# Acid-Catalyzed Isomerization of Pivalaldehyde to Methyl Isopropyl Ketone via a Reactive Protosolvated Carboxonium Ion Intermediate†

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**Abstract:** Quantitative rearrangement of pivalaldehyde to methyl isopropyl ketone is observed in acids such as trifluoromethanesulfonic acid, anhydrous HF, and trifluoroethyl alcohol−$BF_3$ but not in trifluoroacetic acid. Studies in a mixture of trifluoroacetic acid and trifluoromethanesulfonic acid show that acids with $H_o \leq -11$ are able to carry out complete isomerization. These results and density functional theory calculations at the B3LYP/6-31G* level suggest that protonated pivalaldehyde undergoes further protosolvation at higher acidities to a reactive superelectrophilic species resulting in rearrangement. A mechanism for the pivalaldehyde rearrangement to methyl isopropyl ketone in strong protic acids involving a reactive protosolvated superelectrophilic intermediate is suggested. Aspects of the related mechanism of the reaction with isobutane with CO in HF/$BF_3$ medium leading to methyl isopropyl ketone are also discussed.

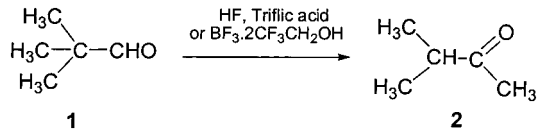
## Introduction

Methyl isopropyl ketone (MIPK) is an efficient high-octane (>100) oxygenate gasoline additive, without many of the undesirable effects of the widely used methyl *tert*-butyl ether (MTBE). One of the preparations of methyl isopropyl ketone involves the rearrangement of pivalaladehyde (trimethylacetaldehyde). Rearrangement of pivalaldehyde (**1**) to methyl isopropyl ketone (**2**), shown in Scheme 1, has been reported by catalysis with aluminum chloride and $H_2SO_4$ by Hoppf et al.[1] Previously Daniloff and Venus-Danilova obtained methyl isopropyl ketone by the reaction of pivalaldehyde in 70% sulfuric acid in a sealed tube at 130 °C.[2]

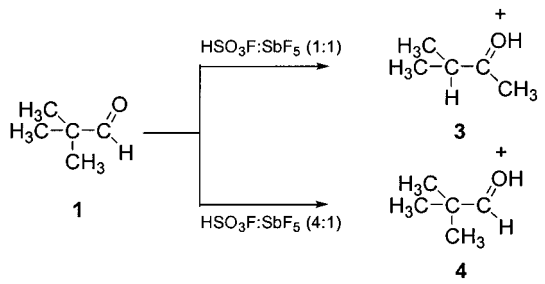
In 1967, Olah et al.[3] reported a study of a series of protonated aliphatic aldehydes by low-temperature $^1$H NMR in the superacid system $HSO_3F-SbF_5-SO_2$. In the case of pivalaldehyde in a 1:1 $HSO_3F-SbF_5$ acid mixture in $SO_2$ solution at −60 °C, no protonated pivalaldehyde was observed but only protonated methyl isopropyl ketone (**3**).[4] Protonated pivalaldehyde (**4**) was observed, however, in the less acidic 4:1 mixture of $HSO_3F-SbF_5$ in $SO_2$ at −70 °C (Scheme 2).

Recently we have found that isobutane undergoes formylation with CO in the presence of $HF-BF_3$ (1:1) and subsequent rearrangement to methyl isopropyl ketone in high yield and high selectivity (Scheme 3).[5] We suggested that the reaction proceeds through the intermediacy of diprotonated or protosolvated pivalaldehyde that undergoes subsequent rearrangement to methyl isopropyl ketone. We now report the effect of acidity on the rearrangement of pivalaldehyde to methyl isopropyl ketone and theoretical calculations for better understanding of the mechanism of the rearrangement.

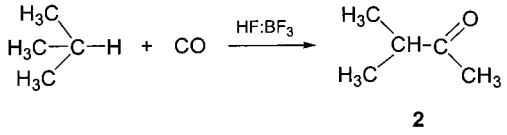
**Scheme 1**




**Scheme 2**




**Scheme 3**




## Results and Discussion

We have found that anhydrous HF, $CF_3SO_3H$, $BF_3$·$2CF_3CH_2OH$, and $BF_3$·$2CF_3CF_2CH_2OH$ complexes are able to effectively isomerize pivalaldehyde to methyl isopropyl ketone even at 0 °C. However, in weaker trifluoroacetic acid (TFA) no isomerization of pivalaldehyde was observed. Since solid superacids

† Considered Chemistry in Superacids, Part 55, For part 54 see ref 17.

(1) Hopff, H.; Nenitzescu, C. D.; Isacescu, D. A.; Cantuiari, I. P. *Chem. Ber.* **1936**, *69*, 2244.

(2) Daniloff, S.; Venus-Danilova, E. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 377.

