Hydride-Transfer Reactions in the Gas Phase. 2.[1] Anchimeric Assistance in the H^- Transfer from 1,1-Dimethylcyclopentane to Alkyl Cations

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The gas-phase hydride transfer from the title compound to several ionic acceptors $GA^+ = CH_5^+$, $C_2H_5^+$, *s*-$C_3H_7^+$, and *t*-$C_4H_9^+$ was studied by mass spectrometric and radiolytic methods in the pressure range 1.1×10^{-8}−700 Torr. Analysis of the irradiated mixtures points to the exclusive formation of rearranged products, with those with methyl migration prevailing over those with ring expansion. Thermochemical considerations, isotope labeling experiments, and deuterium isotope effect measurements concur in defining the detailed mechanism of the gas-phase hydride transfer, which involves significant anchimeric assistance of the methyl and methylene groups adjacent to the reaction center. The primary and the secondary α-D kinetic isotope effects, measured in the hydride transfer from the methylene moieties adjacent to the quaternary carbon of the title compound to either *s*-$C_3H_7^+$ or *t*-$C_4H_9^+$, amount to 2.70 (*s*-$C_3H_7^+$) and 1.89 (*t*-$C_4H_9^+$) and to 1.77 (*s*-$C_3H_7^+$) and 1.15 (*t*-$C_4H_9^+$), respectively. These values are interpreted in terms of a transition state, which is placed rather late along the reaction coordinate, and wherein the assistance of the neighboring (methyl or methylene) group to the departing hydride increases by decreasing the strength of the GA^+ acceptor. The results obtained from the present gas-phase investigation are discussed and compared with those of related gas-phase and solution data.

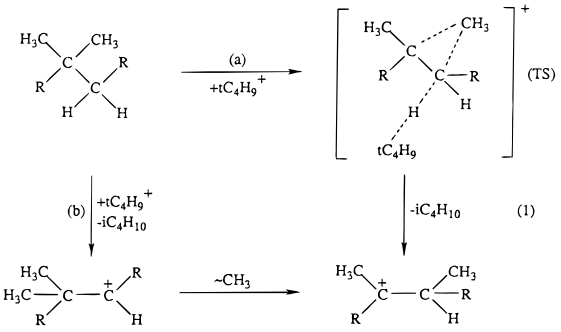
Introduction

As pointed out by Hine,[2] when a reaction would require the intermediacy of a highly unstable species, stepwise bond makings and breakings may be avoided by combining such bond changes into a concerted step. In intramolecular processes, this involves the through-space interaction of neighboring or remote groups to the reaction center and the effect is said to be "neighboring group participation".[3] When neighboring group participation affects the reaction rate by lowering the activation barrier of the rate-limiting concerted step, the group is said to provide *anchimeric assistance*.[3] Thus, according to Capon and McManus,[3] anchimeric assistance is a subdivision of the more general neighboring group participation concept.

Owing to their relevance in many aspects of gas-phase ion chemistry, including stereoisomeric discrimination, many examples of neighboring group participation have been reported in the mass spectrometry literature.[4,5] Isotope effect, selective labeling, and stereospecificity studies indicate that the majority of these processes proceeds via stepwise mechanisms, involving more than one stable intermediate.[6]

No *unambiguous* examples of *anchimeric assistance* in gas-phase ionic reactions are instead reported in these studies, although misuses of the *"anchimeric assistance"* term just to denote neighboring group participation sometimes appear in the relevant publications. This failure is caused by the fact that positive recognition of anchimeric assistance in an ionic reaction demands evaluation of the relevant kinetic parameters at *well-defined reaction temperatures*, as well as assessment of the mechanistic details and of their dependence upon the nature of the reactants.[3]

These essential kinetic and mechanistic pieces of information are seldom accessible at the low-pressure regimes operating in most classical mass spectrometric techniques (≤10 Torr), where ionic species are formed with substantial internal energy hardly relaxed to the rarefied reaction environment on the available time scale and, thus, reacting at an undefined "temperature". Besides, the inherently limited structural resolution of the mass spectrometric methods often hampers the positive assessment of the structural and stereochemical course of the ionic processes.[7] These limitations can be overcome by resorting to the high-pressure radiolytic methodology (≥760 Torr), where the excitation energy of the ionic species can be fully relaxed by fast collisional quenching with a buffer gas and their reactivity determined by standard kinetic procedures, including pressure- and temperature-dependence studies and competition experiments. The actual isolation and characterization of the neutral reaction products provide the necessary information on structure and stereochemistry of the ionic intermediates involved.[7] A demonstration of this capability is provided by the observation that few *unambiguous* pieces of evidence of gas-phase *anchimerically assisted* ionic processes are reported in the literature and most of them based upon high-pressure kinetic investigations using radiolytic methods.[1,8] Among these, the most recent one provided the first unambiguous evidence of methyl-group anchimeric assistance in the gas-phase hydride transfer from the CH_2 of 2,2-dimethylbutane to *tert*-butyl cation (eq 1a; R = CH_3), on the grounds of the over 100-fold increase of the efficiency of the H^- transfer by increasing the system pressure from 4.0×10^{-8} Torr (FT-ICR) to ca. 1 atm (stationary radiolysis).[1]



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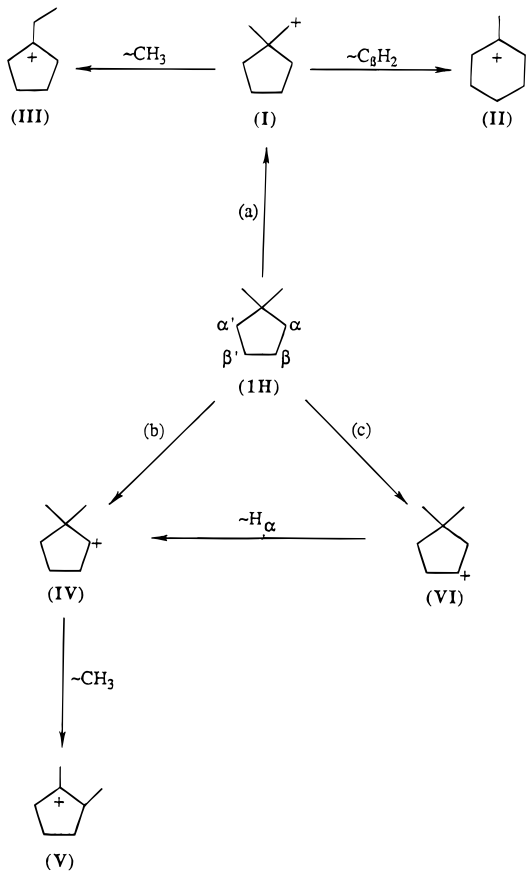
This pressure-dependence criterion is based upon the consideration that the efficiency of a gas-phase ion−molecule reaction ($=k_f/(k_f + k_r)$), involving the formation of a stable, electrostatically bonded ion−neutral complex (INC) is determined by the competition between the evolution of INC to products (k_f), through an internal activation barrier E^*, and its back-dissociation to reactants (k_r), through the pseudobarrier $E°$. This competition depends on both the features of the free energy profile and the experimental conditions. The complex at the top of the internal barrier E^* is a tight complex (low density of states, negative activation entropy), whereas that involved in the back-dissociation is a loose complex (high density of states, positive activation entropy).[7]

At the collision-free limit (approached in the FT-ICR kinetic experiments),[1] the INC is characterized by a constant total energy and angular momentum. Its evolution to reactants or products is essentially governed by entropic, rather than by enthalpic factors. Under such conditions, its crossing of the internal barrier E^* is rather unlikely and thus, the reaction efficiency is generally low. An increase in the reaction pressure (radiolytic experiments)[1] favors the disposal of the excess energy $E°$ of INC by unreactive collisions with the buffer gas (present at 160−700 Torr).[1] Its lifetime increases and its evolution tends to be progressively governed by enthalpic, rather than by entropic factors and, therefore, to follow the lowest activation energy pathway. For exothermic processes with $E^* > E°$, this favors back-dissociation of INC over its conversion to products and, therefore, a negative pressure dependence of the reaction efficiency is observed. For exothermic processes with $E^* < E°$, instead, an increase in the reaction pressure favors conversion of INC to products over its back-dissociation to reactants and, therefore, a positive pressure dependence of the reaction efficiency is observed. Thus, the pressure dependence of the reaction efficiency can be used as a criterion for establishing whether the internal barrier E^* of a gas-phase ion−molecule reaction protrudes above the energy level $E°$ of reactants and, therefore, for throwing light on its detailed mechanism.

