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Protio-2-propyl Dication (Propane Dication, $C_3H_8^{2+}$): Hydrogen/Deuterium Exchange and Theoretical Study. Differentiation of Reactive Gitonic (Proximal) from Stable Distonic (Distant) Dications and the Protosolvolytic Activation of Carbocations[1]

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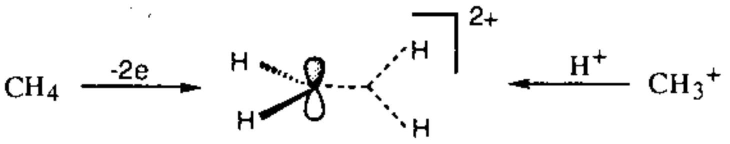
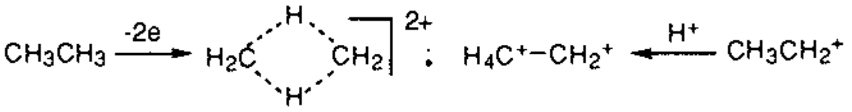
Abstract: Hydrogen/deuterium exchange was observed by ^{2}H-NMR spectroscopy for the long-lived 2-propyl cation when treated with DF in SbF_5/SO_2ClF at –78 °C. As under long-lived stable ion conditions at low temperatures no deprotonation equilibria exist for alkyl cations, protio (deuterio) solvation involving the intermediacy of the protio-(deuterio)-2-propyl dication is suggested to account for the exchange. *Ab initio* calculations at the MP4SDTQ/6-31G**//MP2(FU)/6-31G** level show the protio-2-propyl dication, a gitonic (proximal) dication (as contrasted with usual distonic (distant) dications), to be a remarkably stable minimum structure and support the suggested mechanism for the observed isotopic scrambling.

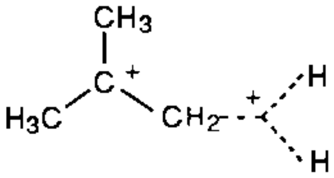
Carbodications play an increasingly important role in chemistry. The solution chemistry of carbodications was reviewed by Prakash, Rawdah, and Olah in 1983.[2a] Gaseous carbodications and their structural aspects were reviewed in 1989 by Lammertsma, Schleyer, and Schwartz.[2b] The methane dication (CH_4^{2+}) is the parent of the protioalkyl dications RH^{2+}. It was studied theoretically[3] with high-level *ab initio* methods and was prepared experimentally in the gas phase *via* 2*e*-ejection from methane.[4] Protonation of the methyl cation can be considered an alternative pathway for the generation of CH_4^{2+}.



The protioethyl dication (ethane dication) $C_2H_6^{2+}$ has also been observed experimentally by charge-stripping mass spectrometric techniques, and the structures of its isomeric forms have been probed by *ab initio* theory. Olah and Simonetta[5a] found an energy minimum for the doubly hydrogen bridged methyl cation dimer (the carbocation analog of diborane). Pople and Schleyer[5b] subsequently showed a second, even slightly more stable carbenium–carbonium form. The species was more fully characterized by us[5c] as a H_2 complex of the ethylene dication.

Recently we have reported the first study of a protioalkyl dication (alkane dication) in superacid solution. The *tert*-butyl cation undergoes upon addition of deuteriated superacid isotopic hydrogen/deuterium exchange.[1] As the stable long-lived *tert*-butyl cation cannot be involved in any deprotonation equilibrium with isobutylene (which would immediately lead to cyclization and oligomerization), the observed isotopic exchange indicates protonation (deuteriation) of methyl C–H bonds (in equilibrium with overall protosolvation of the methyl C–H bonds). The protio-*tert*-butyl dication was found by *ab initio* theory as a surprisingly stable dication,[1] despite charge–charge repulsion in this relatively small carbodication.





In continuation of the our study of protioalkyl dications we have now extended our investigation to the protioisopropyl dication. The 2-propyl cation (**1**) is the simplest long-lived secondary alkyl cation which is stable in superacidic solution. Since only two methyl groups interact with the carbocationic center, **1** is less efficiently stabilized than the *tert*-butyl cation. The gas-phase stability of this ion, based on hydride affinities, is 17.3 kcal/mol lower than that of the *tert*-butyl cation.[6] Ethyl and methyl cations are even less stabilized, and neither has yet been prepared as observable long-lived cations in condensed phase using (slow) spectroscopic methods such as NMR.

