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Protioacyl Dications: Hydrogen/Deuterium Exchange, Rearrangements, and Theoretical Studies[1]

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Abstract: Hydrogen/deuterium exchange was observed by ^{2}H-NMR spectroscopy at the CH_3 groups of the long-lived alkanoyl cations $CH_3CH_2CO^+$ (**4**), $(CH_3)_2CHCO^+$ (**8**), and $(CH_3)_3CCO^+$ (**13**) when treated with excess $DF{\cdot}SbF_5$ superacid. The intermediacy of the corresponding protio(deuterio)acylium dications is suggested to account for the exchanges. Under similar conditions, no exchange was observed in the acetyl ion CH_3CO^+ (**1**) in $DF{\cdot}SbF_5$, but at the same time its electrophilic reactivity is greatly enhanced in superacids. The acetyl cation in a superacidic medium also abstracts tertiary hydrogens of isoalkanes to give protonated acetaldehyde. Density functional theory calculations at the B3LYP/6-31G** level were carried out to support the suggested exchange mechanism as well as lack of exchange in the acetyl cation. On the basis of the calculated results, two alternative mechanisms are also suggested for the Nenitzescu rearrangement of pivaloyl chloride in isobutane with excess $AlCl_3$.

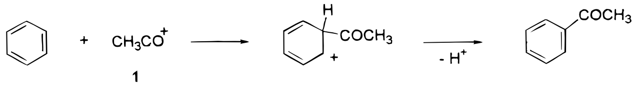
Introduction

Acyl cations RCO^+ (R = alkyl) are the intermediates in Friedel−Crafts type acylations of aromatics.[2] The acetyl cation was first isolated as a stable tetrafluoroborate salt by Seel[3] in 1943. Acyl cations were subsequently extensively studied[4] by various techniques, including IR, NMR, UV, X-ray, and ESCA analysis. These studies have indicated that acyl cations have a nearly linear structure, being resonance hybrids of the linear oxonium ion **I** and oxocarbenium ion **II** forms, with **I** being the predominant contributor to the overall structure.

$$R-C\equiv\overset{+}{O} \longleftrightarrow R-\overset{+}{C}=O$$

I II

As relatively weak electrophiles, acyl ions, such as the acetyl cation CH_3CO^+ (**1**), generally do not react with highly deactivated arenes (*e.g.*, nitrobenzene) or saturated hydrocarbons. It was found, however, that the reactivity of acyl ions is greatly enhanced in a strongly acidic medium. Shudo *et al.*[5] have shown that Friedel−Crafts type acetylation of benzene and chlorobenzene with acetyl hexafluoroantimonate ($CH_3CO^+SbF_6^-$) is greatly enhanced when superacidic CF_3SO_3H is used as the solvent instead of the relatively weak CF_3COOH.



Brouwer and Kiffen[6] have reported the hydride transfer from isobutane to the acetyl cation generated from acetic acid in excess superacidic HF−BF_3. Subsequently, Olah *et al.*[7] found that such reaction does not occur with isolated acylium salts in the absence of superacids in a variety of aprotic solvents such as SO_2, SO_2ClF, AsF_3, and CH_2Cl_2.

To account for the enhanced reactivity of acyl cations under superacid conditions, Olah[7] suggested that the *de facto* reactive intermediate in these reactions is not the acyl cation itself, but rather its O-protonated (*i.e.*, *protosolvated*) form CH_3COH^{2+} (**2**). Protolytic activation of the acetyl ion leads to a highly electron-deficient, *superelectrophilic*, gitonic dication, which is substantially more reactive than its parent monocation.[8]

Vol'pin *et al.* have done extensive work on the activation of acyl ions by Lewis acids.[9] While the 1:1 $CH_3COX-AlX_3$ Friedel−Crafts complex is inactive for the isomerizations of alkanes, the complex $CH_3COX-2AlX_3$ (named "aprotic superacid") containing 2 equiv of AlX_3 was found to be extremely reactive in the low-temperature isomerization of saturated hydrocarbons.[10] Their results indicate that the acetyl cation is highly activated by further O-complexation with a second molecule of AlX_3. Theoretical calculations at the HF/6-31G* level have shown that O-protonation of the acetyl ion leads to a stable dication, $CH_3-{}^+C=O^+-H$, corresponding to the global minimum on the potential energy surface.[11] This agrees with charge-stripping mass spectrometric studies in which the $C_2H_4O^{2+}$ dication has been observed.[12] Interestingly, it was found that the isomer protonated at the C−H bond, ${}^+CH_4-C^+=O$, is 24.6 kcal/mol less stable than the O-protonated acetyl cation.[11]

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(1) Onium Ions. Part 47. Part 46: Wang, Q.; Zhang, H.; Prakash, G. K. S.; Hogen-Esch, T. E.; Olah, G. A. *Macromolecules,* in press.