In the gas-phase hydride transfer from the CH_2 of 2,2-dimethylbutane to *tert*-butyl cation (eq 1a; R = CH_3),[1] the positive pressure dependence of the reaction efficiency excludes the stepwise mechanism 1b, involving formation of an INC between isobutane and the 3,3-dimethyl-2-butyl cation at energy levels protruding above that of the starting reactants ($E^* - E°$ > ca. 1−2 kcal mol^{-1}). The positive pressure trend is rather consistent with a potential energy profile characterized by $E^* - E° < 0$ and, thus, necessarily proceeding through *a concerted, anchimerically assisted mechanism*.

To enlarge the experimental kinetic evidence of alkyl group anchimeric assistance in gas-phase hydride-transfer reactions, the investigation has been now extended to another H^- donor, i.e., 1,1-dimethylcyclopentane (**1H**, eq 1, R−R = $-(CH_2)_3-$), using different H^- acceptors, such as the gaseous acids GA^+ = CH_5^+, $C_2H_5^+$, *s*-$C_3H_7^+$, and *t*-$C_4H_9^+$ ions. In 1,1-dimethylcyclopentane, H^- may be released from three chemically different sites, namely (Scheme 1): (i) the methyl groups (path a); (ii) the $C_\alpha H_2$ and $C_{\alpha'}H_2$ moieties (path b); and (iii) the $C_\beta H_2$ and $C_{\beta'}H_2$ moieties (path c). In principle, the actual occurrence of the corresponding high-energy intermediates **I**, **IV**, and **VI** might be avoided by concerted through-space interaction of vicinal groups with the reaction center. In path a, this would involve the adjacent $C_\alpha H_2$ and $C_{\alpha'}H_2$ groups (yielding directly intermediate **II**) or the methyl moiety (yielding directly intermediate **III**); in path b, the vicinal methyl groups (yielding directly intermediate **V**); in path c, the neighboring α and α′ hydrogens (yielding directly intermediate **IV** and eventually **V**). If this conceivable concerted interaction causes an enhancement of the hydride-transfer rate, by lowering of the corresponding activation barrier relative to the stepwise process, the reaction is "*anchimerically assisted*".

SCHEME 1



It is expected that this study will allow the positive recognition of anchimeric assistance in the various hydride transfers from 1,1-dimethylcyclopentane and discernment of the intrinsic factors determining its occurrence. Additional interest in this gas-phase study arises from the fact that the selected hydride-transfer reaction 1 (R−R = $-(CH_2)_3-$) can represent the gas-phase counterpart of the extensively investigated solvolysis of *gem*-dimethylcyclopentyl arene sulfonate esters, wherein identification of anchimeric assistance is severely hampered by solvation and ion-pairing phenomena.[9]

The kinetic approach adopted in this study has been already presented.[1] It is based upon the preparation of stationary concentrations of the selected hydride acceptor ($GA^+ = CH_5^+$, $C_2H_5^+$, *s*-$C_3H_7^+$, or *t*-$C_4H_9^+$) from γ-radiolysis of the corresponding precursor (CH_4, C_3H_8, or *i*-C_4H_{10}), containing traces (4 Torr) of an effective thermal radical scavenger, i.e., O_2. Its attack on 1,1-dimethylcyclopentane is investigated at 640−700 Torr in the presence of variable concentrations of a powerful nucleophile, i.e., MeOH (0.4−5.1 Torr). Under these conditions, the high collision frequency (ca. 10^{10} s^{-1}) with the bath gas molecules (CH_4, C_3H_8, or *i*-C_4H_{10}) ensures efficient collisional thermalization of the intermediates of sequence 1, whose structure and isomeric distribution can be inferred from the relative abundance of their neutral derivatives after trapping by MeOH.

Experimental Section

Materials. Methane, propane, isobutane, and oxygen were high-purity gases from Matheson Co., used without further

purification. 1,1-Dimethylcyclopentane (**1H**) was synthesized by reduction of the tosylhydrazone of 2,2-dimethylcyclopentanone (Aldrich Chemical Co.) with sodium cyanoborohydride.[10] The same procedure was employed to obtain exclusively 2-deutero-1,1-dimethylcyclopentane (deuterium content > 98%, **1D**) from sodium cyanoborodeuteride (Aldrich Chemical Co.). 1,2-Dimethylcyclopentene was prepared by dehydration of *trans*- and *cis*-1,2-dimethylcyclopentanol (K&K Co.) with phosphoric acid and purified by distillation at 104 °C, 760 Torr.[11] 1-Methylcyclohexanol was purchased from Aldrich Chemical Co. 2,2-Dimethylcyclopentanol was synthesized by reduction of 2,2-dimethylcyclopentanone with lithium aluminum hydride.[12] 3,3-Dimethylcyclopentanol was obtained from reduction of 4,4-dimethyl-2-cyclopenten-1-one (Aldrich Chemical Co.) with sodium borohydride.[13] *trans*- (**2**) and *cis*-1,2-dimethyl-1-methoxycyclopentane (**3**), 1-methyl-1-methoxycyclohexane (**4**), 2,2-dimethyl-1-methoxycyclopentane, and 3,3-dimethyl-1-methoxycyclopentane were obtained from the Williamson reaction on the corresponding alcohols. 1,1-Dimethylcyclopentane (**1H**), 2-deutero-1,1-dimethylcyclopentane (**1D**), and 1,2-dimethylcyclopentene were purified by preparative GLC on a 4-m long, 4-mm i.d. stainless steel column, packed with 5% Carbowax 20M-KOH (2%) on Supelcoport, at 80 °C. Their final chemical purity exceeded 99.95%. Their identity, as well as that of the above alcohols and ethers, was verified by NMR spectroscopy and their chemical and isotopic purity assayed by GLC and GLC-MS on the same columns employed for the analysis of the irradiated mixtures.

Radiolytic Experiments. The gaseous mixtures were prepared by conventional techniques, using a greaseless vacuum line. The reagents and the additives were introduced into carefully outgassed 250-mL Pyrex bulbs, each equipped with a break-seal tip. The bulbs were filled with the required mixture of gases, cooled to the liquid nitrogen temperature, and sealed off. The irradiations were carried out at 37.5 °C in a 220 Gammacell from Nuclear Canada Ltd to a dose of 2×10^4 Gy at a rate of 10^4 Gy h^{-1}, as determined by a neopentane dosimeter. Control experiments, carried out at doses ranging from 1×10^4 to 1×10^5 Gy, showed that the relative yields of products are largely independent of the dose. The radiolytic products were analyzed by GLC, using a HP 5890 A gas chromatograph from Hewlett-Packard, equipped with a flame ionization detector. The following columns were employed: (i) a 100-m long, 0.32-mm i.d. Petrocol DH fused silica capillary column, operated at temperatures ranging from 60 to 120 °C, 3 °C min^{-1}; (ii) a 50-m long, 0.32-mm i.d. PONA fused silica capillary column, operated at temperatures ranging from 60 to 120 °C, 3 °C min^{-1}. The products were identified by comparison of their retention volumes with those of authentic standard compounds, and their identity was confirmed by GLC-MS, using a Hewlett-Packard HP 5970 B mass spectrometer. Their yields were determined from the areas of the corresponding eluted peaks, using individual calibration curves.