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

(4) Olah, G. A.; O'Brien, D. H.; Calin, M. *J. Am. Chem. Soc.* **1967**, *89*, 3586.

(5) (a) Olah, G. A.; Prakash, G. K. S.; Mathew, T.; Marinez, E. R. *Angew. Chem., Int. Ed. Engl.* **2000**, 2647. (b) Olah, G. A. U.S. Patent 6,018,088, 2000.

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**Scheme 4**

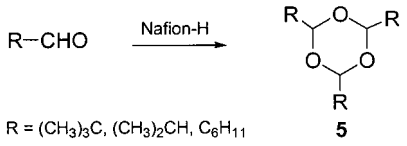



**Table 1.** Effect of Variation of Acidity on the Pivalaldehyde Rearrangement[a]

| $-H_o$ | wt % TFA | wt % TFSA | % pival-aldehyde | % methyl isopropyl ketone |
|---|---|---|---|---|
| 2.7 | 100 | 0 | 100 | 0 |
| 7.7 | 99.1 | 0.9 | 83 | 17 |
| 8.4 | 96.9 | 3.1 | 68 | 32 |
| 9.4 | 92.0 | 8.0 | 29 | 71 |
| 9.7 | 88.6 | 11.4 | 17 | 83 |
| 10.9 | 73.1 | 26.9 | 0 | 100 |
| 11.5 | 56.5 | 43.5 | 0 | 100 |
| 12.5 | 27.2 | 72.8 | 0 | 100 |
| 14.1 | 0 | 100 | 0 | 100 |

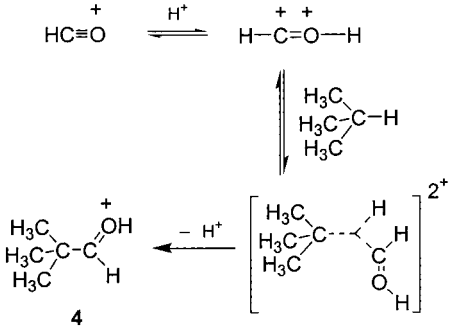
[a] Reaction conditions: 2 h, RT, 1:5 pivalaldehyde:acid.

have the advantage of easy workup and regeneration, Nafion-H was also probed as the acid catalyst in the rearrangement of pivalaldehyde. It was found that Nafion-H, a solid perfluororesinsulfonic acid, catalyzes only the trimerization of pivalaldehyde into a trioxane derivatives in 95% yield instead of isomerization into methyl isopropyl ketone. Preparation of trioxanes is well-known.[6a−e] Nafion-H also catalyzes the trimerization of cyclohexane carboxaldehyde and isobutyraldehyde into their corresponding trioxane derivatives (**5**) under similar conditions (Scheme 4). Interestingly, when the tris-*tert*-butyl-substituted trioxane derived from pivalaldehyde was treated with trifluoromethanesulfonic acid (TFSA), methyl isopropyl ketone was obtained quantitatively.

**Isomerization of Pivaladehyde under Varying Acidities.** Acidities can be conveniently varied by adjusting the relative ratios of trifluoromethanesulfonic acid and trifluoroacetic acid mixtures.[7] To understand the effect of acidity on pivalaldehyde−methyl isopropyl ketone isomerization, we have carried out the reaction in mixtures of differing composition of trifluoromethanesulfonic acid and trifluoroacetic acid. The results are shown in Table 1. According to the Zucker−Hammett postulate[8,9]the rate of an acid-catalyzed reaction is proportional to the Hammett acidity ($H_o$, determined by measuring the half-protonation equilibria of overlapping bases) when the rate-determining step of the reaction involves a protonated species and its steady-state concentration is low. If the rate increases more proportionally to the acidity in the high-acidity region wherein the substrate is completely protonated, we suggest that a new reactive species is formed by a second protonation (or protosolvation) that must also participate in the reaction. Since the trifluoroacetic acid (TFA, $H_o = -2.7$)/trifluoromethanesulfonic acid (TFSA, $H_o = -14.1$) system covers a wide range of acidity, it was possible to test the dependency of the yield of methyl isopropyl ketone upon the acidity of the mixed acid system.

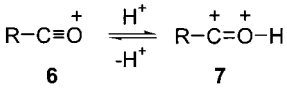
The optimal acidity for the complete rearrangement of pivalaldehyde into methyl isopropyl ketone was found to be at a $H_o$ value of −10.9, close to the superacidity limit of −12 (Table 1). At a Hammett acidity of $H_o = -7.7$, methyl isopropyl ketone was obtained only in 17% yield due to substantial decrease in the rate of isomerization due to lower acidity. Arnett[10] has estimated that protonated aliphatic aldehydes usually have a p$K_a$ of −8.0, whereas Campbell and Edward[11] have shown that the p$K_a$ for protonated methyl isopropyl ketone is −7.1. Therefore, at $H_o = -7.7$, half of pivalaldehyde should be monoprotonated on the basis of its equilibrium concentration. Consequently, the rearrangement of pivalaldehyde does not proceed through its monoprotonated form but must involve a second protonation to form a dicationic or protosolvated species.

