

ARE REACTIONS IN SUPERACID MEDIA DUE TO PROTONS OR TO POWERFUL OXIDISING SPECIES SUCH AS SO_3 OR SbF_5 ?

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Abstract - The concept is questioned that in superacid media hydride ions are abstracted from saturated hydrocarbons solely. Apparently there are two other processes by which carbonium ions can be generated from alkanes in superacids, viz., oxidation by SO_3 or HSO_3F and oxidation by SbF_5 .

INTRODUCTION

Extreme experimental conditions such as low or high pressures and temperatures have always fascinated researchers because of the possibilities they offer compared with the normal experimental conditions-room temperature, atmospheric pressure, etc.

In moving from water as solvent, we are not restricted by conditions such as those affecting acidity in water. It is possible to obtain pH values more basic or more acidic than in water and to exceed the fourteen pH units available in the solvent water. Thus, very acidic pH conditions, of about -25, can be obtained by adding antimony pentafluoride to anhydrous hydrogen fluoride or to fluorosulfuric acid.

Indeed supernatural properties have been ascribed to the enhancement of acidity; the mixture of SbF_5 and HSO_3F has been called "magic acid" by Olah (Ref.1).

Superacid media : definition

As we pass progressively from pure water which has a pH of 7 to a medium whose pH* is close to -25 (equimolar mixture of SbF_5 and HF), the definition of superacidity is arbitrary because there is no clearcut transition between an acid medium and a superacid medium. To obtain high acidities, mineral acids such as H_2SO_4 (and oleums) and HClO_4 have been used at first.

Superacids are, according to Gillespie (Ref.2) more acidic than 100% sulfuric acid, the most frequently used strong acid solvent. The name "superacid" was first suggested by Hall and Conant (Ref.3) for strongly acidic non-aqueous solutions. Because pure H_2SO_4 is not easy to prepare without an excess of either H_2O or SO_3 , I think it is better to use another reference such as liquid hydrogen fluoride or fluorosulfuric acid ($\text{H}_0 \approx -15$). In contemporary usage the term "superacid" is taken to mean mixtures of SbF_5 on the one hand and HF, HSO_3F or $\text{C}_n\text{F}_{2n+1}\text{SO}_3\text{H}$ on the other hand. This usage is predicated by the discovery that addition of antimony pentafluoride to these acids increased their acidity appreciably. We shall assume accordingly that a superacid medium is characterized by a pH < -15 referred to water.

Structure of superacid media

A superacid medium is a strong donor of protons which are very reactive, because they are relatively weakly solvated by the molecules of the solvent

* To simplify matters, I have assumed that pH referred to water is equal to the Hammett acidity function H_0 . This is a rough approximation.

and/or by the lyate ions. When SbF_5 is added to HF or HSO_3F , reactions take place which lead to the formation of various acidic complexes such as HSbF_6 , $\text{HSb}_2\text{F}_{11}$ and $\text{H}(\text{SbF}_5)_2\text{FSO}_3$ (Refs. 1,4,5). The latter compounds are more acidic than HF or HSO_3F because the corresponding complex anions are bigger than F^- or FSO_3^- which involves a loosening of the bond between the proton and its counterion.

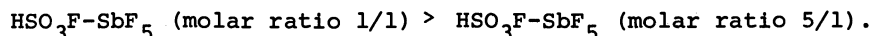
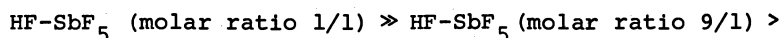
Measure of acidity : Hammett acidity function H_0

The Hammett acidity function H_0 (Ref.6), has been extensively used by Gillespie and coworkers (Refs.7,8) as a measure of the acidity of highly acidic non-aqueous solutions. Typical H_0 values (Ref.8) are listed in the following Table.

