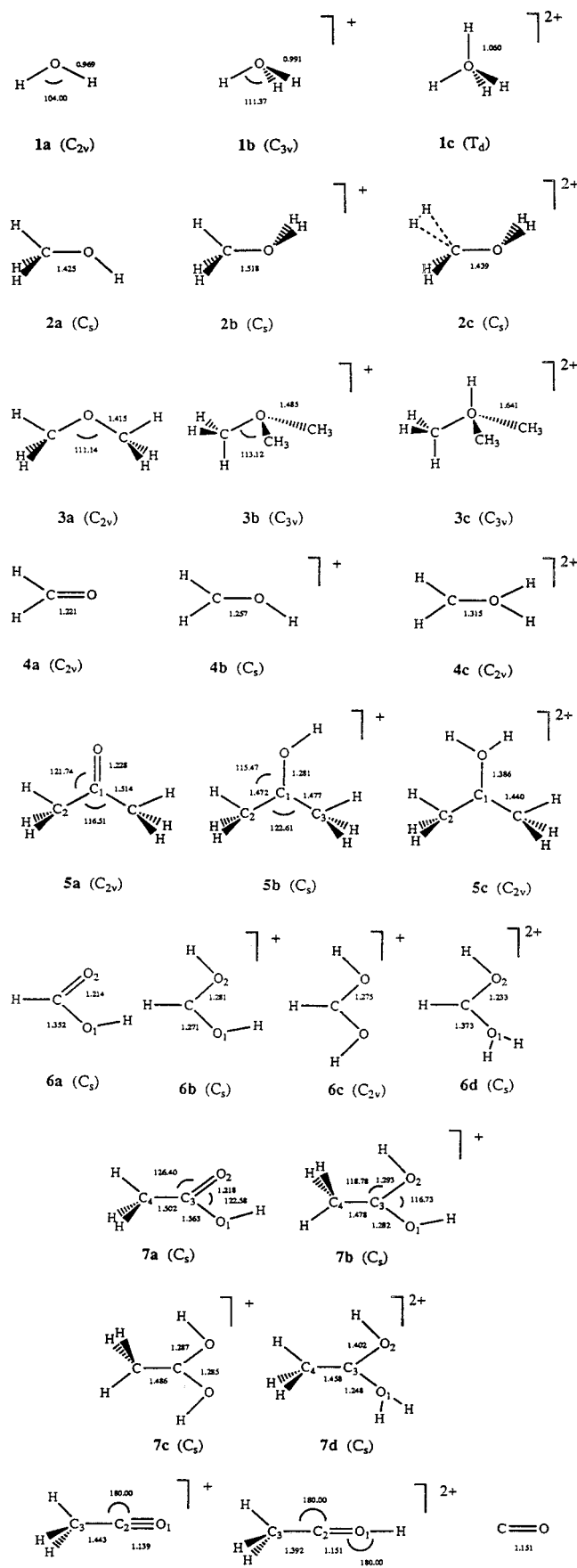


Figure 1. Selected parameters of oxonium and carboxonium compounds and their precursors at the MP2/6-31G* level.

very similar to those calculated and experimentally observed for **1b**. As in the case of **1b**, IGLO is unable to reproduce well the experimental result and gives a slight shielding effect of 2 ppm for **2b** ($\delta^{17}\text{O} -12.5$) with respect to **1a** ($\delta^{17}\text{O} -10.5$).

As shown by previous⁶³⁸ theoretical calculations, diprotonation of **2a** in the gas phase gives preferentially the O,C-protonated dication, $^+\text{CH}_4\text{OH}_2^+$ (**2c**). Both IGLO and GIAO-MP2(qz2p/qz2p) predict a ¹³C NMR chemical shift for the diprotonated species **2c** ($\delta^{13}\text{C}$ 49.9 and 57.7, respectively) that is similar to the calculated ¹³C chemical shift of neutral methanol, **2a** ($\delta^{13}\text{C}$ 51.7 and 58.9, respectively). The GIAO-MP2(qz2p/qz2p)-calculated ¹⁷O NMR chemical shift of **2c** ($\delta^{17}\text{O}$ 16.1) is very close to that calculated for the monoprotonated species **2b** ($\delta^{17}\text{O}$ 14.3). Differentiation between monocation **2b** and dication **2c** by ¹⁷O NMR spectroscopy, therefore, should be difficult.

(ii) Trimethyloxonium and Protonated Trimethyloxonium Ions. The trimethyloxonium ion, $(\text{CH}_3)_3\text{O}^+$ (**3b**), was first prepared by Meerwein² and has been studied extensively by a variety of techniques, including NMR spectroscopy. Our previous⁸ attempts to observe **3b** by ¹⁷O NMR spectroscopy were somewhat inconclusive due to signal broadening are resulted in a tentative assignment of $\delta^{17}\text{O}_{\text{exp}}$ 40.6 to **3b**, indicating a deshielding of 91 ppm with respect to the parent, dimethyl ether, $(\text{CH}_3)_2\text{O}$ (**3a**, $\delta^{17}\text{O}_{\text{exp}}$ -52.5). GIAO-MP2(tzp/dz)-calculated ¹⁷O chemical shifts predict a deshielding at the oxygen atom in **3b** ($\delta^{17}\text{O}$ 12.9) of 21 ppm with respect to the parent, **3a** ($\delta^{17}\text{O}$ -7.6). The order and magnitude of the calculated effect are very similar to those of the GIAO-MP2-calculated deshielding effect at the oxygen atom in other oxonium ions, such as **1b** and **2b**, with respect to their parent compounds. Considering the large difference in magnitude between the experimental (93 ppm) and the calculated (21 ppm) deshielding effects at the oxygen atom in **3b** with respect to **3a**, we have experimentally reinvestigated the ¹⁷O NMR chemical shift of **3b**. Attempts to prepare sufficiently concentrated solutions of $(\text{CH}_3)_3\text{O}^+\text{BF}_4^-$ and $(\text{CH}_3)_3\text{O}^+\text{SbCl}_6^-$ salts in organic solvents such as DMSO or acetonitrile failed due to poor solubility. The $(\text{CH}_3)_3\text{O}^+\text{PF}_6^-$ salt, prepared from $(\text{CH}_3)_2\text{O}$ and PF_5 , however, was found to be considerably more soluble, with a saturated solution of $(\text{CH}_3)_3\text{O}^+\text{PF}_6^-$ being approximately 2 M. Indeed, the ¹⁷O NMR spectrum of the solution recorded over a period of 24 h showed a sharp peak at $\delta^{17}\text{O} -32.1$, which is deshielded by 20.4 ppm compared to the experimental ¹⁷O NMR shift of $(\text{CH}_3)_2\text{O}$ (*vide infra*). This is in excellent agreement with the GIAO-MP2-calculated deshielding effect of 21 ppm.