**Scheme 5**




**Protosolvation and Superelectrophilic Activation.** Extensive studies on the role of various oxonium, sulfonium, and carboxonium dications in superacid-catalyzed reactions have been reported by Hartz et al.[12] In the superelectrophilic formylation of isobutane,[5] the formyl cation in HF−$BF_3$ (1:1) can undergo further protosolvation ($HCO^+\cdots H^+A^-$ or $HC^+{=}O^+H\cdots A^-$) resulting in a very reactive formylating species (superelectrophile). The mechanism suggested involved the insertion of protosolvated formyl cation (diprotonated carbon monoxide dication) into the tertiary C−H bond (with high $\sigma$ reactivity) to produce a protonated pivalaldehyde species, as shown in Scheme 5. This can undergo further protosolvation at the acidity of used HF−$BF_3$ to allow subsequent rearrangement to methyl isopropyl ketone as the final product. Significantly, the carbon atom of the protonated carbonyl group, due to the significant charge delocalization onto the more electronegative oxygen atom, is not sufficiently electron-deficient to bring about carbocationic rearrangement. Only a decrease of neighboring oxygen participation by protonation (protosolvation) of the nonbonded pair of oxygen allows the carbocationic center to develop, thus bringing about the rearrangement (vide infra).

As relatively weak electrophiles, acyl cations do not react with saturated hydrocarbons. Olah has suggested that the de facto reactive intermediates in the reaction of acyl ions with hydrocarbons under superacidic conditions are not the acyl cations themselves but their O-protonated (protosolvated) forms $R-COH^{2+}$ (**7**), which in the extreme case are highly electron-deficient superelectrophilic gitonic dications substantially more reactive than their parent monocations due to substantially decreased neighboring oxygen stabilization.[13] Similarly, Vol'pin et al.[14] found that 2 or more equiv of anhydrous aluminum chloride brings about readily superelectrophilic reaction of acyl cations.




Although no persistent (stable) protioacetyl dications have been observed by NMR spectroscopy, quantum mechanical

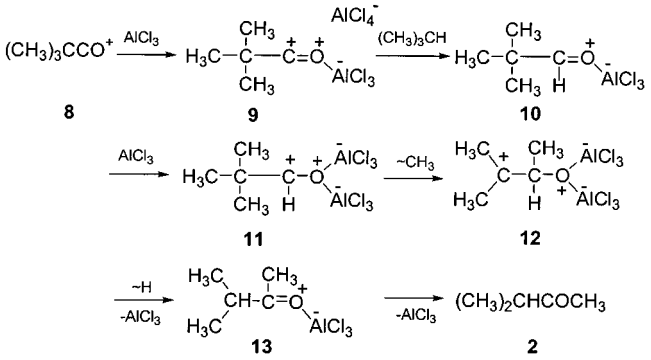
(6) (a) Bevington, J. C. *Q. Rev. Chem. Soc.* **1952**, *6*, 141. (b) Nehring, R. *Chem. Abstr.* **1980**, *92*, 198432h. (c) Ogawa, T. *Chem. Abstr.* **1979**, *90*, 152247g. (d) Saeki, Y.; Fujita, M.; Akiyama, T.; Ueno, Y. *Chem. Abstr.* **1975**, *82*, 64339t (e) Yamashita, Y.; Iwao, K.; Ito, K. *Polymer Bull. (Berlin)* **1978**, *1*, 73; *Chem. Abstr.* **1979**, *91*, 92026t.

(7) Saito, S.; Saito, S.; Ohwada, T.; Shudo, K. *Chem. Pharm. Bull.* **1991**, *39*, 2718.

(8) Zucker, L.; Hammett, L. P. *J. Am. Chem. Soc.* **1939**, *61*, 2791.

(9) Long, F. A.; Paul, M. A. *Chem. Rev.* **1957**, *57*, 935.

**Scheme 6**



calculations have shown that the protonated formyl dication $HCOH^{2+}$ and protonated acetyl dication $CH_3COH^{2+}$ are stable minima. Our studies on acid-catalyzed organic transformations in superacidic trifluoromethanesulfonic acid also support superelectrophilic activation.[15−17]

**Protosolvation of Pivalaldehyde.** Balaban and Nenitzescu[18] reported the formation of methyl isopropyl ketone (**2**) in the reaction of pivaloyl chloride with a large excess of aluminum chloride in the presence of isobutane as a hydride donor. When $SnCl_4$ was used instead of $AlCl_3$, no ketone was formed. A possible mechanism, based on our theoretical calculations,[12] involves hydride abstraction by the O-complexed aprotic superacidic pivaloyl cation−$AlCl_3$ complex (**9**), followed by further complexation to pivalaldehyde−$AlCl_3$ complex (**11**), which in turn undergoes fast rearrangement to methyl isopropyl ketone (**2**) (Scheme 6).

