# Proton acid catalysed hydride transfer from alkanes to methylated benzyl cations

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# PROTON ACID CATALYSED HYDRIDE TRANSFER FROM ALKANES TO METHYLATED BENZYL CATIONS

P. VAN PELT

# PROTON ACID CATALYSED HYDRIDE TRANSFER FROM ALKANES TO METHYLATED BENZYL CATIONS

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE WETENSCHAPPEN AAN DE TECHNISCHE HOGESCHOOL EINDHOVEN, OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF. DR. IR. G. VOSSERS, VOOR EEN COMMISSIE AANGEWEZEN DOOR HET COLLEGE VAN DEKANEN IN HET OPENBAAR TE VERDEDIGEN OP DINSDAG 28 JANUARI 1975 TE 16.00 UUR

DOOR

**PIETER VAN PELT**
GEBOREN TE ROTTERDAM

KRIPS REPRO MEPPEL

DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR
DE PROMOTORS
PROF. DR. H.M. BUCK
en
PROF. DR. G.C.A. SCHUIT

Aan INGRID

Niin päivänä ensimäisnä
itse seppo Ilmarinen
kallistihe katsomahan
ahjonsa alaista puolta
mitä tullehe tullesta,
selvinnehe valkeasta.

On the very first day
he himself, smith Ilmarinen
looked down, looked carefully,
into the bottom of the furnace
if perchance amid the fire
something brilliant had developed.

KALEVALA, RUNO X, 319-324

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# CHAPTER I

## Introduction.

### I.1. REDUCTION AND OXIDATION IN ORGANIC CHEMISTRY AND IN BIOCHEMISTRY.

Oxidation and reduction are fundamental processes accounting for many chemical reactions. In the oxygen-rich atmosphere of the earth, oxidation of compounds is usually easy to bring about. Often oxidation even tends to proceed all the way to the most oxidized compounds that can be derived from a given substrate and oxidation to only a certain level requires the use of more or less complicated control mechanisms. Technologically and biologically the oxidation process is the primary source of energy. Though nuclear fission today and nuclear fusion in the future will become more and more important technological sources of energy, the availability of oxidizable, energy-rich compounds will remain of the utmost importance for all living beings.

These oxidizable compounds (*i.e.* food in a very broad sense) can be formed from oxidized materials ($CO_2$, $H_2O$) by green plants because in their cells the fundamental reductive process of photosynthesis can occur. Many text-books describe this process more or less detailed[1], but a few salient points will be noted here.

The energy of light is captured by chlorophyll in plant cells and used to split water in oxygen, protons and high-energy electrons. Carrier compounds transport the energetic electrons into different photosystems where, among other things, two important high-energy compounds are synthetized, viz. Adenoside-TriPhosphate and Nicotin-amide-Adenosine-Dinucleotide-Phosphate, commonly referred to as ATP and NADPH. (See figure 1.)

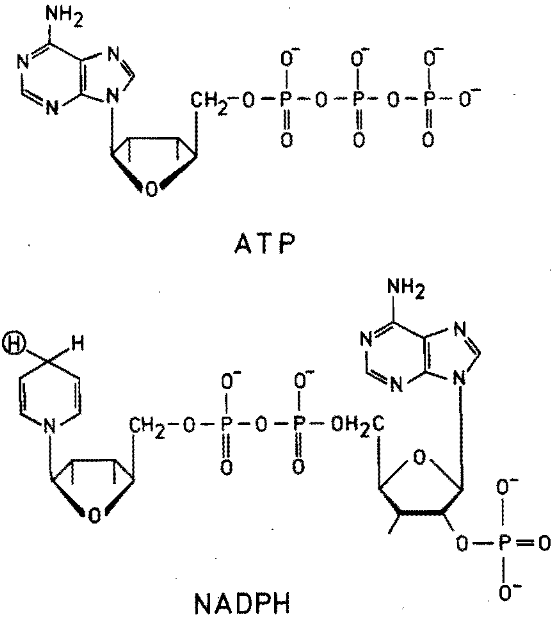


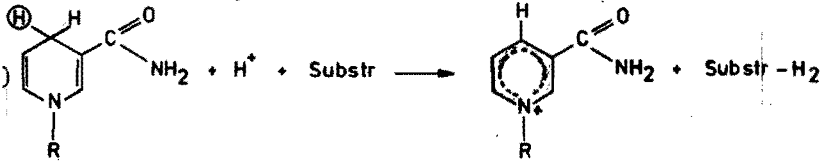
Fig. 1.

In biological systems, ATP serves as an energy-carrier. Splitting of one or more of the anhydride phosphate linkages in ATP releases much free energy, for instance:

(1).... $\text{ATP} \longrightarrow \text{ADP} + P_i$ ; $\Delta G^o = -7.0\ \text{kcal.mole}^{-1}$.

NADPH (or NADH, which is an analogous compound missing the phosphate ester on the 2'-position of the ribose ring) serves as the most important source of hydride ions. Reduction of a substrate is usually accomplished by the transfer of a hydride ion from NADH or NADPH with the concurrent uptake of a proton from the aqueous medium:

(2)



In the glucose producing *Calvin*-cycle[2], reactions (1) and (2) are coupled enzymatically in the reduction of the C=O group of 3-phosphoglycerate to an aldehyde group (glyceraldehyde-3-phosphate). This latter compound is used to form glucose and ribulose-5-phosphate in another enzymatically catalysed process, called the"pentose shunt". Ribulose-5-phosphate is once more energized by ATP and reacts subsequently with free $CO_2$ in an enzymatic process catalysed by diphosphoribulose carboxylase. Two molecules of 3-phosphoglycerate are formed and the *Calvin*-cycle starts anew. Note that the glucose forming reactions are driven by the energy supplied by ATP and the reducing power supplied by NADPH. In this way the energy of light is ultimately stored as reducible compounds. In quite analogous fashion the formation of fats, which represent a class of even more reduced, i.e. energy-richer substances than the sugars, is also driven by ATP and NADPH.

In animal cells the energy stored in reducible compounds (sugars, carbohydrates and fats) is released via accurately balanced oxidative processes. $NAD^+$ serves as the important hydride acceptor (= oxidator) in the mitochondria of animal cells. During these oxidative processes, ATP is formed from ADP and phosphate groups.

In the well known *Krebs*-cycle[2], activated acetic acid, derived from fats and sugars and present as $CoAS{\sim}CO.CH_3$, is "burnt" to $CO_2$ and NADH plus other high-energy compounds (such as GTP and FAD). The energy of NADH is released in a chain of reactions called the "respiratory chain". The stepwise oxidation-reactions in the chain lead to the formation of three molecules of ATP for each molecule of NADH oxidized and the ultimate formation of water from oxygen and the transferred hydride ions plus protons. Though the chain is composed of many complex enzymatic reactions, the overall-reaction may be represented by:

$$(3)\ldots\ \text{Substr.}H_2 + \tfrac{1}{2}O_2 + 3\ \text{ADP} + 3P_i \longrightarrow \text{Substr.} + H_2O + 3\ \text{ATP}.$$

In figure 2 the respiratory chain is schematically drawn and a few important cycle-reactions are included.

The important reactions of the "respiratory chain" involve either hydride transfer reactions or electron transfers, accompanied by proton transfers. In this respect there is no essential difference between these enzymatically catalysed reactions and red/ox reactions in organic chemistry. In the latter case, reduction is also accomplished by the transfer of either "free" hydride ions (i.e. hydrogen with both bonding electrons) or by the cooperative action of electrons and protons. The metalhydrides ($LiAlH_4$, $NaBH_4$, LiH etc.) are reduc-

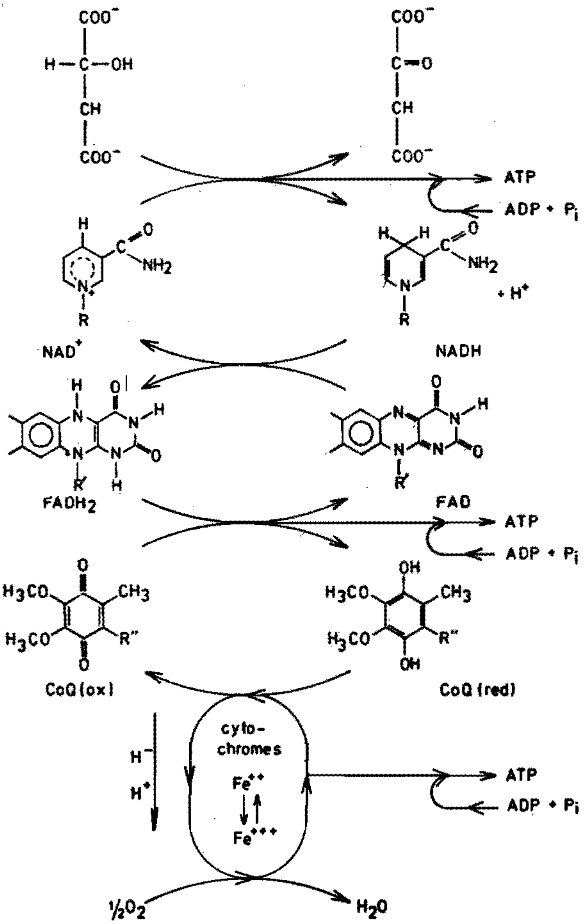


Fig.2. The "respiratory chain".

tors of the first kind, but also many organic compounds forming stable cations (such as cycloheptatriene and triphenylmethane). The alkali and the alkaline earth metals form reductors of the second type (e.g. *Birch*-reduction or reduction via *Grignard*-compounds).

Biochemical reduction by NADH or NADPH always involves the transfer of a hydride ion together with a proton in an enzymatically catalysed reaction. Formally, one can speak of the transfer of an $H_2$ molecule. Two important properties of enzymes are responsible for the catalytic rate enhancement and the stereospecificity of enzymatic reactions, viz. the stereospecific binding on and the bifunctionality of the catalytic site. Most enzymes are very large protein-chains with a very ordered geometry (the so-called tertiary structure) while the reactive site itself is often surprisingly small. As far as we know now, every enzymatic reaction starts with properly orienting the molecule (or molecules) near the catalytic site of the enzyme. In this way the right scene is created for the reaction that is bound to occur or, as one could say, the molecules are oriented in a stimulating surrounding so that reactions, which would require much more drastic conditions otherwise, can proceed very fast and very stereospecific.

As an example consider the reaction between $NAD^+$ and an aldehyde (glyceraldehyde-3-phosphate) catalysed by a dehydrogenase enzyme[3]. (See figure 3). In this reaction $NAD^+$ is first properly oriented and bound on the catalytic site of the enzyme and a sulphur-carbon bond is formed. The incoming aldehyde is protonated, presumably by the thiolic proton, and the hydride transfer per se is accomplished by the fast nucleophilic attack of sulphur on the developping carbenium ion center under the concurrent release of a proton with its pair of bonding electrons (i.e. a hydride ion is transferred). Due to the stereoselective binding on the catalytic site, the hydride ion transfer is also stereospecific. Furthermore, the bifunctionality of the catalytic site is introduced here by the presence of a reducible thiol group, the acidity of which is greatly enhanced by the formation of the sulphur-carbon bond and the presence of an oxidizable group capable of adding to NAD$^+$.

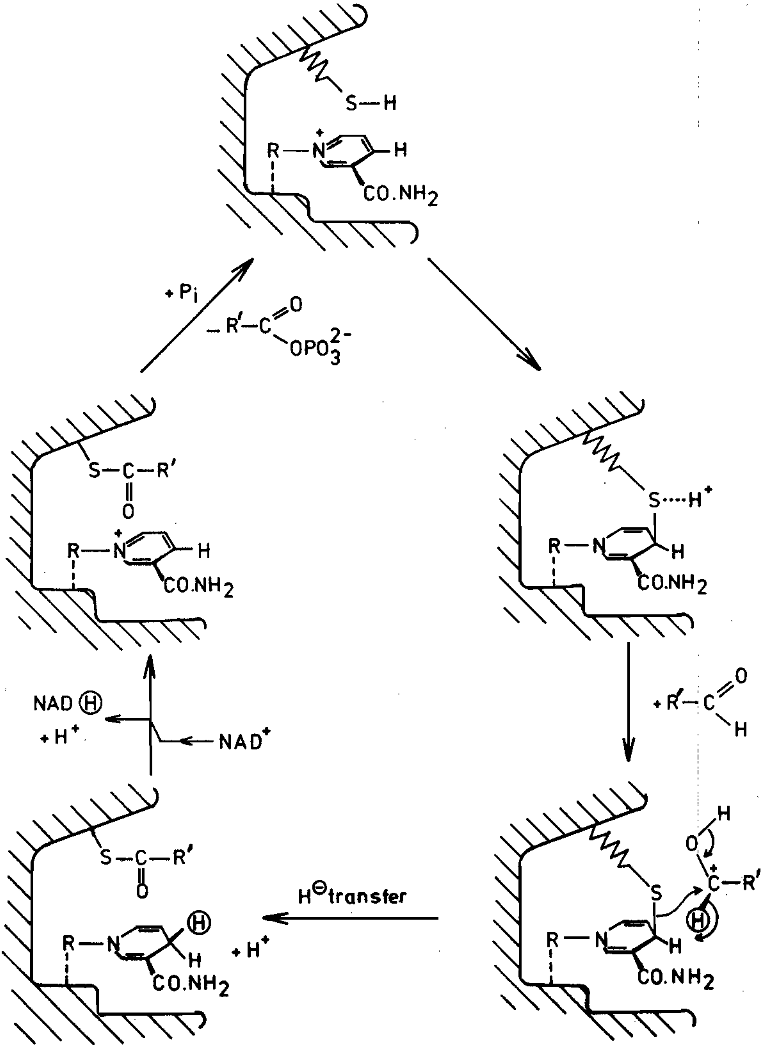


Fig. 3. Dehydrogenase catalysed hydride transfer between NAD$^+$ and glyceraldehyde-3-phosphate.

Reactions occurring in vitro between reducible compounds and hydride donors often also show stereoselectivity. The reduction of ketones by means of *Grignard*-reagents, for instance, proceeds in a stereoselective way. The β-hydrogen atom of the *Grignard*-compound is transferred as an hydride in a cyclic transition state (see figure 4). Deuterium labelling[4] and the use of optically active *Grignard*-reagents[5] revealed the stereospecific nature of the transition state.

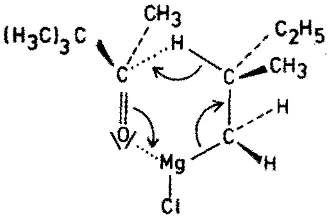


Fig. 4. Reduction of methyl,tert.-butylketone by an optically active *Grignard*-reagent.

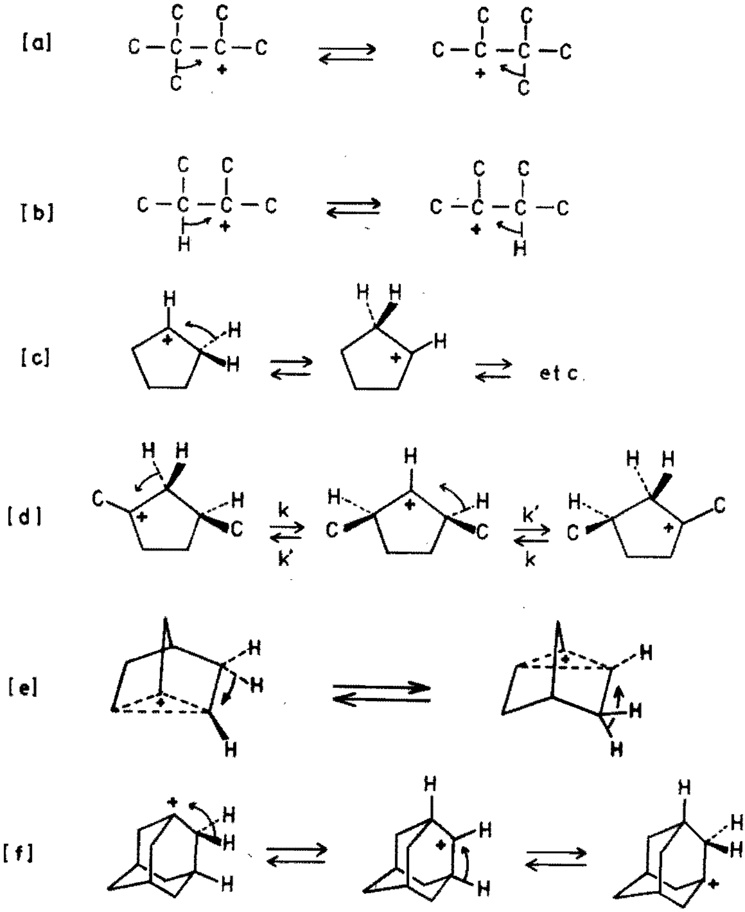
It may be noted that the phenomenon of bifunctionality plays a rôle in these reactions quite analogous to the enzymatically catalysed hydride transfer reactions. Due to bond polarization in the C=O bond, both an acidic and a basic center are present in the same molecule, capable of liganding with the metal and the developping hydride ion at the same time. Thus, cyclic transition states emerge and these features are found back in the well known *Meerwein-Ponndorf* reductions and *Oppenauer* oxidations[6].

Furthermore, it may be noted, that the liberation of the reduced compound (i.e. the alcohol) requires the addition of protons, usually in a discrete second step. Formally, however, we may say that a hydride ion plus a proton are transferred to achieve the reduction of a carbonyl compound to its corresponding alcohol.

## I.2. INTRAMOLECULAR RED/OX REACTIONS IN HYDROCARBONS: HYDRIDE AND ALKIDE SHIFTS.

The generation of carbenium ions (for the nomenclature on carbocations: see ref.7) may be followed by rearrangements leading to more stable products. Either intramolecular or intermolecular hydride or alkide shifts may occur. Both reactions are of fundamental importance for the formation of high-octane fuels in acid catalysed cracking and branching processes carried out in refineries. A few examples of intramolecular shifts are given in figure 5. These examples are merely illustrative; for more detailed information concerning intra- and intermolecular hydrogen- and methyl-migrations, see refs. 8 and 9.

Note that reactions (a) and (b) represent tertiary-tertiary shifts; H-shifts are faster than $CH_3$-shifts, presumably due to steric reasons. Secundary-secundary shifts (c) are also very fast, as indicated by the fact that cyclo-pentyl cations are observed[10] in PMR spectra as singlets ($\delta$ = -4.75 ppm.) at temperatures as low as -130° C. The lower stability of secundary carbenium ions as compared to tertiary ions causes the secundary-tertiary shift (k in (d)) to be rather slow. In the reverse case (k' in (d)) it is quite the opposite: tertiary-secundary shifts are very fast indeed. Non-classical stabilization (as in (e)) lowers the rate of 1,2-hydride shifts tremendously while the same occurs when unfavourable orbital orientation[11] (as in (f)) introduces a high potential barrier for the 1,2-shift. The rather slow proton exchange in hexamethylbenzenium ions (about 18 $sec^{-1}$ at -100° C)[12], which can be regarded as consecutive 1,2-hydrogen shifts, may be due to the above mentioned factors: unfavourable orbital orientation ( in the rigid pentadienyl ring, rotation around C-C bonds is impossible) and the loss of resonance stabilization in the transition state. Both factors may decrease the exchange rate (cf. with tert.-tert. shifts :$10^4$ to $10^5$ $sec^{-1}$ at -100°C).



(a) $k > 5 \times 10^{3}\ \mathrm{sec}^{-1}$ ($-180^{\circ}$C)
(b) $k > 10^{4}\ \mathrm{sec}^{-1}$ ($-100^{\circ}$C)
(c) $k > 10^{4}\ \mathrm{sec}^{-1}$ ($-130^{\circ}$C)
(d) $k \approx 10\ \mathrm{sec}^{-1}$ ($-40^{\circ}$C)
$k' > 10^{4}\ \mathrm{sec}^{-1}$ ($-40^{\circ}$C)
(e) $k = 2.9 \times 10^{-3}\ \mathrm{sec}^{-1}$ ($-2^{\circ}$C)
(f) $k < 2 \times 10^{-5}\ \mathrm{sec}^{-1}$ ($+105^{\circ}$C).

Fig. 5. 1,2-Shifts in alkyl carbenium ions. (from ref. 9 and references cited therein.)

That the occurrence of alkyl carbenium ions is not restricted to strongly acidic conditions and low temperatures is nicely demonstrated by one of the key-steps in the biosynthesis of sterols, viz. the enzymatically catalysed cyclization of squalene to lanosterol. *Bloch* and *Chen*[13] showed that cyclization of squalene in the presence of $^{2}H_2O$ or $H_2{}^{18}O$ did not result in labelled lanosterol, while cyclization in the presence of $^{18}O_2$ gave lanosterol, specifically labelled with $^{18}O$ in the hydroxyl group. *Van Tamelen* and co-workers[14] demonstrated that the first step of the oxidation-cyclization process is the formation of 2,3-epoxysqualene. Once formed, this intermediate can be converted anaerobically to lanosterol. Squalene-epoxydase and epoxysqualene-cyclase, respectively, catalyse these reactions.

As has been noted already (page 5), every enzymatic reaction starts with properly orienting the substrate(s) near the catalytic site of the enzyme. In the case of the cyclization of 2,3-epoxysqualene it has been suggested[15], that the conformation of 2,3-epoxysqualene in the substrate-cyclase complex is such, that the π-orbital interactions favour the formation of proto-lanosterol, presumably in a concerted process. The coiling of the molecule (see figure 6) already resembles the product that is to be formed. Cyclization is initiated by the attack of a proton (or another strong electrophile) on the epoxyde bond, generating a tertiary carbenium ion center on C(2). Presumably in a concerted process, σ-bonds are formed between C(2) and C(7) and between C(6) and C(11), respectively, while the positive charge shifts to C(10). Note that C(6) and C(10) are tertiary centers. In the enzymatic reaction, the third ring is also six-membered indicating ring closure between C(19) and C(15), while a secundary carbenium ion is formed on C(14) in this step. Some unknown interaction between the enzyme and C(14) of epoxysqualene may be operative and, presumably, the favourable orientation of the C(15) π-lobe, which is directed towards the C(10) π-lobe, also forces the formation

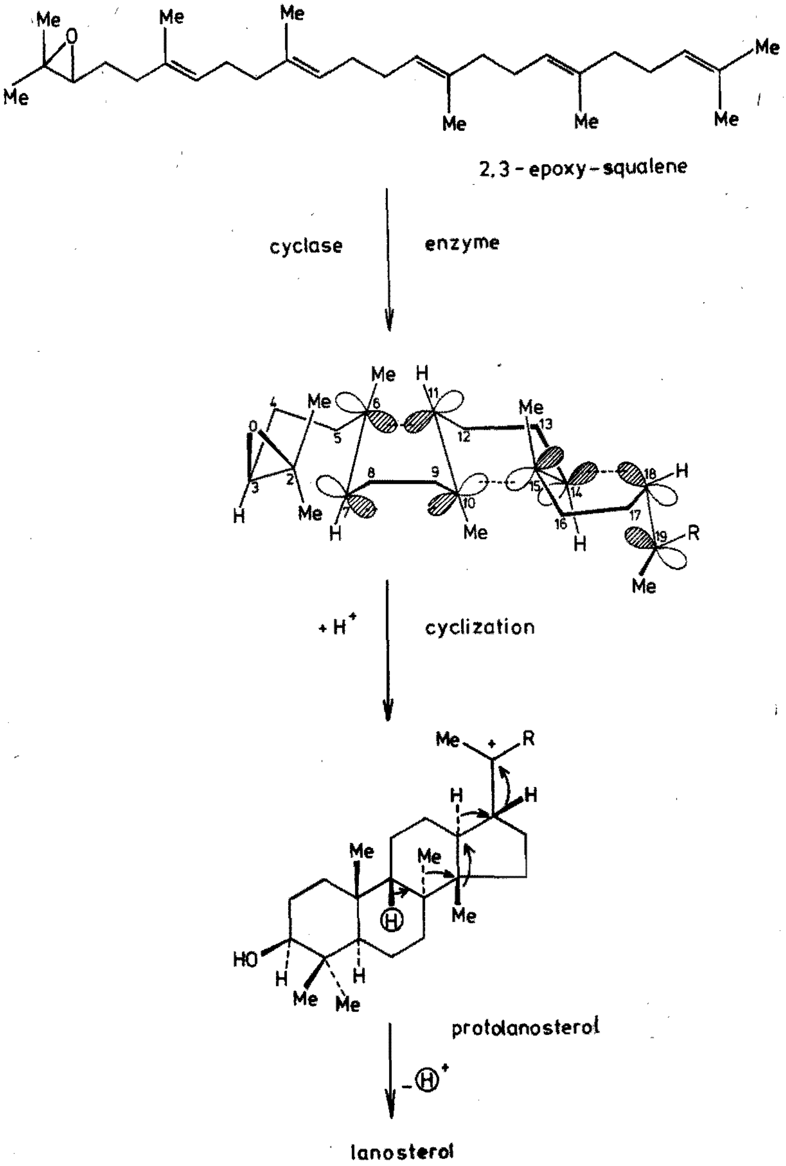


Fig. 6. Enzymatically controlled cyclization of 2,3-epoxy-squalene to protolanosterol.

of a C-C bond between these two carbon atoms. Proto-lanosterol is finally formed upon the attack of C(14) on C(18).

