VOLUME 37 NUMBER 4

ACCOUNTS of CHEMICAL RESEARCH®

APRIL 2004

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Superelectrophilic Solvation

GEORGE A. OLAH*,‡ AND
DOUGLAS A. KLUMPP†

Loker Hydrocarbon Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089, and Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115

Received May 5, 2003

ABSTRACT

Nucleophilic solvation is the interaction of electron-donor solvents with electron-deficient reagents. Electrophilic solvation is the related reverse interaction. Superelectrophilic solvation involves the interaction of electron-donating groups (ligands) of overall electron-deficient species (electrophiles) with strongly electron-acceptor superacids. It occurs with liquid superacids, on solid acids, and even in some enzymatic biological systems. Diminishing neighboring group participation of the electrophilic centers by the affected groups greatly enhances their electrophilic reactivities (superelectrophilic activation), resulting in unusual reactions of substantial interest. Representative examples of superelectrophilic solvation are discussed.

Introduction

The reaction medium can have a profound influence on the outcome of organic chemical reactions.[1] Solvation (the interaction of solvent with the reactants) has been shown to control reaction rates, product yields, and regioselectivities and stereoselectivities in reactions. Solvent effects involving the interaction of electron-donor (nucleophilic) solvents with electron-acceptor (electrophilic) reagents have been widely studied. This in a way stabilizes the electrophiles but at the same time decreases their reactivity. Stability and reactivity are not parallel but opposing properties. The counterpart of nucleophilic solvation, electrophilic solvation is the interaction of reagents of electron-donating ability with electron-acceptor protic acids, which reduces anionic nucleophilicity. It has only more recently been recognized that electron-donating ligands (substituents) of electrophilic reagents can themselves further interact with the superacidic system greatly enhancing electrophilic reactivity. We call it superelectrophilic solvation to differentiate it from what is conventional electrophilic solvation. This new field is gaining significance, hence the timeliness of this Account.

Acid−base interactions are one of the foundations of chemistry. Electron acceptors (i.e., Bronsted or Lewis acids) readily interact with n-donor (nonbonding electron pair donors) as well as with π-donor systems. Superacids can even protonate σ-donors. Interactions leading to protonated and subsequently to diprotonated carbocations or onium ions (as well as related Lewis acid complexed systems) called superelectrophiles were reviewed and are outside the scope of this Account.[2] Superelectrophilic solvation diminishes the intramolecular interactions of neighboring electron-donating substituent groups with electron-deficient centers. It thus decreases Winstein's neighboring group participation and can involve n-, σ-, and π-donor groups. This results in greatly enhanced electrophilic reactivity and higher reaction rates and allows many unusual reactions to take place. In 1975, one of us (G.A.O.) first reported that in superacidic media the acetyl (CH_3CO^+) and the nitronium cations (NO_2^+) display highly enhanced reactivities (vide infra).[3] These results suggested protolytic solvation. Subsequently, the de facto existence of limiting CH_3COH^{2+} and NO_2H^{2+} were also shown.

Concerning the nature of superacid-activated reactions, it should be recognized that they may proceed through superelectrophilic solvation without necessarily forming

George A. Olah is a distinguished professor of chemistry and Director of the Loker Hydrocarbon Research Institute at the University of Southern California. He received the Nobel Prize in Chemistry in 1994 for his work on carbocations and hydrocarbon chemistry. His research interests are in synthetic and mechanistic chemistry with emphasis on hydrocarbon chemistry.

Douglas A. Klumpp (B.S., University of Oklahoma; Ph.D., Iowa State University) was from 1993 to 1996 a postdoctoral research fellow in the Olah group at the University of Southern California. From 1996, he was an assistant professor at California State Polytechnic University, Pomona, and presently is an associate professor of organic chemistry in Northern Illinois University. His research interests are synthetic and mechanistic organic chemistry related to reactive intermediates.

* Corresponding author.
‡ University of Southern California.
† Northern Illinois University.

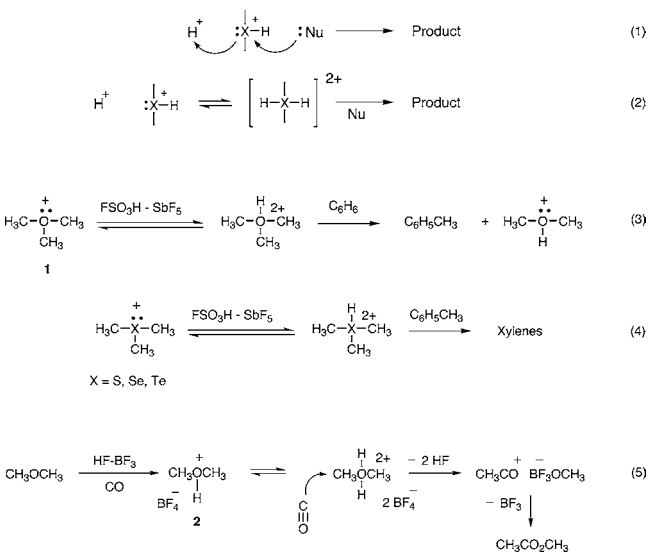
10.1021/ar020102p CCC: $27.50 © 2004 American Chemical Society
Published on Web 02/06/2004

limiting dicationic (doubly electron-deficient) intermediates (eq 1).[2] Lewis acidic electrophiles are uncharged, and with these superelectrophilic solvation avoids charge–charge repulsion effects. The frequently used depiction of protosolvated species as their limiting dications is for simplicity. This does not imply that protosolvation de facto forms these dications in any appreciable concentration (except in limited equilibria), although quantum mechanical calculations have found many of these at energy minima. The reactions of these species can take place with any suitable nucleophile including π-donor arenes and olefins (even when strongly deactivated), n-donor heteroatom containing substrates, and even weak σ-donor alkanes.

Superacids used in superelectrophilic activation are defined as being stronger than 100% H_2SO_4 for Bronsted acids and stronger than $AlCl_3$ for Lewis acids.[4] The use of superacids has enabled previously the preparation and study of many types of long-lived cationic electrophilic species such as carbocations,[5] acyl and carboxonium cations,[6] and varied onium ions such as oxonium, sulfonium, halonium, nitronium, and azonium ions.[7] Their use in superelectrophilic solvation (activation) extends their application to many useful reactions.

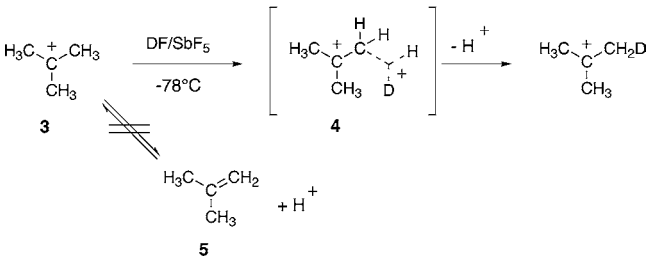
Alkylation with Protosolvated Oxonium Ions and Carbocations

Trialkyloxonium salts (Meerwein salts, R_3O^+ X^-) in the presence of strong acids show substantial increase in their reactivities. These Meerwein salts are excellent alkylating agents for nucleophiles containing heteroatoms but are not capable of C-alkylating aromatic or aliphilic hydrocarbons.[8] When superacids such as FSO_3H-SbF_5 (magic acid, $H_o = -21$ to -24) or $CF_3SO_3H-B(O_3SCF_3)_3$ (triflatoboric acid, H_o -20 to -21) are added, trialkyloxonium ions (**1**) alkylate aromatics such as benzene, toluene or chlorobenzene (eq 3).[9] Weaker acids do not effectively catalyze



the alkylations. Although trialkyloxonium ions have a formal positive charge, the oxygen atom can still act as a

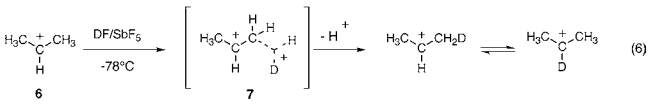
Scheme 1. Superacidic Hydrogen-Deuterium Exchange of the *tert*-Butyl Cation



Lewis base resulting in an interaction between the lone pair electrons on the oxygen and the highly acidic solvating system. Similar results were obtained with the salts of trimethyl sulfonium ($(CH_3)_3S^+$), selenonium ($(CH_3)_3Se^+$), and telluronium ($(CH_3)_3Te^+$) ions.[10] These onium salts methylate toluene in FSO_3H-SbF_5, but with the weaker Bronsted superacid CF_3SO_3H (triflic acid, $H_o = -14.1$), no methylation takes place. The need for extremely high acidity is in accord with the protosolvation of the onium salts (eq 4).

