Proton Acid Catalyzed Hydride Transfer from Alkanes to Methylated Benzyl Cations. 3: Solvated Alkanes as Hydrogen-Donating Intermediates[1]

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Abstract: The hydride-transfer reaction between isobutane (and other tertiary alkanes) and methylated benzyl cations **2-X** (X = OCH_3, CH_3, F, Br, H, NO_2) is shown to be proton acid catalyzed. Scrambling of transferred hydride (or deuteride, tritide) occurs with solvent protons during the actual transfer step per se. The reaction between isobutane or isobutane specifically labeled with deuterium or tritium at the tertiary position and cations **2-X** leads to differently labeled products **3-X**. The amount of scrambling between solvent protons and transferred label depends on the acidity of the solvent, the temperature, and the isotopic mass of transferred hydrogen. Tritiation of the solvent leads to tritiated products **3-X**. A termolecular transition state is postulated for the reaction. In this transition state, a presumably concerted transfer of a proton–hydride pair from a proton acid–alkane complex (solvated alkane) occurs towards the benzyl cation. The distinction between solvated alkanes $(RH{\cdot}HZ)^+$ and free, protonated alkanes $(RH_2)^+$ is discussed. CNDO/2 calculations show that a bonding interaction occurs between a C_s symmetrical protonated isobutane molecule and a benzyl cation at $R = 2.8$ Å. These calculations support the postulated transition state, i.e., the transfer of an activated hydrogen molecule in which strong charge polarization is present or, in other words, an unsymmetrical proton–hydride pair.

Introduction

The existence of CH_5^+ and related five-coordinated carbocations under mass spectrometric conditions is now firmly established.[3,4] CH_5^+ cations are rather stable in a methane plasma, in which it can be generated by high-energy electrons or by H_3^+, acting as a proton source. The low proton affinity of methane (calculated value: 120 kcal mol^{-1})[5] causes CH_5^+ to have a rather high Brönsted acidity. Due to this high Brönsted acidity, CH_5^+ rapidly transfers a proton to virtually every suitable proton acceptor. In chemical ionization mass spectrometry, this property of CH_5^+ is used to generate other carbocations from neutral precursors.[6] It is noteworthy to mention that only a few simple molecules have proton affinities lower than methane, e.g., He (42 kcal mol^{-1})[7] and H_2 (101 kcal mol^{-1}).[8]

Contrary to mass-spectroscopic conditions, the existence of protonated alkanes in solution has not yet been demonstrated directly, for instance by spectroscopic observation of CH_5^+ or related carbocations. The reactions exhibited by alkanes in strongly acidic solutions (proton exchange, H_2 formation, or oligomerization, to mention a few types)[9-14] provide ample indirect evidence, however, for the occurrence of five-coordinated alkanonium ions as intermediates in these reactions, although the transient nature of protonated alkanes yet precluded the determination of their geometry. The assumption that CH_5^+ and, more generally, RH_2^+ ions have the C_s symmetry in solution as well as in the gas phase is based mainly on three arguments, viz. (1) electrophilic attack is supposed to occur predominantly on the main lobes of the sp^3 orbitals of carbon because the electron density is highest there; (2) C_s-like transition states are most likely to occur in some cases for steric reasons; and (3) the energy of CH_5^+ is calculated to be lowest for the C_s symmetry.

Quantum mechanical calculations have been carried out for CH_5^+ assuming different geometries (see Figure 1).[15-19] The C_s symmetry is generally found to have the lowest energy, though the differences between D_{3h} and C_s symmetries are only small: 3.1–10.0 kcal mol^{-1}. In view of the fact that these energy differences are rather small, much weight has been attached to mechanistic arguments in favor of C_s-like transition states for protolytic reactions of alkanes in strong proton acids.

The low or negligible isotope effects observed for proton–deuteron or proton–triton exchange reactions between strong proton acids and CH_3D,[12] C_2H_5D,[13] or $(CH_3)_3CD$[14,20] favor a retention mechanism for these reactions.[21] The rapid dedeuteration of 1,3,5,7-tetradeuterioadamantane in HF/SbF_5 also points to a C_s-like transition state for this reaction.[11] The fact that no methyl transfer occurs between neopentane and *tert*-butyl cations,[13] whereas hydride transfer between isobutane and *tert*-butyl cations is very fast,[22,23] is attributed to steric crowding in the supposed three-center bonded C_s-like transition state for these transfer reactions.[24]

Recently, Cacace and Speranza[25] showed that the gas phase tritio deprotonation of *meso*-1,2-difluoro-1,2-dichloroethane by means of the extremely strong Brönsted acid $^3He^3H^+$ occurs via a retention mechanism. They concluded that triton transfer from $^3He^3H^+$ results in the formation of C_s symmetrical transition states (Figure 2) which form tritiated products retaining their meso configuration.

The present paper deals with some remarkable features of the hydride transfer reaction between isoalkanes and long-lived benzyl cations, such as the pentamethylbenzyl cation.[26] Earlier investigations[27] showed that pentamethylbenzyl cation is rapidly converted into (protonated) hexamethylbenzene when a suitable hydride donor is added to a solution of the benzyl cation in strong anhydrous acids (H_2SO_4, HF, HSO_3F, or CF_3SO_3H). The reaction is fast (half-life typically 2–300 s), clean, and equimolar.[28-29] When isobutane is used as the hydride donor, *tert*-butyl cations are formed smoothly upon the addition of this alkane to a solution of pentamethylbenzyl cation in HSO_3F/SbF_5 (10:1).[30] If the hydride-transfer reaction is carried out in a weaker acid such as HSO_3F, a rapidly equilibrating mixture consisting of *tert*-butyl fluorosulfonate, free *tert*-butyl cation, and SO_3F^- is formed, as evidenced by a broad and temperature-dependent peak in the ^1H NMR spectrum centered at δ 2.1. In the latter case, the addition of a small drop of SbF_5 immediately liberates the free *tert*-butyl cation (δ 4.1).

