Carbocationic Rearrangement of Pivaloyl Cation and Protonated Pivalaldehyde in Superacid Medium: A Novel Solution Equivalent of the McLafferty Rearrangement

George A. Olah, Thomas Mathew, Alain Goeppert, Golam Rasul, and G. K. Surya Prakash

Department of Chemistry, Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California, USA

Pierre Mothé Esteves

Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

Both pivaloyl cation in the presence of hydride donors and protonated pivalaldehyde in superacid media (both aprotic and protic) rearrange to protonated methyl isopropyl ketone involving gitionic dicationic intermediates. In our earlier studies we have found that the rearrangement of pivaladehyde to methyl isopropyl ketone occurs quantitatively in the presence of various superacidic media such as anhydrous HF, triflic acid, boron trifluoride-2,2,2-trifluoroethanol complex (BF_3·$2CF_3CH_2OH$) etc. Our present study with environmentally more benign and stable amine:HF complexes, namely pyridinium poly(hydrogen fluoride) (**PPHF**) (**5**), poly(4-vinylpyridinium) poly(hydrogen fluoride) (**6**), and poly(ethyleniminium) poly(hydrogen fluoride) (**PEIHF**) (**7**) shows that these modified HF equivalents can carry sufficient amount of immobilized HF and provide ample acidity for complete isomerization of pivalaldehyde to methyl isopropyl ketone. Calculations on protioformyl, acetyl and pivaloyl dications at the B3LYP/6-311 ++ G(d,p) and CCSD(T)/6-311 ++ G(d,p)//B3LYP/6-311 ++ G(d,p) levels have been performed to compare the nature of protosolvation of formyl, acetyl, pivaloyl cations and protonated pivaladehyde in superacid media. These studies further suggest protosolvation of protonated pivalaldehyde leading to gitionic dications at high acidities resulting in the carbocatioinic rearrangement. The reported carbocationic rearrangement under superacidic activation represents a novel solution chemistry equivalent of the well known gas-phase McLafferty rearrangement. (J Am Soc Mass Spectrom 2004, 15, 959–965) © 2004 American Society for Mass Spectrometry

Reactivity of acylium ions have been extensively studied in Friedel-Crafts chemistry [1]. Being generally weak in elecrophilic nature, acyl cations such as acetyl cation are relatively less reactive towards deactivated aromatics. However, it has been shown that the reactivity of these electrophiles can be greatly enhanced by using superacidic solvents such as trifluoromethanesulfonic (triflic) acid [2]. Also the acylium salts in superacid media are found to be excellent acylating agents for deactivated aromatics. However, Olah et al. have shown that such reactions do not take place with acylium salts themselves in the absence of superacids in aprotic solvents such as SO_2, SO_2ClF, AsF_3, or CH_2Cl_2 [3].

As we have shown earlier [4, 5], the rearrangement of pivalaldehyde to methyl isopropyl ketone is strictly dependent on the acidity of the medium. Since pivalaldehyde and pivaloyl cation differ only by a hydride ion, it was worthwhile studying by theoretical methods the nature and reactivity of the pivaloyl ion under superacidic conditions as well as in the presence of hydride donors. Unlike protonated (protosolvated) acetylium ion, protonated (protosolvated) trimethylacetylium ion undergoes rearrangement followed by hydride abstraction to give protonated methyl isopropyl ketone under optimal acidic conditions. Trimethylacetyl cation (pivaloyl cation), pivalaldehyde and methyl isopropyl ketone behave in a highly complementary

Published online June 9, 2004

This article is dedicated to Professor McLafferty with friendship and admiration.

Address reprint requests to Dr. G. A. Olah, Department of Chemistry, Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, CA 90089-1661, USA. E-mail: olah@usc.edu

1044-0305/04/$30.00
doi:10.1016/j.jasms.2004.05.002

Received January 19, 2004
Revised April 30, 2004
Accepted May 3, 2004

manner under superacidic conditions. The optimal acidity for the complete rearrangement of pivalaldehyde into methyl isopropyl ketone was found to be at a H_o value of -11[4] close to the Bronsted superacidity limit of -12. Rearrangement of pivalaldehyde (1) to methyl isopropyl ketone (2) has been reported with aluminium chloride and H_2SO_4 [6]. Danilov obtained methyl isopropyl ketone by the reaction of pivalaldehyde in 70% sulfuric acid in a sealed tube at 130 °C [7]. We have studied the rearrangement of pivaladehyde to methyl isopropyl ketone in the presence of various superacidic media such as anhydrous HF, triflic acid, boron trifluoride-2,2,2-trifluoroethanol complex ($BF_3.2CF_3CH_2OH$) etc. [4]. In this paper we report the rearrangement of pivalaldehyde to methyl isopropyl ketone with stable amine:HF complexes. We would like to report a comparitive study of the nature of formyl, acetyl, and pivaloyl cations and protonated pivaladehyde in superacid media using DFT theory emphasizing on the observed acidity requirements for the rearrangement of pivaloyl cation in the presence of hydride donor and protonated pivaladehyde.