The non-enzymatic cyclization of 2,3-epoxysqualene differs from the enzymatic process in that the reaction stops at the formation of a tricyclic compound[16], having a five-membered C ring (see figure 7). Thus, in this case the tertiary carbenium ion center on C(10) attacks C(14), generating the more stable C(15) carbenium ion. On quenching this ion gives mainly the tricyclic alcohol due to deprotonation of the $CH_3$-group on C(15). However, a substantial amount of rearranged product is found, containing a double bond between C(10) and C(11), indicating that in the non-enzymatic ring closure 1,2-hydrogen-shifts are as rapid as deprotonation.

The formation of lanosterol from protolanosterol involves two consecutive 1,2-hydride shifts and two 1,2-methide shifts, and the subsequent removal of hydrogen on C(11) as a proton[17], generating a double bond. This rearrangement is also enzymatically controlled and probably a second catalytic site of the cyclase enzyme is involved[18].

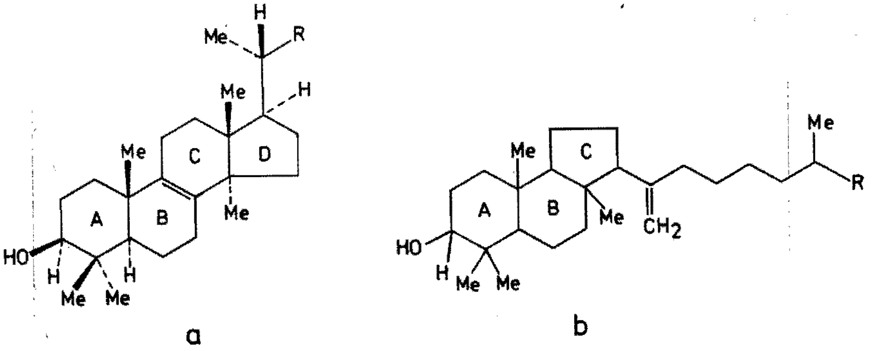


Fig. 7. (a) Lanosterol; (b) Tricyclic product from the non-enzymatic ring closure of 2,3-epoxysqualene.

## I.3. INTERMOLECULAR HYDRIDE TRANSFERS.

According to *Deno* et al.[19] the characteristic features of hydride transfer reactions are: (1) the hydride ion does not exchange with labile protons from the medium nor does it react with these protons to form molecular hydrogen, and: (2) the carbon atom accepting the hydride ion must have an actual or potential open sextet of electrons. Carbenium ions clearly fulfil condition (2), but also any unsaturated carbon compound may be capable of shifting electrons away to neighbouring atoms and thus serve as a hydride acceptor. Olefins and carbonyl compounds often can be readily reduced by hydride-donors under acidic conditions (*Brönsted* or *Lewis* acids may be used).

The rapidity of hydride transfer reactions between (transient) carbenium ions and tertiary alkanes was demonstrated in a very elegant way by *Bartlett, Condon* and *Schneider*[20] in 1944. Within $10^{-3}$ sec., isobutane or propane were formed at $25^{o}$ C when a solution of $AlBr_3$ in isopentane was allowed to react with tert.-butyl chloride or isopropyl chloride. Furthermore, an equivalent amount of tert.-amyl bromide was formed.

Since that time a large number of observations has been published dealing with hydride transfers between tertiary alkanes and alkyl or aryl carbenium ions. It was generally believed that acids were necessary only to generate the carbocations, either due to an oxidizing action (as in the case of the deuteration of the methyl-groups of isobutane in $D_2SO_4$, studied by *Otvös* et al.[21]) or due to its solvolysing or protonating ability (as in the case of the acid catalysed disproportionation of 4,4'-dimethoxy-diphenylmethanol, studied by *Bartlett* et al.[22]).

The introduction, early in the sixties, of very strong acids (such as $HSO_3F$, $HF/SbF_5$ and $HSO_3F/SbF_5$) together with the application of PMR and later $^{13}$CMR spectroscopy resulted in a steadily growing number of publications concerned with carbocations. This field has been reviewed by several authors[8,9,13]. In this connection the work of *Olah* and co-workers and of

*Brouwer, Hogeveen* and colleagues deserves special attention. Actually, hydride transfer belongs to the general class of electrophilic substitution reactions and it goes without saying that knowledge concerning hydride transfer reactions also increases our understanding of electrophilic reactions in general.

Kinetic studies on intermolecular hydride transfers are limited to reversible reactions, with a few exceptions. The reversible hydride exchange between isobutane and tert.-butyl cations has been studied by *Brownstein* and *Bornais*[24] in $SO_2/CH_2Cl_2$ solutions containing $AsF_5$ and by *Olah* et al.[25] in $SO_2ClF$ containing $HSO_3F/SbF_5$ (1:1). In both cases the bimolecular rate constant was found to be about $10^4$ $l.mole^{-1}.sec^{-1}$ at -40° C. Deuteride exchange between 2-$^2$H-isobutane and tert.-butyl cations proved to be about five times slower, indicating a rather small isotope effect ($k_H/k_D$). It may be noted that exchange of label with protons is much slower than the hydride exchange reaction, in accordance with the definition of *Deno*[19].

*Kramer*[26], studying the solvolysis of 2-Cl-2-$CH_3$-pentane in the presence of methylcyclopentane in $HSO_3F/SbF_5$, found 97.6 % of unrearranged 2-methylpentane together with 2.4 % of rearranged product (viz. 3-methylpentane). From the known rate of the methide shift in 2-methylpentyl carbenium ions he estimated the concurrent tertiary-tertiary hydride transfer to have a rate of at least 200 $l.mole^{-1}.sec^{-1}$ at -50° C.

Methylated benzyl cations (e.g. pentamethylbenzyl cations) and some aromatic radical cations (such as perylene$^+$, tetracene$^+$) are excellent hydride acceptors[27]. Isoalkanes react very fast with these cationic hydride acceptors but also secundary alkanes are reactive. Even primary alkanes have been reported to donate hydride ions as well as molecular hydrogen. The reaction between pentamethylbenzyl cations and isobutane is clearly acid catalysed and in $HSO_3F$ the rate is at least 60 $l.mole^{-1}.sec^{-1}$ at -65° C[28].

Intermolecular proton exchange and carbon-hydrogen bond protolysis are important side reactions that may interfere with hydride transfer reactions in strong acids. With deuterated alkanes, the following reactions may occur:

(4)... $R_1\text{-}D + H^+..X^- \longrightarrow R_1^+ + HD + X^-$

(5)... $R_1\text{-}D + H^+..X^- \longrightarrow R_1\text{-}H + D^+..X^-$

(6)... $R_1\text{-}D + R_1^+ \longrightarrow R_1^+ + R_1\text{-}D$

(7)... $R_1\text{-}D + R_2^+ \longrightarrow R_1^+ + R_2\text{-}D$

In principle, all reactions (4)-(7) are reversible, but (4) and (7) can be made quasi-irreversible by a proper choice of the reaction conditions. For $R_1$ = tert.-butyl and $X^-$ = $SbF_6^-$ the rates of reactions (4), (5) and (6) differ markedly under the same reaction conditions . Reaction (6) is by far the fastest with a rate constant[24,25] of about $10^4$ $l.mole^{-1}.sec^{-1}$. at -40° C. Extrapolation to 0° C and assigning the value one to the latter rate constant, relative rate constants of $10^{-8}$, $10^{-6}$ and 1 $l.mole^{-1}.sec^{-1}$, respectively, are calculated for reactions (4)-(6)[31]. These values reflect the much lower deuteride (or hydride) abstracting power of acidic protons, or, in other words, the much higher electrophilicity of alkyl carbenium ions.

The positive charge of protons is undoubtedly delocalized much more than in the case with alkyl cations, due to the much stronger solvation of protons, even in solvents with a very low nucleophilicity. The oligomerization[29] of methane and other alkanes, which occurs in $HSO_3F/SbF_5$ (1:1) at high pressures and temperatures between +60 to +160° C has been attributed to protolytic attack on methane with the formation of transient methyl cations and molecular hydrogen. The formation of trimethylcarbenium ions from isobutane and $SO_2/SbF_5$ at low temperatures, on the other hand, has been ascribed to the hydride abstracting power of $SbF_5$ (*J. Lukas*, quoted in ref. 11). It is known since long that *Lewis* acids, such as $AlCl_3$, $PCl_5$, $BF_3$, $SbCl_5$ and $SbF_5$, are powerful hydride-abstractors (cf. the formation of tropenylium ions[30] from cycloheptatriene and

$SbCl_5$). Therefore, it has been argued that in $HSO_3F/SbF_5$ (1:1) free $SbF_5$ is responsible for the formation of alkyl cations[32].

Tertiary butyl cations react with molecular hydrogen in $HF/SbF_5$ solutions (dilute in $SbF_5$) and the kinetics of this reversible reaction have been investigated by *Hogeveen* et al.[31] Reduction of tert.-butyl cations by $H_2$ was found to be rather slow: $3.5 \times 10^{-4}$ $l.mole^{-1}.sec^{-1}$ at -16 °C, while reduction of cyclopentyl cations or 2-propyl cations is much faster: about $10^{-1}$ $l.mole^{-1}.sec^{-1}$ at -73° C.

## I.4. PROTONATED ALKANES AS INTERMEDIATES IN PROTOLYTIC HYDRIDE TRANSFER REACTIONS.

The existence of $CH_5^+$ and other protonated alkanes under mass-spectrometric conditions nowadays is firmly established[33]: *Field* and *Munson*[34] suggested that $CH_5^+$ can act in the gas-phase either as a *Lewis* acid, abstracting hydride ions from (cyclo)-alkanes with the formation of $CH_4 + H_2$, or acts as a *Brönsted* acid, donating a proton to the alkane with the subsequent removal of this same proton and a hydride as an $H_2$ molecule from the alkane. In the reaction between $CH_5^+$ and cyclo-$C_6D_{12}$, mainly $C_6D_{11}^+$-ions were formed and proton-deuteron scrambling in these ions was not observed. *Field* and *Munson* concluded, that if $CH_5^+$ behaved as a proton donor, the bonding between the entering proton and the cyclo-alkane was rather different from the bonding between the C-atoms and the originally present D-atoms.

*Cacace* and *Speranza*[35] showed, that the gas-phase tritiodeprotonation of meso-1,2-difluoro-1,2-dichloro-ethane by means of the extremely strong *Brönsted* acid $^3He^3H^+$ (generated through the radioactive decay of $^3H_2$) occurs via a retention mechanism. This observation indicates a $C_s$-symmetry for the transition state (see figure 8).

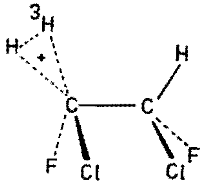


Fig. 8.

The methonium ion ($CH_5^+$) has been the subject of many quantummechanical calculations[36] and the $C_s$-symmetry (see figure 9) is generally agreed to be the most stable of the various possible configurations, though the calculated energy differences are rather small.

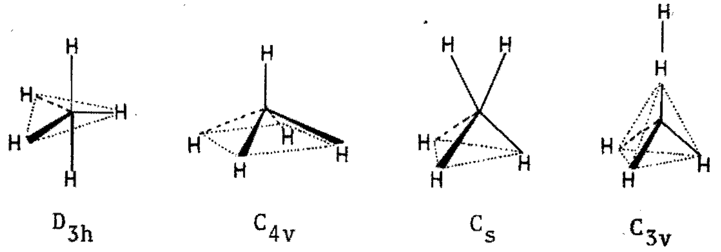


Fig. 9. Some possible geometries for protonated methane ($CH_5^+$).

The existence of $CH_5^+$ and related five-coordinated carbocations in solution remains speculative as these species have never been observed directly by spectroscopic techniques until now. Based on the observed chemistry of methane in very strong proton acids, *Olah* et al.[37] suggested the occurrence of $CH_5^+$ with $C_s$-symmetry as a reactive intermediate. Their main argument for the suggested geometry is, that electrophilic attack will take place on the main lobes of the $sp^3$-orbitals, i.e. in the region in C-C or C-H bonds where the electron density is highest. Furthermore, it has been argued that attack leading to $C_s$-like transition states is more probable for steric reasons[38]. Proton-deuteron exchange in adamantane, labelled on the tertiary positions, corroborates this view.

On the other hand, free $SbF_5$ may be responsible for the observed chemistry of $CH_4$ in $HSO_3F/SbF_5$ (1:1), as $SbF_5$ may abstract $H^-$ from methane, generating $CH_3^+$ ions. The observation that $H_2$ was not evolved in stoichiometric amounts[39] supports this view[9]. It should be noted that, although protolytic reactions may be thought to proceed via $C_s$-like transition states, it is not necessary to assume the same kind of transition states for non-protolytic reactions (e.g. $H^-$-transfer between isobutane and tert.-butyl cations). In the latter case, linear transition states rather than triangular, $C_s$-like transition states may occur due to steric reasons.

The problem of the geometry of penta-coordinated carbon species still seems to be unresolved and even the presence of $CH_5^+$ and related protonated alkanes is speculative. Though many arguments favour $C_s$-like transition states for proton-exchange, hydrogen-formation and hydride exchange reactions (for instance: the low or negligible isotope effects for the proton exchange between deuterated methane[38], ethane[40] and isobutane[28b] with strong proton acids and the low rate for methide-transfer between neopentane and tert.-butyl cations[38] compared with the fast hydride exchange between isobutane and tert.-butyl cations[24,25]), the occurrence of linear transition states can not be ruled out.

The postulated $C_s$-symmetry for five-coordinated alkanonium ions remains controversial, although it should be noted that it is by no means necessary that $C_s$-like transition states should be symmetrical, as has been pointed out by *Olah*[7] on steric grounds and, more recently, by *McIver*[41] based on a group-theoretical analysis.

The hydride transfer reaction between alkanes and methylated benzyl cations showed some remarkable features which prompted a more detailed investigation. A few salient points may be noted concerning the reaction, which forms the subject of this thesis. First of all it turned out, that this hydride transfer reaction is acid catalysed in a true sense, i.e. protons play a rôle in the transition state. From the observation, that the rate of hydride transfer from isoalkanes to pentamethylbenzyl cations was found to depend linearly on the proton-activity $a_{H^+}$ ($\log(k) = -H_0 + \text{constant}$), it followed that one proton participates in a termolecular transition state or intermediate. Furthermore, carrying out the reaction in tritiated acids or with specifically labelled isoalkanes (deuterium as well as tritium were used), scrambled products were obtained. Exchange of transferred hydride (or: deuteride, tritide) was found to occur during the transfer step per se; proton exchange prior to the actual hydride transfer step or after the actual transfer step could be ruled out as a source of scrambling. Finally, variously substituted benzyl cations turned out to be nearly equally reactive towards isobutane and other isoalkanes, in spite of the quite different stabilities of the benzyl cations used. This points out, that the rate limiting step preceeds the actual hydride step.

Another remarkable feature which should be mentioned here is the fact, that quinones could be reduced quantitatively, by isoalkanes in the presence of catalytic amounts of pentamethylbenzyl cations, whereas no reaction at all occurred in the absence of benzyl cations. (See figure 10).
The resemblance of figure 10 with the "respiratory chain" is noteworthy (see figure 2 of this chapter).

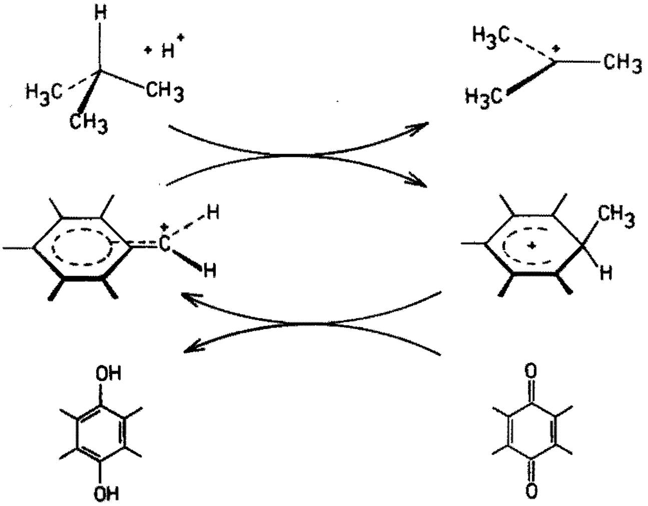


Fig. 10. Catalysed hydride transfer between isobutane and quinones.

It is assumed that the reactivity of benzyl cations is caused by the bifunctionality of the system, i.e. a hydride-accepting group and a proton-accepting group are both present in the same molecule close to each other, enabling the transfer of a transient proton-hydride pair from solvated, or protonated, isobutane molecules. Due to the much smaller polarization of the C=O bonds in quinones, compared to the $C-CH_2^+$ bond of benzyl cations, reduction of quinones requires other hydrogen donors in which the charge separation between the transferable proton-hydride pair is much larger, such as is the case in protonated hexamethylbenzene. In this context, a close parallel is found between these red/ox reactions and enzymatically controlled reductions.

*

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# CHAPTER II

## Generation and Properties of Benzyl Cations.

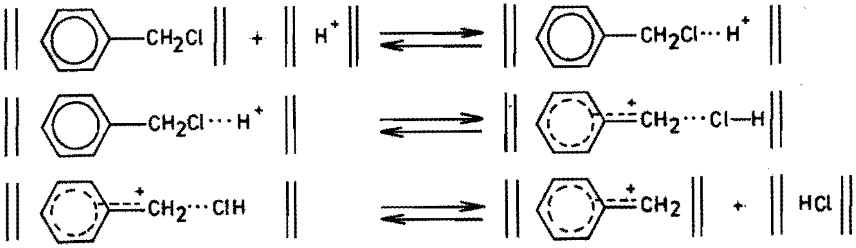
### II.1. INTRODUCTION.

The cleavage of a carbon-halogen bond in benzyl halides has been studied under a wide variety of conditions. Nucleophilic displacement reactions have received special attention[1]. In weakly nucleophilic, polar solvents these reactions usually occur via a $S_N1$-mechanism[2]. Depending on the dielectric constant of the solvent, the nucleophilicity of the leaving group and the stability of the benzyl cation, either free carbenium ions or ion-pairs may be present as reactive intermediates[3].

The generation of benzyl cations as long lived, more or less stable, intermediates requires the use of strong, anhydrous acids as solvents, usually at low temperatures to prevent decomposition of the generated benzyl cations[4]. Either *Brönsted* acids (e.g. $H_2SO_4$, HF, $HSO_3F$ or $CF_3SO_3H$) or *Lewis* acids (such as $SbF_5$, $BF_3$, $PF_5$ or $AlCl_3$) or mixtures of these (the so-called "super-acids" such as $HSO_3F/SbF_5$) are suitable solvents in carbocation chemistry because of their very low nucleophilicity. Liquid $SO_2$ or $SO_2ClF$ may be added as rather inert diluents.

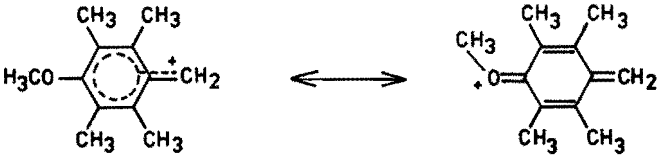
The formation of benzyl cations is either initiated by proton attack on the parent halide followed by cleavage of the C-Cl bond[5], or it is accomplished by the direct abstraction of halide ions by a Lewis acid.

In both cases the rate of bond cleavage is enhanced by solvation of the polar transition state and the energy of the intimate ion-pair initially formed may be further reduced by solvation of the two separated ions. Using *Winstein*'s notation, the process may be visualized as follows:



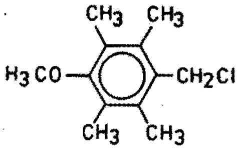
In strong anhydrous acids HCl behaves like a base and protonation[6] of HCl will shift all equilibria to the right. The actual driving force of the solvolytic process is the energy, gained by solvation of the generated ions. As *Gold* has pointed out, this gain in energy may be substantial[7]. The lowering of the energy of the tertiary butyl cation by solvation with water may be in the order of 50 kcal/mole., for example.

Even under the most favourable conditions, such as very low temperatures, very low nucleophilicity of the solvent and the exclusion of moisture, the generation of the primary phenyl carbenium ion (benzyl cation) as a long lived intermediate has never been accomplished until now, due to the concurrent polymerization reaction. Chromium-tricarbonyl complexed benzyl cations[8] and para-methoxy substituted benzyl cations[9] are the only known mono-substituted benzyl cations to date. These ions can be observed as stable particles because the positive charge is extremely well delocalized into the substituents.

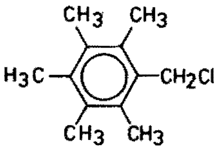


Alternatively, polymerization reactions between benzyl cations and their precursors may be effectively blocked by the introduction of substituents, such as fluorine or methyl, which are poor leaving groups in electrophilic substitution reactions[10]. The substitution of hydrogen by methyl-groups or fluorine not only prevents polymerization, but also stabilizes the cation due to hyperconjugation. Substitution thus may have a twofold effect, viz. delocalization of positive charge and "blocking" of polymerization side reactions.

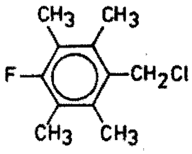
Based on the above mentioned considerations, the following benzylchlorides were chosen as starting materials to study the effect of substituents on their solvolytic behaviour, stability and reactivity towards hydride donors:



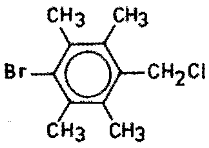
Ia



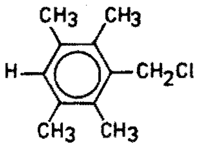
Ib



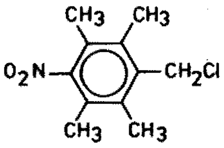
Ic



Id



Ie



If

## II.2. UV/VIS SPECTRA OF SUBSTITUTED BENZYL CATIONS.

Dilute solutions of different substituted 2,3,5,6-tetramethyl benzyl chlorides I(a-f) were prepared in four solvents with increasing acidity: concentrated $H_2SO_4$, an equimolar mixture of $H_2SO_4$ and $HSO_3F$, neat $HSO_3F$ and a mixture of $HSO_3F$ with $SbF_5$ (3.6:1 molar ratio), having Hammett acidities of -12, -13, -15 and -19.5, respectively[11].

On solvolysis compounds I yield the corresponding benzyl cations II, which are intensely coloured (from red to purple-blue) and show characteristic absorptions in the 300-650 nm. region.

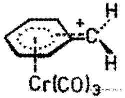
Solutions containing $10^{-4}$ mole.$1^{-1}$ of I(a-f) were made by mixing 10.0 μ 1. of a solution of the parent chloride in $CH_2Cl_2$ with 2.5 ml. acid and the UV/VIS spectra of these solutions were recorded at $14.8^{o}$ C. Increasing absorption at a certain wave-length was taken as evidence for increasing solvolysis, neglecting minor changes due to solvent effects. The results are summarized in table I. Only the data for the two long-wave absorptions are given as these are characteristic for benzyl cations. The absorptions in the 200-300 nm. region may be due to unsolvolysed benzylchlorides as well as to the corresponding cations II. Included in table I are the data for ions IIa, IIb and IId as given by *Olah* et. al.[12] and those of the tricarbonylchromium(0)-complexed benzyl cation[8].

As can be seen in table I, halides Ia and Ib solvolyse completely in every solvent used, whereas Ic and Id solvolyse only partially in concentrated $H_2SO_4$. Quantitative solvolysis of Id occurs in stronger acids, such as $HSO_3F$ and $HSO_3F/SbF_5$. Though Ic solvolyses only partially in $H_2SO_4$, also, more ions IIc are generated in this solvent than is the case with IId as can be judged from the larger calculated molar absorptions. Neglecting solvent effects and using the molar extinction coefficients for the long-wave absorptions of IIc and IId in $HSO_3F/SbF_5$ (in which solvent complete solvolysis occurs, as shown by PMR), one calculates about 10 % solvolysis for Id in concentrated $H_2SO_4$ and about 65 % for Ic under the same conditions.

Compound Ie is merely protonated in $H_2SO_4$ and $H_2SO_4/HSO_3F$ as can be concluded from the light-brown colour of the solution and from the rather intense band at 460 nm. In $HSO_3F$ a

Table I

UV/VIS spectra[a] of solutions of ions II in different acids.