As was found in a previous⁶ theoretical study, the protonated trimethyloxonium dication, $(\text{CH}_3)_3\text{OH}_2^{2+}$ (**3c**), exists as a thermodynamically as well as a kinetically stable species. It has not, however, been observed experimentally. GIAO-MP2-(tzp/dz) chemical shift calculations indicate that the calculated ¹³C chemical shift in the dication **3c** is $\delta^{13}\text{C}$ 133.1 which is 51 ppm deshielded from the monocation **3b** calculated at $\delta^{13}\text{C}$ 81.9. In contrast, GIAO-MP2(tzp/dz) predicts only a small deshielding effect for the ¹⁷O NMR chemical shift in **3c**. Thus, the $\delta^{17}\text{O}$ of **3c** (30.2) is calculated to be deshielded by only 17 ppm compared to the $\delta^{17}\text{O}$ of **3b** (12.9).

Carboxonium Ions. (i) Mono- and Diprotonated Aldehydes and Ketones. Protonated carbonyl compounds belong to the class of carboxonium ions and have been examined extensively in the past by various techniques, including ¹⁷O NMR spectroscopy.^{5,7,8} Carboxonium ions were first studied by Meerwein, and their chemical behavior reflects both their oxonium nature and their carbenium ion nature. Protonated

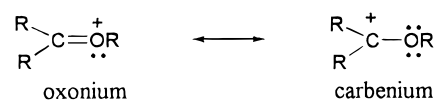


Table 1. Calculated and Experimental ^{17}O and ^{13}C NMR Chemical Shifts of Oxonium and Carboxonium Ions

no.	compound	NMR	IGLO(II) δ	GIAO-SCF δ			GIAO-MP2 δ			exptl ^a δ
				tzp/dz	qz2p/dzp	qz2p/qz2p	tzp/dz	qz2p/dzp	qz2p/qz2p	
1a (C_{2v})	H ₂ O	^{17}O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1b (C_{3v})	H ₃ O ⁺	^{17}O	-2.2	21.7	16.8	18.2	28.2	22.9	24.4	10.2
1c (T_d)	H ₄ O ²⁺	^{17}O	7.7	36.2	30.9	30.2	47.3	39.8	39.2	
2a (C_s)	CH ₃ OH	^{17}O	-10.5	-10.8	-14.2	-13.0	-2.3	-8.1	-6.8	-40.0
		^{13}C	51.7	48.2	49.6	51.9	54.0	57.5	58.9	50.2 ^b
2b (C_s)	CH ₃ OH ₂ ⁺	^{17}O	-12.5	7.5	2.4	4.3	18.1	12.6	14.3	-15.0
		^{13}C	78.4	75.5	77.3	79.6	80.2	83.5	84.5	
2c (C_s)	CH ₄ OH ₂ ²⁺	^{17}O	-12.9	9.6	3.2	7.2	21.2	13.0	16.1	
		^{13}C	49.9	45.6	48.5	51.6	51.4	55.6	57.7	
3a (C_{2v})	(CH ₃) ₂ O	^{17}O	-26.7	-28.0	-31.2	-27.7	-7.6	-14.9	-11.3	-52.5 ^c
		^{13}C	58.5	54.7	56.8	59.6	62.4	66.7	68.8	59.4 ^d
3b (C_{3v})	(CH ₃) ₃ O ⁺	^{17}O	-32.2	-16.5			12.9			-32.1 ^e
		^{13}C	76.6	73.2			81.9			79.3
3c (C_{3v})	(CH ₃) ₃ OH ²⁺	^{17}O	-33.5	-4.2			30.2			
		^{13}C	128.1	124.5			133.1			
4a (C_{2v})	H ₂ C=O	^{17}O	789.6	801.4	793.2	810.8	693.4	684.5	701.3	
		^{13}C	203.1	198.2	204.1	210.4	185.3	193.2	197.7	
4b (C_s)	H ₂ C=OH ⁺	^{17}O	343.7	357.5	356.4	363.1	391.3	387.8	393.0	
		^{13}C	240.6	236.7	241.2	246.0	228.8	235.3	238.3	223.8 ^f
4c (C_{2v})	H ₂ C=OH ₂ ²⁺	^{17}O	179.6	203.0	201.5	207.0	234.3	230.9	235.0	
		^{13}C	266.4	263.0	267.7	271.9	265.3	271.3	273.7	
5a (C_{2v})	(CH ₃) ₂ C=O	^{17}O	669.0	691.9	677.5		637.0	630.7		569.0 ^g
		$^{13}\text{C}_1$		214.8	218.5		198.6	206.1		205.1 ^h
		$^{13}\text{C}_2$		28.7	29.5		31.4	34.7		30.2
5b (C_s)	(CH ₃) ₂ C=OH ⁺	^{17}O	299.0	313.0			342.1			310.3
		$^{13}\text{C}_1$	268.4	264.8			256.3			248.7
		$^{13}\text{C}_2$	30.6	28.9			32.2			30.7
		$^{13}\text{C}_3$	32.5	30.8			35.1			31.9
5c	(CH ₃) ₂ C=OH ₂ ²⁺	^{17}O	156.1	175.8	174.5		192.2	190.8		
		$^{13}\text{C}_1$	291.7	286.7	289.5		278.8	284.3		
		$^{13}\text{C}_2$	37.3	35.0	35.4		41.7	44.3		
6a (C_s)	HCOOH	$^{17}\text{O}_1$	164.6	179.9	179.9	185.0	195.6	193.7	198.9	253.0
		$^{17}\text{O}_2$	417.8	442.0	433.3	441.8	406.2	397.5	405.1	
		^{13}C	173.0	171.3	173.4	179.9	160.2	165.3	170.1	167.6 ⁱ
6b (C_s)	HC(OH) ₃ ⁺	$^{17}\text{O}_1$	198.2	217.0	214.2	221.1	229.3	225.5	231.0	
		$^{17}\text{O}_2$	202.2	217.9	215.3	222.6	233.6	229.5	235.7	
		^{13}C	192.6	191.2	192.3	198.4	183.3	187.5	192.1	177.6 ⁱ
6c	HC(OH) ₂ ⁺	^{17}O	215.6	231.3	227.8	235.1	245.0	240.1	246.0	
		^{13}C	195.7	193.3	194.7	200.6	185.5	190.2	194.6	174.7
6d (C_s)	HC(OH)(OH ₂) ²⁺	$^{17}\text{O}_1$	112.7	135.4	132.7	138.9	146.9	143.0	147.9	
		$^{17}\text{O}_2$	278.3	296.6	293.2	299.7	310.4	306.4	311.4	
		^{13}C	189.7	187.9	188.7	194.9	180.5	184.3	189.1	
7a (C_s)	CH ₃ COOH	$^{17}\text{O}_1$	164.2	179.3			194.3			251.0
		$^{17}\text{O}_2$		411.3	438.4		413.4			
		$^{13}\text{C}_3$	184.3				171.9			176.9
		$^{13}\text{C}_4$	21.2	20.2			20.7			20.8
7b (C_s)	CH ₃ C(OH) ₂ ⁺	$^{17}\text{O}_1$	197.8	215.9			228.3			203.7
		$^{17}\text{O}_2$	201.9	216.0			231.2			
		$^{13}\text{C}_3$	211.3	209.5			202.0			193.0
		$^{13}\text{C}_4$	21.6	20.0			21.7			
7d (C_s)	CH ₃ C(OH)(OH ₂) ²⁺	$^{17}\text{O}_1$	116.6	137.8			148.2			
		$^{17}\text{O}_2$	262.0	279.8			294.2			
		$^{13}\text{C}_3$	213.7	211.5			203.4			
		$^{13}\text{C}_4$	23.3	21.7			24.7			
8a (C_{3v})	CH ₃ CO ⁺	$^{17}\text{O}_1$	354.4	376.1	373.3	379.6	343.8	340.8	345.8	299.5
		$^{13}\text{C}_2$	179.0	178.9	178.8	185.4	155.7	158.5	163.4	150.3
		$^{13}\text{C}_3$	7.9	6.1	5.2	7.9	6.3	7.4	9.1	
8b (C_{3v})	CH ₃ COH ²⁺	$^{17}\text{O}_1$	159.0	185.3	183.3		194.6	190.2		
		$^{13}\text{C}_2$	176.2	175.6	175.6		157.6	160.4		
		$^{13}\text{C}_3$	5.8	4.8	3.7		4.8	5.6		
9 (C_{nv})	C=O	^{17}O	413.8	438.5	433.5	441.6	404.9	397.7	403.6	350.0
		^{13}C	232.9	230.8	229.3	235.8	189.0	191.0	196.1	

