Chemistry in Superacids. V.[1] Evidence for the Protonation of Chlorine, Bromine, Carbon Dioxide, and Xenon in Fluoroantimonic Acid Solution

George A. Olah* and Jacob Shen

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received January 8, 1973

Abstract: Chlorine, bromine, carbon dioxide, and Xe were found to be protonated in HF–SbF_5 solution based on their ability to suppress the isotopic hydrogen–deuterium exchange process of molecular D_2 in the superacid system, as evidenced by the sharp decrease in the amount of HD formed. The suppression effect is discussed according to (1) relative basicities of competing weak bases, (2) ability to quench the intermediate isomeric $(H, D)_3^+$ ions, and (3) solubilities in superacids. Molecular oxygen, whose gaseous proton affinity is lower than that of H_2 (D_2), and molecular N_2, whose gaseous proton affinity is slightly higher than H_2 (D_2), were found to have no suppression effect in the same system.

In our preceding studies, we demonstrated the use of superacids to carry out protolytic processes and also their ability to allow comparison of gaseous ion–molecule reactions with ionic solution chemistry.[1–3] We have also demonstrated that conventionally extremely weak bases such as molecular hydrogen (deuterium),[4] methane,[5] and other saturated hydrocarbons[2] were protonated in superacids, as indicated by isotopic exchange as well as protolytic products obtained, at or below room temperature. The gaseous analogs of protonated hydrogen (deuterium) and methane are commonly observed in many mass spectrometric studies.[6] Under favorable conditions, protonated ethane,[7] propane,[8] and butane[8a,d] have also been observed in the gas phase through proton transfer or other ion–molecule reaction channels.[8a,b] However, the observation of other protonated saturated hydrocarbons, whose existence in superacids has been firmly established in previous studies,[2,3,5] was not so far achieved in the gas phase. On the other hand, there are numerous weak bases whose protonated form has only been observed in the gas phase and has not yet been obtained in solution chemistry.

For a better understanding of the parallelism that may exist between the chemistry in superacids and gaseous molecule–ion chemistry, we have extended our study to the reactions of additional weak bases in superacids. We now present evidence that, for the first time, shows the intermediate formation of protonated molecular chlorine, bromine, carbon dioxide, and xenon in solution chemistry.

Results

As in our previous studies we demonstrated that superacid solutions of D_2 undergo H–D exchange; the D_2–HF–SbF_5 system was chosen as an arbitrary standard in present studies. If added weak bases (B) should be preferentially protonated, H–D exchange should be repressed. In parallel experiments the following four systems were examined and compared to the D_2–HF–SbF_5 system.

D_2–HF–SbF_5 *vs.* B–D_2–HF–SbF_5
(1) B = Cl_2 (2) B = Br_2
(3) B = CO_2 (4) B = Xe

Chlorine. HF–SbF_5 (0.1 mol of 1:1 (mol/mol) was added into each of two 75-ml Monel bombs. Cl_2 (0.05 mol, 15 atm) was then introduced into one of the two bombs. Both were charged subsequently with 15 atm of D_2 and were allowed to undergo exchange reactions as before.[1,4] Isotopic exchange, as was evidenced by HD formation, was measured (by mass spectroscopy) after 24 hr at room temperature to be 32% for the reaction system which did not contain Cl_2 but less than 2% for the system containing Cl_2.

Bromine. Similar experiments were performed for Br_2. While the degree of exchange after 24 hr at room temperature was 32% for the D_2–HF–SbF_5 system free of bromine, it decreased to 2% in the system containing bromine.

In both systems containing Cl_2 or Br_2, respectively, there was no detectable significant amount of HCl or HBr observed during the reactions. The degree of repression of hydrogen–deuterium exchange of D_2 in the HF–SbF_5 system was about 94% in the case of both added Cl_2 and Br_2.