Experimental

Materials

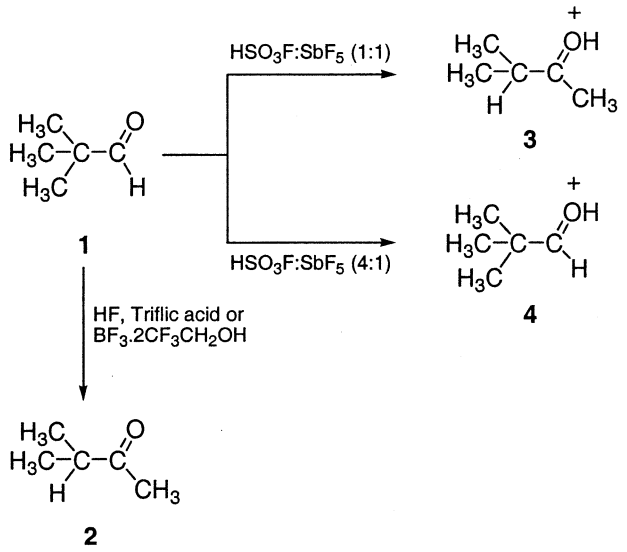
Pyridine, poly(4-vinylpyridine) (2% cross linked), poly(ethylenimine) and pivalaldehyde (all from Aldrich, Milwaukee, WI) were used as received. Anhydrous HF (AHF, Matheson, Newark, CA) was liquified in Nalgene bottles in acetone-dry ice bath (−78 °C) and then used. HF based reagents are quite corrosive and toxic and should be handled with care. The reactions were carried out with well ventilated hoods with proper hand and face protection.

Typical Procedure for the Pivalaldehyde Rearrangement

To a solution of pivalaldehyde (300 mg, 3.5 mmol) in CH_2Cl_2 (4 mL) in a 30 mL Nalgene bottle at 0 °C, 5 g of the acid catalyst (amine:HF complex) was added. The ice bath was removed and the reaction mixture was stirred for 4 hrs at room temperature (22 °C). The mixture was poured slowly and carefully into a minimum amount of ice, neutralized with sodium bicarbonate and extracted with CH_2Cl_2. After drying with $MgSO_4$, CH_2Cl_2 solution was analysed by GC using authentic samples. Quantitative isomerization was observed in each case.

Instrumentation

Analyses were carried out using GC (Varian 3000, 30m DB-5 capillary) and GC/MS (HP-5890 Series II coupled with HP-5971 Series MSD).^{1}H and ^{13}C NMR spectra were obtained on a Varian VXR 300 MHz spectrometer in $CDCl_3$ using TMS as internal standard.



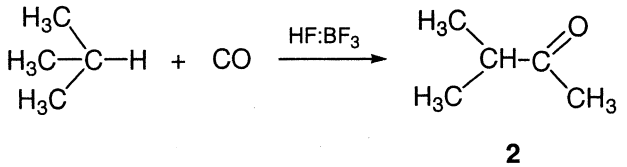
Scheme 1

DFT and Ab Initio Calculations

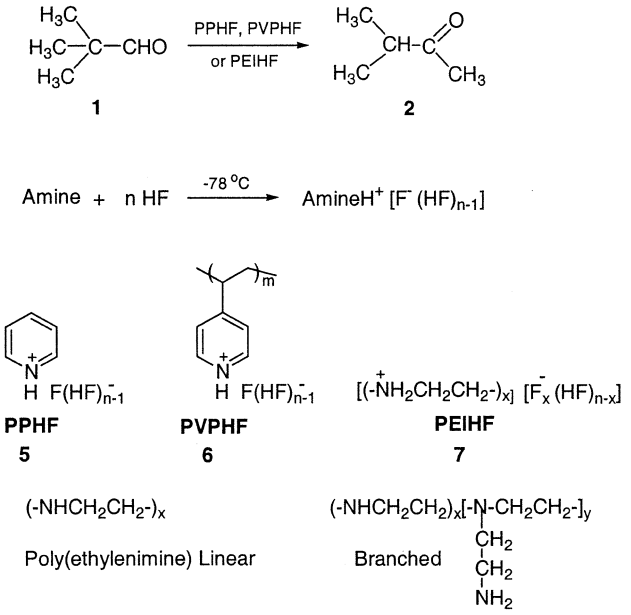
All calculations were performed using the Gaussian 98 program [8]. Geometries of all species investigated were fully optimized at the B3LYP/6-311 ++ G(d,p) level and were characterized as intermediates or transition states on the potential energy surface by the absence or presence of imaginary frequencies, respectively, after vibrational analysis on the optimized geometries. Zero point energies (ZPE) and thermal corrections at 298 K were calculated using the frequencies computed at the B3LYP/6-311 ++ G(d,p) level. Single point energy calculations were carried out at the CCSD(T)/6-311 ++ G(d,p)//B3LYP/6-311 ++ G(d,p) level. Reaction and relative energies refer to enthalpy differences at 298.15 K and 1 atm.