(2) Olah, G. A. *Friedel-Crafts Chemistry*; Wiley-Interscience: New York, 1973.

(3) Seel, F. Z. *Anorg. Allg. Chem.* **1943**, *250*, 331.

(4) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985.

(5) Sato, Y.; Yato, M.; Ohwada, T.; Saito, S.; Shudo, K. *J. Am. Chem. Soc.* **1995**, *117*, 3037.

(6) Brouwer, D. M.; Kiffen, A. A. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 689.

(7) Olah, G. A.; Germain, A.; Lin, H. C.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 2928.

(8) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.

(9) Vol'pin, M.; Akhrem, I.; Orlinkov, A. *New J. Chem.* **1989**, *13*, 771.

(10) Akhrem, I. S.; Orlinkov, A. V.; Afanaseva, L. V.; Vol'pin, M. E. *Dokl. Acad. Nauk SSSR* **1988**, *298* (1), 107.

(11) Lammertsma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4619.

(12) Koch, W.; Frenking, G.; Schwarz, H.; Maquin, F.; Stahl, D. *Int. J. Mass Spectrom. Ion Processes* **1985**, *63*, 59.

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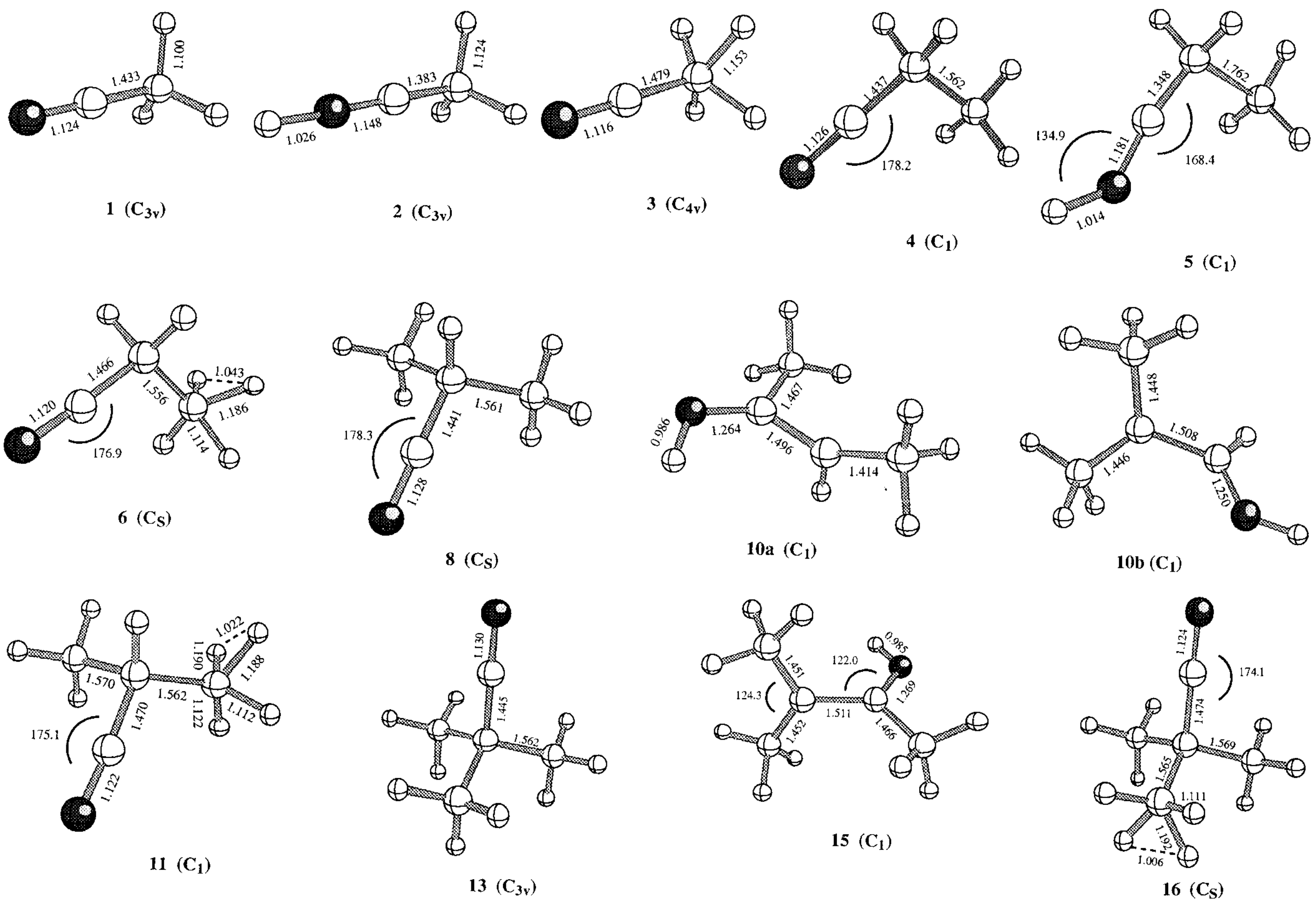


Figure 1. B3LYP/6-31G** optimized geometries of acyl cations and their protonated forms.

