

hexane), and the rest remained at the origin. A similar analysis on cellulose ( $R_f = 0.36$ , 12:7:1 THF/25 mM  $\text{NH}_4\text{HCO}_3$ /2-propanol) gave 1.8% of the radioactivity comigrating with (S)-3-OP and the remainder at the solvent front. A 10- $\mu\text{L}$  sample ( $4 \times 10^5$  dpm) was treated with 0.1 mg of alkaline phosphatase in 400  $\mu\text{L}$  of 1 M diethanolamine, 3 mM  $\text{MgCl}_2$ , pH 10.5, at 37 °C for 48 h. Cold 12-OH was added, and the mixture was extracted with ether. The radioactivity in the extract ( $3.8 \times 10^5$  dmp) coeluted with 12-OH on reversed-phase HPLC.

**Time Course for Incubation of (S)-[1- $^3\text{H}$ ]-OP and 5-OPP with Cell-Free Extracts.** A 3.5-mL portion of cell-free extract containing 30 mg of protein, 110  $\mu\text{g}$  (0.53  $\mu\text{mol}$ ) of (S)-[1- $^3\text{H}$ ]-3-OP (specific activity 7  $\mu\text{Ci}/\mu\text{mol}$ ), and 2.3 mg (4.7  $\mu\text{mol}$ ) of 5-OPP was incubated at 37 °C. Samples (0.2 mL) were taken at 8, 16, 32, 60, 120, 180, 240, 300, 484, 720, and 1120 min and quenched by adding 0.8 mL of 80 mM EDTA. The samples were extracted with 5.5 mL of water-saturated butanol, and the radioactivity in a 0.5-mL portion of the butanol extract was determined. Butanol was removed from the remainder of the extracts with a stream of nitrogen, and the residues were suspended in 200  $\mu\text{L}$  of glycine buffer, pH 10.4. Alkaline phosphatase (50  $\mu\text{g}$ ) was added to each

sample. The samples were incubated at 37 °C for 6 h, extracted in succession with pentane and ether, and analyzed by reversed-phase HPLC.

**Assay for GGGP Synthase.** Assays were run in 150  $\mu\text{L}$  of 50 mM BHDA, pH 7.2, containing 3 mM  $\text{MgCl}_2$ , 1 mM DTT, 150  $\mu\text{M}$  (S)-[1- $^3\text{H}$ ]-3-OP, 200  $\mu\text{M}$  5-OPP, and protein. The mixture was incubated at 37 °C for 10 min, and the reaction was stopped by addition of 100  $\mu\text{L}$  of 0.5 M EDTA. One milliliter of saturated NaCl was added, and the solution was extracted with 3 mL of water-saturated 1-butanol by vortex mixing for 10 s. The layers were allowed to separate, and the radioactivity in a 1-mL portion of the butanol layer was measured by liquid scintillation spectrometry.

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## Role of Oxonium, Sulfonium, and Carboxonium Dications in Superacid-Catalyzed Reactions<sup>1</sup>

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**Abstract:** Energies, electronic structures, gas-phase proton affinities, and isodesmic enthalpies ( $\Delta H_0^{150}$ ) of a series of methyl-substituted oxonium and sulfonium dications and carboxonium dications (di-O-protonated carbonyl compounds) were calculated using ab initio molecular orbital theory. On the basis of computed energetics, the proton affinities and decomposition barriers were also estimated. The role of dicationic superelectrophiles in a number of superacid-catalyzed reactions is discussed.

### Introduction

Oxonium and sulfonium ions are well-recognized intermediates in solution chemistry. Trialkyloxonium salts (Meerwein salts) are widely used alkylating agents for heteroatoms, but not for carbon nucleophiles. However, it was observed in the course of our studies that superacids can greatly enhance their reactivity. For example,  $\text{Me}_3\text{O}^+$  and  $\text{Et}_3\text{O}^+$ , being unreactive toward benzene and toluene under aprotic or low-acidity conditions, readily alkylate them in the presence of superacids.<sup>2</sup>

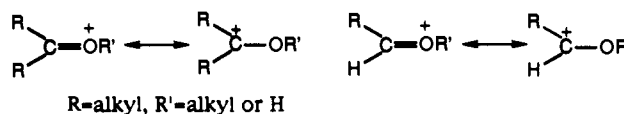
Hydrogen-deuterium exchange experiments of isotopomeric  $\text{H}_3\text{O}^+$  in superacids were found to indicate more rapid exchange upon increase of acidity of the media.<sup>3a</sup> This exchange was suggested to proceed via an associative mechanism involving a tetracoordinated oxonium dication. Similar results were reported also for the hydrosulfonium ion.<sup>3b</sup> On the basis of thermodynamic considerations it was subsequently suggested that  $\text{H}_4\text{O}^{2+}$  could be formed exothermically in sulfonane solutions.<sup>4</sup>

$\text{H}_4\text{O}^{2+}$  and  $\text{H}_4\text{S}^{2+}$  were also subjected to several theoretical investigations.<sup>2,3,5</sup> It was concluded that diprotonation leads to high-lying intermediates with a considerable kinetic barrier toward

dissociation. The generation of these dications in the gas phase as well as in solution was predicted to be possible despite the presence of a dipositive charge.

Whereas destabilization by Coulomb repulsion cannot be alleviated through substituent effects in the case of diprotonated water, (considering the gas-phase-isolated molecule, vide infra), it should be possible to stabilize onium dications by introducing appropriate substituents. Furthermore, related sulfonium dications should be even better suited to accommodate a dipositive charge.

In superacidic systems carboxonium ions show greatly enhanced reactivity.<sup>6</sup> Carboxonium ions (e.g., protonated or alkylated carbonyl compounds) which were first studied by Meerwein are highly stabilized in comparison to alkyl cations.<sup>7</sup> They behave as both oxonium and carbenium ions, with the former nature predominating.



The spectroscopic properties and chemical behavior of these species fully warrant their depiction as delocalized carboxonium ions.



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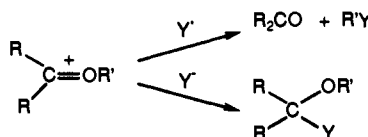
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Table I. Total Energies for Neutral and Mono- and Diprotonated Bases at the MP2/6-31G\*//HF/6-31G\* Level<sup>a</sup>

compd	base	$E_{\text{freebase}}$ (a)	$E_{\text{monoprot}}$ (b)	$E_{\text{diprot}}$ (c)
1	H <sub>2</sub> O	-76.195 96 (12.9) [-76.332 05]	-76.473 82 (20.6) [-76.591 93]	-76.385 58 (25.7) [-76.493 30]
2	MeOH	-115.344 95 (31.0)	-115.644 18 (38.5)	-115.591 82 (41.7)
3	Me <sub>2</sub> O	-154.502 07 (48.3)	-154.813 14 (55.7) -154.826 83 (59.9) <sup>b</sup>	-154.846 54 (64.3) <sup>b</sup>
4	Me <sub>3</sub> O <sup>+</sup>	-193.981 72 (73.0)	-194.025 61 (72.9)	
5	HCHO	-114.165 27 (16.3)	-114.442 83 (24.6)	-114.405 16 (30.1)
6	CH <sub>3</sub> CHO	-153.342 84 (33.5)	-153.642 87 (41.3)	-153.643 80 (46.0)
7	(CH <sub>3</sub> ) <sub>2</sub> CO	-192.521 61 (50.4)	-192.835 41 (57.8)	-192.865 92 (62.3)
8	HCOOH	-189.238 23 (20.8)	-189.526 56 (28.3)	-189.530 34 (33.6)
9	CO	-113.018 03 (3.1) [-113.177 49]	-113.253 54 (10.2) [-113.399 65]	-113.136 63 (14.2) [-113.340 39]
10	CH <sub>3</sub> COOH	-228.415 44 (37.5)	-228.720 08 (44.7)	-228.749 90 (49.8)
11	H <sub>2</sub> CO <sub>3</sub>	-264.294 62 (19.9)	-264.593 36 (31.4)	-264.610 27 (36.3)
12	CO <sub>2</sub>	-188.102 20 (7.1)	-188.307 29 (12.9)	-188.244 68 (16.5)
13	H <sub>2</sub> S	-398.788 21 (9.2) [-398.930 73]	-399.062 53 (16.3) [-399.197 96]	-399.017 24 (21.4) [-399.150 60]
14	MeSH	-437.952 35 (27.8)	-438.249 88 (34.4) -438.265 75 (36.9) <sup>b</sup>	-438.237 06 (38.8) <sup>b</sup>
15	Me <sub>2</sub> S	-477.120 66 (45.7)	-477.437 00 (52.1) -477.457 99 (56.0) <sup>b</sup>	-477.494 78 (61.2) <sup>b</sup>
16	Me <sub>3</sub> S <sup>+</sup>	-516.624 08 (69.4)	-516.690 01 (74.4)	