Formation of pivalaldehyde dication in superacid media (trifluoromethanesulfonic acid or HF−$BF_3$) could also be explained in a similar manner. Theoretical studies at the B3LYP/6-31G* support the mechanism involving a diprotonated pivalaldehyde dication intermediate.

Scheme 7 shows the mechanistic pathways for the reaction, based on the mono- or diprotonated species. To rationalize the experimental results, density functional theory (DFT) calculations were performed, at the B3LYP/6-31G* level with the Gaussian 98 program.[19] Structures for the monoprotonated and diprotonated intermediates and transition states shown in Scheme 6 were fully optimized. The final geometries were subjected to further vibrational analysis that afford the zero-point energy (ZPE) and thermal corrections (298.15 K and 1 atm) for each structure. If not stated otherwise, all energies given refer to enthalpies at 298.15 K and 1 atm. Minima were characterized by the absence of imaginary frequencies. All transition states

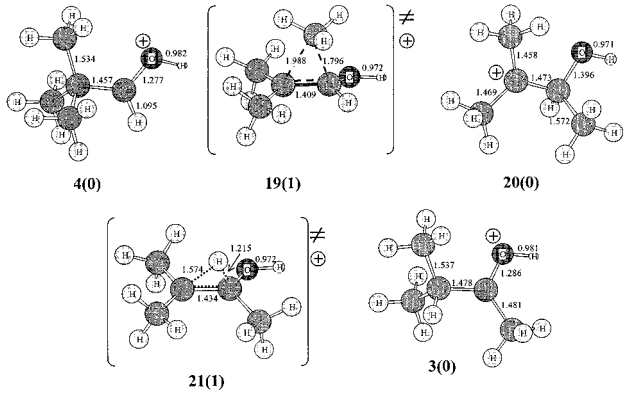


**Figure 1.** Isomeric minimum and transition-state structures calculated for the protonated pivalaldehyde cation (number of found imaginary frequencies in parentheses).

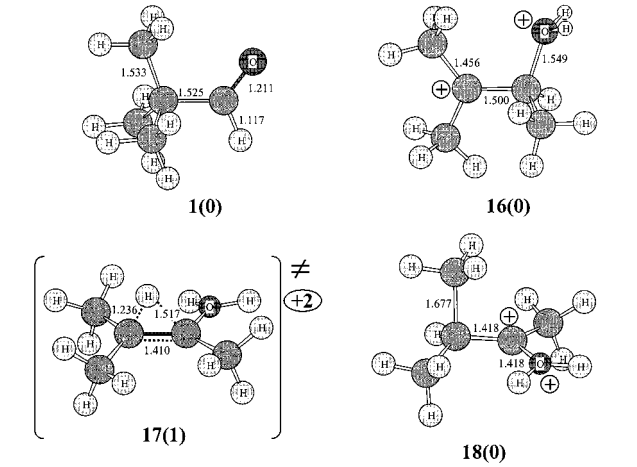


**Figure 2.** Isomeric minimum and transition-state structures calculated for the diprotonated pivalaldehyde cation and the parent pivalaldehyde (number of found imaginary frequencies in parentheses).

presented only one imaginary frequency, whose normal modes are associated with the expected reaction pathway. Figures 1 and 2 contain the optimized geometries for the studied species. The number in parentheses is the number of imaginary frequencies.

Table 2 shows the relative enthalpies for monoprotonated pivalaldehyde and diprotonated pivalaldehyde. Figures 3 and 4 show a description of the potential energy surface (PES) of the rearrangement of the mono- and diprotonated pivalaldehyde, respectively.

Analysis of the PES of the monoprotonated pivalaldehyde (Figure 3) shows a barrier for methyl shift of 9.2 kcal/mol, affording the intermediate **20** in an endothermic process (4.2 kcal/mol). This intermediate undergoes easy rearrangement (activation barrier of 2.3 kcal/mol) to the protonated methyl isopropyl ketone (**3**). The total enthalpy for the rearrangement is exothermic by 15.5 kcal/mol. Thus, the slow or rate-