CO_2 and Xe. Similar parallel experiments were also carried out using equal partial pressures of deuterium and xenon, as well as deuterium and carbon dioxide, in the presence of HF–SbF_5. The extent of the repression of hydrogen–deuterium exchange of D_2 in HF–SbF_5 decreased to 33% upon addition of xenon and to 30% upon addition of carbon dioxide.

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(2) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Amer. Chem. Soc.*, **93**, 1251 (1971).

(3) G. A. Olah, J. R. DeMember, and J. Shen, *J. Amer. Chem. Soc.*, submitted for publication.

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(6) For examples, see (a) J. J. Thomson, *Phil. Mag.*, 24, 209 (1912); (b) V. L. Tal'roze and A. K. Lyubimova, *Dokl. Akad. Nauk SSSR*, **86**, 909 (1952); (c) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Amer. Chem. Soc.*, 85, 3584 (1963); (d) V. Aquilanti, A. Galli, A. Giordini-Giudani, and G. G. Volpi, *J. Chem. Phys.*, **44**, 2307 (1966).

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Discussion

In all the four studied systems, isotopic hydrogen exchange was substantially suppressed or decreased by the added weak bases such as Cl_2, Br_2, CO_2, and Xe. Table I summarizes the degree of repression of hydrogen–deuterium exchange.

Table I. Repression of Hydrogen–Deuterium Exchange of $D_2 + HSbF_6$ by Added Weak Bases

Added base	% repression of exchange
Cl_2	94
Br_2	94
Xe	33
CO_2	30

The fact that neither HCl nor HBr was detected in the reaction systems containing Cl_2 and Br_2 indicates that no protolysis with the solvent acid system, which would lead to their formation, took place.

In our previous investigation,[1,4] we have proposed an ionic chain mechanism similar to the one suggested in gaseous radiolysis studies,[9,10] involving isomeric $(H, D)_3^+$ ions as the proton (deuteron) transfer agents causing the observed exchange process. Thus the D_2–HF–SbF_5 system undergoes exchange according to eq 1–4.

$$\text{initiation} \qquad H^+A^- + D_2 \longrightarrow HD_2^+ + A^- \tag{1}$$

$$\text{propagation} \qquad HD_2^+ + D_2 \longrightarrow HD + D_3^+ \tag{2}$$

$$HD_2^+ + D_2 \longrightarrow D_2 + HD_2^+ \tag{3}$$

$$\text{termination} \qquad HD_2^+, D_3^+ \longrightarrow \text{neutralized by } A^- \tag{4}$$

It is apparent that the formation of isomeric $(H, D)_3^+$ ions *in solution* is essential in order to explain the substantial amount of HD formed in the system.

Thompson and Schaeffer[9] have shown that by adding a small amount of Xe, which has a lower ionization potential as well as a higher proton affinity than those of molecular hydrogen (and deuterium), into H_2–D_2 mixture irradiated by X-rays, the radiation induced exchange process was almost entirely suppressed. The implication was that added Xe, being a stronger base than H_2 and D_2, was able to quench the formed $(H, D)_3^+$ ions and thus efficiently interrupt the exchange chain reaction. On the other hand, the addition of Ar, whose proton affinity[11] is lower than that of H_2 and D_2, had no (or minimal) effect on the isotopic exchange.

We feel our present results can be interpreted in a somewhat similar way. Fluoroantimonic acid, HF–SbF_5, being one of the strongest acidic medium yet investigated, is able to protonate very weak bases such as Cl_2, Br_2, CO_2, and Xe to Cl_2H^+, Br_2H^+, CO_2H^+, and XeH^+, respectively, in competition with or preference over molecular hydrogen and deuterium which have lower basicity. The small concentration of isomeric $(H, D)_3^+$ ions formed, being extremely effective protonating agents, will rapidly proton transfer to the "stronger base" present in the system. Consequently, the chain length of the propagation stage of the ionic hydrogen–deuterium exchange reaction is much shortened or terminated.