<sup>a</sup> Energies are in hartrees. Values in parentheses are zero-point vibrational energies in kcal/mol at the HF/6-31G\*//HF/6-31G\* level scaled by a factor of 0.8929. Values in square brackets are G2 energies in hartrees. <sup>b</sup> At MP2/6-31G\*//MP2/6-31G\*.

Carboxonium ions are ambident electrophiles and can react by transferring the ligand attached to oxygen (H or alkyl or aryl group) to a nucleophile as well as by allowing the nucleophile to be attached to the carbocationic center.



The carbocationic nature of carboxonium ions is weak due to strong delocalization of the oxonium forms. As a result, reactions to the carbocationic center are limited to those by efficient nucleophiles.

*O*-Alkyl carboxonium ions are alkylating agents, whereas acidic carboxonium ions tend to be efficient proton-transfer agents, and nucleophilic attack at the carbocationic center was observed only rarely (vide infra), mostly in their rearrangement reactions in strong acid solutions.

In this paper we discuss the activation of oxonium, carboxonium, and sulfonium ions as a consequence of their further protonation (protolysis). We wish to report the ab initio energies, electronic structures, and proton affinities as well as the isothermic enthalpies and deprotonation barriers of the corresponding dications. We further discuss the role of these dications in superacid-catalyzed reactions.

## Results and Discussion

Ab initio molecular orbital calculations were carried out on an Alliant FX/40 computer by using the GAUSSIAN86<sup>8</sup> and GAUSSIAN90<sup>9</sup> packages of programs. Restricted Hartree-Fock calculations were performed throughout. Structures were typically optimized under appropriate symmetry restrictions first with the HF/3-21G basis set and were subsequently improved at the HF/6-31G\* level. Single-point calculations at the MP2/6-31G\*//HF/6-31G\* level were carried out to include electron correlation. MP2/6-31G\* optimizations were done in cases where the Hartree-Fock level was not reliable in predicting a minimum

structure (vide infra). Although structural differences can be observed with this method, the overall effect on the proton affinities at this level compared to the HF/6-31G\* optimized structures was found to be quite small for selected dications; e.g., the second proton affinity of methanol to H<sub>4</sub>COH<sub>2</sub><sup>2+</sup> changes by only 0.4 kcal/mol from the MP2/6-31G\*//HF/6-31G\* to the MP2/6-31G\*//MP2/6-31G\* level of theory. GAUSSIAN-2 (or G2) theory<sup>10</sup> is a composite method based on a MP2/6-31G\* optimized geometry which is treated in single-point calculations with a variety of basis sets at the post-SCF level. The resulting energies are combined using certain additivity assumptions and improved with zero-point and isogyric corrections. This method has proven to give excellent estimates of the total energy and other properties of small molecules. GAUSSIAN-2 theory was used in this study to reevaluate the total energies, proton affinities, and deprotonation barriers of small dications. The results were also compared to formerly published data. Total energies for the most stable conformers of neutral bases and mono- and dications are summarized in Table I. Vibrational frequencies were calculated at the HF/6-31G\*//HF/6-31G\* level and scaled by a factor of 0.8929 in order to characterize stationary points on the surface as well as to evaluate zero-point vibrational contributions. Gas-phase proton affinities were calculated for 298 K based on MP2/6-31G\*//HF/6-31G\* and GAUSSIAN-2 energies. They are given together with isodesmic enthalpies in Table II. HF/6-31G\* optimized geometries are given in Figure 1.

H<sub>3</sub>O<sup>2+</sup> (1c). Diprotonated water was studied previously,<sup>2</sup> and the tetrahedral isomer was found to be the global minimum. Dissociation was reported to be thermodynamically preferred by -59.2 kcal/mol (HF/6-31G\*), although a kinetic barrier of 39.4 kcal/mol at the same level had to be overcome. The treatment with the GAUSSIAN-2 method makes the deprotonation favorable by -61.9 kcal/mol and lowers the activation energy slightly to 38.2 kcal/mol. The proton affinity calculated for 298 K at the same level is -60.4 kcal/mol. The reexamination of the H<sub>4</sub>O<sup>2+</sup> system is in agreement with previous studies and fully supports experimental results that suggest an associative mechanism for the H/D exchange of H<sub>3</sub>O<sup>+</sup> in superacidic media.

H<sub>4</sub>COH<sub>2</sub><sup>2+</sup> (2c). Diprotonation of methyl alcohol seems to occur primarily on carbon, since the entire HF/6-31G\* singlet surface for CH<sub>3</sub>OH<sub>2</sub><sup>2+</sup> was found to be repulsive. The only stable isomer of CH<sub>3</sub>OH<sub>2</sub><sup>2+</sup> + H<sup>+</sup> involves a pentavalent carbon center, i.e., <sup>+</sup>CH<sub>4</sub>O<sup>+</sup>H<sub>2</sub>.<sup>11</sup> This species was reported to be 36.6 kcal/mol

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**Table II.** Gas-Phase Proton Affinities<sup>12,13</sup> and Isodesmic Enthalpies<sup>14</sup> at the MP2/6-31G\*//HF/6-31G\* Level<sup>a</sup>

compd	base	1st PA <sup>b</sup>		2nd PA, calcd	calcd	
		calcd	exptl		$\Delta H_1^{\text{iso}}$	$\Delta H_2^{\text{iso}}$
1	H <sub>2</sub> O	168.1 (164.6)	166.5	-58.9 (-60.4)	0.0	0.0
2	MeOH	181.8	181.9	-34.6	-13.4	-22.5
3	Me <sub>2</sub> O	189.3	192.1	9.5 <sup>c</sup>	-20.8	-67.8 <sup>c</sup>
4	Me <sub>3</sub> O <sup>+</sup>	29.1				-82.9
5	HCHO	167.4	171.7	-27.7	0.0	0.0
6	CH <sub>3</sub> CHO	182.0	186.6	-2.6	-14.1	-24.2
7	(CH <sub>3</sub> ) <sub>2</sub> CO	191.0	196.7	15.8	-22.7	-42.8
8	HCOOH	174.9	178.8	-1.5	-6.8	-26.0
9	CO	142.2 (140.9)	141.9	-75.9 (-69.3)	26.4	49.0
10	CH <sub>3</sub> COOH	185.4	190.2	15.1	-17.0	-42.3
11	H <sub>2</sub> CO <sub>3</sub>	177.4		7.2	-13.3	-34.3
12	CO <sub>2</sub>	124.4	130.9	-41.4	45.5	15.7
13	H <sub>2</sub> S	166.5 (169.2)	170.2	-32.0 (-28.2)	0.0	0.0
14	MeSH	181.6	187.4	-18.4 <sup>c</sup>	-14.6	-10.4 <sup>c</sup>
15	Me <sub>2</sub> S	193.6	200.6	19.4 <sup>c</sup>	-26.4	-51.5 <sup>c</sup>
16	Me <sub>3</sub> S <sup>+</sup>	37.9				-69.8

<sup>a</sup> All values are in kcal/mol. Values in parentheses are G2 calculated affinities. <sup>b</sup> Proton affinity. <sup>c</sup> At MP2/6-31G\*//MP2/6-31G\*.

less stable than the parent methyloxonium ion at HF/6-31G\*//HF/6-31G\*. This value is slightly improved to 36.2 kcal/mol at MP2/6-31G\*//HF/6-31G\*.