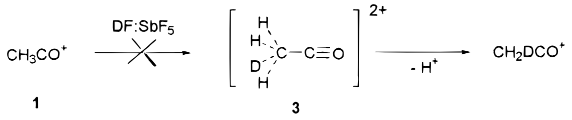
Whereas both experimental and theoretical evidence has been established for the activation of acyl ions by O-protonation, the possibility of C—H protonation in these ions has never been studied experimentally. C—H protonation in acyl ions would lead to highly reactive dications of the type $^{+}RH{-}C^{+}{=}O$ involving a three-center two-electron (3c−2e) bond. Recently,[13,14] we have been able to show by hydrogen/deuterium exchange experiments and theoretical calculations that long-lived stable alkyl cations, such as *tert*-butyl and 2-propyl cations, can undergo C—H protonation to form highly electron deficient protioalkyl dications. Now we report the observation of hydrogen/deuterium exchange by ^{2}H-NMR spectroscopy at the CH_3 groups of the long-lived acylium ions $CH_3CH_2CO^+$ (**4**), $(CH_3)_2CHCO^+$ (**8**), and $(CH_3)_3CCO^+$ (**13**) when treated with excess DF·SbF$_5$ superacid. Protio (deuterio) solvation involving the intermediacy of the corresponding highly electron deficient protio(deuterio)acylium dications is suggested to account for the exchanges. Furthermore, *density functional theory (DFT)* calculations at the B3LYP/6-31G** level were carried out to investigate the suggested mechanism for the observed exchanges. On the basis of the calculated results, two alternative mechanisms are suggested for the Nenitzescu rearrangement[15] of pivaloyl chloride in isobutane with excess $AlCl_3$.

Results and Discussion

In order to investigate the protonation of acylium cations including C—H and C═O bond protonation, we have attempted to observe hydrogen/deuterium exchange in acylium ions CH_3CO^+ (**1**), $CH_3CH_2CO^+$ (**4**), $(CH_3)_2CHCO^+$ (**8**), and $(CH_3)_3CCO^+$ (**13**) when treated with excess DF·SbF$_5$ superacid. Under superacid conditions, acyl cations do not show any deprotonation equilibrium to form the corresponding ketene.[16] In fact, DF·SbF$_5$ is one of the strongest superacid systems known.[4] Thus, the observed hydrogen/deuterium exchange in acylium ions under these conditions therefore cannot proceed via a deprotonation−reprotonation mechanism, but would involve the protonation of a C—H bond to form dication intermediates containing a three-center two-electron (3c−2e) bond.

To gain better insight into the effect of protosolvation on the structure of acylium cations, DFT calculations were carried out on the parent acylium ions and their protonated forms. Geometry optimizations were initially performed at the B3LYP/6-31G* level and subsequently at the B3LYP/6-31G** level. Geometries are summarized in Figure 1. Total energies (−au), ZPEs (kcal/mol), proton affinities (kcal/mol), and relative energies (kcal/mol) of the ions are given in Table 1.

Protonation (Deuteriation) of Acetyl Cation CH_3CO^+. Acetyl hexafluoroantimonate was treated with excess DF·SbF$_5$ superacid at 20 °C. No hydrogen/deuterium exchange was observed by ^{2}H-NMR even after 4 weeks.



Attempted proton/deuterium exchange in weaker acids such as CF_3SO_3D or D_2SO_4 was also not successful. Under these

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[13] Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1993**, *115*, 6985.

[14] Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S.; Burkhart, M.; Lammertsma, K. *J. Am. Chem. Soc.* **1994**, *116*, 3187.

[15] Balaban, A. T.; Nenitzescu, C. D. *Justus Liebigs Ann. Chem.* **1959**, *625*, 66.

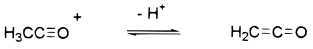
[16] Olah, G. A.; Alemayehu, M.; Wu, A.; Farooq, O.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 8042.