Results and Discussion

In 1967, Olah et al. [9], reported studies on a series of protonated aliphatic aldehydes by low temperature ^{1}H-NMR using the HSO_3F-SbF_5-SO_2 superacid system. In the case of pivalaldehyde using a HSO_3F-SbF_5 (1:1) acid mixture in SO_2 solution at −60 °C, no protonated pivalaldehyde signals were observed and, instead, peaks due to protonated methyl isopropyl ketone (**3**) were observed (Scheme **1**). Protonated pivalaldehyde (**4**) was prepared in a less acidic HSO_3F-SbF_5 (4:1) mixture in SO_2 at −70 °C.

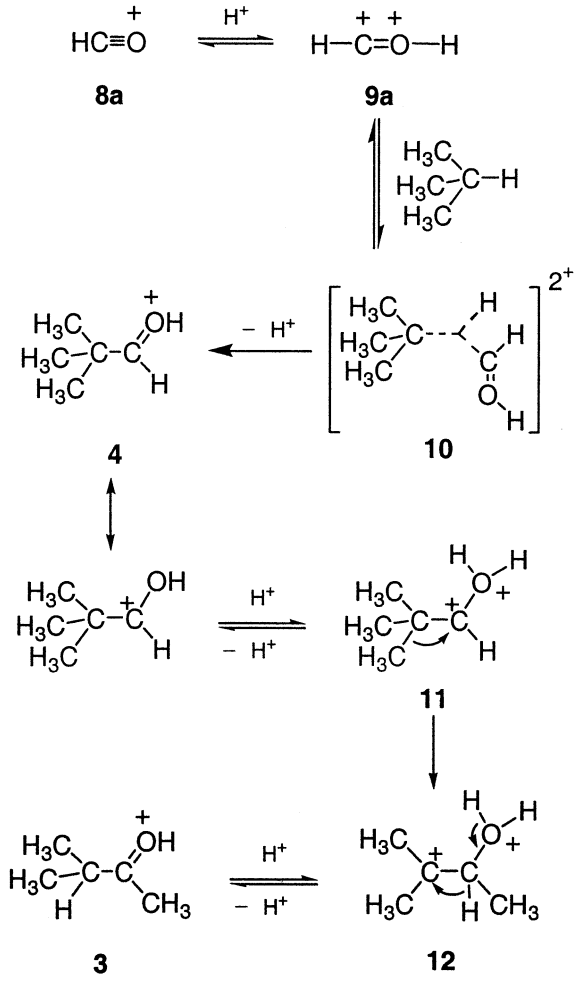


Scheme 2



Scheme 3

We have recently found that isobutane undergoes formylation and rearrangement with CO in the presence of $HF.BF_3$ (1:1) to give methyl isopropyl ketone (**2**) in high yield and high selectivity (Scheme **2**) [10]. We suggested that the reaction proceeds through the intermediacy of gitionic diprotonated pivalaldehyde, which undergoes subsequent rearrangement to methyl isopropyl ketone. We explained the effect of acidity on pivalaldehyde rearrangement to methyl isopropyl ketone by monitoring the rearrangement under varying acidities provided by mixtures of trifluoroacetic acid and trifluoromethanesulfonic acid [4].

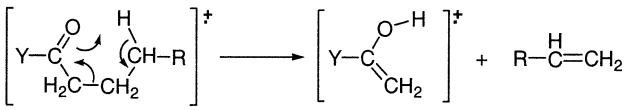


Scheme 4

Rearrangement Study in Amine:HF Complexes

Quantitative isomerization of pivalaldehyde to isopropyl methyl ketone was observed in anhydrous HF ($-H_0$ = 15). However use of liquid hydrogen fluoride carry serious environmental and safety risks. With this in mind, extensive efforts have been made to develop suitable liquid or solid HF based catalysts, which are environmentally more benign and stable [11, 12]. These modified forms of HF, namely, pyridinium poly(hydrogen fluoride) (**PPHF**) (**5**) [13] poly(4-vinylpyridinium) poly(hydrogen fluoride) (**6**) [14], and poly(ethyleniminium) poly(hydrogen fluoride) (**PEIHF**) (**7**) were prepared from pyridine, poly(4-vinylpyridine) and poly(ethylenimine), respectively, to alleviate the volatility and toxicity of anhydrous HF (Scheme **3**). The efficacy of isomerization of pivalaldehyde has been tested with all of these polymeric HF complexes. Since these catalysts were found to carry out isobutane-isobutylene alkylation very efficiently to produce high octane gasoline, it is clear that these systems do possess the required acidity for high octane alkylation process ($-H_0 > 12$) [15] and therefore for the isomerization of pivalaldehyde also. PVPHF (**6**) can be considered a solid HF equivalent and the reaction can be easily carried out at room temperature. In all these cases we have observed quantitative isomerization. We have used amine:HF complexes (1:22 ratio with respect to N) and these were found to give optimum acidity for smooth and complete isomerization. Scheme **3** shows a comparative analysis of the superelectrophilic activation of formyl, acetyl, and pivaloyl cations and protonated pivalaldehyde.