(H<sub>3</sub>C)<sub>2</sub>OH<sub>2</sub><sup>2+</sup> (**3c**). Diprotonated dimethyl ether failed to converge to a stable structure at the Hartree-Fock level. However, at the MP2/6-31G\*//MP2/6-31G\* level a stable O,O-diprotonated isomer exists. The second proton affinity of 9.5 kcal/mol suggests that the formation of diprotonated dimethyl ether in the gas phase is an exothermic process.

(H<sub>3</sub>C)<sub>3</sub>OH<sup>2+</sup> (**4b**). Protonated trimethyloxonium ion exists at HF/6-31G\* as a thermodynamically as well as kinetically stable species. At the MP2/6-31G\*//HF/6-31G\* level a stabilization of -27.6 kcal/mol relative to the trimethyloxonium ion is predicted. This makes **4b** the thermodynamically most favored oxonium dication. The  $\Delta H_2^{\text{iso}}$  value (Table II) indicates that the proton transfer from H<sub>3</sub>O<sup>2+</sup> to (H<sub>3</sub>C)<sub>3</sub>O<sup>+</sup> is exothermic by 82.9 kcal/mol. Deprotonation of **4b** occurs via a transition state that was found to be 101.5 kcal/mol above the parent dication. The transition state **4c** was located and confirmed with a frequency calculation. Structural details are given in Figure 2.

(H<sub>3</sub>C)<sub>4</sub>O<sup>2+</sup> (**4d**). The tetramethyloxonium dication was found to be a stable minimum at HF/6-31G\*. The total energy at MP2/6-31G\*//HF/6-31G\* of -233.21462 hartrees is 57.9 kcal/mol higher than the energy for the system (H<sub>3</sub>C)<sub>3</sub>O<sup>+</sup> + H<sub>3</sub>C<sup>+</sup>.

HCHOH<sub>2</sub><sup>2+</sup> (**5c**). Di-O-protonated formaldehyde is isoelectronic with ethylene. In agreement with the reported results,<sup>15a</sup> the global minimum of the dication has a planar C<sub>2v</sub> symmetry. The increase in C-O bond length on first protonation is 0.048 Å (4%), and a further 0.073 Å (6%) on second protonation is observed. The C-O bond length (1.305 Å) in diprotonated form **5c** is between the C=O double bond length in formaldehyde (1.184 Å) and the C-O single bond length in methanol (1.339 Å). The deprotonation barrier toward O-H and C-O dissociation

for the dication **5c** was calculated to be 62.6 and 101.8 kcal/mol, respectively, at the MP2/6-31G\*//HF/6-31G\* level.<sup>15a</sup>

Similar to HCHOH<sub>2</sub><sup>2+</sup>, ethylene and substituted ethylene dications have been calculated by Frenking.<sup>16</sup>

CH<sub>3</sub>CHOH<sub>2</sub><sup>2+</sup> (**6c**). Di-O-protonated acetaldehyde dication (**6c**) should be relatively more stable than di-O-protonated formaldehyde (**5c**) due to methyl hyperconjugative stabilization. Methyl hyperconjugation in **6c** increased the C-O bond length by 0.03 Å compared to that of **5c**. This suggests that the methyl hyperconjugation further increases the single-bond character of the C-O bond in **6c**. In fact the energy difference in going from CH<sub>3</sub>CHOH<sup>+</sup> to CH<sub>3</sub>CHOH<sub>2</sub><sup>2+</sup> is exothermic by 0.6 kcal/mol, whereas in going from HCHOH<sup>+</sup> to HCHOH<sub>2</sub><sup>2+</sup> it is endothermic by 23.6 kcal/mol.

(CH<sub>3</sub>)<sub>2</sub>COH<sub>2</sub><sup>2+</sup> (**7c**). Diprotonated acetone is isoelectronic with the *tert*-butyl cation. The calculated C-O bond length in **7c** is 1.359 Å, 0.02 Å longer than that of **6c**, indicating more hyperconjugation in **7c** compared to **6c**. The largest second proton affinity, that of monoprotonated acetone (15.8 kcal/mol), and the largest  $\Delta H_2^{\text{iso}}$  value, that of **7c** (-42.8 kcal/mol), within this series of carboxonium ions (Table II) indicates the possibility of the relatively easy formation of diprotonated acetone as intermediate.

Krivdin, Facelli, et al. also carried out recently<sup>17</sup> a theoretical study of the protonation of acetone and calculated NMR chemical shifts and coupling constants for the mono- and diprotonated species. Experimentally (by NMR) no diprotonated acetone could be observed. This is, however, not unexpected as its equilibrium concentration could be extremely low.

HC(OH)(OH)<sub>2</sub><sup>2+</sup> (**8c**). Diprotonated formic acid can be considered as a donor-acceptor complex of H<sub>2</sub>O and diprotonated CO (HCOH<sup>2+</sup>). The second proton affinity of monoprotonated formic acid and the  $\Delta H_2^{\text{iso}}$  value of **8c** were calculated to be -0.2 and -26.0 kcal/mol, respectively.

HCOH<sup>2+</sup> (**9c**). Diprotonated CO (**9c**), which is isoelectronic with acetylene, has been calculated previously<sup>15</sup> with results similar to those reported here. We have applied the G2 procedure<sup>10</sup> to calculate the molecular energy and dissociation barrier of **9c**. Total G2 energies and the MP2/6-31G\* optimized structures are given in Figure 3. The proton affinity of CO at G2 was calculated to be 140.9 kcal/mol, which compares well with the experimental value of 141.9 kcal/mol. The calculated proton affinity of HCO<sup>+</sup> is -69.3 kcal/mol at the same level. HCOH<sup>2+</sup> (**9c**) lies 70.8 kcal/mol above HCO<sup>+</sup> + H<sup>+</sup>. The G2 method gives a deprotonation barrier for conversion of **9c** to HCO<sup>+</sup> + H<sup>+</sup> via transition-state **9e** that is significantly lower (19.5 kcal/mol) than the alternative barrier via **9f** (46.3 kcal/mol) to COH<sup>+</sup> + H<sup>+</sup>.

(12) Proton affinities (PA) of the reaction B + H<sup>+</sup> → BH<sup>+</sup> have been calculated from the following formula:

$$PA = -\Delta H_{298} = -\Delta E_0^{\text{elec}} - \Delta ZPE + 5/2RT$$

where the  $\Delta E_0^{\text{elec}}$  term includes all electronic effects, the term  $\Delta ZPE$  is the difference in zero-point energies for B and BH<sup>+</sup>, and the final term is the temperature correction. All of the calculations reported here are for a temperature of 300 K; Dixon, D. A.; Komornicki, A.; Kraemer, W. P. *J. Chem. Phys.* **1984**, *81*, 3603.

