SCIENCE

Superacids

Acids up to billions of times stronger than sulfuric acid have opened up fascinating new areas of chemistry.

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Until recently, chemists generally considered mineral acids, such as sulfuric, nitric, perchloric, and hydrofluoric acids, to be the strongest acid systems attainable. That view has changed considerably as extremely strong acid systems—hundreds of millions, even bil-

very closely to the degree of transformation of a base with its conjugate acid, keeping in mind that this will depend on the base itself and on medium effects. The advantage of this method was shown in the 1930's by Hammett and Deyrup (4), who investigated the proton donor

Summary. Superacids, although first referred to as early as 1927, were only extensively studied in the last decade. Acidities up to 10^{12} times that of sulfuric acid have now been obtained. The extremely low nucleophilicity of the counterions in superacidic systems is especially useful for the preparation of stable, electron-deficient cations, particularly carbocations. Many of these cations, which were formerly detectable only in the gas phase, can now be studied in solution. Novel organic syntheses that are not possible in ordinary acidic media can also be achieved in superacids, including syntheses of economically important hydrocarbons. The unique ability of superacids to bring about hydrocarbon transformations, even to activate methane to undergo electrophilic oligocondensation, can open up new fields in chemistry.

lions of times stronger than sulfuric acid—have been discovered. The object of this article is to give a general overview of the chemistry of these superacids. Reviews have appeared describing individual superacid systems and their chemistry (1–3).

A number of methods are available for estimating acidity in solution. The best known one is the direct measurement of hydrogen ion activity (a_{H+}) used in defining the pH.

$$p\mathrm{H} = -\log a_{H+} \quad (1)$$

This can be achieved by measuring the potential of a hydrogen electrode in equilibrium with a dilute acid solution. In highly concentrated acid solutions, however, the pH concept is no longer applicable, and the acidity must be related

ability of the H_2O–H_2SO_4 system over the whole concentration range by measuring the extent to which a series of nitroanilines were protonated. This was the first application of the very useful Hammett acidity function

$$H_0 = p\mathrm{K}_{BH+} - \log \frac{BH^+}{B} \quad (2)$$

Here the $p\mathrm{K}_{BH+}$ is the dissociation constant of the conjugate acid (BN^+), and BH^+/B is the ionization ratio, which is generally measured by spectroscopic means [ultraviolet, nuclear magnetic resonance (NMR), and more recently dynamic NMR]. The Hammett acidity function is a logarithmic scale on which 100 percent sulfuric acid has an H_0 of -11.9 and anhydrous HF has an H_0 of -11.0.

Protic (Bronsted) Superacids

The acidity of sulfuric acid solution can be increased by the addition of solutes that behave as acids in the system; that is

$$HA + H_2SO_4 \rightleftarrows H_3SO_4^+ + A^-$$
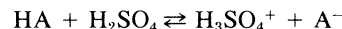
These solutes increase the concentration of the highly acidic $H_3SO_4^+$ cation just as the addition of an acid to water increases the concentration of the oxonium ion, H_3O^+. Fuming sulfuric acid (oleum) contains a series of such acids, the polysulfuric acids, the simplest of which is disulfuric acid, $H_2S_2O_7$ (5), which ionizes as a moderately strong acid in sulfuric acid

$$H_2S_2O_7 + H_2SO_4 \rightleftarrows H_3SO_4^+ + HS_2O_7^-$$
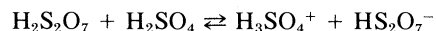
Higher polysulfuric acids, such as $H_2S_3O_{10}$ and $H_2S_4O_{13}$, also behave as acids and appear somewhat stronger than $H_2S_2O_7$. The value of the acidity function H_0 increases continuously up to and beyond the composition of $H_2S_2O_7$ as SO_3 is added to H_2SO_4.

In 1927, Hull and Conant (6) observed that weak organic bases such as carbonyl compounds (ketones and aldehydes) are capable of forming salts with perchloric acid in nonaqueous solvents. Because of the ability of perchloric acid in nonaqueous systems to protonate such weak bases, they called this acid system a superacid. According to Gillespie and coworkers (5, 7–9), who did much pioneering work on inorganic aspects of acid systems, all protic acids stronger than 100 percent sulfuric acid should be classified as superacids. Thus perchloric acid ($HClO_4$), fluorosulfuric acid (HSO_3F), and trifluoromethanesulfonic acid (CF_3SO_3H) are considered to be superacids.

Highly concentrated perchloric acid ($H_0 \simeq -13.0$) is also an extremely strong oxidizing agent, and its contact with organic compounds must be considered extremely dangerous. This is because of the ease of formation of covalent per-

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chlorates of the type R_3COClO_3 (where R is an alkyl or aryl group), which are thermally unstable and can give rise to violent explosions. We will not discuss further the chemistry of perchloric acid in this article; however, it has been reviewed (10). Fluorosulfuric acid and trifluoromethanesulfonic acid have acidities comparable to or higher than that of perchloric acid without the associated dangers of the latter.

Fluorosulfuric acid. Fluorosulfuric acid (1) is one of the strongest protonic acids known ($H_0 = -15.6$). Of all the simple Bronsted acids studied so far, only disulfuric acid ($H_2S_2O_7$) appears to be more acidic than fluorosulfuric acid. Its other advantages include a conveniently

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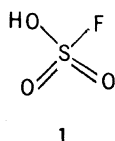
wide liquid range ($-89°$ to $+163°C$) and a viscosity (1.56 centipoise at 25°C) lower than that of sulfuric acid systems. It is readily available, relatively inexpensive, easily purified by distillation, and if pure (free from HF) it does not etch glass.

The low freezing point ($-89°C$) has proved to be advantageous in the study of protonation (3), particularly of weak bases such as carbonyl compounds and aromatic hydrocarbons. At ambient temperatures proton exchange reactions in acids are generally much too fast to allow the detection of protonated weak bases. Near the freezing point of fluorosulfuric acid, however, many proton exchange reactions are slowed down sufficiently to be studied by NMR spectroscopy. Another advantage of fluorosulfuric acid is that it is not as good a sulfonating agent toward organic compounds as $H_2S_2O_7$, particularly at low temperatures. Most of the applications of fluorosulfuric acid are discussed in the section on Bronsted-Lewis superacid mixtures.

Trifluoromethanesulfonic acid (triflic acid). This acid (2) was first prepared (11) by the oxidation of bis(trifluoromethylthio)mercury with aqueous hydrogen peroxide. Commercially, it is pre-

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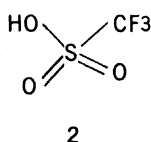
pared by electrochemical fluorination of methanesulfonic acid (12), and it can also be prepared from trichloromethanesulfonyl chloride (Cl_3SO_2Cl) with HF followed by hydrolysis. It is a colorless liquid

that boils at 162°C, fumes in moist air, and is converted to a stable monohydrate, which is a solid at room temperature. Triflic acid and its conjugate bases have extreme thermal stability and are resistant to both oxidative and reductive cleavage. Strong nucleophiles are not known to displace fluoride from triflic acid or its derivatives. However, it is capable of forming covalent derivatives. It has an H_0 value of -14.6 (2). Other properties of triflic acid, such as a relatively low freezing point ($< -35°C$) and viscosity (2.87 centipoise) compared with sulfuric acid, have made it a highly useful solvent for the generation of cation radicals (13) and carbocations. It is also extensively used as an acidic catalyst for chemical syntheses (2).