The results reported in this paper show that the hydride transfer from isoalkanes toward pentamethylbenzyl cations (**2-CH**$_3$, see Scheme I) is acid catalyzed. Furthermore, transfer of labeled hydride (deuteride or tritide) is accompanied by extensive proton scrambling with solvent protons during the

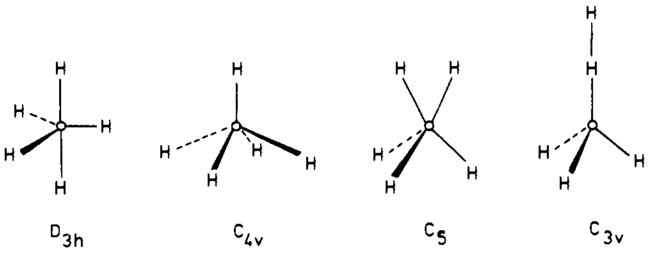
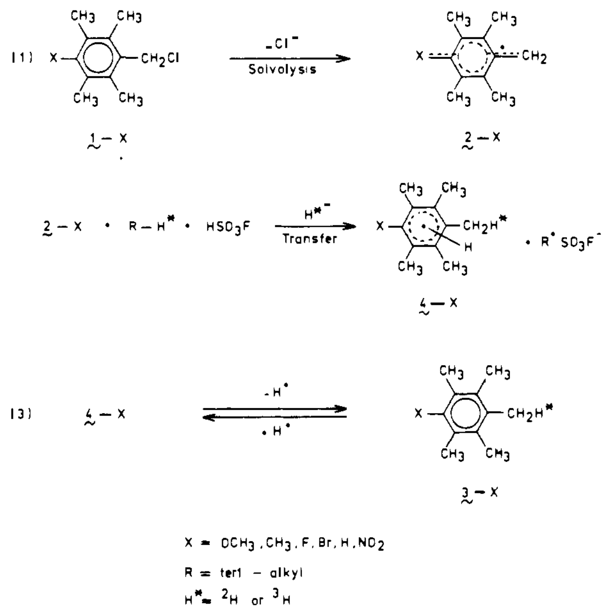


Figure 1.

Scheme I



actual hydride transfer step per se.

To our knowledge, this is the first unambiguous case of proton scrambling occurring *during* a hydride transfer reaction. Deno et al.[31] stated as a general rule that hydride ions do *not* exchange with (labile) protons from the solvent *nor* react with protons with concomitant formation of H_2 during hydride-transfer reactions. Indeed, all hydride-transfer reactions studied until now seem to follow this rule. For instance, the reversible deuteride transfer between [2-^{2}H]isobutane and *tert*-butyl cations, which is very fast (10^4 l mol^{-1} s^{-1} at −40 °C[23]), is virtually undisturbed by the presence of the very acidic solvent HSO_3F/SbF_5 (1:1). Dedeuteration of [2-^{2}H]isobutane does occur, but is much slower (4.5×10^{-4} l mol^{-1} s^{-1} at 0 °C[20]) and should be regarded merely as a side reaction. The irreversible deuteride transfer from [2-^{2}H]isobutane to ions **2**-CH_3 offers a quite different picture: proton scrambling is nearly as fast as the transfer reaction itself and can not be regarded simply as a side reaction, but should be considered to form an integral part of the whole reaction.

Various para-substituted 2,3,5,6-tetramethylbenzyl chlorides (**1**-X) were used as precursors for benzyl cations **2**-X (see Scheme I). Solvolysis of **1**-X in strong anhydrous acids (HSO_3F, HSO_3F/SbF_5, or SbF_5, diluted with SO_2 or SO_2ClF) yields long-lived ions **2**-X at low temperatures (−60 °C). ^{1}H NMR and uv spectra of these ions have been reported elsewhere.[32,33] The stability of ions **2**-X depends strongly on the para substituent and was determined in a qualitative way by means of uv spectroscopy[33] to be: **2**-OCH_3 > **2**-CH_3 > **2**-F > **2**-Br ≃ **2**-H > **2**-NO_2. The observed differences in ^{1}H NMR chemical shifts between the unsolvolyzed CH_2Cl group and the -CH_2^+ group increase in this same order and CNDO/2 calculations show that the positive charge is less accommodated by the substituted phenyl ring going from **2**-OCH_3 to **2**-NO_2. All ions exhibit a fast hydride-transfer reaction when an isoalkane is added, as shown by ^{1}H NMR and uv spectra and by analysis of the quenched products. For practical reasons, the reaction between **2**-CH_3, which is rather stable, and isobutane was studied into detail. The conclusions from this investigation are believed to be also generally applicable to the other ions **2**-X and other hydride-donating isoalkanes.

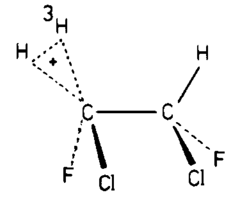


Figure 2.