Fourier Transform Mass Spectrometric (FT-ICR) Experiments. The FT-ICR kinetic experiments were performed with a Bruker Spectrospin Apex TM 47e FT-MS equipped with an external source and a cylindrical (60-mm length, 60-mm diameter) "infinity cell",[14] situated between the poles of a superconducting magnet operated at 4.7 T. The kinetic experiments were performed at the nominal temperature of 300 K. The alkyl cation reactant was generated in the external ion source by 70 eV electron impact on the corresponding neutral precursor at the nominal source pressure of 1×10^{-5} Torr and transferred into the FT-ICR cell containing 1,1-dimethylcyclopentane at $(1.1-1.3) \times 10^{-8}$ Torr. Propane was introduced into the FT-ICR cell by a pulsed magnetic valve to collisionally quench any vibrationally and translationally excited ionic intermediate. After a half second pumping time, the alkyl cation reactant was isolated from the plasma by sequential broad-band ejection and "single shots"[15] and allowed to react with 1,1-dimethylcyclopentane. In this way the decrease of the logarithm of the relative abundance of the starting alkyl cation with the reaction time appears approximately linear, as required for thermally equilibrated reactants. The concentration of 1,1-dimethylcyclopentane in the FT-ICR cell was determined from the pressure measured by the ionization gauge located in the high-vacuum pumping line of the FT-ICR cell housing, corrected by using independently measured calibration factors.[16]

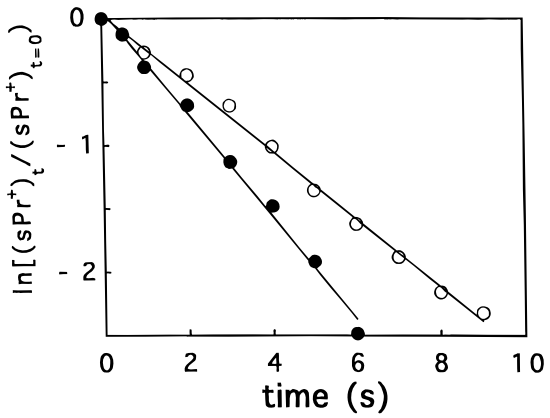


Figure 1. Time dependence of the $\ln[(s\text{-}C_3H_7^+)_t/(s\text{-}C_3H_7^+)_{t=0}]$ ratio following attack of thermalized $s\text{-}C_3H_7^+$ ions on 1,1-dimethylcyclopentane **1H** (**1H** partial pressure = 1.1×10^{-8} Torr (open circles); 1.3×10^{-8} Torr (full circles)).

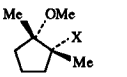
Results

FT-ICR Experiments. No detectable formation of $C_7H_{13}^+$ products was observed after 30 s reaction time, when $t\text{-}C_4H_9^+$ ions are introduced and thermalized into a FT-ICR cell containing 1.3×10^{-8} Torr of 1,1-dimethylcyclopentane **1H**. This implies that, after ca. 17 collisions,[17a] the extent of the conceivable hydride transfer from **1H** to $t\text{-}C_4H_9^+$ is well below the mass spectrometric detection limit (ca. 1% of the $t\text{-}C_4H_9^+$ peak). Thus, the upper limit of the efficiency of the process, expressed by the ratio between the observed bimolecular rate constant (k_{obs}) and the calculated collision rate constant ($k_{coll} = 14.0 \times 10^{-10}$ cm^{-3} $molecule^{-1}$ s^{-1}),[17a] can be placed around 6×10^{-4}.

On the contrary, thermal $s\text{-}C_3H_7^+$ ions react efficiently with **1H** under FT-ICR conditions, yielding exclusively the $C_7H_{13}^+$ product. The kinetic curves shown in Figure 1 refer to experiments carried out at **1H** partial pressures of 1.3×10^{-8} Torr (full circles) and 1.1×10^{-8} Torr (open circles). The slopes of the curves, referring to the logarithm of the fraction of starting $s\text{-}C_3H_7^+$ ion as a function of time, over the corresponding [**1H**] concentration, provide directly the bimolecular rate constant of the hydride transfer process (k_{obs}) which amounts to 9.9×10^{-10} cm^{-3} $molecule^{-1}$ s^{-1}. The hydride-transfer efficiency can be estimated from the relevant collision rate constant ($k_{coll} = 15.4 \times 10^{-10}$ cm^{-3} $molecule^{-1}$ s^{-1}) as amounting to 0.64.

Radiolytic Experiments. Radiolytic experiments were carried out to investigate the kinetics and the mechanism of the hydride-transfer 1 (R−R = $-(CH_2)_3-$) in the high-pressure range, by applying traditional procedures such as the trapping of the ionic intermediates by a powerful nucleophile (MeOH)

TABLE 1: Product Yields from the Gas-Phase Attack of GA^+ Ions on 1,1-Dimethylcyclopentane

Run No.	System Composition[a]				Product Yields, (%)[b]						Total Absolute Yield, %[c]
											
	Substrate (torr)	Bulk Gas (torr)	GA^+	MeOH (torr)	2 (X=H)	2 (X=D)	3 (X=H)	3 (X=D)	4 (X=H)	4 (X=D)	
i	1H (7.4)	CH_4 (633)	$C_nH_5^{+d)}$	2.0	41.7		36.7		21.6		72
ii	1H (8.3)	C_3H_8 (650)	$sC_3H_7^+$	4.5	41.8		42.3		15.9		21
iii	1H (8.3)	C_3H_8 (650)	$sC_3H_7^+$	1.2	44.2		39.6		16.2		20
iv	1H (8.3)	C_3H_8 (665)	$sC_3H_7^+$	0.4	44.8		41.5		13.7		29
v	1H (6.6)	CH_4 (600) C_3D_8 (80)	$sC_3D_7^+$	0.4	41.1	0.8	39.6	0.4	18.1	n.d.[e]	17
vi	1H (6.7)	CD_4 (600) C_3D_8 (90)	$sC_3D_7^+$	0.4	40.9	0.4	39.4	n.d.	19.2	n.d.	42
vii	1H (7.4)	iC_4H_{10} (668)	$tC_4H_9^+$	1.3	47.2		44.8		8.0		10
viii	1D (4.3)	CH_4 (660)	$C_nH_5^{+d)}$	0.9	4.4	36.7	6.8	34.2	0.5	17.4	22
ix	1D (6.7)	C_3H_8 (685)	$sC_3H_7^+$	5.1	5.9	41.8	5.4	37.0	0.4	9.5	17
x	1D (6.7)	C_3H_8 (685)	$sC_3H_7^+$	2.0	5.4	39.8	5.6	39.4	0.2	9.5	24
xi	1D (7.0)	C_3H_8 (665)	$sC_3H_7^+$	0.5	5.8	40.5	6.3	39.2	0.2	8.0	18
xii	1D (7.6)	iC_4H_{10} (650)	$tC_4H_9^+$	1.5	5.9	40.4	8.1	35.7	1.8	9.0	7

[a] O_2: 4 Torr. Radiation dose: 2×10^4 Gy (dose rate: 1×10^4 Gy h^{-1}). [b] Percent values as the ratios between the absolute yield of each product and the combined yields of all products identified. Each value is the average of several determinations, with an uncertainty range of ca. 5% of the value. [c] The absolute yields are estimated from the percent ratio of the products, expressed as their $G_{(M)}$ values (the number of molecules *M* produced per 100 eV of absorbed energy) and the literature $G_{(GA^+)}$ values.[18] [d] $n = 1, 2$. [e] n.d. = below detection limit, ca. 0.2%.

after a given reaction time and the isolation and structural discrimination of their neutral end products. The composition of the reaction systems and the absolute yields of products, expressed as the ratio between their $G_{(M)}$ values (number of molecules formed/100 eV absorbed energy) and that of their GA^+ precursors,[18] as well as their isomeric distribution are reported in Table 1. The ionic nature of the radiolytic products of Table 1 is ensured by addition to the gaseous mixtures of ca. 0.5 mol % of O_2, a powerful thermal radical scavenger, and it is demonstrated by the sharp decrease of the overall product yields (over 80%) caused by addition to the gaseous mixture of 0.4 mol % of NMe_3, an efficient positive ion interceptor.