Protolytic activations can also be achieved in case of primary and secondary oxonium ions. This has been shown to be an important aspect of the superacid-catalyzed chemistry of alcohols.[11] Protosolvation is also suggested in the superacid-catalyzed carbonylation of dimethyl ether (or methanol) to form methyl acetate (eq 5).[12] The methyloxonium ion (**2**) is itself not reactive toward CO. However, superelectrophilic activation allows it to react with carbon monoxide.

The reactions of C–C and C–H σ-bonds are of fundamental importance in the chemistry of hydrocarbons.[13] In superacids, alkanes can undergo isomerization, cracking, and oligomerization reactions through steps involving σ-bond protonations. In these reactions, carbocationic intermediates play a key role. Several recent studies have demonstrated that interaction of their σ-bonds can also be involved via protosolvation in superacidic media enhancing their reactivity. The *tert*-butyl cation (**3**) is well-known as a stable species in superacids. However when the *tert*-butyl cation is generated in an SbF_5/SO_2ClF solution and 1:1 DF/SbF_5 is added, the *tert*-butyl cation undergoes slow but well characterized (^1H and ^2H NMR) hydrogen–deuterium exchange (Scheme 1).[14] To account for the isotopic exchange in the superacidic system where no deprotonation equilibrium with isobutylene (**5**) can take place, protonation (deuteration) of the *tert*-butyl cation (**3**) to the protio-*tert*-butyl dication (**4**) or corresponding protosolvation must occur. In a similar respect, 2-chloropropane can be ionized in SbF_5/SO_2ClF to the 2-propyl cation (**6**), and subsequent addition of 1:1 DF/



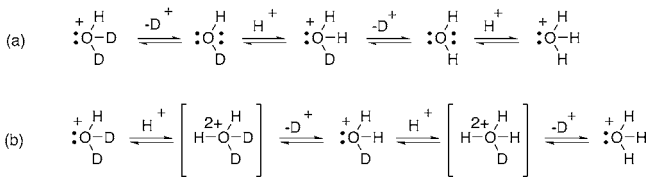
SbF_5 leads to hydrogen–deuterium exchange (5% exchange after 72 h at -78 °C).[15] The exchange can be envisaged to occur by reactions at the C–H bond via the

dication **7** (eq 6). Alkyl cations such as the *tert*-butyl cation and 2-propyl cation (**6**) are significantly stabilized by hyperconjugative C−H and C−C σ-back-donation into the empty carbocationic p-orbitals. Protosolvation involving σ-bonds can diminish hyperconjugative stabilization and thus lead to activated carbocationic species.

Hydrogen Exchange in Protosolvolysis of the Hydronium and Sulfonium Ions

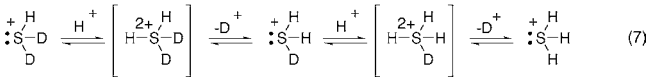
In understanding the chemistry of protosolvolytically activated alkyloxonium ions, the protonation of the parent hydronium ion (H_3O^+) to the tetrahydridooxonium dications (H_4O^{2+}, diprotonated water) is of fundamental significance.[2] The isotopomeric ions H_2DO^+, and HD_2O^+ exhibit no hydrogen/deuterium exchange when the ions are formed in $HSO_3F{:}SbF_5$ ($H_o = -21$); however, in even stronger superacidic medium ($HF/DF{-}SbF_5$, $H_o = -25$), hydrogen/deuterium exchange is observed.[16] Two mechanisms are possible for the observed H/D exchange (Scheme 2): (a) deprotonation−protonation equilibria

Scheme 2. Two Possible Mechanisms for H/D Exchange of the Hydronium Ion in Superacids



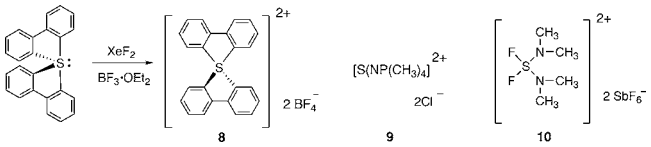
involving neutral molecules and monocations or (b) protonation−deprotonation equilibria involving monocations exchanging H and D through H_4O^{2+} dications. Because H/D exchange only occurs at the highest acidities (i.e., with $HF/DF{-}SbF_5$ but not with $HSO_3F{:}SbF_5$) and deprotonation to form water is not feasible in these systems, the results suggest that isotopic exchange takes place via isotopomeric H_4O^{2+} or corresponding protosolvated H_3O^+ species. This is in accord with theoretical studies, which have predicted H_4O^{2+} to be a kinetically stable species (Koch and Schwarz and Olah et al.).[17]

Similar to the studies involving protosolvation of hydronium ion, hydrogen/deuterium exchange experiments have suggested the protosolvation of H_3S^+ involving H_4S^{2+} (eq 7).[18] The existence of intermediate H_4S^{2+} is further



(7)

supported by the recent reports of stable organosulfurane-(IV) dications (**8**−**10**).[19−21] Salt **8** is prepared by the oxidation of the neutral organosulfurane with XeF_2 to



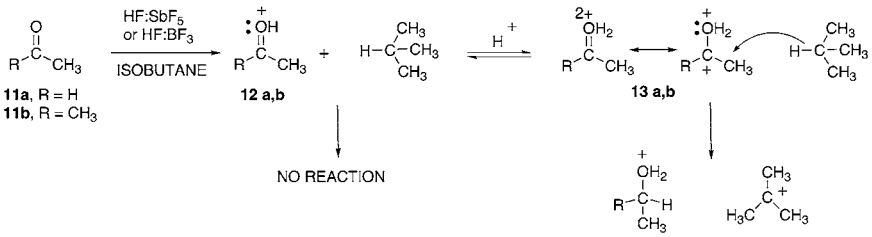
obtain the product **8** as a crystalline solid. X-ray diffraction studies of **8** revealed a tetrahedral geometry at the sulfur and determined the C−S bond length to be 1.753 Å, which is comparable to C−S single bond lengths. Schmidbaur and his associates have even been able to prepare and study by X-ray crystallography the tetraaurated derivatives $\{O[o\text{-}CH_3{-}C_6H_4)_3PAu]_4\}^{2+}$ and $\{S[C_6H_5)_3PAu]_4\}^{2+}$, analogues of both H_4O^{2+} and H_4S^{2+}, respectively.[22] These studies indicate that H_4X^{2+} species in the limiting cases are isolable real intermediates (energy minima) and not only transition states. In superacidic systems, they and their analogues can also be considered to be protosolvated H_3X^+ onium ions with some contribution of the dicationic species.

Alkylation with Protosolvated Carboxonium Ions and Their Analogues

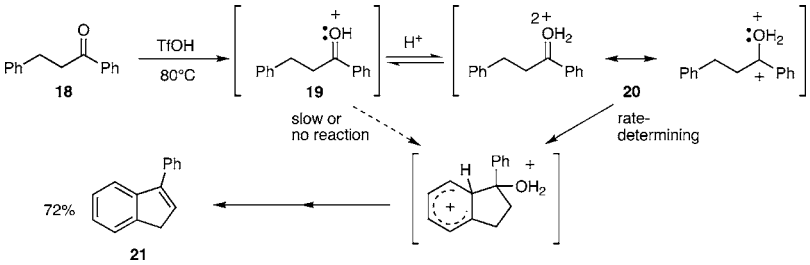
Considerable evidence has been reported to suggest that electrophilic solvation can activate carboxonium ions.[23] It has been long recognized that carboxonium ions are highly stabilized by strong oxygen participation and therefore are much less reactive compared to alkyl cations. For example, trivalent carbocations are efficient hydride abstractors that generate related carbocations from tertiary isoalkanes. In contrast, carboxonium ions do not abstract hydride from isoalkanes when they are reacted in aprotic solvents (also estimated to be thermodynamically unfavorable). When acetaldehyde or acetone (**11a,b**) is treated with isobutane in $HF{:}SbF_5$ or $HF{:}BF_3$, the *tert*-butyl cation is formed (Scheme 3).[24] These considerations lead to the mechanistic proposal involving the protosolvation of the carboxonium ions (**12a,b**) forming superelectrophilic species (**13a,b**), enabling hydride abstraction to occur. Similar reactions have also been observed for formaldehyde and its ionized products.[24b]

