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Reduction of Antimony Pentafluoride by Alkanes: Implications for Mechanisms in Superacid Chemistry

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Reductions of SbF_5 in HF proceed only very slowly in the presence of H_2 as the lone reducing agent, but the addition of certain alkanes causes a large increase in the rate of reduction. For example, a 1:10 mixture of SbF_5/HF gives only about 2% Sb(V) reduction by reaction with H_2 at 5.8 atm partial pressure after 4 h at 50 °C. About ten times as much reduction occurs when a mixture of hexane and cyclohexane (9:1) is added to the reaction. Other hydrocarbons gave the following reductions (wt %) in a 0.5-h reaction time: propane, 2.1; *n*-butane, 1.9; isobutane, 9.0; isobutane (no applied H_2), 9.0. These results are discussed in terms of either a direct hydride abstraction from alkane by SbF_5 or a series of single electron transfer steps.

The ionization of alkanes in superacids, such as SbF_5/HF and SbF_5/FSO_3H, has been formulated as occurring by the loss of hydrogen (H_2) from a protonated alkane.[1] Although the protonation mechanism is considered to be quite well-established, skeptics have continued to raise doubts about its exclusivity. Other processes, oxidations by SbF_5, SO_3, or FSO_3H and the like, have been suggested.[2-5] The results of the present work give support to the arguments of the skeptics and raise additional doubts about the exclusivity of the protonation mechanism for the ionization of alkanes.

$$HF + SbF_5 \rightleftharpoons H^+ SbF_6^-$$

$$R^1R^2CH_2 + H^+ \rightleftharpoons R^1R^2CH_3^+ \rightleftharpoons R^1R^2CH^+ + H_2$$

Perhaps the opening of the controversy can be dated with the suggestion of the direct hydride mechanism by Holmes and Pettit[2] in a study of cycloheptatriene. Other workers later extended the idea to explain reactions of lower alkanes in "neat" SbF_5.[3,4] In contrast, Olah has interpreted his oligocondensation of methane[6] and many other reactions of paraffins in superacids in terms of the protonation mechanism for ionization.[1] He argued that SbF_5 cannot be made sufficiently free of HF to preclude operation of the protonation mechanism; i.e., even if hydride abstraction were to occur in a very pure sample of SbF_5, the reaction would produce HF from collapse of the intermediate SbF_5H^- and cause a change to the protonation mechanism for further ionization.

$$CH_4 + SbF_5 \rightleftharpoons CH_3^+ + SbF_5H^-$$

$$SbF_5H^- \rightarrow SbF_3 + HF + F^-$$

$$\text{or } H^+ + SbF_5H^- \rightleftharpoons SbF_5 + H_2$$

Bobilliart, Thiébault, and Herlem[7] have found that FSO_3H alone is reduced by butane and by pentane with production of SO_2. Larsen, Pagni, and co-workers have shown that cycloheptatriene is oxidized by FSO_3H to produce tropylium ion and SO_2.[8] This result led them to examine the reaction of isobutane in SbF_5/FSO_3H mixtures. Neither hydrogen nor SO_2 were observed, but cycloheptatriene did cause production of SO_2 this system.

Herlem has presented an argument[5] that, in superacid solutions, SbF_5 is a stronger oxidizing agent than the hydrogen ion.

One might expect that an important test for the protonation mechanism would be the measurement of hydrogen produced by the second step in the ionization. In fact, the lower alkanes produce only traces of hydrogen in contact with superacids. This apparent stoichiometric deficiency in hydrogen production has been attributed by Olah[1] to uptake of "nascent" hydrogen by the acid, causing reduction of SbF_5 in an SbF_5/HF system.

There is an appearance of disagreement as to whether SbF_5 is reduced by H_2. Olah reported that "neat" SbF_5 can be reduced quantitatively by 50 atm of H_2 at room temperature in 24 h,[1] but other workers have reported that H_2 does not reduce systems such as HSO_3F, FSO_3H/SbF_5, and HF/SbF_5.[9] A possible reason for this difference is that SbF_5 is stabilized toward reduction by interaction with strongly coordinating solvents such as HF or FSO_3H, expecially in dilute solutions.