Acid	$-H_0$
H_2SO_4	11.93
$\text{H}_2\text{S}_2\text{O}_7$	14.14
HSO_3F	15.07
HSO_3F (10% SbF_5)	18.94

Since the pioneering work of Gillespie no progress has been reported on systems containing more than 10% of SbF_5 in HSO_3F . The difficulties encountered in direct measurement of the BH^+/B ratio by u.v. spectroscopy and the unavailability of weak bases with overlapping log I values are the reasons for reduced reliance on acid-base indicators. Recently Sommer *et al.* (Ref.9) have reported a new method of determination of the BH^+/B ratio using a dynamic NMR technique. The principle is based on the well known fact that the barrier to rotation around a single bond with some π character is very sensitive to all factors which enhance π electron delocalisation (Ref.10). Sommer and coworkers have evaluated the acidity of $\text{HSO}_3\text{F}-\text{SbF}_5$ mixtures in a range between 8 to 25 moles percent of SbF_5 . Their values agree with those of Gillespie and show a continuous increase in acidity on addition of SbF_5 . A discrepancy observed in the 9 - 10% region may be explained by poor accuracy due to the use of diprotonated indicators in the u.v. determinations.

Extrapolation to higher SbF_5 concentrations yields, for magic acid, a H_0 value of -25. By studies of protonation of β -diketones and acid-catalysed isomerizations of hydroxyallyl and alkyltetrahydrofuryl cations (Fig.1), Brouwer *et al.* (Refs. 11,12) have shown that the order of decreasing acidity was:



Another measure of the acidity of superacids called the $R_0(H)$ function has been inferred from measurements of the hydrogen electrode potential versus the ferrocene-ferricinium potential (or of any reference system which is assumed to be independent of the solvent). Although SbF_5 is not a strong acid per se (Ref.16) its addition to HF , HSO_3F , $\text{CF}_3\text{SO}_3\text{H}$, $\text{C}_n\text{F}_{2n+1}\text{SO}_3\text{H}$ (Ref.17) enhances the acidity of these, as shown by using a set of Hammett indicators or potentiometric measurements.

Interest and properties of superacid media

Ten years ago Olah gave a fantastic impetus to studies of reactions in superacids. Thus it has become possible to protonate very weak bases, to study the stereochemistry of the strongest acceptor site of a molecule, and to observe carbocations and their rearrangements etc.

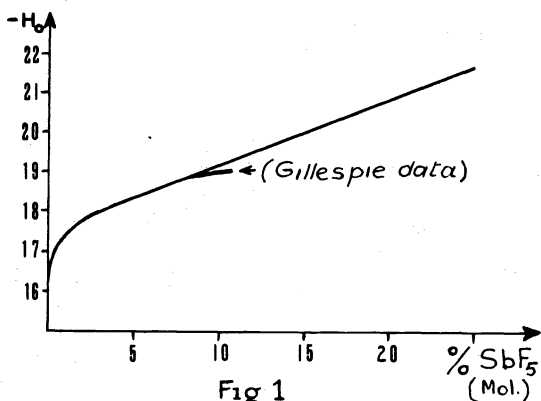


Fig 1 Acidity of the FSO₃H-SbF₅ mixture

Moreover, the availability of protons which is due to the fact that they are poorly solvated has another consequence; the proton becomes concomitantly a powerful oxidant. Indeed at room temperature, the potential of the electrochemical reduction of the proton varies linearly with -0.06 pH or $+ 0.06 \text{ H}_0$. Consequently when $\text{pH} < -15$, this potential is considerably higher than in water. It must be pointed out that the enhancement of acidity is accomplished by adding antimony pentafluoride which is a strong oxidant.

By allowing superacids to react with alkanes, the most stable carbocations are obtained. These correspond to the most ramified hydrocarbons which have the best octane number - thus superacid media catalysts seem able to solve the problem of tetraethyl-lead free gasoline. As a matter of fact, with such catalysts the isomerisation rate of *n*-pentane can reach 85%, which is the thermodynamic limit. Since *n*-pentane is the major constituent of gasoline a complete conversion of this compound into *isopentane* which possesses a high octane number should avoid the use of anti-detonating additives.