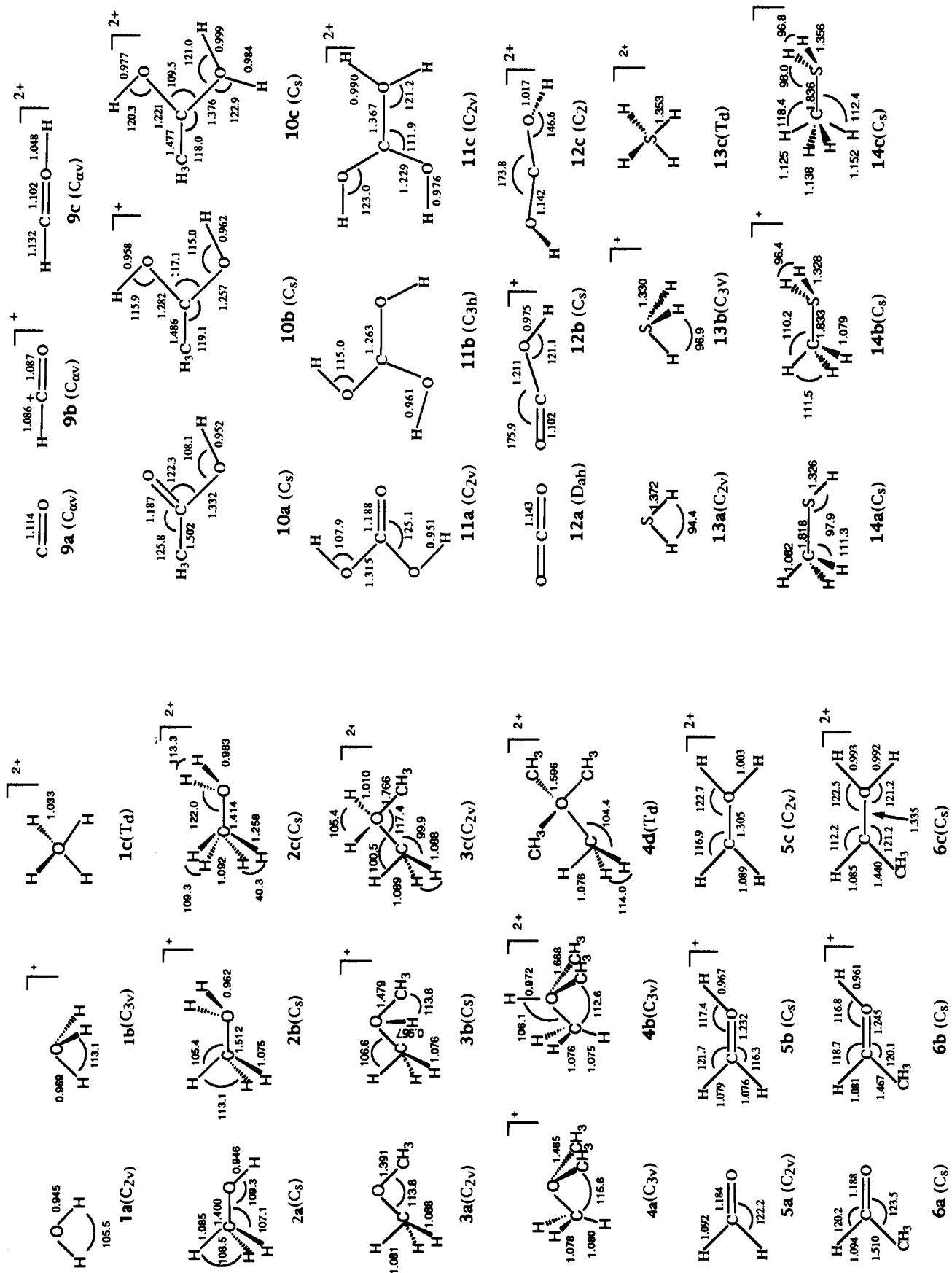
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(17) Krivdin, L. B.; Zinchenko, S. V.; Kalabin, G. A.; Facelli, J. C.; Tufno, M. F.; Contreras, R. H.; Yu, A.; Denisov, O. A.; Gavriluk, V. I.; Mamatyuk, J. *J. Am. Chem. Soc.*, submitted.



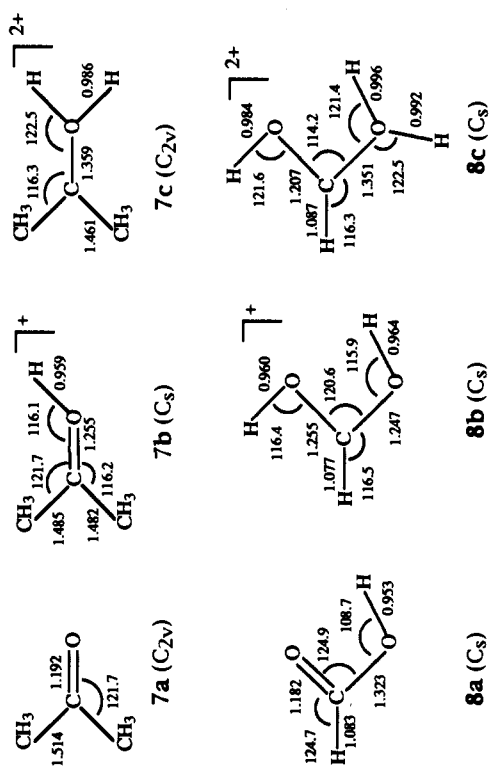


Figure 1. HF/6-31G\* optimized structures (of the most stable isomers) of the free (a) and mono- (b) and diprotonated (c) bases. Bond lengths are in angstroms, and bond angles are in degrees. Structures 3c, 14c, and 15c were optimized at MP2/6-31G\*.

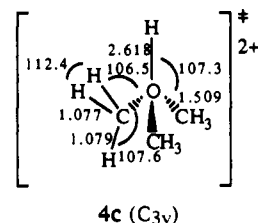


Figure 2. Structural parameters for the  $(\text{CH}_3)_3\text{OH}_2^+$  deprotonation transition state calculated at HF/6-31G\*.

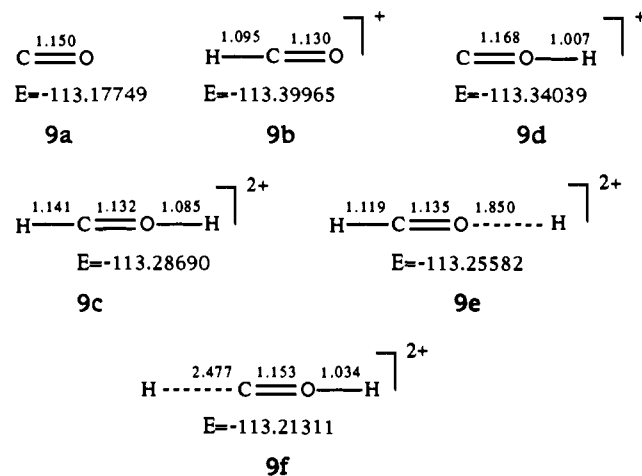


Figure 3. MP2/6-31G\* optimized structures and G2 calculated energies (hartrees) of 9a-f.

$\text{CH}_3\text{C}(\text{OH})(\text{OH}_2)^{2+}$  (10c). Similar to diprotonated formic acid (8c), diprotonated acetic acid (10c) can be viewed as a donor-acceptor complex of  $\text{H}_2\text{O}$  and protonated acetyl cation ( $\text{CH}_3\text{COH}_2^+$ ). As expected, methyl substitution on 8c increased the proton affinity and the  $\Delta H_2^{160}$  value of 10c by 16.6 and 10.2 kcal/mol, respectively, compared to unsubstituted diprotonated formic acid (8c).