(10) Arnett, E. M. Quantitative Comparisons of Weak Organic Bases. *Prog. Phys. Org. Chem.* **1963**, *1*, 223.
(11) Campbell, H. J.; Edward, J. T. *Can. J. Chem.* **1960**, *38*, 2109.
(12) Hartz, N.; Rasul, G.; Olah, G. A. *J. Am. Chem. Soc.* **1993**, *115*, 1277.
(13) Olah, G. A.; Burrichter, A.; Rasul, G.; Prakash, G. K. S.; Hachoumy, M.; Sommer, J. *J. Am. Chem. Soc.* **1996**, *118*, 10423.
(14) (a) Vol'pin, M.; Akhrem, I.; Orlinkov, A. *New J. Chem.* **1989**, *13*, 771. (b) Akhrem, I. S.; Orlinkov, A. V.; Afanaseva, L. V.; Vol'pin, M. E. *Dokl. Acad. Nauk. SSSR* **1988**, *298* (1), 107.
(15) (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.
(16) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.
(17) Hwang, J. P.; Prakash, G. K. S.; Olah, G. A. *Tetrahedron* **2000**, *56*, 7199.
(18) (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.
(19) 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.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

**Scheme 7.** Proposed Mechanistic Scheme for the Pivalaldehyde Rearrangement by (a) Monoprotonated Pathway and (b) Superelectrophilic Activation (protosolvation) of the Monoprotonated Pivalaldehyde

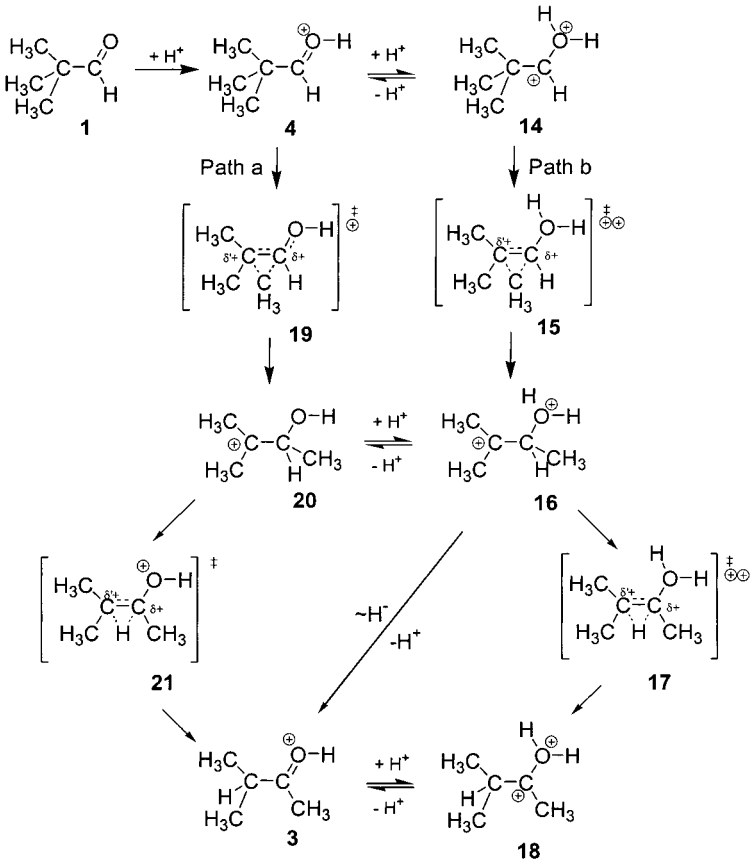



**Table 2:** Relative Energies for Mono- and Diprotonated Pivalaldehyde

| monoprotonated pivalaldehyde | | diprotonated pivalaldehyde | |
|---|---|---|---|
| species | $\Delta H°$(298 K), kcal/mol | species | $\Delta H°$(298 K), kcal/mol |
| **4** | 0.0 | **14** | ~48[a] |
| **[19]‡** | 9.2 | **[15]‡** | *b* |
| **20** | 4.2 | **16** | 0.0 |
| **[21]‡** | 6.5 | **[17]‡** | 27.6 |
| **3** | −15.5 | **18** | 23.7 |

[a] Not a stable species (see text for discussion). [b] Not found in the PES.

determining step of the reaction corresponds to the methyl shift of the monoprotonated pivalaldehyde.

The second O-protonation of the protonated pivalaldehyde by strong acids would lead to the formation of the gitonic dication **14**. The most stable species found in the potential energy surface of diprotonated pivalaldehyde (Figure 4) is the distonic cation **16**. Gitonic diprotonated pivalaldehyde **14** was not found as a minimum in the PES. All attempts for its optimization afforded the most stable distonic cation **16**, which is the global minimum on the PES (see Scheme 6). Formation of the gitonic dication **14** increases the electrophilic character of the protonated carbonyl group that leads to the methyl group (C−C bond overlaps with the $\pi$ system of the C═O group; see Figure 3) shift to the carbonyl carbon and alleviates the electron demand in the adjacent position. The intramolecular Coulombic (charge−charge) repulsion in the gitonic dication is also diminished. Nevertheless, to estimate the relative stability of the gitonic cation **14** in relation to the other species on the potential energy surface, geometry optimization with the $H_3C-C-C$ bond angle constrained at several angles was performed