Key questions then are the following: is SbF_5 reduced in a superacid such as the SbF_5/HF system; and if so, is the reduction caused by direct reaction between an alkane and the SbF_5 or by a reaction of SbF_5 with H_2 produced from a protonated alkane? A demonstration of SbF_5 reduction by alkanes instead of H_2 would have important mechanistic implications for the ionization process itself.

How can one distinguish reductions caused by an alkane from reductions caused by H_2 produced from a protonated alkane? A helpful approach to separating these effects has developed from a fortuitous use of hydrogen in industrial isomerization processes. In a prospective industrial isomerization process one would normally use moderate hydrogen pressure (2–10 atm) over the acid mixture to prevent the buildup of acid-soluble oily byproducts that cause loss of acid strength and activity. Fortuitously the addition of this H_2 allows one to "swamp" the system with much more H_2 than would be produced by alkane ionization alone. This has proved to be helpful in separating the reductive effect of alkanes from that of H_2.

Results and Discussion

In the following experiments the superacid (1:10 mole ratio of SbF_5/HF) was allowed to contact 1.4 times its weight of a hydrocarbon feed. The feed, unless otherwise specified, is a mixture of 9:1 *n*-hexane/cyclohexane. The acid-feed mixture

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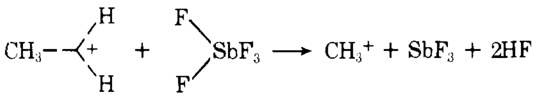
was stirred in an autoclave at 50 °C under 5.8 atm of H_2. In a simulation of a commercial isomerization process, the acid was used to isomerize more than one batch of the hydrocarbon mixture. At the end of a 0.5-h reaction period, the stirrer was shut off, the mixture was allowed to settle, and the hydrocarbon layer was drawn off through a sample tube located at the interface between the two liquids. The acid remaining in the autoclave was then reused with another batch of hydrocarbon. This process was repeated until a total of eight batches of the hydrocarbon mixture had been processed over the acid for 0.5 h per batch, a total reduction time of 4 h for the acid. The acid was then quenched with water and analyzed for Sb(III) by permanganate titration. A set of three such identical experiments gave SbF_5 reductions of 18.5, 19.4, and 17.1%. These results were then compared with a type of experiment in which the acid was merely stirred with the same hydrogen pressure as before for 4 h without exposure to any hydrocarbons at all. A set of three such experiments gave SbF_5 reductions of 2.3, 1.4, and 2.0%.

This accelerating effect of the alkane mixture upon SbF_5 reduction was seen in single-batch experiments as well. A 1-h run with the same kind of acid mixture used before with the same hydrocarbon mixture under the same conditions gave 8.05% reduction, but extending the reaction time to 4.4 h and increasing hydrogen pressure almost sevenfold to 40 atm gave only 7.3% SbF_5 reduction when the alkane mixture was omitted.

In the long multiple-batch runs a small amount of black, coke-like solid was produced.

Other experiments showed that the rate of SbF_5 reduction depends upon the type of hydrocarbon in the reaction. The following experiments were all done with the same kind of acid mixture under 5.8 atm of H_2 at 50 °C, but reaction times were all only 0.5-h total for a single batch of alkane on a single batch of fresh acid. The reaction time was deliberately kept short to minimize changes in the alkane composition during the reaction period. Two identical experiments with *n*-butane gave 1.5 and 1.9% reduction. Although these percentages seem low, note that reaction time is one-eighth that described above with the hexane/cyclohexane mixture. A single experiment with propane gave 2.1% reduction. Isobutane, presumably more reactive because of chain branching, gives values of 9.0 and 8.6% reduction in duplicate tests. Isobutane also gave 9.0% reduction when the experiment was repeated without applied hydrogen pressure. A similar test with isobutane under considerably greater (15 atm) hydrogen pressure brought the SbF_5 reduction to only 11.3%. It seems quite clear that the alkane is of greater importance in these reductions than the hydrogen pressure.