Extensive theoretical as well as experimental studies on the role of various oxonium, sulfonium and carboxonium dications in superacid-catalysed reactions have been carried out recently [16]. In the superelectrophilic formylation of isobutane, the formyl cation in $HF:BF_3$ (1:1) can undergo further protosolvation ($HCO^+ \ldots H^+A^- \approx HC^+{=}O^+H \ldots A^-$) resulting in a very reactive formylating species (a superelectrophile) [10]. The mechanism suggested involves the insertion of protosolvated formyl cation into the tertiary C–H bond (with high σ reactivity) to produce the protonated pivaladehyde species **4**. This can undergo further protosolvation at the required optimum acidity (supplied by $HF:BF_3$

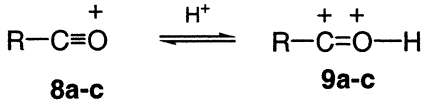


Scheme 5. McLafferty rearrangement.

system) to assist subsequent rearrangement to methyl isopropyl ketone as the final product (Scheme 4).

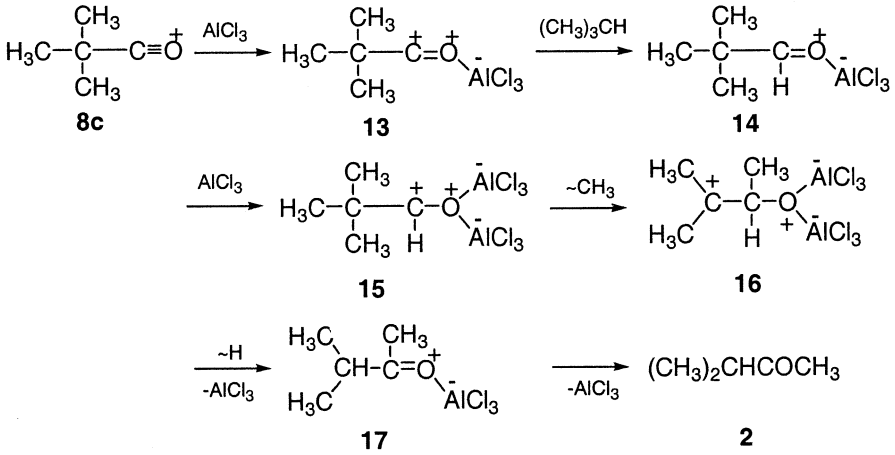
Though pivalaldehyde-methyl isopropyl ketone rearrangement is a carbocationic rearrangement (involving 1,2-hydrogen, methyl shifts) without any skeletal fragmentation, this process is comparable to McLafferty rearrangement (in carbonyl compounds having γ-hydrogen) or various fragmentations of neutral molecules in the gas phase (involving radical cations) [17] (Scheme 5).

Over the past decade Olah et al. have explored extensively the nature and behavior of acyl ions in superacid medium [4, 5, 16, 18]. They suggested that the *de facto* reactive intermediate in the reaction of acyl ions under superacidic conditions is not simple acyl cations itself, but its O-protonated (protosolvated) form R-COH^{2+} (**9a–c**), which is a highly electron deficient superelectrophilic gitonic dication substantially more reactive than its parent monocation [5].