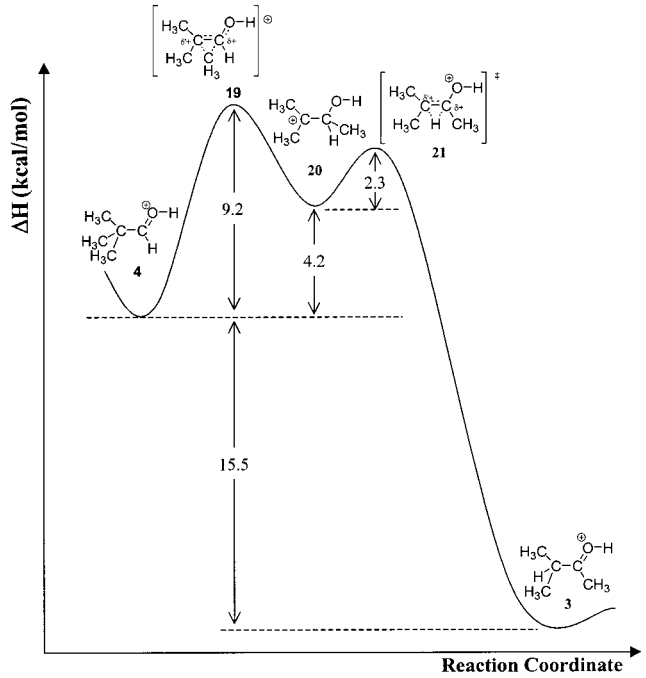



**Figure 3.** Potential energy surface (reaction coordinate) for the rearrangement of monoprotonated pivalaldehyde to protonated methyl isopropyl ketone.

(see Figure 5). It can be noted that there is no minimum upon variation of the angle $\theta$, suggesting that the second protonation of the pivalaldehyde affording the gitonic dication **14** leads, in a barrierless process, to the most stable distonic dication **16**. Nevertheless, once this dication is formed, the hydride shift rearrangement, through transition state **17** affording the dication

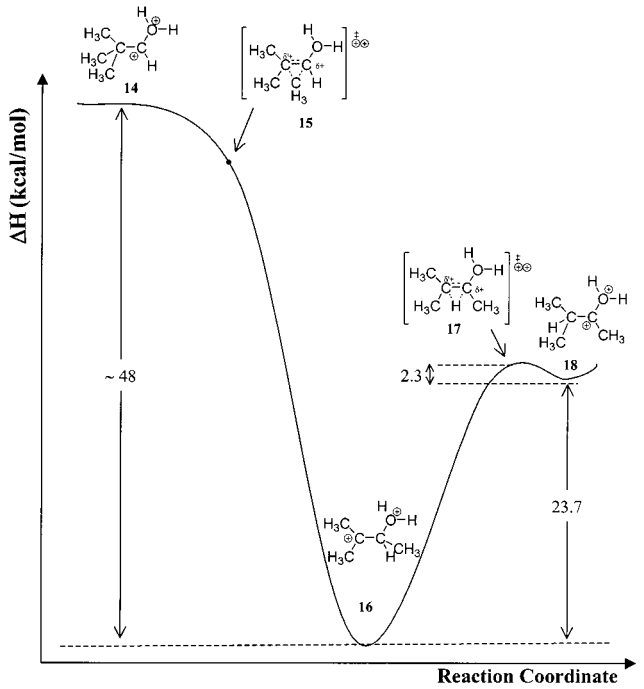



**Figure 4.** Potential energy surface (reaction coordinate) for the rearrangement of the diprotonated pivalaldehyde to the diprotonated methyl isopropyl ketone.

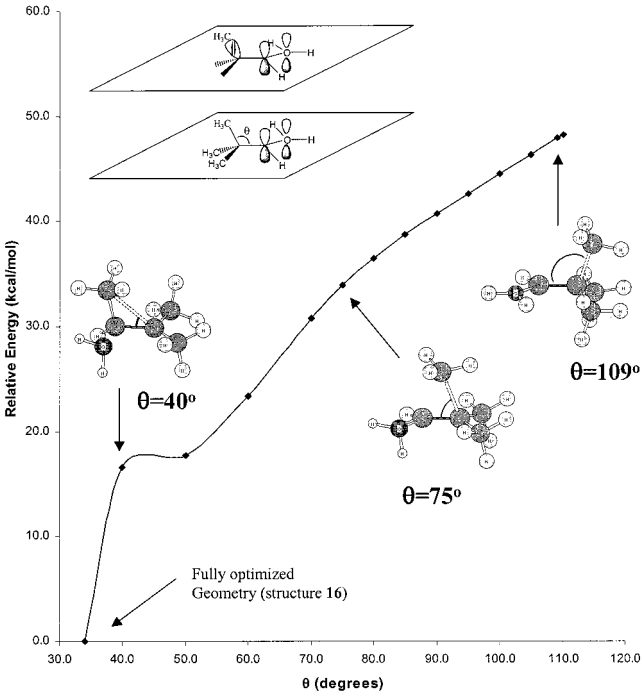
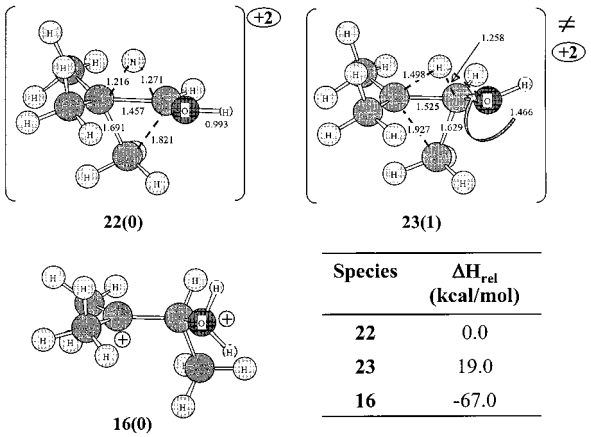