Introduction of gaseous isobutane into a purple-blue solution of **2**-CH_3 in HSO_3F leads to the quantitative formation of protonated hexamethylbenzene (**4**-CH_3) within a few seconds at −75 °C. This sets a lower limit of about 10^2 l mol^{-1} s^{-1} to the bimolecular reaction rate constant at this temperature, or $\Delta G^{\ddagger}_{200}$ is about 13 kcal mol^{-1}.[34]

Results

I. Acid Catalysis. As noted already, the reaction between isoalkanes and methylated benzyl cations is rather fast in HSO_3F or other strong acids (with $H_0 < -15$) even at low temperatures. In weaker acids (e.g., H_2SO_4) **2**-CH_3 reacts notably slower with isoalkanes. Three acidic solvents were therefore chosen in the range $-11 > H_0 > -14$ to study the influence of the solvent acidity on the rate of hydride transfer from different isoalkanes towards cation **2**-CH_3, viz. 100% H_2SO_4, a 2:1 mixture and a 1:2 mixture of H_2SO_4 with HSO_3F. The Hammett acidities of these solvents were taken to be −11.9, −12.9, and −13.2, respectively.[35]

In a typical experiment, 0.5 ml of a CCl_4 solution of alkane (3 mol l^{-1}) was rapidly dispersed into a dilute solution of **2**-CH_3 in acid (0.05 mol l^{-1}) at 0 °C. The change in color of **2**-CH_3 (purple-blue) to **4**-CH_3 (faint yellow) was measured in time and from these data the pseudo-first-order rate constant k_{obsd} for the hydride-transfer reaction was calculated. A logarithmic plot of k_{obsd} vs. H_0 gives straight lines with slopes between 0.65 and 0.78 (see Figure 3). According to Liler,[36] acid-catalyzed reactions are characterized by $\log(k_{\text{obsd}}) = -aH_0 +$ constant, irrespective of the fact whether protonation is rate determining or not. The value a equals the number of protons participating in the reaction and therefore should have an integral value ($a = 1$) in the case of one proton catalyzing the reaction. The slopes experimentally found differ from $a = 1$, but this deviation is not too serious because of the errors involved in the determination of the points of Figure 3, but also because the derivation of Liler's equation involves the assumption that the ratio of the activity coefficients of the base (here, the alkane) and the protonated base is equal to the ratio of the activity coefficients of the indicator base and its protonated form used to determine the Hammett acidity. This assumption is probably invalid, as the concentration of alkane is rather high. In similar cases, slopes smaller than unity are often found.[33]

The observed dependence of the overall reaction rate k_{obsd} suggests that one proton participates in the hydride-transfer reaction, in accordance with a suggestion made earlier that a proton escorts the hydride ion from the alkane to the benzyl cation.[26]

II. Hydride–Proton Scrambling. The reaction between [2-^{2}H]isobutane and solutions of **2**-CH_3 in different strong

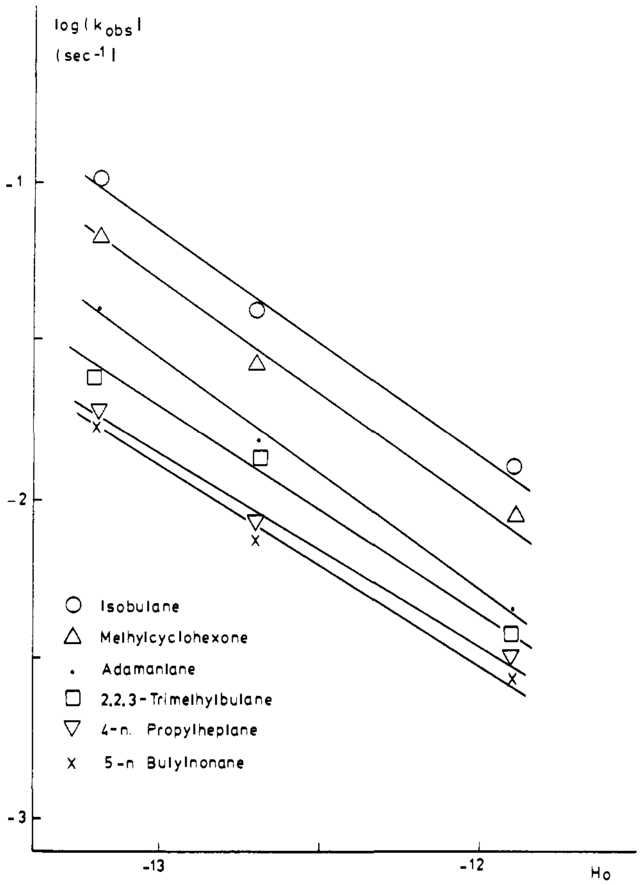


Figure 3.

Table I. Deuterium Analyses of **3**-CH_3 Obtained after D^- Transfer from [2-^{2}H]Isobutane to **2**-CH_3 in Different Acids at Various Temperatures

		Percentage[b]	
Acid	Temp, °C[a]	Undeuterated	Monodeuterated
HSO_3F	−60	21	78
	−45	57	42
	−30	63	35
HSO_3F/SO_2 (1:2)	−60	14	85
CF_3SO_3H	−40	51	46
SbF_5/SO_2 (1:2)[c]	−70	10	89

[a] Temperature of the cooling bath; estimated accuracy: ±2 °C. [b] Determined with a GEC-AEI MS-902 double focusing mass spectrometer, operating at 6.2-eV ionization potential; accuracy about 0.5%. [c] Contains traces of water as impurities; see text.