Several recent reports have described kinetic studies suggesting protosolvated carboxonium ion intermediates. Divinyl ketones are known to cyclize to 2-cyclopentanones in acid-catalyzed electrocylization reactions. The Nazarov and related reactions often require forcing conditions of high acidity and high temperatures and O-protonated

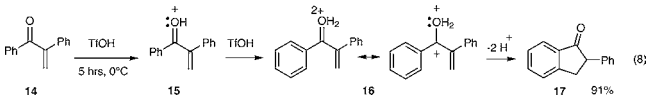
Scheme 3. Proposed Mechanism for the Superacid-Catalyzed Hydride Transfer from Isobutane to Carbonyl Compounds



Scheme 4. Proposed Mechanism for the Cyclization of 1,3-Diphenyl-1-propanone (18)



cationic intermediates have been proposed. In reactions of a series of 1-phenyl-2-propen-1-ones catalyzed by superacidic triflic acid (CF_3SO_3H), 1-indanones were obtained in generally good yields (eq 8).[25] In kinetics



studies, 1-phenyl-2-propen-1-ones were reacted in solutions of varying acidity and in all cases the cyclizations were found to exhibit first-order kinetics. The rate constants were found to be dependent on the acid strength over the range of acidities from $H_o = -9$ to -13. These results are consistent with the Zucker−Hammett hypothesis, which states that reaction rates are proportional to acidity if the reactive species (protonated intermediates) are formed in low concentrations and are involved in the rate-determining step.[25] Given that the carbonyl group is almost fully protonated at $H_o = -9$, the increasing rate suggests the involvement of a protosolvated reactive intermediate (**16**).

1,3-Diphenyl-1-propanone (**18**) was found to give the cyclization product **21** in good yield from reaction in superacid (Scheme 4).[26] The acid-catalyzed cyclization shows a dramatic dependency on the acidity of the reaction medium: a yield of 72% in 100% CF_3SO_3H ($H_o = -14.1$); a yield of 7% in 6% w/w CF_3SO_3H−94% CF_3CO_2H ($H_o = -8.7$); a yield of 0% in 100% CF_3CO_2H ($H_o = -2.7$). The cyclodehydration reaction was also examined in kinetics studies, and between the range of $H_o = -8.2$ and -14.1, the reaction rate constant was found to increase linearly with acidity. These results also suggest the protosolvated species **20** to be involved in the rate-determining cyclization step (Scheme 4).

When the unsaturated acetal **22** is reacted with superacid at −60 °C and irradiated, a photostationary state is observed consisting of the two stereoisomers **23a** and **23b** (Scheme 5).[27] Evaluation of the kinetics of stereomutation shows good first-order kinetics, and the rate constant increases with acidity. Consequently, dication **24** is proposed.

A number of synthetically useful conversions have been reported in which protosolvated carboxonium ion intermediates are involved (Table 1). Limiting dicationic intermediates in which the positive charge centers are in close proximity are called *gitonic* (close by) superelectrophiles. When the positive charge centers are separated by two or more carbon atoms, they are *distonic* (distant)

Scheme 5. Role of Dication (24) in the Stereomutation of the Oxonium Ion (23b)

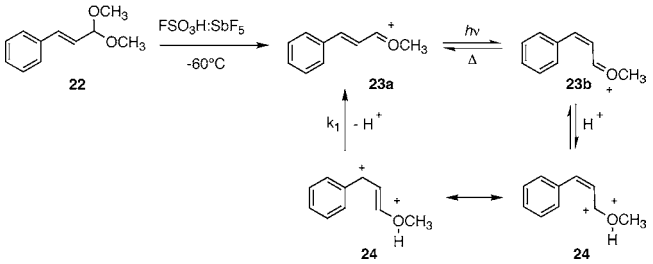
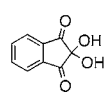
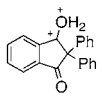
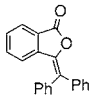
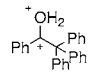
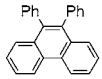
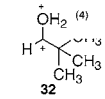
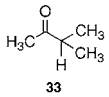
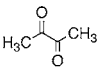
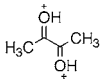
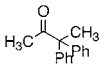
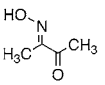
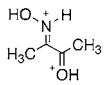
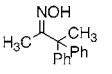
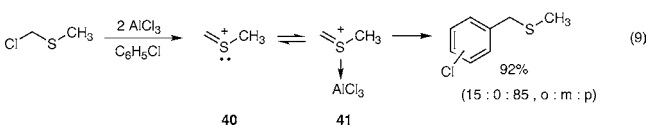


Table 1. Superacid-Catalyzed Conversions Involving Protosolvated Carboxonium Ion Intremediates and Related Dicationic Systems

STARTING MATERIAL	PROPOSED INTERMEDIATES	PRODUCT	YIELD
 25	 26	 27	98%
28	 29	 30	99%
31	 32	 33	100%
 34	 35	 36	94%
 37	 38	 39	75%

superelectrophiles. Such superelectrophiles are involved in the series of studied reactions.[28−32]

Thiocarboxonium ions have received less attention than the carboxonium ions, but it was shown that they can also undergo protosolvation or Lewis acidic electrophilic solvation.[33] With a 2:1 molar excess of $AlCl_3$, chloromethyl methyl sulfide reacts rapidly with arenes to give methylthiomethylation products (eq 9). The alkylating

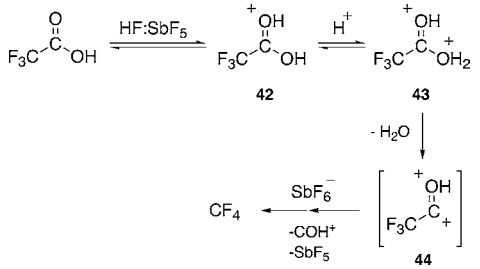


ability of chloromethyl methyl sulfide is greatly enhanced

by using excess Lewis acid. Along with NMR studies, these results suggest an electrophilic solvation involving the reactive electrophilic species (**41**).

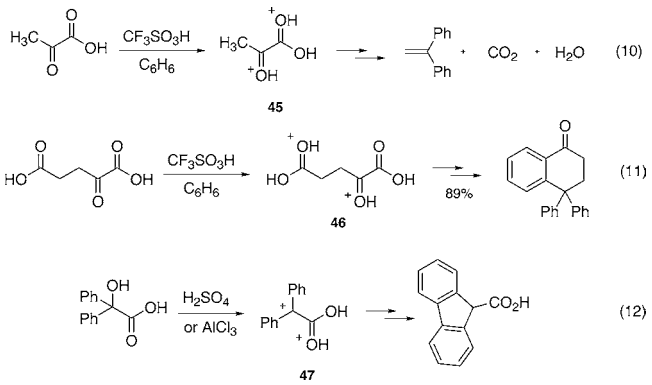
Protosolvation has also been shown in the acid-catalyzed formation of acyl cations from the corresponding carboxylic acids. For example, tetrafluoromethane is formed in the reaction of trifluoroacetic acid (CF_3CO_2H) with FSO_3H-SbF_5 (50 mol % SbF_5; Scheme 6).[34] These