The 2-propyl cation can be readily obtained from the ionization of corresponding propyl halides in superacidic medium.[7] The formation of free alkyl cations in superacidic media, as opposed to exchanging donor–acceptor complexes, was demonstrated *inter*

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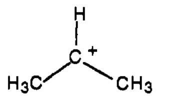
alia by their NMR chemical shift data and analysis of the ^{13}C-NMR coupling constants of the ion.[7] The temperature-dependent ^{1}H-NMR spectrum of the 2-propyl cation (**1**) in SbF_5/SO_2ClF solution revealed rapid interchange of the methine and methyl protons.[8] It was considered that the rearrangement involves an equilibrium between the primary 1-propyl and secondary 2-propyl cations. An alternative mechanism involving a protonated cyclopropane intermediate was not ruled out in the study and was further substantiated by ^{13}C-scrambling studies. It was found, by NMR spectroscopy, that the ^{13}C-label was uniformly distributed over all three carbon atoms when [2-^{13}C]2-chloropropane was ionized at −60 °C.[7] The intermediacy of protonated cyclopropane was subsequently corroborated by further independent labeling experiments.[9] The structures and energetics of the $C_3H_7^+$ system was also investigated at various levels of theory.[10] To rationalize the isotope scrambling, four structural isomers of the $C_3H_7^+$ hypersurface corresponding to the 2-propyl cation (**1**), 1-propyl cation (**2**), corner-protonated cyclopropane (**3**), and edge-protonated cyclopropane (**4**) were considered by Koch et al.[10a] They found the 2-propyl cation (in C_2 symmetry) to be the global energy minimum and to be 7.2 kcal/mol more stable than corner-protonated cyclopropane **3** (MP4/6-311G**//MP2/6-311G** + ZPE), which agrees well with gas-phase studies.[11] Edge-protonated cyclopropane is only 1.4 kcal/mol less stable than cation **3**, which implies rapid H-exchange on the cyclopropane frame. The 1-propyl cation was characterized as a transition structure for C-scrambling in the propyl cation **1**, with which it has an energy difference of 19.3 kcal/mol (MP4/6-311G** + ZPE),[10a] a value that is slightly larger than the 16.3 kcal/mol determined in superacid media.[12] These data suggest a high activation energy for C-scrambling and the involvement of protonated cyclopropane to explain H- and C-scrambling in the superacid-solvated 2-propyl cation.



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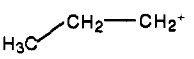

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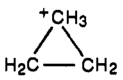

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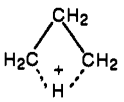

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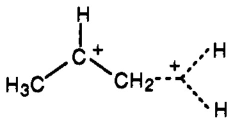
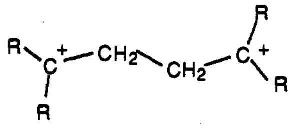
The above-mentioned results suggest that formation of protonated cyclopropane from the 2-propyl cation is a facile process. On the basis of our present work we have now also considered alternative mechanistic pathways for the scrambling process in the propyl cation.

Protosolvolytic activation, of the 2-propyl cation in superacidic media, would lead in the limiting case to the gitonic (*vide infra*) protio-2-propyl dication. It can also be derived by two-electron oxidation of propane. High energy electron impact ionization studies of propane have shown that the initially formed propane dication is not stable under these conditions. It reacts under hydrogen loss to give $[C_3H_{2,3,4}]^{2+}$ ions.[13a] The high distortion of the dication, initially formed in the Franck–Condon process, and the fact that the secondary ions lie within its manifold, were suggested to account for the failure to observe a stable $[C_3H_8]^{2+}$ fragment. The related ethane dication $C_2H_6^{2+}$ (*i.e.* protonated ethyl cation), however, is kinetically more stable and was studied extensively by experimental[13b–e] and theoretical[4,13f–h,14,15] methods.

The search for the propane dication, $C_3H_8^{2+}$, involving protonation (deuteriation) of the 2-propyl cation in superacidic solutions is the subject of this study. The possible formation of the protio-2-propyl dication was also probed by theoretical calculations. The resulting evidence suggests that further protonation of the 2-propyl cation is indeed possible under superacidic conditions, leading to a superelectrophilic gitonic dication. It is suggested to call proximal reactive carbodications as gitonic dications (based on the Greek yeitonic, pronounced gitonic), as contrasted with distant distonic dications in which the charge centers are generally separated by at least two carbon atoms.