Table II. Deuterium and Tritium Analyses of **3**-CH_3 Obtained after D^- Transfer from [2-^{2}H]Isobutane to **2**-CH_3 in Different Tritiated Acids at Various Temperatures

		Percentage[b]	
Acid	Temp, °C[a]	Monodeuterated	Tritiated
HSO_3F	−65	83	24
	−50	60	37
	−45	42	56
	−30	35	68
HSO_3F/SbF_5 (5:1)	−65	61	27
	−55	42	49
HSO_3F/SO_2 (2:1)	−65	84	14
	−50	81	13
HSO_3F/KSO_3F (5:1)	−45	83	7

[a] Temperature of the cooling bath; estimated accuracy: ±2 °C. [b] Deuterium percentage accuracy about 0.5%; tritium percentage is accurate ±2–5%, depending on the tritium activity.

acids at various temperatures yields only partially deuterated product **3**-CH_3. Table I shows the percentages of monodeuterated and undeuterated hexamethylbenzene obtained after quenching the reaction mixtures. It may be noted that the yield of **3**-CH_3, based on the starting material **1**-CH_3, was nearly quantitative in all cases (more than 95% after purification). Furthermore, the degree of deuteration of isobutane on the 2 position was better than 98%, as no protio compound could be detected by ^{1}H NMR or Raman spectroscopy.

From the results in Table I one concludes that some scrambling process interferes with the D^- transfer reaction; else 98% monodeuteration should be found in each case. The fact that deuteride transfer is also incomplete in SbF_5/SO_2 may be due to the presence of proton-containing impurities, presumably water, in this solvent. The rigorous exclusion of atmospheric water was found to be very difficult under our experimental conditions (closed reaction vessel, purged with dry N_2), as the acids used are extremely hygroscopic.

In a separate experiment, [2-^{2}H]isobutane was added to solutions of specifically labeled 2,3,4,5,6-pentamethyl[α-^{2}H]benzyl cation in HSO_3F. After quenching with water and purification of product **3**-CH_3, mass spectrometric analysis showed that the hexamethylbenzene was partially monodeuterated and partially dideuterated. At −45 °C, the ratio of monodeuterated to dideuterated **3**-CH_3 was 58:41%; this ratio was 64:35% at −30 °C. Comparison with Table I shows that labeling of ion **2**-CH_3 has no effect on the amount of scrambling observed. Furthermore, from a proton-decoupled ^{13}C NMR spectrum of a mixture of monodeuterated and dideuterated **3**-CH_3 containing approximately equal percentages of both species, it was found that both deuterium atoms in the dideuterated species belong to the same methyl group, showing that indeed deuteride was transferred to the benzylic center.

Higher temperatures and higher acidities favor the scrambling between protons and transferred deuteride. To study this effect more clearly, a set of experiments was carried out in which deuterated isobutane was added to solutions of **2**-CH_3 in tritiated acids. Tritiated HSO_3F was prepared by the addition of a small amount of HTO (5 μl with a specific activity of 5 mCi ml^{-1}) to 25 ml of freshly distilled acid. After quenching of the reaction mixtures, product **3**-CH_3 was purified (chromatography over Al_2O_3 with ligroin as eluent, followed by sublimation in vacuo) and the deuterium content was determined as before. Moreover, each sample was checked on tritium content. The relative ^{3}H percentages were calculated as the ratios of measured molar activity in **3**-CH_3 to the molar activity in the solvent. Table II summarizes the results.

The results of Table II agree well with those of the preceding table: extensive loss of label occurs, especially at higher temperatures and/or higher solvent acidities. Furthermore, the amount of tritium incorporated into **3**-CH_3 is nearly equal to the amount of deuterium lost during the reaction, indicating that indeed protons from the acidic solvent substitute transferred deuteride ions.

The influence of isotopic mass on the hydride-transfer reaction was briefly studied by treating solutions of ions **2**-X (X = OCH_3, CH_3, Br, and NO_2) in HSO_3F at −70 °C with *either* a mixture of [2-^{2}H]isobutane and [2-^{3}H]isobutane *or* a mixture of [2-^{1}H]isobutane and [2-^{3}H]isobutane. In either case, products **3**-X were purified by column chromatography (Al_2O_3, ligroin) and the relative tritium percentages were

Table III. Relative Tritium Percentages in **3**-X, Formed via the Reaction between ^3H-Labeled Protio- or Deuterioisobutane and Ions **2**-X in HSO_3F at −70 °C

	Percentage tritium	
Product	Mixture $^1H/^3H$	$^2H/^3H$
3-OCH_3	3 ± 1	52.1 ± 0.3
3-CH_3	4 ± 1	62.5 ± 0.3
3-Br	5 ± 1	69.5 ± 0.5
3-NO_2[a]	11 ± 2	70 ± 3

[a] The nitro compound **3**-NO_2 gave appreciable quenching of the scintillator solution, resulting in a low counting efficiency (about 2%, as determined with an internal standard) and, consequently, a lower accuracy.

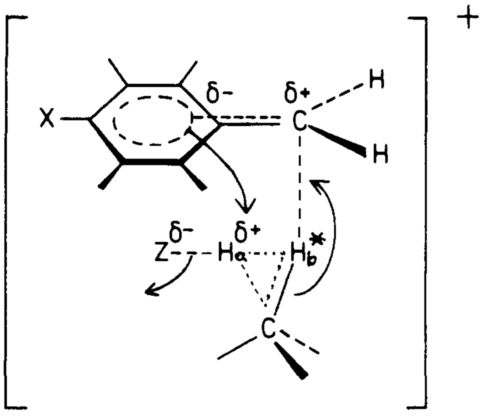


Figure 4.

determined, based on the molar activity of the alkane mixtures. Table III summarizes the results.

