Electrophilic Reactions at Single Bonds. XI. Hydrogen–Deuterium Exchange of $H_2(D_2)$ in Superacids Involving Isomeric $(H,D)_3^+$ Ions[1]

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Abstract: Molecular hydrogen and deuterium were found to undergo exchange reactions in superacids at room temperature, as indicated by HD formation. The following seven systems were studied: (1) $H_2 + DF–SbF_5$; (2) $H_2 + D_2SO_4–SbF_5$; (3) $H_2 + FSO_3D–SbF_5$; (4) $D_2 + HF–SbF_5$; (5) $D_2 + H_2SO_4–SbF_5$; (6) $D_2 + FSO_3H–SbF_5$; (7) $H_2 + D_2 + HF–SbF_5$. The exchange reaction indicates the intermediacy of isomeric $(H,D)_3^+$ ions in superacid solutions.

The H_3^+ ion was first discovered by Thomson[2] in 1912 in his hydrogen-discharge studies. In fact, it is the first observed gaseous ion–molecule reaction product. The reaction sequence (1) was established in 1925

$$H_2^+ + H_2 \longrightarrow H_3^+ + H \qquad (1)$$

by Hogness and Lunn.[3] Since then very extensive mass spectrometric and other related studies of H_2, D_2, HD, and their mixtures have been carried out in an effort to study either thermodynamic or kinetic aspects of ion–molecule reactions of $(H, D)_3^+$ cations.[4–15]

The gaseous proton affinity of H_2[5] was first measured in 1941 by Russell, Fontana, and Simons,[6a] who studied the scattering of low velocity protons in hydrogen to calculate a proton affinity value of 80.7 kcal, which is comparable to more recent values obtained through photoionization studies[6b] and ion cyclotron resonance studies.[7] Latter icr studies[7] and tandem mass spectrometric studies[8] have also dealt with proton affinity of D_2 and have taken into account the possible excited states of the D_3^+ ion. The rate constant of reaction 1 has been calculated[9] and determined experimentally.[6b,10] Detailed kinetic analysis of reactions 1–3 as well as their rate constants have been

$$D_2^+ + D_2 \longrightarrow D_3^+ + D \qquad (2)$$

$$HD^+ + HD \longrightarrow H_2D^+ + D \qquad (3a)$$

$$HD^+ + HD \longrightarrow HD_2^+ + H \qquad (3b)$$

studied recently by icr spectrometry.[10a] The possible reactions that isomeric $(H, D)_3^+$ ions may undergo in the gas phase in encountering neutral molecules other than hydrogen, such as N_2,[10d,f,11] noble gases,[6,7 10d,f,11c,12] hydrocarbons,[13] alcohols,[14] and benzene and its simple derivatives[15] have been studied extensively by mass spectrometry, radiolysis, and icr spectrometry.

Despite the numerous investigations in the gas phase, no solution chemistry of these ions was to our knowledge so far observed.

Gillespie and Pez reported[16] that according to their solubility, cryoscopic, and nmr spectroscopic measurements, $FSO_3H–SbF_5–SO_2$ ("magic acid[17]") is not a sufficiently strong proton donor to protonate a series of weak bases, including molecular hydrogen. Their investigations, however, related only to observe H_3^+ as a stable, detectable intermediate in what would be macroscopic concentrations. They certainly do not rule out protonation of hydrogen (deuterium) to H_3^+ $(D_3)^+$ as a metastable species (transition state) or its presence in low concentration, not detectable with the methods used.[16]

Recently superacids have been shown to be able to protonate all saturated hydrocarbons, including methane.[17] The methonium ion (CH_5^+) is commonly