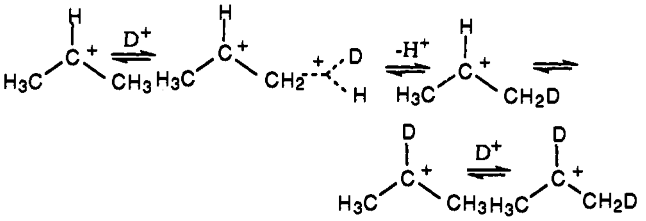
gitonic propane dication



distonic 1,4-butane dication

Results and Discussion

2-Chloropropane was ionized in SbF_5/SO_2ClF solution at −78 °C to the 2-propyl cation, and subsequently 1:1 DF/SbF_5 was added. The deuterium/hydrogen exchange that took place in the ion was monitored by ^{2}H-NMR spectroscopy. After 72 h at −78 °C (the temperature was not raised to avoid any decomposition of the ion) the ion indicated (see Figure 1) about 5% deuterium incorporation (determined using external acetone-d_6 standard). The intermediacy of the protonated 2-propyl dication is considered to account for the observed exchange. The exchange involves both methine and methyl protons, although initial deuteriation is considered in the methyl group, followed by rapid interchange of the methyl and methine hydrogens (deuteriums). Two possible pathways for isotope exchange can also be ruled out. A deprotonation–reprotonation equilibrium involving propene should result in fast oligomerization of propene in the presence of excess isopropyl cation, competing with the observed exchange. No such reaction was, however, observed under the experimental conditions, indicative of the absence of any propene in the system.



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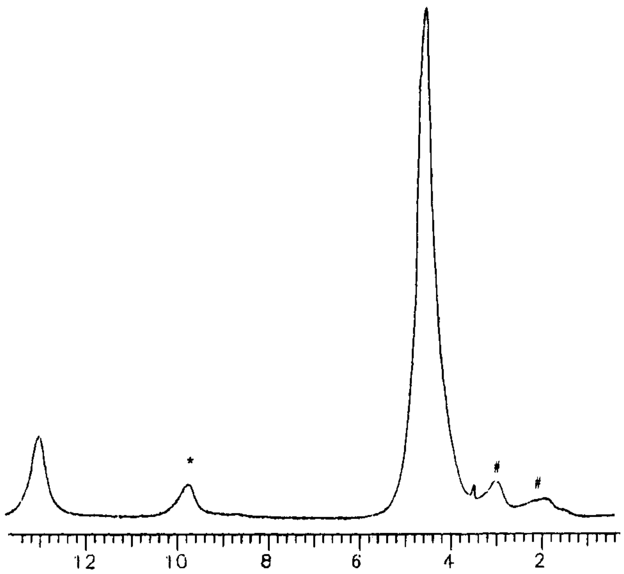
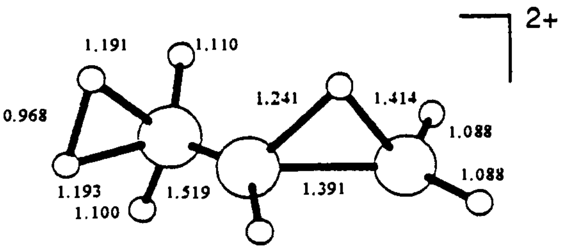


Figure 1. ^{2}H-NMR spectrum (30.7 MHz) of the 2-propyl cation after hydrogen/deuterium exchange with DF in SbF_5/SO_2ClF (* acid peak, # impurities).

Furthermore, 1:1 DF/SbF_5 is one of the strongest superacid systems known.[16a] The experimental proton affinity of propene of 179.5 ± 0.8 kcal/mol[16b] and the calculated PA of 177.8 kcal/mol[10a] make the deprotonation of the 2-propyl cation in excess superacid energetically extremely unfavorable. Rearrangement involving protonated cyclopropane, by a diprotonation–deprotonation (deuteriation), can also be ruled out on the basis of the instability of cyclopropane under high acidity conditions. This was demonstrated[17] by hydrogen/deuterium exchange studies of cyclopropane in strong deuteriated acids,[17a] where the slow initial protonation was followed by fast ring opening. Only one deuterium *per* molecule was incorporated into the products, indicating that, under these conditions, protonation–deprotonation equilibria do not occur. The proton affinity of cyclopropane, which was previously measured to be 179.8 kcal/mol[16] and calculated (178.0 kcal/mol),[10a] illustrates the unfavorable thermodynamics for a deprotonation–protonation equilibrium.