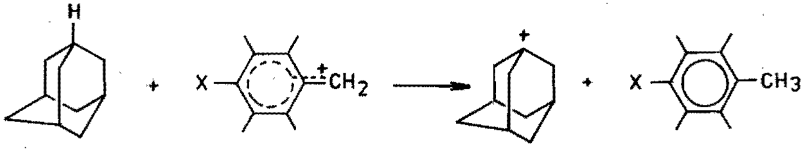
| Acid | $H_2SO_4$ (neat) | $HSO_3F/H_2SO_4$ (1:1) | $HSO_3F$ (neat) | $HSO_3F/SbF_5$ (3.6:1) | $HSO_3F/SbF_5$ (1:1,-50°) |
|---|---|---|---|---|---|
| Chloride | This work | | | | Ref. 12. |
| Ia | 435(0.10) | 430(0.12) | 425(0.11) | --- | 420(0.07) |
| | 335(2.30) | 330(2.40) | 335(2.50) | --- | 334(2.40) |
| Ib | 510(0.15) | 500(0.16) | 515(0.18) | 529(0.21) | 520(0.21) |
| | 334(1.50) | 330(1.40) | 330(1.60) | 330(1.60) | 330(1.70) |
| Ic | 475(0.14) | 470(0.15) | 480(0.17) | 480(0.17) | --- |
| | 315(0.79) | 315(1.05) | 315(1.45) | 315(1.45) | --- |
| Id | 490(0.02) | 480(0.16) | 510(0.20) | 540(0.24) | 540(0.24) |
| | 345(0.22) | 350(0.70) | 365(1.70) | 364(1.40) | 364(1.20) |
| Ie | --- | 460(0.55) | 545(0.13) | 545(0.18) | --- |
| | 335(0.10) | 340(0.70) | 320(0.81) | 320(1.00) | --- |
| If | --- | 410, sh. | 420, sh. | 420, sh. | --- |
| | 345(0.10) | 350(0.40) | 345(0.74) | 330(0.85) | --- |
|  | 514(0.04) | dec. | --- | --- | --- |
| | 348(0.15) | dec. | --- | --- | --- |

[a] $\lambda_{max}$ in nm., calculated molar absorption (x $10^{-4}$) between brackets.

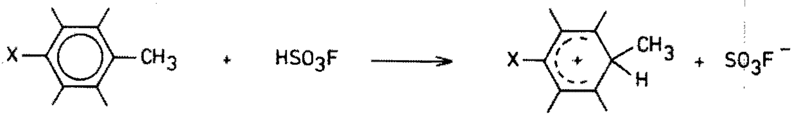
purple-blue solution is obtained showing a different spectrum with $\lambda_{max}$ at 545 nm. Addition of $SbF_5$ leads to increased absorption at this wave-length, pointing to increased solvolysis. Generation of cation IIf is extremely difficult , even in $HSO_3F/SbF_5$, due to the $NO_2$-substituent. Protonation of If predominates in strong acids (vide infra) and this side reaction presumably prevents solvolysis to a large extent.

At this point, the striking similarity between the UV/VIS spectra of cation IIb and of the $Cr(CO)_3$-complexed benzyl cation is noteworthy. The calculated absorptions of benzyl$^+$ are: 420(0.08), 290(0.55), 206(0.01) and 200(0.27) (nm, (oscillator strenght))[13,14]. Introduction of 5 $CH_3$-groups or complexation with $Cr(CO)_3$ leads to the same shift: 90 nm. *Hanazaki* and *Nagakura*[14] observed a same red-shift in α,α,2,4,6-pentamethylbenzyl cations and attributed this shift to steric hindrance between the ortho- and α-methyl groups. In the case of cation IIb, and especially for the $Cr(CO)_3$-complexed benzyl cation, this can hardly be a good explanation. Rather it must be assumed , that strong charge-transfer occurs from the substituents to the lowest vacant MO of the benzyl cation. Thus $Cr(CO)_3$ may be considered as an extremely good electron donor in accordance with the "metallic" character of this group. This charge-transfer stabilizes the cation tremendously ($\Delta$ $pK_a$ = 6 according to *Trahanovsky*[8]), but also considerably lowers the reactivity towards hydride donors.

To check if any unwanted side reactions had occurred between compounds I and the solvent, or cations II (sulphonation, formation of diphenylmethyl compounds or polymerization) a small amount of adamantane in $CH_2Cl_2$ was added to the $HSO_3F$-solutions of I(a-f) and the UV/VIS spectra were recorded subsequently. Adamantane is known to be an excellent hydride donor, stable in $HSO_3F$, while the adamantyl cation does not absorb above 200 nm. The UV/VIS spectra of the resulting solutions showed unambiguously the formation of the proton complexes of compounds III in each case.



II III



III IV

The UV/VIS spectra of pure reference compounds III in $HSO_3F$ at 14.8° C were nearly identical with those of the compounds formed from ions II via hydride transfer. This indicates that in no case irreversible side reactions had occurred and that compounds I either solvolyse cleanly or at the most undergo reversible protonation in the acids used.

The introduction of a stream of isobutane in dilute solutions of $Cr(CO)_3$-complexed benzyl cations in $H_2SO_4$ did not give any visible reaction within a few minutes. Only slow decomposition was observed after about 5 minutes, but this decomposition also occurs in the absence of hydride donors. This lack of reactivity supports the view of *Trahanovsky*[8] that stabilization of benzyl cations by $Cr(CO)_3$ is effected through electron-donation, leading to a decrease of the positive charge in the $CH_2$-group of the complexed benzyl cation.

## II.3. PMR MEASUREMENTS.

Solvolysis of chlorides I(a-f) could be accomplished in non-nucleophilic solvents at low temperatures. The ease of formation of cations II is, of course, strongly dependent on the para-substituent. Therefore, solvents with increasing solvolytic power had to be used going from Ia to If. The PMR data of Chlorides I(a-f) and of benzyl cations II(a-f) are summarized in table II.

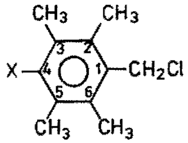
## Table II

PMR spectra[a,b] of chlorides I(a-f) and cations II(a-f).

| -X | | $\delta(CH_2Cl)$<br>$\delta(CH_2^+)$ | $\delta(CH_3)^{2,6}$ | $\delta(CH_3)^{3,5}$ | $\delta(X)$ | Solvent[d] |
|---|---|---|---|---|---|---|
| $-OCH_3$ | I | 4.75 | 2.30 | 2.20 | 3.70 | (1) |
| | II[c] | 8.25 | 3.00 | 2.70 | 5.05 | (2) |
| $-CH_3$ | I | 4.80 | 2.30 | 2.45 | 2.30 | (1) |
| | II[c] | 8.70 | 2.70 | 2.35 | 2.70 | (2) |
| -F | I | 4.55 | 2.15 | 2.00(d,1.5) | -- | (1) |
| | II | 8.70(d,2.5) | 2.80 | 2.30(d,1.5) | -- | (3) |
| -Br | I | 4.65 | 2.40 | 2.30 | -- | (1) |
| | II[c] | 9.05 | 2.90 | 2.70 | -- | (3) |
| -H | I | 4.70 | 2.20 | 2.15 | 7.00 | (1) |
| | II | 9.10 | 2.75 | 2.40(d,2.0) | 8.45 | (4) |
| $-NO_2$ | I | 4.75 | 2.10 | 2.35 | -- | (1) |
| | II | 9.40 | 2.75 | 2.55 | -- | (4) |

a. Shifts (in ppm.) relative to TMS. Multiplcity and J (in Hz.), between brackets.

b. The numbering is as follows:



c. See also ref. 12.

d. (1): $SO_2$, -65°; (2): $HSO_3F$ with 10 vol. % $SO_2$ or $SO_2ClF$, -65°; (3): $HSO_3F/SbF_5$ (about 5:1 molar ratio) with 10 vol. % $SO_2ClF$, -65°; (4): $SO_2$ or $SO_2ClF$ with $SbF_5$, -70°. After the recording of the PMR spectra TMABr was added in each case.

The PMR data of ions IIa, IIb and IId agree well with those published by *Olah* et al.[12], except for small differences (0.1-0.2 ppm. downfield), ascribable to our use of internal reference as opposed to *Olah*'s use of external TMS.

In the case of Ie and If, protonation occurred as a side reaction in strong proton acids. Upon the addition of about 20 vol.% $HSO_3F$ to a solution of Ie in $SO_2$ at -70°, para-protonated Wheland complex IV is formed immediately. The PMR spectrum shows temperature dependent line broadening of the absorptions of $HSO_3F$ ($\delta$= 10.6 ppm.) and of the aliphatic $-CH_2$ group (3.9 ppm.), indicating fast intermolecular proton exchange between Ie and the acid. (See figure 1).

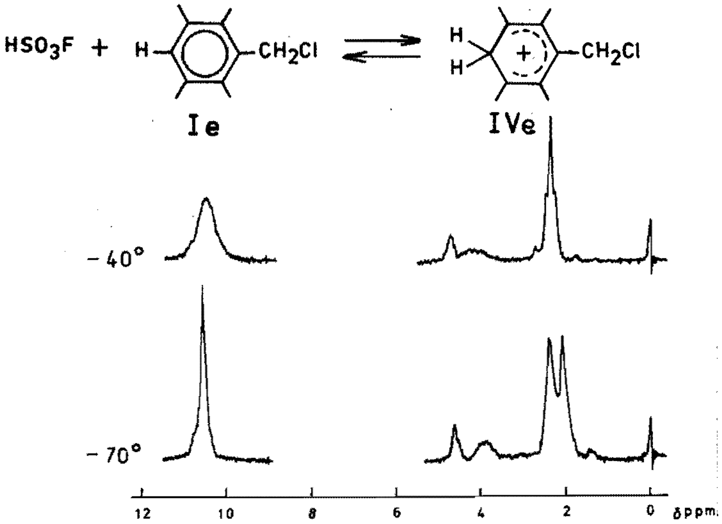


Fig. 1. Proton exchange between $HSO_3F$ and complex IV in $SO_2$ with 20 vol. % acid.

The assignment of the peaks at 4.6 and 3.9 ppm. to $-CH_2Cl$ and $-CH_2$, respectively, is based on the fact that a $SO_2$ solution of α,α-dideutero-2,3,5,6-tetramethylbenzyl chloride with 20 vol.% $HSO_3F$ gives the same PMR spectrum except for the absorption at 4.6 ppm. This latter absorption thus must be due to the $-CH_2Cl$ group of complex IV.

The fast exchange between Ie and $HSO_3F$ at -40° points to a decreased basicity of this compound compared with, for instance, pentamethylbenzene or durene. These latter compounds show negligible exchange at -80° in $HSO_3F$ as follows from their PMR spectra. At low temperatures, solvolysis and protonation of Ie are competing processes in $HSO_3F$. The fact that solvolysis is not observed in rather concentrated solutions (0.1 molar) indicates that protonation dominates and prevents the generation of cation IIe to a large extent.

Compound If is protonated on the $NO_2$-group in $HSO_3F/SO_2$ at -60 °C and shows nearly the same spectrum as a solution of If in $CDCl_3$. At -25 °C, fast proton exchange causes the methyl signals to coalesce. In $HSO_3F/SbF_5$ (1:1), a broad signal at about 7.5 ppm. is observed, presumably due to the formation of strong donor-acceptor complexes between $SbF_5$ and the $CH_2Cl$ of If. In this case, protonation of the $NO_2$-group may also suppress solvolysis to a large extent.

Due to these protonation side reactions, cations IIe and IIf could only be obtained in $SO_2ClF/SbF_5$ solution at -70°. When a mixture of $HSO_3F/SbF_5$ (1:1) was added to a solution of Ie and If in $SO_2$ at low temperatures, solvolysis was obscured by side reactions, viz. protonation and formation of complexes with $SbF_5$.

## II.4. THE STABILITY OF SUBSTITUTED BENZYL CATIONS.

The remarkable stability of the pentamethylbenzyl cation IIb is demonstrated by the fact that the ion does not decompose when a solution of IIb in $HSO_3F$ is heated at 75 °C for 15 minutes[12]. On the other hand, If is quite reluctant to solvolyse smoothly even in $SO_2ClF/SbF_5$ due to the strong destabilizing action of the nitro-substituent. Two observations point out that the stability of ions II decreases in the order: IIa > IIb > IIc > IId ≃ IIe > IIf, viz. the observed solvolytic behaviour (stronger acids are needed in this order to get complete solvolysis in dilute solutions) and the observed differences in PMR chemical shifts between the $-CH_2Cl$ group and the $-CH_2^+$ group. (See table III).

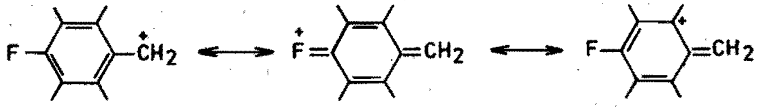
Table III

$^1H$ and $^{19}F$-chemical shift differences for ions II(a-f) and $p\text{-}X\text{-}C_6H_4.CF_2^+$ cations, respectively.

| Para-subst. | $\Delta$ ($^1H$)$^{a)}$ | $\Delta\rho^{b)}$ | $\Delta$ ($^{19}F$)$^{c)}$ |
|---|---|---|---|
| $-OCH_3$ | 3.50 | --- | --- |
| $-CH_3$ | 3.90 | 324.6 | --- |
| -F | 4.15 | 327.3 | 69.7 |
| -Cl | --- | 326.4 | 72.1 |
| -Br | 4.40 | --- | 72.3 |
| -J | --- | --- | 73.0 |
| -H | 4.40 | 347.9 | 75.6 |
| $-NO_2$ | 4.65 | 345.4 | --- |

a) $\Delta$ ($^1H$) = $\delta$ ($CH_2Cl$) - $\delta$ ($CH_2^+$), in ppm., from table II.
b) $\Delta\rho$ = $\rho$ ($CH_2Cl$) - $\rho$ ($CH_2^+$), in $10^3$ electron units, as calculated in the CNDO/2 approximation.
c) $\Delta$ ($^{19}F$) = $\phi$ ($CF_3$) - $\phi$ ($CF_2^+$), in ppm., from ref. 15.

The strong charge delocalization by the para-methoxy group is apparent from the rather small downfield shift of the $CH_2^+$ protons upon ionization, while the nitro-group is seen to be the least stabilizing substituent, as expected. The observation that para-fluorine accomodates positive charge better than para-bromine needs some comment. *Olah*[15] deduced from the experimentally found $^{19}F$ chemical shift differences between para-substituted benzyl,α,α-difluoro cations and their precursors that halogen back-donation increased from iodine to fluorine. For cation IIc this would mean that the quinoid structure IIc(2) becomes less important in going from para-F to para-J.



**IIc**(1) **IIc**(2) **IIc**(3)

However, structure IIc(2) implies the formation of a fluoronium-like particle and this is incompatible with the known strong electronegativity of fluor. This kind of mesomeric charge delocalization was also rejected by *Mikhailow*[16] in his review dealing with carbon-halogen bonds. It was shown that the concepts of mesomerism, when applied to these bonds, frequently led to contradictory explanations. According to *Mikhailow*'s view, halogen effects must be explained by the fact that the bulkier halides have less favourable overlap with the orbitals of the carbon atom to which they are bonded.

CNDO/2 calculations, however, show that chlorine donates slightly more negative charge to the benzylic center than fluorine. In polar solvents this inductive electron-donation may be strongly counteracted by solvation. Noting that the bulkier halides are much more polarizable, stronger solvation of the para-halide substituent will tend to fix charge on the outside of the atom and this charge will be blocked from the positive center. Thus, stronger solvation of bulkier halides would lead to larger downfield shifts of the $-CH_2^+$ or $-CF_2^+$ group in the benzyl cation.

Referring again to the paper by *Gold*[7], it may be stated as a quite general rule, that the total energy of a conglomerate of ions and solvent molecules will be lowered both by solvation and by delocalization, the two processes operating in opposite directions: delocalization spreads out charge while solvation leads to charge localization. In different cases, different compromises between the two processes may prove to be favourable.

The reluctance of Id to solvolyse as compared with Ic then reflects the stronger solvation of bromine which leads to a diminished tendency of bromine to delocalize positive charge during the (solvolytic) transition state.

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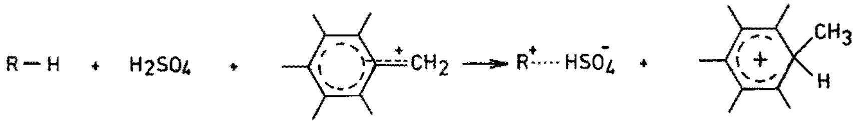
# CHAPTER III

## Alkanes as Hydride Donors; PMR Spectroscopy.

### III.1. INTRODUCTION.

In 1964, *Buck*[1] discovered that a purple-blue solution of pentamethylbenzyl cations in $H_2SO_4$ turned yellow immediately after the addition of isooctane. Hexamethylbenzene was formed via a fast hydride transfer according to reaction (1):

(1)



II

III

*Malchick* and *Hannan*[2], studying the alkylation of para-cresol, found that isopentane inhibited the concurrent formation of bismethylene-phenols. They explained this effect by assuming that a rapid hydride transfer occurs between the isoalkane and transient benzyl cations so that these latter reactive species were removed from the medium before they could couple with para-cresol. Reaction (1), however, showed unambigously that this reaction indeed takes place.

A wide variety of hydride donors was found to react with IIb, for example: isoalkanes, 9,10-dihydroanthracene, cycloheptatriene and even molecular hydrogen[3] The reaction with isoalkanes is very smooth whereas $H_2$ reacts much slower. The reported reactivity of methane is questionable as no trace of tritium could be detected in hexamethylbenzene formed via a reaction between tritiated $CH_4$ and IIb in $HSO_3F$

As will be shown in chapter IV the hydride transfer reaction between benzyl cations and isoalkanes is acid catalysed. In $HSO_3F$ the reaction is completed within a few seconds at -65° C and ions II(a-f) form products III(a-f) in high yield upon the addition of isobutane. Due to their basicity, compounds III are protonated in strong acids and *Wheland* complexes IV are formed.

In sections 2 and 3 of this chapter the PMR spectra of compounds IV and the basicity of compounds III will be discussed.

The effect of miscellaneous hydride donors (other than isoalkanes) will be discussed in section 4.

## III.2. PENTAMETHYL,X-BENZENES FROM CATIONS II AND ISOBUTANE.

Solutions of chlorides I(a-f) in liquid $SO_2$ or $SO_2ClF$ were mixed with $HSO_3F$ or $HSO_3F/SbF_5$ at -75° C and an equivalent amount of isobutane was added. Frequently an isobutane/nitrogen mixture was used to ensure good mixing of the solution and to avoid side reactions of isobutane with the acid (for instance: hydrogen evolution[4]). The mixture usually changed colour within 10 seconds and subsequently the PMR spectrum was taken at low temperature. Table IV summarizes the PMR data of protonated compounds III(a-f).

Quenching of the acidic solutions of III(a-f) in cold water or methanol and extraction with n-heptane generally yielded rather pure pentamethyl,X-benzene (80-95%). In the case of If, however, the pentamethyl,nitro-benzene formed via the hydride transfer reaction was sometimes contaminated with unreacted If. This was not the case when isobutane was added very slowly (about 2-4 minutes) to a solution of If in $HSO_3F/SbF_5$.

Pentamethyl,methoxybenzene forms para protonated Wheland complex IVa in $HSO_3F$ in which oxygen carries a formal positive charge. The fact that the PMR spectrum shows no trace of proton exchange at all accessible temperatures (-80° up to - 10 °C) and the inequivalence[5] of the two $CH_3$ groups ortho to the methoxy substituent point to strongly hindered rotation around the O-C bond of IVa. (See figure 2 for the PMR spectrum of IVa.)

Table IV

PMR spectra[a)] of compounds III(a-f) in strong acids[b)] at -70° C.

| -X | $\delta(CH_3)^{2,6}$ | $\delta(CH_3)^{3,5}$ | $\delta(X)^4$ | $\delta(H)$ | $\delta(CH_3)^1$ |
|---|---|---|---|---|---|
| $-OCH_3$ | 2.15 | 2.4, 2.6 | 4.55 | 4.15(q.,7)[c)] | 1.55(d.,7) |
| $-CH_3$ | 2.85 | 2.55 | 3.00 | 4.30(q.,7) | 1.90(d.,7) |
| -F | 2.70 | 2.25(d.,1.5) | --- | 4.35(q.,8) | 1.75(d.,8) |
| -Br[d)] | 2.40 | 2.70 | --- | 4.60(br.) | 2.80 |
| -H | 2.20 | 2.50 | 4.45(q.,4) | | 2.65(t.,4) |
| $-NO_2$ | 2.70 | 2.95 | --- | 14.6[e)] | 2.85 |

a) Shifts in ppm., relative to TMS. TMABr (= $(CH_3)_4N^+.Br^-$) as internal standard; $\delta^{TMS}$ = 3.2 ppm.

b) $HSO_3F/SO_2$ or $HSO_3F/SbF_5$ (5:1) with $SO_2ClF$ as cosolvent.

c) Multiplicity and J(in Hz.).

d) A complex pattern was observed between 3.0 and 2.1 ppm. The main species is believed to be IVd(1) (see figure 4).

e) Nitracidium proton, only observable in $HSO_3F/SbF_5$ (1:1) at -75 °C.

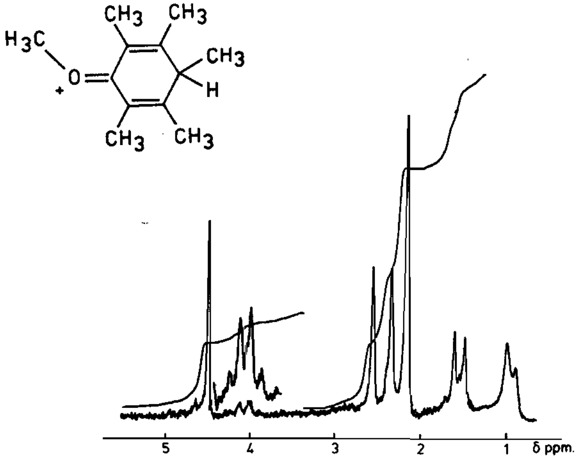


Fig. 2. PMR spectrum of IVa in $HSO_3F/SO_2$ at -65° C.

The fluorine substituent in pentamethyl,fluoro-benzene (IIIc) enhances the basicity of the para carbon atom of the ring as can be concluded from the formation of rather stable Wheland complex IVc upon protonation of IIIc in $HSO_3F/SbF_5$ (5:1) at $-65^{\circ}$ C. (See figure 3). A four-bond coupling between $^{19}F$ and the $CH_3$ groups ortho to the fluorine is observed ($J_{F\text{-}C\text{-}C\text{-}C\text{-}H} = 1.5$ Hz.) but coupling between $^{19}F$ and the aliphatic $CH.CH_3$ group is virtually absent. That five- and six-bond coupling is too small to detect (or even absent) can be inferred from the fact that irradiation of the doublet at 1.75 ppm. results in the collaps of the quartet at 4.35 ppm. to a sharp singlet without observable splitting and *vice versa*.

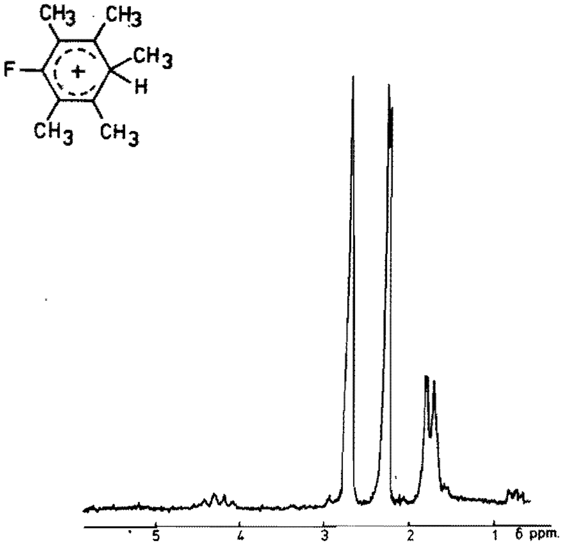
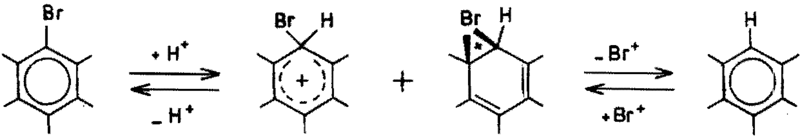


Fig. 3. PMR spectrum of IVc in $HSO_3F/SbF_5$ (5:1) at $-65^{\circ}$ C.

In protonated hexamethylbenzene (IVb) a small splitting of 2 Hz. has been reported due to the coupling between the aliphatic C-H proton and the para-$CH_3$ group[6], but in $HSO_3F$/$SbF_5$ (5:1) diluted with $SO_2$ this coupling was not observable even at -75° C. Line broadening due to the viscosity of the solvent may account for the absence of observable splittings or, alternatively, the different solvation of IVb in $HSO_3F$/$SbF_5$ as compared with $HF/SbF_5$ or $HF/BF_3$ may lead to a more distorted geometry of the cyclohexadienyl cation. In the former solvent, $[H_2SO_3F\text{-}SbF_5]^+$ is thought to be the protonating agent while the much less bulky $H_2F^+$ ions are the protonating agents in $HF/BF_3$ or $HF/SbF_5$. The bulkier agents will lead to more steric repulsion in cations such as IVb and IVc and this will lead to smaller splittings[7]. In this context mention may be made of the work of *van der Lugt* et al[8]., who reported para-protonation of biphenyl in $HSO_3F/SbF_5$ and ortho-protonation of the same compound in $HF/BF_3$, and explained this behaviour on steric grounds.