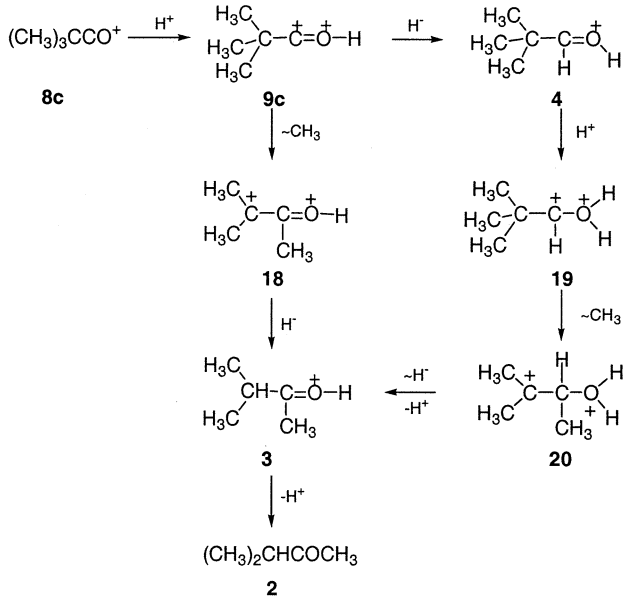


Results obtained during our recent studies on acid catalyzed organic transformations using triflic acid clearly support the superelectrophilic activation of electrophiles in superacidic systems [18–20]. Activation of acyl ions by Lewis acids has been studied extensively by Vol'pin et al. [21] and they found that in the low temperature isomerization of saturated hydrocarbons, a 1:1 CH_3COX-AlX_3 Friedel-Crafts complex was found to be inactive where as CH_3COX-$2AlX_3$ (1:2) complex was found to be highly reactive due to the superelectrophilic character of the acetylium ion by further O-complexation with a second molecule of $AlCl_3$. Theoretical calculations at the HF/6-31G* level have shown that O-protonation of the acetyl ion leads to a stable but highly electron deficient, superelectrophilic gitonic dication, $CH_3-C^+=O^+-H$ (**9b**) which corresponds to a global minimum on the potential energy surface [22]. This is in complete agreement with charge-stripping mass spectrometric studies in which $C_2H_4O^{2+}$ dication has been characterized experimentally [23]. Electron-impact double ionization of dinitrogen pentoxide, N_2O_5, investigated using ion-ion coincidence spectroscopy coupled with time-of-flight mass spectrometry, showed the formation and dissociation of $N_2O_5^{2+}$ dication [24]. Protosolvation of nitronium ion leading to protonitronium dication, NO_2H^{2+} has been identified by Olah et al. [25]. Charge stripping mass spectrometric technique has been effectively used by Schwarz et al. to generate $Cu(H_2O)^{2+}$ and $Cu(NH_3)^{2+}$ dications [26]. Existence of CCl_4^{2+} dications has also been observed during electron ionization of CCl_4 and their gas phase stability has been supported by ab initio MO calculations [27].

Similar to Vol'pin's study, Balaban and Nenitzescu [28] in the late 1950s studied the behavior of the trimethylacetyl chloride (pivaloyl chloride) with a large excess of aluminium chloride in presence of isobutane as hydride donor and observed the formation of methyl isopropyl ketone (**2**). No ketone was isolated when $SnCl_4$ was used instead of $AlCl_3$. One of the two possible mechanisms, based on our theoretical calculations [5], shows that the reaction involves direct hydride abstraction by the O-complexed aprotic superacidic pivaloyl cation-$AlCl_3$ Complex (**13**), followed by further complexation to protosolvated pivalaldehyde-$AlCl_3$ Complex (**15**), which, in turn, undergoes rapid rearrangement to methyl isopropyl ketone (**2**) (Scheme 6).



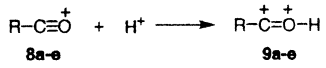
Scheme 6



Scheme 7

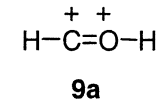
In general, under superacidic conditions protosolvated pivaloyl cation can assume two pathways, either initial 1,2-methyl shift followed by hydride abstraction from the hydride donor to give the protonated methyl isopropyl ketone or the initial hydride abstraction to give protonated trimethylacetaldehyde (pivalaldehyde) followed by further protonation, 1,2-methyl shift, 1,2-hydride shift and deprotonation sequentially to give the protonated methyl isopropyl ketone. Though both the mechanisms appear to be endothermic, previous calculations at the B3LYP/6-31G** level show that the 1,2-gitonic dication (**9c**) undergoes spontaneous rearrangement to form thermodynamically more stable 1,3-distonic dication (oxocarbenium dication) (18) which was found to be the global minimum on the $C_5H_{10}O^{2+}$ surface. Present computational studies at the CCSD(T)/6-311 ++ G(d,p)//B3LYP/6-311 ++ G(d,p) level of the formyl, acetyl, and pivaloyl cations and their protonated forms could explain the properties and behavior during superelectrophilic activation and subsequent changes of these cations in superacid media (Scheme 7).

In order to verify the stability of these species, we have performed high level *ab initio*/DFT calculations, at the CCSD(T)/6-311 ++ G(d,p)//B3LYP/6-311 ++ G(d,p) level, for the protonation of the acyl cations. Results are shown below.

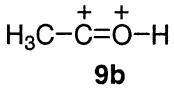


	R	ΔH(25 °C) (kcal/mol)
a	H	70.6
b	CH_3	34.9
c	$(CH_3)_3C$	-1.8
d	CH_3CH_2	22.1
e	$(CH_3)_2CH$	[a]

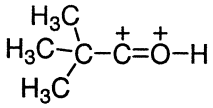
We found that the protonation energies decrease steeply from smaller R groups to bulkier ones. We found that the O-protonated pivaloyl dication (**9c**) is actually not a stable species, rearranging spontaneously to the distonic dication **18**. The data for **9c** above refer to the structures obtained by optimization of the geometry considering symmetry restrictions (C_{3v}). This was done in order to obtain a geometry for the protonated pivaloyl cation, which allows us to estimate the energy for O-protonation, despite the fact that it is not possible to have this species as a true intermediate on the potential energy surface, since it has two imaginary frequencies (NIMAG = 2). It is interesting to note that the pivaloyl cation (**8c**) would be further protonated exothermically if it would be a true intermediate. This indicates that once O-protonation of the pivaloyl cation takes place, the system spontaneously rearranges to the distonic dication, **18**.