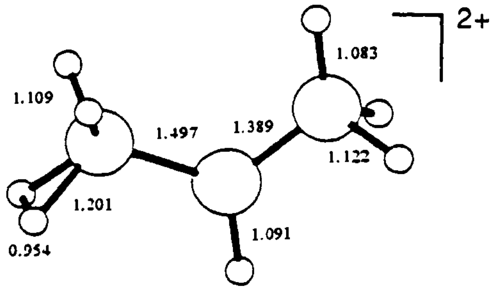
To further probe the nature of the protonated 2-propyl dication (propane dication), *ab initio* theoretical calculations using the Gaussian 92 series of programs were used.[18,19] Structure optimizations and vibrational frequencies were calculated at the all-electron MP2(full)/6-31G* level of theory, followed by optimization at MP2(full)/6-31G** with final energy evaluations at frozen-core MP4(fc)/6-31G** (Table 1). The 2-propyl cation **1** was included to facilitate comparisons. The larger hydrogen-polarized basis set (6-31G**) was employed for a more accurate representation of the hyperconjugative effects in the dications. All geometrical parameters are given at MP2(full)/6-31G**, and all relative energies are at MP4 corrected for 0.95-scaled zero-point energies (ZPEs), except when indicated otherwise.



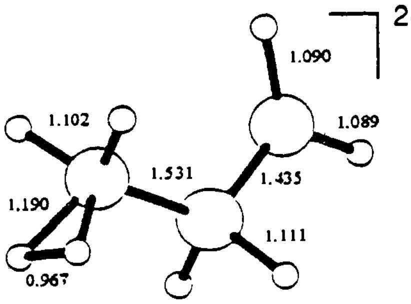
5 C_1

The global *ab initio* energy minimum for the propane dication is structure **5**. This dication is virtually isoenergetic with the 2-propyl cation **1** at the highest level of theory employed. Thus, the mono- and dication are thermodynamically equally viable when considered as isolated species. This, of course, not only illustrates the likely coexistence of the 2-propyl cation and the propane dication but more importantly renders very strong support for the observed proton–deuterium exchange of the 2-propyl cation under superacidic conditions.

To determine the kinetic stability of dication **5** and to provide further support for the experimentally observed H/D- and ^{13}C-scrambling in the 2-propyl cation, a broader survey of the $C_3H_8^{2+}$ potential energy surface is required and several stationary points were identified. In addition to the methonium-substituted ethyl cation **5**, three minima (**6**, **9**, and **10**) and three transition structures (**7**, **8**, and **11**) were identified.



6 C_s



7 C_s

Because the bonding patterns of dications are generally different from those of monocations, the discussion is facilitated by highlighting common structural features that are easily recognizable in a building block approach.[2b,20] Such an approach has been shown to lead to general classes of dications like the methonium-substituted cations (CH_4^+-R^+),[20] hydrogenated dications, and diborane-type structures in addition to methylated dications.[21,22] Propane dication structures are no exception, and

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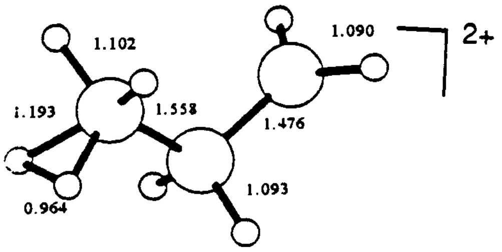
Table 1. Total (in –hartrees) and Relative (in kcal/mol) Energies and Zero-Point Vibrational Energies (in kcal/mol) for $C_3H_7^+$ and $C_3H_8^{2+}$ Isomers