Higher homologous perfluoroalkanesulfonic acids. The higher homologs of triflic acid, $C_nF_{2n+1}SO_3H$, are also superacids, but their acidity decreases with increasing molecular weight (14). The acidities on the H_0 scale of CF_3SO_3H, $C_2F_5SO_3H$, $C_4H_9FSO_3H$, and $C_5F_{11}SO_3H$ are -14.6, -14.5, -12.7, and -11.7, respectively. The C_1 to C_4 acids are liquids at room temperature; the C_6 to C_8 acids are solids with relatively low melting points. Addition of metal fluorides of higher valence, such as antimony, tantalum, or niobium pentafluoride, greatly enhances the acidity of all these systems. Addition of 3 to 5 percent (by weight) antimony pentafluoride, for example, causes an increase of at least 10^5 in acidity.
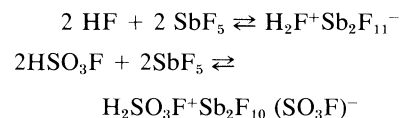
Lewis Superacids

The study of Friedel-Crafts reactions led to the realization (15) that only nonbonded electron pair donors such as alkyl halides can readily coordinate with Lewis acid catalysts ($AlCl_3$ or BF_3), whereas with bonded electron pair donors such as olefins and aromatics, protic acid catalysis is needed. In a generalized sense, however, acids are electron acceptors, and thus no a priori differentiation between Bronsted (protic) and Lewis acids seems to be justified. In extending the concept of superacidity to Lewis acid halides, it is suggested that those stronger than anhydrous aluminum chloride (the most commonly used Friedel-Crafts acid) should be categorized as superacids. These superacidic Lewis acids include such higher-valence halides as antimony, arsenic, tantalum, niobium, and bismuth pentafluorides. It should always be kept in mind that superacidity encompasses both Bronsted and Lewis acid systems.

Conjugate Bronsted-Lewis Superacids

In most Lewis acid-catalyzed systems, as in the reactions of saturated or unsaturated hydrocarbons, the actual catalysts are the strong conjugate acids of Lewis acid halides with proton sources such as H_2O or HCl, which are nearly always present in the system—that is, $H^+AlCl_4^-$, $H^+BF_4^-$, and so on (in their solvated forms). These conjugate Friedel-Crafts acids have H_0 values estimated at about -15 to -16. They are stronger acids than the usual mineral acids. For example, xylenes are not isomerized by mineral acids but are readily isomerized by Friedel-Crafts conjugate acid systems. In 1952 McCauley and Lien (16) demonstrated the usefulness of acid systems such as $HF-BF_3$ in hydrocarbon transformation reactions.

Two superacid systems used very frequently are HSO_3F-SbF_5 (Magic Acid) (17) and $HF-SbF_5$ (fluoroantimonic acid). The acidity of anhydrous HF and HSO_3F increases drastically on the addition of Lewis acid fluorides such as SbF_5, which form large complex fluoro anions that facilitate dispersion of the negative charge (7, 9, 18).

$$2\ HF + 2\ SbF_5 \rightleftharpoons H_2F^+Sb_2F_{11}^-$$
$$2HSO_3F + 2SbF_5 \rightleftharpoons$$
$$H_2SO_3F^+Sb_2F_{10}\ (SO_3F)^-$$

The acidity function of HSO_3F increases from -15.6 to -21.0 on addition of 25 mole percent SbF_5 (19, 20), as shown in Fig. 1. Extrapolation of the HSO_3F-SbF_5 curve in Fig. 1 would lead to an H_0 value of about -25 for Magic Acid. Fluoroantimonic acid is even stronger. As shown in Fig. 1, with 4 mole percent SbF_5 the H_0 value for $HF-SbF_5$ is already -21.0, a thousand times stronger than the value for fluorosulfuric acid with the same SbF_5 concentration. At present it is difficult to estimate the acidity of 1:1 $HF-SbF_5$, but a value of -28 can be predicted (20) on the basis of isomerization kinetics data. Thus, these superacidic systems can be 10^{16} times stronger than 100 percent sulfuric acid

Related superacid systems in which SbF_5 is replaced by AsF_5, TaF_5, NbF_5, or BF_3 are lower in acidity than Magic Acid and fluroantimonic acid. For example, BF_3 forms no stable conjugate acid with HSO_3F. However, $HF-TaF_5$, $HF-NbF_5$, and $HF-BF_3$ are very useful superacids that are nonreducible and will not cause oxidative side reactions.

The conjugate superacids of triflic acid with Lewis acid halides such as SbF_5 also have greatly increased acidity, and they have been used to prepare high-oc-

tane alkylates from reactions of alkanes or alkylaromatic hydrocarbons with olefins (21). The CF$_3$SO$_3$H-SbF$_5$ system is also useful for the isomerization of straight-chain (or slightly branched) alkanes to their more highly branched isomers of higher octane numbers (22), a reaction important in the petroleum industry. With NbF$_5$ and TaF$_5$, triflic acid forms catalytic systems that are capable of converting benzene or toluene to ethylbenzene (22).

Solid Superacids

Acidic oxides such as silica and silica-alumina were used extensively as solid acid catalysts in the past and are not discussed in this article (23). However, solid acid systems considerably stronger than these have been developed recently and can be categorized as solid superacids.

As chemical applications of liquid superacids became important, efforts were made to attach superacids to solid supports. There have been considerable difficulties in achieving this goal. For example, BF$_3$-based systems such as HF-BF$_3$ cannot be well adsorbed onto solid supports because the highly volatile BF$_3$ is easily desorbed. However, SbF$_5$, TaF$_5$, and NbF$_5$ have much lower vapor pressures and are thus much more adaptable to being attached to solids. Because of their extreme chemical reactivity, SbF$_5$, HF-SbF$_5$, and HSO$_3$F-SbF$_5$ can be attached preferentially only to fluoridated alumina, fluorinated polyolefin resin, graphite, or fluorinated graphite (23, 24). On such carriers, at temperatures as low as 70°C, HF-SbF$_5$ and HSO$_3$F-SbF$_5$ readily isomerize straight-chain alkanes such as n-heptane or n-hexane. Similar systems are also effective as alkylation catalysts for alkanes with alkenes. Solid superacids based on TaF$_5$ or NbF$_5$ are more stable than those based on SbF$_5$ because of their resistance to reduction. Solid perfluorinated resin sulfonic acid catalysts, such as those based on the acid form of DuPont's Nafion ion membrane resin CF$_3$(CF$_2$)$_x$-O-CF$_2$CF$_2$SO$_3$H, and higher perfluoroalkane sulfonic acids, such as perfluorodecanesulfonic acid, are also gaining interest as solid superacid catalysts (4).

Preparation of Carbocations in
Superacids

Superacids such as Magic Acid or fluoroantimonic acid have made it possible to prepare stable, long-lived carbo-

cations, which are too reactive to exist as stable species in less acidic solvents. Stable superacidic solutions of a large variety of carbocations, including alkyl cations such as the tert-butyl cation (3) (trimethylcarbenium ion) or the isopropyl cation (4) (dimethylcarbenium ion), have been obtained (25). Some of the

CH$_3$—C$^+$(CH$_3$)CH$_3$ H—C$^+$(CH$_3$)CH$_3$

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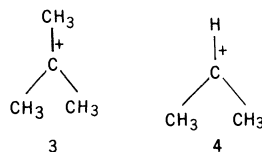
carbocations, as well as related acyl cations and acidic carboxonium ions, that have been prepared in superacidic solutions or even isolated from them as stable salts are shown in Fig. 2. Spectroscopic techniques such as ^{1}H and ^{13}C NMR and infrared, ultraviolet, and electron spectroscopy have been employed to characterize carbocations (10). Typical alkyl and cycloalkyl cations gener-

ated and studied in these superacidic media are shown in Fig. 3, and the ^{1}H NMR spectra of 3 and 4 as well as the tert-amyl cation and the tricyclopropylmethyl cation are shown in Fig. 4.