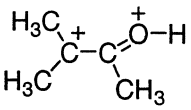
9a



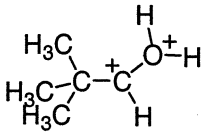
9b



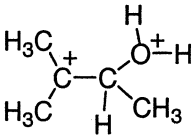
9c



18

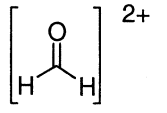


19

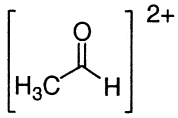


20

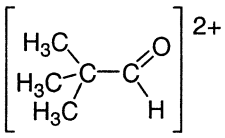
The above diprotonated species are also isomeric to the dications of the parent aldehydes **21**, **22**, and **23**, respectively. In principle, generation of such ions may be possible in the gas phase by double ionization of parent aldehydes.



21



22



23

However, our calculations show that only the dication of formaldehyde (**21**) would be a stable species. Other dications, **22** and **23**, are also susceptible to fragmentation similar to various fragmentation reactions of neutral molecules or molecular ions such as simple bond cleavage, McLafferty rearrangement (in carbonyl compounds having γ-hydrogen), retro-Diels-Alder reactions (in cycloalkenes) etc. due to steric or stability considerations to form stable ion species, which are quite common in the gas phase [17]. Structures **22** and **23** undergo coulombic explosion into R^+ and HCO^+ spontaneously in a barrierless process. Our calculations also show that the rearrangement of **21** into