**Figure 5.** Variation of the energy of the diprotonated pivalaldehyde as a function of the angle $\theta$.

**18**, is made difficult by charge−charge repulsion. Thus, it would be energetically preferable that the dication **16** undergo concerted hydride shift and deprotonation to afford protonated methyl isopropyl ketone (**3**). These results can explain why the yield for the rearranged product increases with the increasing acidity of the reaction medium. The slow step for this process is expected to be the second protonation (protosolvation) of protonated pivalaldehyde, which is preferred with stronger acids. From the constrained angle variation geometry optimization study, one could estimate the relative energy of the gitonic dication **14** (obtained from the geometry with $\theta = 109.47°$) to




| Species | $\Delta H_{rel}$ (kcal/mol) |
|---|---|
| **22** | 0.0 |
| **23** | 19.0 |
| **16** | -67.0 |

**Figure 6.** Structures calculated (MP2(full)/6-31G*) for the insertion of $HCOH^{2+}$ (diprotonated CO) into the tertiary C−H bond of isobutane (**22**) and the transition state (**23**) for rearrangement into the dication **16** (number of found imaginary frequencies in parentheses). Relative enthalpies (298.15 K and 1 atm) calculated at MP2(full)/6-31G* level are also shown.

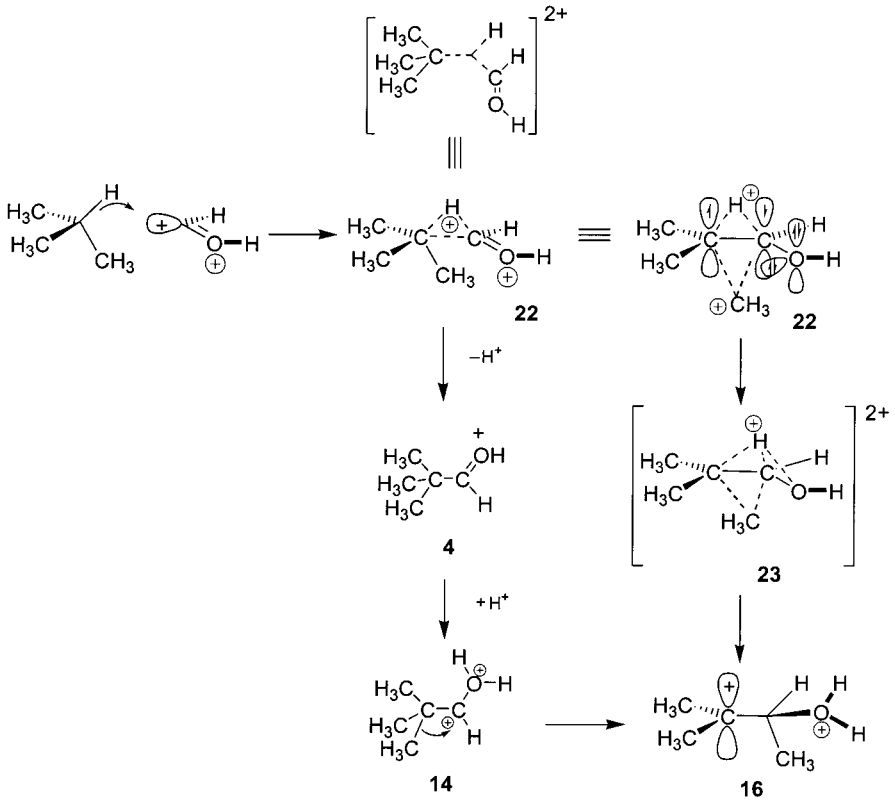
be 48 kcal/mol higher in energy than the distonic dication **16**. One should note, however, that only protosolvation of the monoprotonated species could be sufficient to promote the rearrangement, which significantly would decrease this energy, especially when stronger superacids are used.