Pentamethyl,bromo-benzene (IIId) presumably forms a mixture of different ions in $HSO_3F/SbF_5$ (5:1). Protonation on carbon carrying a $CH_3$-group can be ruled out as the characteristic doublet in the region $\delta$ = 2.0-1.5 ppm. is not observed. The spectrum consists of small broadened absorptions at 4.6 and 6.2 ppm. and more intense absorptions in the region where aromatic $CH_3$-groups absorb usually, at $\delta$ = 3.05, 2.95 and 2.50 and at $\delta$ = 2.80, 2.70 and 2.40 ppm. These two sets of absorptions are believed to belong to two different species as each set has an estimated integral ratio of 1:2:2 and, furthermore, as one set has a larger intensity (as a whole) in $HSO_3F/SbF_5$ while the other set diminishes at the same time. The solubility of IIId in $HSO_3F$ or $HSO_3F/SbF_5$ is low and the absorptions are rather broad -this may be due to the nuclear quadrupole moment of Br together with the viscosity of the solvent at the low temperatures- so that accurate integrals could not be obtained.

Drowning the acidic solution in water gave IIId mixed with some pentamethylbenzene (about 5 to 10 %). Methanolysis with cold $CH_3OH$ (-65 °C) gave more debrominated product IIIe (up to 30%) together with IIId, as found by GLC and PMR. All these facts suggest that considerable amounts of another cation were formed, besides product IVd(1). Because of the absorption at 6.2 ppm. this other cation is suggested to be bromonium ion IVd(2). (See figure 4). The PMR spectrum of 1,1,3-trimethylethylenebromonium ion[9] shows signals at 6.58 ppm.(tert. proton, quartet, J= 6 Hz.), 2.62 ppm. ($CH_3$ in the 3-position, doublet, J= 6 Hz.) and 3.10 ppm.( two methyl groups, singlet). The strong resemblance in the chemical shifts of the two different bromonium ions seems to support our suggestion of ion IVd(2) as the second species present in solutions of IIId in $HSO_3F/SbF_5$.



IIId IVd (1) IVd (2) IIIe

Figure 4.

Cation IIf is presumably present only in low concentrations in solutions of If in $HSO_3F$ as this ion is not observed by PMR. Nevertheless, on the addition of isobutane,pentamethyl,nitrobenzene is rapidly formed. Protonation of IIIf occurs in the $NO_2$ group in $HSO_3F/SbF_5$ (1:1) diluted with 10 vol. % $SO_2ClF$. The nitracidium proton absorbs at $\delta = 14.6$ ppm. at -70° and the $-NOOH^+$ group seems to be frozen in a position perpendicular to the phenyl ring as the ortho methyl-groups absorb at the same field. Alternatively, rapid intramolecular proton exchange in the $NOOH^+$ group may lift any inequivalency of the ortho-methylgroups. In protonated nitro-mesitylene, the same phenomenon is observed[10]. The collaps of the methyl signals at temperatures above -30 °C in $HSO_3F/SO_2$ may also be due to intermolecular proton exchange.

Figure 5 shows the two possible configurations for protonated IIIf. At this point it may also be noted that the formation of IIIf from If goes markedly slower than, for instance, that of IIIb from IIb.

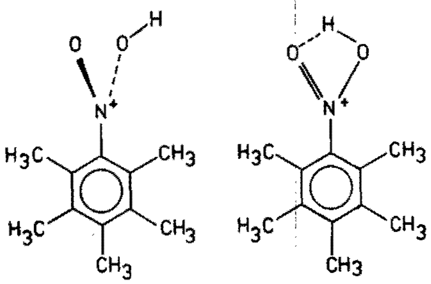


Fig .5

## III.3. THE BASICITY OF AROMATIC HYDROCARBONS.

Compounds III(a-f) are all acting as weak bases and form rather stable cyclohexadienyl cations (*Wheland* σ-complexes) upon protonation in $HSO_3F$ or $HSO_3F/SbF_5$ at low temperatures. Products III, originating from the hydride transfer towards cations II, are rapidly and nearly quantitatively transformed into their conjugate acids IV (with the exception of IIIf which is protonated on the $NO_2$ group). Thus the reversible reactions leading from halides via solvolysis to cations II and, subsequently, via hydride transfer to products III become quasi-irreversible due to the "terminating" protonation reaction in strong acids.

The reverse process, i.e. the formation of carbenium ions upon the protonation of neutral molecules has been observed with triphenylmethanes[11]. In $HSO_3F/SbF_5$ triphenylmethane cleaves readily to $(C_6H_5)_2\text{-}CH^+$ ions and benzene. Para-methoxy substituted triphenylmethanes show the same reaction even in $H_2SO_4$. The high stability of the diphenylmethyl cations compared with the stability of the protonated triphenylmethanes is the driving force for this reversed Friedel-Crafts reaction. In the case of the primary benzyl cations, the reaction with benzene, anisole or durene, for instance, always leads to the expected diphenylmethanes which indicates the low stability of the benzyl cations compared to the stability of the protonated end-product.

In IIIa the $CH_3O$-substituent clearly enhances the basicity of the para-position of the aromatic ring as the PMR spectrum of IVa does not change from -80° up to -15° in $HSO_3F/SO_2$ and even in neat $HSO_3F$ at +35° the PMR spectrum is virtually the same. At higher temperatures, however, IVa starts to exchange protons as judged from the broadening of the $CH.CH_3$ signals.

The fluoro-substituent in IIIc also enhances the basicity of the para-position of the aromatic ring, but IVc exhibits quite rapid proton exchange in $HSO_3F/SbF_5$ (5:1) at temperatures above -40 °C. From this it may be concluded that IIIa is much more basic than IIIc.

Similarly, the observed rapid proton exchange in solutions of IIIe in $HSO_3F/SbF_5$ (5:1) above -55° to -50° points to an even lower basicity of IIIe as compared with IIIc and, certainly, with IIIa. It is tacitly assumed that the exchange processes for the different ions IVa, IVc, IVd, IVe are intermolecular and have nearly the same activation parameters. From the work of *MacLean* and *Mackor*[7b] it may be seen that this is true for compounds differing not too much in basicity, such as durene, hexamethylbenzene and mesitylene. Using the same solvent ($HSO_3F/SbF_5$ (5:1)), the temperature where the $CH.CH_3$ doublet collapses may be taken as a measure for the basicity of the dissolved compound.

Presumably, pentamethyl,bromo-benzene IIId is less basic than IIIc and IIIe, though this cannot be concluded with certainty from the PMR spectra. The low solubility of IIId in strong acids , however, also suggests this. Nitro compound IIIf is the least basic of the six compounds

Hexamethylbenzene is thought to be slightly more basic than pentamethylbenzene ($\log(K_b)_i$ = +0.6 and +0.4 for IIIb and IIIe, respectively[12]), but the rapid intramolecular proton exchange in hexamethylbenzenium ions can not be suppressed entirely, even in $HSO_3F/SbF_5$ (1:1) at -80°. Though this behaviour has been attributed to tunneling[7b], it was found that deuterated IVb in $DSO_3F/SO_2ClF$ did not show a clear deuterium splitting for the $CD.CH_3$ signal even at -90°. This indicates that $D^+$ exchange is still rather fast. If, however, proton tunneling really is occurring one would expect deuteron exchange to be at least 20 or 30 fold slower[13] and the deuterium splitting of about 1 Hz. would be observable at this low temperature. Remembering that methyl-substitution lowers the basicity of the carbon atom to which the $CH_3$ group is attached and, at the same time, enhances the basicity of carbon atoms ortho and para in the ring, it would be expected that IIIb has a lower basicity than IIIe. The rapid intramolecular proton exchange then may point to a decreased basicity and would put IIIb somewhere between IIIe and IIId.

On the basis of the PMR data the following order of basicity emerges for compounds III:

IIIa > IIIc > IIIe > IIIb > IIId > IIIf.

## III.4. OTHER HYDRIDE DONORS.

Cations II react rapidly with isoalkanes (isobutane, adamantane, methylcyclohexane and 2,2,3-trimethylbutane, for instance) and it may be noted that the nature of the alkane does not matter very much as long as there is a tertiary hydrogen in the molecule. The rate of the hydride transfer reaction diminishes, however, when bulkier alkanes are used (e.g. 2-methylpropane reacts faster than 4-n.propylheptane or 5-n.butylnonane). This is attributed to steric hindrance leading to a larger entropy of activation for the hydride transfer reaction.

With methane a slow reaction occurs when cation IIb in $HSO_3F$ or $HSO_3F/SbF_5$ (5:1) is allowed to react at -70 °C and a methane pressure of about 20 atm. Quenching of the acidic solution after about 90 to 150 minutes gave yields of 35 to 50 % of hexamethylbenzene. The crude product ususally contained also considerable amounts of pentamethylbenzyl alcohol or halide Ib. Carrying out the same reaction with tritiated $CH_4$ (prepared from $CH_3MgJ$ and tritiated water) gave hexamethylbenzene in which no tritium could be detected. This suggests that some unknown impurity rather than methane itself reacts with cation

IIb. The low rate of the reaction indicates that this impurity, whatever it may be, is not an isoalkane, anyway.

Under the same conditions (-70°, 20 atm. pressure, $HSO_3F/SbF_5$) molecular hydrogen reacts within 45-60 minutes and gives nearly quantitative yields of hexamethylbenzene. It may be noted, that reaction of $H_2$ with cation IIb in tritiated $HSO_3F$ does not lead to tritiated hexamethylbenzene; only unlabelled product IIIb is formed.

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# CHAPTER IV

## The Influence of the Acidity; Transfer of Isotopic Hydrogen.

### IV.1. INFLUENCE OF THE ACIDITY OF THE SOLVENT ON THE REACTION-RATE OF THE HYDRIDE TRANSFER REACTION BETWEEN ALKANES AND PENTAMETHYLBENZYL CATIONS.

As has been 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, for instance in sulphuric acid, cation IIb reacts notably slower with isoalkanes. The rate of the hydride transfer reaction thus was thought to depend on the acidity of the solvent employed. This dependence was studied by noting the time, necessary to complete the hydride transfer reaction between several alkanes and pentamethylbenzyl cations in different acidic solvents.

In concentrated $H_2SO_4$ or mixtures of $H_2SO_4$ with $HSO_3F$, halide Ib solvolysed quantitatively to cation IIb, as was shown in chapter II. The time at which the hydride transfer is essentially complete can be monitored conveniently by the change in colour (from purple-blue to yellow) which occurs when the last traces of pentamethylbenzyl cation disappear.

Concentrated $H_2SO_4$ was prepared by mixing reagent grade $H_2SO_4$ with 60 % oleum until the conductivity was minimal[1]: $1.05 \times 10^{-3}$ Mho.cm$^{-1}$. Freshly distilled $HSO_3F$ was mixed with 100 % $H_2SO_4$ in volume ratios of 1:2 and of 2:1, respectively. The *Hammett*-acidities of these three solvents were taken to be: -11.9, -12.9 and -13.2, respectively, as determined by *Gillespie* et al[2]. As traces of water or other basic impurities, or a slight excess of oleum, may lower or enhance the acidity of 100 % $H_2SO_4$ considerably, the $H_0$ value of this solvent may differ about 0.2 to 0.4 units. The $HSO_3F/H_2SO_4$ mixtures are much less sensible to impurities, as far as the acidity is concerned.

In a typical experiment, 0.5 ml. of a solution of halide Ib in $CCl_4$ (0.5 mole.$l^{-1}$) was added to 5.0 ml. of the acid at 0° C. Upon shaking of the heterogeneous mixture, the halide dissolved into the acid layer and solvolysed completely. To the purple-blue solution of pentamethylbenzyl cations (about 0.05 mole.$l^{-1}$), 0.5 ml. of a solution of alkane in $CCl_4$ was added (3 mole.$l^{-1}$) and the mixture was again vigorously shaken to ensure dissolution of the alkane. The time at which the colour of the pentamethylbenzyl cations disappeared was noted. The results are summarized in table V.

Table V

Overall-reaction times at 0° C for different alkanes with solutions of IIb (0.05 mole.$l^{-1}$) in $H_2SO_4$ or $HSO_3F/H_2SO_4$ mixtures.

| Alkane | t(sec) | t(sec) | t(sec) |
|---|---|---|---|
| Acidity | $H_0$ =-11.9 | $H_0$ =-12.7 | $H_0$ =-13.2 |
| Isobutane | 80 | 25 | ≈10 |
| Methylcyclohexane | 90 | 35 | ≈15 |
| Adamantane | 220 | 65 | 25 |
| 2,2,3-Trimethylbutane | 250 | 75 | 40 |
| 4-n.Propylheptane | 310 | 120 | 55 |
| Cyclohexane | >360 | >300 | ≈250 |
| n-Heptane | >600 | >360 | >300 |

A plot of $^{10}\log$ (t) <u>versus</u> $H_0$ gave straight lines with slopes of about 0.60 to 0.74. As the reaction between the alkane and pentamethylbenzyl cations may be considered to be pseudo first-order (both the acid and the alkane are present in excess), the overall-reaction time t is inversely proportional with the reaction rate R of the hydride transfer reaction. Formally, a first-order reaction takes infinite time to go to completion, but from the integrated rate-law:

$(1)\ldots\ \ln(A/A_0) = -k.t$

it follows, that:

$(2)\ldots\ t = c/k$

in which c $(= \ln(A_0/A))$ is an arbitrary constant, assuming A to be equal in each case. As every experiment was performed in the same way, this assumption seems reasonable. From the plots of the overall-reaction time t versus $h_0$, the relation between these two parameters is found to be:

$(3)\ldots\ {}^{10}\log(t) = a.H_0 + c'$ or: $(4)\ldots\ (t) = c'.(h_0)^{-a}$

in which c' is a constant and a is the slope of the line given by the $^{10}\log(t)$ vs. $H_0$ plots.

Using (2), (4) can be rewritten to:

$(5)\ldots\ {}^{10}\log(k) = -a.H_0 + c''$

Now, assume that the reaction between an alkane (A) and pentamethylbenzyl cations (B) proceeds in two steps, the first step being a rapid protonation equilibrium:

$$A + H^+ \overset{K}{\rightleftharpoons} AH^+$$

$$AH^+ + B \xrightarrow{k} X^{\neq} \longrightarrow \text{Products.}$$

the rate of reaction per unit volume of solution would be:

$(6)\ldots R = k_{obs}.\ C_A = k.(AH^+)$

with $k_{obs}$ is the observed first-order rate constant, k the rate constant of the rate-determining step, $C_A$ the stoichiometric concentration of reactant A and $(AH^+)$ the concentration of protonated alkane. From transition state theory it follows, that:

$(7)\ldots\ R = (kT/h).(X^{\neq})$

with $(X^{\neq})$ is the concentration of activated complex.

Introducing activity coefficients ($f$), K and $K^{\neq}$ can be written as:

$$(8)\ldots\ K = \frac{(H^+).(A)}{(AH^+)} . \frac{f_{H^+}.f_A}{f_{AH^+}}$$

$$(9)\ldots\ K^{\neq} = \frac{(X^{\neq})}{(AH^+)} . \frac{f_{\neq}}{f_{AH^+}}$$

If the concentration of protonated alkane is very small, $(AH^+)$ may be given by:

$$(10)\ldots\ (AH^+) = \frac{(A)\ a_{H^+}}{K} . \frac{f_A}{f_{AH^+}} = \frac{(X^{\neq}).f_{\neq}}{K^{\neq}.f_{AH^+}}$$

Thus, $(X^{\neq})$ is given by:

$$(11)\ldots(X^{\neq}) = \frac{K^{\neq}}{K} . \frac{(A).a_{H^+}.f_A}{f_{\neq}}$$

and, using (7) and (11), the observed rate constant becomes:

$$(12)\ldots\ k_{obs} = (kT/h) . \frac{K^{\neq}}{K} . \frac{a_{H^+}.f_A}{f_{\neq}}$$

Noting that, by definition,:

$$(13)\ldots\ H_0 = -{}^{10}\log(a_{H^+}).(f_{Ind}/f_{Ind.H^+})$$

it follows, that:

$$(14)\ldots\ {}^{10}\log(k_{obs}) = -H_0 + \text{constant}$$

<u>if</u> $(f_A/f_{AH^+})$ is equal to $(f_{Ind}/f_{Ind.H^+})$, <u>i.e</u>. if the indicator base, used to determine the *Hammett*-acidity of the solvent behaves the same as the alkane as regards activity coefficients.

Experimentally, it was found that $^{10}\log(t)$ plotted *versus* $H_0$ gave straight lines with slopes between 0.60 and 0.74. Thus, experimentally, expression (5) was found:

$$(5) \ldots {}^{10}\log(k) = -a.H_0 + c''$$

instead of the previously derived expression (14). The deviation of the experimentally found slopes a from unity may arise from the fact, that alkanes will behave differently from indicator bases which are normally used in $H_0$-determinations. Assumption of equality between $(f_A/f_{AH^+})$ and $(f_{Ind}/f_{IndH^+})$(A= alkane and Ind= indicator base) may therefore be not valid. Especially the activity coefficient $f_A$ of the unprotonated alkane may be considerably smaller than one in view of the rather large concentrations of alkane in the acidic solvents, which are expected to be nearly saturated with alkane. The fact that the largest deviations of unit-slope are found with methylcyclohexane, 2,2,3-trimethylbutane and tri-n.propylmethane agrees with this as these alkanes are presumably less soluble than isobutane (solubility about 0.2 mole.$l^{-1}$ in $HSO_3F$) or adamantane. The latter compound contains four tertiary C-H bonds per molecule and actually, the observed reactivity of adamantane should be corrected for this. As the slope of the log(t) *vs.* $H_0$ line remains the same, this correction has been omitted.

In a first approximation, the reaction rate for the hydride transfer reaction is proportional to the proton-activity. The dependence of R on $a_{H^+}$ indicates a *termolecular transition state for the hydride transfer between isoalkanes and methylated benzyl cations in which one proton participates*.(see figure 1.)

The observed reaction rate for the reaction:

$$(15) \quad A + B + H^+ \longrightarrow \text{Products}$$

may be expressed as:

$$(16) \ldots \; R = C.(a_A).(a_B).(a_{H^+}).\ \exp(\Delta S^{\neq}/R - \Delta H^{\neq}/RT)$$

where $a_A$ and $a_B$ are the activities of isoalkane and pentamethylbenzyl cation, respectively, $a_{H^+}$ is the proton-activity and

$\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the activation enthalpy and entropy of the reaction. The constant C includes (*kT/h*) and activity coefficients $f_{Ind}/f_{Ind.H^+}$ .

The observation that bulkier alkanes, such as adamantane, 2,2,3-trimethylbutane and 4-n.propylmethane, react slower than, for instance, isobutane may be due <u>either</u> to differences in the activity coefficients <u>or</u> to the smaller solubility of these alkanes in strong acids. Also differences in $\Delta H^{\neq}$ or $\Delta S^{\neq}$ may play a rôle, but as in no case a very much slower rate was observed when the temperature was lowered from +25° C to -70° C (using neat $HSO_3F$), $\Delta H^{\neq}$ may be assumed to be rather small, presumably not larger than 3 to 5 $kcal.mole^{-1}$. A difference of 0.6 $kcal.mole^{-1}$ then would lead to differences in the rate of a factor 3, but a difference of 2 $cal.^{o}K^{-1}.mole^{-1}$ in $\Delta S^{\neq}$ would give the same result. In view of the termolecular nature of the transition state, a rather large activation entropy must be expected and a small change in $\Delta S^{\neq}$ seems to be much more likely than relatively large changes in $\Delta H^{\neq}$.

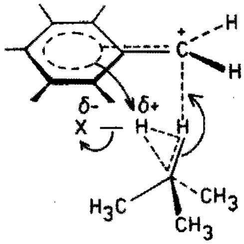


Fig.1. Termolecular transition state for the reaction between isobutane and pentamethylbenzyl cations in strong acids.

As will be shown in the following part of this chapter, the participation of protons in the transition state leads to the incorporation of hydrogen isotopes, originating from the labelled acid, into the products of the hydride transfer reactions, and this observation supports the here postulated transition state.

## IV.2. LABELLING EXPERIMENTS WITH HYDROGEN ISOTOPES.

The use of hydrogen isotopes (deuterium and tritium) for the study of hydride or proton transfers makes it possible to measure the position and the amount of transferred particles. Furthermore, the occurrence and magnitude of isotope effects gives valuable information about the reaction paths that are followed. Side-reactions, such as concurrent proton exchange, rearrangements or reactions with impurities, may escape experimental observation under normal conditions but are easily discovered when hydrogen labelling is employed.

When solutions of pentamethylbenzyl cations in $HSO_3F$ were treated with equimolar amounts of 2-$^2$H-isobutane, deuteride transfer occurred[3] and deuterated hexamethylbenzene was formed. Quenching of the acidic solutions with water and purification of the precipitated hexamethylbenzene gave yielded 75 to 90 % of essentially pure III (mpt.160-165$^o$ C; pure hexamethylbenzene has mpt. 165.8$^o$ C, but traces of impurity are known to have a rather large influence on the melting point).

In the mass-spectrum of hexamethylbenzene, the principal peak observed at low ionization potential (6.20 eV) occurs at m/e = 162, i.e. the parent peak. Satellites at m/e = 163 and 164 are caused by $^{13}$C containing $(C_{12}H_{18}^+)$-ions. Under the same conditions, mixtures of differently deuterated hexamethylbenzenium ions give peaks at m/e = 162, 163, 164 etc. Correcting for the known $^{13}$C content, the percentage of undeuterated, monodeuterated, dideuterated etc. molecules can be calculated with an accuracy of about 0.1 %. The analysis of deuterated hexamethylbenzene, obtained from the reaction of 2-$^2$H-isobutane and pentamethylbenzyl cations in various strong acids (see table VI) showed, that with increasing temperature, less deuteride transfer had occurred. Thus, deuteride transfer is accompanied by hydride transfer in spite of the fact that the used deuteride donor (2-$^2$H-isobutane) is deuterated better than

95 %, as evidenced by the absence of detectable amounts of protio-compound either observable by PMR or by Raman-spectroscopy. Analysis of 2-$^2$H-isobutane by means of mass-spectroscopy proved to be very unsatisfactory, due to the ease with which tertiary-butyl cations are formed in the mass-spectrometer, even at very low ionization potentials.

Table VI

$^2$H-analyses of hexamethylbenzene formed via deuteride transfer from 2-$^2$H-isobutane to cations IIb.

| Acid | t (° C) | $d_0$ | $d_1$ | $d_2$ | $d_3$ |
|---|---|---|---|---|---|
| $HSO_3F$ (neat) | -60 | 21.2 | 78.3 | 0.5 | --- |
| | -45 | 56.8 | 42.4 | 0.8 | --- |
| | -30 | 63.0 | 35.0 | 1.7 | 0.3 |
| $HSO_3F/SO_2$ (1:2 v/v) | -60 | 14.0 | 85.0 | 1.0 | --- |
| $SbF_5/SO_2$ (1:2 v/v) | -70 | 10.4 | 89.1 | 0.5 | --- |
| $CF_3SO_3H$ | -40 | 51.4 | 46.0 | 2.5 | 0.2 |

At first sight, the fact that deuteride transfer is not 100 % in $SbF_5/SO_2$ might point to imperfect deuteration of isobutane, but it will be shown that traces of water or other proton-containing impurities may lead to the formation of HF in this solvent and the same scrambling behaviour will be observed as in the other acidic solvents.

To ascertain whether or not proton exchange occurs between 2-$^2$H-isobutane and the acid, a set of experiments was carried out in which the deuterated alkane was added to solutions of pentamethylbenzyl cations in tritiated $HSO_3F$ at different temperatures. In some cases, $SbF_5$, $KSO_3F$ or $SO_2$ was added to enhance or to lower the acidity of the solvent and thus to promote or to prevent proton exchange reactions. Tritiation was accomplished by adding a small amount of tritiated water

( 5 µl. with a specific activity of 5 $mCi.ml^{-1}$) to freshly distilled $HSO_3F$ (25 ml.). Hexamethylbenzene was prepared via deuteride transfer from 2-$^2$H-isobutane to cation IIb in these tritiated acids in exactly the same way as before and the tritium content as well as the deuterium content of purified samples was determined[3]. Table VII shows the results.

## Table VII

$^2$H and $^3$H content of hexamethylbenzene formed via deuteride-transfer to cations IIb in tritiated acids.

| Acid | t(° C) | % $^2$H | % $^3$H(rel.) |
|---|---|---|---|
| $HSO_3F$ | -65 | --- | 25.4 |
| | -65 | 83.2 | 24.3 |
| | -50 | 60.4 | 37.4 |
| | -45 | 42.4 | 56.3 |
| | -30 | 35.2 | 68.0 |
| $HSO_3F/SbF_5$ (5:1) | -65 | 61.2 | 27.0 |
| | -55 | --- | 39.0 |
| $HSO_3F/SO_2$ (2:1) | -65 | 84.3 | 14.0 |
| | -50 | 81.2 | 13.0 |
| $HSO_3F/KSO_3F$ (5:1) | -45 | 82.9 | 7.0 |
| | -40 | --- | 7.1 |

The calculation of the relative tritium percentages was carried out as follows. Known amounts of tritiated $HSO_3F$ were mixed with methanol at low temperature (-50 to -40° C) to obtain dilute solutions of about 5 % by weight. Small samples were taken from these mixtures and the tritium content determined in the usual way, using Instagel as the solvent. Tritium contents were always expressed as $dpm.mole^{-1}$. As proton exchange between the methyl-groups of hexamethylbenzene or pentamethylbenzyl cations is negligible (vide infra), only one site is left for the uptake of a tritide ion per molecule, i.e. the reactive $CH_2^+$-group. Because $HSO_3F$ is present in large excess, complete benzyl cations (IId and IIf) give rise to compounds III which contain slightly more tritium.