Scheme 6. Superacid-Catalyzed Formation of CF_4 from Trifluoroacetic Acid

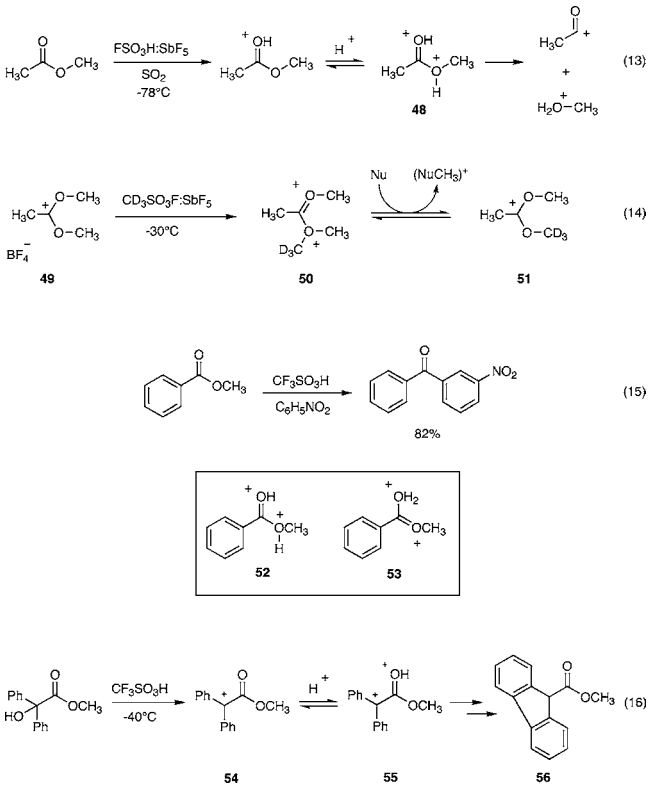


results were interpreted as the protonation of CF_3CO_2H to form ion **42**, subsequent protosolvation involving the gitonic dication **43**, and dissociation to the protiotrifluoroacetyl cation **44**, which ultimately leads to CF_4. In a similar respect, protosolvation has been suggested in the superacid-induced formation of the acetyl cation from acetic acid and the formation of the transient formyl cation from formic acid.[2,6]

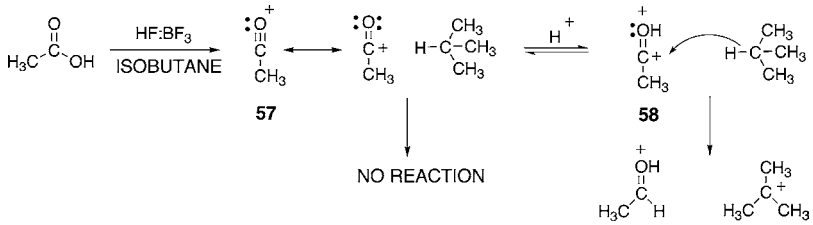
Carboxylic acids can also form a variety of distonic superelectrophilic intermediates by protonation of the carboxylic acid group and ionization of adjacent functional groups. α-Keto acids generate reactive electrophilic (**45**, **46**) species capable of condensing with arenes in high yields (eqs 10 and 11).[35] Benzilic acid gives fluorine-9-carboxylic acid almost quantitatively (eq 12) in excess H_2SO_4 or $AlCl_3$ via dication **47**.[36] A high degree of delocalization of positive charge through the phenyl rings in **47** facilitates this 4π electron electrocyclization.



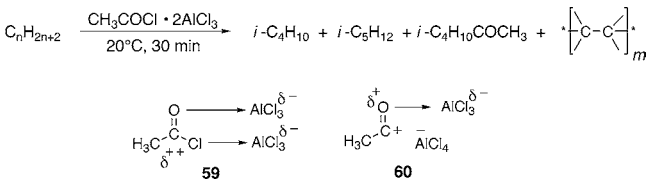
Acid-catalyzed ester cleavage has been extensively studied in organic chemistry, and recently evidence has emerged to suggest that protosolvation (electrophilic solvation) can play a role in this chemistry. In low-temperature NMR studies, methyl acetate is found to be completely protonated at the acyl oxygen in superacidic $FSO_3H/SbF_5/SO_2$ solution.[37] There is no indication of an equilibrium with the neutral ester or the ether protonated isomer. However even at −78 °C, protonated ethyl acetate undergoes slow acyl oxygen cleavage to acetyl cation and methyl oxonium ion (eq 13). This suggests further protolytic activation via the superelectrophilic gitonic carboxonium dication (**48**). Further evidence for dicationic intermediates comes from a study of the 1,1-dimethoxyethyl cation (**49**) and its reaction with $CD_3F:SbF_5/SO_2$ (eq 14).[37] At −30 °C, slow methyl exchange occurs at the methoxy oxygen. Since demethylation (to form the neutral ester) is unlikely in such highly acidic solution, the methyl exchange is best interpreted by electrophilic solvation of **49** by the $CD_3F:SbF_5/SO_2$ and methylation to give the dication **50**. Subsequent demethylation then gives the exchange product **51**. Superelectrophilic intermediates have also been proposed in the reaction of some esters. For example, a recent report describes the conversions of methyl benzoate to benzophenone products (70−93% yields) from reactions in superacid (eq 15).[38] To explain the high level of electrophilic reactivity of this system, the protosolvated species **52** and **53** are proposed as possible intermediates. In the acid-catalyzed cyclization of some ethylene dications, protonation of the ester group is thought to be a key activation step.[39] Reaction of α-(methoxycarbonyl)diphenylmethanol with CF_3SO_3H ($H_o = -14.1$) gives the fluorene product (**56**) in 94% yield (eq 16). The yield of the product **56** drops with decreasing acidity. Moreover, the kinetics of the cyclization was studied, and the cyclization rate was found to increase linearly with acidity between $H_o = -11$ and $H_o = -13$. The linear rate correlation provides strong evidence for the protonation of the monocationic intermediate (**54**). Theoretical studies suggest that formation of the dication **55** lowers the barrier



Scheme 7. Proposed Mechanism for the Superacid-Induced Hydride Transfer from Isobutane to Acetyl Cation



Scheme 8. Lewis Acidic Solvation of the Acetyl Cation Inducing Alkane Reactions

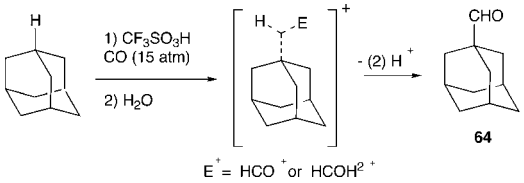


to conrotatory electrocyclization by about 8 kcal/mol and thus facilitates the conversion to **56**.

Reactions with Protic or Lewis Acid Solvated Acyl Cations or Carbon Monoxide

Like carboxonium ions, acyl cations are relative weak electrophiles that are effectively stabilized by resonance.[40] Although acetyl salts are capable of reacting with benzene and activated arenes, the acetyl cation generally does not react with weaker nucleophiles such as deactivated arenes or saturated alkanes. However, there are several reports of activation of acyl cations by superacids. For example, hydride transfer from isobutane to the acetyl cation has been reported when the reaction is carried out in excess $HF-BF_3$ (Scheme 7),[3] yet hydride transfer does not occur in aprotic solvents such as SO_2, SO_2ClF, or CH_2Cl_2. Our earlier studies have shown that acetyl salts such as CH_3CO^+ SbF_6^- exhibit significantly higher reactivities in protic superacids ($H_o < -12$) when compared to weaker acids ($H_o > -12$).[6] These results are consistent with a protosolvation of the acetyl cation with the Bronsted superacid. The monocationic species (**57**) is unreactive, while the dicationic species (**58**) can abstract hydride. In addition to protosolvation, the activation of the acetyl cation can be accomplished with Lewis acids. As Vol'pin found, reaction of CH_3COCl with two or more equivalents of $AlCl_3$ with alkanes leads to isomerization and other electrophilic reactions (Scheme 8).[41] Since the reaction does not occur when one equivalent of $AlCl_3$ is used, the results have been interpreted as evidence for an electrophilic solvation involving a dicationic complex (**59** or **60**). These results are also consistent with the protosolvation of the acetyl cation.