Table 1. Total Energies (−au), ZPEs (kcal/mol), Proton Affinities (kcal/mol), and Relative Energies (kcal/mol) of Acyl Cations and Their Protonated Forms[a]

molecule	B3LYP/ 6-31G*	B3LYP/ 6-31G**	ZPE[b]	E_{rel}[c]	PA[d]
1 (CH_3CO^+)	152.923 54	152.928 18	27.0	0.0	−25.8
2 (CH_3COH^{2+})	152.877 17	152.8886 1	29.5	27.3	
3 (CH_4CO^{2+})	152.849 67	152.858 95	29.8	46.2	
4 ($CH_3CH_2CO^+$)	192.246 65	192.253 89	44.6	0.0	9.4
5 ($CH_3CH_2COH^{2+}$)	192.224 77	192.238 93	47.7	12.5	
6 ($CH_4CH_2CO^{2+}$)	192.256 58	192.270 68	47.2	−7.9	
8 ($(CH_3)_2CHCO^+$)	231.5686 4	231.578 60	61.7	0.0	16.4
10a ($(CH_3)_2CC(OH)H^{2+}$)	231.628 35	231.645 37	65.5	−38.1	
10b ($CH_3CHC(OH)CH_3{}^{2+}$)	231.618 58	231.635 81	64.8	−32.8	
11 ($CH_3(CH_4)CHCO_2{}^+$)	231.588 73	231.606 04	64.0	−14.9	
13 ($(CH_3)_3CCO^+$)	270.889 40	270.902 12	78.6	0.0	22.5
15 ($(CH_3)_2CC(OH)CH_3{}^{2+}$)	270.980 43	270.000 56	81.9	−58.5	
16 ($CH_4(CH_3)_2CCO^{2+}$)	270.918 02	270.938 61	80.5	−21.0	

[a] All structures were characterized as minima on the potential energy surface (NIMAG = 0). [b] Zero-point vibrational energies at the B3LYP/6-31G*//B3LYP/6-31G* level scaled by a factor of 0.96. [c] Relative energy at the B3LYP/6-31G**// B3LYP/6-31G** + ZPE level. [d] Proton affinity at the B3LYP/6-31G**//B3LYP/6-31G** level and at 300 K: PA = $-\Delta E - \Delta ZPE + (5/2)RT$.

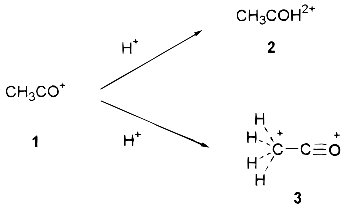
conditions a deprotonation−reprotonation involving ketene was anticipated. However, under these conditions acetyl cation undergoes hydrolysis to acetic acid.



Otvos and his associates[17] have observed such exchange in isobutane in D_2SO_4 involving isobutylene as an intermediate which leads to H/D exchange only on the methyl groups. On the other hand, in deuterated superacids H/D exchange occurs both on methyne and on methyl groups.

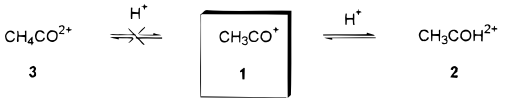
To understand lack of H/D exchange in the acetyl cation, we have carried out theoretical calculations. The structural parameters of acetyl ion CH_3CO^+ (**1**) at the B3LYP/6-31G** level are in agreement with previous[18] *ab initio* calculations at the MP2/6-31G* level and with X-ray structures obtained for salts $CH_3CO^+\ SbCl_6^-$ [19] and $CH_3CO^+\ SbF_6^-$.[20] The calculated C−O bond length of 1.124 Å at the B3LYP/6-31G** level is slightly longer than the experimental value of 1.109 Å in $CH_3CO^+SbCl_6^-$ salt.

Protonation of acetyl ion CH_3CO^+ (**1**) may take place at two different sites. O-protonation of **1** results in the formation of the protioacetyl dication **2**. Protonation of the C−H bond in **1** results in a dication of type **3**.

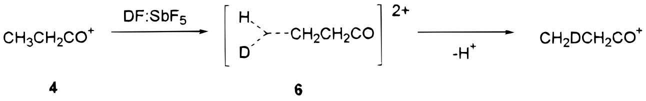


The protioacetyl dication CH_3COH^{2+} (**2**) has been observed[12] in the gas phase by charge-stripping mass spectrometry and has previously[11,21] been calculated at the HF/6-31G* level as the global minimum for $C_2H_4O^{2+}$. We found little change in the geometry of **2** when going from the Hartree−Fock level to the B3LYP level. The C−O bond length of 1.148 Å in **2** at the B3LYP/6-31G** level is essentially the same as that of carbon monoxide (CO), indicating triple bond character. Due to C−H hyperconjugation, a significant shortening of the CH_3−C bond in **2** (1.383 Å) is found as compared to that of the parent acetyl ion **1** (1.433 Å).

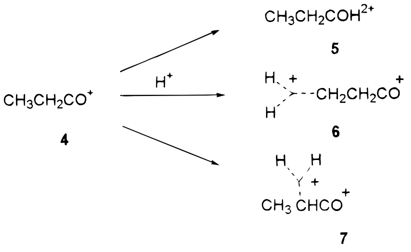
C−H protonation of the acetyl cation **1** leads to dication **3** which was calculated to be a stable minimum at the B3LYP/6-31G** level. In agreement with previous[21] calculations at the HF/6-31G* level, optimization at the B3LYP/6-31G** level gave a C_{4v} structure with no localized 3c−2e bonds. Optimization at the correlated MP2/6-31G* level also resulted in a C_{4v} structure for dication **3**. At the B3LYP/6-31G** level, dication **3** was found to be 18.9 kcal/mol less stable than the O-protonated isomer **2**. This is consistent with the lack of any observable hydrogen/deuterium exchange in acetyl ion **1** with DF•-SbF_5 since the substantial energy difference between dications **2** and **3** suggests the absence of C−H protonation (deuteriation).