## Table VIII

Relative $^3$H-content of compounds III, obtained via reaction of cations II with $^3$H-labelled isobutane (or: 2-$^2$H-isobutane) in neat $HSO_3F$ at -70° C.

| Compound | % $^3$H (rel.)[a)] | % $^3$H (rel.)[b)] |
|---|---|---|
| IIIa | 4.5; 2.0 | 52.1 |
| IIIb | 2.9; 4.9; 2.8 | 62.5 |
| IIId | 3.7; 5.0 | 69.5 |
| IIIf | 11.4; 9.0; 13.6 | 70. (±3) |

a) With a mixture of 2-$^1$H-isobutane/2-$^3$H-isobutane.
b) With a mixture of 2-$^2$H-isobutane/2-$^3$H-isobutane.

The fact that a much higher relative tritium percentage is found in products from the reaction with $^3$H-containing 2-$^2$H-isobutane than in the same products obtained from the reaction with $^3$H-labelled protio-isobutane points to a significant isotope effect for the hydride transfer reaction. The slightly higher tritium content of products IIId and IIIf points to increasing selectivity with decreasing stability of the benzyl cations.

It may be assumed that the low stability of, for instance, cation IIf leads to a high reactivity towards the hydride-donor, i.e. to a lowering of the energy of the transition state or the intermediate, in which hydride transfer takes place. The apparent slowness of the reaction may very well point to solvolysis as the rate determining step for the overall reaction. This point will be discussed further in chapter VI.

## IV.3. PROTON EXCHANGE BETWEEN STRONG PROTON ACIDS AND HYDROCARBONS.

The observation that deuteride or tritide transfer from labelled alkane towards methylated benzyl cations in $HSO_3F$ is accompanied by extensive loss of label may in principle be due to several reasons. At first sight, the results of the reaction between labelled isobutane and pentamethylbenzyl cations (see tables VI and VIII) may be explained by the following assumptions:

a) 2-$^2$H-isobutane may contain small amounts of protiocompound (up to 5 %) as an impurity, in spite of the fact that great care was taken in the preparation of the deuterated compound. Such small amounts would be hardly visible in PMR spectra or Raman spectra so that the presence of unlabelled isobutane in the deuterated alkane can not be ruled out with certainty.

b) Large isotope effects for the hydride transfer reaction would then lead to relatively large amounts of unlabelled hexamethylbenzene.

Assumption b) leads to an $k_H/k_T$ of about 25 at -70° C, based on the fact that hexamethylbenzene, prepared via hydride/ tritide transfer from $^3$H-labelled isobutane contains about 4 % tritium (see table VIII). Using the relation of *Swain*[6], $\log(k_H/k_T) = 1.44 \times \log(k_H/k_D)$, the hydrogen-deuterium isotope effect would be about 9, and the deuterium-tritium isotope effect would be about 2.7. Based on these values 2.5 % of protio-impurity in 2-$^2$H-isobutane would give rise to about 22 % of unlabelled hexamethylbenzene and the reaction between $^3$H-labelled 2-$^2$H-isobutane and pentamethylbenzyl cations would yield about 40 % of tritiated product. Actually, 52 % is found( see table VIII).

Assumption b) seems to hold reasonably well, but the observation that also tritium originating from the acid is found back in the products III and the observation that the amount of transferred deuteride decreases with increasing temperature (cf. tables

VI and VII) point out that assumptions a) and b) alone can not explain all the experimental data.

In a first approximation, isotope effects are given by: $k_H/k_D = \exp(-\Delta E/RT)$, where ΔE is equal to the difference in zero-point energy of the C-H and the C-D bonds that are broken in the reaction. It is at once seen that the differences in the rate caused by isotope effects become smaller at higher temperatures and relatively more deuterium would be expected to be transferred at higher temperatures. Experimentally, the reverse is observed (cf. tables VI and VII).

Proton exchange, either between the acid and the labelled alkane or between the acid and the labelled compounds III may occur, prior or after the hydride transfer step, respectively. Both exchange reactions were separately studied (vide infra) but it turned out that proton exchange between $HSO_3F$ and isobutane on the one hand or hexamethylbenzene on the other hand both are slow processes at low temperatures (beneath -30° C). As a third possibility, therefore, proton exchange during the hydride step per se must be considered. First the experimental data will be given which form the basis for the discussion of the reaction mechanism in chapter VI.

Proton exchange between the methyl-groups of hexamethylbenzene (and, presumably, those of other methylated benzenes as well) and $HSO_3F$ can be ruled out because quenching of a solution of unlabelled IIIb in tritiated $HSO_3F$ (at -40° C) gave back the starting material with negligible tritium content after an exchange time of about 10 minutes. The recovered compound had an activity of $1.9 \times 10^4$ dpm.mole$^{-1}$, i.e. 0.09 % of the activity of the acid employed. Taking into account that there are 18 equivalent C-H bonds in hexamethylbenzene, this amounts to less than $0.5 \times 10^{-2}$ % exchange per C-H bond. The findings of *Ginzburg* et al[7] agree with this. They found that hexamethylbenzene could not be tritiated when a solution of this compound was refluxed in $^3H$-labelled $CF_3COOH$ for a few hours.

Using the relation given by *Duffield* and *Calvin*[8]:

(17) $k = -(1/t).(1/a+b).\ln(1-x/x_\infty)$

the rate of exchange between hexamethylbenzene (0.5 $\text{mole.l}^{-1}$) and $HSO_3F$ (14 $\text{mole.l}^{-1}$) can be estimated at $-40^o$ C. At t = 10 minutes, the mole fraction $x/x_\infty$ that has exchanged is $0.5 \times 10^{-4}$, and k is calculated to be $1.3 \times 10^{-8}$ $\text{l.mole}^{-1}.\text{sec}^{-1}$ at $-40^o$ C per C-H bond.

Hexamethylbenzene is nearly quantitatively protonated in $HSO_3F$ and proton-attack on hexamethyl benzenium ions will take place predominantly on the meta $CH_3$-groups. The transition state of the proton exchange reaction will involve the five-coordinated carbon species, pictured in figure 2.

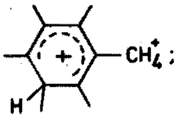
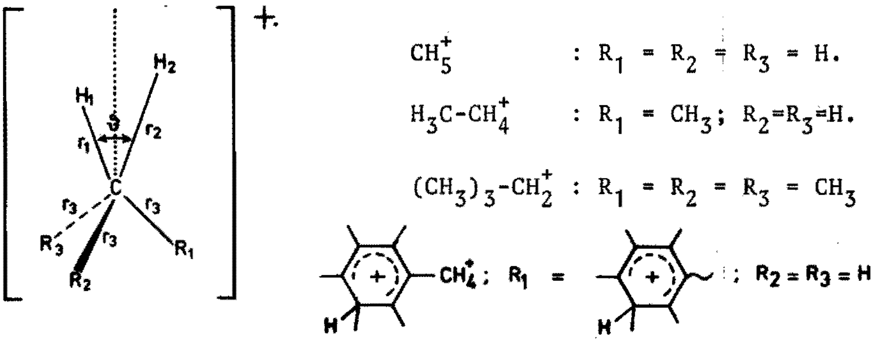


Fig. 2. Transition state for proton exchange in hexamethylbenzenonium ions.

The dedeuteration of $CH_3D$ has been studied by *Hogeveen* and *Bickel*[9] in $HF/SbF_5$ (11:1). Extrapolation of their data gives $k = 1.5 \times 10^{-7}$ $\text{l.mole}^{-1}.\text{sec}^{-1}$ at $-40^o$ C for this exchange reaction. The dedeuteration of $C_2H_5D$ in the same solvent has an extrapolated rate constant of $4.5 \times 10^{-6}$ $\text{l.mole}^{-1}.\text{sec}^{-1}$ at $-40^o$ C.[10] These proton exchange reactions are believed to proceed via closely related transition states (see figure 3).

The observation that $CH_3D$, $C_2H_5D$ and $(CH_3)_3CD$ are dedeuterated with comparable rates[9,10,11] under the same conditions ($HF/SbF_5$ (11:1) at $0^oC$: $k = 0.2 \times 10^{-4}$, $7 \times 10^{-4}$ and $50 \times 10^{-4}$ $\text{l.mole}^{-1}.\text{sec}^{-1}$, respectively) led *Brouwer* and *Hogeveen*[12] to the conclusion that the five coordinated carbon atom in the transition states (figure 3) carries little or no positive charge. Otherwise, charge delocalization by $CH_3$-groups would lead to differently stabilized transition states and, consequently, much larger rate differences would have been expected.

Taking into account the lower acidity of $HSO_3F$ ($H_0$ =-15)[13] compared with the acidity of $HF/SbF_5$ (11:1) (which is estimated to be about 10 to 100 times higher), the experimentally found rate of proton exchange of hexamethylbenzene in $HSO_3F$ ($1.3 \times 10^{-8}$ $l.mole^{-1}.sec^{-1}$ at $-40^{o}$ C) may be as much as 100 times larger in $HF/SbF_5$ (11:1). Thus, the rate of this proton exchange is quite comparable with the rate of dedeuteration of $C_2H_5D$ and the positively charged cyclohexadienyl-fragment is seen to have little or no influence on the energy of the transition state relative to the energy of the reactants. Again, this points to little or no positive charge of the five-coordinated carbon atom in the transition state as pictured in figure 3.



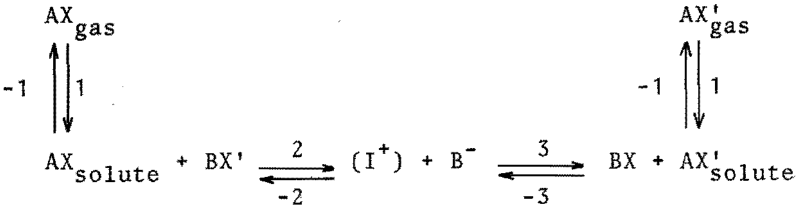
$CH_5^+$ : $R_1 = R_2 = R_3 = H$.

$H_3C\text{-}CH_4^+$ : $R_1 = CH_3$; $R_2 = R_3 = H$.

$(CH_3)_3\text{-}CH_2^+$ : $R_1 = R_2 = R_3 = CH_3$

Fig. 3. Transition state ($C_s$-symmetry) for proton exchange reactions.

As has already been stated, proton exchange between labelled isobutane and $HSO_3F$ is too slow to account for the observed scrambling in labelled products III, obtained from the hydride transfer reaction between benzyl cations and labelled isobutane. Experimentally, this was confirmed by measuring the rate of tritiation of isobutane gas[4] in the presence of tritiated $HSO_3F$. The heterogeneous exchange reaction between a gas AX and an acid BX' can be followed by analysing gas samples provided that the gas-solute equilibrium is fast compared with the rate-determining step ($k_2$) of the exchange reaction. Scheme A vizualizes the reactions which are relevant in the system.



Scheme A.

The pseudo first-order rate constant k' and the bimolecular rate constant $k_2$ are given by:

(18) $k' = (-1/t).\ln(1-x/x_\infty) = (K/K+1).(k_2/2).(a'+b)$

with $K = k_{-1}/k_1$ is the gas-solute equilibrium constant, a' and b are the concentrations of AX and BX in the liquid phase and $x/x_\infty$ is the fractional exchange at time t. For experimental details and the derivation of (18): see appendix A. Table IX summarizes the results.

### Table IX

Pseudo first-order and bimolecular rate constants (k' and $k_2$) for the exchange reaction between isobutane gas and $^3HSO_3F$.

| Temp. ($^\circ$ C) | k' ($sec^{-1}$) | $k_2$ ($l.mole^{-1}.sec^{-1}$) |
|---|---|---|
| -5 | 52 $x10^{-5}$ | 25 $x10^{-5}$ |
| 0 | 93 $x10^{-5}$ | 45 $x10^{-5}$ |
| +5 | 180 $x10^{-5}$ | 89 $x10^{-5}$ |
| +25 | 745 $x10^{-5}$ | 390 $x10^{-5}$ |

From table IX, the following activation parameters were calculated: $\Delta H^{\neq} = 13.7$ $kcal.mole^{-1}$ and $\Delta S^{\neq} = -22$ $cal.mole^{-1}.^oK^{-1}$.

The dedeuteration of 2-$^{2}$H-isobutane was followed by taking samples at suitable time-intervals and analysing these by means of PMR spectroscopy. At 0° C, the rate of this reaction was found to be 32 x$10^{-5}$ l.mole$^{-1}$.sec$^{-1}$. Comparing this value with the rate of the tritio-deprotonation ($k_2$ = 45 x$10^{-5}$ l.mole$^{-1}$.sec$^{-1}$), a small isotope effect of about 1.5 can be calculated . This is in agreement with the observation by *Hogeveen* et al.[9,10,12] of negligible isotope effects in the dedeuteration reactions of methane and ethane.

The dedeuteration of 2-$^{2}$H-isobutane was also briefly studied by *Hogeveen* et al.[11] in a mixture of Freon and $HF/SbF_5$ (25:1). At 0° C a half life of about 3.5 hours can be calculated from their data, whereas in $HSO_3F$ the tritio-deprotonation has a $t_{\frac{1}{2}}$ of about 10 minutes. This points to a higher acidity of $HSO_3F$ compared to $HF/SbF_5$ (25:1). The rate difference of a factor 20 amounts to a difference in $H_0$ of about 1.4 units, i.e. $H_0$ ($HF/SbF_5$(25:1)) = -13.6 (± 0.2) based on a $H_0$ value[13] for $HSO_3F$ of -15.0 (± 0.1).

That proton exchange between labelled isobutane and $HSO_3F$ is indeed a slow process at temperatures below -10° C was also confirmed by PMR spectra of solutions of 2-$^{2}$H-isobutane in $SO_2$-$HSO_3F/SbF_5$ (5:1) at -15 °C. Even after 45 minutes the deuterium splitting of 1 Hz. remained clearly visible and no trace of protio-alkane could be detected. The reported fast proton exchange[3] is in error; it was found that freshly distilled $HSO_3F$ oxidized isobutane to a slight extent due to traces of $SO_3$ in the solution. Under these conditions, traces of tert.-butyl cation are formed and the observed line-broadening and doublet-collaps is caused by rapid hydride exchange between these traces of tert.-butyl cation and dissolved isobutane.
This reversible hydride exchange was studied by *Olah* et al.[4], who reported a bimolecular rate constant of $10^4$ l.mole$^{-1}$.sec$^{-1}$ for this reaction at -40° C. in $HSO_3F/SbF_5$ (1:1) diluted with $SO_2ClF$.

Thus, proton exchange between the alkane and the acid can be ruled out as the source of the observed scrambling of label in compounds III.

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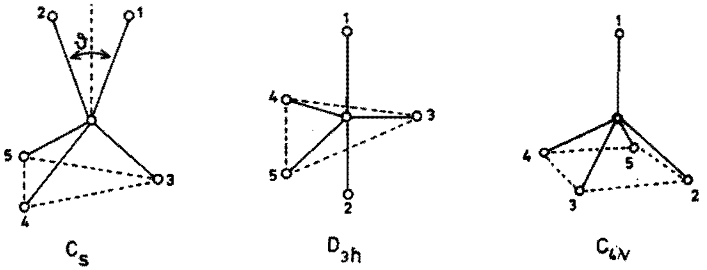
# CHAPTER V

## Quantummechanical Calculations.

### V.1. ALKANES AND PROTONATED ALKANES.

The observation of protonated methane in the mass-spectrometer[1] (in 1966) and the postulated intermediacy of $CH_5^+$ and related five-coordinated carbocations during protolytic reactions between alkanes and so-called "super-acids" (in 1968)[2], triggered theoreticians to perform quantummechanical calculations on these species. It was hoped that these calculations would show which geometry for $CH_5^+$ was energetically preferred and, furthermore, calculated charge densities were supposed to give valuable information aimed at a better understanding of the observed chemistry of methane in very strong proton acids.

Three different geometries were usually adopted as a starting point, viz. the $C_s$-symmetry, the $D_{3h}$-symmetry or the $C_{4v}$-symmetry, pictured in figure 1.



$C_s$ $D_{3h}$ $C_{4v}$

Fig. 1. Some symmetries adopted for five-coordinated carbocations.

*Gamba* et al.[3], using the semi-empirical CNDO/2 method of

*Pople*, *Santry* and *Segal*[4], calculated the $C_s$-symmetry to be about 10 kcal.mole$^{-1}$ more stable than the $D_{3h}$-symmetry. Ab-initio calculations, performed by *van der Lugt* and *Ros*[5] also showed the $C_s$-symmetry to be more stable than both the $D_{3h}$ and the $C_{4v}$-symmetry (3.5 and 0.3 kcal.mole$^{-1}$, respectively), but the results of *Mulder* and *Wright*[6] appeared to be at variance with these results. The latter authors concluded that the energy differences between the three adopted symmetries for $CH_5^+$ were so small that none of them was more favourable than another. Later, *Pople* et al.[7] performed more refined ab-initio calculations and found the $C_s$-symmetry to be definitely more stable than the $D_{3h}$ and the $C_{4v}$-symmetries. All reported calculations give geometrical parameters, very similar to each other, with the exception of the calculations of *Pople* et al., in which a much smaller angle for $H_1CH_2$ and slightly longer bond-lengths for C-$H_{1,2}$ was found.

As calculations on isobutane or protonated isobutane have not yet been published, it was decided to carry out some CNDO/2 calculations on these molecules. To check the reliability of the parametrization of the used programme, first $CH_4$ and $CH_5^+$ were calculated. For methane, tetrahedral symmetry ($T_d$) was calculated and the C-H bond-length was varied between 1.04 and 1.14 Å. Table X shows the results of the calculations.

The minimal energy for $CH_4$ was calculated to be -10.115 a.u. for a bond length of 1.09 Å (± 0.02 Å) for C-H. This geometry agrees well with that, calculated by *Pople* et al.[7], but the energy is calculated much too high. It may be noted, however, that ab-initio calculations are much more suited for the determination of absolute energies, but within the same framework, the CNDO/2 method is also suitable for the calculation of energy-differences. Bond polarization causes carbon to have a slight excess of electron-density in $CH_4$. Though this may enhance electrophilic attack on carbon, considerable electrostatic shielding may arise from the positively charged hydrogen atoms towards attacking, positively charged electrophiles.

Table X

Calculated energy$^{a)}$ and charge densities$^{b)}$ in $CH_4$ ($T_d$-symmetry).

| r(C-H), Å | 1.04 | 1.08 | 1.09 | 1.10 | 1.14 |
|---|---|---|---|---|---|
| $E_{tot.}$ | -10.107 | -10.109 | -10.115 | -10.115 | -10.114 |
| $E_{elec.}$ | -19.663 | -19.743 | -19.558 | -19.557 | -19.452 |
| $E_{bind.}$ | - 1.387 | - 1.390 | - 1.395 | - 1.394 | - 1.393 |
| μ(Deb.) | 0.028 | 0.001 | 0.003 | 0.003 | 0.024 |
| ρ(C) | - 0.050 | - 0.053 | - 0.047 | - 0.048 | - 0.045 |
| ρ(H) | + 0.0125 | + 0.013 | + 0.011 | + 0.011 | + 0.010 |

a) Energy in Hartrees, 1 Hartree = 1 a.u. = 628 kcal.mole$^{-1}$.

b) Charges in electron-units; a positive sign denotes a deficiency of electron density in the valence shell, a negative sign denotes a surplus.

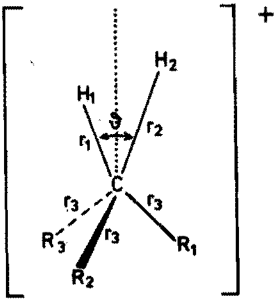


Fig. 2. $C_s$-symmetry for protonated alkanes

For $CH_5^+$, a $C_s$-like symmetry was adopted (see figure 2) and CNDO/2 calculations were performed for various angles $\theta$ and for different bond-lengths $r_1$, $r_2$ and $r_3$. The results are summarized in table XI. The geometry with minimum energy ($\theta=56^o$ ($\pm 4^o$) and $r_1=r_2=1.17$ Å, $r_3=1.10$ Å) agrees well with that calculated by *Gamba* et al.[3], *van der Lugt* and *Ros*[5] and *Mulder* and *Wright*[6], though different methods of calculation were used by these different authors.

Rotation of $H_1$,$H_2$ around the twofold axis did not change the total energy within $10^{-3}$ a.u., indicating that this rotation has only a very small energy barrier, not exceeding 50 cal.mole$^{-1}$. *Pople* et al.[7] also concluded to nearly free rotation of the $CH_3$ and the $H_2$ parts of the molecule with respect to each other and described $CH_5^+$ as "a hydrogen molecule attached to a $CH_3^+$ ion". In view of the calculated charge distribution in $CH_5^+$, this is a somewhat over-simplified view and it would be more correct to speak of a cationic $H_2$ molecule attached to a strongly polarized methyl radical. According to the calculations of *Pople* et al.[7], the H-H distance of the supposed hydrogen molecule is about 0.85 Å, whereas our calculations give a H-H distance of 1.10 Å. Note that the distance, as calculated by *Pople* et al. is rather close to the equilibrium-value in $H_2$ (0.746 Å), but the H-H distance, calculated by CNDO/2 methods is rather close to that of $He_2^+$: 1.08 Å. The stretching as well as the charge in the $H_2$ part of $CH_5^+$ ion points to considerable weakening of the C-H bonds in this ion, in accordance with the grossly increased negative charge of the carbon atom of $CH_5^+$ compared to $CH_4$.

For protonated methane , the results of CNDO/2 calculations showed the $D_{3h}$-symmetry to be about 3.5 kcal.mole$^{-1}$ less stable than the $C_s$-symmetry. *Gamba* et al[3] even calculated an energy-difference of about 10 kcal.mole$^{-1}$ and *Pople* et al.[7] found a value of about 3.7 kcal.mole$^{-1}$. Table XII summarizes our results of calculations on $CH_5^+$ and gives the results of *Gamba* et al.[3], *van der Lugt* and *Ros*[5] and *Pople*

# Table XI

Calculated energies[a)] and charge distributions[b)] in $CH_5^+$ ($C_s$-symmetry).

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $r_1$, Å | 1.09 | 1.10 | 1.10 | 1.10 | 1.12 | 1.17 | 1.30 | 1.37 |
| $r_2$, Å | 3.26 | 2.00 | 1.40 | 1.10 | 1.12 | 1.17 | 1.30 | 1.37 |
| $3_3$, Å | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 |
| $\theta$(degr.) | 10 | 30 | 40 | 58 | 58 | 56 | 45 | 36 |
| $E_{tot.}$ | -10.132 | -10.305 | -10.447 | -10.467 | -10.474 | -10.484 | -10.471 | -10.450 |
| $E_{elec.}$ | -20.899 | -21.891 | -22.801 | -23.293 | -22.203 | -22.949 | -22.522 | -22.383 |
| $E_{bind.}$ | - 0.773 | - 0.946 | - 1.088 | - 1.108 | - 1.116 | - 1.126 | - 1.113 | - 1.091 |
| $\mu$(Deb.) | 13.92 | 5.688 | 3.472 | 2.450 | 2.510 | 2.796 | 3.305 | 3.462 |
| $\rho(C)$ | + 0.010 | - 0.009 | - 0.098 | - 0.204 | - 0.199 | - 0.170 | - 0.100 | - 0.026 |
| $\rho(H_1)$ | + 0.058 | + 0.087 | + 0.235 | + 0.301 | + 0.301 | + 0.305 | + 0.300 | + 0.278 |
| $\rho(H_2)$ | + 0.853 | + 0.553 | + 0.371 | + 0.308 | + 0.309 | + 0.310 | + 0.302 | + 0.279 |
| $\rho(H_3)_{av.}$ | + 0.026 | + 0.124 | + 0.164 | + 0.197 | + 0.196 | + 0.185 | + 0.166 | + 0.156 |

a) Energies in Hartrees, 1 Hartree = 628 kcal.mole$^{-1}$.

b) Charge-densities in electron-units; see also note b), table X.

et al.[7] for comparison.

Calculation of the energy of $CH_5^+$ with constant $r_1$ and variable angle and bond-length $r_2$ simulates the protonation-deprotonation reaction:

(1) $CH_4 + H^+ \rightleftarrows CH_5^+$

The entering proton gains electrondensity at the expense of the four, originally present hydrogen atoms. Formation of the fifth bond lowers the total energy of the system and from our data the proton affinity is calculated to be about 232 kcal. mole$^{-1}$. As ab initio calculations are known to be superior to CNDO/2 calculations, as far as energies are concerned, the proton affinity calculated by *Pople* et al.[7] may be considered as more reliable; from their data the following reaction enthalpies may be derived:

(2) $CH_5^+ \rightarrow CH_4 + H^+$ -118 kcal.mole$^{-1}$.