Aromatic and homoaromatic cations and carbodications. According to Hückel's (4n+2) electron rule, if a carbocation has aromatic character, it is stabilized by resonance. Some aromatically stabilized Hückeloid systems generated in superacid media along with some carbodications are shown in Fig. 5.

Static or equilibrating carbocations. Some carbocations tend to undergo fast degenerate rearrangements through intramolecular hydrogen or alkyl shifts to the related identical (degenerate) structures (26). The question arises whether these processes involve equilibrations between limiting "classical" ion intermediates, whose structures can be adequately described by Lewis-type two-electron, two-center bonds separated by
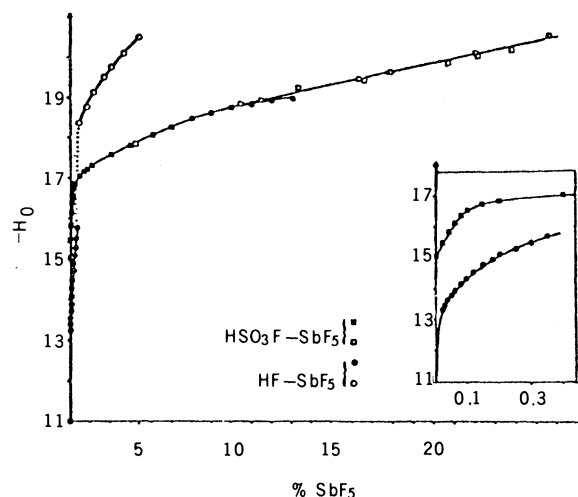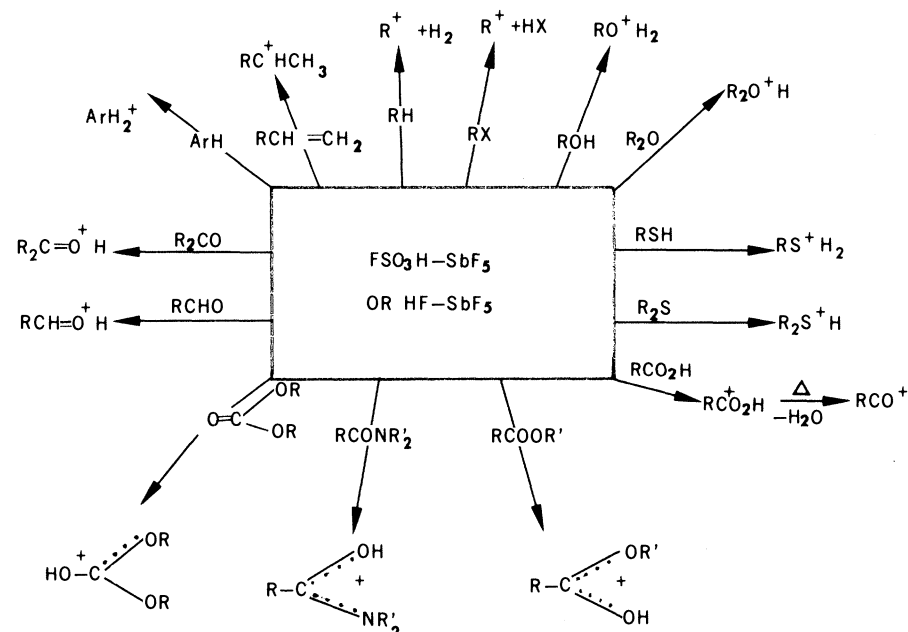

Fig. 1 (left). Relative acidities of HF and HSO$_3$F on addition of SbF$_5$. Fig. 2 (below). Some carbocations generated in superacids.

low-energy transition states, or whether intermediate "nonclassical" hydrogen- or alkyl-bridged carbonium ions are involved, which also require the presence of two-electron bonds between three or more centers for their description (27–30). It is difficult to answer this question by NMR spectroscopy because of its slow time scale; however, NMR has been used to delineate structures where degenerate rearrangements lead to averaged shifts and coupling constants. Also, Saunders and Kates (30) recently introduced an ingenious technique in which deuterium labeling perturbs the degenerate equilibria, allowing one to differentiate between classical and nonclassical equilibrating cations (the perturbation is minimal in the case of nonclassical equilibrating ions).

Faster methods, such as infrared and Raman spectroscopy and especially ESCA (electron spectroscopy for chemical analysis), are particularly useful for investigating these systems (31). Some typical examples are depicted in Fig. 6.

Heteroatom-stabilized cations. Heteroatom-substituted carbocations are strongly stabilized by electron donation from the nonbonded electron pairs of the heteroatoms adjacent to the cationic center. For example

$$R_2C^+ - X \leftrightarrow R_2C = X^+$$
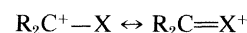
where X can be Br, OR, NR_2, SR, F, or Cl (where R is an alkyl or aryl group). The stabilizing effect is enhanced when two or three electron-donating heteroatoms coordinate with the electron-deficient center. Some examples are shown in Fig. 7.

Hydrocarbon Transformation Reaction

The astonishing acidity of Magic Acid and related superacids allows protonation of exceedingly weak bases. Not only all conceivable π-electron donors (such as olefins, acetylenes, and aromatics) but also weak σ-electron donors (such as saturated hydrocarbons, including the parent alkane, methane) are protonated. The ability of superacids to protonate saturated hydrocarbons (alkanes) rests on the ability of the two-electron, two-center covalent bond to share its bonded electron pair with empty orbital (p or s) of a strongly electron-deficient reagent such as a protic acid:

$$R-H + H^+ \rightleftarrows \left(R \cdots \overset{H}{\underset{H}{\triangle}} \right)^+$$
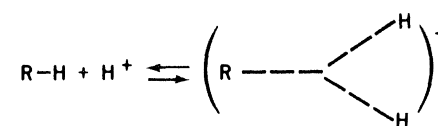
Superacids are suitable reagents for chemical transformation, particularly of hydrocarbons.

Isomerization. The isomerization of hydrocarbons is of practical importance (15). Isomeric dialkylbenzenes, such as xylenes, are starting materials for plastics and other products. Generally, only one of the possible isomers is used as the starting material, and thus there is a need for intraconversion (isomerization). Straight-chain alkanes with five to eight carbon atoms have considerably lower octane numbers than their branched isomers, and hence there is a need to convert them into the higher-octane branched isomers. Isomerizations are generally carried out under thermodynamically controlled conditions and lead
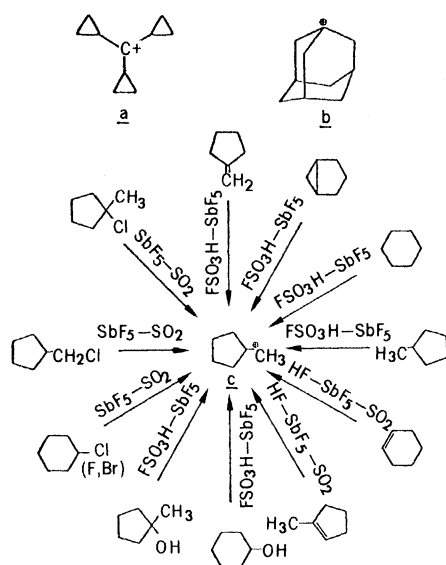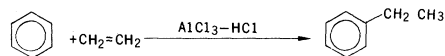