Protonation (Deuteriation) of Propionyl Cation $CH^3CH_2CO^+$. Propionyl chloride (CH_3CH_2COCl) was reacted with DF•SbF_5 solution at 20 °C, and the resulting long-lived stable propionyl cation $CH_3CH_2CO^+$ (**4**) was characterized by ^{1}H- and ^{2}H-NMR spectroscopy (δ(^{1}H) 3.26, qt; 1.09, tr). The solution was kept at 20 °C, and no decomposition of the ion was observed under these conditions. Hydrogen/deuterium exchange at the methyl positions in ion **4** was observed by ^{2}H-NMR as indicated by a peak at 1.11 ppm whose intensity increased with time. After 12 days, about 2.5% deuterium incorporation at the CH_3 groups in **4** was observed (determined using external acetone-d_6 standard). No exchange was found at the methylene hydrogens in **4**. The intermediacy of the C−H deuterated propionyl cation **6** is considered to account for the observed exchange at the methyl position in **4**.



The geometry of propionyl cation $CH_3CH_2CO^+$ (**4**) at the B3LYP/6-31G** level is in agreement with previous[18] *ab initio* calculations at the Hartree−Fock level and with an X-ray structure obtained[22] for the salt $CH_3CH_2CO^+GaCl_4^-$. The calculated C−O bond length of 1.126 Å in **4** agrees well with the experimental value of 1.099 Å in $CH_3CH_2CO^+GaCl_4^-$. Protonation of propionyl ion $CH_3CH_2CO^+$ (**4**) can take place at three different sites. O-protonation of **4** results in the formation of gitonic[8] dication **5**. C−H protonation at the methyl position in **4** results in a distonic[8] dication of type **6**, whereas C−H protonation at the methylene position leads to a gitonic dication of type **7**.



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(17) Otvos, J. W.; Stevenson, D. P.; Wagner, C. D.; Beeck, O. *J. Am. Chem. Soc.* **1951**, *73*, 5741.

(18) Lien, M. H.; Hopkinson, A. C. *J. Org. Chem.* **1988**, *53*, 2150.

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

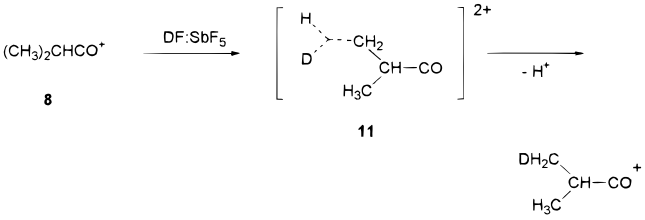
(20) Boer, F. P. *J. Am. Chem. Soc.* **1966**, *88*, 1572.

(21) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1986**, *108*, 5808.

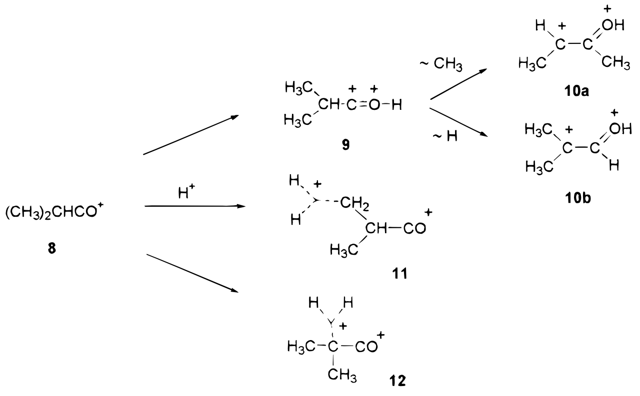
(22) LeCarpentier, J.-M.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 1430.

The global minimum on the potential energy surface for $C_3H_6O^{2+}$ at the B3LYP/6-31G** level is the C−H protonated isomer **6**, being 20.4 kcal/mol more stable than the O-protonated isomer **5**. Dication **6** (C_s symmetry) has a 3c−2e bond in its minimum energy structure. The O-protonated isomer **5** is characterized by a significant shortening of the CH_3−C bond in **5** (1.348 Å) as compared to that of the parent propionyl ion **4** (1.437 Å) due to C−H and C−C hyperconjugation. The C−O bond length of 1.181 Å in **5** is essentially the same as that of carbon monoxide CO (1.188 Å at the B3LYP/6-31G** level), indicating triple bond character. No minimum structure could be located for the methylene C−H protonated isomer **7** at B3LYP/6-31G** level because of its immediate dissociation into ions CH_3CO^+ and CH_3^+. As expected, and consistent with the observed hydrogen/deuterium exchange, the C−H protonated propionyl dication **6** is better stabilized compared to the C−H protonated acetyl dication **3** due to less charge−charge repulsion.