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observed in the gas phase. Taking 229 ± 3 kcal/mol as the gaseous heat of formation of CH_5^+,[18] the proton affinity of methane could be estimated as 111 ± 3 kcal/mol. The experimental value of the intrinsic proton affinity of H_2 is not presently available. The limits, however, could be placed as 80 ± 4 kcal/mol $\leqslant PA(H_2)^\dagger \leqslant 88$ kcal/mol when referenced to $(H_3^+)^\dagger$ which has at least 10–20 kcal/mol of vibrational excited energy.[7] Since the heat of formation of the ground state H_3^+ ion is lower than that of the vibrationally excited $(H_3^+)^\dagger$ ion, the intrinsic proton affinity of H_2 could be expected to be 10–20 kcal/mol more than $PA(H_2)^\dagger$. Schwartz and Schaad[19] have calculated a lower limit on the proton affinity of ground-state H_2, $PA(H_2) \geqslant 96$ kcal/mol, assuming the equilateral triangle configuration. This value is in reasonable agreement with the above mentioned estimation. Therefore the difference between $PA(CH_4)$ and $PA(H_2)$ would be expected to be less than 0.5 eV. Since methane recently was found able to be protonated in superacid systems,[17] it seemed reasonable to expect that molecular hydrogen could also be protonated under similar conditions.

Hogeveen[20] has found no evidence for hydrogen–deuterium exchange when molecular D_2 was treated with HF–SbF_5 in excess HF solution, an acid system obviously weaker than the 1:1 (mol/mol) superacids used in our studies.

In our studies we were able to observe the hydrogen–deuterium exchange of molecular H_2 and D_2, respectively, in 1:1 superacids at room temperature as evidenced by observation of HD formation. Data clearly indicate that protonation and deuteronation of hydrogen and deuterium must take place in solution. Consequently, these studies indirectly substantiate H_2D^+ and HD_2^+, as well as H_3^+ and D_3^+ formation, in the high acidity solution chemistry of hydrogen and deuterium, at least as transition states in the kinetic exchange process.

Experimental Section

A. Materials. Antimony pentafluoride was obtained from the Allied Chemical Co. and was twice distilled before use. D_2 and HD were obtained from Matheson and Merck, Sharp and Dohme, Ltd., respectively, and were analyzed for purity (>99%) before use by mass spectrometry. Fluorosulfuric acid-*d* and deuterium fluoride were prepared by exchange with sulfuric acid-d_2 and from reacting CaF_2 with D_2SO_4, respectively.

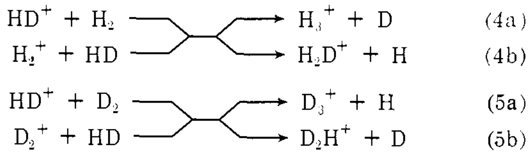
B. Hydrogen–Deuterium Exchange with Superacids. In a typical experiment, 10 g of 1:1 (mol/mol) deuteron or proton acid–SbF_5 was placed in a 75-ml Teflon-lined Monel autoclave. The autoclave was then evacuated to a pressure of ∽40 Torr. About 14 atm of hydrogen (or deuterium) was introduced, and the reaction vessel was sealed and shaken at 25° for an average of 18 hr. Gas samples taken were analyzed by mass spectroscopy.

C. Reaction of a Mixture of H_2 and D_2 with Superacids. An equimolar mixture of H_2 and D_2 was allowed to react in HF–SbF_5 solution. At 25° and 14 atm combined H_2 and D_2 pressure, gas samples were taken at each of the 14-hr, 34-hr, and 98-hr runs, and were analyzed for HD formation.

D. Analysis of Gas Mixtures. (1) Mass Spectrometric Analysis. Conventional mass spectrometric analyses of gas samples were carried out on a Consolidated Engineering Corp. Model 21-620 mass spectrometer. Sensitivities of H_2, HD, and D_2 were calibrated by using pure reagent gases.

(2) Ion Cyclotron Resonance Spectrometric Analysis. A Varian Associates icr spectrometer equipped with a flat cell was also used to perform gas sample analysis. Ion cyclotron single resonance spectra were recorded at either high pressure (10^{-5} Torr) or low pressure ($\leqslant 10^{-7}$ Torr). Since the reaction vessel has been evacuated before the reaction started, and since the gas samples were taken at liquid nitrogen temperature after each run, practically all gas samples contained only isomeric hydrogens.