$\text{C}(\text{OH})_2(\text{OH}_2)^{2+}$  (11c). The global minimum of diprotonated carbonic acid corresponds to the planar  $\text{C}_{2v}$  geometry 11c and can be considered as a donor-acceptor complex of  $\text{H}_2\text{O}$  and diprotonated  $\text{CO}_2$  ( $\text{C}(\text{OH})_2^{2+}$ ) (12c). The C—OH<sub>2</sub> bond length (1.367 Å) of 11c is slightly greater than the C—OH bond length (1.339 Å) of neutral methanol, whereas the C—OH bond length (1.229 Å) of 11c is between the normal C—O and C=O bond lengths, indicating the delocalization of the second charge between the two oxygen atoms (of C—OH).

$\text{HOCO}^{\text{H}}\text{H}^+$  (12c). The global minimum of diprotonated  $\text{CO}_2$  corresponds to the dihydroxycarbonyl dication 12c with  $\text{C}_2$  symmetry. This ion was also calculated previously<sup>18</sup> by Koch and Schwarz, and our results are similar to theirs. The deprotonation barrier was found to be 38.0 kcal/mol at the MP4/6-311G\*\*//HF/6-31G\* level.<sup>17</sup> The dicationic complex of  $\text{CO}^+ + \text{H}_2\text{O}^+$  is 11.1 kcal/mol less stable than 12c at the same level.

$\text{H}_4\text{S}^{2+}$  (13c). Diprotonated hydrogen sulfide was previously found as a high-lying minimum (25.2 kcal/mol, MP4SDTQ/6-31G\*\*//HF/6-31G\*) with a deprotonation barrier of 59.2 kcal/mol at the same level.<sup>4</sup> The GAUSSIAN-2 method predicts 13c to be 29.7 kcal/mol less stable than the hydrosulfonium ion. The deprotonation barrier was found to be 56.2 kcal/mol, and the proton affinity at the same level was estimated to be -28.2 kcal/mol.

$\text{H}_4\text{CSH}_2^{2+}$  (14c). The second protonation of methyl sulfide occurs at the carbon center, similar to the methyloxonium dication. However, the stationary point on the HF/6-31G\* surface proved to be a transition state. MP2/6-31G\* optimization led to a minimum that is destabilized by 19.9 kcal/mol relative to the methylsulfonium ion.

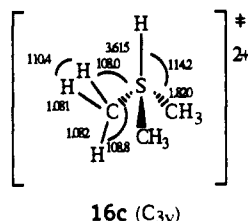
16c (C<sub>3v</sub>)

Figure 4. Structural parameters for the (CH<sub>3</sub>)<sub>3</sub>SH<sub>2</sub><sup>2+</sup> deprotonation transition state calculated at HF/6-31G\*.

(H<sub>3</sub>C)<sub>2</sub>SH<sub>2</sub><sup>2+</sup> (15c). Diprotonation of dimethyl sulfide at MP2/6-31G\*\*//MP2/6-31G\* is favored by 17.9 kcal/mol in the gas phase.

(H<sub>3</sub>C)<sub>3</sub>SH<sup>2+</sup> (16b). Protonation of the trimethylsulfonium ion leads to a stable intermediate at HF/6-31G\*. The proton affinity for (CH<sub>3</sub>)<sub>3</sub>S<sup>+</sup> at MP2/6-31G\*\*//HF/6-31G\* is 37.9 kcal/mol. The transition state for the deprotonation was calculated to be 95.5 kcal/mol above (CH<sub>3</sub>)<sub>3</sub>SH<sup>2+</sup> at the same level. The transition structure 16c is given in Figure 4.

(H<sub>3</sub>C)<sub>3</sub>S<sup>2+</sup> (16d). Methylation of trimethylsulfonium ion gives a high-lying intermediate with a total energy of -555.90387 hartrees which is located 28.5 kcal/mol above the (H<sub>3</sub>C)<sub>3</sub>S<sup>+</sup> + H<sub>3</sub>C<sup>+</sup> system at MP2/6-31G\*\*//HF/6-31G\*.

Considerable barriers for the proton loss of dications were reported earlier.<sup>15a,c,19</sup> It was shown theoretically by Dunitz and Ha<sup>20</sup> that bonding interactions can counteract strong electrostatic charge-charge repulsion sufficiently to result in kinetically stable species. Previously it was suggested that calculated barriers are overestimated at the Hartree-Fock level.<sup>15c</sup> Correlated levels lower the activation energy slightly, but even with G2 theory significant barriers exist for smaller dications. At HF/6-31G\*\*//HF/6-31G\* the deprotonation barrier for HCOH<sup>2+</sup> is 22.7 kcal/mol.<sup>15a</sup> The G2 method still calculates a gas-phase barrier of 19.5 kcal/mol.

Even experimentally<sup>21</sup> it was observed that, upon an increase of charge, the bonding situation can be improved and kinetically stable species can result. Gas-phase studies of the He<sub>2</sub><sup>2+</sup> system showed that the dication is stabilized by a kinetic barrier of 33.2 kcal/mol, although dissociation is preferred by as much as 200.0 kcal/mol.

The reason for the kinetic stability of small dications was previously discussed<sup>19</sup> in terms of effective nuclear charge. It was suggested that a fractional increase in nuclear charge leads to stronger bonding and a decrease of the equilibrium internuclear distance. The activation barriers were furthermore interpreted<sup>22</sup> as the result of two opposing factors, e.g., the energy gained in the formation of a new bond and the Coulomb repulsion of two charged fragments.

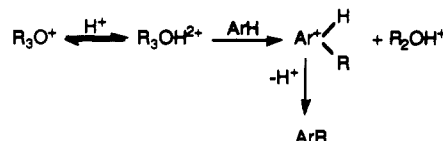
It must be further recognized that the calculational data referred to dilute gas conditions and thus do not fully relate to the condensed state. Solvation or clustering effects may have a major influence. In particular in small dications, solvation tends to diminish the effect of charge-charge repulsion and thus could bring H<sub>4</sub>O<sup>2+</sup>, for example, into a thermodynamically more accessible region. Superacid solutions of H<sub>3</sub>O<sup>+</sup> could be highly clustered structures. Thus, the H<sub>4</sub>O<sup>2+</sup> protons might be shared by more than one H<sub>3</sub>O<sup>+</sup> in a dynamic fashion.

The theoretical data for H<sub>4</sub>O<sup>2+</sup> show it to be a T<sub>d</sub> minimum energy structure which may be difficult to generate, without substantial cluster stabilization. The electrostatic repulsion associated with the protonation of H<sub>3</sub>O<sup>+</sup> is also the probable cause of H<sub>4</sub>O<sup>2+</sup> so far eluding gas-phase detection. Electrostatic repulsion is much less pronounced for clustered species. This was substantiated by the H<sup>+</sup>/D<sup>+</sup> exchange studies of H<sub>3</sub>O<sup>+</sup> in sup-

eracidic media. Protosolvation resulting in delocalizing the excess positive charge over a larger "cluster" can be responsible for superelectrophilic activation.

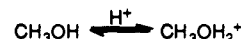
The effect of the counterions certainly has an important influence on the equilibrium between dications and monocations. However, it should be noted that an exceedingly delocalized and weak nucleophile like SbF<sub>6</sub><sup>-</sup> or related Sb<sub>2</sub>F<sub>11</sub><sup>-</sup> might not compete efficiently with the rather localized lone pairs of the monocations. If these anions were valid bases, the exchange of H<sub>4</sub>O<sup>2+</sup> in DF-SbF<sub>5</sub> should not be accelerated by an increase of the acidity of the solution. The accelerated exchange rate suggests that monocations can very well compete with large, weak nucleophiles like SbF<sub>6</sub><sup>-</sup>, since all protons are initially solvated by the counterions.