Fig. 3 (left). Alkyl and cycloalkyl cations. (a) The tricyclopropylmethyl cation was the first cyclopropylmethyl cation to be observed by NMR spectroscopy (52). (b) Bredt's rule (53) in its original form seems to exclude the possibility of formation of positive carbenium ion centers at bridgehead positions. Indeed, bridgehead halides proved to be extremely unreactive under solvolytic conditions. However, 1-fluoroadamantane (as well as 1-haloadamantanes) gives the stable 1-adamantyl cation in superacid solution (3). The stability of the ion is explained by the overlap of the empty p lobe with the back lobes of three bridgehead C–H bonds [σ-Π hyperconjugation]. (c) The tertiary 1-methyl-1-cyclopentyl cation (54) is very stable in superacids and can be generated from a variety of starting materials. Fig. 4 (below). Proton NMR spectra of (a) *tert*-butyl cation (3), (b) *tert*-amyl cation, (c) isopropyl cation, and (d) tricyclopropylmethyl cation. The frequency was 60 MHz in (a) to (c) and 300 MHz in (d).
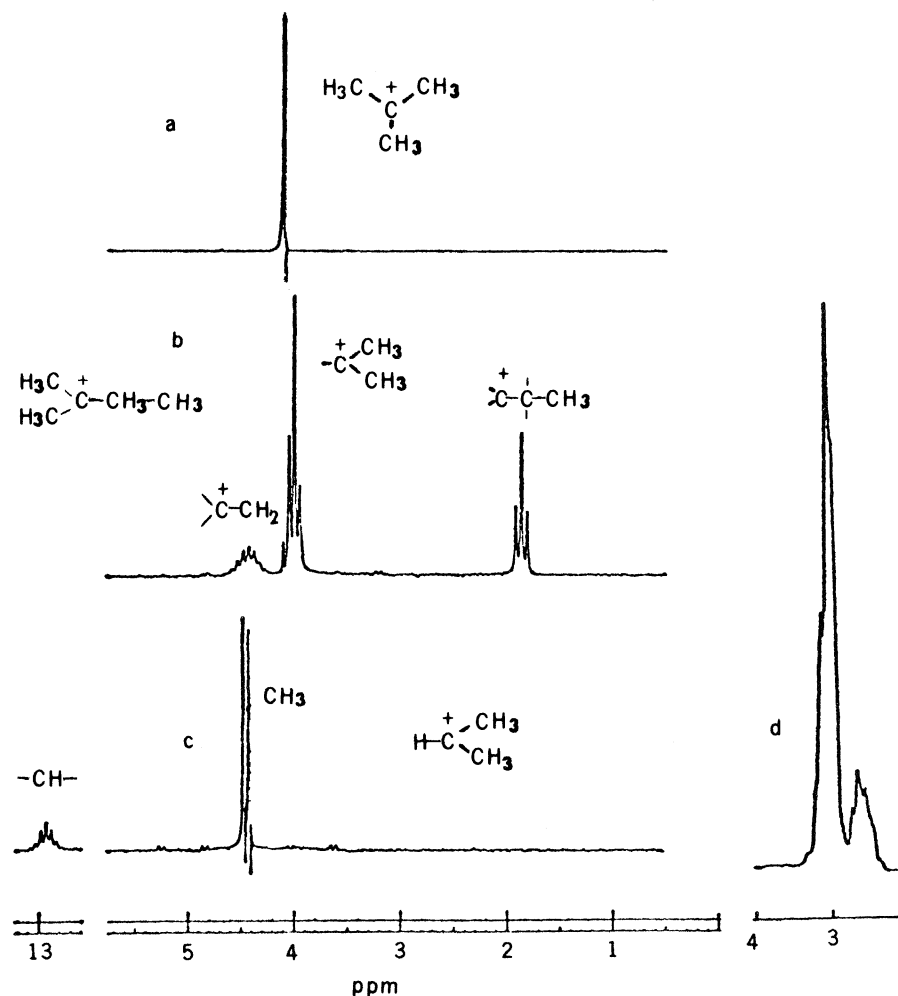
to equilibria. The equilibria favor increased amounts of the higher-octane branched isomers at lower temperatures.

Conventional acid-catalyzed isomerization of alkanes can be effected with various systems. Superacid-catalyzed reactions can be carried out at much lower temperatures, even at or below room temperature, and thus provide more of the branched isomers. This is of particular importance in preparing lead-free gasoline. Increasing the octane number by this means is preferable to doing so by the addition of higher-octane aromatics or olefins, which may pose environmental or health hazard problems (32). Isomerization of alkylaromatics can also be effectively carried out with superacids (15, 33).

Alkylation. Alkylation of aromatics is carried out industrially on a large scale; an example is the reaction of ethylene with benzene to produce ethylbenzene, which is then dehydrogenated to styrene, the monomer used in producing polystyrene. Traditionally, these alkyla-

tions have been carried out in solution with a Friedel-Crafts acid catalyst such as AlCl$_3$. However, these processes are quite energy-consuming, form complex mixtures of products, and require large amounts of catalyst, most of which is tied up as complexes and can be difficult or impossible to recover. The use of a solid superacidic catalyst permits clean, efficient heterogenous alkylations with no complex formation.

Aliphatic alkylation is widely used to produce high-octane gasolines and other hydrocarbon products (34, 35). Conventional paraffin-olefin (alkane-alkene) alkylation is an acid-catalyzed reaction which involves the addition of a tertiary alkyl cation generated from an isoalkane (through hydride abstraction) to an olefin. An example of such a reaction is the isobutane-ethylene alkylation, yielding 2,3-dimethylbutane. The mechanism of such reactions has been elucidated by Schmerling (36).