(3) $CH_5^+ \rightarrow CH_4^+ + H^\cdot$ - 83 kcal.mole$^{-1}$.

(4) $CH_5^+ \rightarrow CH_3^+ + H_2$ - 16 kcal.mole$^{-1}$.

Though quantummechanical calculations may be fairly suited for the explanation of mass-spectrometric data, application to phenomena occurring in solutions must be done with great care due to the fact that solvation-effects may interfere. However, the conditions prevailing in solvents with a very low nucleophilicity[8] resemble gas-phase conditions to a large extent and calculations may be more significant for reactions occurring under these conditions.

Even in solvents with a very low nucleophilicity, however, deprotonation of $CH_5^+$ will be more easy than $H_2$-formation, because reaction (2) will be coupled to a reaction in which a nucleophile takes up the proton. It may be assumed, that the net effect of both coupled reactions will be a gain in energy if the proton affinity of the nucleophile is larger than that of methane. Deprotonation of $CH_5^+$, which is a rather

## Table XII

Geometry, energy^a) and charge distribution^b) of $CH_5^+$ ($C_s$ and $D_{3h}$-symmetries).

| Symmetry | $C_s$ | $D_{3h}$ | $C_s$ | $D_{3h}$ | $C_s$ | $D_{3h}$ | $C_s$ | $D_{3h}$ |
|---|---|---|---|---|---|---|---|---|
| Ref. | This work | | (3) | | (5) | | (7) | |
| $r_1=r_2$, Å | 1.17 | 1.125 | 1.21 | 1.16 | 1.17 | 1.13 | 1.24 | 1.12 |
| $r_3=r_4=r_5$, Å | 1.10 | 1.125 | 1.14 | 1.14 | 1.10 | 1.12 | 1.08 | 1.11 |
| θ(degr.) | 56 | -- | 50 | -- | 58 | -- | 40.1 | -- |
| $E_{tot.}$ | -10.484 | -10.479 | -10.206 | -10.190 | -40.2896 | -40.2842 | -40.3272 | -40.3157 |
| ρ(C) | - 0.170 | - 0.246 | - 0.164 | - 0.261 | - 1.113 | - 1.367 | --- | --- |
| $\rho(H)_{1,2}$ | + 0.307 | + 0.317 | + 0.299 | + 0.312 | + 0.436 | + 0.561 | --- | --- |
| $\rho(H)_{3,4,5}$ | + 0.185 | + 0.203 | + 0.189 | + 0.212 | + 0.413 | + 0.415 | --- | --- |

a) Energies in Hartrees, 1 Hartree = 1 a.u. = 628 kcal.mole$^{-1}$.

b) Charge-densities in electron-units; see also note b), table X.

stable ion under low-pressure conditions in the gas phase[9,10], occurs readily in the presence of suitable proton-acceptors[10]. Calculations[7] show that most simple molecules (e.g. $C_2H_6$, $C_2H_4$, $H_2O$, $NH_3$, HF) have a higher proton affinity than $CH_4$ and, thus, $CH_5^+$ acts as a very strong Brönsted acid in the presence of these compounds. One important exception may be noted here: $H_2$ molecules have a lower proton affinity than $CH_4$ in view of the fact, that $CH_5^+$ is formed from $H_3^+$ and $CH_4$, as demonstrated by *Aquilanti* and *Volpi*[9]. In accordance with this, H-D exchange between $H_2$ (or $D_2$) and very strong proton acids is extremely slow[8].

At very low pressures or in the absence of suitable proton-acceptors, $CH_5^+$ decomposes readily to $CH_3^+$ and $H_2$ (reaction (4)). This reaction has a very low activation energy, supposedly even smaller than 16 $kcal.mole^{-1}$ as a positive entropy effect may arise: for the formation of two particles from one ion, T x S is estimated to be 4 to 8 $kcal.mole^{-1}$ at room temperature and even more at elevated temperatures.

In solution, $CH_5^+$ will be very unstable and proton transfer will occur more readily than $H_2$ formation. This is in agreement with the fact, that dedeuteration of $CH_3D$ occurs at a measurable rate at 25° C in HF/$SbF_5$ (11:1) ($k = 3.9 \times 10^{-4}$ $l.mole^{-1}.sec^{-1}$) while the formation of $H_2$ or HD is not observed under these conditions[11]. Assuming $H_2F^+$ to be the most acidic species in HF/$SbF_5$ proton exchange may be thought to involve two steps (reaction (5)).

$$(5)\quad \text{a)}\ CH_3D + H_2F^+ \longrightarrow CH_4D^+ + HF + E_1$$

$$\text{b)}\ CH_4D^+ + F^- \longrightarrow CH_4 + DF + E_2$$

where $E_1$ and $E_2$ are the differences in proton affinity of HF and $CH_4$ and of $F^-$ and $CH_4$, respectively. The net gain in energy, i.e. $E_1 + E_2$ is equal to the difference in the proton affinities of HF and $F^-$ and, as $F^-$ is certainly more basic than HF, reaction (5) will be energetically favourable.

From the calculations of *Pople* et al.[7], $E_1$ is found to be -2 kcal.mole$^{-1}$ (or lower) and it may be assumed that (5) a) is rate determining in view of the fact, that $E_2$ will be much larger than +2 kcal.mole$^{-1}$.

Hydrogen evolution (reaction (6)) is also initiated by proton attack (step a)), but step b) is different:

$$(6)\quad a)\quad CH_4 + H_2F^+ \longrightarrow CH_5^+ + HF + E_1$$

$$b)\quad CH_5^+ \longrightarrow CH_3^+ + H_2 + E_3$$

However, the net gain in energy, $E_1 + E_3$, is about -18 kcal.mole$^{-1}$, or slightly more if the entropy is taken into account. It is by no means certain, though, that step a) is rate determining also for reaction (6). The observation, that proton exchange between $CH_4$, $C_2H_6$, $(CH_3)_3CH$ and protonated hexamethylbenzene on the one hand and strong proton acids on the other hand have rate constants which differ not very much (at the most a factor 100), then points out that a common intermediate is formed in the rate determining step of the proton exchange reaction, viz. the five-coordinated carbocation. The observed differences might be due to the small differences in σ-basicity of the different compounds. Scheme 1 summarizes reactions (2) to (6).

CNDO/2 calculations of isobutane and of protonated isobutane involved the optimalization of the geometry of isobutane (the C-C bond length and the tertiary C-H bond were varied) and the determination of the geometry with minimal energy of $C_s$-symmetry protonated isobutane. The C-H bond length in the $CH_3$ groups was fixed at 1.09 Å and tetrahedral angles were assumed for the tert.-butyl group throughout the calculations. Table XIII gives the results.

From table XIII, the energy of protonated isobutane is calculated to be 0.400 Hartrees lower than that of the parent compound, indicating a proton affinity of 245 kcal.mole$^{-1}$. Actually, the proton affinity of isobutane may be much smaller (cf. the experimentally observed[7] proton affinities of

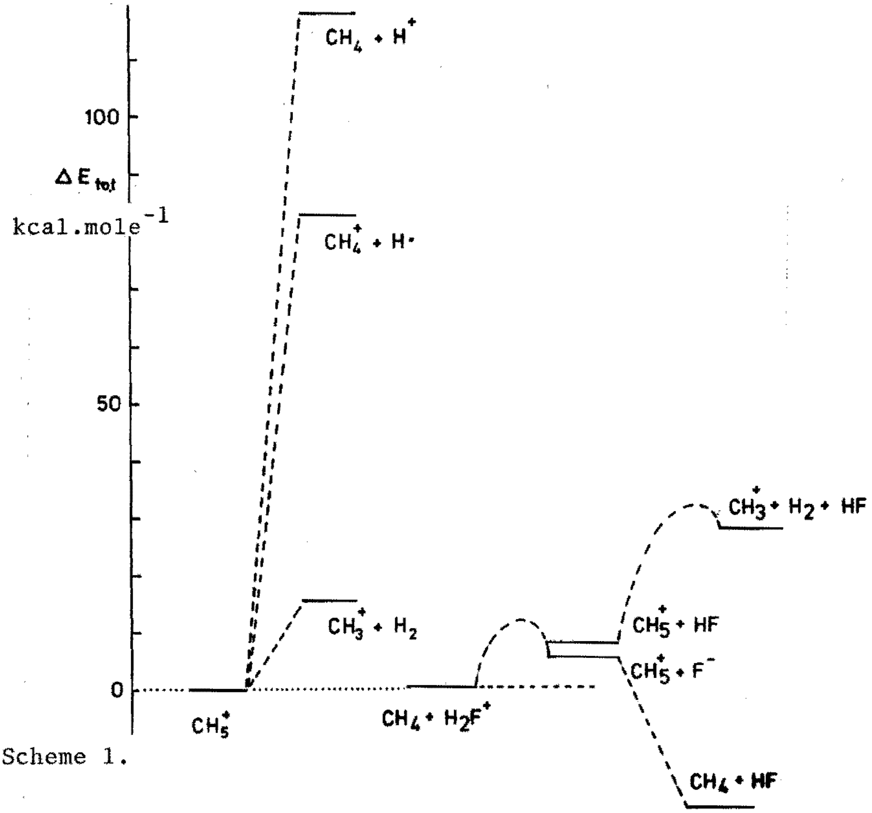
Table XIII

Energies[a] and charge distributions[b] in isobutane and in protonated isobutane ($C_s$-symmetry).

| | Isobutane | Protonated isobutane | | | | | |
|---|---|---|---|---|---|---|---|
| $r_1$, Å | 1.10 | 1.171 | 1.171 | 1.171 | 1.171 | 1.00 | 1.35 |
| $r_2$, Å | | 1.171 | 1.171 | 1.171 | 1.171 | 1.00 | 1.35 |
| $r_3$, Å | 1.54 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 |
| θ(degr.) | -- | 37 | 45 | 58 | 64 | 58 | 58 |
| $E_{tot.}$ | - 36.136 | - 36.498 | - 36.528 | - 36.536 | - 36.535 | - 36.439 | - 36.489 |
| $E_{elec.}$ | -116.225 | -123.557 | -123.508 | -123.569 | -123.596 | -124.625 | -122.497 |
| $E_{bind.}$ | - 5.088 | - 4.8116 | - 4.842 | - 4.850 | - 4.849 | - 4.753 | - 4.803 |
| μ(Deb.) | 0.163 | 1.811 | 1.778 | 1.589 | 1.499 | 1.327 | 1.829 |
| ρ(C) | + 0.050 | + 0.050 | + 0.030 | + 0.005 | - 0.002 | - 0.045 | + 0.052 |
| $\rho(H)_{1,2}$ | - 0.011 | + 0.250 | + 0.256 | + 0.254 | + 0.252 | + 0.262 | + 0.252 |
| $\rho(CH_3)_{av.}$ | - 0.013 | + 0.175 | + 0.181 | + 0.185 | + 0.194 | + 0.201 | + 0.175 |

a) Energy in Hartrees, 1 Hartree = 1 a.u. = 628 $kcal.mole^{-1}$.

b) Charge-densities in electron-units; see also note b), table X.



Scheme 1.

$NH_3$ and of $H_2O$: 207 and 164 kcal.mole$^{-1}$, respectively). Comparison with the proton affinity of methane, calculated in the same way, shows isobutane to be more basic than methane. The difference in the calculated proton affinities is about 13 kcal.mole$^{-1}$. The proton affinity of ethane is about 20 kcal.mole$^{-1}$ larger than that of methane[11]. In view of the known fact that CNDO/2 calculations usually yield energies and energy-differences which are smaller than the more refined ab initio treatment, the calculated difference in proton affinity between methane and isobutane is in agreement with the trend that higher homologs of methane have a higher basicity.

The larger rate of proton exchange and of hydrogen formation exhibited by isobutane in strong acids, compared to the same reactions with methane, may be due partly to the higher basicity of the former compound. The much larger stability of tert.-butyl cations compared with $CH_3^+$ (due to better solvation in solution[12]), however, will also favour the latter reaction.

## V.2. PROTONATED ISOALKANES AS REACTIVE HYDROGEN-DONATING INTERMEDIATES.

The experimental observations on the hydride transfer between isobutane and methylated benzyl cations, presented in the preceding chapters, can be summarized by the following statements:

*1) the rate of the hydride transfer reaction is linearly dependent on the Hammett acidity of the solvent, indicating that one proton (or: one acid molecule) participates in the transition state of the rate determining step;*

*2) the observed scrambling of transferred label is neither due to proton exchange between labelled alkane and the solvent prior to the actual hydride transfer step nor due to exchange between the labelled end-product (e.g. hexamethylbenzene) and the solvent.*

It may be noted that statement 1) does not describe an geometry for the transition state, nor does it explicitly say that the proton and the hydride ion are transferred in a concerted way. However, statement 2) leaves as the only acceptable alternative the assumption, that the observed scrambling of label occurs during the hydride transfer step per se. From this, it follows that the exchanging particles must be in close contact to each other and furthermore, some intermediate with a finite lifetime must be involved. As any chemical process, no matter how fast, takes some time to occur, it seems more proper to speak of scrambling of label occurring in an intermediate than to use the concept of transition states in this respect.

By definition, transition states are states with an infinitely short lifetime as these represent points in the multidimensional energy-geometry space where changes along the reaction coordinate only lower the total energy of the reacting system, i.e. transition states represent saddle points in the energy-geometry space[13]. In practice, high-energetic intermediates and related transition states resemble each other very closely and it is not easy to differentiate among them in many cases.

CNDO/2 calculations were performed on a number of substituted benzyl cations in order to see the influence of various substituents on the charge distribution in these cations. No extensive search was made for minimal geometries, however, so that the calculated energies are only of qualitative value. Table XIV lists some representative charge densities on carbon atoms in the phenyl ring and on carbon and hydrogen of the $CH_2$ group. It should be noted that for the first four calculations a slightly different parametrization of the CNDO/2 program was used in which a lower ionization-potential was assigned to carbon than in the other calculations. As a consequence, the latter calculations overestimate the electron-density on $C_5$ and underestimate the electron-density on the H atoms of the $CH_2$ group. The total charge of the $CH_2$ group remains the same in both calculations however, and as can be seen from table XIV considerable charge transfer occurs in each case from the phenyl ring to the electron-deficient $CH_2$ group.

In a separate calculation, using a CNDO/2 program with which also transition metals could be handled, benzyl cation and $Cr(CO)_3$-complexed benzyl cation was calculated. These calculations showed that the positive charge of the $CH_2$ group dropped from +0.52 to +0.42 charge units on complexation, whereas the total charge on the $Cr(CO)_3$ group increases from +0.27 to +0.48 electron-units on solvolysis of the benzyl chloride complex. Stabilization of the benzyl cation by the $Cr(CO)_3$ group thus is due to electron-donation of this group and not due to charge delocalization over the phenyl ring. In table XIV a definite trend is observed in the calculated charges on the $CH_2$-group, indicating increasing charge deloca-

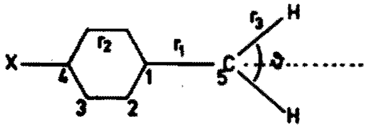
Table XIV

Charge distribution[a)] in different benzyl cations[b)].

| Substituents | $\rho(C_1)$ | $\rho(C_2)$ | $\rho(C_3)$ | $\rho(C_4)$ | $\rho(C_5)$ | $\rho(CH_2)$ |
|---|---|---|---|---|---|---|
| None | 3 | 99 | - 10 | 128 | 250 | 450 |
| p-Cl | 2 | 112 | - 14 | 184 | 228 | 410 |
| p-F | - 6 | 124 | - 60 | 359 | 224 | 406 |
| p-$CH_3$ | - 2 | 109 | - 36 | 180 | 211 | 381 |
| 3,5-$(CH_3)_2$ | 42 | - 89 | 74 | - 53 | - 54 | 354 |
| p-$NO_2$-II[c)] | -22 | 93 | 12 | 11 | - 74 | 328 |
| 2,6-$(CH_3)_2$ | -26 | 167 | 199 | 44 | - 84 | 314 |
| p-F-2,6-$(CH_3)_2$ | -39 | 177 | -253 | 315 | - 91 | 307 |
| p-H-II | -11 | 104 | - 3 | - 52 | - 88 | 303 |
| p-Cl-II | -20 | 91 | 0 | 46 | - 98 | 291 |
| p-F-II | -29 | 106 | - 57 | 244 | -103 | 285 |
| 2,4,6-$(CH_3)_3$ | -36 | 156 | -228 | 229 | -106 | 280 |
| p-$CH_3$-II | -14 | 108 | - 48 | 136 | -109 | 271 |

a) Electron-deficiencies, in $10^3$ electron-units.

b) CNDO/2 calculations, based on the following geometry:



$r_1 = r_2 = 1.40$ Å
$r_3 = 1.09$ Å
$\vartheta = 120°$

$r_{C_4-X}$ from ref. 14.

c) II = 2,3,5,6-tetramethyl-.

lization in these ions due to the substituents. The calculated charge of $CH_2$ is believed to be a good measure for the stability of the ions as observed in solvolytic experiments (see chapter II). The experimentally observed PMR shifts of the $CH_2^+$-group also agree qualitatively with the order of calculated charge densities in this group.

In view of the fact that positive charge will be best accomodated by electron-donating groups on the ortho- or para-positions, the instability of the 3,5-dimethylbenzyl cation, which hav not been observed as long-lived ion until now, is in agreement with the large positive charge of $CH_2$ as calculated. On the other hand, it is seen that the introduction of a $NO_2$-group on the para-position more than offsets the stabilizing action of two $CH_3$-groups on the ortho-positions. Furthermore, the delocalization of positive charge is seen to increase by para-substitution in the order: $NO_2 < H < Cl < F < CH_3$, which reflects the order of stability, found in chapter II. Substitution of $CH_3$ groups on the meta-position has only little effect on the stability of benzyl cations, as follows also from solvolytic experiments .

Table XIV shows, that the carbon atom $C_1$ carrying the $CH_2$-group becomes slightly negative in all cations II and some negative charge is also calculated for the meta-carbon atoms of the phenyl ring. However, the diminished availability of $\pi$-electrons makes it very unlikely that ring protonation of benzyl cations can occur to a measurable extent. On this basis, the possibility of a reaction between proton-benzyl cation complexes and isobutane molecules can be ruled out as an explanation for the observed proton-acid catalysis.

On the other hand, the reactivity of methane and other simple alkanes towards super-acids, as well as the quantum-mechanical calculations performed for $CH_5^+$ and $(CH_3)_3CH_2^+$, point out that protonated alkanes can be present as (transient) intermediates in strong acidic solutions.

Therefore, the reaction between protonated isobutane and a benzyl cation was simulated by calculating the total energy for these two ions in the CNDO/2 approximation. Approach of $C_s$-symmetry protonated isobutane towards benzyl cation along an axis perpendicular to the benzyl cation was taken as a model for the acid catalysed hydride transfer reaction between isobutane and pentamethylbenzyl cations. Figure 3 gives the charge distribution for the system at minimum energy.

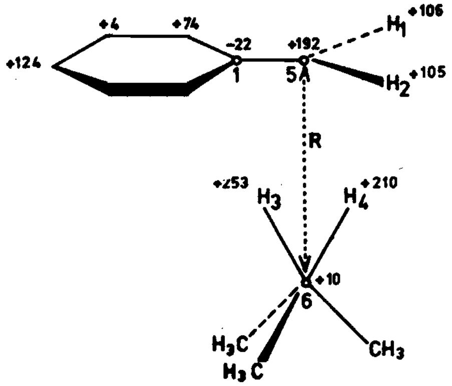


Fig. 3. Benzyl cation and protonated isobutane ($C_s$), approaching each other; R = 2.8 Å. Charge-densities in $10^{-3}$ electron units.

It was found that the total energy of the system, after an initial rise for decreasing R, showed a discrete minimum at R = 2.8 Å. Figure 4 shows a plot of the energy-difference of the system, compared with the energy of the two separate particles with the same geometry (R = ∞). The results of these calculations suggest that at R = 2.8 Å a stable intermediate is formed as separation of the two particles has an activation energy of about 7 kcal.mole$^{-1}$. In this intermediate, the distances between $C_5$ and $H_{3,4}$ and between $C_1$ and $H_3$ are 1.75 and 1.95 Å, respectively, i.e. well within the range of incipient carbon-hydrogen bonds. Furthermore, a drift of electron-density occurs in the $C_6$-$H_{3,4}$ bonds and in the $C_1$-$C_5$ bond of the protonated alkane and the benzyl cation, respectively. Table XV lists some calculated charge densities for protonated isobutane, approaching the benzyl cation.

Table XV

Charge distribution[a)] and energy[b)] of benzyl cation and protonated isobutane, approaching each other. (See figure 3).

| Distance R, Å | ∞ | 10 | 4 | 2.8 | 2.4 |
|---|---|---|---|---|---|
| $E_{tot.}$, a.u. | -91.044 | -90.992 | -90.930 | -90.935 | -87.767 |
| $E_{rel.}$, kcal.mole$^{-1}$ | 0 | 30.3 | 71.5 | 68.7 | 3,277. |
| $\rho(C_5)$ | +250 | +250 | +217 | +192 | +154 |
| $\rho(C_1)$ | + 3 | + 3 | - 5 | - 22 | - 35 |
| $\rho(C_6)$ | + 5 | + 6 | + 14 | + 10 | + 87 |
| $\rho(H_1)$ | +100 | +100 | + 99 | +105 | +112 |
| $\rho(H_2)$ | +100 | +100 | + 99 | +105 | +112 |
| $\rho(H_3)$ | +255 | +249 | +235 | +253 | +335 |
| $\rho(H_4)$ | +254 | +249 | +223 | +210 | +147 |
| $\rho$(total)[c)] | +967 | +957 | +882 | +853 | +912 |

a) Electron-deficiencies, in $10^3$ electron-units.

b) Energies in Hartrees, 1 Hartree = 628 kcal.mole$^{-1}$.

c) $\rho$(total) = the sum of the listed charges.

The results of these calculations point out, that considerable charge rearrangement occurs when the two positive particles approach each other. The initially equivalent hydrogen atoms $H_3$ and $H_4$ become an incipient hydride and proton, while the total charge in the reaction-center (i.e. carbon atoms $C_1$, $C_5$ and $C_6$ and hydrogens $H_1$, $H_2$, $H_3$ and $H_4$) diminishes. Further charge delocalization over the three methyl·

groups of the incipient tert.-butyl cation and the phenyl ring thus releases electrostatic repulsion between the two like-charged particles.

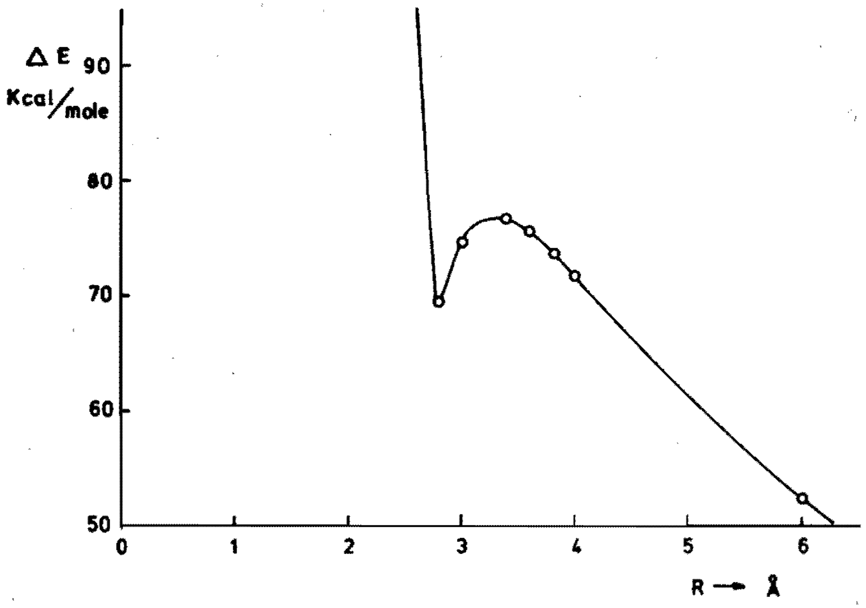


Fig. 4. $\Delta E_{tot.}$, kcal.mole$^{-1}$, of a protonated isobutane molecule approaching a benzyl cation.

It may be noted, that the approach of a benzyl cation and a protonated isobutane molecule (as presented here) is a rather crude model. A more refined treatment of the system should take into account, that nearly all bond lengths and bond angles change during the reaction. For instance, the five-coordination of $C_6$ will become a three-coordination as a tertiary butyl cation is formed upon hydride transfer. A change in coordination also occurs on $C_1$ and $C_5$, which become an aliphatic $CH.CH_3$ part of protonated toluene. However, even from the crude model employed here, valuable information about the driving force of the hydride transfer reaction can be derived.

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# CHAPTER VI

## Discussion and Concluding Remarks.

### VI. SOLVATED ALKANES AS HYDROGEN DONORS.

The low rate of proton exchange between methane[1], ethane[2] and isobutane[3] and strong acids and the low rate of hydrogen - formation for isobutane[4] in proton acids is qualitatively in agreement with the calculated low proton affinity of alkanes[5]. High-energetic, five-coordinated carbon species are assumed as transition states or intermediates for these reactions. The fact that the rate of these reactions depends strongly on the acidity of the solvent, but depends very little on the substituents attached to the reaction center, added to the observed chemistry of alkanes in strong acids (see page 17-18), all point to $C_s$-like geometries for protonated alkanes.