Chemical behaviour of alkanes in superacid solutions

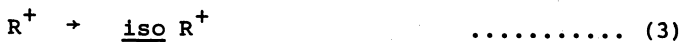
In superacid media, alkanes behave like bases. Thus the first step is a protonation reaction,



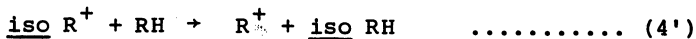
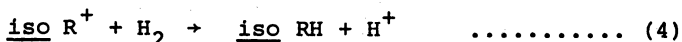
The $[\text{RH}_2]^+$ species is unstable and leads to the formation of the carbocation R^+ with concomitant loss of a hydrogen molecule



For saturated hydrocarbons $\text{C}_n\text{H}_{2n+2}$ with $n \geq 5$ the isomerisation reaction (3) can take place



If an excess of H_2 is present, (or if an excess of alkane molecules are present) the following reaction can occur.



Reactions (1) and (2) are merely oxidation reduction processes. This becomes apparent when one writes the reaction in the form,



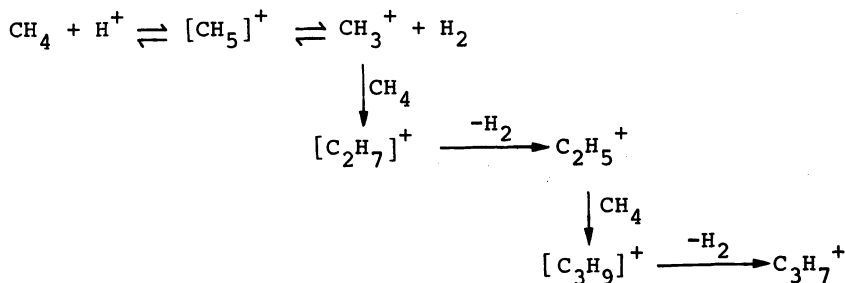
Reaction (5) is the sum of the following half reactions;



In the case of reaction (4') carbocations R^+ can attack further alkane molecules to yield oligomerized molecules thus,



thus, in 1968, Olah & Schlosberg (Ref.18) claimed that they were able to oligomerize methane in magic acid. The overall process is outlined in the following scheme.



Scheme I

etc.

With other alkanes, Olah et al. (Ref.19) found that oligocondensation reactions take place with increasing ease, on going from methane, to ethane, to propane, to butane, etc.

Isomerisation and oligomerisation of paraffins occur via carbocations which are oxidized species compared to the alkanes. As a result carbocations can be generated by protonation as well as by powerful oxidants.

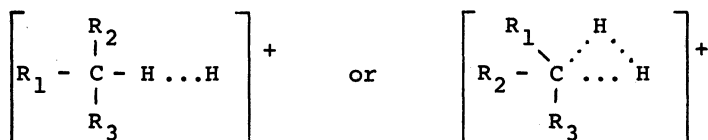
Thus Olah's reactions can be initiated not only by protonation but also by strong oxidising agents. Because SbF_5 itself is a strong oxidant, the identity of the chemical species involved in the creation of carbocations is important from a theoretical and practical point of view; the isomerisation of *n*-pentane and *n*-hexane and the oligocondensation of lower alkanes are reactions of industrial interest.

Mechanism of hydride abstraction from parafins

The abstraction of hydride ion from saturated hydrocarbons by strong acids to yield stable carbonium ions was first reported in the years 1962/3. A mechanism was proposed consisting of a protonation of the saturated hydrocarbon followed by elimination of H_2 and formation of a carbonium ion. Applications aroused immediate interest (Ref.22).

The direct observation of stable alkylcarbonium ions has challenged many research workers. Olah et al. (Ref.20) and researchers from the Shell Company (Ref.21) succeeded in this endeavour. Extensive investigations were reported by Brouwer and Hogeveen (Ref.23) on the system HF-SbF_5 and by Olah and Lukas (Ref.24).

Hogeveen and coworkers (Ref.25) have suggested a linear or triangular configuration for the protonated species involved in hydride abstraction but were unable to distinguish whether it was a transition state or longer lived intermediate,



The triangular configuration was strongly endorsed by Olah who considered it to be a distinct intermediate.