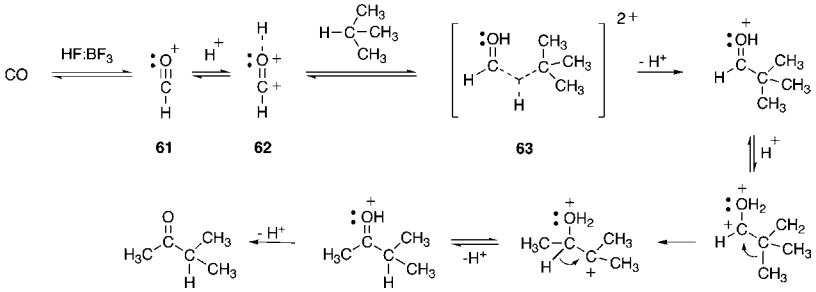
The reactions of carbon monoxide in superacids have been of substantial interest in synthetic and mechanistic studies.[2] Carbon monoxide can be protonated at the carbon to yield the formyl cation (**61**, HCO^+), and its direct observation has been reported in $HF-SbF_5$ solution using high-pressure NMR spectroscopy.[42] While the formyl cation is considered to be sufficiently electrophilic to react with arenes (Gatterman–Koch formylation), a more electrophilic protosolvated species is needed in reactions with saturated hydrocarbons (Scheme 9). For example, isobutane is converted to methyl isopropyl ketone in high yield by the reaction of carbon monoxide with $HF-BF_3$.[43] Since $HF-BF_3$ is not capable of ionizing isobutane to the *tertiary*-butyl cation directly, the results are consistent with the formation of the protosolvated formyl cation (**62**). Formylation then occurs by reaction of **62** with the carbon–hydrogen bond (**63**) giving protonated pivaldehyde, which then rearranges to methyl isopropyl ketone. Pivaldehyde itself has been shown to isomerize to methyl isopropyl ketone in superacid.[30] Similarly, the protosolvated formyl cation (or limiting protoformyl dication) is proposed in the conversion of adamatane to 1-adamantanecarboxaldehyde (**64**, eq 17).[44] The yield of **64** increases



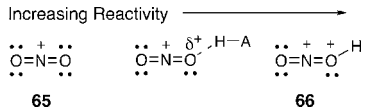
(17)

with acidity (9% in CF_3SO_3H; 21% in $CF_3SO_3H-SbF_5$), and deuterium-labeling experiments ruled out a mechanism involving the formation of the 1-adamantyl cation and hydride abstraction from adamantane.

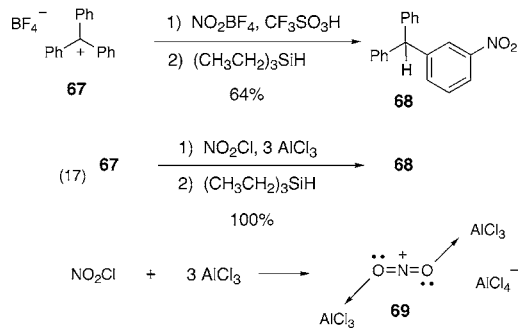
Scheme 9. Proposed Mechanism for the Formylation of Isobutane and Rearrangement to Methyl Isopropyl Ketone



Scheme 10. Protosolvation of the Nitronium Ion



Scheme 11. Superelectrophilic Nitration of the Trityl Cation (67)



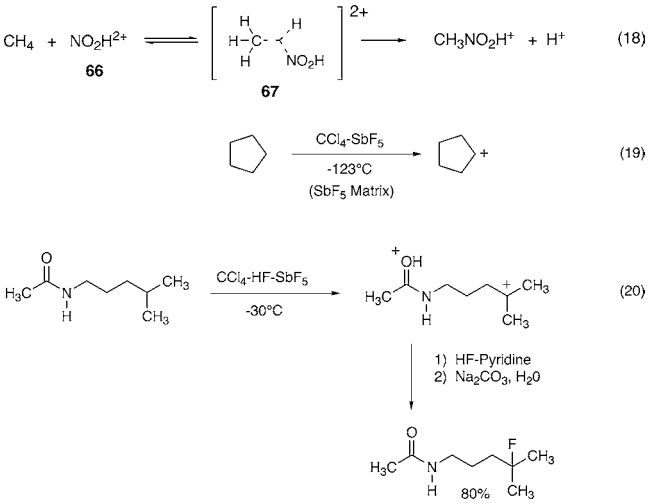
Nitrations with Protic or Lewis Acid Activated Nitronium Ion

In 1974, the first observation of the enhanced electrophilic reactivity of nitronium salts (**65**) in superacid was reported,[45] and the protosolvation of the nitronium ion was later suggested (**66**, NO_2H^{2+}, Scheme 10).[3] More recently, a mixture of nitric acid and triflatoboric acid (2 $CF_3SO_3H-(CF_3SO_3)_3B$; $H_o = -20.5$)[46] was shown to nitrate deactivated arenes in high yields, and the reactivity of this system was attributed to the formed protonitronium dication (NO_2H^{2+}). A similar conclusion is made from the nitration of the trityl cation (**67**) with nitronium salts in superacid (Scheme 11).[47] When nitronium tetrafluoroborate is reacted with the trityl cation in CH_2Cl_2 or sulfolane, nitration does not occur due to the deactivating effects of the carbenium ion center of **67**. Nitration is achieved by activation with triflic acid giving **68**. Nitration is also affected quantitatively by reaction of NO_2Cl with 3 mol excess $AlCl_3$ suggesting Lewis acidic electrophilic solvation of the nitronium cation (**69**). Remarkably, nitronium salts have been shown to react with even methane under superacidic conditions (eq 18).[48] The mechanism of nitration is thought to proceed via a two-electron three-center bond carbocationic transition state (**67**) formed by insertion of dication **66** into the C−H σ-bond of methane.

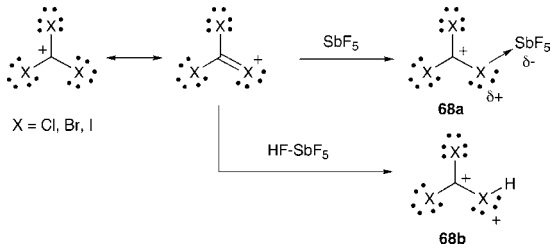
The activation of the nitronium ion (**65**, NO_2^+) is a consequence of the interaction of the oxygen nonbonded pair electrons with superacidic Bronsted or Lewis acids (Scheme 10). Protonation (or coordination by Lewis acid) weakens the N−O π-bond character and results in the bending of the linear nitronium ion and rehybridization of the nitrogen from sp to sp^2.[49] The rehybridization creates a developing p orbital on the nitrogen, which is capable of interacting with weak π-donor or σ-donor nucleophiles. High-level theoretical calculations have shown the protonitronium dication (**66**) to be a kinetically stable species with an estimated (gas-phase) barrier to deprotonation of 17 kcal/mol.[50] These calculations also found the optimized structure to have a bent structure with a O−N−O bond angle of about 172°. Recently, the protonitronium dication (**66**) was observed by Schwarz in the gas phase by electron impact mass spectrometry.[50] Attempts to directly observe **66** under superacidic conditions by ^{15}N NMR and FT-IR (Raman) spectroscopy have shown only moderate effects by the superacids. This suggests that the protonitronium ion (**66**) if formed is only in very low equilibrium concentrations even in the strongest superacids where the nitronium ion is protosolvated.

Superelectrophilic Solvation of Halogenated Systems

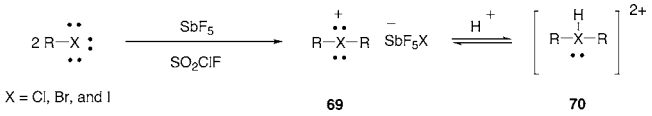
Superelectrophilic solvation has also been suggested involving halogenated ions. The trihalomethyl cations CX_3^+ (X = Cl, Br, I) were shown to have enhanced reactivities in superacid solution, while polyhalomethanes in the presence of excess $AlBr_3$ or $AlCl_3$ exhibit the properties of aprotic superacids.[51] The trihalomethyl cations are capable of hydride abstraction from alkanes and alkyl groups when the reactions are done in the presence of Bronsted or Lewis superacids (eqs 19 and 20),[52] while complex systems such as $CBr_4 \cdot 2AlBr_3$, $CCl_4 \cdot 2AlCl_3$, and others have been shown to efficiently catalyze the cracking, isomerization, and oligomerization of alkanes and cycloalkanes.[53] Electrophilic solvation (**68a,b**, Scheme 12) can be envisaged for these systems. Dialkylhalonium ions (**69**) can be prepared and even isolated as stable species by reacting an excess of haloalkane with strong Lewis acid halides such as SbF_5 (Scheme 13).[54] Protosolvated species such as **70** have been proposed as gitonic superelectrophilic intermediates and have been