Analysis at high sample pressure is made possible by comparing the icsr spectra of gas samples with those of pure H_2 or pure D_2. The ion–molecule reactions that may occur in pure H_2 or D_2 can only lead to the formation of H_3^+ (*m/e* 3) ion or D_3^+ (*m/e* 6) ion through reaction 1 or 2. The ion–molecule reactions in pure HD and in either HD–H_2 or HD–D_2 system, however, will always lead to the formation of HD_2^+ (*m/e* 5) ion and H_2D^+ (*m/e* 4) ion through reaction 3–5, in addition to the formation of H_3^+ and D_3^+ ions.



For reaction systems where H_2 only is used as gaseous reactant, any amount of ions of *m/e* 4 or 5 present in the high pressure icsr spectra would indicate the presence of HD molecules in the gas sample. Since generally it is improbable that D_2 exists as impurity in H_2 reagent gas, and since reaction sequence 4 is still observable in the icr spectrometer even when partial pressure of HD is lower than 10^{-7} Torr, the above described analysis could be more sensitive (although less quantitative) than the conventional mass spectrometric analysis.

When D_2 is employed as reactant gas, the mass peaks of D_2^+ and H_2D^+ overlap. Furthermore, since there is always H_2 residue in the sample inlet system, the reactions between H_2 and D_2 could also give rise to H_2D^+ as well as HD_2^+. Therefore, for reaction systems where D_2 is the gaseous reactant, only a substantial amount of increase of peak intensity at *m/e* 5 in the icsr spectra of the gas sample could be taken as the indication for the formation of HD. In the reaction systems studied, the amount of HD formed is always sufficient to indicate its own presence by giving rise to substantial increase of the *m/e* 5 peak indicative of HD_2^+.

Icr analysis at low pressure ($<10^{-7}$ Torr), where ion–molecule reactions are minimized, is in principle the same as mass spectroscopic analysis.

The analytical method used has also been calibrated by use of known mixtures of H_2, D_2, and HD.

Results

Six systems were investigated in our study of hydrogen–deuterium exchange monitoring the reactions by the use of mass spectroscopy: (1) H_2 + FSO_3D–SbF_5; (2) H_2 + D_2SO_4–SbF_5; (3) H_2 + DF–SbF_5; (4) D_2 + FSO_3H–SbF_5; (5) D_2 + H_2SO_4–SbF_5; (6) D_2 + HF–SbF_5.

A. H_2 + FSO_3D–SbF_5 and D_2 + FSO_3H–SbF_5. About 14 atm of H_2 (D_2) was introduced into an evacuated 75-ml Teflon-lined Monel autoclave which contained 10 g of 1:1 (mol/mol) FSO_3D–SbF_5 (FSO_3H–SbF_5). After the autoclave was shaken at 25° for 18 hr, gas samples analyzed by mass spectroscopy showed an average (three runs) of 3% HD for both H_2 + FSO_3D–SbF_5 and D_2 + FSO_3H–SbF_5.

B. H_2 + D_2SO_4–SbF_5 and D_2 + H_2SO_4–SbF_5. Parallel experiments with those described in section A gave gas samples that contained less than 1% of HD, as were analyzed by mass spectroscopy. To run the reactions at higher temperatures (>50°) is not generally favorable because the reduction of SbF_5 to SbF_3 and HF (DF) is then much accelerated. The amount of hydrogen–deuterium exchange was still less than 1% after 72 hr.

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High pressure ion cyclotron single resonance spectra of gas samples from the $H_2 + D_2SO_4$–SbF_5 system gave strong peaks at *m/e* 4 and 5, which were not observed for gas samples taken from the same reaction system at the start of the reaction. Experimental data thus clearly show that HD indeed has been formed in the exchange rection of $H_2 + D_2SO_4$–SbF_5.

C. H_2 + DF–SbF_5 and D_2 + HF–SbF_5. Similar parallel experiments for H_2 + DF–SbF_5 and D_2 + HF–SbF_5 showed substantial amount of HD formation as compared with reaction systems A and B. The degree of hydrogen–deuterium exchange is 23% after 18 hr, and increased to 40% after 72 hr. From the extent of the exchange reaction, the relative acid strength of the used systems is HF–SbF_5 > FSO_3H–SbF_5 > H_2SO_4–SbF_5.