These results clearly show that H_2 is not the principal cause of the reductions observed. The proposal cited earlier, that SbF_5 reduction results from uptake of H_2 by the SbF_5, is clearly untenable. Although this conclusion does give support to the arguments of skeptics such as Herlem,[5] who have argued for a direct oxidation of alkanes by SbF_5, it does not allow one to completely exclude the possibility of reduction occurring by reaction of a protonated alkane intermediate with the SbF_5.



$$\mathrm{CH_3}{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\langle +}} + \overset{\mathrm{F}}{\underset{\mathrm{F}}{\rangle}}\mathrm{SbF_3} \longrightarrow \mathrm{CH_3^+ + SbF_3 + 2HF}$$

Although a great deal of literature has been published using the pentacoordinate carbon interpretation for reactions of lower alkanes, there is little reason to reject the direct hydride mechanism (or, as an alternative, a series of single-electron transfers) out of hand. The arguments for the protonated alkane intermediate have largely been arguments against the direct hydride transfer mechanism. Olah has indicated that antimony hydrides are "known to be most unstable compounds," because of the "extreme weakness of the Sb–H bond."[1] In fact, antimony hydrides appear not to be so unstable as to preclude their possible intermediacy. Stibine, SbH_3, though it is somewhat thermally unstable, can be obtained at room temperature. It can even be prepared by treating antimony trihalides with $LiAlH_4$,[10] a reaction that would almost certainly involve antimony halohydride intermediates. Since SbF_5 is a much more vigorous oxidizing agent than antimony trihalides, it seems highly likely that it would yield stibine with even greater vigor under the same conditions. Such a reaction would also have a high likelihood of involving antimony halohydride intermediates.

The ionization potentials of the lower alkanes are so large (about 10.55 eV)[11] that any mechanism involving single-electron transfers might seem totally unfeasible, but such gas phase measurements can be misleading when extrapolated to condensed phases. When there are large differences in solvation between reactant and products, a reaction will be more favored in solution than such gas phase data might indicate. Such effects of differential solvation are illustrated by the report of Briggs, Yamdagni, and Kebarle[12] that aniline is a stronger base by several orders of magnitude than methylamine in the gas phase, directly opposite to the situation in solution. A number of possible intermediate antimony fluoride ions, such as SbF_5^{2-} and SbF_4^-, are known to exist.[13] Finally, any concern about gas phase ionization potentials must be weighed against Herlem's calculation[5] showing that SbF_5 is a stronger oxidizing agent than H^+ in HF solution.

It seems important at this point to remain open to all of the mechanistic possibilities until more complete evidence is obtained.

Experimental Section

The hydrocarbons used were Phillips Pure Grade (min 99 mol %). The antimony pentafluoride, supplied by Ozark-Mahoning, was freshly distilled before use in an all-Teflon still supplied by Berghof/America. Hydrogen fluoride was supplied by Air Products.

General Procedures for Antimony Pentafluoride Reactions. Antimony pentafluoride (39.0 g, 0.18 mol) was weighed into a tared 150 mL stainless steel sample cylinder equipped with a valve on each end. Hydrogen fluoride (37 g, 1.85 mol) was then distilled into the sample cylinder by immersing the cylinder in ice water after connecting it to the HF supply cylinder. The acid mixture was then fed by argon pressure into a 300 mL Magnedrive autocalve made of Hastelloy C, supplied by Autoclave Engineers. The autoclave was stirred at 2500 rpm using the factory-supplied impeller plus an extra Teflon stirring blade about 5.5 cm up from the factory-supplied impeller. The acid mixture was heated to 50 °C. The temperature was controlled by an iron–constantan thermocouple connected to a West Gardsman controller that regulated steam flow through a solenoid valve. The steam was allowed to mix with tap water and flow through a heating coil on the outside of the autoclave. Careful balance of steam and water pressures and flow rates allowed the temperature to be held so nearly constant that "drift" was not detectable on a Leeds & Northrup 8693 potentiometer (est. ±0.1 °C). At reaction temperature the hydrocarbon feed (when used) was forced into the autoclave from a tared sample cylinder in the same manner as the acid mixture. The autoclave was then pressurized with the required amount of hydrogen. At the end of the reaction time the hydrogen pressure was released. The reaction mixture was cooled and then quenched by pressuring ca. 70 mL of water into the sealed system. The autoclave was then opened for removal and separation of the organic and aqueous phases. The organic phase (when present) was washed with 15% hydrochloric acid. The wash liquid was combined with the aqueous phase collected from the autoclave for volumetric measurement. An aliquot of this aqueous solution was analyzed for Sb(III) by titration with standardized potassium permanganate solution. Another aliquot was analyzed for total antimony by atomic absorption on a Perkin-Elmer 603 spectrometer.