The effect of added weak bases in suppressing the exchange process may depend on (a) the relative basicities of additives relative to that of molecular hydrogen (deuterium) and (b) the reversibility of the proton transfer reaction (5) and its like in superacid systems. The

$$H_3^+ + B \rightleftharpoons H_2 + BH^+ \tag{5}$$

$$B = Cl_2, Br_2, CO_2, Xe$$

first factor will determine to what extent the added weak base will compete with molecular hydrogen (deuterium), the initial protonating step. The second factor determines how effectively an added base can hinder the propagation step by quenching the intermediate $(H, D)_3^+$ ions. If proton transfer from isomeric $(H, D)_3^+$ ions to an added base is rapid and the equilibrium of the proton transfer reaction (5) tends to be to the right, chain propagation will be substantially reduced. However, if reaction 5 can be easily reversed, then the propagation chain length will not be reduced as much as in the previous case and consequently substantial hydrogen–deuterium exchange (evidenced by HD) still may be observed as long as isomeric $(H, D)_3^+$ ions are being formed in the system. The reversibility of reaction 5 in superacids may largely depend on how much the endothermicity of the reaction can be overcome by solvation effects.[12]

An additional factor, which may also be important in determining the degree to which the isotopic exchange is suppressed, is the concentration of the competing weak bases in the superacid solution.[15] Gillespie and Pez[16] have studied the solubility of a series of weak bases in superacids. They found the solubility of H_2, Xe, N_2, and O_2 to be negligible but that of CO_2 to be much higher in superacid solutions. While a 0.2 *M* solution of CO_2 in FSO_3H–SbF_5 was obtained at room temperature and atmospheric pressure, the concentrations of H_2, Xe, N_2, and O_2 were all found to be less than 1 ml of gas/100 ml of superacid. In our present study the values of suppression of exchange by Xe are higher than those by CO_2 at comparable time durations in parallel runs, despite the fact that the concentration of Xe in HF–SbF_5 is considerably less than that of CO_2. The reverse of proton transfer reaction 5 for CO_2 in superacids must be more important than for Xe. This indicates that xenon has a proton affinity which is higher than that of CO_2.

The solubility of Cl_2 and Br_2 in superacids is not known. However, in parallel runs, a simultaneous tenfold decrease of the pressure (concentration) of Cl_2 (or Br_2) and a tenfold increase of CO_2 had no significant effect on the repression values of H–D exchange. As

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(9) S. O. Thompson and O. A. Schaeffer, *J. Amer. Chem. Soc.*, **80**, 553 (1958).

(10) T. Terao and R. A. Back, *J. Phys. Chem.*, **73**, 3884 (1969).

(11) M. T. Bowers and D. D. Elleman, *J. Amer. Chem. Soc.*, **92**, 7258 (1970).

(12) The gas-phase proton affinities (PA) are not exactly known for Cl_2, Br_2, and CO_2. However, PA(CO_2) was shown to be higher than PA(N_2).[13] The gas-phase proton affinity of Xe is less than that of CH_3Cl.[14] Taking $\Delta H_f(H_3^+)$ = 260 kcal/mol and PA(Xe) $\leqslant$ 160 kcal/mol, the reverse of reaction 5 for Xe is calculated to be endothermic by no more than 54 kcal/mol in the gas phase.

(13) J. A. Burt, J. L. Dunn, J. J. McEwen, M. M. Sutton, A. E. Roche, and H. I. Schiff, *J. Chem. Phys.*, **52**, 6062 (1970).

(14) T. O. Tiernan and P. S. Gill, *J. Chem. Soc.*, **50**, 5042 (1969).

(15) We are greatly grateful to one referee who emphasized the importance of this very factor.

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

a consequence, we feel that the role of solubility in these cases is of minor importance. That Cl_2 and Br_2 can suppress the isotopic hydrogen–deuterium exchange more successfully then Xe or CO_2 is mainly due to their higher relative basicities than those of Xe, CO_2, and H_2 (D_2) in superacids.