The significance of the reported study lies in our better understanding of superacid-catalyzed conversions of oxonium, sulfonium, and carboxonium ions. Trialkyloxonium ions, i.e., Meerwein salts, are excellent alkylating agents for heteroatoms but are not capable of C-alkylating aromatic or aliphatic compounds. In conjunction with strong protic acids such as FSO<sub>3</sub>H, CF<sub>3</sub>SO<sub>3</sub>H, or FSO<sub>3</sub>H·SbF<sub>5</sub> (Magic Acid), they were found to readily alkylate aromatics. Benzene and toluene have been methylated and ethylated with trimethyl- and triethyloxonium salts in the presence of Magic Acid.<sup>1</sup> The methylation of toluene gave an isomer distribution of 60% *o*-, 11% *m*-, and 21% *p*-xylene, indicative of a typical aromatic substitution involving a highly reactive electrophilic reagent. The protolytic activation of trialkyloxonium ions can be taken as indicative of the protosolvation of the oxygen lone pair which enhances the electrophilicity of the alkyl group. Lewis acid complexation can have a similar effect.

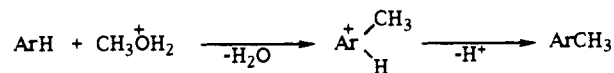


Acid-catalyzed alkylation of aromatics with alcohols is well-known. Whereas tertiary (and secondary) alcohols react with relative ease following a carbocationic mechanism, alkylation with primary alcohols is generally achieved only in the case of more reactive aromatics, and even then under forcing conditions.

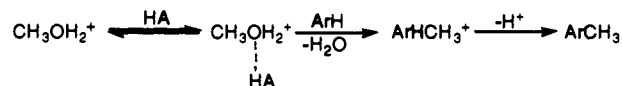
Protonation of methyl alcohol gives the very stable, well-defined methyloxonium ion under superacidic, stable ion conditions.



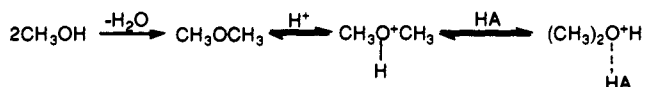
The reactivity of the methyloxonium ion with nucleophiles is reflected in proton transfer or nucleophilic S<sub>N</sub>2-like displacement giving methylated products.



It is significant to note that in superacidic media, including solid superacids, methylation of aromatics is greatly facilitated. This can reflect activation through protosolvation of the nonbonded electron pair on oxygen, allowing the methyl group to C-alkylate aromatics.



Alternatively, methyl alcohol can dehydrate under the acidic conditions to give dimethyl ether, which then forms dimethyloxonium ion, (CH<sub>3</sub>)<sub>2</sub>OH<sup>+</sup>, and through its protosolvation another reactive methylating agent is formed.



The methyloxonium ion in superacidic media readily undergoes ionic hydrogenation, giving methane.<sup>23a</sup> As cleavage giving the

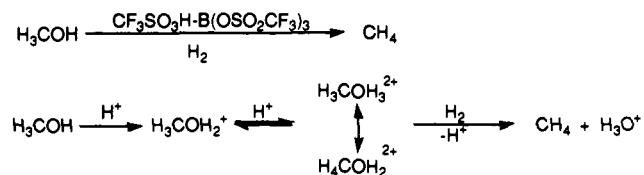
(19) Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1321.

(20) Dunitz, T. K.; Ha, T. K. *J. Chem. Soc., Chem. Commun.* 1972, 568.

(21) Radom, L.; Gill, P. M. W.; Wong, M. W.; Nobes, R. H. *Pure Appl. Chem.* 1988, 28, 183. Yagisawa, H.; Sato, H.; Watanabe, T. *Phys. Rev.* 1977, A16, 1352.

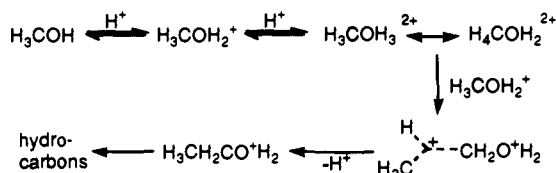
(22) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986; p 397.

free methyl cation ( $\text{CH}_3^+$ ) is prohibitive for energetic reasons, the reaction is best interpreted to proceed through the protonated methyloxonium dication.



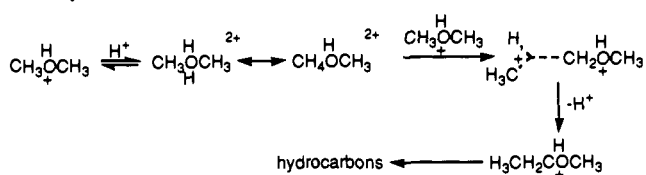
As indicated by the present theoretical calculation, diprotonation of methyl alcohol gives preferentially the O,C-diprotonated dication, i.e.,  $^+\text{CH}_4\text{OH}_2^+$ , but some contribution from protosolvated  $\text{CH}_3\text{OH}_3^{2+}$  is possible in superacidic solution.

The chemical behavior of methyl alcohol (and dimethyl ether) in superacids is indeed indicative of protolytic activation of the related methyloxonium ions. When methyl alcohol (or dimethyl ether) is reacted with superacids ( $\text{HF}\cdot\text{SbF}_5$ ,  $\text{FSO}_3\text{H}\cdot\text{SbF}_5$ ,  $\text{TaF}_5$ ,  $\text{NbF}_5$ , and others) under forcing conditions (100–300 °C), some methane is obtained. Pearson, when reacting methyl alcohol or trimethyl phosphate with phosphorus pentoxide or polyphosphoric acid, respectively, at 190 °C, obtained  $\text{C}_3$ – $\text{C}_9$  alkanes as well as toluene and  $\text{C}_8$ – $\text{C}_{10}$  aromatics.<sup>23b</sup> Electrophilic methylation of methyl alcohol itself is expected only on oxygen, giving dimethyl ether. Further protolytic formation of free  $\text{CH}_3^+$  is, for energetic reasons, improbable. It is therefore considered that in superacidic media, where methyl alcohol is completely protonated, the methyloxonium ion,  $\text{CH}_3\text{OH}_2^+$ , itself will undergo methylation in the C–H bond. The active methylating agent is provided by protosolvation or some diprotonation equilibrium resulting in a superelectrophilic methylating agent. According to calculated results the O,O-diprotonated form of methanol is not a stable species in the gas phase. In superacidic solution, however, it may contribute to account for the observed C-methylation.

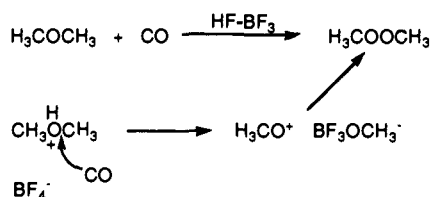


Once the first  $\text{C}_1$  to  $\text{C}_2$  conversion is achieved, ethyl alcohol will give readily the observed hydrocarbon products (by further alkylation or through dehydration to ethylene and its well-recognized acid-catalyzed electrophilic chemistry).

Dimethyl ether is expected to react similarly to methyl alcohol. Of course, intermolecular acid-catalyzed dehydration of methyl alcohol is well recognized to give dimethyl ether. Protolytic activation of dimethyl ether can take place similarly to that of methyl alcohol.



Similar activation is probably involved in the carbonylation of dimethyl ether (or methyl alcohol) in superacidic solutions to methyl acetate.



Trimethyloxonium ion does not react with CO, except when activated by superacids.

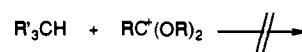
Trialkylsulfonium ions are weak alkylating agents at best. They do not alkylate aromatic hydrocarbons. Laali et al., however, found that, similarly to their oxonium analogs in the presence of superacids, they are greatly activated and alkylate aromatics with ease.<sup>24</sup> Protic activation of the sulfonium ions to their dications is thus indicated. Similarly the reactivity of  $\text{CH}_3\text{SH}$  and  $(\text{CH}_3)_2\text{S}$  is equally enhanced by superacids.

The carbocationic reactivity of carboxonium ions is greatly enhanced by their protosolvation (protonation) in superacidic solutions.