It was deduced unquestionably from these results that the formation of carbonium ions from hydrocarbons in strong acids was uniquely due to hydride abstraction by a proton.

But many experiments were at variance with these facts.

In the Laboratoire de Chimie Analytique, Bobilliart and coworkers (Ref.26) tried to oligomerize lower alkanes by electrochemical initiation. Since oligomerisation occurs via carbocation intermediates, as, e.g., in scheme No.I, it was expected that Olah's reactions could be obtained by preparing carbonium ions via electrochemical oxidation of the corresponding saturated hydrocarbons. The solvent chosen for the anodic electrolysis was pure fluorosulfuric acid ($H_0 = -15$). It was believed that such a solvent was relatively inert towards paraffins, compared with magic acid ($H_0 = -25$). It came to light that this premise was wrong.

During electrolysis of light alkanes, we found that a chemical reaction interfered with the desired electrochemical process. With *n*-butane and *n*-pentane we observed that isomerisation and polymerisation occurred even without electrolysis. A careful investigation revealed that the hydrocarbons were oxidized to carbonium ions (which explains isomerisation and polymerisation) with concomitant production of sulfur dioxide. We detected no trace of hydrogen.

The only way to rationalize our results was to assume that oxidation of paraffins to carbocations by SO_3 occurred. The SO_3 originated from the dissociation of fluorosulfuric acid.

At the same time, Larsen, Bouis, Watson and Pagni (Ref.27) found similar results with cyclo-heptatriene in pure fluorosulfuric acid. The oxidation of cyclo-heptatriene to tropylium ion by SO_3 led these workers to study carefully the reaction of isobutane in mixtures of HSO_3F and SbF_5 where isobutane is converted smoothly to the tert-butyl carbocation. Larsen et al. observed neither hydrogen nor sulfur dioxide. However, cyclo-heptatriene did yield SO_2 during the formation of tropylium ion. These results indicate clearly that carbocation formation was not proceeding via hydride abstraction by protons.

In actual fact, even in magic acid, hydrogen is not produced in amounts required by the stoichiometry: $R_1R_2R_3C-H + H^+ \rightleftharpoons R_1R_2R_3C^+ + H_2$

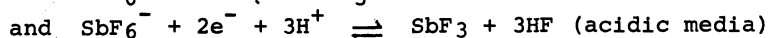
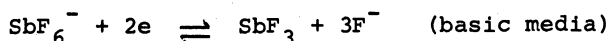
According to Olah (Ref.24) the stoichiometry deficiency was due to the fact that "nascent" hydrogen reduces the acid. However it has been shown earlier (Ref.25) that hydrogen does not reduce acid systems such as HSO_3F , HSO_3F-SbF_5 , $HF-SbF_5$.

In 1973 Lukas, Kramer and Kouwenhoven (Ref.21) pointed out that a number of results obtained with the two acid systems $HF-SbF_5$ (molar ratio $> 10/1$) and HSO_3F-SbF_5 (1/1) are not compatible with the protonation scheme; for example methane was found to oligomerize in HSO_3F-SbF_5 but not in $HF-SbF_5$, although the hydrogen-deuterium exchange takes place in both systems. These authors postulated that a fundamentally different mechanism may account for the reactions of saturated hydrocarbons in strong acids. They have shown (Ref.21) that hydride abstraction from alkanes can be effected by SbF_5 alone.

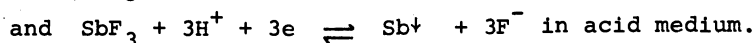
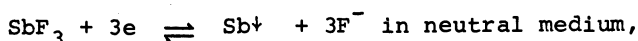
It is in this context that Thiébault (Ref.28) undertook, a year ago, an electrochemical study of the behaviour of antimony pentafluoride dissolved in pure hydrogen fluoride. Why hydrogen fluoride rather than fluorosulfuric acid? Because addition of SbF_5 to fluorosulfuric acid leads to complicated reactions which produce the species SbF_6^- , $Sb_2F_{11}^-$, $SbF_5 \cdot (SO_3F)^-$ and $(SbF_5) \cdot 2SO_3F^-$. The $HF-SbF_5$ system is simpler inasmuch as only two complex anions are formed viz., SbF_6^- and $Sb_2F_{11}^-$. For this reason we have used the $HF-SbF_5$ system for investigating the oxidising power of SbF_5 compared to the oxidising power of the proton in superacid media.