Scheme 12. Activation of Trihalomethyl Cations



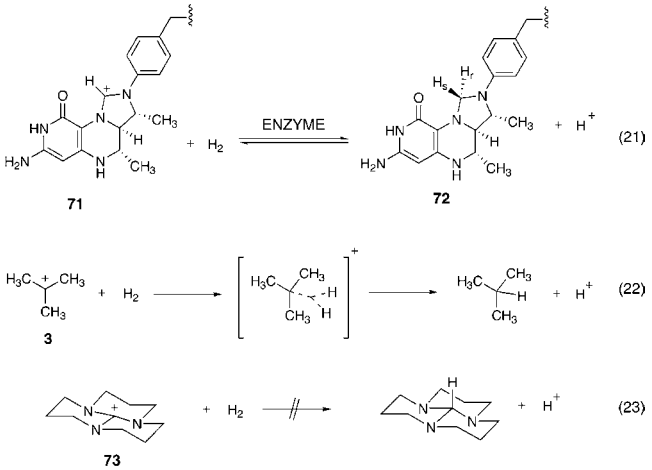
Scheme 13. Activation of Halonium Ions



studied by theoretical methods.[55] In the HF−SbF_5 superacid-catalyzed carbonylation reaction of alkanes, when bromide ion is added into the reaction mixture, the reaction rate increases greatly.[56] This can be best interpreted to be a consequence of the protolytic activation of H_2Br^+ via the gitonic trihydrobromonium dication H_3Br^{2+}, though it was suggested by the authors that the enhanced reactivity may be due to the formation of "Br^+".[2]

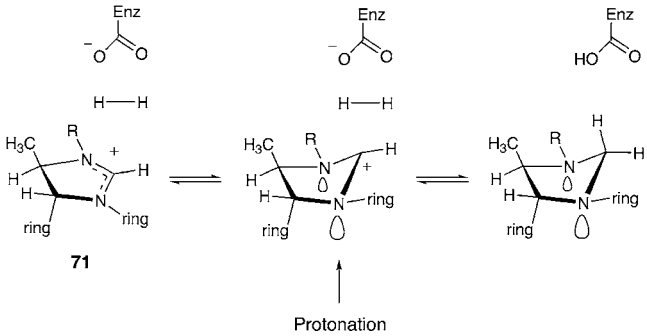
Enzymatic Analogues of Protosolvolytic Reactions

In studies of a metal-free hydrogenase enzyme, a reaction mechanism has been proposed by Thauer et al. that invokes a process remarkably similar to protosolvation reactions in superacid.[57] The chemistry is part of an enzymatic system that converts CO_2 to methane. It was found that N^5,N^{10}-methenyl tetrahydromethanopterin (**71**) undergoes an enzyme-catalyzed reaction with H_2 by hydride transfer to the pro-R position and release of a proton to give the reduced product **72** (eq 21). Authors



pointed out that, despite the low nucleophilicity of H_2, cations such as the *tert*-butyl cation (**3**) are sufficiently electrophilic to react with H_2 via a two-electron three-center bond (eq 22). However, because of stabilization from adjacent nitrogen atoms, cations such as the guanidinium system (**73**) do not react with H_2 (eq 23). Since N^5,N^{10}-methenyl tetrahydromethanopterin (**71**) should also exhibit significant stabilization of the cationic site, its reactivity with molecular hydrogen is somewhat surprising. It was suggested that protonation of one or both of the adjacent nitrogen base sites could generate a more electrophilic system (Scheme 14). This would result in decreased neighboring group stabilization and increased electrophilicity.

Scheme 14. Proposed Mechanism for the Enzymatic Protolytic Activation of Cation 71



Solid Acid-Catalyzed Analogues of Protosolvolytic Reactions

Our discussion of electrophilic solvation has centered on the effect of superacids in solution chemistry. However, solid superacids may also participate in electrophilic solvation. One of these is the hydrogen form of DuPont's perfluorinated resin sulfonic acid Nafion-H, which is frequently used as an acidic catalyst. It contains acidic SO_3H groups clustered together in pockets capable of interacting with electrophilic reagents not unlike solution systems. Certain zeolites such as Mobil's ZSM-5 contain Bronsted or Lewis acid sites in close proximity enabling the formation of highly reactive intermediates through bi- and multidentate interactions.

Conclusions

In summary, a growing body of evidence suggests that many electrophilic reagents even when positively charged are capable of further interaction (coordination) with strong Bronsted or Lewis acids resulting in superelectrophilic solvation and thus activation. These proto- and Lewis acidic solvation equilibria can involve n-donor, π-donor, and even σ-donor ligands or substituents of the electrophilic reagents. Similar activation involving some transition metal catalysts has also been recently suggested.[58] While in some cases the equilibria may involve distinctly formed species having full dipositive charge (i.e., superelectrophiles), superelectrophilic solvation may only involve weaker interactions resulting however in enhanced electrophilic reactivity. An important aspect of these interactions is diminished neighboring group participation and thus activation of the electron-deficient centers (electrophilic sites). The reactivity of the parent electrophiles can be much increased by proto- or, in general, superelectrophilic solvation. It is suggested to call this superelectrophilic solvation to differentiate it from conventional electrophilic solvation, which is decreasing nucleophilic reactivity of basic reagents. Whereas superelectrophilic solvation of organic and inorganic systems is discussed in our Account mainly in solution chemistry, similar activation can also occur with solid acids or even in some enzymatic systems.

References

(1) (a) *Highlights in Solute−Solvent Interactions*; Linert, W., Ed.; Springer-Verlag: Wien, Austria, New York, 2002. (b) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, Federal Republic of Germany, New York 1988.

(2) Olah, G. A. Superelectrophiles. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767−922.

(3) Olah, G. A.; Germain, A.; Lin, H. C.; Forsyth, D. Electrophilic Reactions at Single Bonds. XVIII.[1] Indication of Protosolvated de Facto Substituting Agents in the Reactions of Alkanes with Acetylium and Nitronium Ions in Superacidic Media. *J. Am. Chem. Soc.* **1975**, *97*, 2928−2929.

(4) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985; Chapter 1.

(5) Prakash, G. K. S., Schleyer, P. v. R., Eds. *Stable Carbocation Chemistry*; Wiley: New York, 1997.

(6) Olah, G. A., Schleyer, P. v. R., Eds. *Carbonium Ions*; Wiley-Interscience: New York, 1968−1976; Vol. 5.

(7) Olah, G. A.; Laali, K. A.; Wang, Q.; Prakash, G. K. S. *Onium Ions*; Wiley: New York, 1998.

(8) Granik, V. G.; Pyatin, B. M.; Glushkov, R. G. The Chemistry of Trialkyloxonium Tetrafluoroborates. *Russ. Chem. Rev.* **1971**, *40* (9), 747−759.

(9) (a) Olah, G. A.; De Member, J. R.; Mo, Y. K.; Svoboda, J. J.; Schilling, P.; Olah, J. A. Onium ion. VII. Dialkylhalonium ions. *J. Am. Chem. Soc.* **1974**, *96*, 884−892. (b) Olah, G. A.; Rasul, G.; Burrichter, A.; Prakash, G. K. S. Attempted Hydrogen−deuterium Exchange of the Protio-timethyloxonium Dication $(CH_3)_3OH_2^{+2}$, a Study of the Methylating Ability of $(CH_3)_3O^+$ in Superacids and Theoretical Investigations. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 4099−4103.

(10) Laali, K.; Chen, H. Y.; Gerzina, R. J. Methylation of Aromatics with Me_3S^+, Me_3Se^+, and Me_3Te^+ in Superacid Media. *J. Organomet. Chem.* **1988**, *348*, 199−204.

(11) (a) Kaspi, J.; Montgomery, D. D.; Olah, G. A. Heterogeneous Catalysis by Solid Superacids. 5. Methylation of Benzene and Methyl Benzenes with Methyl Alcohol over a Perfluorinated Resin Sulfonic Acid (Nafion-H) Catalyst. *J. Org. Chem.* **1978**, *43*, 3147−3150. (b) Pearson, D. E. Conversion of Methanol into Hydrocarbon. *J. Chem. Soc., Chem. Commun.* **1974**, 397. (c) Olah, G. A.; Laali, K. A.; Wang, Q.; Prakash, G. K. S. *Onium Ions*; Wiley: New York, 1998; p 435.