III. Quantum Mechanical Calculations. The observed catalysis of the hydride-transfer reaction by one, presumably solvated, proton (e.g., $(H\cdot SO_3FH)^+$) indicates a termolecular transition state for this reaction. The observed rapid scrambling between protons and transferred hydride ions strongly suggests that the catalyzing proton is in very close proximity to the incipient hydride ion, so that a strong interaction can exist between these two particles (see Figure 4). As a crude model for this transition state we calculated the energy of protonated isobutane approaching a benzyl cation by the CNDO/2 method. First, the energy of the two separate particles was calculated, optimizing the relevant bond lengths and angles. For protonated isobutane the C_s symmetry was assumed, analogous to CH_5^+. The optimized geometries of protonated isobutane and the benzyl cation are given in Figure 5, together with the calculated energies and charge distributions. For comparison, the geometry of CH_5^+ is included. Note the striking similarity between CH_5^+ and protonated isobutane as regards geometry and charge distribution.

The geometries for which a minimum energy was calculated were used in subsequent calculations, in which the total energy of the two particles was calculated for distances R between 10 and 2.6 Å. A plot of ΔE_{tot} (i.e., the total energy for finite R minus the energies of the separate particles) shows a local minimum at R = 2.8 Å (see Figure 6). The charge distribution corresponding with R = 2.8 Å is shown in Figure 7. The local minimum in ΔE_{tot} suggests that for R = 2.8 Å a more or less stable intermediate is formed.

Separation of the two particles has an "activation energy" of about 7 kcal mol^{-1}. For distances R smaller than 2.8 Å a sharp increase in ΔE_{tot} occurs due to electron-electron repulsion terms, but in a more refined treatment a changing

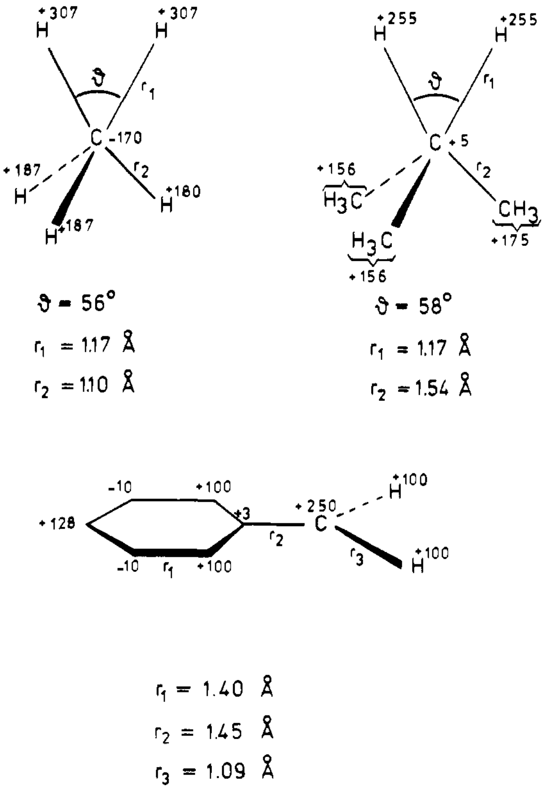


Figure 5.

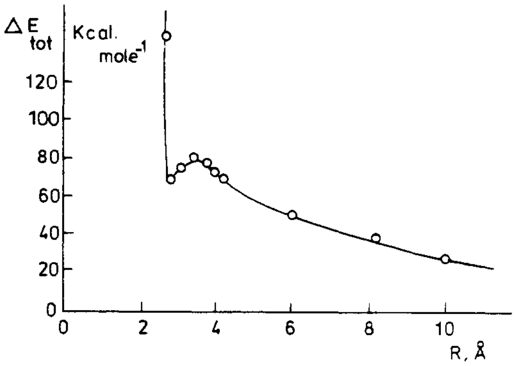


Figure 6.

geometry of the two particles should be taken into account as R becomes smaller than about 4 Å. In the situation pictured in Figure 7, the distances between C(5) and H(3,4) and C(1) and H(3) are 1.75 and 1.95 Å, respectively, i.e., well within the range of incipient C–H bonds. A drift of electron density in the C(6)–H(3,4) bonds and the C(1)–C(5) bond is seen to occur. More positive charge is localized on the ortho carbons of the phenyl ring and the three methyl groups of the alkyl moiety. This leads to a weakening of the electrostatic repulsion between the two like-charged particles. Furthermore, H(3) becomes more positive, i.e., more proton-like, while H(4) becomes less positive, i.e., more hydride-like, upon formation of the complex at R = 2.8 Å.

The results of the CNDO/2 calculations suggest that the initially equivalent hydrogens H(3) and H(4) become an incipient proton and hydride, respectively. It may be stressed that the model, as treated here, is rather crude. The most significant simplification is the assumption of a protonated, five-coordinated isobutane as the attacking agent. As will be shown (vide supra) a much more realistic model would contain a solvated isobutane, i.e., an isobutane molecule in which the tertiary C–**H** bond interacts with a proton that is still bound to its

