Chemistry in Super Acids. IV.[1] Exchange of Hydrogen and Deuterium in HF (DF)–SbF_5, FSO_3H (FSO_3D)–SbF_5, and H_2SO_4 (D_2SO_4)–SbF_5 Solutions

Sir:

The gas-phase ion–molecule chemistry of H_3^+ and the related D_3^+, H_2D^+, and HD_2^+ ions has been well investigated starting with the hydrogen-discharge studies of Thomson.[2] In particular, detailed mass spectroscopic studies of hydrogen, deuterium, and their mixtures have been carried out.[3,4] No solution chemistry of these ions, however, was to our knowledge so far observed.

Gillespie and Pez[5] recently reported that according to their solubility, cryoscopic, and nmr spectroscopic measurements FSO_3H–SbF_5–SO_3 is not a sufficiently strong proton donor to protonate a series of weak bases, including hydrogen. Whereas their observations seem to disprove H_3^+ as a stable, detectable intermediate in what would be macroscopic concentrations, they certainly do not rule out protonation of hydrogen to H_3^+ as a metastable species (transition state) or its presence in low concentrations, not detectable with the methods used.[5]

We wish to report our data on the hydrogen–deuterium exchange of molecular hydrogen and deuterium in super acid systems at room temperature as evidenced by observation of HD formation. Data clearly indicate that protonation (deuteronation) of hydrogen and deuterium must take place in solution. Consequently, we believe that 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 processes.

Six systems were investigated in our study monitoring hydrogen–deuterium exchange 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; and (6) D_2 + HF–SbF_5. Ten grams 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 in individual runs evacuated to a pressure of <40 μ. About 14 atm of hydrogen (or deuterium) was introduced, and the reaction vessel was sealed and shaken at room temperature for the average of 18 hr. Gas samples taken were analyzed by mass spectroscopy (Consolidated Engineering Company Model 21-620 mass spectrometer was used for the analysis). Analysis of the gas mixtures was also carried out at 10^{-6} Torr on a Varian Associates icr spectrometer, under conditions to minimize ion–molecule reactions of hydrogen (deuterium). The analytical method used was calibrated by use of known mixtures of H_2, D_2, and HD.[6]

All systems gave evidence for the exchange reactions shown by the formation of HD.

$$H_2 + D^+ \rightleftharpoons [H_2D^+] \rightleftharpoons HD + H^+$$
$$D_2 + H^+ \rightleftharpoons [D_2H^+] \rightleftharpoons DH + D^+$$

The hydrogen–deuterium exchange, observed as HD, under reaction conditions kept identical (14 atm, 25°, 18 hr), amounted to an average (of three parallel experiments) of 23% in the HF–SbF_5 (DF–SbF_5) system, 3% in the FSO_3H–SbF_5(FSO_3D–SbF_5) system, and less than 1% in H_2SO_4–SbF_5 (D_2SO_4–SbF_5). Exchange was increased to 40% in HF–SbF_5 (DF–SbF_5) after running the reaction at room temperature for 72 hr.

When an equimolar mixture of H_2 and D_2 was allowed to react in HF–SbF_5 solution, HD formation by exchange of D_2 took place much faster. At 25° at 14 atm combined H_2 and D_2 pressure exchange of D_2 to HD was 29% after 14 hr, 57% after 34 hr, and 72% after 98 hr. Data indicate that H_3^+ was formed *via* protonation of H_2 and acted as a transfer protonating agent to D_2, in what is well known as an ionic chain reaction of radiation-induced hydrogen–deuterium exchange.[7] From the extent of exchange

$$H_3^+ + D_2 \rightleftharpoons H_2 + D_2H^+ \rightleftharpoons HD + D^+, \text{etc.}$$

reaction, the acid strength of the used systems is in the order HF–SbF_5 > FSO_3H–SbF_5 > H_2SO_4–SbF_5.

Reactions can generally not be run at higher temperatures as reduction of SbF_5 to SbF_3 and HF (DF) is then much accelerated. Whereas hydrogen–deuterium exchange of the solvent acid system and loss of hydrogen and deuterium due to reduction of SbF_5 is thus unavoidable, there seems to be no way to explain the room temperature $H_2 + D^+ \rightarrow HD \leftarrow H^+ + D_2$ exchange without the suggested protonation (deuteronation) mechanism.

Conroy's calculations[8] showed that the most stable configuration for H_3^+ is trigonal with the charge equally shared over the whole surface of the system. It is thus reasonable to suggest trigonal tricenter bond structures for the closely related D_2H^+ and DH_2^+ ions which would lead to facile isotopic exchange.

We feel that these results further extend the parallelism which is becoming obvious between chemistry in super acids and gaseous molecule–ion reactions. The similarities between CH_5^+ and H_3^+ are also noteworthy. Evidence presented for formation of H_3^+ in solution chemistry may have implications concerning the effect of hydrogen in catalytic reactions, like isomerization and alkylation. In this regard it is noteworthy that the ability of aluminum chloride to activate molecular hydrogen was observed previously.[9] 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). Hydro isomerizations observed on noble metal hydrogenation catalysts may also involve H_3^+ formation.

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(3) O. Luhr, *J. Chem. Phys.*, **3**, 146 (1935), and numerous subsequent studies.[4]

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Acknowledgment. The Petroleum Research Fund administered by the American Chemical Society and Esso Research and Engineering Company are thanked for partial support given for this work and Dr. Frank Fields for stimulating discussions.