(12) Bagno, A.; Bukla, J.; Olah, G. A. Superacid-Catalyzed Carbonylation of Methane, Methyl Halides, Methyl Alcohol, and Dimethyl Ether to Methyl Acetate and Acetic Acid. *J. Org. Chem.* **1990**, *55*, 4284−4289.

(13) Olah, G. A.; Molnár, A. *Hydrocarbon Chemistry*; Wiley: New York, 1995.

(14) Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S. Protio-*tert*-butyl Dication ($(H_3C)_3C^+CH_4^+$): Hydrogen−Deuterium Exchange and Theoretical Study. The Role of Protosolvation on Alkyl Cation Reactivity in Superacid Solution. *J. Am. Chem. Soc.* **1993**, *115*, 6985−6986.

(15) Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S.; Burkhart, M.; Lammertsma, K. Protio-2-propyl Dication (Propane Dication, $C_3H_8^{2+}$): Hydrogen/Deuterium Exchangne and Theoretical Study. Differentiation of Reactive Gitonic (Proximal) from Stable Distonic (Distant) Dications and the Protosolvolytic Activation of Carbocations. *J. Am. Chem. Soc.* **1994**, *116*, 3187−3191.

(16) Olah, G. A.; Prakash, G. K. S.; Barzaghi, M.; Lammertsma, K.; Schleyer, P. v. R.; Pople, J. A. Protonated Hydronium Dication, H_4O^{2+}. Hydrogen−Deuterium Exchange of $D_2H^{17}O^+$ in $HF:SbF_5$ and $DH_2{}^{17}O^+$ in $DF:SbF_5$ and Theoretical Calculations. *J. Am. Chem. Soc.* **1986**, *108*, 1032−1035.

(17) Koch, W.; Heinnich, N.; Schwarz, H.; Maquin, F.; Stahl, D. Combined Experimental and ab Initio Molecular Orbital Studies on Gaseous OH_n^{2+} Species ($n = 1-4$). *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 305−316.

(18) Olah, G. A.; Prakash, G. K. S.; Marcelli, M.; Lammertsma, K. The Tetrahydridosulfonium Dication, H_4S^{2+}. Hydrogen−Deuterium Exchange of DH_2S^+ in $FSO_3D:SbF_5$ and D_2HS^+ in $FSO_3H:SbF_5$ and Theoretical Calculations. *J. Phys. Chem.* **1988**, *92*, 878−880.

(19) Sato, S.; Ameta, H.; Horn, E.; Takahashi, O.; Furukawa, N. First Isolation and Molecular Structure of Bis(2,2′-biphenylylene)-sulfuranyl Bis(tetrafluoroborate) $[8\text{-}S\text{-}4(C4)]^{2+}$. *J. Am. Chem. Soc.* **1997**, *119*, 12374−12375.

(20) Henle, H.; Hoppenheit, R.; Mews, R. $[(Me_2N)_2SF_2]^{2+}$, a Sulfur (VI) Dication. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 507−508.

(21) Folkerts, H.; Hiller, W.; Herker, M.; Vyoishchikov, S. F.; Frenking, G.; Dehnicke, K. $S(NPMe_3)_4^{2+}$: The First Structure Determination of a Dication of Hexavalent Sulfur. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1362−1363.

(22) (a) Grohmann, A.; Riede, J.; Schmidbaur, H. Electron-deficient Bonding at Pentacoordinate Nitrogen. *Nature* **1990**, *345*, 140. (b) Zeller, E.; Beruda, H.; Schmidbaur, H. Tetrahedral Gold Cluster [Au4]2+: Crystal Structure of $\{[(tert\text{-}Bu)_3PAu]_4\}^{2+}(BF_4^-)\cdot 2CHCl_3$. *Inorg. Chem.* **1993**, *32*, 3203−3204.

(23) Hartz, N.; Rasul, G.; Olah, G. A. Role of Oxonium, Sulfonium, and Carboxonium Dications in Superacid-Catalyzed Reactions. *J. Am. Chem. Soc.* **1993**, *115*, 1277−1285.

(24) (a) Brouwer, D. M.; Kiffen, A. A. HYDRIDE TRANSFER REACTIONS II. Hydride Transfer from Alkanes to Methyloxocarbonium Ion. *Recl. Trav Chim. Pays-Bas* **1973**, *92*, 689−697. (b) Brouwer, D. M.; Kiffen, A. A. HYDRIDE TRANSFER REACTIONS III. Rates of Hydride Transfer from Isobutane to Hydroxycarbonium Ions. *Recl. Trav Chim. Pays-Bas* **1973**, *92*, 809, 906. (c) Olah, G. A.; Germain, A.; Lin, H. C.; Forsyth, D. Electrophilic Reactions at Single Bonds. XVIII.[1] Indication of Protosolvated de Facto Substituting Agents in the Reactions of Alkanes with Acetylium and Nitronium Ions in Superacidic Media. *J. Am. Chem. Soc.* **1975**, *97*, 2928−2929.

(25) Suzuki, T.; Ohwada, T.; Shudo, K. Superacid-Catalyzed Electrocyclization of 1-Phenyl-2-propen-1-ones to 1-Indanones. Kinetic and Theoretical Studies of Electrocyclization of Oxonium-Carbenium Dications. *J. Am. Chem. Soc.* **1997**, *119*, 6774−6780.

(26) Saito, S.; Sato, Y.; Ohwada, T.; Shudo, K. Friedel−Crafts-Type Cyclodehydration of 1,3-Diphenyl-1-propanones. Kinetic Evidence for the Involvement of Dication. *J. Am. Chem. Soc.* **1994**, *116*, 2312−2317.

(27) Blackburn, C.; Childs, R. F. Acid-Catalyzed Stereomutations about the C(2)−C(3) Bond of 3-Aryl-1-methoxyallyl Cations. Dication Formation by Oxygen Protonation. *J. Chem. Soc., Chem. Commun.* **1984**, 812−813.

(28) Klumpp, D. A.; Fredrick, S.; Lau, S.; Prakash, G. K. S.; Jin, K. K.; Bau, R.; Olah, G. A. Acid-catalyzed Condensations of Ninhydrin with Aromatic Compounds. *J. Org. Chem.* **1999**, *64*, 5152−5155.

(29) Klumpp, D. A.; Baek, D. N.; Prakash, G. K. S.; Olah, G. A. The Preparation of Condensed Aromatics by the Superacidic Dehydration Cyclization of Aryl Pinacols and Epoxides. *J. Org. Chem.* **1997**, *62*, 6666−6671.

(30) Olah, G. A.; Mathew, T.; Marinez, E. R.; Esteves, P. M.; Etzkorn, M.; Rasul, G.; Prakash, G. K. S. Acid-Catalyzed Isomerization of Pivaldehyde to Methyl Isopropyl Ketone via a Reactive Protosolvated Carboxonium Ion Intermediate. *J. Am. Chem. Soc.* **2001**, *123*, 11556−11561.

(31) Yamazaki, T.; Saito, S.; Ohwada, T. Acid-catalyzed Reactions of 1,2-Dicarbonylethanes with Benzene. Ethylene Dication Electrophiles. *Tetrahedron Lett.* **1995**, *36* (32), 5749−5752.

(32) Ohwada, T.; Yamazaki, T.; Suzuki, T.; Saito, S.; Shudo, K. Structures and Reactivities of Ethylene Dication Electrophiles. *J. Am. Chem. Soc.* **1996**, *118*, 6220−6224.

(33) Olah, G. A.; Wang, Q.; Neyer, G. Superelectrophilic Methylthiomethylation of Aromatics with Chloromethyl Methyl Sulfide/Aluminum Chloride ($MeSCH_2Cl$:2 $AlCl_3$) Reagent. *Synthesis* **1994**, 276−278.

(34) Prakash, G. K. S.; Rasul, G.; Burrichter, A.; Laali, K. K., Olah, G. A. Ab Initio/IGLO/GIAO-MP2 Studies of Fluorocarbocations: Experimental and Theoretical Investigation of the Cleavage Reaction of Trifluoroacetic Acid in Superacids. *J. Org. Chem.* **1996**, *61*, 9253−9258.