^a Taken from ref 8 unless otherwise noted. ^b ^{13}C NMR original data have been converted by using the formula $\delta(\text{TMS}) = 194.6 - \delta(\text{CS}_2)$. ^c Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*, 4th ed.; Thieme Verlag: New York, 1991. ^d Delseth, C.; Kintzinger, J.-P. *Helv. Chim. Acta* **1978**, *61*, 1327. ^e Olah, G. A.; Doggweiler, H.; Felberg, J. D.; Fröhlich, S. *J. Org. Chem.* **1985**, *50*, 4847. ^f This study. ^g Taken from ref 40. ^h Kintzinger, J.-P. In *Oxygen NMR Characteristic Parameters, in NMR-17. Oxygen-17 and Silicon-29*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer Verlag: New York, 1981. ⁱ Taken from ref 42. ^j In 88% aqueous solution, taken from: lauterbur, P. C. *J. Chem. Phys.* **1957**, *27*, 217. ^k Taken from ref 44.

ketones and aldehydes play an important role as reaction intermediates and are involved in the acid-catalyzed hydration, nucleophilic addition, and ketal-forming reactions of the carbonyl group as well as in the formation of semicarbazones, hydrazones, and Schiff bases.³⁹

Despite strong theoretical support for their existence, diprotonated ketones and aldehydes have not been observed experimentally by NMR, presumably due to the low equilibrium concentration of these extremely reactive electrophiles, even in superacid medium.

(a) Mono- and Diprotonated Formaldehyde. Protonation of formaldehyde, H₂CO (**4a**), has been studied previously

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Table 2. Calculated Total Energies (in Hartrees) of Oxonium and Carboxonium Ions at the MP2/6-31G* Level

no.	compound	energy	no.	compound	energy
1a (<i>C_{2v}</i>)	H ₂ O	76.196 85	6a (<i>C_s</i>)	HCOOH	189.241 78
1b (<i>C_{3v}</i>)	H ₃ O ⁺	76.475 11	6b (<i>C_s</i>)	HC(OH) ₂ ⁺	189.529 57
1c (<i>T_d</i>)	H ₄ O ²⁺	76.387 25	6c (<i>C_{2v}</i>)	HC(OH) ₂ ⁺	189.525 17
2a (<i>C_s</i>)	CH ₃ OH	115.346 14	6d (<i>C_s</i>)	HC(OH)(OH) ₂ ²⁺	189.533 44
2b (<i>C_s</i>)	CH ₃ OH ₂ ⁺	115.645 85	7a (<i>C_s</i>)	CH ₃ COOH	228.418 94
2c (<i>C_s</i>)	CH ₄ OH ₃ ²⁺	115.593 91	7b (<i>C_s</i>)	CH ₃ C(OH) ₂ ⁺	228.723 13
3a (<i>C_{2v}</i>)	(CH ₃) ₂ O	154.503 46	7c (<i>C_s</i>)	CH ₃ C(OH) ₂ ⁺	228.716 59
3b (<i>C_{3v}</i>)	(CH ₃) ₃ O ⁺	193.983 64	7d (<i>C_s</i>)	CH ₃ C(OH)(OH) ₂ ²⁺	228.753 33
3c (<i>C_{3v}</i>)	(CH ₃) ₃ OH ²⁺	194.027 96	8a (<i>C_{3v}</i>)	CH ₃ CO ⁺	152.477 97
4a (<i>C_{2v}</i>)	H ₂ CO	114.167 75	8b (<i>C_{3v}</i>)	CH ₃ COH ²⁺	152.414 56
4b (<i>C_s</i>)	H ₂ COH ⁺	114.444 63	9 (<i>C_{nv}</i>)	CO	113.021 22
4c (<i>C_{2v}</i>)	H ₂ COH ₂ ²⁺	114.406 62			
5a (<i>C_{2v}</i>)	(CH ₃) ₂ CO	192.523 91			
5b (<i>C_s</i>)	(CH ₃) ₂ COH ⁺	192.837 42			
5c (<i>C_{2v}</i>)	(CH ₃) ₂ COH ₂ ²⁺	192.868 44			

