

Chemistry in Super Acids. IV.¹ Exchange of Hydrogen and Deuterium in HF (DF)-SbF₅, FSO₃H (FSO₃D)-SbF₅, and H₂SO₄ (D₂SO₄)-SbF₅ Solutions

Sir:

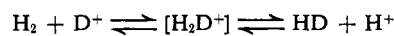
The gas-phase ion-molecule chemistry of H₃⁺ and the related D₃⁺, H₂D⁺, and HD₂⁺ ions has been well investigated starting with the hydrogen-discharge studies of Thomson.² In particular, detailed mass spectroscopic studies of hydrogen, deuterium, and their mixtures have been carried out.^{3,4} No solution chemistry of these ions, however, was to our knowledge so far observed.

Gillespie and Pez⁵ recently reported that according to their solubility, cryoscopic, and nmr spectroscopic measurements FSO₃H-SbF₅-SO₃ is not a sufficiently strong proton donor to protonate a series of weak bases, including hydrogen. Whereas their observations seem to disprove H₃⁺ as a stable, detectable intermediate in what would be macroscopic concentrations, they certainly do not rule out protonation of hydrogen to H₃⁺ 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 H₂D⁺ and HD₂⁺, as well as H₃⁺ and D₃⁺ 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) H₂ + FSO₃D-SbF₅; (2) H₂ + D₂SO₄-SbF₅; (3) H₂ + DF-SbF₅; (4) D₂ + FSO₃H-SbF₅; (5) D₂ + H₂SO₄-SbF₅; and (6) D₂ + HF-SbF₅. Ten grams of 1:1 (mol/mol) deuterium or proton acid-SbF₅ 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 H₂, D₂, and HD.⁶

All systems gave evidence for the exchange reactions shown by the formation of HD. The hydrogen-deu-



terium 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-SbF₅ (DF-SbF₅) system, 3% in the FSO₃H-SbF₅ (FSO₃D-SbF₅) system, and less than 1% in H₂SO₄-SbF₅ (D₂SO₄-SbF₅). Exchange was increased to 40% in HF-SbF₅ (DF-SbF₅) after running the reaction at room temperature for 72 hr.

When an equimolar mixture of H₂ and D₂ was allowed to react in HF-SbF₅ solution, HD formation by exchange of D₂ took place much faster. At 25° at 14 atm combined H₂ and D₂ pressure exchange of D₂ to HD was 29% after 14 hr, 57% after 34 hr, and 72% after 98 hr. Data indicate that H₃⁺ was formed *via* protonation of H₂ and acted as a transfer protonating agent to D₂, in what is well known as an ionic chain reaction of radiation-induced hydrogen-deuterium exchange.⁷ From the extent of exchange



reaction, the acid strength of the used systems is in the order HF-SbF₅ > FSO₃H-SbF₅ > H₂SO₄-SbF₅.

Reactions can generally not be run at higher temperatures as reduction of SbF₅ to SbF₃ 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 SbF₅ is thus unavoidable, there seems to be no way to explain the room temperature H₂ + D⁺ → HD ← H⁺ + D₂ exchange without the suggested protonation (deuteronation) mechanism.

Conroy's calculations⁸ showed that the most stable configuration for H₃⁺ 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 D₂H⁺ and DH₂⁺ 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 CH₅⁺ and H₃⁺ are also noteworthy. Evidence presented for formation of H₃⁺ 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⁺AlCl₃OH⁻ or the like). Hydro isomerizations observed on noble metal hydrogenation catalysts may also involve H₃⁺ formation.

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(2) J. J. Thomson, *Phil. Mag.*, **21**, 225 (1911); **24**, 209 (1912).

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

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(5) R. J. Gillespie and G. P. Pez, *Inorg. Chem.*, **8**, 1233 (1969).

(6) Obtained from Matheson and Merck Sharp and Dohme, Ltd., of Canada, respectively.

(7) S. O. Thomson and O. A. Shaeffer, *J. Amer. Chem. Soc.*, **80**, 553 (1958); *Radiat. Res.*, **10**, 671 (1959); see also P. H. Dawson and A. W. Teckner, *J. Chem. Phys.*, **37**, 672 (1962); V. Aquilanti, A. Galli, A. Giardini-Guidoni, and G. G. Vopli, *ibid.*, **43**, 1969 (1965); W. M. Jones, *ibid.*, **47**, 4675 (1967); T. Terao and R. A. Back, *J. Phys. Chem.*, **73**, 3884 (1969).

(8) H. Conroy, *J. Chem. Phys.*, **40**, 603 (1964).