The recent revival of interest in strong acid chemistry is further exemplified by the discovery (37) that lower alkanes such as methane and ethane can be poly-condensed in Magic Acid at 50°C, yielding mainly C$_4$ to C$_{10}$ hydrocarbons of the gasoline range. The proposed mechanism (Fig. 8) necessitates the intermediacy of protonated alkanes (pentacoordinated carbonium ions), at least as transition states. Until now, these ions have been observed only by mass spectrometry (37). Because of the high
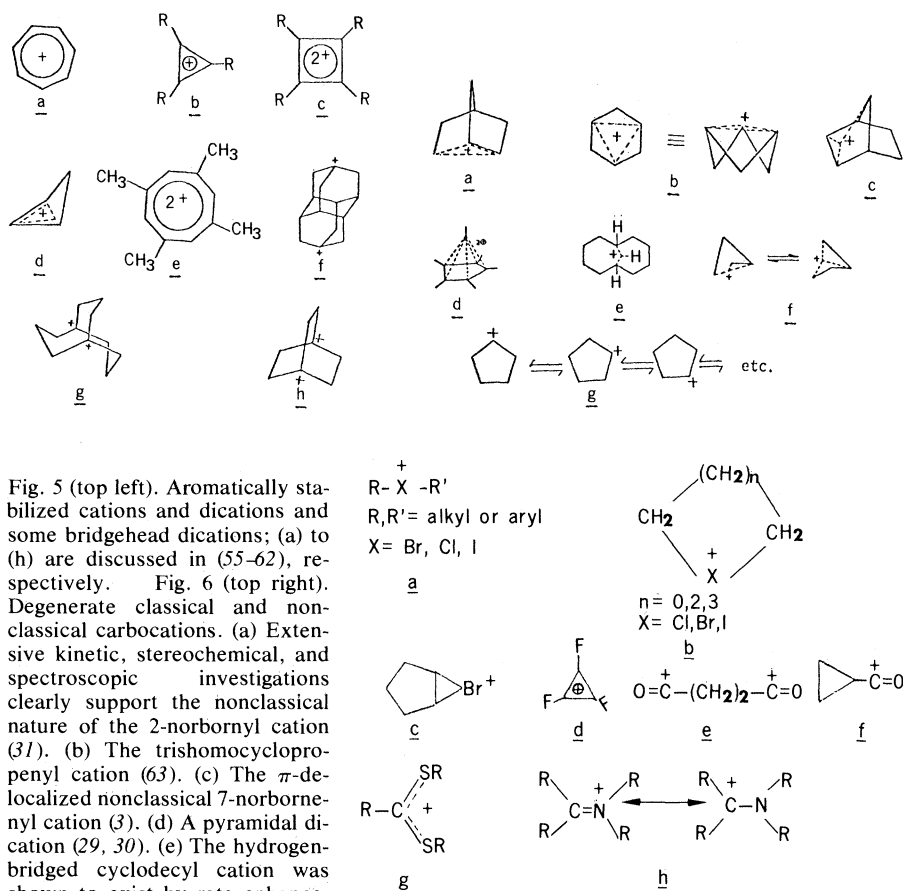
Fig. 5 (top left). Aromatically stabilized cations and dications and some bridgehead dications; (a) to (h) are discussed in (55–62), respectively. Fig. 6 (top right). Degenerate classical and nonclassical carbocations. (a) Extensive kinetic, stereochemical, and spectroscopic investigations clearly support the nonclassical nature of the 2-norbornyl cation (31). (b) The trishomocyclopropenyl cation (63). (c) The π-delocalized nonclassical 7-norbornenyl cation (3). (d) A pyramidal dication (29, 30). (e) The hydrogen-bridged cyclodecyl cation was shown to exist by rate enhancement in solvolysis and by direct spectroscopic observation (64). (f) Rapidly equilibrating bicyclobutonium cations (65). (g) Rapidly equilibrating classical cyclopentyl cation (3). Fig. 7 (bottom right). Heteroatom-stabilized cations: (a) to (d) are described in (66), (e) and (f) in (67), (g) in (68), and (h) in (69).

reactivity of primary and secondary ions under these conditions, the alkylation reaction is complicated by hydride transfer and related competing reactions. However, in this mechanism it is implicit that an energetic primary cation will react directly with methane or ethane. This opens the door to new chemistry through activation of these traditionally passive molecules.

A convenient way to prepare an energetic primary cation is to react ethylene with superacid. This has been used (38) with HF-TaF$_5$ catalyst to achieve ethylation of methane in a flow system at 50°C. With a methane-ethylene mixture (85:15), propane is the major product. This reaction clearly is a direct alkane alkylation through a pentacoordinated carbocation (Fig. 9). Alkylation of ethylene by an incipient methyl cation can be ruled out because the yield of propylene and polymeric material was only a few percent. Methane alone does not react under these conditions, and ethylene alone yields mainly a mixture of products with higher molecular weights.

When a 1:9 ethylene-ethane mixture is treated with the same catalyst, normal butane is formed with high selectivity.

This again shows that no primary butyl cation is formed from ethylation of ethylene (Fig. 10) and that the ethyl cation alkylates ethane in a C–H bond through a pentacoordinated carbonium ion. These results clearly suggest that carbonium ions or tight ion pairs of a related pentacoordinated nature (37) are the reacting species and alkylations can proceed without the concurrent isomerization characteristic of trivalent alkyl cations.

Polymerization. The key initiation step in cationic polymerization of alkenes is the formation of a carbocationic intermediate (39), which can then interact with excess monomer to start propagation. The mechanism of the initiation of cationic polymerization and polycondensation has been extensively studied. Trivalent carbenium ions play the key role, not only in the acid-catalyzed polymerization of alkenes, but also in the polycondensation of arenes (π-bonded monomers) as well as the cationic polymerization of ethers, sulfides, and nitrogen compounds (nonbonded electron-pair donor monomers). On the other hand, pentacoordinated carbonium ions play the key role in the electrophilic reactions of σ-bonds (single bonds), in-
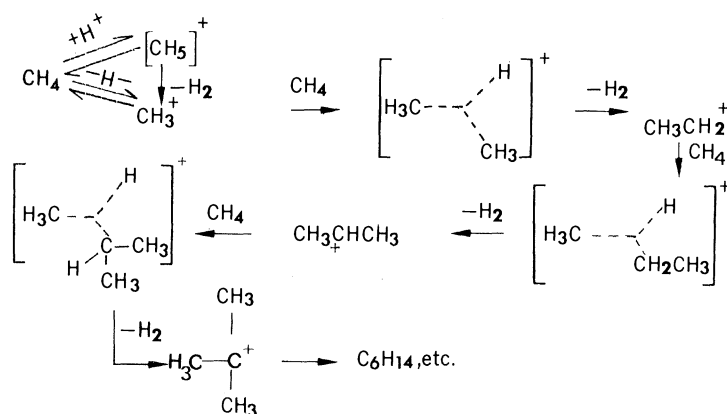
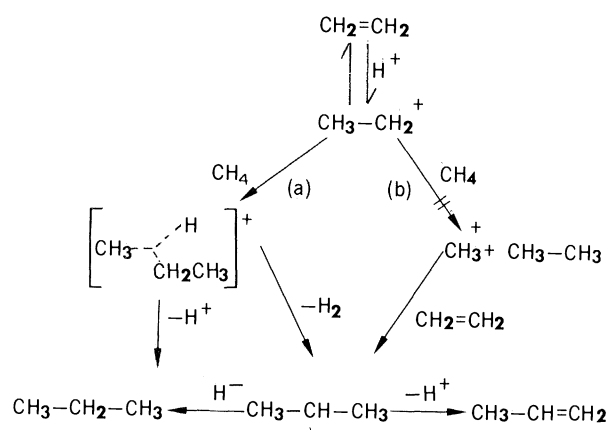Fig. 8 (left). Methane oligocondensation reaction. Fig. 9 (right). Ethylene-methane alkylation.
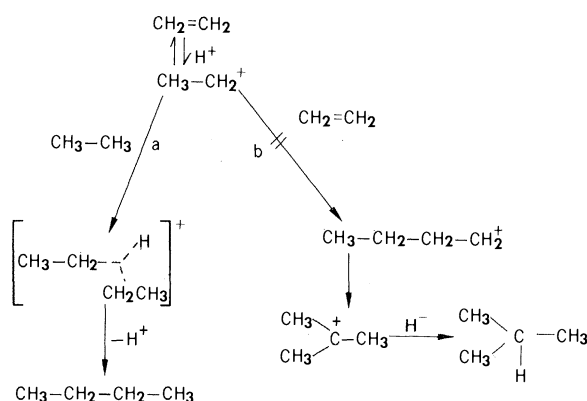
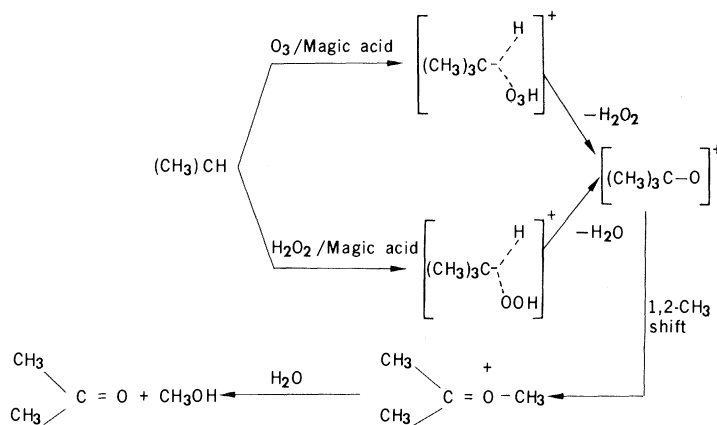Fig. 10 (left). Ethylene-ethane alkylation. Fig. 11 (right). Conversion of isobutane into acetone and methyl alcohol.

cluding the oligocondensation of alkanes and the cocondensation of alkanes and alkenes (40, 41).