theoretically⁶ and by ¹³C NMR spectroscopy.⁴⁰ The calculated geometry of H₂COH⁺ (**4b**) is in agreement with the previously⁴¹ reported results obtained at the Hartree–Fock level. Both GIAO-MP2(qz2p/qz2p)- and IGLO(II)-calculated ¹³C NMR chemical shifts for **4b** (δ¹³C 238.3 and 240.6, respectively) are in close agreement with the reported experimental ¹³C NMR shift, δ¹³C_{exp} 223.8. In the prediction of the ¹⁷O NMR chemical shift in **4b**, however, GIAO-MP2 and IGLO differ significantly from each other. GIAO-MP2(qz2p/qz2p) predicts a shielding effect of 308 ppm in **4b** (δ¹⁷O 393.0) with respect to the parent, **4a** (δ¹⁷O 701.3). This prediction is in line with the experimentally observed ¹⁷O NMR shielding by 260 ppm in a number of protonated carbonyl compounds.⁸ Though pointing in the right direction, IGLO vastly overestimates this effect by predicting a shielding of 446 ppm at the carbonyl oxygen atom in **4b** (δ¹⁷O 343.7) upon protonation of **4a** (δ¹⁷O 789.6). The diprotonated species, H₂COH₂²⁺ (**4c**), is isoelectronic with ethylene (global minimum, planar *C_{2v}* symmetry^{6,41}). Both IGLO and GIAO-MP2 predict a further deshielding in ¹³C NMR by 30 ppm in the dication, **4c** (δ¹³C 266.4 and 273.7, respectively) with respect to the monocation, **4b** (δ¹³C 240.6 and 238.3, respectively). The GIAO-MP2(qz2p/qz2p) ¹⁷O NMR chemical shift in **4c** (δ¹⁷O 235.0) is calculated to be further shielded by 158 ppm with respect to **4b** (δ¹⁷O 393.0). **4c** should, therefore, be detectable by ¹³C and ¹⁷O NMR spectroscopy, but fast exchange between the mono- and diprotonated forms must be taken into account.

(b) Mono- and Diprotonated Acetone. Acetone [(CH₃)₂CO **5a**], and its mono- [(CH₃)₂COH⁺, **5b**] and diprotonated [(CH₃)₂COH₂²⁺, **5c**] forms have recently been investigated theoretically by Krivdin *et al.*,⁴² who employed the *noncorrelated* LORG method to calculate ¹⁷O and ¹³C NMR chemical shifts. However, the LORG-calculated ¹⁷O chemical shifts showed substantial deviation from the experimentally observed chemical shifts, whereas the ¹³C NMR chemical shifts were in excellent agreement with the experimnt. The LORG-calculated ¹⁷O shifts are comparable to those obtained by the IGLO method in this study (see Table 1) and overestimate the ¹⁷O NMR shielding effect on the carbonyl oxygen upon protonation by more than 100 ppm. GIAO-MP2 vastly improves these results, predicting a shielding effect of 295 ppm in protonated acetone, (CH₃)₂COH⁺ (**5b**, δ¹⁷O 342.0) with respect to **5a** (δ¹⁷O 637.0). This compares well with the experimentally observed shielding of 260 ppm in **5b** (δ¹⁷O_{exp} 310.0) as compared to **5a** (δ¹⁷O_{exp} 569.0) and supports the conclusions drawn from previous⁸ ¹⁷O NMR studies, *i.e.*, that the protonated carbonyl group retains

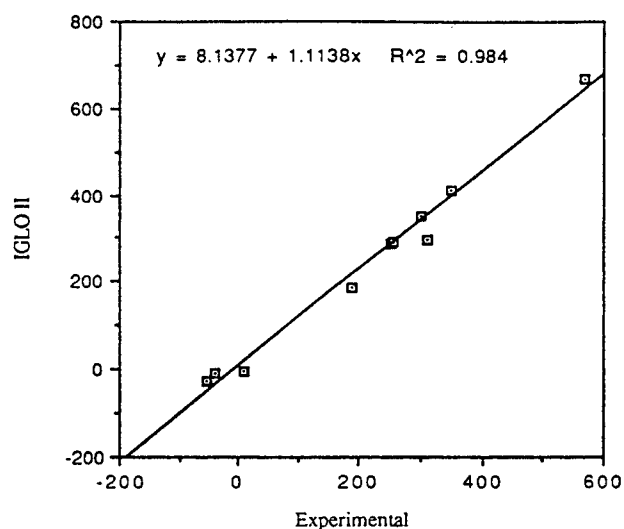
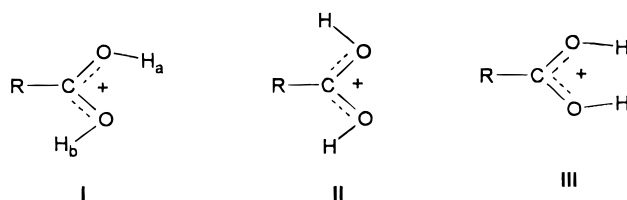


Figure 2. Oxygen-17 NMR chemical shifts: IGLO(II) vs experimental correlation.

substantial carbon–oxygen π-bond character and that the hydroxycarbenium ion resonance is only a minor contributor to the overall structure. The calculated effects of mono- and diprotonation on the ¹⁷O NMR chemical shift of acetone are very similar in nature and magnitude to those of mono- and diprotonated formaldehyde (**4b,c**). Both IGLO and GIAO-MP2-(tzp/dz) predict a further deshielding by 25 ppm at the carbonyl carbon in **5c** (δ¹³C 291.7 and 278.8, respectively) as compared to **5b** (δ¹³C 268.4 and 256.3, respectively). Similar to diprotonated formaldehyde (**4c**), GIAO-MP2 calculations at the tzp/dz level predict a further shielding in the ¹⁷O NMR chemical shift of **5c** (δ¹⁷O 192.2) by 150 ppm with respect to the monoprotonated species, **5b** (δ¹⁷O 342.1).