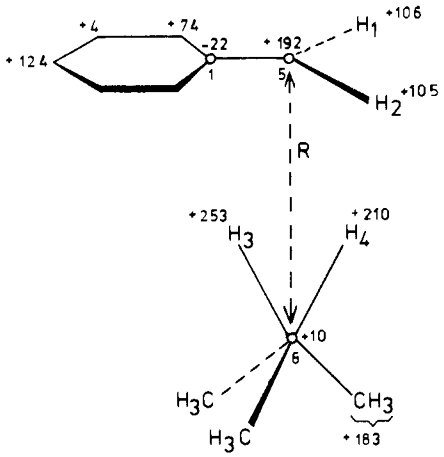
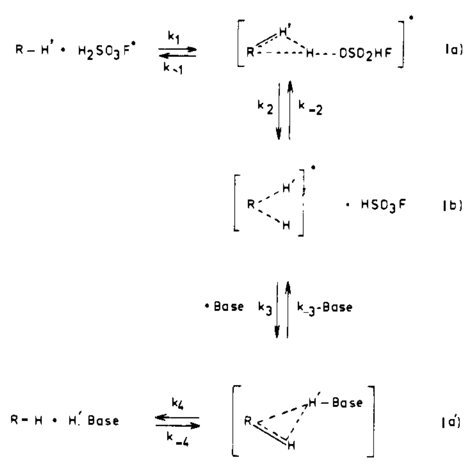


Figure 7.

Scheme II



conjugate base. However, in view of the prohibitively long computing times in treating such a model, we adopted the crude model as presented here. Though admittedly somewhat oversimplified, our crude model reflects one important property of the transition state as pictured in Figure 4, viz. the possibility of an interaction between the (bound) proton-like hydrogen H(a) (or H(3)) and the π system of the phenyl ring (or C(1)).

Discussion

Various explanations for the observed loss of label during the hydride-transfer reaction between isobutane and ions **2**-X may be given. For instance, proton–deuteron exchange between labeled isobutane and acid may occur concomitantly with the deuteride-transfer reaction. In an earlier stage of our investigations this seemed to offer a good explanation for our observations.[34] The reported fast proton exchange between isobutane and HSO_3F is in error, however: traces of SO_3 in freshly distilled HSO_3F presumably oxidize the alkane to the *tert*-butyl cation and the observed doublet collapse mentioned[34] is simply due to a fast hydride exchange between isobutane and *tert*-butyl cations, present in the solution in minute quantities.[23] In fact, proton–triton exchange between isobutane and HSO_3F is quite slow: $k(0\ °C) = 5 \times 10^{-4}$ l mol^{-1} s^{-1}.[20] Hogeveen et al.[14] found that [2-^{2}H]isobutane was dedeuterated in Freon-HF/SbF_5 with a half-time of about 3.5 h at 0 °C. ^{1}H NMR spectra of [2-^{2}H]isobutane in SO_2ClF containing some HSO_3F/SbF_5 (5:1) show no sign of the protio compound after 45 min at −15 °C. These facts taken together with the high rate of the hydride-transfer reaction between isoalkanes and ions **2**-X rule out an explanation based on proton exchange between acid and alkane for the scrambling observed during the hydride-transfer reactions between isoalkanes and ions **2**-X.

Dedeuteration or detritiation of products **3**-X or **4**-X may also be ruled out as a source of scrambling. As a check, hexamethylbenzene was dissolved in tritiated HSO_3F at −40 °C and the solution quenched after 10 min. The tritium percentage of recovered **3**-X was only 0.09% and from this value a rate constant for the proton-exchange reaction of about 1.3×10^{-8} l mol^{-1} s^{-1} may be calculated using the procedure of Duffield and Calvin.[37]

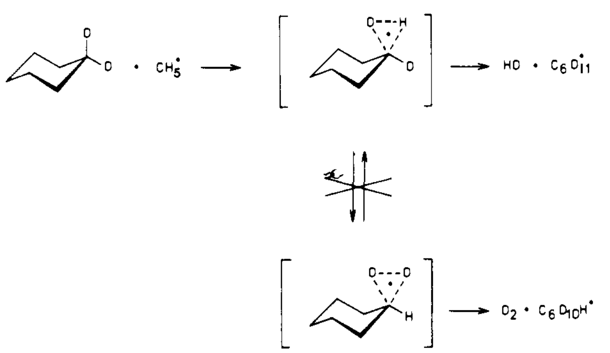
The very low rate of proton exchange between **3**-CH_3 and strong acids is in accordance with the findings of Ginzburg et al.[38] that **3**-CH_3 can not be tritiated measurably by refluxing this compound in ^{3}H-labeled CF_3COOH for over 3 h.

It has been noted already that our experimental data point out, in our opinion, that the hydride-transfer reaction between isoalkanes and benzyl cations **2**-X proceeds via a termolecular transition state, as pictured in Figure 4. In this transition state, an interaction exists between the catalyzing proton and the incipient hydride ion. However, this interaction is not so strong that molecular hydrogen is formed during the reaction. At this point a clear distinction should be made between our proposed transition state and the five-coordinated alkanonium ions occurring during protolytic reaction of alkanes in superacids. In the latter case, high-energetic transition states must be involved in view of the rather low rates encountered for proton exchange, hydrogen formation, or oligomerization reactions. The high-energetic nature of alkanonium ions (such as CH_5^+) is qualitatively in agreement with the low proton affinity of alkanes.[4,15,39]