Alkylation and oligocondensation reactions of alkanes giving higher-molecular-weight alkanes have been achieved (40–42)—for instance, the oligocondensation of methane, which was discussed in the preceding section. When higher proportions of alkanes are treated in relation to the superacid used, they undergo oligocondensation with increasing ease. The oligocondensation of lower alkanes to give polyalkanes is a reaction of substantial practical interest; by this reaction, natural gas can be converted into branched liquid hydrocarbons in the gasoline range or into other hydrocarbon products. A study of alkane polycondensation in Magic Acid (43) has shown that highly branched polyalkanes with molecular weights up to 700 can be obtained by reacting a gaseous alkane (C_1 to C_4) with the liquid acid, even at room temperature.

The first step of this polycondensation reaction involves protonation of the alkane, with subsequent formation of one molecule of hydrogen, at the expense of the superacid used. This difficulty can be overcome, as pointed out by Olah

et al. (37), by adding a small amount of an olefin such as ethylene to the reaction mixture as initiator. Roberts and Calihan (41) also showed that methane undergoes polycondensation in the presence of alkenes such as propene, 1-butene, or 2-methylpropene, giving polyalkanes containing block methylene groups (at least four straight-chain CH_2 units).

Superacids in Organic Syntheses

Since their discovery (3), stable carbocations were known to be readily quenched by various nucleophiles. These reactions, which were first used to confirm the structure of the ions, proved to be very useful in organic syntheses. The selectivity of the reactions is based on the fact that generally only the thermodynamically more stable ions are formed under the reaction conditions, resulting in high selectivity. The new functional group created in the superacid medium will itself undergo protonation, and thus be protected against any further electrophilic attack. In this way, a number of new selective reactions with high yields were achieved, as shown in the following examples.

Dienone-phenol rearrangement. This isomerization is of substantial importance in natural product syntheses, usually catalyzed by a strong base. The reaction occurs with good yields in polycyclic systems under superacidic conditions, as shown by Gesson and Jacquesy (44).
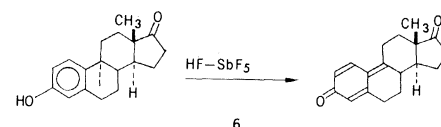
Reduction. Hydride ion transfer to carbocations is a well-known reaction in hydrocarbon chemistry. This reaction has been used successfully in superacid to reduce α,β-unsaturated ketones with methylcyclopentane as the hydride donor (43). Superacid-catalyzed reduction of aromatics, as shown by
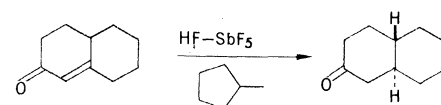
Wristers (45), requires both a hydride donor and hydrogen
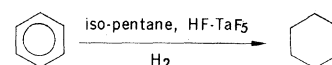
Carbonylation. The reaction between carbocations and carbon monoxide affording oxocarbenium ions (acyl cations) is a key step in the well-known Koch-Haaf react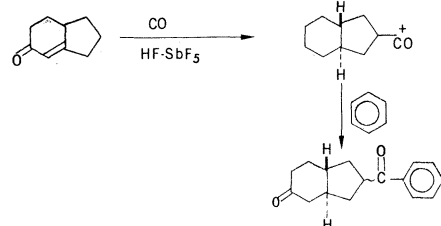ion for the preparation of carboxylic acids from alkenes (46). It has been thoroughly studied by Hogeween (46) under superacidic conditions. The reaction has recently been applied to functionalize nonactivated carbon atoms (47).


Oxidation. Novel oxidations of hydrocarbons in superacids with ozone or hydrogen peroxide have been investigated (48). Protonated ozone $(O_3H)^+$ or hydrogen peroxide $(H_3O_2)^+$ attacks the single σ-bond, resulting in oxygen insertion. These reactions can be followed by a protolytic transformation, such as the conversion of isobutane into acetone and methyl alcohol (Fig. 11) (48). By a similar procedure, aromatics (ArH) are also hydroxylated in high yields at low temperature

$$ArH \xrightarrow[\text{HSO}_3\text{F–SO}_2\text{ClF}]{\text{H}_2\text{O}_2} ArOH$$
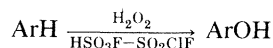
Miscellaneous reactions. Many acid-catalyzed reactions can be advantageously carried out by using solid superacids instead of conventional acid systems. The reactions may be in either the gaseous or liquid phase. For example, several simple procedures were recently reported (49) in which Nafion-H solid acid was used in alkylation, transbromination, nitration, acetalization, hydration, and so on.

Superacids in Inorganic Chemistry

Halogen cations. It has often been postulated that the monoatomic ions I^+, Br^+, and Cl^+ are the reactive intermediates in halogenation reactions of aromatics and alkenes. The search for such species has led to the discovery of I_2^+ and other related halogen cations, which are stable in superacids (50). The I_2^+ cation may be generated by the oxidation of I_2 with $S_2O_6F_2$ in HSO_3F solution

$$2 I_2 + S_2O_6F_2 \rightarrow 2 I_2^+ + 2 SO_3F^-$$
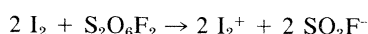
and a stable blue solution of this cation can also be obtained by oxidizing iodine with 65 percent oleum. In a less acidic medium, the I_2^+ cation disproportionates to more stable oxidation states. The electrophilic Br_2^+ cation is obtainable only in the very strong superacid Magic Acid or fluoroantimonic acid, and it disproportionates in HSO_3F. The Cl_2^+ cation, which is much more electrophilic, has not yet been observed in solution. Monoatomic halogen cations seem to be too unstable to be directly observed.

Cations of other nonmetallic elements. Elemental sulfur, selenium, and tellurium give colored solutions when dissolved in a number of strongly acidic media. It has been shown (51) that S_{16}^{2+}, S_8^{2+}, S_4^{2+}, Se_8^{2+}, Te_4^{2+}, and Te_6^{2+} are present in such solutions. These cations are formed by oxidation of the elements by $H_2S_2O_7$ or $S_2O_6F_2$; for example

$$4 S + 6 H_2S_2O_7 \rightarrow S_4^{2+} + 2 HS_3O_{10}^- + 5 H_2SO_4 + SO_2$$
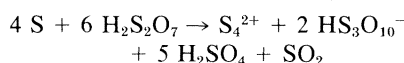
Like the halogen cations, the sulfur, selenium, and tellurium cations are highly electrophilic and undergo disproportionation in media with any appreciable basic properties, although, as would be anticipated, the ease of disproportionation increases in the order tellurium < selenium < sulfur.