Mono- and Diprotonated Carboxylic Acids and Acyl Cations. Carboxylic acids are protonated in superacids to form stable carboxonium ions, for which three different conformers (**I–III**) are possible.⁵ NMR studies^{43,44} indicate that structure



I is the predominant conformer, whereas structure **III** is not

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 (41) Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 5484.
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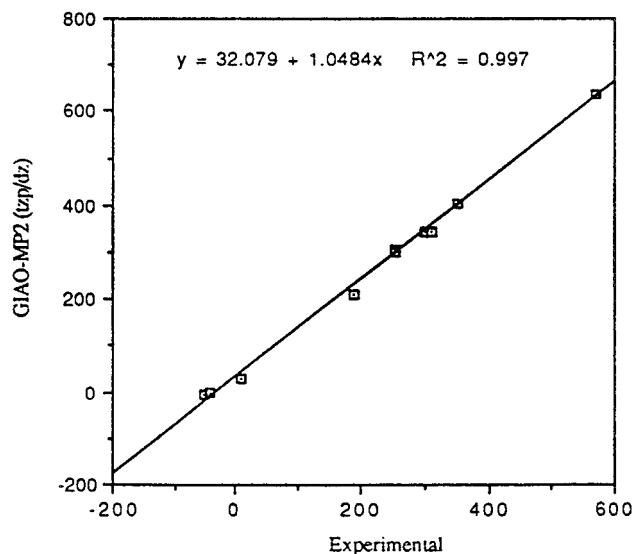


Figure 3. Oxygen-17 NMR chemical shifts: GIAO-MP2(tzp/dz) vs experimental correlation.

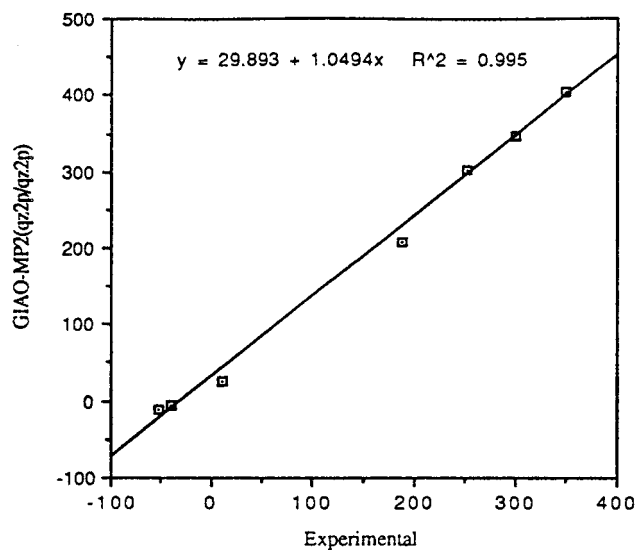
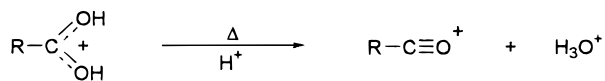


Figure 4. Oxygen-17 NMR chemical shifts: GIAO-MP2(qz2p/qz2p) vs experimental correlation.

observed. As with protonated ketones, the charge is predominantly localized on oxygen. The ^{13}C NMR chemical shift of the carboxylic carbon is slightly deshielded (20 ppm) upon protonation, indicating that less charge is localized on this carbon than on the carbonyl carbon in protonated ketones.⁴⁵ In ^{17}O NMR spectroscopy, only one oxygen resonance is observed in carboxylic acids due to fast proton exchange. A shielding of about 50 ppm is observed for each oxygen upon protonation.⁸ Upon raising the temperature of the superacid solutions, cleavage to related acyl cations (RCO^+) via dehydration is observed.⁵



Acyl cations have been extensively studied by various techniques including IR, NMR, UV, X-ray, and ESCA analysis.^{5,7,8,46,47} These studies have indicated that the acyl cations

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(46) Olah, G. A.; Germain, A.; White, A. M. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1976; Vol. 5, p 2049 and references therein.

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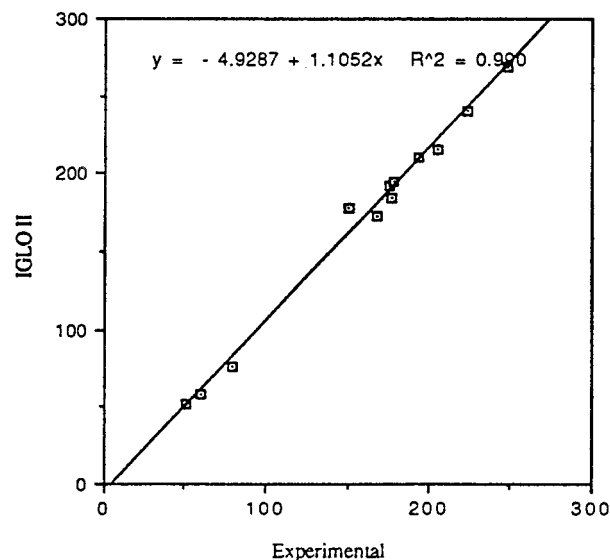


Figure 5. Carbon-13 NMR Chemical Shifts: IGLO(II) vs experimental correlation.

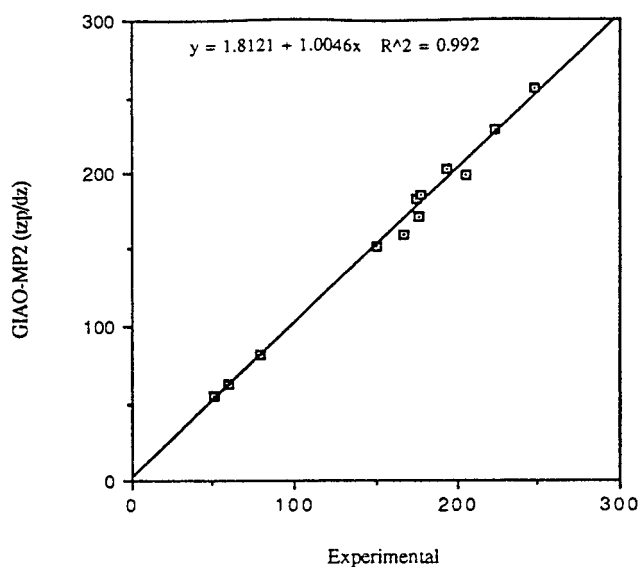
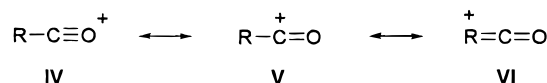


Figure 6. Carbon-13 NMR Chemical Shifts: GIAO-MP2(tzp/dz) vs experimental correlation.

are resonance hybrids of the oxonium ion (**IV**), oxocarbenium ion (**V**), and ketene-like forms, $\text{R} = \text{aryl}$, alkenyl, or alkynyl, (**VI**), with **V** as the predominant contributor to the overall structure.