Although the +5 oxidation state of antimony is not electroactive at a platinum electrode in hydrogen fluoride solutions it is possible to evaluate the redox potential of the couple Sb(+III)/Sb(+V). From the results (see legend of figure 1) Sb(+V) is a stronger oxidant than the proton in highly acidic media. Thus SbF_5 can evidently function as an oxidising agent when carbonium ions are generated in superacid media.

The electrochemical oxidation of elementary antimony yields exclusively Sb(III+) and Sb(III+) does not disproportionate whatever the pH. Thus Sb(V) is a stronger oxidant than Sb(III), and the reduction of Sb(V) produces Sb(III). In the presence of HF, SbF_5 yields SbF_6^- and $\text{Sb}_2\text{F}_{11}^-$, when $[\text{SbF}_5] < 1\text{M}$. SbF_6^- ions are the predominant species, whose reduction proceeds via the reactions,



The electrochemical oxidation of elementary antimony to Sb(III) is possible. The electrochemical reduction of Sb(III) to Sb(O) is likewise possible via the reactions,



The geometry of the corresponding potential plot (Curve 2 of Fig.2) is described by the equation,

$$\begin{aligned} E(\text{V}) &= -0.95 + 0.054 \log(\text{F}^-) \\ &= -0.95 + 0.054 \text{pF}^-, \end{aligned}$$

while the oxidation potential of the proton (Curve 1 of Fig.2) is described by

$$E(\text{V}) = -0.75 + 0.054 \text{pF}^-$$

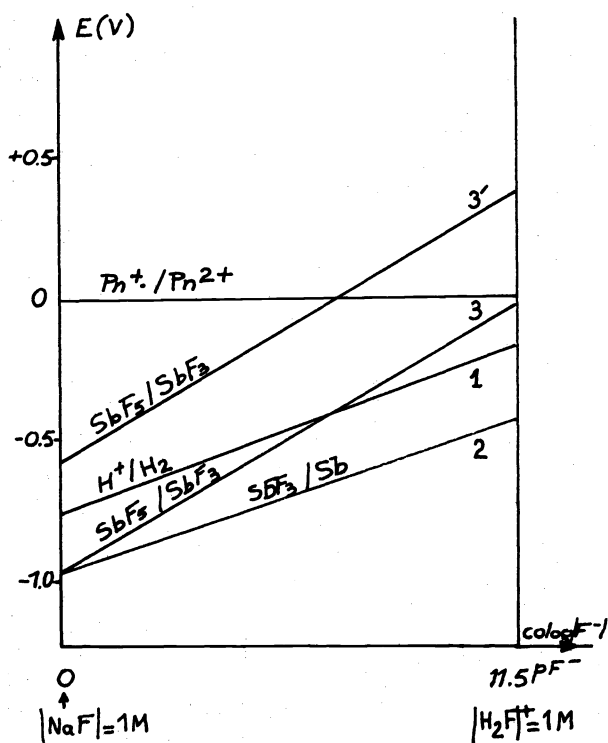


Fig. 2

The equation of the corresponding potential plot (lines (3) and (3') of Fig.2) is

$$E(V) = C + \frac{3}{2} \times 0.054 \text{ pF}^-$$

It follows that C is equal to or greater than -0.95 V; thus curve (3) represents the lower limit of the oxidising potential of Sb(V+).

Conclusion

In view of the situation outlined in this paper much work remains to be done to establish unequivocally the mechanisms by which carbonium ions are formed in superacid media. We can conclude, however that four processes exist by which carbonium ions can be generated from hydrocarbons in acid and superacid solutions :

- 1) hydride abstraction by a proton,
- 2) oxidation by SbF_5 ,
- 3) oxidation by SO_3 in the presence of HSO_3F
- 4) electrochemical oxidation of the hydrocarbon.