An outstanding feature of the product patterns of Table 1 is the complete absence of both 2,2-dimethyl-1-methoxycyclopentane and 3,3-dimethyl-1-methoxycyclopentane among the radiolytic products, irrespective of the concentration of MeOH (0.4−5.1 Torr). Analysis of the GLC-MS fragmentation pattern of the radiolytic products excludes also the occurrence of methyl (1-methylcyclopentyl)methyl ether, as well as of any cyclopentane derivatives containing the ethyl moiety, including 1-ethyl-1-methoxycyclopentane. Instead, nearly equal amounts of both *trans*- (**2H**) and *cis*-1,2-dimethyl-1-methoxycyclopentane (**3H**) are invariably formed under all conditions, together with minor yields of 1-methyl-1-methoxycyclohexane (**4H**, 8.0−21.6%). The relative abundance of **4H** does not depend much on the MeOH partial pressure (entries ii−iv of Table 1), but it rather increases with the strength of the GA^+ acid, i.e., in the order t-$C_4H_9^+$ < s-$C_3H_7^+$ < $C_nH_5^+$. Replacement of s-$C_3H_7^+$ with s-$C_3D_7^+$, as the hydride ion acceptor, in the experiments with **1H** does not lead to any significant incorporation of the D label into the ethereal products (≤0.8%, entries v and vi of Table 1). Equal proportions of *trans*- (**2H**) and *cis*-1,2-dimethyl-1-methoxycyclopentane (**3H**) are obtained as well from $C_nH_5^+$(n = 1,2)-protonation of 1,2-dimethylcyclopentene. No detectable formation of 1-methyl-1-methoxycyclohexane (**4H**) was observed from this starting substrate.

The same product pattern observed with **1H** is obtained when using 2-deuterio-1,1-dimethylcyclopentane (**1D**), as the hydride (or deuteride) donor. Analysis of the GLC-MS fragmentation pattern of the radiolytic products reveals the predominant formation of almost equimolar amounts of deuterated *trans*- (**2D**) and *cis*-1,2-dimethyl-1-methoxycyclopentane (**3D**), accompanied by smaller equimolar yields of their unlabeled analogues **2H** (4.4−5.9% (values corrected for the initial ca. 2% H content in **1D**)) and **3H** (5.4−8.1% (values corrected for the initial ca. 2% H content in **1D**)). Deuterated 1-methyl-1-methoxycyclohexane (**4D**) is formed as well (8.0−17.4%), whereas its unlabeled analogue **4H** is barely detectable (0.2−1.8% (values corrected for the initial 2% H content in **1D**)). The observation that in the majority of the experiments, the [**4D**]/[**4H**] yield ratios largely exceed that expected for statistical uptake of a ring hydrogen by GA^+ (i.e., [**4D**]/[**4H**] = 7), suggests that 1-methyl-1-methoxycylohexane arises predominantly from the loss of a hydride ion originally belonging to a methyl group of 1,1-dimethylcyclopentane, while any conceivable contribution from the loss of one of its ring hydrogens seems to play a negligible role.

Discussion

Nature of the GA^+ Acceptors. The nature and distribution of the stable GA^+ ions from ionization of each individual bulk component of the gaseous mixture have been intensely investigated in a variety of mass spectrometric and radiolytic studies.[18,19] γ-Radiolysis of CH_4 produces known yields of both CH_5^+ ($\Delta H_f°$ (standard formation enthalpy) = 216 kcal mol^{-1})[20] and $C_2H_5^+$ ions ($\Delta H_f°$ = 215.6 kcal mol^{-1}),[20] which are powerful Brønsted (proton affinity (PA) = 131.6 kcal mol^{-1} (CH_4); 162.6 kcal mol^{-1} (C_2H_4))[20] and Lewis acids. In 1 atm of CH_4 and at 298 K, the CH_5^+ ions are present predominantly in the monosolvated [CH_5^+•CH_4] form (ca. 85%, $\Delta H_f°$ = ca. 191 kcal mol^{-1}), amounting the free CH_5^+ ions to only 15% of the ionic species.[21] In the same systems, $C_2H_5^+$ ions are obtained mostly in the free state, together with ca. 13% in the monosolvated [$C_2H_5^+$•CH_4] form ($\Delta H_f°$ = ca. 192 kcal mol^{-1}).[22] When traces of C_3H_8 are introduced in the CH_4 mixtures at atmospheric pressure, both CH_5^+ and $C_2H_5^+$ ions rapidly abstract a hydride ion from C_3H_8 yielding quantitative amounts of s-$C_3H_7^+$ ($\Delta H_f°$ = 190.9 kcal mol^{-1}).[20] In 1 atm of C_3H_8 and at 298 K, complete clustering between the s-$C_3H_7^+$ ions and their parent C_3H_8 molecules leads to the [s-$C_3H_7^+$•C_3H_8] adduct ($\Delta H_f°$ = ca. 152 kcal mol^{-1}).[23] No significant clustering between the s-$C_3H_7^+$ ions and the CH_4 molecules takes place

in the methane/propane mixtures.[22] γ-Radiolysis of i-C_4H_{10} produces known yields of t-$C_4H_9^+$ ions (ΔH_f° = 165.8 kcal mol^{-1}).[20] In 1 atm of i-C_4H_{10} and at 298 K, nearly one-half of the t-$C_4H_9^+$ ions remains in the free state (ca. 48%), while the other half adds to an i-C_4H_{10} molecule forming a loosely bonded [t-$C_4H_9^+$•i-C_4H_{10}] adduct (ΔH_f° = ca. 126 kcal mol^{-1}).[23] Later on, thermochemical considerations will indicate that almost all the free and the solvated ions described above may actually act as hydride acceptor toward **1H**.

Reaction Kinetics. In both the radiolytic and the FT-ICR experiments, the GA^+ ions undergo many unreactive collisions with their bulk precursor and, therefore, are thermally equilibrated with the reaction medium before interacting with 1,1-dimethylcyclopentane.