(35) Klumpp, D. A.; Garza, M.; Lau, S.; Shick, B.; Kantardjieff, K. Electrophilic Chemistry of Biologically Important α-Keto Acids. *J. Org. Chem.* **1999**, *64*, 7635−7637.

(36) Ohwada, T.; Shudo, K. Substituted Ethylene Dications. Structures of Phenylmethyl Cations Substituted with an Electron-Withdrawing Group on the Cation Center. *J. Am. Chem. Soc.* **1989**, *111*, 34−40.

(37) Olah, G. A.; Hartz, N.; Rasul, G.; Burrichter, A.; Prakash, G. K. S. Ester Cleavage in Superacidic Media Involving Diprotonated *Gitionic* Carboxonium Dications. *J. Am. Chem. Soc.* **1995**, *117*, 6421−6427.

(38) Hwang, J. P.; Prakash, G. K. S.; Olah, G. A. Trifluoromethanesulfonic Acid-Catalyzed Novel Friedel−Crafts Acylation of Aromatics with Methyl Benzoate. *Tetrahedron* **2000**, *56*, 7199−7203.

(39) Ohwada, T.; Suzuki, T.; Shudo, K. Superacid-Catalyzed Electrocyclization of Diphenylmethyl Cations to Fluorenes. Kinetic and Theoretical Revisit Supporting the Involvement of Ethylene Dications. *J. Am. Chem. Soc.* **1998**, *120*, 4629−4637.

(40) Olah, G. A., Schleyer, P. v. R., Eds. *Carbonium Ions*; Wiley-Interscience: New York, 1968−1976; Vol. 5; pp 2049−2133.

(41) Vol'pin, M.; Akhrem, I.; Orlinkov, A. Aprotic Organic Superacids − Efficient Reagents and Catalysts for Transformations of Alkanes and Cycloalkanes under Mild Conditions. *New J. Chem.* **1989**, *13*, 771−790.

(42) de Rege, P. J. F.; Gladysz, J. A.; Horvath, I. T. Spectroscopic Observation of the Formyl Cation in a Condensed Phase. *Science* **1997**, *276*, 776−779.

(43) Olah, G. A.; Prakash, G. K. S.; Mathew, T.; Marinez, E. R. Superacid-Catalyzed Selective Formylation-Rearrangement of Isoalkanes with Carbon Monoxide to Branched Ketones. *Angew. Chem., Int. Ed.* **2000**, *39*, 2547−2548.
(44) Farooq, O.; Marcelli, M.; Prakash, G. K. S.; Olah, G. A. Superacid-Catalyzed Electrophilic Formylation of Adamantane with Carbon Monoxide Competing with Koch-Haaf Carboxylation. *J. Am. Chem. Soc.* **1988**, *110*, 864−867.
(45) Olah, G. A.; Lin, H. C. Synthetic Methods and Reactions; XI. A Convenient Direct Preparation of 1,3,5-Trinitrobenzene from *m*-Dinitrobenzene by Nitration with Nitronium Tetrafluoroborate in Fluorosulfuric Acid Solution. *Synthesis* **1974**, 444.
(46) Olah, G. A.; Orlinkov, A.; Oxyzoglou, A. B.; Prakash, G. K. S. Nitration of Strongly Deactivated Aromatics with Superacidic Mixed Nitric-Triflatoboric Acid ($HNO_3/2CF_3SO_3H-B(O_3SCF_3)_3$). *J. Org. Chem.* **1995**, *60*, 7348−7350.
(47) Olah, G. A.; Wang, Q.; Orlinkov, A.; Ramaiah, P. Superelectrophilic Nitration of the Triphenylcarbenium Ion. *J. Org. Chem.* **1993**, *58*, 5017−5018.
(48) Olah, G. A.; Ramaiah, P.; Prakash, G. K. S. Electrophilic Nitration of Alkanes with Nitronium Hexafluorophosphate. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 11783−11785.
(49) Olah, G. A.; Rasul, G.; Aniszfeld, R.; Prakash, G. K. S. Protonitronium Dication (NO_2H^{2+}). *J. Am. Chem. Soc.* **1992**, *114*, 5608.
(50) Weiske, T.; Koch, W.; Schwarz, H. Experimental Evidence for the Existence of the Protonitronium Dication ($HONO^{2+}$) in the Gas Phase and ab Initio Molecular Orbital Calculations of Its Potentrial Energy Surface. *J. Am. Chem. Soc.* **1993**, *115*, 6312−6316.
(51) Olah, G. A.; Rasul, G.; Yudin, A. K.; Burrichter, A.; Prakash, G. K. S.; Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Vol'pin, M. E. Trihalomethyl Cations and Their Superelectrophilic Activation. *J. Am. Chem. Soc.* **1996**, *118*, 1446−1451 and references therein.
(52) (a) Vancik, H.; Percac, K.; Sunko, D. E. Chloromethyl Cations in Cryogenic SbF_5 Matrixes and the Generation of Carbocations from Hydrocarbons. *J. Am. Chem. Soc.* **1990**, *112*, 7418−7419. (b) Martin, A.; Jouannetaud, M.-P.; Jacquesy, J.-C. Fluorination or Hydroxylation of non Activated C−H Bonds in Amides and Ketones using CCl_4 or NBS in Superacids. *Tetrahedron Lett.* **1996**, *37*, 2967−2970. (c) Sommer, J.; Bukala, J. Selective Electrophilic Activation of Alkanes. *Acc. Chem. Res.* **1993**, *26*, 370−376. (d) Culman, J. C.; Simon, M.; Sommer, J. Selective Carbonylation of Propane in Superacidic Media *via* Hydride Abstraction by the Chlorocarbocations: CCl_3^+ and $CHCl_2^+$. *J. Chem. Soc., Chem Commun.* **1990**, 1098−1100.
(53) Akhrem, I. S.; Churilova, I. M.; Vitt, S. V. Oxidative Transformations of Cyclohexane, Methylcyclopentane, and Pentane, on Treatment with Superelectrophiles Based on Polyhalomethane and Aluminum Halides. *Russ. Chem. Bull., Int. Ed.* **2001**, *50*, 81−87.
(54) (a) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985; Chapter 1. Olah, G. A.; Laali, K. A.; Wang, Q.; Prakash, G. K. S. *Onium Ions*; Wiley: New York, 1998. Olah, G. A.; De Member, J. R.; Mo, Y. K.; Svoboda, J. J.; Schilling, P.; Olah, J. A. Onium ion. VII. Dialkylhalonium ions. *J. Am. Chem. Soc.* **1974**, *96*, 884−892. Olah, G. A.; Rasul, G.; Burrichter, A.; Prakash, G. K. S. Attempted Hydrogen−deuterium Exchange of the Protiotimethyloxonium Dication ($(CH_3)_3OH_2^{+2}$, a Study of the Methylating Ability of $(CH_3)_3O^+$ in Superacids and Theoretical Investigations. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 4099−4103. (b) Olah, G. A. *Halonium Ions*; Wiley-Interscience: New York, 1975.
(55) Olah, G. A.; Rasul, G.; Hachoumy, M.; Burrichter, A.; Prakash, G. K. S. Diprotonated Hydrogen Halides (H_3X^{2+}) and Gitionic Protio Methyl- and Dimethylhalonium Dications ($CH_3XH_2^{2+}$ and $(CH_3)_2$-XH^{2+}): Theoretical and Hydrogen−Deuterium Exchange Studies. *J. Am. Chem. Soc.* **2000**, *122*, 2737−2741.
(56) Bukula, J.; Culmann, J.-C.; Sommer, J. Selective Carbonylation of Propane in HF-SbF_5: The Role of of Carbon Monoxide in the Halogen-promoted Activation Step. *J. Chem. Soc., Chem. Commun.* **1992**, 481−483.
(57) Berkessel, A.; Thauer, R. K. On the Mechanism of Catalysis by a Metal-Free Hydrogenase from Metrhogenic Archaea: Enzymatic Transformation of H_2 without a Metal and Its Analogy to the Chemistry of Alkanes in Superacid. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2247−2250.
(58) Negishi, E. Principle of Activation of Electrophiles by Electrophiles through Dimeric Association − Two Are Better than One. *Chem.—Eur. J.* **1999**, *5*, 411.

AR020102P