D. H_2 + D_2 + HF–SbF_5. HD formation in this system is the fastest of all the systems studied. At 25° after 14 hr 29% HD is formed.

Discussion

All the six systems studied gave evidence for exchange of molecular hydrogen and deuterium in superacids at room temperature. The exchange reaction takes place most readily in HF–SbF_5 or DF–SbF_5.

The radiation-induced atomic exchange in hydrogen gas has been studied previously and was interpreted in terms of a simple hydrogen atom chain reaction.[21] It has been proven later[22,23] that, although hydrogen atom chain reaction is well established in the photochemical and thermal systems, in the case of radiation-induced processes exchange occurs almost entirely by an ionic chain mechanism. For example, when xenon was added to a H_2–D_2 mixture irradiated by X-rays, it suppressed almost entirely the exchange processes by readily accepting a proton from H_2^+. Even a large amount of Ar, whose proton affinity is smaller than H_2, had nearly no effect.[23] The ionic mechanism has also been proven by high pressure mass spectrometric studies, glow discharge studies,[24] and studies with tritium β-rays.[25] However, our observation that H_2 or D_2 readily undergoes exchange with superacids at room temperature is the first time that similar ionic mechanism is found to operate in solution involving isomeric $(H, D)_3^+$ ions, as is illustrated in eq 6–9

$$\text{initiation}\quad H^+A^- + D_2 \longrightarrow HD_2^+ + A^- \qquad (6)$$

$$\text{propagation}\quad HD_2^+ + D_2 \longrightarrow \begin{cases} HD + D_3^+ & (7) \\ D_2 + HD_2^+ & (8) \end{cases}$$

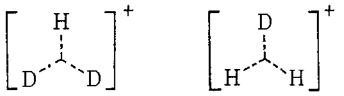
$$\text{termination}\quad HD_2^+,\ D_3^+ \longrightarrow \text{neutralized by } A^- \qquad (9)$$

where A^- represents the anions present in the superacid solutions. When H_2 and D_2 both are present in the system, available propagation channels will be increased through the exchange cycle (10). As a consequence, H–D mixture underwent hydrogen–deuterium exchange with superacids in a much accelerated way, as was evidenced by the increasing amount of HD formed in the $H_2 + D_2$ + HF–SbF_5 system.

$$\begin{tikzcd}
D_3^+ \arrow[d, shift right, "H_2"'] & D_2H^+ \arrow[l, "D_2"'] \arrow[dl, shift right, "H_2"'] \arrow[d, shift right, "H_2"'] \\
H_2D^+ \arrow[u, shift right, "D_2"'] \arrow[ur, shift right, "D_2"'] \arrow[r, "H_2"'] & H_3^+ \arrow[u, shift right, "D_2"']
\end{tikzcd} \qquad (10)$$

More quantitative kinetic studies are difficult due to unavoidable reduction of SbF_5 by H_2 or D_2, which is slow at 25°. However, there seems to be no way to explain the room temperature $H_2 + D^+ \rightleftharpoons HD + H^+$ (or $D_2 + H^+$) exchange without the suggested protonation (or deuteration) mechanism.

Both Conroy's[26a] and Schwartz and Schaad's[19] calculations have shown that the most stable configuration for H_3^+ is trigonal with the charge equally shared over the whole surface of the system. Christoffersen and Shull's[26b] study relating to the nature of the chemical bonding in H_3^+ indicated that the electronic charge at the center of the molecule is greater than that at the midpoint of a line between nuclei. This is evidenced by their calculated electron-density contours for the ground-state H_3^+ ion. Therefore, one appropriate description of the bonding arrangement in H_3^+ would be a set of three "bonds" pointing from the nuclei to the center of the molecule, rather than by bonds along the lines between the nuclei. It is thus reasonable to suggest similar three-center bound structures for the closely related D_2H^+ and DH_2^+ ions which can lead to facile isotopic exchange in acidic solution.



(Of course experimental observation of H–D exchange *per se* cannot prove the trigonal nature of the transition state, as contrasted with a linear one.)