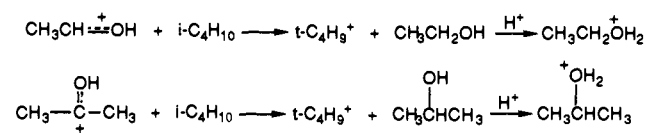
Trivalent carbocations (carbenium ions) are well recognized as efficient hydride abstractors, generating for example from tertiary isoalkanes the related new carbocations



In contrast, carboxonium ions, being weaker electrophiles, show no hydride-abstrating ability against isoalkanes when reacted in aprotic solvents ( $\text{SO}_2$  or  $\text{SO}_2\text{ClF}$ ).

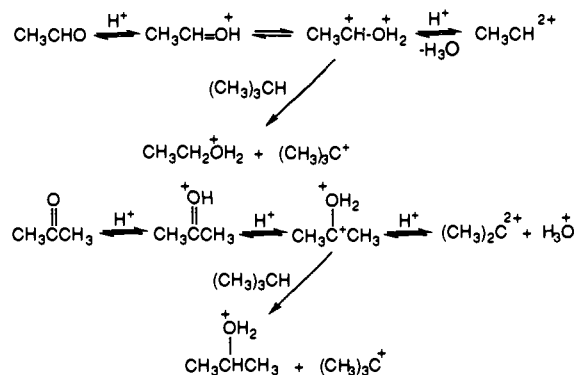


The reactivity of carboxonium ions, however, is greatly increased in superacidic solutions. Brouwer and Kiffen<sup>25</sup> observed that acetaldehyde and acetone readily reacted in 9:1  $\text{HF}\cdot\text{SbF}_5$  or  $\text{HF}\cdot\text{BF}_3$  solutions with isobutane to give *tert*-butyl cation in the presumed reactions



Brouwer and Kiffen stated, "The hydride transfer from an alkane molecule to a hydroxycarbenium ion to form an alkyl-carbenium ion and an alcohol molecule is thermodynamically a very unfavorable reaction. The equilibrium of this reaction as such would lie completely to the side of the starting compounds. It is the high degree of the protonation of the alcohol that renders the hydride transfer thermodynamically possible."

It is now suggested on the basis of the low carbocationic reactivity of the methylcarboxonium ( $\text{CH}_3\text{CHOH}^+$ ) and dimethylcarboxonium ( $(\text{CH}_3)_2\text{COH}^+$ ) ions that the hydride-transfer reactions which were observed in excess superacid solutions were de facto induced by diprotonated acetaldehyde or acetone, respectively.

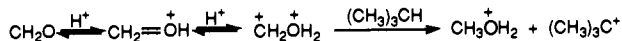


These reactions are thermodynamically favorable (vide infra), and protonated alcohols are formed directly in the hydride-transfer reaction itself (and not by subsequent protonation of neutral alcohol products). The diprotonated carbonyl compounds act as extremely reactive superelectrophiles.

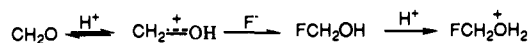
Protonated formaldehyde reacts similarly.

(23) (a) Olah, G. A.; Wu, A.-h. *Synlett* 1990, 599–600. (b) Pearson, D. E. *J. Chem. Soc., Chem. Commun.* 1974, 397.

(24) Laali, K.; Chen, H. Y.; Gerzina, R. J. *J. Org. Chem.* 1987, 52, 4126.  
(25) Brouwer, D. M.; Kiffen, A. A. *Recl. Trav. Chim. Pays-Bas* 1973, 92, 809.

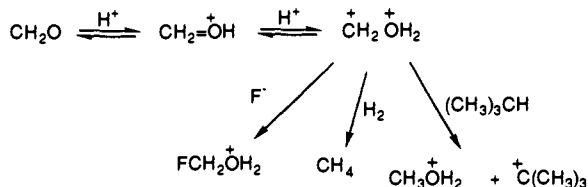


Olah and Mateescu observed<sup>26</sup> that when monomeric formaldehyde was reacted with 3:1 HF·SbF<sub>5</sub> or HSO<sub>3</sub>F·SbF<sub>5</sub> (containing some HF) in SO<sub>2</sub>ClF solution at -78 to 40 °C, protonated fluoromethyl alcohol, FCH<sub>2</sub>OH<sub>2</sub><sup>+</sup>, was obtained. It was assumed at the time that the reaction proceeded with formation of fluoromethyl alcohol, which was subsequently protonated.

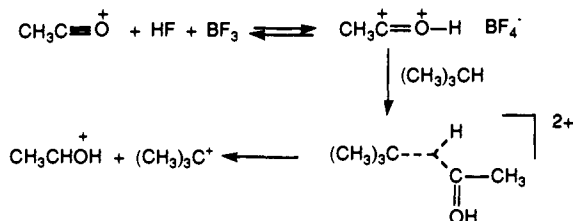


The reaction with HCl gave similarly protonated chloromethyl alcohol, ClCH<sub>2</sub>OH<sub>2</sub><sup>+</sup>.<sup>27</sup>

It is now suggested that the more probable course of the reactions involves the much more reactive diprotonated (protosolvated) formaldehyde. Formaldehyde is also readily reduced under ionic hydrogenation conditions even at room temperature to methyloxonium ion (and subsequently to methane).<sup>27</sup> Monoprotonated formaldehyde possesses too weak a carbocationic nature to be able to account for the reactions.



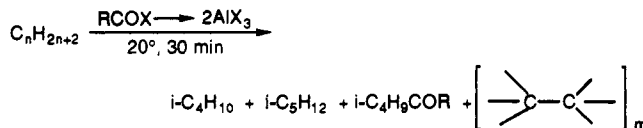
Brouwer and Kiffen<sup>28</sup> have also reported the hydride-transfer reaction of isobutane with the acetyl cation (CH<sub>3</sub>CO<sup>+</sup>), generated from acetic acid in excess HF·BF<sub>3</sub>. Olah et al.<sup>29</sup> found that such a reaction does not occur with isolated acetyl cations in aprotic solvents such as SO<sub>2</sub>, SO<sub>2</sub>ClF, AsF<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>. Further, the hydride abstraction from isobutane by the acetyl cation is endothermic by 8.5 kcal/mol (in the gas phase). It was therefore suggested that the reaction occurs by protosolvation of the acetyl cation by the superacidic HF·BF<sub>3</sub> system.



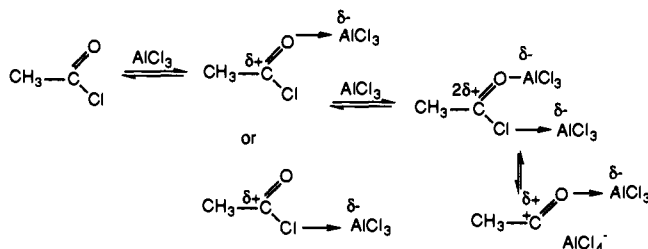
A stable protoacetyl dication has not been observed by NMR spectroscopy. However, theoretical calculations have shown that C<sub>2</sub>H<sub>4</sub>O<sup>2+</sup> is a global minimum.<sup>30</sup> This agrees with charge-stripping mass spectrometric studies wherein the C<sub>4</sub>H<sub>4</sub>O<sup>2+</sup> dication has been observed. Interestingly, the C-protonated isomer (involving a C—H)<sup>+</sup>CH<sub>4</sub>—C<sup>+</sup>=O is only 24.6 kcal/mol less stable than the O-protonated acetyl cation.