Nevertheless, under collision-free conditions (FT-ICR; pressure $\leq 1.3 \times 10^{-8}$ Torr), the electrostatic interaction energy liberated in the formation of the INC between GA^+ and 1,1-dimethylcyclopentane cannot be dissipated to the reaction medium. Most of it is stored as excess internal energy among the INC degrees of freedom. It follows that the phenomenological kinetic parameters measured in the FT-ICR experiments do not refer to a defined reaction temperature (thermal kinetics) but rather represent microscopic rate constants averaged over a non-Boltzmann excitation energy distribution.[7] Besides, a portion of the electrostatic interaction energy liberated in the formation of the INC is employed to counterbalance the increase of the rotational energy of the complex, due to the conservation of the total angular momentum.[24] Thus, not all the INC interaction energy is spendable to overcome E^*, and hence the reaction efficiency may be further lowered. For the systems investigated, it is estimated that, at room temperature, the effect of conservation of total angular momentum on the reaction efficiency never exceeds 1 order of magnitude.[24,25]

Instead, at the high pressures typical of the radiolytic experiments (640−700 Torr), the high collisional frequency (ca. 10^{10} s^{-1}) with the bulk gas allows fast disposal of the excess translational, vibrational, and rotational energy of the INC before its conversion to products. It follows that the kinetic and mechanistic information obtained under these conditions refers to thermally equilibrated systems and can be adequately correlated with similar processes occurring in solution.[7] The efficiencies of the thermal processes occurring in the radiolytic experiments are represented by the total absolute yields of products of Table 1, which reflect the conversion extent of their ionic precursors in the time interval between the generation of the ions and their trapping by MeOH (ca. 3×10^{-9} s).[17b] The absolute yield values, reported in Table 1, indicate that, while with s-$C_3H_7^+$, as the hydride acceptor, the reaction efficiency slightly decreases (from 0.6 to 0.2−0.4) by increasing the buffer gas pressure from ca. 10^{-8} to 700 Torr, with t-$C_4H_9^+$ it increases by over 3 orders of magnitude, i.e., by a factor which cannot be attributed exclusively to the effect of conservation of total angular momentum under the FT-ICR conditions (ca. 10^{-8} Torr), but which rather depends on the specific mechanistic path followed by the hydride-transfer reaction under largely different pressure conditions.

Ion Termochemistry and Reaction Mechanism. In view of the unavailability of experimental thermochemical data concerning the conceivable cyclopentyl ion intermediates **I**, **III**, **IV**, and **VI** of Scheme 1, their formation enthalpies are estimated using a method based on the isodesmic substitution[26] approach. Thus, for **IV**, the heats of formation of 1,1-dimethylcyclopentane, cyclopentyl cation, and cyclopentane are known.[20] Assuming that replacement of the CH_2 moiety adjacent to the vacant orbital in cyclopentyl cation by the CMe_2 group produces no change in the heat of formation apart from that associated to the inherent stability of the two radicals, it results a ΔH°_f value of 177 kcal mol^{-1} for **IV**. A correction for the stabilizing effect of two electron-releasing methyl groups of CMe_2 on the positive charge of 6 kcal mol^{-1} is made, consistent with calculation on similar systems. This leads to a corrected value of 171 kcal mol^{-1} for ΔH°_f of **IV**. Recourse to the same procedure provides the quoted formation enthalpies for 3,3-dimethylcyclopentyl cation **VI** (ΔH°_f = 175 kcal mol^{-1}), 1-ethylcyclopentyl cation **III** (ΔH°_f = 159 kcal mol^{-1}), and for the hypothetical (1-methylcyclopentyl)methyl cation **I** (ΔH°_f = 197 kcal mol^{-1}). The formation enthalpies used for evaluating the thermochemistry of the reactions of Scheme 1 are listed in Table 2.

TABLE 2: Thermochemical Data (kcal/mol^{-1}) (Estimated Values in Italic)

Species	ΔH°_f	Ref.	Species	ΔH°_f	Ref.
CH_4	-17.8	20a	CH_5^+	216	20a
C_2H_6	-20.1	20a	$C_2H_5^+$	215.6	20a
C_3H_8	-25.0	20a	$sC_3H_7^+$	190.9	20a
iC_4H_{10}	-32.1	20a	$tC_4H_9^+$	165.8	20a
 (1H)	-33	20b	$[CH_5^+ \cdot CH_4]$	191	21
			$[C_2H_5^+ \cdot CH_4]$	192	22
 (I)	*197*	see text	$[sC_3H_7^+ \cdot C_3H_8]$	152	23
			$[tC_4H_9^+ \cdot iC_4H_{10}]$	126	23
 (III)	*159*	see text			
 (IV)	*171*	see text	 (V)	158	20a
 (VI)	*175*	see text	 (II)	157	20a

According to the reported values, all pathways of Scheme 1, involving the $C_nH_5^+$ (n = 1, 2) acceptor, are thermochemically allowed (ΔH° (standard reaction enthalpy) ≤ -6 kcal mol^{-1}), except perhaps that involving hydride abstraction from a methyl group of **1H** by [CH_5^+•CH_4] (path a) (ΔH° = 3 kcal mol^{-1}).[27] If this latter pathway is actually energetically precluded, the [CH_5^+•CH_4] cluster ($G_{(M)} = 0.85 \times 1.9$[18a] = ca. 1.62) is able to abstract only the ring hydride ions (ΔH°(kcal mol^{-1}) = −23 (path b); −19 (paths c)), whereas the residual free CH_5^+ ions ($G_{(M)} = 0.15 \times 1.9$ = ca. 0.28) are able to abstract all the hydrogens of **1H** (ΔH°(kcal mol^{-1}) = −4 (path a); −30 (path b); −26 (paths c)). $C_2H_5^+$ ions, either free ($G_{(M)} = 0.87 \times 0.9$[18a] = ca. 0.8) and in the CH_4-solvated form ($G_{(M)} = 0.13 \times 0.9$ = ca. 0.1), are able to abstract all the hydrogens of **1H** (ΔH°(kcal mol^{-1}) = −6 (free) and 0 (solv) (path a); −32 (free) and −26 (solv) (path b); −28 (free) and −22 (solv) (paths c)). Within the hypothesis that the exothermic attack on 1,1-dimethylcyclopentane by the methane ions is totally indiscriminate, the expected [**4**]/([**2**] + [**3**]) product ratios would range around 0.22, a value which is close to the measured one (0.27 (**1H**), Table 1). These findings are consistent with a rather unselective hydride-transfer pattern from 1,1-dimethylcyclopentane to the methane ions, although its detailed mechanism remains still undefined.[27] The rather stable intermediate **III** does not seem to be kinetically accessible on the potential energy surface describing path a, as demonstrated by the complete absence of its methoxy derivative among the reaction products.[28] Formation of the methoxy derivatives of the much less stable species **I**, **IV**, and **VI** is not observed either, thus suggesting

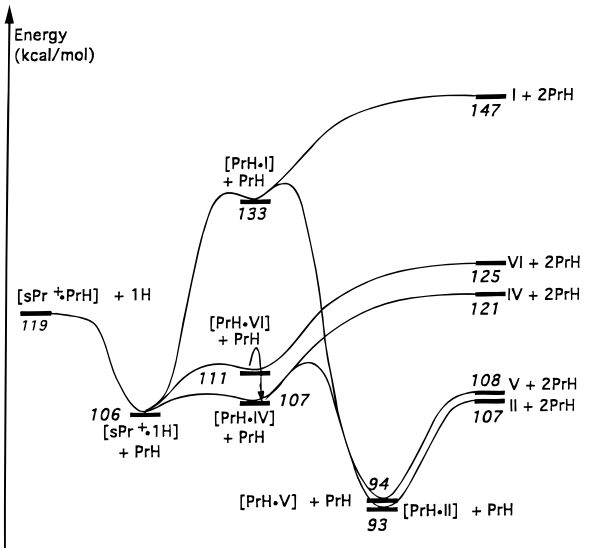


Figure 2. Potential energy profile for the gas-phase reaction between *s*-$C_3H_7^+$ ions and 1,1-dimethylcyclopentane **1H**. The figures in italic refer to the total standard formation enthalpy of the corresponding species.