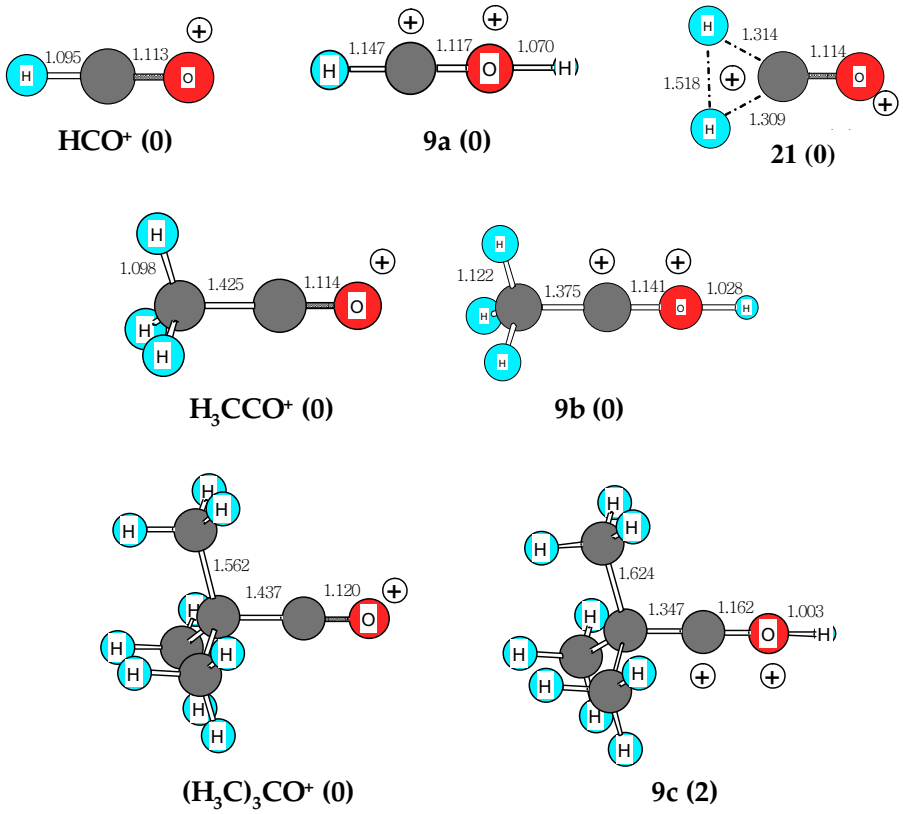


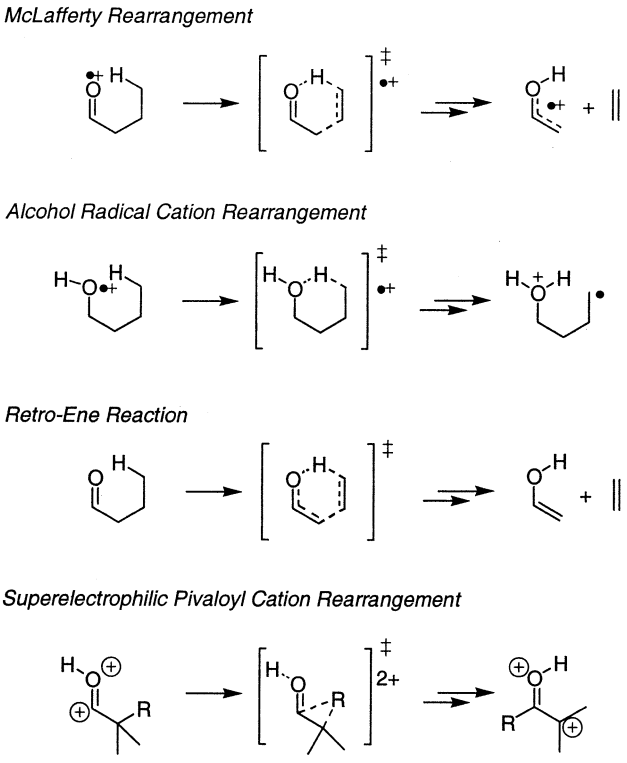
Figure 1. Geometries obtained at B3LYP/6-311 ++ G(d,p) for the acylium ions and its dications formed upon protonation (number of found imaginary frequencies in parenthesis) and the dication of formaldehyde.

9a is exothermic by −78.3 kcal/mol. The geometries obtained after optimization are shown in Figure 1.

By protonating on oxygen of the acylium ions, shortening of the R–COH bonds is observed, as well as an increase in the CO bond length. The C–H or the C–C bonds in the R group also lengthen due to hyperconjugative interactions. This is very similar to the CO, C–H, and C–C bond lengthening in the McLafferty rearrangement. The cases where in the R groups are relatively electron rich, a bridged structure or even a 1,2-shift can be expected, since it leads to stable distonic dication, where charges are relatively far away from each other, thus alleviating intramolecular charge-charge repulsion.

Attempted optimization of **19** failed due to rearrangement into more stable Structure **20**. Subsequent 1,2-hydride shift to afford **3** is predicted to be endothermic by 23.5 kcal/mol.

The similarity of the McLafferty rearrangement and related reactions with the superelectrophilic pivaloyl cation rearrangement can be seen in Scheme 6. While those reactions usually involve a γ-hydrogen shift followed by α,β carbon-carbon cleavage, in the pivaladehyde rearrangement there is a α,β carbon-carbon cleavage, but the alkyl group shifts to the doubly deficient carbonyl group, leading to a single dicationic species (Scheme 8).



Scheme 8

The lengthening of the α,β C–C bond is also observed in the transition states and precursors reported in early theoretical studies of the McLafferty rearrangement [29].

Conclusions

Studies on acylium cations and their behavior under superacidic conditions (aprotic or protic) show that further protolytic activation at the O-site of formyl, acetyl, and pivaloyl cation/protonated pivalaldehyde leads to highly electron deficient, protosolvated superelectrophilic species (gicationic dications) which are many-fold more reactive than the parent monocation. Protolytic activation makes formyl and acetyl cations superelectrophilic acylating agents for Friedel-Crafts acylation on deactivated systems. Since O-protonated pivaloyl dication is a highly unstable species, the immediate rearrangement of pivaloyl cation/protonated pivalaldehyde towards methyl isopropyl ketone takes place under suitable conditions.

Acknowledgments

The authors gratefully acknowledge support of this work by Loker Hydrocarbon Research Institute.