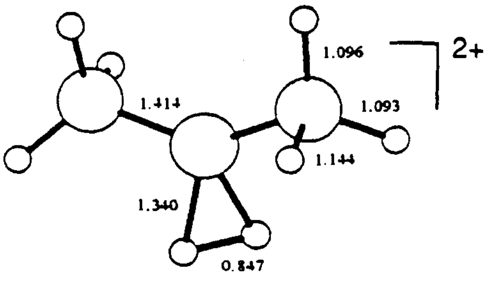
	MP2/6-31G*//MP2-6-31G*			MP2/6-31G**//MP2/6-31G**		MP4/6-31G**//MP2/6-31G**		
	abs	ZPE	rel	abs	rel	abs	rel	E_{rel}[a]
1	117.760 65 (0)	[56.95]	–4.14	117.814 91	3.33	117.854 75	3.33	–0.5
5	117.754 05 (0)	[61.03]	0.00	117.820 25	0.00	117.860 06	0.00	0.0
6	117.745 60 (0)	[60.00]	5.27	117.809 41	6.78	117.850 31	6.09	5.1
7	117.753 71 (1)	[60.84]	0.19	117.818 25	1.26	117.859 36	0.44	0.3
8	117.737 70 (1)	[61.84]	10.23	117.802 60	11.04	117.844 21	9.91	10.7
9	117.685 20 (0)	[56.40]	43.17	117.749 14	44.62	117.790 77	43.49	39.1
10	117.739 35 (0)	[63.24]	9.22	117.800 61	12.30	117.836 84	14.56	16.7
11	117.719 99 (1)	[61.16]	21.40	117.783 90	22.78	117.822 89	23.34	23.5
H_2	1.144 141 (0)	[6.48]		1.157 661		1.164 56		
$C_3H_6^{2+}$ [b]	116.548 99 (0)	[43.74]	38.28[b]	116.590 38	45.37[b]	116.627 93	42.42[b]	36.5[b]

[a] Relative energies corrected for 0.95-scaled MP2(full)/6-31G* ZPEs. [b] Propylidene dication, relative energy is for the $C_3H_8^{2+}$ dehydrogenation of **5**.

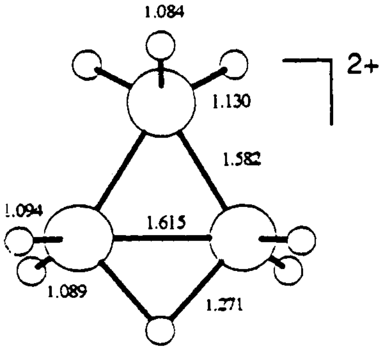
isomeric structures can be envisioned as composed of (a) CH_4^{2+} + ethylidene or CH_4^+-substituted ethyl cations, (b) CH_4^{2+} + ethylene or hydrogenated cyclopropyl dications, and (c) methylated diborane-like $C_2H_6^{2+}$, all of which resemble previous $C_3H_6^{2+}$ and $C_3H_4^{2+}$ studies.[23,24]



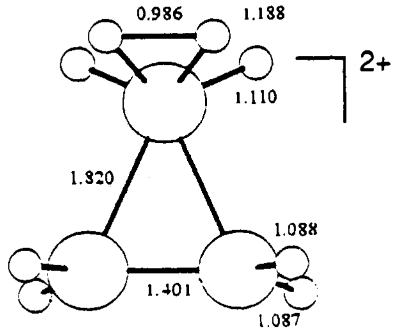
8 C_s



9 C_2



10 C_s



11 C_s

The gitonic dication **6** (C_s symmetry), which is the formal product of α-protonation of the 2-propyl cation, is hyperconjugatively stabilized by 5.1 kcal/mol upon H-bridging to give the global minimum energy structure **5**, while further transfer of this bridging hydrogen from an α- to a β-carbon results in distonic **7**, which is only 0.3 kcal/mol less stable than **5**. Consequently, rapid H/D-scrambling in the protio-2-propyl dication is expected. The bishyperconjugative stabilization[23] in **7** is reflected in the 10.4 kcal/mol energy difference with structure **8**, in which the carbenium center is 90° rotated.