Diprotonated carboxylic acids have not been observed experimentally. However, a diprotonation equilibrium has been indicated in the ionization processes of formic and acetic acids.¹⁵ The protonation and diprotonation reactions of formic and acetic acids were also studied theoretically.^{6,48}

(a) Mono- and Diprotonated Formic Acid. Monoprotonated formic acid, $\text{HC}(\text{OH})_2^+$ (**6b**), has been observed by NMR as a stable ion in $\text{FSO}_3\text{H}/\text{SbF}_5$ and HF/BF_3 solutions.^{46,49,50} In our calculations, structure **6b** was found to be the global minimum, differing only by a few kilocalories per mole (2.76 kcal/mol) from isomer **6c**. This is in agreement with previ-

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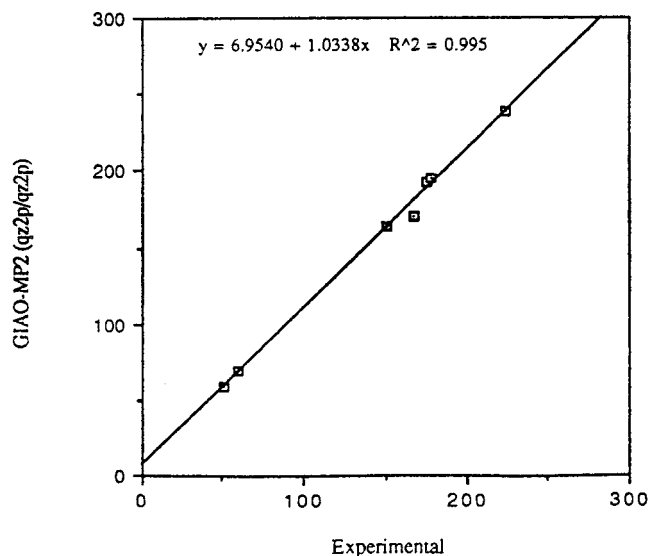


Figure 7. Carbon-13 NMR chemical shifts: GIAO-MP2(qz2p/qz2p) vs experimental correlation.

ously⁴⁶ reported NMR studies. **6b** is characterized by two carbon–oxygen bonds of nearly equal length (1.281 and 1.271 Å, respectively), corresponding to a bond length in between a carbon–oxygen double and single bond. The GIAO-MP2-calculated shielding effect for each oxygen in **6b** ($\delta^{17}\text{O}_{\text{av}}$ 233.4) is 69 ppm with respect to the parent, HCO_2H (**6a**, $\delta^{17}\text{O}_{\text{av}}$ 302.0), which is in line with the experimentally observed shielding of 50 ppm for each oxygen in acetic and propionic acids IGLO overestimates this shielding effect and predicts a shielding of 91 ppm for the oxygen atoms in **6b** ($\delta^{17}\text{O}_{\text{av}}$ 200.2) with respect to **6a** ($\delta^{17}\text{O}_{\text{av}}$ 291.2).

Diprotonated formic acid, $\text{HC}(\text{OH})(\text{OH}_2)^{2+}$ (**6d**), can be considered as a donor–acceptor complex of H_2O and diprotonated carbon monoxide (HCOH^{2+}) and has been calculated previously⁶ at the Hartree–Fock level. No significant changes in geometry occur when going from the HF to MP2 level. While the C–OH bond retains substantial double bond character (1.233 Å), the C–OH₂ bond exhibits a considerable elongation (1.373 Å) compared to the corresponding carbon–oxygen bonds in the monoprotated species, **6b**. Both IGLO and GIAO-MP2 predict a deshielding of 30 ppm for the ¹³C NMR chemical shift at the carboxy carbon in dication **6d** ($\delta^{13}\text{C}$ 266.4 and 273.7) relative to monocation **6b** ($\delta^{13}\text{C}$ 240.6 and 238.3). The GIAO-MP2- and IGLO-calculated ¹⁷O NMR chemical shifts indicate a significant difference in the nature of the two oxygens in the diprotonated species: the ¹⁷O NMR chemical shift of the oxygen atom bearing one hydrogen atom (O₂ in **6d**) was calculated (GIAO-MP2) at $\delta^{17}\text{O}$ 311 (compared to $\delta^{17}\text{O}$ 236 in **6b**), which corresponds to a 30% increase of the carbon–oxygen π -bond order. On the other hand, the GIAO-MP2-calculated chemical shift of the oxygen atom bearing two hydrogens (O₁ in **6d**) is $\delta^{17}\text{O}$ 148 ppm (compared to $\delta^{17}\text{O}$ 231 in **6b**), reflecting a decrease in carbon–oxygen π -bond order of ~35%. IGLO gives similar results. Despite this difference in ¹⁷O chemical shifts, the average calculated chemical shift of both oxygen atoms ($\delta^{17}\text{O}_{\text{av}}$ 229.7) differs only insignificantly from the GIAO-MP2 shift found for the monoprotated species **6b** ($\delta^{17}\text{O}_{\text{av}}$ 233). Due to fast proton exchange and averaging of the resonances, ¹⁷O NMR spectroscopy is most likely not suitable for the detection of diprotonated formic acid (**6d**).