References

1. Olah, G. A. Friedel-Crafts Chemistry; Wiley-Interscience: New York, 1973.
2. Sato, Y.; Yato, M.; Ohwada, T.; Saito, S.; Shudo, K. *J. Am. Chem. Soc.* **1995,** *117,* 3037.
3. Olah, G. A.; Germain, A.; Lin, H. C.; Forsynth, D. A. *J. Am. Chem. Soc.* **1975,** *97,* 2928.
4. Olah, G. A.; Mathew, T.; Marinez, E. R.; Esteves, P. M.; Etzkorn, M.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **2001,** *123,* 11556.
5. Olah, G. A.; Burrichter, A.; Rasul, G.; Prakash, G. K. S.; Hachoumy, M.; Sommer, J. *J. Am. Chem. Soc.* **1996,** *118,* 10423.
6. Hopff, H.; Nenitzescu, C. D.; Isacescu, D. A.; Cantuiari, I. P. *Chem. Ber.* **1936,** *69,* 2244.
7. Daniloff, S.; Venus-Danilova, E. *Ber. Dtsch. Chem. Ges.* **1926,** *59,* 377.
8. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.7*; Gaussian, Inc.: Pittsburgh PA, 1998.
9. Olah, G. A.; O'Brien, D. H.; Calin, M. *J. Am. Chem. Soc.* **1967,** *89,* 3582.
10. Olah, G. A.; Prakash, G. K. S.; Mathew, T.; Marinez, E. R. *Angew. Chem. Int. Ed. Engl.* **2000**, 2647. (Olah, G. A., U.S. Patent 2000, 6018088).
11. (a) Hirschmann, R. F.; Miller, J.; Jones, R. E. *J. Am. Chem. Soc.* **1956,** *78,* 4956. (b) Aranda, G.; Jullien, J.; Martin, J. A. *Bull. Soc. Chim. Fr.* **1965,** *1890.* (c) ibid. **1956,** 2850. (d) Bergstrom, C. G.; Nicholson, R. T.; Dodson, R. M. *J. Org. Chem.* **1963,** *28,* 2633. (e) French Patent, FR 1370827. (*Chem. Abstr.* **1965,** *62,* 2712h).
12. (a) Balicheva, T. G.; Borodin, P. M.; Pologikh, I. V. *Yad. Magn. Rezon.* **1969**, 49. (b) Hecht, S. S.; Rothman, E. S. *J. Org. Chem.* **1975,** *38,* 395. (c) French Patent, FR 1374591. (*Chem. Abstr.* **1965,** *62,* 9212a). (d) Van der Akken, M.; Jellinek, F. *Recl. Trav. Chim. Pays. Bas* **1967,** *86,* 275. (e) Thomas, R. K. *Proc. R. Soc. London, Ser. A* **1971,** *322,* 137. (f) Politanskii, S. F.; Ivanyk, G. D.; Sarancha, V. N.; Shevchuk, V. U. Z. *Org. Khim.* **1974,** *10,* 693.
13. Olah, G. A.; Welch, J. T.; Vankar, Y. D.; Nojima, M.; Kerekes, I.; Olah, J. A. *J. Org. Chem.* **1979,** *44;* 3872 and references cited therein. (Olah, G. A., U.S. Patent 1991, 5073674).
14. (a) Olah, G. A.; Li, X.-Y. *Synlett* **1990**, 267. (b) Olah, G. A.; Li, X.-Y.; Wang, Q.; Prakash, G. K. S. *Synthesis* **1993**, 693.
15. Olah, G. A., U.S. *Patent* **2002,** 15415.
16. Hartz, N.; Rasul, G.; Olah, G. A. *J. Am. Chem. Soc.* **1993,** *115,* 1277.
17. (a) McLafferty, F. W.; Bursey, M. M.; Kimball, S. M. *J. Am. Chem. Soc.* **1966,** *88,* 5022. (b) McLafferty, F. W., Ed. In Interpretation of Organic Mass Spectra, 2nd ed.; Benjamin: Reading: MA, 1973. (c) Boer, F. P.; Shannon, T. W.; McLafferty, F. W. *J. Am. Chem. Soc.* **1968,** *90,* 7239. (d) McAdoo, D. J.; Witiak, D. N.; McLafferty, F. W. *J. Am. Chem. Soc.* **1977,** *99,* 7265. (e) Hendon, W. C.; Grayson, C. R.; Manion, J. M.; Jerald, M. *J. Org. Chem.* **1967,** *32,* 526.
18. Hwang, J. P.; Prakash, G. K. S.; Olah, G. A. *Tetrahedron* **2000,** *56,* 7199.
19. Olah, G. A. *Angew. Chem. Int. Ed. Engl.* **1993,** *32,* 767.
20. (a) Olah, G. A.; Rasul, G.; York, C.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995,** *117,* 11211. (b) Olah, G. A.; Klumpp, D. A.; Neyer, G.; Wang, Q. *Synthesis* **1996,** *321.* (c) Klumpp, D. A.; Beak, D. N.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1997,** *62,* 6666.
21. (a) Vol'pin, M. E.; Akhrem, I. S; Orlinkov, A. V. *New J. Chem.* **1989,** *13,* 1771. (b) Akhrem, I. S.; Orlinkov, A. V.; Afanaseva, L. V.; Vol'pin, M. E. *Dokl. Acad. Nauk SSSR* **1988,** *298(1),* 107.
22. Lammertsma, K. *J. Am. Chem. Soc.* **1984,** *106,* 4619.
23. Koch, W.; Frenkling, G.; Schwarz, H.; Maquin, F.; Stahl, D. *Int. J. Mass Spectrom. Ion Processes* **1985,** *63,* 59.
24. O'Connor, C. S. S.; Jones, Nykola C.; Price, Stephen D. *Chem. Phys.* **1997,** *214,* 131.
25. Prakash, G. K. S; Rasul, G; Burrichter, A; Olah, G. A. *ACS Symposium Series* **1996**, *623,* 10.
26. Schroder, D.; Schwarz, H.; Wu, J.; Wesdemiotis, C. *Chem. Phys. Lett.* **2001,** *343,* 258.
27. Guenat, C.; Maquin, F.; Stahl, D.; Koch, W.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1985,** *63,* 265.
28. (a) Balaban, A. T.; Nenitzescu, C. D. *Justus Liebigs Ann. Chem.* **1959,** *625,* 66. (b) 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.
29. (a) Ha, T.; Radloff, C.; Nguyen, M. T. *J. Phys. Chem.* **1986,** *90,* 2991. (b) Dorigo, A. E.; McCarrick, M. A.; Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1990,** *112,* 7508. (c) Liu, R. F.; Pulay, P. *J. Comput. Chem.* **1992,** *13,* 183.