The mechanism proposed for the rearrangement of pivalaldehyde into methyl isopropyl ketone[5,13] (Scheme 3) involves further protosolvation of the protonated aldehyde at higher acidities. The reaction does not take place in 100% trifluoroacetic acid. Upon addition of trifluoromethanesulfonic acid, the acidity of the system and the rate of isomerization to methyl isopropyl ketone are increased. The increasing yield of methyl isopropyl ketone with increasing acidity suggests a mechanistic pathway involving further protonation of the monoprotonated aldehyde. Pivalaldehyde is first O-protonated, giving a highly stabilized carboxonium ion **4**, but due to stabilization by the neighboring oxygen, rearrangement does not occur. Subsequent further protonation (protosolvation) at higher acidity gives the gitonic dication **14**. The gitonic dication, being a high-lying energetic species, undergoes a concerted methyl shift to give the lower-lying distonic dication **16**, which undergoes further hydride shift and deprotonation to give the product, methyl isopropyl ketone **2**.

As the diprotonated pivalaldehyde is also proposed to be involved as an intermediate in the reaction of isobutane with CO in $HF-BF_3$ systems (Scheme 5), we performed calculations for this reaction. These calculations were carried out at the MP2-(full)/6-31G* level, following the same procedures described for the B3LYP level.

The insertion of the diprotonated CO into the tertiary C−H of isobutane (Scheme 8) afforded, according to MP2(full)/6-31G* calculations, species **22** (Figure 6). This species was found to be a minimum in the PES at this level of theory. It is interesting to note that one of the methyl groups in structure **22** indicates some interaction with the electron-deficient carbon of the diprotonated CO, as expressed in the relatively short C···C(OH) distance of 1.821 Å (Figure 6). This system can be imagined as the enolic form of the 2-methylpropanal, with a proton ($H^+$) on one face of the C=C double bond and a $CH_3^+$ cation on the other face. This system could afford in one single step the distonic carbodication **16** (which would further directly give methyl isopropyl ketone), through transition state **23** (Scheme 8). This would be an alternative pathway for the

**Scheme 8**



formation of the methyl isopropyl ketone from isobutane in CO/HF/$BF_3$ system, without necessarily forming pivalaldehyde as an intermediate. The previously proposed reaction pathway (Scheme 5) would involve the deprotonation of structure **22**, forming the protonated pivalaldehyde, which by subsequent reprotonation and rearrangement would afford the protonated ketone (Scheme 8). The structure of transition state **23** was successfully characterized at the MP2 level, and it is shown in Figure 6. This transition state was calculated to be 19.0 kcal/mol higher in energy than the intermediate **22**, and the $\Delta H$ for the formation of species **16** from **23** was calculated as −67.0 kcal/mol.

## Conclusion

The present study shows that higher acidities are required for the rearrangement of pivalaldehyde to methyl isopropyl ketone and offers a mechanistic scheme involving the formation of highly reactive protonated (protosolvated) pivalaldehyde. The mechanism for the direct formation of methyl isopropyl ketone from the reaction of isobutane with CO in the HF−$BF_3$ system was also probed theoretically.

## Experimental Section

Trifluoroacetic acid (Aldrich) and trifluoromethanesulfonic acid (3M) were distilled before use. Anhydrous HF (AHF, Matheson) was condensed in Nalgene bottles cooled in an acetone−dry ice bath. $BF_3$ (Matheson), 2,2,2-trifluoroethanol (Aldrich), 3,3,3,-trifluoropropanol (Aldrich), and pivalaldehyde (Aldrich) were used as received. Analyses were carried out by gas chromatography (GC) (Varian 3000, 30m DB-5 capillary) and gas chromatography/mass spectrometry (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 tetramethylsilane (TMS) as internal standard. All the calculations were performed with the Gaussian 98 program.[19] All geometries were fully optimized at the B3LYP/6-31G* level. The final geometries were subject to further vibrational analysis, which afford the zero-point energy (ZPE) and thermal corrections (298.15 K and 1 atm) for each structure.

Typical procedure for the pivalaldehyde rearrangement was as follows: To 10 mL of the acid catalyst in a 30 mL Nalgene bottle at 0 °C was added 2.0 mL of pivalaldehyde. The ice bath was removed and the reaction mixture was stirred for 2 h at room temperature (22 °C). The reaction mixture was poured slowly into a minimum amount of ice, neutralized with sodium bicarbonate, and extracted with ether. After drying with $MgSO_4$, ether solution was analyzed by GC using authentic samples.

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**Supporting Information Available:** Tables S1 and S2 including absolute energies, ZPE, thermal corrections to 298.15 K and 1 atm, absolute entropies, and imaginary frequencies for the transition states, and the values of the potential energy of the diprotonated pivalaldehyde in function of the $H_3C-C-CHO$ bond angle. This information is available free of charge via the Internet at http://pubs.acs.org.

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