On the other hand, the high rate of hydride transfer between isobutane and pentamethylbenzyl cations in $HSO_3F$ and the smooth electro-chemical oxidation of alkanes in this solvent[6], point to the existence of another intermediate in solutions of alkanes in strong proton acids. The latter reactions are also acid catalysed and involve transition states or intermediates which contain one proton or one proton acid molecule.

Many chemical observations about reactions of alkanes in strongly acidic solutions are explained readily if the following equilibria are assumed to exist in, for instance, $HSO_3F$ solutions of alkanes (see figure 1):

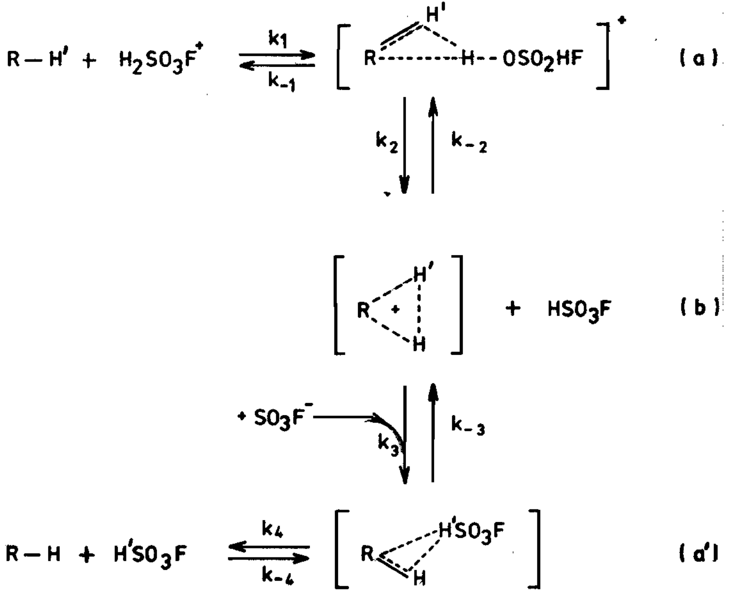


Fig. 1. Proton exchange between alkane and $HSO_3F$.

Due to the high-energetic nature, species (b) can be expected to be present only in low concentrations and with suitable proton-acceptors (such as $SO_3F^-$ ions, for instance) protonated molecules (b) are rapidly deprotonated. In solvents with a very low nucleophilicity, $H_2$ formation can occur also but proton exchange is usually faster than the former reaction which points to the very high acidity of species (b). Under mass-spectrometric conditions hydrogen formation can become predominant, especially with protonated propane and protonated (iso)butane.

*Aquilanti* and *Volpi*[7] were able to observe protonated methane and ethane in the mass-spectrometer, but protonated or deuterated propane or (iso)butane decomposed so rapidly that these species were not observed. Their observation that deuterated propane, for instance, formed in the reaction between $D_3^+$ and propane, gave only low amounts (less than 20%) of deuterated propyl cations $H_3C\text{-}CD^+\text{-}CH_3$ and the later observation of *Field* and *Munson*[8] that protonated cyclo-$C_6D_{12}$, formed in the reaction between $CH_5^+$ and the deuterated alkane, did not yield $C_6D_{10}H^+$ ions in the hydrogen forming reaction:

$$(1) \quad C_6D_{12} + CH_5^+ \longrightarrow C_6D_{12}H^+ + CH_4 \longrightarrow C_6D_{11}^+ + HD + CH_4$$

all point to an inequivalency of the carbon-hydrogen bonds in five-coordinated carbocations which are just formed. According to *Field* and *Munson*, "... it would appear that if $CH_5^+$ donates a proton it does not become at all equivalent to the other hydrogens in the (cyclohexane) molecule..." (ref. 8, page 4279).

In solution chemistry, the same phenomenon is encountered. The observation of *Pletcher* *et al.*[6] that the anodic oxidation of alkanes in $HSO_3F$ solution is acid catalysed, was ascribed by them to a rate determining protonation equilibrium preceding the fast electron-transfer steps at the anode:

$$(2) \quad R\text{-}H + HSO_3F \underset{k_b}{\overset{k_f}{\rightleftharpoons}} RH_2^+ + SO_3F^-$$

$$(3) \quad RH_2^+ \longrightarrow [RH_2^{++}] + e^- \longrightarrow R^+ + 2\,H^+ + 2\,e^-$$

From the dependence of the half-wave potential $E_{\frac{1}{2}}$ on the concentration of $SO_3F^-$ it was inferred that one proton participated in the rate determining step, and from the steady-state limiting current *Pletcher* *et al*. estimated a lower limit for $k_f$ of $2.5 \times 10^3$ sec.$^{-1}$ at 25° C. Formation of protonated alkanes at such a rate is in contradiction with the observed low rate of proton exchange of alkanes, a reaction that proceeds *via* the same intermediate, unless one makes the unreasonable assumption that deprotonation is rate determining in the latter case.

Rather it must be assumed that a second species is present in solutions of alkanes in strong acids which is more readily formed than "free" protonated alkanes and thus is much less energetic than $RH_2^+$ ions. It is postulated here that solvated alkanes (a) or alkane-proton acid adducts are formed prior to the formation of "free" $RH_2^+$. The suggested reaction mechanism for proton exchange between alkanes and strong acids (figure 1) resembles the mechanism for electrophilic substitution, species (a) being comparable with π-complexes while species (b) resemble Wheland σ-complexes.

The unexpected high solubility[1,2,3] of the lower alkanes in $HSO_3F$ and $HF/SbF_5$ mixtures, as compared with the low solubility of gaseous alkanes in water[9], also suggests some specific interaction between solute and solvent in the former case. In view of the high dielectric constant of strong anhydrous acids, strong solvation of dissolved particles must be expected and the electron-demand exhibited by protons in $HSO_3F$ and especially in $H_2SO_3F^+$ ions may lead to adducts between alkanes and these proton donors in $C_s$-like geometries in which electron-density of C-H bonds is shared with protons in three-center bonds.

The postulated alkane-proton acid adducts can also be considered as intimate ion-pairs consisting of a strongly solvated protonated alkane (see figure 2). Proton exchange, i.e. the reaction (a)→(b)→(a'), then would involve desolvation of (a) which would inevitably lead to an increase of the internal energy of the separated ion-pair.

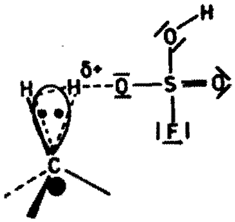


Fig. 2.

It has been noted already that the reaction between labelled isobutane and cations II in $HSO_3F$ leads to scrambled products. Neither proton exchange between the alkane and the acid, nor proton exchange between product and acid could account for the observed scrambling. These facts strongly suggest that some exchange of hydrogen isotopes occurs during the hydride transfer step per se. The assumption of "free", five-coordinated $RHD^+$ species as a hydrogen-donating intermediate must be rejected on several grounds. The most important argument is the high-energetic nature of these species. The formation of species (b) (see figure 1) is very slow as indicated by the rather low rate of proton exchange reactions. Secondly, labelling percentages of 50% would arise in all experiments (if the assumption is made of negligible isotope effects) when the symmetrical $C_s$-structure for intermediate (b) is assumed. If it is assumed that isotope effects are not negligible, the situation becomes even worse, for then the heavier isotopes would have a much smaller chance of being transferred as a hydride, especially at low temperatures, and deuteration would always be smaller than 50%. Actually, the reverse is observed for the reaction with 2-$^2$H-isobutane.

*Kurz* and *Kurz*[10] pointed out, in a theoretical treatment of proton transfer reactions, that different modes of proton transfer can be discerned depending on the size of the reactants, the activation energy of the reaction and the dielectric properties of the solvent (the dielectric constant $\varepsilon$ and the microscopic relaxation time $\tau$). Their treatment was based on an electrostatic model in which a charge is transferred from one site to another site in a cylindrical cavity surrounded by a continuous dielectricum. The results of their treatment are equally well applicable to hydride transfer reactions as only the sign of the transferred charge is reversed in the latter case. According to the model of *Kurz* and *Kurz*, a fast hydride transfer between bulky reactants will be coupled to the rotational fluctuations in the surrounding solvent if this solvent has a high dielectric constant and a rather large relaxation time. The polarization of the solvent will be such that the internal charge distribution of the activated complex will be completely in equilibrium with its environment at all points along the reaction coordinate. In other words, the duration of the transfer event will be much longer than the natural duration of a C-H vibration ($10^{-13}$ sec.) in view of the fact that the microscopic relaxation time $\tau$ of $HSO_3F$ may be assumed to be much longer than $10^{-13}$ sec.

Normally, isotopic scrambling between transferred hydride ions and labile protons from the acidic solvent is not observed, as has been pointed out by *Deno* <u>et</u> <u>al</u>.[11]. The reported hydride transfer between 2-$^2$H-isobutane and tert.-butyl cations in strongly acidic solutions[12,13,14] corroborates this. This latter reaction is not really acid catalysed, however, and the transfer event may occur so fast that protons from the solvent do not have a chance to interfere and to catch electrons from the transferred hydride. Though *Olah* <u>et</u> <u>al</u>.[12] postulate a three-center bonded transition state for the $H^-$ transfer between isobutane and tert-butyl cations, a linear transition state cannot be ruled out. (See figure 3).

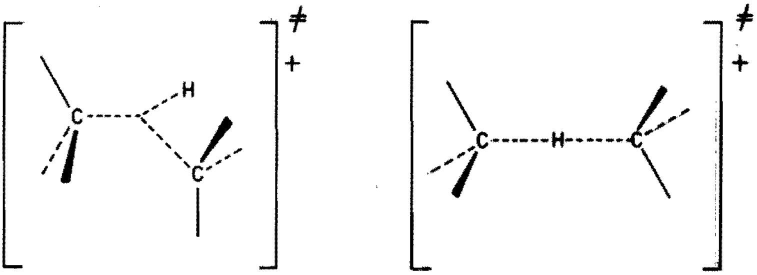


Fig. 3. Possible transition states for $H^-$ transfer between isobutane and tert.-butyl cations.

Observation of a rather low kinetic isotope effect $(k_H/k_D) = 5$ for the hydride transfer between isobutane and tert.-butyl cations[12] is in excellent agreement with the predictions of the theory of *Kurz* and *Kurz*[10] that solvent coupled transfer reactions will have isotope effects that are lowered by a factor of 3 or more compared with the isotope effects that would normally be expected.

The fact that scrambling is observed <u>during</u> the hydride transfer between isobutane and methylated benzyl cations points out that the acid molecule (or solvated proton), present in the termolecular intermediate,can interact with the incipient hydride ion. Figure 4 shows the suggested transition state.

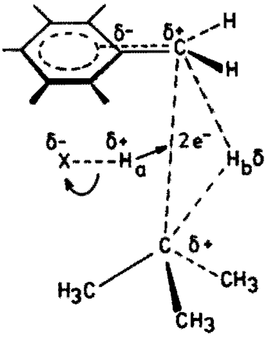


Fig. 4. Transition state for the transfer of a $H^-..H^+$ pair between solvated isobutane and cation IIb, indicating the scrambling route.

It is suggested that the incipient hydride ion can exchange electrons with the electron-deficient proton $H_a$ which is in very close proximity to the transferred hydride $H_b$. In stronger acids, proton $H_a$ becomes "harder" as it is less strongly bonded to its conjugate base, and increased interaction of $H_a$ with $H_b$ will lead to increased scrambling as is actually observed. On the other hand, heavier isotopes of hydrogen $H_b$ will interact more strongly with the carbon atom of the $(CH_3)_3C$ part of the system due to a lower zero-point vibrational energy in the C-D or C-T bond. Differences in zero-point energy are in the order of 0.3 to 0.45 $kcal.mole^{-1}$ compared to the C-H bond, and these rather small energy terms may lower the rate of transfer relatively much in view of the small activation energies involved. Substitution of $H_b$ by heavier isotopes $^2H_b$ or $^3H_b$ then leads to increased scrambling as is actually observed (cf. table VIII of chapter IV). Isotopic substitution of $H_a$, for instance by tritiation of the acid, does not have a notable effect on the scrambling behaviour (cf. table VII of chapter IV) as the bond between proton $H_a$ and its conjugate base $X^-$ is very weak and thus is not sensitive for isotope effects.

Though the model used in chapter V to calculate the energy of a benzyl cation approaching a protonated isobutane molecule (figure 3 of chapter V) is not exactly coincident with the postulated transition state (figure 4 of this chapter), it may be inferred from the calculated charge densities that a proton-hydride pair is transferred in a more or less concerted way. The driving force for this process is thought to be the strong polarization present in the benzylic $C-CH_2^+$ bond which polarizes entering hydrogen-like molecules to form a hydride-proton pair. The observation that isoalkanes react much faster than molecular $H_2$ and furthermore, that no tritium is incorporated when hexamethylbenzene is formed from pentamethylbenzyl cations and $H_2$ (20 atm., -60° C) in tritiated $HSO_3F/SbF_5$ (5:1), indicates similar transition states (see figure 5). The lower rate of the reaction with $H_2$ must be ascribed to the fact that entering hydrogen molecules must be polarized and stretched to form a $H^--H^+$ pair, whereas in the reaction with solvated isoalkanes, this situation is already present in the beginning of the reaction.

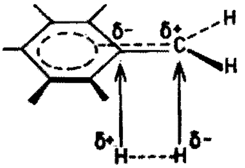


Fig. 5. Transition state for the reaction between methylated benzyl cations and $H_2$.

From the reported activation enthalpies and entropies of reactions (4) to (6), the free energies of activation at -40° C are found to be: 9.1 (± 1) $kcal.mole^{-1}$, 18.7 (± 1.5) $kcal.mole^{-1}$ and 12.4 (± 2.5) $kcal.mole^{-1}$, respectively.

(4) $(CH_3)_3C\text{-}H + (CH_3)_3C^+ \longrightarrow (CH_3)_3C^+ + (CH_3)_3C\text{-}H$

$\Delta H^{\neq} = 4.0$ $kcal.mole^{-1}$, $\Delta S^{\neq} = -22$ e.u. (ref. 12)

(5) $(CH_3)_3C\text{-}H + {}^3HSO_3F \longrightarrow (CH_3)_3C\text{-}{}^3H + HSO_3F$

$\Delta H^{\neq} = 13.3$ $kcal.mole^{-1}$, $\Delta S = -22$ e.u. (ref. 3)

(6) $(CH_3)_3C\text{-}H + HSO_3F +$ pentamethylbenzyl$^+$ $\longrightarrow$ Products

$\Delta H^{\neq} = 2$ to 4 $kcal.mole^{-1}$, $\Delta S^{\neq} = -40$ to -55 e.u..

Assuming that part of the free energy of activation in reaction (6) is necessary for the formation of a solvated isobutane molecule and another part is needed for the hydride transfer step per se, and assuming furthermore that the free energy of activation for this latter step is about the same as the free energy of activation for reaction (4), the $\Delta G^{\neq}$ for the formation of solvated alkane is about 3.5 $kcal.mole^{-1}$. A schematical energy diagram is shown in fig. 6.

Summarizing the postulated reaction mechanism for the hydride transfer reaction between (iso)alkanes (or $H_2$) and methylated benzyl cations, three rules may be seen to govern the rate of these reactions:

1. Strong polarization of the benzylic $C\text{-}CH_2^+$ bond forces incoming hydrogen-like molecules to become a proton-hydride pair.
2. Solvation of C-H bonds in alkanes by strongly acidic hydrogen weakens the carbon-hydrogen bond that is "protonated" and promotes heterolytic splitting of this bond.
3. A solvent-coupled mechanism retards the transfer of the proton-hydride pair sufficiently that some scrambling may occur.

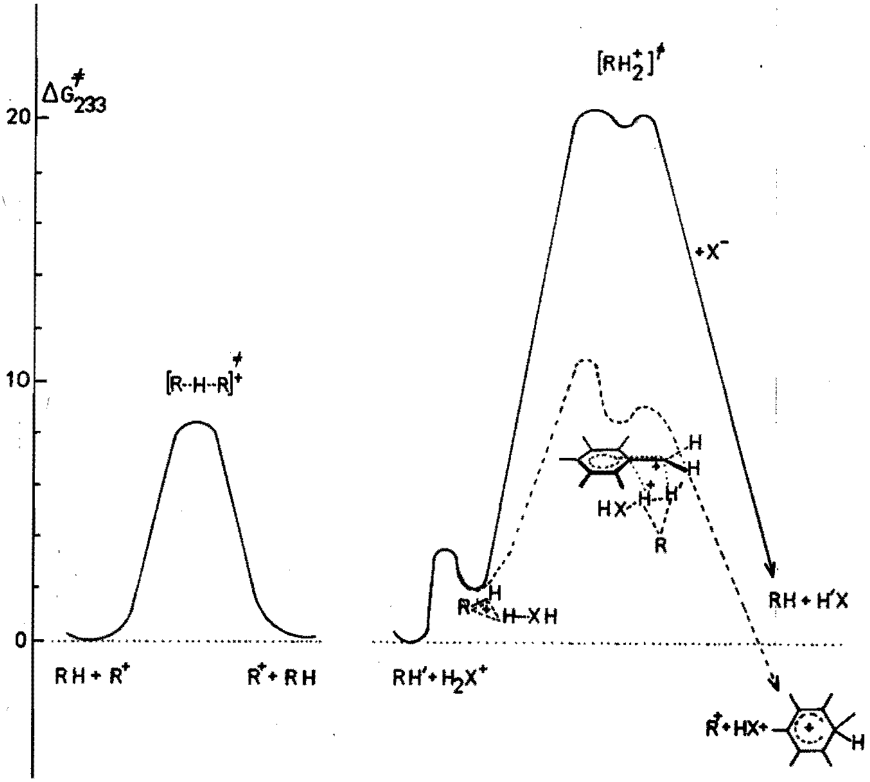
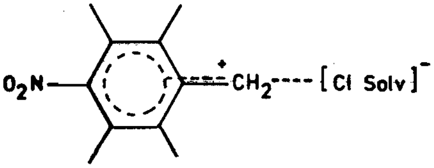


Fig. 6. $\Delta G^{\neq}_{233}$ for reactions (4), (5) and (6).

According to rule 1, benzyl cations substituted with alkyl groups on the benzylic center (e.g. α,α-dimethylbenzyl cations) are not reactive, due to the charge delocalizing action of these substituents. It may be expected that α,α-difluorobenzyl cations are likewise not reactive. According to rule 2, a higher proton affinity of the alkane enhances the rate of the reaction which explains the low reactivity of $CH_4$ and of $C_2H_6$ and the high reactivity of isobutane. According to rule 3, labelling of the acidic medium has no effect on the reaction rate, but isotope effects do occur if the hydride donor is labelled.

## VI. 2. SOME CONCLUDING REMARKS.

As has been noted in chapter III, the stability of the 4-$NO_2$-2,3,5,6-tetramethylbenzyl cation is much lower than that of, for instance, the pentamethylbenzyl cation. Solvolysis of halide If in $HSO_3F$ is not achieved as evidenced by UV and PMR spectra. Nevertheless, a rapid reaction takes place with isobutane and other tertiary alkanes and products IIIf are formed, though the rate of this reaction is lower than, for instance, with IIb. It may be assumed that either small concentrations of IIf, or strongly polarized donor-acceptor complexes of If and acid molecules, resembling tight ion-pairs, are present in solutions of If in $HSO_3F$. The fact that the rate is not very much slower (at the most a factor 100) than the reaction rate of the hydride transfer between isobutane and cations IIb,suggests the occurrence of ion-pairs rather than that of free cations IIf in $HSO_3F$. As has been pointed out by *Lichtin* et al.[15], the reactivity of ion-pairs in displacement reactions will be lower than the reactivity of free ions, though the decrease of the rate is usually not very large.



The here suggested occurrence of ion-pairs in solutions of halides 1(a-f) in $HSO_3F$ could not be established with certainty, but measurements of the conductivity of dilute solutions of halides Ia or Ib in pure $HSO_3F$ revealed that the equivalent conductivity $\Lambda_{eq.}$ did not give straight lines when plotted against $(c)^{\frac{1}{2}}$ in the region of $c = 0.1 \times 10^{-4}$ to $100 \times 10^{-4}$ mole.$1^{-1}$. The measurements were carried out at low temperatures ($-40^\circ$ and $-75^\circ$ C) and, though the reproducibility of the different runs was rather bad, the same trend was observed each time, viz. a curvature in the plots of $(c)^{\frac{1}{2}}$ against $\Lambda_{eq.}$ indicating a larger equivalent conductivity in the more dilute solutions. This suggests that in the more concentrated solutions of halides Ia and Ib in $HSO_3F$, solvolysis into free cations II is incomplete at low temperatures, i.e. halides Ia and Ib behave as weak electrolytes under these circumstances. The observation of complete solvolysis,judged from PMR spectra or UV spectra does not rule out the existence of rapidly equilibrating ion-pairs, as these spectroscopic techniques are not very well suited to discriminate between free ions or ion-pairs in solutions.

Assuming that halide If solvolyses only to a slight extent in $HSO_3F$ and forms predominantly ion-pairs between cations IIf and solvated $Cl^-$ ions, the lower reactivity towards isobutane can be explained. However, noting that in the reaction between $^3$H-labelled isobutane or $^3$H-labelled 2-$^2$H-isobutane less scrambling of label is observed in product IIIf than for instance in product IIIa and IIIb, this latter observation points to a faster hydride transfer step per se. As the amount of scrambling during the transfer of the hydride-proton pair is only indicative for the rate of this process, but not for the overall-rate of the whole reaction, the overall-rate may be influenced by other factors, such as the rate of solvolysis of the halide and the reactivity of the particular benzyl cation involved. In view of the fact that substituent effects are of minor importance as far as the overall-rate of the hydride transfer reaction is concerned, solvolysis as a rate determining process seems to be ruled out. The observed differences in the overall reaction rate may be caused either by the occurrence of different concentrations of free cations II or by rather small differences in reactivity of ion-pairs formed by the variously substituted benzyl cations II.

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# CHAPTER VII

## Experimental Part.

### APPARATUS.

PMR spectra were recorded on a Varian A-60a NMR spectrometer or on a Varian T-60 spectrometer, equipped with a variable temperature accessory. The T-60 was equipped with a Perma-lock, a spin-decoupler and a low temperature probe. NMR spectra of benzyl cations IIe and IIf were taken on a Varian HA-100 spectrometer connected to a Digilab Fourier Transform computing system.

UV spectra were recorded on a Perkin-Elmer 124 spectrophotometer with a thermostated cell-holder.

Tritium was determined with a Packard 3015 liquid scintillation counter. Efficiencies were measured either by the channels ratio method of an external standard, or by an internal ($^3$H)toluene standard.

Deuterium analyses were performed in Leiden, at the Gorlaeus laboratories, by Dr. Klebe and Dr. van Thuyl. Use was made of a GEC-AEI MS-902 double focussing mass spectrometer, operating at low ionization potential (6.2 eV for hexamethylbenzene). The intensity of the parent peaks was measured with an ion-current meter attached on the collector line. The accuracy of the deuterium determinations was about 0.5%.

Conductivity measurements were carried out with a Philips GM 4249 conductivity-meter.

## MATERIALS.

Fluorosulphuric acid ($HSO_3F$) (Schuchardt) and $CF_3SO_3H$ (Fluka) were distilled at atmospheric pressure under a stream nitrogen; the boiling points of these acids are: 167 and 164$^{o}$ C, respectively. Due to their hygroscopicity, the storage time of these acids is limited to about 10 days and therefore, mainly freshly distilled acids were used.

$SO_2ClF$ (Cationics Inc.) and $SbF_5$ (Aldrich) were used as obtained. Isobutane gas (Matheson) of purity better than 99.5% was used throughout. Hydrogen, methane and other hydride donors (such as adamantane, methylcyclohexane and 2,2,3-trimethylmethane) were used as obtained from different commercial sources.

Tritiated water with and activity of 5 mCi.ml$^{-1}$ was supplied by Amersham (G.B.).

Deuterated isobutane was prepared from tert.-butyl bromide via the *Grignard*-compound (made in tetrahydrofurane solution). Evaporation of excess THF from the solution of the *Grignard*-compound at low pressure and subsequent addition of $D_2O$ (Merck, purity better than 99.9% deuterium) gave deuterated isobutane gas. The gas was collected in a cold trap ($CO_2$/acetone) and distilled once to remove traces of THF.

Tritiated 2-$^{2}$H-isobutane was prepared in the same way, but 10 µl. of tritiated water was added to the $D_2O$. Tritiated 2-$^{1}$H-isobutane was obtained via proton exchange between isobutane and tritiated $HSO_3F$.

## BENZYL CHLORIDES I(a-f).

Para-methoxy-2,3,5,6-tetramethylbenzyl chloride (Ia) was prepared from 2,3,5,6-tetramethylphenol (durophenol) in two steps. Firstly the phenol was methylated in $CH_2Cl_2$ solution by means of 2,2,2-trimethoxy-4-methyl-1,2-oxaphospholene-4 according to the method of *Voncken*[1]. Washing with water and removal of the methylene chloride yielded quantitatively the durophenol-methyl ether. This procedure was found to be superior to that used by *Olah* et al.[2], viz. methylation of durophenol by dimethylsulphate and sodium hydroxide[3].