(9) L. W. Wright, S. W. Weller, and G. A. Mills, *Ind. Eng. Chem.*, **49**, 1054 (1957).

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(10) Postdoctoral Research Associate, 1968–1969.

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

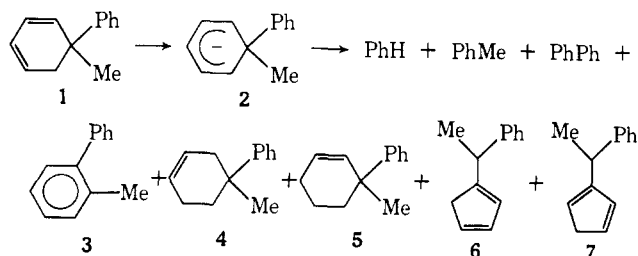
Sir:

The elucidation of the factors¹ (e.g., charge distribution,² ion pairing³) 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-cyclohexadiene⁴ (**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 spectrum⁵ 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, C₂ and C₄ vinyl, $J_{12} = 8$ Hz, $J_{23} = 6$ Hz), complex multiplet at 6.16–6.54 (3 H, C₁, C₃, and C₅ 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

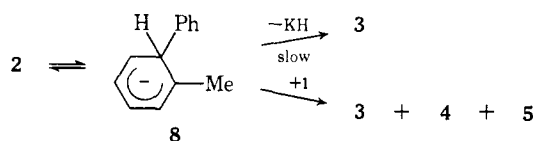
they are readily interconverted (thermally)⁸ under the glpc conditions used for isolation.



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 intramolecular¹⁰ migration of a substituent at C₆ (probably phenyl^{11,12}) in **2**, followed by loss of potassium hydride.

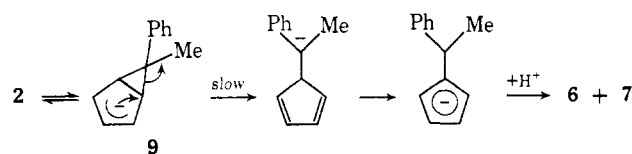
Cyclohexenes **4** and **5** are very minor products but, along with **3**, are much more prominent when **1** (rather than potassium amide) is in excess. This is consistent with a relatively rapid (and reversible¹³) 1,2-phenyl migration followed by intermolecular hydride transfer to **1** (Scheme I).¹⁴ The formation of cyclopentadienes

Scheme I



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 II



(8) (a) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963); (b) W. R. Roth, *Tetrahedron Lett.*, 1009 (1964); (c) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

(9) Cf. (a) H. Pines and H. E. Eschinazi, *J. Amer. Chem. Soc.*, **78**, 5950 (1956); (b) R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *ibid.*, **91**, 4535 (1969).

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

(11) (a) E. Grovenstein, Jr., and G. Wentworth, *J. Amer. Chem. Soc.*, **89**, 1852, 2348 (1967), and earlier papers; (b) T. F. Crimmins, W. S. Murphy, and C. R. Hauser, *J. Org. Chem.*, **31**, 4273 (1966).

(12) Phenyl migration is preferred over methyl migration because the activated complex for the former process is "aromatic" due to a "Möbius" interaction of the C₁, C₆, and phenyl *p* orbitals. For molecular orbital calculations see ref 1a and N. F. Phelan, H. H. Jaffé, and M. Orchin, *J. Chem. Educ.*, **44**, 626 (1967).

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

(14) Cf. J. E. Hofmann, P. A. Argabright, and A. Schriesheim, *Tetrahedron Lett.*, 1005 (1964).

(15) For electrocyclicizations of pentadienyl anions, see (a) R. B. Bates and D. A. McCombs, *ibid.*, 977 (1969); (b) D. H. Hunter and S. K. Sim, *J. Amer. Chem. Soc.*, **91**, 6202 (1969).

(16) Recent evidence suggests that **9** should preferentially revert to **2** (D. J. Atkinson, M. J. Perkins, and P. Ward, *Chem. Commun.*, 1390 (1969)).

(1) Reviews: (a) H. E. Zimmerman, "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 345; (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965; (c) H. F. Ebel, *Fortschr. Chem. Forsch.*, **12**, 387 (1969).

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(3) (a) M. Szwarc, *Accounts Chem. Res.*, **2**, 87 (1969); (b) M. Szwarc, "Carbanions, Living Polymers, and Electron-Transfer Processes," Wiley, New York, N. Y., 1968, Chapter V.

(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^b by reduction, acetylation, pyrolysis, and base-promoted isomerization (cf. S. W. Staley, *J. Amer. Chem. Soc.*, **89**, 1532 (1967)).