We also attempted, in similar experiments, suppression of isotopic hydrogen exchange using O_2 and N_2 as additives. However, there was essentially no suppression effect on the exchange process in the D_2–HF–SbF_5 system. Molecular oxygen was recently shown to have lower proton affinity in the gas phase than molecular hydrogen.[13] The proton affinity of molecular nitrogen, which is approximately 116 kcal/mol,[17] was also shown to be lower than that of CO_2.[13] Assuming comparable limited solubilities in superacids,[16] present results suggest that molecular oxygen and nitrogen have somewhat lower (or similar) basicities than molecular hydrogen and deuterium in superacids. The isotopic hydrogen-exchange reaction thus cannot indicate whether limited protonation of these extremely weak bases is taking place.

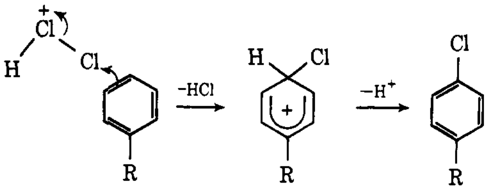
Having extremely low nucleophilicity, the superacid system employed in this study has minimized solvent effects.[3] The relative strength of the series of weak bases studied in it qualitatively shows a trend parallel to that of their gas-phase basicities.

Conclusion. The present study further extends the parallelism between the chemistry in superacids and gaseous ion–molecule reactions. While Cl_2H^+ and Br_2H^+ were to our knowledge not previously reported, CO_2H^+ and XeH^+ were known in the gas phase.[13,14,18] Evidence for their existence in solution chemistry, however, is now presented for the first time. It is interesting to consider that besides the well known dihydrohalonium ions (H_2X^+), the monohydrodihalonium ions (HX_2^+) are now shown to exist in solution chemistry. Trihalogen cations X_3^+ are well known.[19] A tabulation of reported triatomic halonium and hydrohalonium ions is given in Table II.

Table II. Triatomic Halonium and Hydrohalonium Ions

H_2F^+		
H_2Cl^+	Cl_2H^+	Cl_3^+
H_2Br^+	Br_2H^+	Br_3^+
H_2I^+		I_3^+

Cl_2H^+ and Br_2H^+ may play important roles in acid-catalyzed chlorinations and brominations, respectively, as the active halogenating agents. Their reactions with aromatics, for example, can be considered as a displacement reaction by the aromatic substrate acting as the nucleophile.



Evidence for the protonation of Xe to ^+XeH in HF–SbF_5 is the first report to show the n-donor ability of a noble gas in ionic solution chemistry.

With proof obtained in the present study for formation of XeH^+, the scope of known onium ions in ionic solution chemistry was extended to the noble gases. It is of interest to list onium ions of group IVa–VIIIa elements so far observed in solution chemistry (Table III).

Table III. Onium Ions in Ionic Solution Chemistry

IVa	Va	VIa	VIIa	VIIIa
CH_5^+	NH_4^+	OH_3^+	FH_2^+	
SiH_5^+	PH_4^+	SH_3^+	ClH_2^+	
	AsH_4^+	SeH_3^+	BrH_2^+	
		TeH_3^+	IH_2^+	XeH^+

Protonated carbon dioxide, CO_2H^+, is considered of particular importance because of its expected carboxylating ability, which is, indeed, indicated in ongoing research to be reported.

Experimental Section

Antimony pentafluoride and fluoroantimonic acid were spectrograde, donated by Cationics, Inc., Cleveland, Ohio. D_2 was obtained from the Matheson Gas Co., and was analyzed for purity (>99%) by mass spectrometry.

Study of Repression of Hydrogen–Deuterium Exchange in the Presence of Added Bases. In a typical experiment, 0.1 mol of 1:1 (mol/mol) HF–SbF_5 was added into each of two 75-ml Monel bombs which were then evacuated to a pressure of 40 Torr or less. Into one bomb, about 15 atm of Cl_2 (0.05 mol) was introduced. Each reaction vessel was then charged with about 14 atm of deuterium gas and was shaken at room temperature. Gas samples taken at different time durations were analyzed by a Consolidated Engineering Corp. Model 21-260 mass spectrometer.

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