On the other hand, the high rate of the acid-catalyzed hydride-transfer reaction between isoalkanes and ions **2**-X and the rapid anodic oxidation of alkanes in HSO_3F, which reaction was shown by Pletcher et al.[40] to be also acid catalyzed, point out that different and less energetic transition states or intermediates are involved. We suggest that the following equilibria exist in solutions of alkanes in strong proton acids (e.g., HSO_3F) (see Scheme II). It is assumed that the formation of free protonated alkane RH_2^+ (species b) is preceded by the formation of solvated alkanes a in much the same way that Wheland σ complexes are preceded by more loosely bonded π complexes during electrophilic-substitution reactions. Species b should be considered as transition states rather than as intermediates under all conditions, except maybe under the extremely nonnucleophilic conditions prevailing in the mass spectrometer. The high-energetic nature of protonated alkanes RH_2^+ prevents the buildup of any detectable concentrations of these species in solutions, because always some suitable base will be present (e.g., SO_3F^- ions) that acts as proton scavenger towards RH_2^+ cations. Even under mass spectrometric conditions, RH_2^+ ions seem to be unsymmetrical contrary to what may be expected on the ground of quantum mechanical calculations. In this respect it is noteworthy that Field and Munson[4] observed no $C_6D_{10}H^+$ ions when protonated cyclo-C_6D_{12} decomposed unimolecularly into HD and hexyl cations in the mass spectrometer (see Scheme III). According to Field and Munson, entering protons immediately leave the deuterated cyclohexane molecule together with one deuteron and its electron pair. The observation of Aquilanti and Volpi[3] that propane, deuterated by D_3^+, gave only low amounts (less than 20%) of $H_3CCD^+CH_3$ cations under mass spectrometric conditions also points to an unsymmetrical geometry of the intermediate $(H_3CCH_2DCH_3)^+$ ions in this case.

The unsymmetrical nature of protonated alkanes occurring in the mass spectrometer supports the suggested occurrence of solvated alkanes a in solutions of alkanes in strong proton acids. If the methane or hydrogen plasma inside the mass spectrometer is considered as a kind of very nonnucleophilic

Scheme III



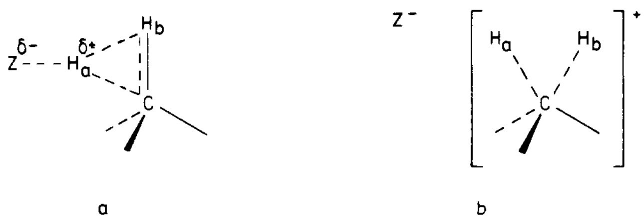


Figure 8.

"solvent", any residual interaction between CH_4 or H_2 molecules and protonated alkane RH_2^+ may be looked upon as a kind of "solvation", leading to an unsymmetrical behavior in the subsequent decomposition of the protonated alkane.[41] In the same way, protonation of C–H σ bonds will not be complete in solutions also in the sense that some interaction will remain between the proton on the σ bond and its original conjugate base. Hydrogens H_a and H_b will be more equivalent if the interaction between H_a and its conjugate base Z is weaker (see Figure 8a). In the limit of infinitely strong acids HZ, protonated alkanes will be completely symmetrical with respect to H_a and H_b and resemble a complex between a H_2^+ ion and an alkyl radical (Figure 8b).

The acid-catalyzed hydride transfer from isoalkanes toward benzyl cations **2**-X may now be visualized as an attack of solvated alkane on the benzyl cation, leading to a transition state as pictured in Figure 4. All experimental data, i.e., the proton acid catalysis, the observed scrambling of transferred hydride, and the dependence of the scrambling on acidity and temperature, point out that a more or less concerted transfer of a proton–hydride pair occurs during the reaction. In stronger acids, a decreased interaction between H_a and its conjugate base Z leads to increased interaction with incipient hydride H_b (and hence, increased scrambling), but also to an increased interaction with the aromatic π system (and hence, a different polarization of the C_{ar}–CH_2 bond), leading to an increased tendency of the CH_2 group to accept a hydride ion. The basicity of the tertiary C–H bond of the alkane plays a dominant role. Therefore, secondary or primary alkanes are much less reactive hydride donors.[42]

In this connection one may regard the participating proton as bifunctional in the sense that first the alkane is activated by solvation of a tertiary σ bond, while the same proton, at a later stage of the reaction, activates the benzyl ion by solvating its π system.

NOTE: The occurrence of protonated ions **2**-X was suggested by Professor G. A. Olah as an interesting alternative explanation for the reactivity of benzyl cations towards isoalkanes. He rightly argued that the electron deficiency of the benzylic center would be enormously enhanced by protonation because of the destruction of conjugative delocalization, which otherwise makes the pentamethylbenzyl cation (and related ions) rather stable. Though *neither* protio-solvated isoalkanes *nor* protonated (or protio-solvated) benzyl cations were detected by ^1H NMR, and though the basicity of the benzyl π system presumably plays a not yet completely understood role in the transition state (Figure 4), the assumption of protonated ions **2**-X as the reactive species is, in our view, unlikely on the following grounds.

(1) The observed rapid scrambling during the hydride-transfer step per se strongly suggests that catalyzing proton and (incipient) hydride are physically very close to each other, i.e., within a range of, say 3 Å. This rules out meta-protonated dicationic species (in which the distance between proton and benzylic center is about 4–5 Å), but α-protonated species may still fit in this picture. According to CNDO/2 calculations the electron density of the α position is relatively high compared to other positions, though not as high as the meta positions in most cases. Thus, a weak interaction between protons and the α position of benzyl cations can not be excluded rigorously.

(2) The fact that widely differing para substituents X have only very little influence on the amount of scrambling observed, and furthermore, that the scrambling is least with the least-basic compound **2**-NO_2 (see Table III), points out that the interaction between the π system of the benzyl cation and the participating proton is nearly the same in each case if compared to the interaction between proton and incipient hydride. If the basicity of the benzyl cation would play a crucial role, a much stronger interaction between proton and ion **2**-OCH_3 would be expected than, for instance, with ion **2**-NO_2, and a proportionally decreased interaction with hydride ions, as it may be expected that a more tightly bound proton will show a decreased tendency to interfere in the hydride-transfer event. As may be noted from Table III, the opposite is observed experimentally.