(b) Mono- and Diprotonated Acetic Acids. Monoprotated acetic acid, $\text{CH}_3\text{C}(\text{OH})_2^+$ (**7b**), has been observed experimentally in superacid media by ¹H, ¹³C, and ¹⁷O NMR spectroscopy.^{5,7,8} In agreement with reported NMR studies,⁴³ which show the presence of two conformers, **7b,c**, with **7b**

predominating over **7c** by a factor of 19:1, we found structure **7b** as the global minimum, differing in energy from structure **7c** by 4.11 kcal/mol. The IGLO(II)- and GIAO-MP2-calculated ¹³C chemical shifts ($\delta^{13}\text{C}$ 211.3 and 202.0, respectively) correlate well with the experimental ¹³C NMR chemical shift for **7b** of $\delta^{13}\text{C}_{\text{exp}}$ 193.0. GIAO-MP2 shows some improvement over IGLO(II) with regard to the ¹³C chemical shift of the carboxylic carbon in **7b**. The calculated effect of protonation on the ¹⁷O chemical shifts in acetic acid, $\text{CH}_3\text{CO}_2\text{H}$ (**7a**), is similar in nature to that found for formic acid (**6a**, *vide infra*). Both IGLO and GIAO-MP2 predict a shielding at both oxygens in **7b** ($\delta^{17}\text{O}_{\text{av}}$ 199.9 and 229.8, respectively) upon protonation by 88 and 74 ppm, respectively, as compared to **7a** ($\delta^{17}\text{O}_{\text{av}}$ 287.8 and 303.9, respectively). The order of magnitude and the direction of this effect compare well with the experimentally observed shielding effect at both oxygens in **7b** ($\delta^{17}\text{O}_{\text{exp}}$ 203.7) of 47 ppm with respect to **7a** ($\delta^{17}\text{O}_{\text{exp}}$ 251.0). This implies a loss of about 20–25% in π -bond order for each carbon–oxygen bond, which is very similar to the loss of π -bond character indicated by the computed ¹⁷O shifts for the protonation of formic acid.

Diprotonated acetic acid (**7d**) can be visualized⁶ as a donor–acceptor complex of H_2O and the protonated acetyl cation ($\text{CH}_3\text{COH}^{2+}$) and has not been observed experimentally. The global minimum **7d** is characterized by a long C–OH₂ bond of 1.402 Å and a shorter C–OH bond of 1.248 Å. This is reflected also in the ¹³C and ¹⁷O NMR chemical shifts. Both IGLO(II) and GIAO-MP2(tzp/dz) predict little change in the ¹³C chemical shift of the carboxylic carbon when going from **7b** ($\delta^{13}\text{C}$ 268.4 and 256.3, respectively) to **7d** ($\delta^{13}\text{C}$ 291.7 and 278.8, respectively), indicating that the second positive charge is almost exclusively located on the oxygen atom bearing two hydrogens. GIAO-MP2 predicts a ¹⁷O chemical shift of $\delta^{17}\text{O}$ 294 for the oxygenation in **7d** bearing one hydrogen (compared to $\delta^{17}\text{O}$ 231 in **7b**) and a chemical shift of $\delta^{17}\text{O}$ 148 for the oxygen atom bearing two hydrogens (compared to $\delta^{17}\text{O}$ 228 in **7b**). IGLO(II) gives similar results. The magnitude and direction of the calculated ¹⁷O chemical shifts in diprotonated acetic acid (**7b**) are very similar to those calculated for diprotonated formic acid (**6d**). As for **6d**, fast proton exchange and averaging of the signals in the experimental ¹⁷O NMR spectrum result in an average ¹⁷O chemical shift that differs only insignificantly from the calculated shift found for the monoprotated species, **7b**.

(c) Acetyl Ion and Protoacetyl Dication. The calculated structure of acetyl ion, CH_3CO^+ (**8a**), is in agreement with previous^{6,51} calculations and with X-ray structures^{52,53} obtained for salts such as $\text{CH}_3\text{CO}^+\text{SbF}_6^-$ and $\text{CH}_3\text{CO}^+\text{SbCl}_6^-$. The calculated C–O bond length of 1.139 Å (experimental bond length, 1.109 Å in $\text{CH}_3\text{CO}^+\text{SbCl}_6^-$) resembles that found in carbon monoxide (**9**) and indicates substantial triple-bond character of the C–O bond. ¹³C NMR and ESCA studies, however, indicate that charge is also partially localized on carbon. The experimental ¹³C chemical shift of the carboxonium carbon at $\delta^{13}\text{C}$ 150.3 is well reproduced by the GIAO-MP2 method ($\delta^{13}\text{C}$ 158.5 at the qz2p/dzp level). IGLO is off by 30 ppm ($\delta^{13}\text{C}$ 179 at level II) compared to the experimental value (see Table 1). Previous ¹⁷O NMR studies⁸ of the acetyl cation in $\text{HF}/\text{SbF}_5/\text{SO}_2$ solution have led to the conclusion that the π -bond order of the C–O bond in **8a** is in between that of a carbon–oxygen double and triple bond. This is confirmed by both IGLO(II) and GIAO-MP2(qz2p/dzp) calculations: taking the calculated GIAO-MP2 ¹⁷O NMR chemical shift of **9** ($\delta^{17}\text{O}$ 397) as a model for carbon–oxygen triple bonds, one observes

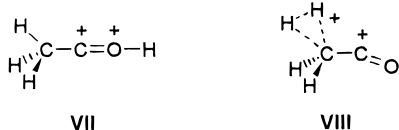
(51) Olah, G. A.; Burcher, A.; Rasul, G.; Prakash, G. K. S.; Hachoumy, M.; Sommer, J. *J. Am. Chem. Soc.* **1996**, *118*, 10423.

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(53) LeCarpentier, J.-M.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 1421.

a shielding of 55 ppm for **8a** ($\delta^{17}\text{O}$ 340.8). This is in excellent agreement with the experimentally observed shielding of 50 ppm in **8a** ($\delta^{17}\text{O}_{\text{exp}}$ 299.5) with respect to carbon monoxide ($\delta^{17}\text{O}_{\text{exp}}$ 350.0) and indicates that the C–O bond character in the acetyl cation is less than that of a C–O triple bond but considerably more than that of a C–O double bond.