Durophenol-methyl ether was converted to Ia by heating 10 grams of the compound in concentrated HCl with 5 grams of 35% formaline under stirring for 4 hours at 65° C. Recrystallization (3 times) from ligroin gave pure white product Ia; yield: 70%, mp. 108-109° C. Analysed for $C_{12}H_{17}ClO$: Calcd: C, 67.76; H, 8.05. Found: C, 67.82; H, 8.18.

Pentamethylbenzyl chloride (Ib) was prepared according to the method of *Benington* et al.[4]. Pentamethylbenzene (K&K or Aldrich) was chloromethylated in concentrated HCl by means of formaldehyde. At this point it should be mentioned that a warning has been published concerning the use of acidic formaldehyde solutions. Heating of these solutions may lead to the formation of highly carcinogenous bis-chloromethyl ether[5]. Working in a good fume cupboard is absolutely imperative for chloromethylation reactions in general.

Para-bromo-2,3,5,6-tetramethylbenzyl chloride (Id) was prepared from bromodurene[6] by chloromethylation using standard methods[2].

2,3,5,6-Tetramethylbenzyl chloride (Ie) was prepared by the method of *Benington* et al.[4]. Repeated recrystallizations were necessary to obtain a pure product (mp. 69.3° C).

Para-fluoro-2,3,5,6-tetramethylbenzyl chloride (Ic) was prepared in seven steps, starting with durene.
(a) Durene was converted into dinitrodurene according to the method described in Organic Syntheses, Vol. II, page 254.
(b) Reduction of dinitrodurene in ethanol by means of sodium disulfide afforded 95% pure nitro,amino-durene[7].
(c) Para-nitro-2,3,5,6-tetramethylbenzenediazonium tetrafluoro-

borate was prepared by diazotation of nitro,aminodurene in 25% $H_2SO_4$ with $NaNO_2$ at 0° C, followed by the addition of an excess of a saturated $NaBF_4$ solution in water, filtering and drying in air.

(d) Thermolysis of the diazonium salt mixed with an equal weight of sea sand (in the fume cup board!) and extraction of the solid left in the flask gave crude nitro,fluorodurene. Chromatography over a silica column with petroleum ether as eluens gave pure, white nitro,fluoro-durene; yield: 35 to 55%, mp. 97-98° C.

(e) Nitro, fluoro-durene was catalytically reduced in ethanol solution by means of $H_2$ gas (10 atm.) and Pd/C catalyst in a Parr apparatus. Quantitative conversion to fluoro,aminodurene was obtained.

(f) Diazotation of this latter compound in 25% $H_2SO_4$ with $NaNO_2$ at 0° C followed by the addition of a large excess of $H_3PO_2$ afforded 70% crude product after 3 days at room temperature. Washing a solution of crude fluorodurene with $Na_2CO_3$ solution followed by steam distillation gave essentially pure product. Subsequent chromatography over $Al_2O_3$ with ligroin as eluens gave 40% fluorodurene; mp. 51-52° C.

(g) Fluorodurene was converted into Ic by chloromethylation following the method of *Suzuki*[8]. A solution of fluorodurene in monochloromethyl ether (about 1 g of product in 10 g solvent) was cooled (0° C) and 60% oleum was added with stirring The warm, brown solution was poured on crushed ice and extracted with chloroform, washed with water and dried. Evaporation of the solvent gave crude Ic. Recrystallization from petroleum ether (60/80) gave pure product Ic; mp. 64-66° C.

The overall yield of steps (a) to (g) is about 4 to 6%, based on starting material, i.e.durene.

Para-nitro-2,3,5,6-tetramethylbenzyl chloride (If) was prepared from nitro-durene[9] according to the method of *Suzuki*[8]. A yield of 65% of If was obtained after recrystallization from petroleum ether (60/80); mp. 110-111° C.

The reported direct mono-nitration of durene by means of nitronium tetrafluoroburate in superdry sulfolane (tetrahydrothiophene,1,1-dioxide)[10] was unsuccessful. The combined result of three attempts to obtain nitrodurene in this way was a meagre 0.5% of pure product based on durene. The main product of the nitration reaction was 2,3,5,6,2',4',5'-heptamethyl, diphenylmethane, as was evidenced by PMR spectra[11].

$Cr(CO)_3$-complexed benzyl alcohol was prepared via the method of *Strohmeier*[12] in a specially constructed reaction vessel. Either direct complexation of benzyl alcohol with chromiumhexacarbonyl in diglyme solution or reduction of $Cr(CO)_3$-complexed methylbenzoate by means of $LiAlH_4$ in ether was employed. Both methods gave only low yields (about 20%) of pure product.

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# APPENDIX A.

## HETEROGENEOUS EXCHANGE OF ISOTOPES BETWEEN SUBSTRATES WITH ONE EXCHANGEABLE SITE.

Consider an equilibrium between a gas and a solution of that gas in a solvent. Between the solvent and the solute, an atom or group X can be exchanged for isotopically labelled X'.

$$\begin{tikzcd}
AX_{gas} \arrow[d, shift right, "k_1"'] & & & AX'_{gas} \arrow[d, shift left, "k_4"] & \\
AX_{solute} \arrow[u, shift right, "k_{-1}"'] & + \quad BX' \arrow[r, shift left, "k_2"] & (I^+) \quad + \quad B^- \arrow[l, shift left, "k_{-2}"] \arrow[r, shift left, "k_3"] & AX'_{solute} \arrow[l, shift left, "k_{-3}"] \arrow[u, shift left, "k_{-4}"] & + \quad BX
\end{tikzcd}$$

Make the following assumptions:

(1) Exchange occurs only in the solution.

(2) The rate of equilibration of AX and AX' in the gas phase and in solution is fast compared with the overall-rate of the exchange reaction.

(3) The steady state theory applies to intermediate $(I^+)$

(4) The gas-solute equilibrium is independent of isotopic substitution, *i.e.* $k_1 = k_4$ and $k_{-1} = k_{-4}$ .

If the initial concentration of AX' is zero, the rate of appearance of AX' in the solution is given by:

$$(5)\quad \frac{d(AX'_s)}{dt} = k_3.(I^+).(B^-) - k_{-3}.(AX'_s).(BX) + k_4.(AX'_g) - k_{-4}.(AX'_s)$$

Applying condition (3), the concentration of $(I^+)$ is given by:

$$(6) \quad (I^{+}) = \frac{k_2.(AX_s).(BX') + k_{-3}.(AX'_s).(BX)}{(k_3 + k_{-2}).(B^{-})}$$

Thus, the rate of appearance of AX' can be given by:

$$(7) \quad \frac{d(AX'_s)}{dt} = \frac{k_3.k_2}{(k_3+k_{-2})}.(AX_s).(BX') - \frac{k_{-2}.k_{-3}}{(k_3+k_{-2})}.(AX'_s).(BX) +$$

$$+ k_4.(AX'_g) - k_{-4}.(AX'_s).$$

Putting $\rho = k_{-2}/k_3$ and $\sigma = \frac{k_{-2}.k_{-3}}{k_2.k_3} = (k_{-3}/k_2).\rho$, expression (7) can be simplified to:

$$(8) \quad \frac{d(AX'_s)}{dt} = \frac{k_2}{(1+\rho)}.\left[(AX_s).(BX') - \sigma.(AX'_s).(BX) - \frac{d(AX'_g)}{dt}\right]$$

Applying conditions (2) and (4), the concentrations of AX and AX' in the gas phase or the liquid phase are given by:

$$(9) \quad (AX_s) = K.(AX_g) \text{ and } (AX'_s) = K.(AX'_g) \text{ with } K = (k_{-1}/k_1)$$

The rate of appearance of AX' in the <u>gas phase</u> follows from (8) and (9):

$$(10) \quad \frac{K+1}{K}.\frac{d(AX'_g)}{dt} = \frac{k_2}{(1+\rho)}.\left[(AX_g).(BX') - \sigma.(AX'_g).(BX)\right]$$

Introducing the following abbreviations:

a = the total amount of gas, in moles.
p = the volume of the liquid phase, in liters.
q = the volume of the gas phase, in liters.

and noting that AX' and BX' are present only in trace amounts, the concentrations at time zero and time t are given by:

$$(BX')_0 = y_0 \quad \text{and} \quad (BX')_t = f.y_0 \text{ mole.l}^{-1} \quad (0 < f < 1)$$

$$(BX)_0 = b \quad \text{and} \quad (BX)_t = (BX)_0 = b \text{ mole.l}^{-1}.$$

$$(AX_s)_0 = (K.a.q)/(K.p + q) \text{ mole.l}^{-1} \text{ and } (AX_s)_t = (AX_s)_0$$

$$(AX_g)_0 = (a.q)/(K.p + q) \text{ mole.l}^{-1} \text{ and } (AX_g)_t = (AX_g)_0$$

$$(AX'_s)_t = (K.(1-f).p.y_0)/(K.p + q) \text{ mole.l}^{-1}$$

$$(AX'_g)_t = ((1-f).p.y_0)/(K.p + q) \text{ mole.l}^{-1}$$

Equation (10) can be written as :

$$(11) \quad \frac{K+1}{K}.\frac{d(AX'_g)}{dt} = \frac{k_2}{(1+\rho)}.\left[\frac{a.q.f.y_0}{K.p + q} - \sigma.(AX'_g).b\right]$$

The fraction (f) that has exchanged at time t is:

$$(12) \quad f = \left(1 - \left[\frac{(AX'_g)_t.(K.p + q)}{p.y_0}\right]\right)$$

Using (12), (11) becomes:

$$(13) \quad \frac{K+1}{K}.\frac{d(AX'_g)}{dt} = \frac{k_2}{(1+\rho)}.\left[\frac{(aq + \sigma bp)}{p} . \frac{apqy_0}{(Kp+q).(aq + \sigma bp)} - (AX'_g)_t\right]$$

which integrates to:

$$(14) \quad \frac{K+1}{K}. \ln\left[\frac{apqy_0}{(K+1).(aq + \sigma bp)} - (AX'_g)_t\right] = \frac{k_2}{(1+\rho)}.\frac{[aq + \sigma bp]}{p}.t + C.$$

Using the following boundary conditions:

(15) for $t \to \infty$, $(AX'_g)_t = (AX'_g)_{eq} = x_\infty$

(16) for $t \to \infty$, $\ln(\ldots.) \to -\infty$ and $(AX'_g)_{eq} = \dfrac{apqy_0}{(K+1).(aq + \sigma bp)}$

(17) for $t=0$, $(AX'_g) = 0$, and $C = -\ln(AX'_g)_{eq} = -\ln(x_\infty)$

the integrated rate law (14) becomes:

$$(18)\quad -\frac{1}{t}.\ln(1 - x/x_\infty) = \frac{k_2}{(1+\rho)}.\ (a'+\sigma b).\frac{K}{K+1}. \quad \text{with } a' = aq/p$$

Neglecting isotope effects, <u>i.e</u>. putting $\rho=\sigma=1$, equation (18) is simplified to:

$$(19)\quad k' = -\frac{1}{t}.\ln(1-x/x_\infty) = \frac{K}{K+1}.\ \frac{k_2}{2}.\ (a' + b)$$

From equation (19), it can be inferred that it is sufficient to measure any observable which is linear with the concentration of AX' in the gas phase. If X' is a radioactive isotope, the activity in standard gas samples withdrawn from the gas phase at suitable time-intervals and at equilibrium serves as a useful measure for the amount of exchanged gas.

Experimentally, the tritio-deprotonation of isobutane gas was followed by contacting dry isobutane gas (1 l.=0.05 mole) with tritiated $HSO_3F$ (14.7 ml.=0.25 mole, activity 1.7 $\times 10^7$ dpm. $mole^{-1}$) at 1.08 atm. and temperatures between -5 and +25 $^oC$. The acid layer was stirred (magnetically) and several 10.0 ml samples were taken from the gas phase during each run. Every isobutane sample was washed with aqueous KOH to remove any traces of acid and dissolved into toluene scintillator fluid. After 6 to 24 hours, when equilibrium was attained, $x_\infty$ was determined by taking a few more samples from the gas phase.

Plotting $\ln(1-x/x_\infty)$ versus t the pseudo first-order rate constant k' was obtained (equation (19)). The solubility of isobutane was determined by weighing an evacuated flask containing a known amount of $HSO_3F$. The flask was filled with isobutane until a slight over-pressure of 7 to 9 cm. Hg, vigorously shaken and more isobutane was added if necessary. Weighing and correcting for the weight of the gas phase gave the amount of isobutane dissolved in the acid: 0.18 and 0.17 mole.$l^{-1}$, at 20 and 0 $^{o}$C, respectively. From this, a' is calculated to be 2.8, 3.0 and 3.2, at 25, 5 and -5 $^{o}$C. Using b = 17 mole.$l^{-1}$, the second-order rate constants $k_2$ were calculated from k' (equation (19)).

The results have been given in table IX. See also ref. 4 of chapter IV.

## SUMMARY.

The reactivity of saturated hydrocarbons towards benzyl cations is the subject of this thesis. In strong acidic solution, hydride transfer occurs from tertiary and secundary alkanes to benzyl cations. This heterolytic splitting of carbon-hydrogen bonds is enhanced considerably by increasing the acidity of the medium and is influenced by two factors, viz. the basicity of the alkane and the polarization in the benzylic C-$CH_2$ bond.

The concept of bi-functionality, emerging from enzymatically catalysed bio-reactions, is used to explain the reactivity of stable benzyl cations towards polarized, solvated isoalkanes. Kinetic investigations and tracer experiments show that the hydride transfer reaction between alkanes and methylated benzyl cations proceeds via a termolecular transition state (or intermediate) in which one proton or acid molecule participates. The observation of scrambling of hydrogen isotopes during the hydride transfer step per se strongly supports the postulated reaction mechanism.

Quantummechanical calculations by means of the semi-empirical CNDO/2 method indicate the transfer of a proton-hydride pair, presumably in a concerted way, from a protonated alkane with $C_s$-symmetry towards the polarized benzylic C-$CH_2$ bond. It is suggested that in acidic solutions, alkane-proton acid adducts (or strongly solvated protonated alkanes) rather than free protonated alkanes are the reactive intermediates in the hydride transfer reaction.

When isobutane is allowed to react with benzyl cations in tritiated proton acids, tritium is incorporated in the products derived from the benzyl cation. Thus, the actual transfer step of the proton-hydride pair is sufficiently slow that scrambling in this ion-pair may occur. A solvent-coupled re-

action mechanism, caused by strong ionic solvation of the transition state, is postulated to govern the rate of transfer of the proton-hydride pair.

An attempt has been made to rationalize the observed rate differences between proton exchange reactions shown by alkanes in strong proton acids and the hydride transfer reaction, occurring between alkanes and benzyl cations in strong acids. The large difference in rate between these two types of reaction is attributed to the occurrence of different five-coordinated carbon species. The formation of free, highly energetic five-coordinated carbonium ions (such as for instance $CH_5^+$) is postulated to be rate determining for proton exchange and hydrogen evolution reactions. The formation of strongly solvated alkanes (which form in a way the low-energetic precursors of the protonated alkanes) is postulated to be a necessary step prior to hydride transfer towards benzyl cations. In this context, a resemblance is suggested between these two kinds of species and π- and σ-complexes, which occur during electrophilic reactions with aromatic compounds.

In agreement with the postulated reaction mechanism, the (much slower) reaction between benzyl cations and molecular $H_2$ is <u>not</u> accompanied by scrambling when the reaction is carried out in tritiated acid. Thus, this latter reaction is believed to consist of a heterolytic splitting of a hydrogen molecule in a proton-hydride pair, which is transferred towards the benzyl cation in a concerted way.

## SAMENVATTING.

Onderwerp van dit proefschrift is de onverwachte reactiviteit van verzadigde koolwaterstoffen tegenover benzyl kationen. Opgelost in sterke protonzuren blijken tertiaire en secundaire alkanen in een snelle reactie hydride ionen over te dragen naar het benzyl kation. Deze heterolytische splitsing van koolstof-waterstof bindingen wordt aanzienlijk versneld door verhoging van de zuurgraad van de oplossing en wordt bepaald door twee factoren, te weten: de basiditeit van de alkaan en de polarisatie in de benzyl C-$CH_2$ binding.

Het verschijnsel van de bi-functionaliteit, zoals dit naar voren komt in enzymatisch gekatalyseerde bio-reakties, staat model om de reactiviteit van benzyl kationen tegenover gepolariseerde, gesolvateerde alkanen te verklaren. Kinetische onderzoekingen en isotopen-overdrachts experimenten tonen aan, dat de hydride-overdracht verloopt via een termoleculaire overgangstoestand of intermediair, waarin een proton of zuur molecule voorkomt. De waargenomen uitwisseling van waterstof isotopen gedurende de eigenlijke hydride-overdracht vormt een sterk argument voor het gepostuleerde reaktiemechanisme.

Quantummechanische berekeningen (CNDO/2 methode) geven aan, dat er een proton-hydride paar wordt overgedragen, vermoedelijk in één stap, vanuit een geprotoneerd alkaan met een $C_s$-symmetrie naar de gepolariseerde benzyl C-$CH_2$ binding. In sterk zure oplossingen zijn eerder alkaan-proton zuur adducten (of sterk gesolvateerde, geprotoneerde alkanen) de reaktieve intermediairen voor de hydride-overdrachtsreaktie, dan vrije, geprotoneerde alkanen.

Voert men de reaktie tussen isobutaan en benzyl kationen uit in getritieerd zuur, dan blijkt het product dat ontstaat uit het benzyl ion, tritium te bevatten. De conclusie is, dat de eigenlijke overdrachts-stap van het proton-hydride paar

voldoende langzaam is, zodat isotopen-uitwisseling kan plaatsvinden. Een koppeling tussen het omringende medium en het over te dragen proton-hydride paar, veroorzaakt door een sterke solvatatie van de overgangstoestand, wordt dan bepalend voor de snelheid van de overdrachts-stap.

Gepoogd is de waargenomen snelheidsverschillen te verklaren tussen enerzijds proton-uitwisselingsreakties, zoals alkanen die vertonen in sterke proton zuren, en anderzijds de hydride-overdrachtsreaktie tussen alkanen en benzyl kationen. Het grote verschil in reaktie-snelheid tussen deze twee reaktie-types wordt toegeschreven aan het voorkomen van verschillende vijf-gecoördineerde koolstof-deeltjes. Gepostuleerd wordt, dat de vorming van vrije, hoog-energetische carbonium ionen, zoals bijv. $CH_5^+$, de snelheidsbepalende stap is voor de proton-uitwisseling en voor waterstof-vormende reakties. De vorming van sterk gesolvateerde alkanen, die als het ware de laag-energetische voorlopers van geprotoneerde alkanen zijn, wordt gepostuleerd als een noodzakelijke stap die vooraf gaat aan de eigenlijke hydride-overdracht naar benzyl kationen. In dit verband wordt een analogie getrokken tussen deze twee soorten deeltjes en π- en σ-complexen, welke voorkomen tijdens electrofiele reakties met aromatische verbindingen.

De veel langzamere reaktie tussen moleculaire waterstof en benzyl kationen wordt <u>niet</u> vergezeld van isotopen-uitwisseling als de reaktie wordt uitgevoerd in getritieerd zuur. Dit is in overeenstemming met het gepostuleerde reaktiemechanisme; de reaktie met $H_2$ bestaat uit het heterolytisch splitsen van een waterstof molecule in een proton-hydride paar dat naar het benzyl kation wordt overgedragen.

## CURRICULUM VITAE.

Na het behalen van het einddiploma gymnasium β aan het St.-Janscollege te Den Haag in 1960 trad ik in dienst van de Kon./Shell. Aan het K.S.L.A. werd de opleiding tot leerling-analist gevolgd en aansluitend was ik werkzaam aan het K.S.E.P.L. te Rijswijk, met een onderbreking voor het vervullen van mijn militaire dienstplicht.

In oktober 1964 werd aangevangen met de studie in de scheikunde aan de Rijksuniversiteit te Leiden. In 1967 werd het kandidaatsexamen G afgelegd (scheikunde met natuurkunde en wiskunde als bijvakken).

De hoofvakstudie werd verricht aan de afdeling physische chemie van Prof. Dr. C.J.F. Bötcher en behelsde de studie van het dielectrische relaxatiegedrag van verdunde oplossingen van heptanolen in het hoogfrequente radiogolven gebied.

De bijvakstudie werd verricht aan de afdeling voor theoretische organische chemie van Prof. Dr. L.J. Oosterhof. Aldaar werd een aanvang gemaakt met het onderzoek van de hydride overdracht van alkanen naar gemethyleerde benzyl kationen. Dit onderzoek stond onder leiding van Dr. H.M. Buck en resulteerde later in de, in dit proefschrift beschreven, promotiestudie.

In het cursusjaar 1967-1968 gaf ik 12 uur per week les aan het St.-Janscollege te Den Haag. Van 1968 tot 1970 was ik als assistent verbonden aan de afdeling voor physische chemie van Prof. Dr. C.J.F. Bötcher.

In maart 1971 werd het doctoraalexamen scheikunde afgelegd (hoofdvak physische chemie, bijvakken quantumchemie en numerieke wiskunde).

Het in dit proefschrift beschreven onderzoek werd begonnen in april 1971.

## COLOPHON.

Aan de totstandkoming van dit proefschrift hebben velen bijgedragen. Met name wil ik hier mijn dank uitspreken tegenover:

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STELLINGEN.

1. Het verwaarlozen van de spin-polarisatie in σ-bindingen van organo-fosfor radicalen leidt tot foutieve interpretaties van de ESR spectra van deze radicalen.

   T.F. Hunter and M.C.R. Symons, J. Chem. Soc., A, 1770 (1967).
   C. Thomson and D. Kilcast, Chem. Comm., 214 (1971).
   C. Jongsma, H.G. de Graaf and F. Bickelhaupt, Tetrahedron Letters, 14, 1267 (1974).

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2. De snelheid waarmee de anodische oxidatie van alkanen in sterke proton-zuren plaats vindt is onverenigbaar met de suggestie van Pletcher en medewerkers, dat deze reactie via vrije, geprotoneerde alkanen verloopt.

   J. Bertram, J.P. Coleman, M.F. Fleischmann and D. Pletcher, J. Chem. Soc. (Perkin I), 347 (1973).
   P. van Pelt and H.M. Buck, Rec. Trav. Chim., 91, 195 (1972).

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3. De stabiliteit van geprotoneerde 2,3-di-*tert.*-butyl-episulfides in sterke proton-zuren, zowel als de $^{1}H$- en $^{13}C$-NMR spectra van deze ionen, wijzen op sterke ladingsdelocalizatie over de C-atomen van de thiiraan-driering.

   P. Raynolds, S. Zonnebelt, S. Bakker and R.M. Kellogg, J. Amer. Chem. Soc., 96, 3146 (1974).

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4. De verdringing van ionen uit de watermantel rondom vaste deeltjes, gedispergeerd in waterige zoutoplossingen, wordt door de conductometrische experimenten van Horne en Young niet overtuigend aangetoond.

   R.A. Horne and R.P. Young, Electrochim. Acta, 17 (4), 763 (1972).

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5. De verklaring die van Tamelen geeft voor de selectiviteit waarmee squaleen eindstandig wordt geëpoxydeerd, n.l. dat deze reactie verloopt via opgerolde squaleen-conformaties, wordt onvoldoende gesteund door spectroscopische onderzoekingen; eerder moet worden aangenomen, dat de selectiviteit berust op een kinetisch gecontroleerde reactie leidend tot het energetisch gunstigste epoxy-squaleen.

E.E. van Tamelen, Acc. Chem. Res., 1, 111 (1968).
M. van Dommelen, Afstudeerverslag TH Eindhoven, okt. 1974.

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6. Het katalytische effect van H-mordeniet en andere zure zeolieten op de isomerisatie van *n*-alkanen tot *iso*-alkanen wordt door de aanwezigheid van zure SiOH groepen in de holten van de katalysator onvoldoende verklaard; sterke electrostatische velden in de katalytisch actieve holten verhogen lokaal de proton-activiteit dermate, dat de vorming van vijf-gecoördineerde carbonium ionen als initierende stap voor de isomerisatie-reactie mogelijk wordt.

H.W. Kouwenhoven, Papers of the Conference on Molecular Sieves, pag. 529, (1973).
E. Dempsey, Papers of the Conference on Molecular Sieves, pag. 293 (1967).

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7. Een wetenschapsbeleid op lokaal niveau, gebaseerd op een prioriteiten schema voor het wetenschappelijk onderzoek, zal stimulerend werken op het formuleren van een goed functionerend zwaartenpuntenbeleid binnen de afdelingen of sub-faculteiten van hogescholen, resp. universiteiten.

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8. Het gebruik van verschillende huisartsen in de regio Eindhoven om zure voedingen voor te schrijven voor pasgeborenen is ten onrechte gegrond op de overweging, dat deze voeding caries in het zich ontwikkelende gebit zal tegengaan.

P. van Pelt                                Eindhoven, 28 januari 1975.