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Registry No.—SbF_5, 7783-70-2; propane, 74-98-6; *n*-butane, 106-97-8; isobutane, 75-28-5; hexane, 110-54-3; cyclohexane, 110-82-7.

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Mechanism of the Oxidative Cyclization of *N′*-(*p*-Hydroxyphenyl)-2-(phenylamino)-5-methyl-*p*-benzoquinone Diimine in Aqueous Solution

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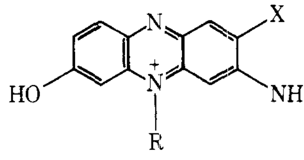
The title compound undergoes intramolecular cyclization in aqueous solution to give a quantitative yield of 2-amino-8-hydroxy-3-methyl-10-phenylphenazinium salt. In the absence of any other oxidant, the rate-controlling step between pH 8 and 12 is aerial oxidation of the intermediate 2-amino-8-hydroxy-3-methyl-10-phenyl-5,10-dihydrophenazine to the product, whereas outside this pH range the cyclization step is rate controlling.

In a recent publication,[1] we proposed a mechanism for formation of 2-amino-8-hydroxyphenazines (**1**) from *N′*-(*p*-hydroxyphenyl)-2-amino-*p*-benzoquinone diimines (**2**).



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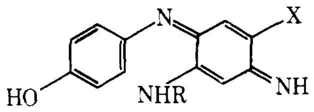

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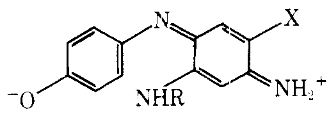

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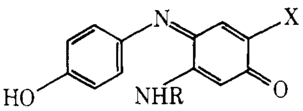

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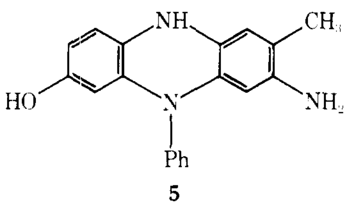

5

We were unable to study the 2-*N*-phenyl diimine (**2**, X = Me, R = Ph) above pH 8.5 due to the rapid reaction rate, but over the pH range 6–8 only data consistent with the proposed mechanism were obtained. We have now extended the study of this diimine to cover the full pH range and have found anomalous results at pH > 8 which lead us to a more detailed mechanism for the cyclization reaction.

Results and Discussion

Spectra and Products. At pH > 10, the title diimine rapidly converted to the phenazine. Therefore, spectral data of the diimine at high pH were difficult to obtain. At lower pH the diimine was considerably more stable and two ionic forms were observed: a red cation (λ 518 nm) and a blue zwitterion (λ 675 nm). By rapidly injecting diimine into buffers of different pH and then scanning a selected part of the visible spectrum, the pK_a was estimated as 8. Using this same technique, the diimine anion was shown to be red with a pK_a around 12 (estimated at 650 nm since phenazine formation is relatively slow up to pH 12 and its spectrum does not interfere at this wavelength). These data are consistent with those of previously reported analogues. The high reactivity of the diimine precludes further structural characterization.

Over the pH range 5–13, the diimine cyclized quantitatively to the phenazinium salt (**1**, R = Ph, X = Me). The phenazine spectrum has been described previously[2] and shows a zwitterion [λ 513 nm (log ε 4.48), pK_a 5.4] at high pH and a cation [λ 498 nm (log ε 4.25) and 436 (4.16)] at lower pH.

Kinetics of Cyclization. Unlike with analogous diimines, the spectrophotometric course of the cyclization reaction was not simple. Between pH 8 and 12, scans of the visible spectrum of a reacting solution showed no isosbestic point, and loss of the spectrum of the diimine was considerably faster than appearance of phenazine. Kinetic analysis showed that both imine loss and phenazine formation followed first-order kinetics but that derived rate constants could be as much as a factor of 50 apart depending on the solution pH. Below pH 7.5, the spectrophotometric scans showed a clean isosbestic point and the rate constant was independent of wavelength. As the pH was raised, the rate of loss of imine increased dramatically so that the half-life was only a few seconds at pH 12. However, the rate of phenazine formation changed little over this pH range, only beginning to increase noticeably above pH 12. First-order rate constants for loss of imine (k') and phenazine formation (k'') are given in Table I.

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