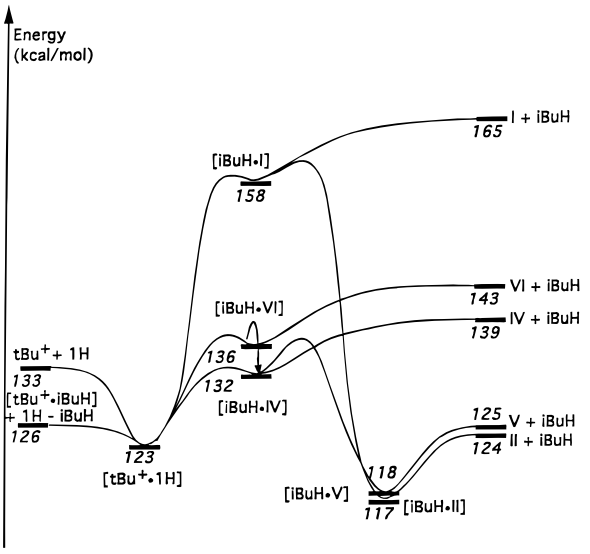
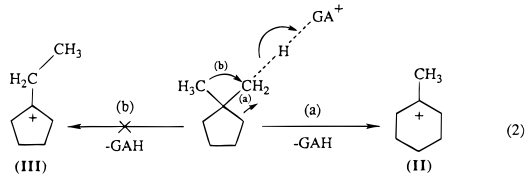


Figure 3. Potential energy profile for the gas-phase reaction between *t*-$C_4H_9^+$ ions and 1,1-dimethylcyclopentane **1H**. The figures in italic refer to the total standard formation enthalpy of the corresponding species.

that either structures **I**, **IV**, and **VI** are not accessible along the $C_nH_5^+$(n = 1, 2)-**1H** reaction coordinate or, if they are, they are completely converted into the more stable forms **II** and **V** within the time of their interception by the MeOH nucleophile (ca. 3×10^{-9} s).[17b]

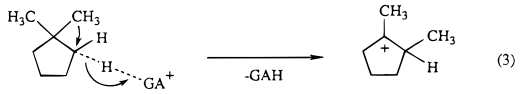
A more informative picture is obtained from analysis of the potential energy profiles reported in Figures 2 and 3, concerning respectively the attack of [*s*-$C_3H_7^+$•C_3H_8] and of the *t*-$C_4H_9^+$/[*t*-$C_4H_9^+$•*i*-C_4H_{10}] pair on **1H**. The profiles refer to the hypothetical stepwise reaction mechanism depicted in Scheme 1. The depths of the potential wells corresponding to INCs, e.g., [*s*-$C_3H_7^+$•**1H**] and [*t*-$C_4H_9^+$•**1H**], were obtained from the classical ion-molecule interaction theory,[29] after calibration of the calculation method using the experimentally measured potential well depths of the [*s*-$C_3H_7^+$•C_3H_8] and [*t*-$C_4H_9^+$•*i*-C_4H_{10}] adducts.[23,30] No precise measurements of the activation barriers of Figures 2 and 3 are available. Nevertheless, the activation barrier for the conceivable **VI** → **IV** 1,2-hydrogen shift can be taken as approximately equal to that measured in the degenerate rearrangement of unsubstituted cyclopentyl cation (≤2.8 kcal mol^{-1}),[31] whereas that of the **IV** → **V** and **I** → **II** 1,2-alkyl (or alkenyl) group shifts as equal to that measured in the degenerate rearrangement of 2,3,3-trimethylbutyl-2 cation (ca. 6 kcal mol^{-1}).[32] The activation barrier of gas-phase intracluster hydride-ion transfer [GAH•**I** (or **VI**) (or **IV**)] → [GA^+•**1H**] has been found to be strictly correlated to the corresponding reaction enthalpy.[18i] For exothermic processes ($-\Delta H° > 3$ kcal mol^{-1}), involving unencumbered H^- donors, the activation barrier, if existing at all,[23] rarely exceeds 2 kcal mol^{-1}.[18i,33]

According to the relevant energy profiles, neither [*s*-$C_3H_7^+$•C_3H_8] (Figure 2) nor the *t*-$C_4H_9^+$/[*t*-$C_4H_9^+$•*i*-C_4H_{10}] pair (Figure 3) are energetically able to abstract a hydride ion from the methyl groups of **1H** via the hypothetical stepwise mechanism involving the high-energy primary species **I**. This is because the relevant energy barriers protrude by no less than 14 and 25 kcal mol^{-1}, respectively, above that of back-dissociation of starting reagents. Nonetheless, substantial amounts of **4H**, whose formation implies necessarily the hydride abstraction from the methyl groups of **1H** (path a of Scheme 1), were recovered in both systems (Table 1). In analogy with the conclusions reached in related investigations,[1] formation of **4H** can be only accounted for by anchimeric assistance of the $C_\alpha H_2$ group (or the $C_{\alpha'}H_2$ one) of **1H** to the departure of the hydride ion from a CH_3 moiety of the donor to the GA^+ acceptor. This implies that interaction of either [*s*-$C_3H_7^+$•C_3H_8] or the *t*-$C_4H_9^+$/[*t*-$C_4H_9^+$•*i*-C_4H_{10}] pair with the methyl groups of **1H** leads directly to **II** via the concerted mechanism 2a, whose activation free energy must therefore lie not only below that of their hypothetical stepwise process but also below the corresponding back-dissociation barrier. $C_\alpha H_2$-group anchimeric assistance to the hydride loss from the CH_3 of **1H** (eq 2a) supersedes that involving the other methyl group (eq 2b) and leading directly to intermediate **III**, as demonstrated by the absence of its ethereal derivative among the radiolytic products.



(2)

A similar conclusion is reached as regards the mechanism of formation of the ionic precursor **V** of ethers **2H** and **3H** from attack of the *t*-$C_4H_9^+$/[*t*-$C_4H_9^+$•*i*-C_4H_{10}] pair on **1H** (Figure 3). Here, the stepwise mechanisms involving the intermediacy of either the [*i*-C_4H_{10}•**VI**] adduct (followed by rapid intracluster **VI** → **IV** isomerization) (path c of Scheme 1) or, directly, the [*i*-C_4H_{10}•**IV**] adduct (path b of Scheme 1) would require overcoming an activation barrier of at least 5 kcal mol^{-1} above that of back-dissociation to the starting reagents. The corresponding free energy gap is even larger since stepwise conversion of [*t*-$C_4H_9^+$•**1H**] to [*i*-C_4H_{10}•**V**] via either [*i*-C_4H_{10}•**VI**] or [*i*-C_4H_{10}•**IV**] proceeds through a "tight" transition state (negative activation entropy), whereas its back-dissociation involves a "loose" transition structure (positive activation entropy).[34] In this case, the efficiency of the stepwise process should follow a negative pressure dependence, rather than the experimentally observed positive pressure dependence (reaction efficiency: ca. 6×10^{-4} at 10^{-8} Torr; 0.07−0.10 at ca. 700 Torr). Thus, it can be concluded that attack of the *t*-$C_4H_9^+$/[*t*-$C_4H_9^+$•*i*-C_4H_{10}] pair on **1H** leads directly to the intermediate [*i*-C_4H_{10}•**V**] through a concerted mechanism (eq 3), involving an activation barrier