The stability of the nontraditional structure **5** is further highlighted when compared with the β-protonated 2-propyl cation **9** (C_2 symmetry), which is less stable by 39.1 kcal/mol. This formally dioxidized propane, the dimethyl derivative of the methane dication, is not likely to be formed in the condensed phase nor in the gas phase. Structure **9** is best represented as a H_2-complexed $CH_3CCH_3^{2+}$, which is evident from the 0.847-Å short H–H distance and the correspondingly 1.340-Å long methylene C–H bonds. The dehydrogenation of **9** to this cross-hyperconjugatively[23] stabilized propylidene dication is exothermic by 2.6 kcal/mol, which may explain why in the gas phase only dehydrogenated C_3-dications have been observed in high energy electron impact studies on propane.[2b,25]

An alternative structure similar to **9** is H_2-complexed $CH_3CH_2CH^{2+}$. However, this species should be less stable than **9** and was not considered for theoretical scrutiny.

Carbon scrambling requires the formation of cyclic dication structures, of which two were identified. The methyl-substituted diborane-like dication structure **10** (*cf.* the ethane dication), which can also be viewed as edge,corner diprotonated cyclopropane, is a modest 16.7 kcal/mol less stable than **5**. The energy difference between these two structures is remarkably similar to the observed activation energy of 16.3 ± 0.4 kcal/mol for C-scrambling. Alternatively, α,β-migration of a CH_4^+-methonium group can

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be considered, but because transition structure **11** is 23.5 kcal/mol less stable than **5**, rendering this a less likely process to occur.

Conclusions

The effect of π-conjugation (as in allyl cations) and nonbonded electron pair (n) back-donation (as in haloalkyl cations) is well understood and documented in carbocations. Alkyl cations are stabilized by hyperconjugative C–H and C–C σ-bond back-donation into the empty carbocationic p-orbital. Solvation of electrophiles until now was always considered to be nucleophilic in nature, *i.e.* involving electron donor solvents or reagents. Protolytic solvation of electrophiles capable of further coordination was, however, shown to result in enhanced superelectrophilic reactivity.[26] It is now demonstrated that not only electrophiles capable of π- or n-donor interactions but even hydrocarbon cations capable of further σ-coordination can be potentially activated. In the limiting case protolytic interaction of alkyl cations in superacids can *de facto* result in formation of protioalkyl dications (alkane dications), as demonstrated by isotopic hydrogen–deuterium exchange studies and theoretical calculations. In ions, such as the protio-*tert*-butyl and protio-isopropyl dications despite charge–charge repulsion there is remarkable bonding interaction. Hydrogen/deuterium exchange experiments in highly acidic superacids and theoretical calculations have shown that the protonation of the 2-propyl cation leads to a stable protio-2-propyl dicationic intermediate. It is of course not necessary for protolytic activation to involve complete formation of alkane dications. Protosolvation of alkyl cations in strongly acid systems involving C–H (or C–C) bonds can contribute to superelectrophilic activation of the alkyl cations. At the same time, as shown in the present study, the gitonic protio-2-propyl dication (propane dication) is unexpectedly stable. This may explain why certain carbocationic conversions of saturated aliphatic hydrocarbons (such as alkane isomerizations or alkylations) show preference to solution acid catalyzed conditions, which proceed well at modest temperatures. In contrast, with solid acid catalyzed processes, where protolytic activation plays lesser role, the reactions can be carried out only at more elevated temperatures.

Experimental Section

^{1}H-NMR and ^{2}H-NMR spectra were obtained at 200.0 and 30.7 MHz, respectively. The ^{1}H-NMR and ^{2}H-NMR chemical shifts were referenced to an external acetone-d_6 signal.

Starting Materials. SO_2ClF was available as described in earlier studies.[1] SbF_5 (Allied-Signal) was doubly distilled and stored in Teflon bottles. 2-Chloropropane was obtained from Aldrich and was used as received.

Preparation of the 2-Propyl Cation and Isotope Exchange Studies. 2-Chloropropane (~10 mg) was dissolved in SO_2ClF (1 mL) at −78 °C in an NMR tube. Addition of an 8-fold excess of SbF_5 in SO_2ClF (0.5 mL) under vigorous stirring gave the 2-propyl cation. Subsequently, DF/SbF_5 (0.1 mL) was added, and the hydrogen/deuterium exchange was monitored over a period of 72 h with ^{2}H-NMR. At the end of the period the solution showed (Figure 1) ~5% deuterium incorporation (using acetone-d_6 as external standard) involving both the methine and methyl groups (in the ratio 1:6).

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Supplementary Material Available: Cartesian coordinates of the optimized structures **5–11** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[26] Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767 and references therein.