Recently the H_5^+ ion has been observed by mass spectrometry.[27] It appears that H_3^+ with the three-center bound configuration acts as a clustering center for H_2 molecules. A recent *ab initio* quantum mechanical calculation[28] has supported this model of H_5^+, and employed this model to calculate the binding energy of the H_5^+ molecule–ion. The result is in good agreement with the experimental value.[29]

Sixty years after H_3^+ had been observed in the gas phase, for the first time its role in ionic solution chemistry is emerging in superacid systems. We feel that our results further extend the parallelism which is becoming evident between chemistry in superacids and gaseous ion–molecule chemistry. The similarities between the structures of CH_5^+ and H_3^+ are noteworthy. CH_5^+ indeed can be considered as methylated H_2 and was discussed in our preceding work. Two electron three-center bonded carbonium ion forma-

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tion is general in carbocation chemistry. Similar structures are also found in boron hydride chemistry. For example, the structure of BH_5 is similar to that of CH_5^+.[30] The orbital description of the $B_5H_{10}^+$ ion also involves a framework of $B_5H_9^+$ and H^+ is added at B_1 to form a three-center bond constructed from two s orbitals on H atoms and a p orbital extented along the symmetry axis.[31]

The formation of H_3^+ ion in solution chemistry may have implications concerning the effect of hydrogen in catalytic reactions, isomerization and alkylation. For example, the ability of aluminum chloride to activate molecular hydrogen was observed previously.[32] Our work may clarify the nature of this activation as aluminum chloride always contains enough moisture to act as a strong Brønsted acid ($H^+AlCl_3OH^-$ or the like). Hydroisomerizations observed on noble metal hydrogenation catalysts may also involve formation of H_3^+. The well-recognized effect of hydrogen pressure to decrease protolytic cracking processes can be considered as quenching of carbenium ion centers by H_2, *i.e.*, alkylation of the H–H bond resulting in alkane formation.

Acknowledgment. Support of our work by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged.

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Electrophilic Reactions at Single Bonds. XII.[1a] Hydrogen–Deuterium Exchange, Protolysis (Deuterolysis), and Oligocondensation of Alkanes with Superacids[1b]

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Abstract: Twenty-one alkanes, including methane, ethane, propane, butane, 2-methylpropane, 2-methylbutane, and 2,2-dimethylpropane, were studied in FSO_3H–SbF_5 and HF–SbF_5 (SO_2ClF) as well as in the corresponding deuterated superacid systems. Hydrogen–deuterium exchange and protolysis, followed frequently by oligocondensation, were observed, indicating the general reactivity of C–H and C–C single bonds toward superacid systems. All data indicate frontside electrophilic attack on the involved bonds involving pentacoordinated carbonium ions.

Two types of electron donor ability have been recognized: π- as well as n-donor (unshared electron pair donor) ability.[2] The reactivity of olefins, acetylenes, and aromatic hydrocarbons toward electrophiles lies in the π-electron-donor abilities of the unsaturated C═C and C≡C bonds and π-aromatic systems. Compounds with unshared pairs of electrons on heteroatoms, as well as carbanions or singlet carbenes, represent the major types of n-donor substrates most frequently encountered. Both types are characterized in that an electron-releasing substituent group will facilitate the electron-donor ability while an electron-withdrawing group will decrease it.

The acid-catalyzed transformation reactions of saturated hydrocarbons (fragmentation, alkylation, isomerization) are generally considered to be carbocation reactions involving trivalent carbenium ions. Whitmore[3] and subsequently Bartlett, Condon, and Schneider[4a] as well as Schmerling[4b] in landmark publications developed the mechanistic concepts of acid-catalyzed alkane alkylations, isomerizations, and fragmentations. The major steps in the mechanism are the intermolecular transfer of hydride ion from a tertiary position in an isoparaffin to a carbenium ion and the ease of shift of a hydrogen atom or alkyl group from one carbon atom to another.

Contrary to frequent textbook references to electrophilic aliphatic substitution of saturated compounds, authenticated examples are limited to reactions involving organometallic compounds, such as organomercurials.[5] Protolytic reactions, such as hydrogen exchange,[6] migration of double bonds,[7] and keto–enol tautomerization,[8] involve either π- or n-donor inter-

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