Protonation (Deuteriation) of Isobutyryl Cation $(CH_3)_2CHCO^+$. Isobutyryl ion $(CH_3)_2CHCO^+$ (**8**) was obtained by reacting isobutyryl chloride with excess DF•SbF_5 solution at −10 °C. The long-lived stable ion was characterized by ^{1}H- and ^{2}H-NMR spectroscopy (δ(^{1}H) 3.50, sep; 1.12, d), and no decarbonylation reaction to form the corresponding secondary carbocation was observed under these conditions. Hydrogen/deuterium exchange at the methyl positions in ion **8** was observed by ^{2}H-NMR as indicated by a peak at 1.18 ppm whose intensity increased with time. After 12 days, about 3% deuterium incorporation at the methyl positions in **8** was observed. No exchange was found at the methyne hydrogen in **8**. The intermediacy of the C−H deuterated propionyl cation **11** is suggested to account for the observed exchange at the methyl position in **8**.

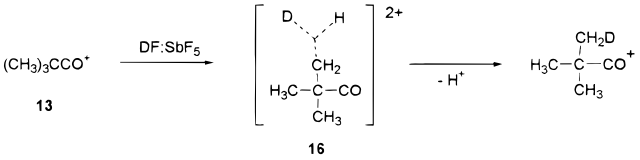


Protonation of isobutyryl ion $(CH_3)_2CHCO^+$ (**8**) may result in three different dications: O-protonated gitonic dication **9**, C−H protonated distonic dication **11**, and C−H protonated gitonic dication **12**.

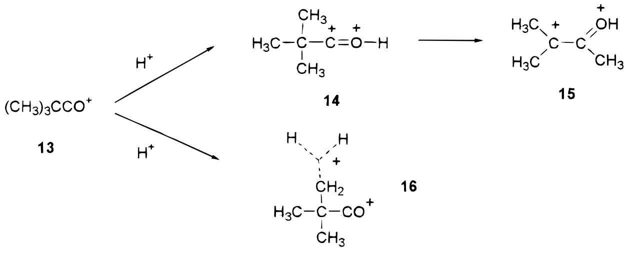


The geometry of isobutyryl ion $(CH_3)_2CHCO^+$ (**8**) at the B3LYP/6-31G** level is in agreement with previous[23] *ab initio* calculations at the HF/3-21G* level and with an X-ray structure obtained[22] for the salt $(CH_3)_2CHCO^+SbCl_6^-$. Attempts to find a stable minimum for the O-protonated species **9** failed because of rearrangement (methyl shift) to form the more stable oxocarbenium dication **10a**. Alternatively, and thermodynamically even more favorable, **9** can undergo a hydride shift to form oxocarbenium ion **10b**, which was found to be the global minimum on the $C_4H_8O^{2+}$ surface (*vide infra*). C−H protonation at the methyl positions, however, leads to a stable distonic dication, **11**, at the B3LYP/6-31G** level, which is characterized by a 3c−2e bond at the CH_3 carbon. The C−O bond length of 1.122 Å resembles that of carbon monoxide (1.188 Å at the B3LYP/6-31G** level) and indicates triple bond character. The methylene C−H protonated isomer **12** was found not to be a stable minimum structure at the B3LYP/6-31G** level because of its dissociation into ions $CH_3CH_2CO^+$ and CH_3^+ similar to the propionyl system.

Protonation (Deuteriation) of Pivaloyl Cation (CH^3)$_3$CCO$^+$. Pivaloyl chloride ($(CH_3)_3CCOCl$) was reacted with DF•SbF_5 solution at −10 °C, and the resulting long-lived stable pivaloyl cation $(CH_3)_3CCO^+$ (**13**) was characterized by ^{1}H- and ^{2}H-NMR spectroscopy (δ(^{1}H) 1.13, s). The solution was kept at −10 °C, and no decarbonylation of the acylium ion to form *tert*-butyl cation was observed under these conditions. Hydrogen/deuterium exchange at the methyl positions in ion **13** was observed by ^{2}H-NMR as indicated by a peak at 1.11 ppm whose intensity increased with time. After 8 days, about 3.5% deuterium incorporation at the methyl positions in **13** was observed. The intermediacy of the C−H deuterated propionyl dication **16** is considered to account for the observed exchange at the methyl position in **13**.



In theory, protonation of pivaloyl cation $(CH_3)_3CCO^+$ (**13**) can occur at two different sites. O-Protonation of **13** results in the formation of gitonic dication **14**. Protonation of the methyl C−H bond in **13** leads to a distonic dication of type **16**.