Experimental Section

Apparatus. ^1H NMR spectra were recorded on a Varian A-60a or on a Varian T-60 NMR spectrometer, equipped with a variable temperature accessory. ^1H NMR spectra of **2**-H and **2**-NO_2 were taken on a Varian HA-100 connected to a Digilab Fourier transform computing system. Uv spectra were recorded with a Perkin-Elmer 124 spectrometer. Tritium was determined with a Packard 3015 liquid scintillation counter. Instagel (Packard) was used as scintillator fluid and efficiencies were determined *either* with the channels ratio method of an external standard *or* by means of an internal [^3H]toluene standard. Deuterium analyses were performed on a GEC-AEI MS-902 double focusing mass spectrometer at 6.2-eV ionization potential. The intensity of the parent peaks was measured with an ion-current meter attached in the collector line and corrected for natural ^{13}C abundancy.

Materials. HSO_3F and CF_3SO_3H (Schuchardt and Fluka) were distilled at atmospheric pressure under a stream of N_2 and used fresh. SO_2ClF (Cationics Inc.) and SbF_5 (Aldrich) were used as obtained. Isobutane gas (Matheson) of purity better than 99.7% was used throughout. Various other hydride donors (such as adamantane, methylcyclohexane, 2,2,3-trimethylbutane, and 4-*n*-propylheptane) were used as obtained from different commercial sources. Tritiated water (5 mCi ml^{-1}) was obtained from Amersham (U.K.). Deuterated isobutane was prepared from *tert*-butyl bromide via the Grignard compound (made in THF) by reaction with D_2O Merck, 99.95% D). The gas was collected in a cold trap (CO_2/acetone) and fractionated once to remove traces of THF. Tritiated deuterioisobutane was prepared in the same way, but 10 μl of tritiated water was added to the D_2O. Tritiated isobutane was prepared by proton–triton exchange of isobutane over tritiated HSO_3F and subsequent purification of the gas.

Benzyl chlorides were prepared as described elsewhere.[33] For the preparation of **1**-OCH_3, 2,3,5,6-tetramethylphenol was used as starting compound. The phenol was methylated in CH_2Cl_2 by means of 2,2,2-trimethoxy-4-methyl-1,2-oxaphosphol-4-ene according to the method of Voncken.[43] This method was found to be superior to the method of Graebe,[44] viz. methylation by dimethyl sulfate and sodium hydroxide. Chloromethylation of durophenol methyl ether yielded **1**-OCH_3: mp 109.5 °C.

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(41) **Note:** Recently, Kebarle and Hiraoka (*J. Am. Chem. Soc.*, **97**, 4179 (1975)) noted the occurrence of $CH_5(CH_4)_n{}^+$ clusters in a methane plasma containing $CH_5{}^+$ ions. Solvation of $CH_5{}^+$ by one CH_4 molecule was found to be energetically favorable ($\Delta G° = 1.2$ kcal mol^{-1}), while the addition of a second CH_4 molecule is less favorable ($\Delta G° = -1.4$ kcal mol^{-1}). Still weaker interactions are found for clusters with $n = 3, 4, \ldots$. From their data one would conclude that asymmetric solvation (i.e., $CH_5{}^+CH_4$) is more likely to be found than a symmetric configuration ($CH_5{}^+(CH_4)_2$).
(42) **Note:** The calculated proton affinities of CH_4 and C_2H_6 are 120 and 149 kcal mol^{-1}, respectively.[5] Though no data are available for propane or isobutane, the latter compounds are certainly more basic in view of the fact that protolytic reactions (e.g., in HSO_3F/SbF_5) proceed much more rapidly with these alkanes than with methane or ethane.
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Carbanions. Electron Transfer vs. Proton Capture. 4. Products of Base-Catalyzed Reactions of Various 9-Substituted Fluorenes with Aromatic Nitro Compounds

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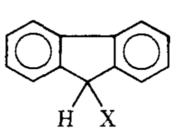
Abstract: Fluorenes substituted in the 9 position with CH_3O-, CH_3-, $(CH_3)_2CH$-, H_2N-, and HO- react with potassium methoxide and aromatic nitro compounds in oxygen-free methanol. The reaction products are dimers, diphenylene-*N*-arylnitrones, trisubstituted hydroxylamines, mono- and disubstituted azoxy compounds, and dehydrogenation products. These are shown to arise from 9-substituted fluorenyl radicals produced by one-electron oxidation of the corresponding carbanions. The radicals undergo coupling, reaction with reduction products from the nitro compounds, or transfer a second electron.

It is well established that carbanions undergo one-electron transfer reactions to aromatic nitro compounds to give the radical anion of the nitro compound.[1] The fate of the carbanion derived radicals has not been thoroughly explored. In our efforts[2] to use electron-transfer oxidation as a probe of carbanion environment, we felt that it would be valuable in each case to provide a complete identification of reaction products. The present paper serves this function for the reaction of several 9-substituted fluorenide ions with aromatic nitro compounds.



1a, X = $-OCH_3$
b, X = $-CH_3$
c, X = $-CH(CH_3)_2$
d, X = $-NH_2$
e, X = $-OH$

Results and Discussion

When **1a–e** were treated with potassium methoxide in methanol in the presence of nitrobenzene or 3,5-dichloronitrobenzene (DCNB) under anaerobic conditions, compounds **2–7** were formed in the amounts listed in Table I. We suggest