References and Notes

1. R. J. Gillespie, *Acc. Chem. Res.* **1**, 202 (1968); *Can. Chem. Educ.* **4**, 9 (April 1969).
2. R. D. Howells and J. D. McCown, *Chem. Rev.* (1977), p. 69.
3. G. A. Olah, *Chem. Eng. News* **45**, 761 (27 March 1967); *Science* **168**, 1298 (1970); *Carbocations and Electrophilic Reactions* (Wiley, New York, 1973).
4. L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.* **54**, 2721 (1932).
5. R. J. Gillespie and E. A. Robinson, in *Non-Aqueous Solvent Systems*, T. C. Waddington, Ed. (Academic Press, New York, 1965), p. 117; R. J. Gillespie and T. E. Peel, *Adv. Phys. Org. Chem.* **9**, 1 (1972).
6. N. F. Hull and J. B. Conant, *J. Am. Chem. Soc.* **49**, 3047 (1927).
7. R. J. Gillespie and T. E. Peel, *ibid.* **95**, 5173 (1973).
8. R. J. Gillespie and K. C. Malhotra, *J. Chem. Soc.* (1967), p. 1994.
9. R. J. Gillespie, in *Proton Transfer Reactions*, V. Gold, Ed. (Chapman & Hall, London, 1975), p. 27.
10. G. N. Dorofeenko, S. V. Krivun, V. I. Dulenko, Yu. A. Zhadanov, *Russian Chem. Rev.* **34**, 88 (1965).
11. R. N. Hazeldine and J. M. Kidd, *J. Chem. Soc.* (1954), p. 4228.
12. T. Gramstad and R. N. Hazeldine, *ibid.* (1976), p. 173; T. Gramstad, *Tidsskr. Kjemi Bergves. Metall.* **18**, 157 (1958); *Chem. Abstr.* **50**, 13982h (1956).
13. G. C. Yang and A. E. Pohland, *J. Phys. Chem.* **76**, 1504 (1972).
14. J. Grondin, R. Sagnes, A. Commeyras, *Bull. Soc. Chim. Fr.* (1976), p. 1779.
15. G. A. Olah, *Friedel-Crafts Chemistry* (Wiley, New York, 1973).
16. D. A. McCauley and A. P. Lien, *J. Am. Chem. Soc.* **74**, 6246 (1952).
17. Registered trademark of Cationics Inc., Columbia, S.C.
18. A. Commeyras and G. A. Olah, *J. Am. Chem. Soc.* **90**, 2929 (1968).
19. J. Sommer, P. Rimmelin, T. Drakenberg, *ibid.* **98**, 2671 (1976); J. Sommer, S. Schwartz, P. Canivet, P. Rimmelin, *ibid.* **100**, 2576 (1978).
20. D. M. Brouwer and J. A. van Doorn, *Recl. Trav. Chim. Pays-Bas* **97**, 894 (1972).
21. G. A. Olah, U.S. patent 3,708,553 (1973); *Chem. Abstr.* **78**, 123979 (1973).
22. J. E. Mahan and J. R. Norell, U.S. patent, 3,838,489 (1974).
23. They are reviewed in (*15*), pp. 343-355.
24. J. M. Oelderik, U.S. patent 3,394,202 (1968); G. A. Olah, U.S. patents 3,766,286 and 3,708,553 (1973); G. A. Olah, J. Kaspi, J. Bukala, *J. Org. Chem.* **42**, 4187 (1977).
25. G. A. Olah, E. B. Baker, J. C. Evans, W. S. Toglyesi, J. S. McIntyre, I. J. Bastieu, *J. Am. Chem. Soc.* **86**, 1360 (1964).
26. For reviews, see G. A. Olah and P. v. R. Schleyer, Eds., *Carbonium Ions* (Wiley, New York, 1968), vol. 1; (1970), vol. 2; (1972), vol. 3; (1973), vol. 4; (1976), vol. 5; D. Bethell and V. Gold, *Carbonium Ions, an Introduction* (Academic Press, New York, 1967).
27. R. N. Grimes, *Carboranes* (Academic Press, New York, 1970); T. P. Nevell, E. de Salas, C. L. Wilson, *J. Chem. Soc.* (1939), p. 1188.
28. S. Winstein and D. S. Trifian, *J. Am. Chem. Soc.* **71**, 2053 (1949); S. Winstein, *Q. Rev. Chem. Soc.* **23**, 1411 (1969); D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.* **9**, 179 (1972).
29. H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.* **8**, 413 (1975).
30. M. Saunders and M. Kates, *J. Am. Chem. Soc.* **100**, 7082 (1978).
31. G. A. Olah, *Acc. Chem. Res.* **9**, 41 (1976).
32. These are covered in the standards and regulations of the Occupational Safety and Health Administration.
33. V. A. Koptyug, *Isomerization of Aromatic Compounds* (Israel Program for Scientific Translations, Jerusalem, 1965).
34. L. F. Albright and A. R. Goldsby, Eds., *Industrial and Laboratory Alkylations* (American Chemical Society, Washington, D.C., 1977).
35. Union Carbide Company process.
36. L. Schmerling, *J. Am. Chem. Soc.* **66**, 1422 (1944).
37. G. A. Olah and R. H. Schlosberg, *ibid.* **90**, 2726 (1968).
38. M. Siskin, R. H. Schlosberg, W. P. Kocsi, preprint of paper presented at the Symposium on New Hydrocarbon Chemistry, American Chemical Society San Francisco meeting, 29 August to 3 September 1976; R. H. Schlosberg, M. Siskin, W. P. Kocsi, F. J. Parker, *J. Am. Chem. Soc.* **98**, 7723 (1976).
39. G. A. Olah, *Makromol. Chem.* **175**, 1039 (1974); J. P. Kennedy, *Polymer Chemistry of Synthetic Elastomers*, J. P. Kennedy and E. G. M. Tornquist, Eds. (Wiley, New York, 1968), part 1, p. 291; J. P. Kennedy and R. S. Squires, *J. Macromol. Sci. Chem.* **1**, 805 (1967); D. C. Pepper, in *Friedel-Crafts and Related Reactions*, G. A. Olah, Ed. (Wiley, New York, 1964), vol. 2, pp. 1293-1349; P. H. Plesch, paper presented at the IUPAC Symposium on Macromolecules, Helsinki, July 1972.
40. G. A. Olah, Y. Halpern, J. Shen, Y. K. Mo, *J. Am. Chem. Soc.* **93**, 1251 (1971); *ibid.* **95**, 4960 (1973).
41. D. T. Roberts, Jr., and L. E. Calihan, *J. Macromol. Sci. Chem.* **7**, 1629 (1973); *ibid.*, p. 1641.
42. J. G. Speight, P. Kovacic, F. W. Koch, *J. Macromol. Sci. Rev. Macromol. Chem.* **5**, 295 (1971).
43. J. M. Loustard, N. H. Douteau, J. C. Jacquesy, R. Jacquesy, P. Longevialle, *Tetrahedron Lett.*, (1975), p. 2029.
44. J. P. Gessori and J. C. Jacquesy, *Tetrahedron* **29**, 3631 (1973).
45. J. Wristers, *J. Am. Chem. Soc.* **97**, 4312 (1975).
46. H. Hogeveen, *Adv. Phys. Org. Chem.* **10**, 29 (1973).
47. J. J. Coustard and J. C. Jacquesy, *J. Chem. Res.* (1977), p. 280.
48. G. A. Olah, D. G. Parker, N. Yoneda, *Angew. Chem. Int. Ed. Engl.* **12**, 909 (1978).
49. G. A. Olah, J. Kaspi, J. Bukala, *J. Org. Chem.* **42**, 4187 (1977); J. Kaspi and G. A. Olah, *ibid.* **43**, 3142 (1978); J. Kaspi, D. D. Montgomery, G. A. Olah, *ibid.*, p. 3147; G. A. Olah, R. Malhotra, S. C. Narang, *ibid.*, p. 4628; G. A. Olah and J. Kaspi, *Nouv. J. Chim.* **2**, 581 (1978); G. A. Olah and D. Meidar, *Synthesis* (1978), p. 358; G. A. Olah, T. Keumi, D. Meidar, *ibid.*, p. 929.
50. R. J. Gillespie and M. J. Morton, *Q. Rev.* (1971), p. 553.
51. R. J. Gillespie and J. Passemore, *Acc. Chem. Res.* **4**, 413 (1971).
52. N. C. Deno, H. G. Richey, Jr., S. Liu, J. D. Hodge, J. J. Houser, M. J. Wisotsky, *J. Am. Chem. Soc.* **84**, 2016 (1962); C. U. Pittmann, Jr., and G. A. Olah, *ibid.* **87**, 2998 (1965); G. A. Olah, P. W. Westerman, J. Nishimura, *ibid.* **96**, 3548 (1974).
53. J. Bredt, J. Houben, P. Levy, *Chem. Ber.* **35**, 1286 (1902); J. Bredt, H. Thouet, J. Schmitz, *Justus Liebigs Ann. Chem.* **437**, 1 (1924).
54. G. A. Olah and J. Lukas, *J. Am. Chem. Soc.* **90**, 933 (1968).
55. G. Merling, *Chem. Ber.* **24**, 3108 (1891); D. v. E. Doering and L. H. Knox, *J. Am. Chem. Soc.* **76**,