IR studies of the acetyl cation show significant shifts of the CO frequencies depending on the acidity of the system, indicating protosolvation.¹⁸ Shudo *et al.*⁵⁴ have shown that Friedel–Crafts-type acetylation of benzene and chlorobenzene with acetyl hexafluoroantimonate ($\text{CH}_3\text{CO}^+\text{SbF}_6^-$) is greatly enhanced when using superacidic $\text{CF}_3\text{SO}_3\text{H}$ as solvent instead of the relatively weak CF_3COOH . Previous^{38,51} theoretical calculations have shown that O-protonation of the acetyl ion leads to a stable dication ($\text{CH}_3-\text{C}^+=\text{O}^+-\text{H}$), corresponding to the global minimum on the potential energy surface. This agrees with charge-stripping mass spectrometric studies in which the $\text{C}_2\text{H}_4\text{O}^{2+}$ dication has been observed.⁵⁵ Recently,⁵¹ we have investigated the possibility of C–H protonation in CH_3CO^+ by hydrogen/deuterium exchange experiments and density functional theory methods. Interestingly, it was found that the isomer **VIII**, protonated at the C–H bond, $^+\text{CH}_4-\text{C}^+=\text{O}$, is 18.9 kcal/mol less stable than the O-protonated acetyl cation, **VII**.⁵¹ The MP2/6-31G*-calculated C–O bond length of 1.151



Å in **8b** is essentially the same as that of **9** (1.151 Å), indicating triple-bond character. A significant shortening of the CH_3-C bond in **8b** (1.392 Å) is found as compared to the same bond in the parent acetyl ion, **8a** (1.443 Å), due to hyperconjugation. Both IGLO(II) and GIAO-MP2(qz2p/dzp) predict little change in the ^{13}C NMR chemical shift at the carboxonium carbon in the dication **8b** as compared to the monocation **8a**. The GIAO-MP2(qz2p/dzp)-calculated ^{13}C chemical shift in **8b** is $\delta^{13}\text{C}$ 160.4, which is essentially the same as that calculated for the parent monocation, **8a**, at $\delta^{13}\text{C}$ 158.5. The ^{17}O NMR-calculated chemical shifts for dication **8b**, however, are substantially different from those calculated for monocation **8a**. GIAO-MP2-(qz2p/tzp) predicts a further shielding for the oxygen atom in **8b** ($\delta^{17}\text{O}$ 190.2) by 150 ppm as compared to the acetyl monocation, **8a** ($\delta^{17}\text{O}$ 340.8). The IGLO-calculated difference in ^{17}O chemical shifts between **8a** and **8b** is even larger, predicting a shielding effect of 200 ppm for the oxygen atom in **8b** ($\delta^{17}\text{O}$ 159.0) as compared to **8a** ($\delta^{17}\text{O}$ 354.4). As predicted by IGLO and GIAO-MP2 calculations, **8b** should be distinguishable from **8a** by ^{17}O NMR spectroscopy.

Chemical Shift Correlation. The GIAO-MP2-calculated ^{17}O and ^{13}C NMR chemical shifts are in excellent agreement with the experimental data (Table 1 and Figures 2, 3, 6, and 7). The GIAO-SCF- (Table 1) and IGLO(II) (Table 1 and Figures 2 and 5) calculated chemical shifts also correlate very well with the experimental data. In particular, GIAO-MP2 shows a significant improvement in the $\delta^{13}\text{C}$ of the carbonyl carbon in protonated carbonyl compounds and in the $\delta^{17}\text{O}$ of saturated oxonium ions and protonated aldehydes and ketones (*vide infra*).

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The choice of basis set was found to be important, especially in the GIAO-MP2 calculation of $\delta^{17}\text{O}$. GIAO-MP2 was found to give more accurate $\delta^{17}\text{O}$ with the qz2/qz2p basis than with the less expensive tzp/dz basis set (Figures 3 and 4). On the other hand, there is not much change in the $\delta^{13}\text{C}$ of the molecules investigated when going from the tzp/dz to the qz2p/qz2p basis set (Figures 6 and 7).

Conclusions

The ^{17}O and ^{13}C NMR chemical shifts of a series of oxonium and carboxonium ions such as R_3O^+ , R_2COH^+ , $\text{RC}(\text{OH})_2^+$, and CH_3CO^+ ($\text{R} = \text{H}$ and CH_3) and their corresponding diprotonated species were investigated using IGLO and GIAO-MP2 methods. The data were compared with the available solution phase experimental data of the monocations. Based on the calculations, the ^{17}O NMR chemical shift of trimethyloxonium ion ($(\text{CH}_3)_3\text{O}^+$) was reinvestigated experimentally and reassigned to $\delta^{17}\text{O} -32.1$. Furthermore, the structures and energies of a number of oxonium and carboxonium dications as well as the effect of diprotonation on the ^{17}O and ^{13}C NMR chemical shifts are also reported.

Experimental Part

$(\text{CH}_3)_3\text{O}^+\text{BF}_4^-$ (Aldrich), $(\text{CH}_3)_3\text{O}^+\text{SbCl}_6^-$ (Aldrich), $(\text{CH}_3)_2\text{O}$ (Matheson), PF_5 (Matheson), and acetone- d_6 (99.9% D, Cambridge Isotope) were commercially available products and were used as received. Volatile materials used in this work were manipulated in well-passivated (with ClF_3 and HF) vacuum lines constructed from Teflon-PFA with injection-molded fittings and valves. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox.

^{17}O NMR spectra were obtained on a Varian Associates Unity-300 spectrometer equipped with a 10 mm variable temperature probe at 40.7 MHz. NMR spectra were referenced to H_2O ($\delta^{17}\text{O}$ 0). All calculations were carried out using the GAUSSIAN 94⁵⁶ and ACES II⁵⁷ packages of programs.

Preparation of $(\text{CH}_3)_3\text{O}^+\text{PF}_6^-$. Trimethyloxonium hexafluorophosphate was prepared from dimethyl ether and phosphorus pentafluoride in a way similar to a previously⁵⁸ reported procedure. PF_5 (20 mmol) and $(\text{CH}_3)_2\text{O}$ (20 mmol) were condensed in a 300 mL round-bottom flask at -196°C . The flask was sealed and kept at constant temperature (35°C ; oil bath). After 6 days, volatile products were removed *in vacuo* at -196°C for 1 h and, after the mixture was allowed to slowly warm to room temperature, at 50°C (oil bath) for 3 h, giving a white crystalline solid. Yield: 42% (1.74 g, 8.4 mmol).

NMR Study of $(\text{CH}_3)_3\text{O}^+$. A saturated solution of $(\text{CH}_3)_3\text{O}^+\text{PF}_6^-$ salt in CD_3CN was prepared ($\sim 2\text{ M}$) and transferred under inert gas atmosphere into a 10 mm NMR tube for ^{17}O NMR analysis at ambient temperature. ^{17}O NMR (in $\text{DMSO}-d_6$): $\delta^{17}\text{O} -32.1$ (s).

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