The pivaloyl cation $(CH_3)_3CCO^+$ (**13**) has previously been calculated by *ab initio* methods at a low level of theory.[24] Attempts to find a stable minimum at the B3LYP/6-31G** level for the O-protonated species **14** failed because of spontaneous rearrangement to form the thermodynamically more stable oxocarbenium dication **15**, which was found to be the global minimum on the $C_5H_{10}O^{2+}$ surface. C−H protonation at the methyl positions, however, leads to a stable distonic dication, **16**, at the B3LYP/6-31G** level with a 3c−2e bond at the CH_3 carbon. The C−O bond length of 1.124 Å resembles that of carbon monoxide (1.188 Å at the B3LYP/6-31G** level) and indicates triple bond character.

In 1959 *Balaban and Nenitzescu*[15] reported the formation of methyl isopropyl ketone in the reaction of pivaloyl chloride with

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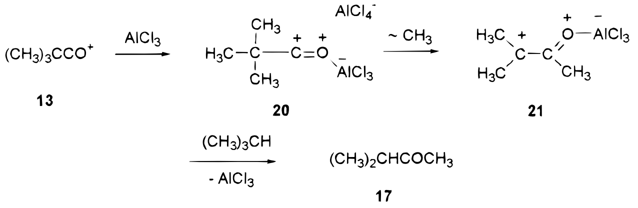
(23) Bouchoux, G.; Hoppiliard, Y. *J. Phys. Chem.* **1988**, *92*, 5869.

(24) Radom, L. *Aust. J. Chem.* **1974**, *27*, 231.

Scheme 1



a large excess of aluminum chloride in the presence of isobutane as the hydride donor. The reaction was carried out at room temperature and under CO pressure (140 atm) in order to suppress decarbonylation of the pivaloyl chloride. When $SnCl_4$ was used instead of $AlCl_3$, no rearrangement product was observed.

$$(CH_3)_3CCOCl \xrightarrow[\text{isopentane}]{AlCl_3\ \text{(excess)}} (CH_3)_2CHCOCH_3$$

17

Two possible reaction mechanisms were proposed.[15] The first mechanism involves the initial ionization of pivaloyl chloride to pivaloyl cation **13** which then undergoes a 1,2 methyl shift to form the corresponding tertiary carbenium ion **18**. Hydride abstraction from isopentane finally leads to the formation of methyl isopropyl ketone (**17**).

$$(CH_3)_3CCO^+ \xrightarrow{\sim CH_3} (CH_3)_2\overset{+}{C}COCH_3 \xrightarrow{H^-} (CH_3)_2CHCOCH$$

13 **18** **17**

Alternatively, it was suggested hydride abstraction from isopentane can also occur right after the initial formation of pivaloyl cation **13** to form trimethyl acetaldehyde (**19**). Rearrangement of **19** then leads to the formation of methyl isopropyl ketone (**17**). Both mechanisms, however, appear to be endothermic as proposed.

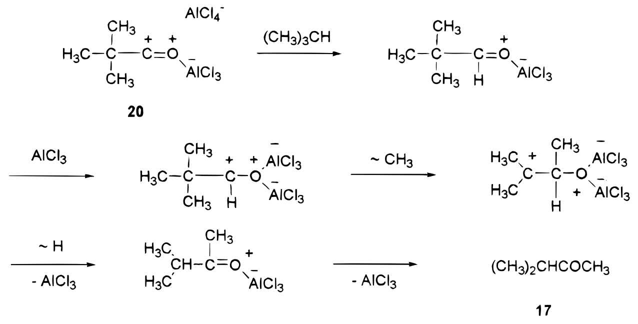
$$(CH_3)_3CCO^+ \xrightarrow{H^-} (CH_3)_3CCHO \xrightarrow{\sim} (CH_3)_2CHCOCH_3$$

13 **19** **17**

On the basis of our theoretical calculations, we now suggest two alternative pathways for the Nenitzescu[25] rearrangement. Our calculations at the B3LYP/6-31G** level have shown that O-protonated pivaloyl cation **14** immediately rearranges into the more stable distonic dication **15**. Rearrangement of pivaloyl cation **13** to form carbenium ion **18**, on the other hand, is thermodynamically unfavorable by 15.6 kcal/mol at thee B3LYP/6-31G** level of theory. These results could inidicate that the pivaloyl cation **13** formed initially in the reaction is highly activated by further O-complexation with a second molecule of $AlCl_3$ (the equivalent of protonation or protosolvation). The aprotic superacid complex **20** thus formed readily undergoes a 1,2 methyl shift to form the more stable complex **21** (Scheme 1). Finally, hydride abstraction from isopentane leads to the observed methyl isopropyl ketone **17**. This pathway would also explain the fact that no rearrangement product was observed when the weaker Lewis acid $SnCl_4$ was used instead of $AlCl_3$.