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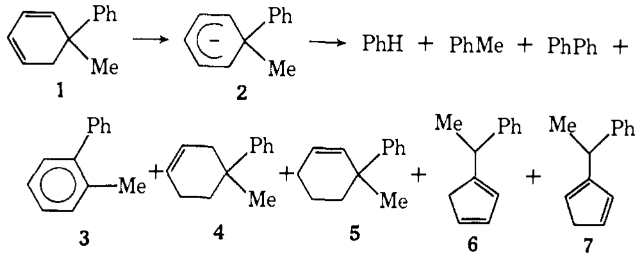
Reactions of the 6-Methyl-6-phenylcyclohexadienyl Anion. Role of the Counterion

Sir:

The elucidation of the factors[1] (*e.g.*, charge distribution,[2] ion pairing[3]) which determine the reactivity of carbanions has received an increasing amount of attention. We wish to report results which demonstrate that the title anion can undergo a variety of competitive inter- and intramolecular reactions at ambient temperature and that these reactions are greatly influenced by the counterion.

When 5-methyl-5-phenyl-1,3-cyclohexadiene[4] (**1**) is added to an approximately threefold excess of potassium amide in liquid ammonia at *ca.* −33° a deep-red solution is produced, the nmr spectrum[5] of which corresponds to what is expected for the 6-methyl-6-phenylcyclohexadienyl anion (**2**): multiplet at τ 2.3–3.2 (5 H, phenyl), apparent doublet of doublets (XX′ portion of an AA′BXX′ system) at 4.08 (2 H, C_2 and C_4 vinyl, J_{12} = 8 Hz, J_{23} = 6 Hz), complex multiplet at 6.16–6.54 (3 H, C_1, C_3, and C_5 vinyl), and singlet at 8.75 (methyl), partially obscured by the solvent absorption. Although there are no other peaks if the spectrum is obtained immediately after formation of the anion, additional signals can be observed after several hours.

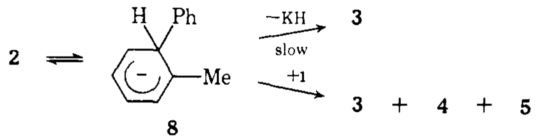
When the potassium salt of **1** is allowed to stand at 25° for 49 hr with a *ca.* tenfold excess of potassium amide a complex mixture of at least eight compounds is obtained in 75–90% yield.[6] Each component which was >1–2% of the mixture was isolated by glpc and identified by comparison of its infrared or nmr spectrum with that of an authentic sample.[7] Cyclopentadienes **6** and **7** were identified as an equilibrium mixture since they are readily interconverted (thermally)[8] under the glpc conditions used for isolation.



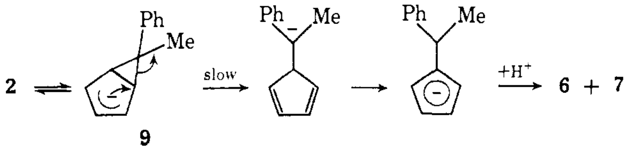
The formation of benzene and toluene and of biphenyl can be explained by loss of phenylpotassium and of methylpotassium,[9] respectively. *o*-Methylbiphenyl (**3**) can arise by intramolecular[10] migration of a substituent at C_6 (probably phenyl[1,11,12]) in **2**, followed by loss of potassium hydride.

Cyclohexenes **4** and **5** are very minor products but, along with **3**, are much more prominent when **1** (rather than potassium amide) is in excess. This is consistent with a relatively rapid (and reversible[13]) 1,2-phenyl migration followed by intermolecular hydride transfer to **1** (Scheme I).[14] The formation of cyclopentadienes **6** and **7** is particularly noteworthy and can be explained by an initial disrotatory electrocyclic ring closure,[15] followed by a rate-limiting cleavage of a perimetrical cyclopropyl bond.[16]

Scheme I



Scheme II



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(4) Prepared from 4-methyl-4-phenyl-2-cyclohexenone ((a) R. L. N. Harris, F. Komitsky, Jr., and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 4765 (1967); (b) F. G. Bordwell, R. R. Frame, R. G. Scamehorn, J. G. Strong, and S. Meyerson, *ibid.*, **89**, 6704 (1967)) by lithium aluminum hydride reduction followed by *p*-toluenesulfonic acid catalyzed dehydration.

(5) Trimethylamine, taken as τ 7.87, was used as an internal standard.

(6) Undecane and tridecane were present as internal standards.

(7) (a) *o*-Methylbiphenyl (**3**): I. R. Sherwood, W. F. Short, and R. Stansfield, *J. Chem. Soc.*, 1832 (1932); (b) cyclopentadienes **6** and **7**: K. Hafner, *Justus Liebigs Ann. Chem.*, **606**, 79 (1957); (c) cyclohexenes **4** and **5** were prepared from 4-methyl-4-phenylcyclohexanone[4b] by reduction, acetylation, pyrolysis, and base-promoted isomerization (*cf.* S. W. Staley, *J. Amer. Chem. Soc.*, **89**, 1532 (1967)).

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(10) The product mixture did not change significantly under conditions of 40-fold dilution nor was any *m*- or *p*-methylbiphenyl detected.

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(13) The reversibility of this migration derives from the expected greater stability of **2** relative to **8**.

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