Apart from Brønsted acid activation, the acetyl cation (and other acyl ions) can also be activated by Lewis acids. While the 1:1 CH<sub>3</sub>COX—AlX<sub>3</sub> Friedel-Crafts complex is inactive for the isomerization of alkanes, a complex with a molar excess of AlX<sub>3</sub> was found by Volpin et al. to be<sup>31,32</sup> extremely reactive toward isomerization of saturated hydrocarbons. They called the

CH<sub>3</sub>COX—AlX<sub>3</sub> complex an aprotic superacid. This indicates that the acetyl cation is further activated by O-complexation with a second molecule of AlX<sub>3</sub>.

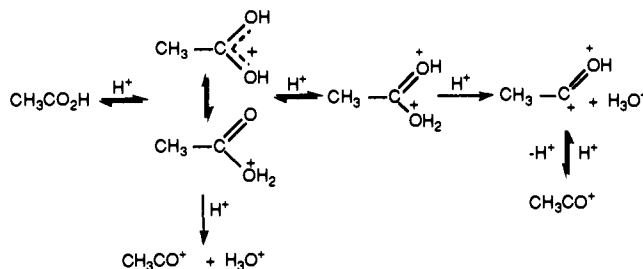


The ionization of acyl (such as acetyl) chloride with excess AlCl<sub>3</sub> can also be considered to involve bidentate interaction.



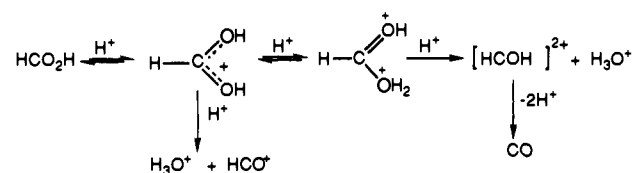
In superacidic solution the protolysis of carboxylic acids to acyl cations proceeds through the protonated acids, i.e., alkyl-carboxonium ions RC<sup>+</sup>(OH)<sub>2</sub> (vide infra).

Acetic and other carboxylic acids O-protonate in superacids to stable, observable (by NMR) carboxonium ions.<sup>33</sup> Cleavage to related acyl cations is observed by increasing the temperature of the solutions. A diprotonation equilibrium can play a role in the protolytic ionization process.



Cleavage of diprotonated acetic acid would proceed through the bent protoacetyl dication (CH<sub>3</sub>COH<sup>2+</sup>), which would explain the observed high reactivity of the system toward alkanes.

Formic acid is of particular interest as its protolysis after observing the parent carboxonium ion at low temperature leads to generation of CO, without observation of the formyl cation (vide infra).



Diprotonated CO, i.e., HCOH<sup>2+</sup>, can indeed be the de facto reactive formylating agent in the observed superacidic formylation of adamantane.<sup>34</sup>

In related work Shudo et al. recently suggested<sup>35</sup> that in the Gattermann reaction of aromatics diprotonated HCN is the de facto reagent. HCNH<sub>2</sub><sup>2+</sup> was first theoretically studied by Schwarz.<sup>36</sup> Diprotonated nitriles, RCNH<sub>2</sub><sup>2+</sup>, similarly were suggested to be involved.

(26) (a) Olah, G. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1971**, *93*, 781.

(b) Olah, G. A.; Yu, S. H. *J. Am. Chem. Soc.* **1975**, *97*, 2793.

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In conclusion, protolytic (electrophilic) activation of onium, carboxonium, and related ions results in doubly electron deficient (dipositive) *superelectrophiles* whose reactivity greatly exceeds that of their parents observed in aprotic or conventional acidic media. The definition of the term *superelectrophile* is arbitrary,<sup>37</sup> as is that of superacids, but it reflects the remarkably enhanced reactivity. *Superelectrophiles* are highly reactive, energetic, high-lying intermediates and should be differentiated from low-lying, stable intermediates, which are frequently observable (even with relatively slow physical methods) or even isolable, but they are not necessarily the de facto reagents without further activation. The term "reactive intermediate" (used loosely in the past) should

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be differentiated from "stable intermediate". The discussed onium and carboxonium dications are not considered to be "stable intermediates". They can, however, be present in superacidic solutions in very low equilibrium concentrations, facilitated by protosolvation (clustering). Further related "electrophilic assistance" by superacids, without necessarily forming fully developed dipositive intermediates, must also be considered.

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**Supplementary Material Available:** Archive entries of the optimized structures of 1-16 (9 pages). Ordering information is given on any current masthead page.

## Chemistry, Kinetics, and Spectroscopy of Highly Hindered Diarylcarbenes. The Case of Decachlorodiphenylcarbene

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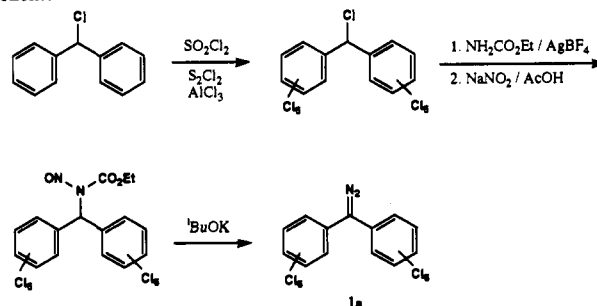
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**Abstract:** Bis(pentachlorophenyl)diazomethane (**1a**) was prepared, and reactivities of perchlorodiphenylcarbene (**2a**) generated by photolysis of **1a** were investigated not only in terms of product analysis but also by using flash photolysis techniques. Although the major reaction found for **2a** was dimerization forming perchlorotetraphenylethylene and was essentially similar to that observed for 2,2',4,4',6,6'-hexachlorodiphenylcarbene (**2b**), product distribution clearly indicated that the carbenic center in **2a** is more rigidly protected than that in **2b** by the four ortho chloro substituents which are buttressed by the four meta chloro groups. Irradiation of **1a** in a 2-methyltetrahydrofuran glass at 77 K resulted in the appearance of the absorption due to triplet **2a** at 356, 493, and 525 nm. Flash photolysis of **1a** in benzene solution produced a transient absorption due to **2a** at 357 nm, which decayed in second order in accordance with the product analysis data. The rate constant for dimerization of **2a** was determined to be  $2.5 \pm 0.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , 3 orders of magnitude smaller than that of unsubstituted diphenylcarbene. The triplet carbene (**2a**) was trapped by oxygen to generate the perchlorobenzophenone oxide showing its maximum at 390 nm ( $t_{1/2} = 510 \pm 9 \text{ ms}$ ) and also by 1,4-cyclohexadiene to produce bis(perchlorophenyl)methyl radical ( $\lambda_{\text{max}} 376 \text{ nm}$ ) with the rate constant of  $6.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ .

The enormous effect of perchlorophenyl groups on the stability of arylmethyl radicals has been well documented by a series of reports by Ballester and his co-workers.<sup>1</sup> Thus, perchlorotriphenylmethyl has been shown to have its half-life on the order of 100 years in solution at room temperature in contact with air and is therefore termed as an inert free radical. In this light, the perchlorophenyl group is expected to exert a similar stabilizing effect on triplet arylcarbene.

In 1964, Zimmerman and Paskovich<sup>2</sup> generated 2,2',4,4',6,6'-hexachlorodiphenylcarbene (HCD) in the hope of insulating the valence-deficient center from its environment. Although the approach did not afford an isolable carbene, the divalent species exhibited unique behavior. In solution, this carbene did not react with the parent diazo compound to give azine but dimerized instead. The chemistry found for HCD is thus in sharp contrast with that found for other diarylcarbenes<sup>3</sup> and is interpreted as reflecting its highly congested divalent center ob-

Scheme I



viously due to the presence of four chlorine groups at the ortho positions. Naturally one would expect that the carbenic center must be more crowded as one introduces four chlorine groups at the meta positions which can buttress the four ortho chlorine groups.<sup>4,5</sup> Thus, we generated decachlorodiphenylcarbene, and its reactivities were investigated not only by product analysis but also by using flash photolysis techniques.

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