Alternatively, **20** could directly hydride abstract to $AlCl_3$-complexed pivaldehyde which upon further $AlCl_3$ activation undergoes consecutive CH_3 and H shifts to give finally the isopropyl methyl ketone (**17**) (Scheme 2).

Scheme 2



In fact, Olah *et al.* have previously[26] shown that protonated pivaldehyde rearranges to protonated isopropyl methyl ketone in strong superacids such as Magic Acid (1:1 molar $FSO_3H\cdot SbF_5$). On the other hand, in weaker Magic Acid (4:1 molar $FSO_3H\cdot SbF_5$) only protonated pivaldehyde was observed, indicating clearly protolytic activation in the stronger acid which promotes rearrangement.

Conclusions

Hydrogen/deuterium exchange was observed by ^2H-NMR spectroscopy at the CH_3 groups of the long-lived acylium ions $CH_3CH_2CO^+$ (**4**), $(CH_3)_2CHCO^+$ (**8**), and $(CH_3)_3CCO^+$ (**13**) when treated with excess $DF\cdot SbF_5$ superacid. C−H bond protonation/deuteriation involving the intermediacy of the corresponding protio(deuterio)acylium dications is suggested to account for the exchanges. Under similar conditions, no exchange was observed in the acetyl ion CH_3CO^+ (**1**) in $DF\cdot SbF_5$. The lack of hydrogen/deuterium exchange in CH_3CO^+ (**1**) is consistent with theoretical calculations at the B3LYP/6-31G** level which showed that the O-protonated isomer CH_3COH^{2+} (**2**) is more stable by 18.9 kcal/mol as compared to the C−H protonated isomer CH_4CO^{2+} (**3**), resulting in greatly increased electrophilic reactivity. On the basis of the calculated results, two alternative mechanisms are suggested for the Nenitzescu[15] rearrangement of pivaloyl chloride in isobutane with excess $AlCl_3$, which involves the activation of pivaloyl cation **13** by further O-complexation with a second molecule of $AlCl_3$ to form the aprotic superacid complex **20** which further either hydride abstracts or rearranges to finally give the isopropyl methyl ketone product.

Experimental Section

Propionyl chloride, isobutyryl chloride, and pivaloyl chloride are commercially available products (Acros) and were distilled prior to use. Anhydrous HF (Setic Labo), D_2O (Acros), CF_3SO_3D (Aldrich), D_2SO_4 (Aldrich), and benzoyl chloride (Lancaster) were used as received. Antimony pentafluoride (Allied-Chemical) was doubly distilled prior to use. $CH_3CO^+SbF_6^-$ was prepared from acetyl chloride and anhydrous hexafluoroantimonic acid as described previously.[27] DF was prepared from benzoyl fluoride and D_2O as reported.[28] Benzoyl fluoride was prepared from benzoyl chloride and anhydrous HF as reported.[29]

^1H and ^2H NMR spectra were obtained on a Bruker AM 400 spectrometer equipped with a variable temperature probe at 400 and 61.4 MHz, respectively. Five millimeter Quartz NMR tubes were used for samples containing DF. NMR spectra were obtained with respect to TMS by using an acetone-d_6 capillary as the external standard.

Geometries and structures were determined by DFT[30] methods using the GAUSSIAN 94[31] package of programs. All geometries were fully

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(25) Nenitzescu, C. D.; Balaban, A. T. In *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley: New York, 1964; Vol. III (No. 1), pp 1033−1152.

(26) Olah, G. A.; O'Brien, D. H.; Calin, M. *J. Am. Chem. Soc.* **1967**, *89*, 3582.

(27) Olah, G. A.; Svoboda, J. *Synthesis* **1972**, 306.

(28) Olah, G. A.; Kuhn, S. J. *Z. Anorg. Allg. Chem.* **1956**, *287*, 282.

(29) Olah, G. A.; Kuhn, S. J. *Org. Synth.* **1965**, *45*, 3.

optimized at the B3LYP/6-31G** level. Zero-point vibrational energies at the B3LYP/6-31G* level were scaled by a factor of 0.96.

H/D Exchange Experiments with DF·SbF$_5$. The appropriate precursor (ca. 150 mg) was placed in a Kel-F tube and cooled to −78 °C in a dry ice/acetone bath. Approximately 2 mL of DF·SbF$_5$ (2.5:1 molar solution) was added to the solution at −78 °C. The ensuing mixture was vigorously stirred (Vortex stirrer) under periodic cooling. After the sample was characterized by ^{1}H- and ^{2}H-NMR spectroscopy at −15 °C, it was kept at constant temperature (see the text) and periodically monitored by ^{1}H- and ^{2}H-NMR spectroscopy.

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(30) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(31) *Gaussian 94*, Revision A.1: Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T. A., Peterson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. J. P., Head-Gordon, M., Gonzalez, C., Pople, J. A., Eds.; Gaussian, Inc.: Pittsburgh, PA, 1995.