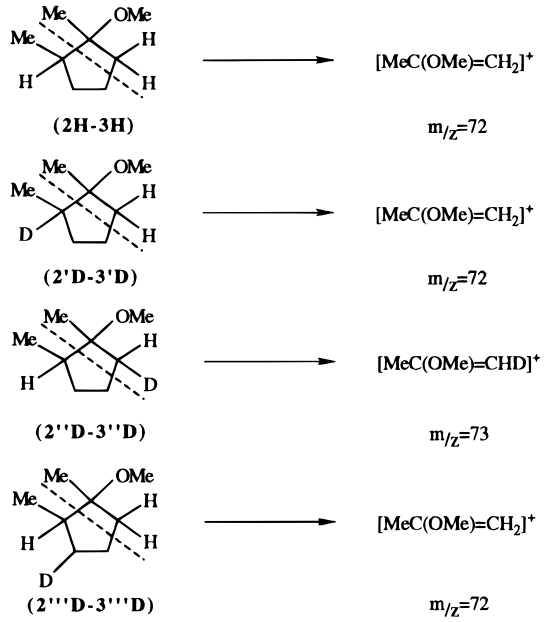
(3)

much lower than those of the conceivable stepwise pathways, via the higher energy [*i*-C_4H_{10}•**VI**] and [*i*-C_4H_{10}•**IV**] intermediates. *Since the concerted pathway 3 involves a rate-determining step with an activation barrier significantly lower than those of the conceivable stepwise routes*, the process can be rightfully labeled as *anchimerically assisted*.

Analysis of the potential energy profiles involving the [*s*-$C_3H_7^+$•C_3H_8] species (Figure 2), as the hydride acceptor, while suggesting a similar anchimerically assisted mechanism 2a for the hydride transfer involving the methyl group of the donor, does not allow us to reach any straightforward conclusions as to whether the process involving the ring hydrogens is concerted or not. In fact, for these reactions, the internal energy barriers of the conceivable stepwise paths, involving either the [C_3H_8•**VI**] adduct (followed by rapid intracluster **VI** → **IV** isomerization) (path c of Scheme 1) or, directly, the [C_3H_8•**IV**] one (path b of Scheme 1), do not protrude above the reactants energy, and therefore the observed pressure dependence of the reaction efficiency can satisfy both hypotheses. Nevertheless, discrimination between the concerted and the stepwise mechanism can be obtained from the results of Table 1 (entries v and vi) concerning the attack of [*s*-$C_3D_7^+$•C_3D_8] on **1H**. These are characterized by the almost exclusive formation of unlabeled ethers **2H** and **3H**, whereas their deuterated analogues **2D** and **3D** are barely detectable. On the grounds of the energy profiles shown in Figure 2, in fact, any conceivable [C_3D_7H•**IV**], formed either directly, by hydride abstraction from the $C_\alpha H_2$ moiety of **1H** (path b of Scheme 1), or via rapid intracluster **VI** → **IV** isomerization (path c of Scheme 1), is expected to rapidly undergo a sort of internal return to the adduct [*s*-$C_3D_7^+$••**1H**] (and, of course, its [*s*-$C_3D_6H^+$••**1D**] isotopomer),[35] before its rate-limiting conversion to the [propane•**V**] isomer. It follows that a significant incorporation of the deuterium label should be observed in both the ethereal products and the starting 1,1-dimethylcyclopentane. The lack of any significant D incorporation in these compounds after irradiation speaks against the occurrence of the [propane•**IV**] structure, formed either directly from hydride transfer from the $C_\alpha H_2$ moiety of **1H** to the *s*-propyl ion, or indirectly through the [propane•**VI**] structure. On these grounds, formation of intermediate [C_3H_8•**V**] is believed to proceed through the concerted mechanism 3.

Kinetic Isotope Effects (KIEs). An additional piece of evidence in favor of the intervention of anchimeric assistance in these gas-phase hydride-transfer reactions arises from the evaluation of the kinetic isotope effects (KIEs), using 2-deutero-1,1-dimethylcyclopentane as the starting substrate. The evaluation of the primary (PKIE) and secondary kinetic isotope effects (SKIE) is based upon the mass spectrometric fragmentation pattern of *trans*- and *cis*-1,2-dimethyl-1-methoxycyclopentanes arising from attack of GA^+ on **1D** in the presence of MeOH. A significant fragment from 70 eV electron impact on the unlabeled ethers **2H** and **3H** is $[MeC(OMe)=CH_2]^+$ ($m/z = 72$) Chart 1.[36] The same peak is observed in the mass fragmentation of the *cis*- and *trans*-2-deutero-1,2-dimethyl-1-methoxycyclopentane (**2′D**−**3′D** in Chart 1), obtained from gas-phase $C_nD_5^+$ (n = 1,2)-deuteronation of 1,2-dimethyl-cyclopentene in the presence of methanol. Mass spectra of *trans*- and *cis*-1,2-dimethyl-1-methoxycyclopentanes from attack of GA^+ on **1D** in the presence of MeOH are instead characterized by the presence of the base peak at $m/z = 72$ ($[MeC(OMe)=CH_2]^+$ from **2H**−**3H**, **2′D**−**3′D**, and **2‴D**−**3‴D** of Chart 1), accompanied by a less abundant fragment at $m/z = 73$ ($[MeC(OMe)=CHD]^+$ from **2″D**−**3″D** of Chart 1). Both ethers **2H** and **3H** from **1H** display identical fragmentation patterns, coinciding, mutatis mutandis, within ca. 2% with those of **2D** and **3D** from **1D**. Thus, for instance, the $[m/z = 72]/[m/z = 128]$ and the $[m/z = 72]/[m/z = 113]$ intensity ratios from ethers **2H** and **3H** are nearly identical to the $([m/z = 72] + [m/z = 73])/[m/z = 129]$ and the $([m/z = 72] + [m/z = 73])/[m/z = 114]$ ones from **2D** and **3D**, respectively. It is concluded that the presence and the position of a deuterium label in **2D** and **3D** do not influence appreciably their fragmentation patterns and, therefore, the relative abundance of the $m/z = 72$ and $m/z = 73$ peaks closely reflects the relative distribution of the ethers of Chart 1.

CHART 1



From the reaction pattern shown in Scheme 2, and within the very reasonable assumption that trapping of intermediates **VH**, **V′D**, and **VD** by MeOH and neutralization of the ensuing derivatives are relatively fast steps of the reaction sequences, it results that:

$$\Theta = [MeC(OMe)=CH_2]^+/[MeC(OMe)=CHD]^+ = (k_D + k_H^{\alpha} + k_H^{\alpha'})/k_H^{\alpha'}$$

The $k_D/(k_H^{\alpha} + 2k_H^{\alpha'})$ ratio is expressed by the $\Phi = ([\mathbf{2H}] + [\mathbf{3H}])/([\mathbf{2D}] + [\mathbf{3D}])$ fraction. Therefore, since $k_D = \Phi(k_H^{\alpha} + 2k_H^{\alpha'})$, Θ can be expressed by the following equation:

$$\Theta = (1 + \Phi)(k_H^{\alpha}/k_H^{\alpha'}) - (1 + 2\Phi)$$

which, if rearranged, gives

$$k_H^{\alpha'}/k_H^{\alpha} = (1 + \Phi)/[\Theta - (1 + 2\Phi)]$$

In the same way, the $k_H^{\alpha'}/k_D$ can be expressed by the following equation:

$$k_H^{\alpha'}/k_D = (1 + \Phi)/[\Phi(\Theta + 1)]$$

Now, in consideration of the negligible $C_{\alpha'}HD$ kinetic effect (a γ-deuterium effect)[37] expected on the $k_H^{\alpha'}$ (Scheme 2), the $k_H^{\alpha'}$ can be taken as equal to the rate constant for the hydride transfer from the $C_\alpha H_2$ moiety of **1H** to GA^+. In this way, the $k_H^{\alpha'}/k_D$ and the $k_H^{\alpha'}/k_H^{\alpha}$ ratios express respectively the primary (PKIE)