3203 (1954); H. J. Dauben, Jr., F. A. Godecki, K. M. Harmon, D. L. Person, *ibid*. **79**, 4557 (1957).
56. R. Breslow and C. Yuan, *J. Am. Chem. Soc.* **80**, 5991 (1958); R. Breslow, J. T. Groves, G. Ryan, *ibid*. **89**, 5048 (1967).
57. G. A. Olah and J. S. Straral, *ibid*. **98**, 6290 (1976).
58. _____, G. Liang, *ibid*. **96**, 6233 (1974); G. A. Olah, J. S. Staral, R. J. Spear, G. Liang, *ibid*. **97**, 5489 (1975).
59. G. A. Olah, J. S. Staral, L. A. Paquette, *ibid*. **98**, 1267 (1976); G. A. Olah, J. S. Staral, G. Liang, L. A. Paquette, W. P. Melega, J. J. Carmody, *ibid*. **99**, 3349 (1977).

60. G. A. Olah, G. D. Mateescu, G. Sipos, P. v. R. Schleyer, in preparation.
61. G. A. Olah, G. Liang, P. v. R. Schleyer, E. M. Engler, M. J. S. Dewar, R. M. Bingham, *J. Am. Chem. Soc.* **95**, 6829 (1973).
62. G. A. Olah, G. Liang, P. v. R. Schleyer, W. Parker, C. I. F. Watt, *ibid*. **99**, 966 (1977).
63. S. Masamune, M. Sakai, A. V. K. Jones, T. Nakashima, *Can. J. Chem.* **52**, 855 (1974); G. A. Olah, G. K. S. Prakash, T. N. Rawdah, J. C. Rees, D. Whittaker, *J. Am. Chem. Soc.* **101**, 3935 (1979).
64. R. P. Kirchen and T. S. Sorensen, *J. Am. Chem. Soc.* **100**, 6761 (1978).
65. G. A. Olah, C. L. Jeuell, D. P. Kelley, R. D.

Porter, *ibid*. **94**, 146 (1972); J. S. Staral *et al.*, *ibid*. **100**, 8016 (1978).
66. G. A. Olah, *Halonium Ions* (Wiley, New York, 1975).
67. H. Perst, in *Oxonium Ions in Organic Chemistry* (Academic Press, New York, 1971); in *Carbonium Ions*, G. A. Olah and P. v. R. Schleyer, Eds. (Wiley, New York, 1976), vol. 5, pp. 1961–2047.
68. G. A. Olah, D. H. O'Brien, C. U. Pittmann, *J. Am. Chem. Soc.* **89**, 2996 (1967).
69. R. J. Gillespie and T. Birchall, *Can. J. Chem.* **41**, 158 (1963); U. Müller and K. Dehnicke, *Angew. Chem.* **78**, 825 (1960); *Angew. Chem. Int. Ed. Engl.* **5**, 841 (1966).

The Rise of the Angiosperms: A Genecological Factor

The combination of insect pollination and closed carpels may provide a unique selective mechanism.

David L. Mulcahy

To what factors do the angiosperms owe their preeminent position in present world floras? Numerous angiospermous characteristics have been suggested as being contributory toward, or even decisive in, the evolutionary rise of this group. These include insect-pollinated flowers, closed carpels, double fertilization, true endosperm, vessel elements, broad leaves, defensive alkaloids, and bird-dispersed fruits (*1–3*).

There can be no doubt that many of these hypotheses contain more than a modicum of truth but, in this article, I propose yet another one, a hypothesis that depends on, and thereby adds significance to, two outstanding character-istics of the primitive angiosperms: insect pollination and the closed carpel. My hypothesis is that insect pollination and the closed carpel, in combination, provide a mechanism that greatly in-tensified selection pressures among the microgametophytes. Thus, the micro-gametic phase of the life cycle served as a barrier against poorly functioning hap-loid genomes and hence benefited the re-mainder of the life cycle.

To understand the operation and the consequences of this mechanism, it is necessary to consider some character-istics of a wind-pollinated preangio-spermous species, similar perhaps to those that presumably gave rise to the

Summary. In the primitive angiosperms, closed carpels are believed to have evolved as protection for ovules, which would otherwise be injured by animal pollina-tors. The hypothesis is presented that, whatever the origin and other functions of angiosperms, insect pollination and closed carpels may, in combination, reduce the influence of random variation on pollen tube competition, thus enhancing the ability of natural selection to act on the gametophytic phase of the life cycle. The micro-gametophytic phase represented by vast numbers of haploid individuals can then serve, by insect pollination and closed carpels, as a screen against any genome not functioning with a high degree of metabolic vigor. Poorly balanced genomes could thus be eliminated at relatively little cost. Insect-pollinated angiosperms would there-fore benefit from positive aspects of sexual recombination. Such a system may have allowed the angiosperms to undergo their rise to dominance.

early angiosperms. Typically vast num-bers of pollen grains would have been produced since only a miniscule fraction of these randomly moving grains could ever reach a receptive surface. Those grains that did reach receptive surfaces would most likely have done so singly and, because such pollinations might have occurred over a long period of time, the first grains to arrive could have en-joyed a head start, compared to later ar-rivals. Thus, the success or failure of a particular microgametophyte was influ-enced by chance. Upon arrival, the wind-borne pollen was passively carried to the megasporangium either by falling upon or being drawn to it by contraction of a pollination droplet.

In each of these above-mentioned characteristics, an insect-pollinated angi-osperm is in direct contrast with a wind-pollinated preangiosperm. In the angio-sperm, for example, fairly large numbers of grains will have reached receptive sur-faces, not by deposition of single grains, but rather by masses of pollen deposited simultaneously by insect visitors. Fur-thermore, upon reaching a receptive sur-face, pollen grains, because of the closed carpels, of necessity produce pollen tubes that grow through fairly long sec-tions of stylar tissues.

While the transition from wind-polli-nated preangiosperm to insect-pollinated angiosperm may have had many con-sequences, my hypothesis suggests some of the most significant effects may have been upon the nature of interactions be-tween microgametophytes. For ex-ample, with insect pollinations, more pollen grains would reach receptive sur-faces (stigmas) so that competition among microgametophytes would be in-tensified. Furthermore, the simultaneous arrival on the stigma of many pollen grains would generate, in itself, an epi-sode of intense competition. Finally, the long passage through the style, as is ex-plained below, would provide an ex-