It is obvious that the first three processes can occur simultaneously. The first process is interesting from an industrial point of view if the second process does not play a role, because process 2 involves a loss in catalyst activity.

REFERENCES

1. A. Commeyras and G.A. Olah, J. Amer. Chem. Soc. **91**, 2929 (1969): see Ref. 2; the name "Magic acid (R)" has been used by research students in Olah's laboratory. Magic acid (R) is a registered trade mark of Cationics Inc. (Cleveland. Ohio - USA).
2. R.J. Gillespie, Acc. of Chem. Res. **1**, 202 (1968).
3. N.F. Hall and J.B. Conant, J. Amer. Chem. Soc. **49**, 3047 (1927).
4. R.C. Thompson, J. Barr, R.J. Gillespie, J.B. Milne and R.A. Rothenbury, Inorg. Chem. **4**, 1641 (1965).
5. P.A.W. Dean and R.J. Gillespie J. Amer. Chem. Soc. **92**, 2362 (1970).
6. L.P. Hammett and A.J. Deyrup, J. Amer. Chem. Soc. **54**, 2721 (1932).
7. R.J. Gillespie, T.E. Pell and E.A. Robinson J. Amer. Chem. Soc. **93**, 5085 (1971).
8. R.J. Gillespie and T.E. Peel J. Amer. Chem. Soc., **95**, 5173 (1973).
9. J. Sommer, P. Rimmelin and T. Drakenberg J. Amer. Chem. Soc. in the press.
10. E.S. Gore, D.J. Blears and S.S. Danyluck, Can. J. Chem. **43**, 2135 (1965).
11. D.M. Brouwer, Rec. Trav. Chim., **87**, 225 (1968).
12. D.M. Brouwer and J.A. Doorn, Rec. Trav. Chim. **89**, 553, 896 (1970).
13. A. Vaillant, J. Devynck and B. Tremillon, Anal. Lett. **6**, 1095 (1973).
14. A. Vaillant, J. Devynck and B. Tremillon, J. Electroanal. Chem. **57**, 219 (1974).
15. M. Herlem and A. Thiébault, J. Electroanal. Chem. in the press.
16. J.P. Masson, J. Devynck and B. Tremillon J. Electroanal. Chem. **64**, 193 (1975).
17. J. Grondin, R. Sagnes, and A. Commeyras to be published.
18. G.A. Olah and R.H. Schlosberg, J. Amer. Chem. Soc. **90**, 2726 (1968).
19. G.A. Olah, Y. Halpern, J. Shen and Y.K. Mo. J. Amer. Chem. Soc. **95**, 4960 (1973).
20. G.A. Olah, Angew. Chem. Internat. Ed. **12**, 173 (1973) see literature cited in Ref.24.
21. See Ref.1, J. Lukas, P.A. Kramer and A.P. Kouwenhoven Rec. Trav. Chim. **92**, 44 (1973).
22. J.M. Oelderik, E.L. Mackor, J.C. Platteeuw and A. van der Wiel, Brit. P. 981.311 Appl. June 62 (see also U.S.P., 201.494) see C.A. **61**, 515 g.
23. D.M. Brouwer and H. Hogeveen Progr. in Phys. Chem. **9**, 179 (1972).
24. G.A. Olah and J. Lukas, J. Amer. Chem. Soc. **89**, 2227 (1967); **89**, 4739 (1967); **90**, 933 (1968).
25. H. Hogeveen, C.J. Gaasbeek and A.F. Bickel, Rec. Trav. Chim. **88**, 703 (1969).
26. F. Bobilliart, A. Thiébault and M. Herlem C.R. Acad. Sc. Paris, Série C, **278**, 1485 (1974).
27. J.W. Larsen, P.A. Bouis, C.R. Watson and R.M. Pagni J. Amer. Chem. Soc. **96**, 2284 (1974).
28. A. Thiebault and M. Herlem, to be published.