SCHEME 2

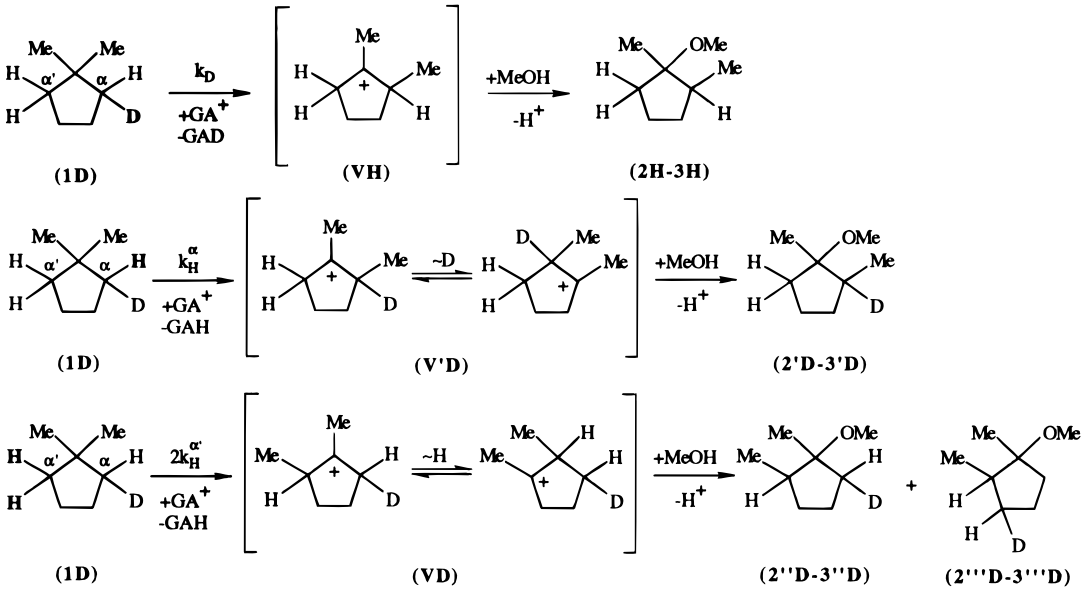


TABLE 3: First-Order Rate Constants (Θ)[a] and Product Yield (Φ)[a] Ratios and Deuterium Isotope Effects in the Hydride Transfer from the $C_\alpha H_2$ of 1,1-Dimethylcyclopentane to the GA^+ Acceptors (37.5 °C)

run no.	GA^+	(Θ)	(Φ)	$'k_H^\alpha/k_D$	$'k_H^\alpha/k_H^\alpha$
ix	*s*-$C_3H_7^+$	1.970	0.143	2.69	1.67
x	*s*-$C_3H_7^+$	1.919	0.139	2.81	1.78
xi	*s*-$C_3H_7^+$	1.919	0.152	2.60	1.87
			av	2.70 ± 0.11	1.77 ± 0.10
xii	*t*-$C_4H_9^+$	2.400	0.184	1.89	1.15

[a] See text.

and the secondary α-D kinetic isotope effect (SKIE) in reaction 3. The relevant values are summarized in Table 3, together with the corresponding Φ and Θ factors.

The significant PKIE observed in the hydride transfer from 1,1-dimethylcyclopentane to the *s*-$C_3H_7^+$ and *t*-$C_4H_9^+$ acceptors, essentially related to the virtual hydride stretching motion,[38] provides further evidence in favor of a concerted, anchimerically assisted mechanism. In fact, on the grounds of the energy profiles of Figures 2 and 3, the hypothetical stepwise sequence (b) of Scheme 1 would proceed via a fast [GA^+•**1H**] ↔ [GAH•**IV**] preequilibrium step, followed by the rate-limiting [GAH•**IV**] → [GAH•**V**] intracluster isomerization. Within this hypothesis, the overall rate constant of the stepwise hydride transfer would be directly proportional to the k_iK_{eq} product, where k_i is the [GAH•**IV**] → [GAH•**V**] isomerization rate constant, and K_{eq} is the [GA^+•**1H**] ↔ [GAH•**IV**] pseudoequilibrium constant. The k_i constant is unaffected by replacement of the leaving hydride by a deuteride ion in the stepwise sequence b of Scheme 1. The effect might be sizable on K_{eq}, depending upon the force field of the *s*-C_3H_7−H and *t*-C_4H_9−H bonds relative to that of the C_α−H bonds of 1,1-dimethylcyclopentane.[39] Since the force field of homologue bonds, e.g., the C−H bonds, is proportional to the corresponding dissociation energy,[40] that of the C_α−H bonds of 1,1-dimethylcyclopentane is just below that of the GA−H bonds (GA = *s*-C_3H_7 and *t*-C_4H_9). On these grounds, K_{eq} would display only a *limited inverse* isotope effect ($K_{eq}^H \leq K_{eq}^D$), if any. It follows that, within the hypothesis of a hydride-transfer reaction proceeding via the stepwise sequence (b), the measured rate constant would be affected by a *small inverse* isotope effect as well ($k_iK_{eq}^H \leq k_iK_{eq}^D$). On the contrary, the *normal* primary isotope effect, measured for the hydride-transfer rate constant from the radiolytic experiments ($k_H^{\alpha'}/k_D = 1.89-2.70$, Table 3) excludes that the occurrence of the hypothetical stepwise route b in favor of a concerted, anchimerically assisted mechanism with a transition state involving a significant C_α−H bond rupture in 1,1-dimethylcyclopentane.

Unlike PKIE, inference of transition-state geometries from SKIEs is more complicated. The magnitude of SKIEs may be partitioned into variable translational, rotational, and vibrational contributions from all the transition-state moieties, although, for those involving C_α−H bonds, vibrational motion plays a predominant role.[38] Accordingly, following Streitwieser's formulation,[41a] a normal SKIE mainly reflects the out-of-plane bending (wagging) motion of the C_α−H bonds, as a response of the extent of sp^3-sp^2 C_α rehybridization at the transition state. In this framework, the relatively large SKIE ($k_H^{\alpha'}/k_H^\alpha = 1.77$) shown in entries ix−xi of Table 3 indicates that, in the transition state of the concerted hydride transfer from the $C_\alpha H_2$ moiety of **1H** to *s*-$C_3H_7^+$, the C_α−H wagging motion is nearly completely free.[41] This implies that the relevant transition structure is characterized by a limited anchimeric assistance of the methyl groups of **1H** to the leaving hydride ion. The lower $k_H^{\alpha'}/k_H^\alpha = 1.15$, measured with *t*-$C_4H_9^+$, indicates that the same interaction is much more developed in the corresponding transition state. Here, the accompanying decrease of the PKIE ($k_H^{\alpha'}/k_D$ from 2.70 (*s*-$C_3H_7^+$) to 1.89 (*t*-$C_4H_9^+$)) reflects a parallel effect (Hammond postulate effect) on the reaction surface, which is consistent with a transition structure resembling the [*i*-C_4H_{10}•**V**] one and placed later along the reaction coordinate relative to that leading to the [C_3H_8•**V**] adduct.

In conclusion, both PKIE and the SKIE in the hydride transfer reaction 3 with GA^+ = *s*-$C_3H_7^+$ and *t*-$C_4H_9^+$ indicate that the reaction is anchimerically assisted by the adjacent methyl groups. In the departure of the C_α−H hydride ion, the anchimeric assistance of the vicinal methyl groups, although only partially developed, plays a decisive role. In fact, it provides that limited energy push necessary to break completely the residual $C_\alpha\cdots H\cdots GA^+$ bonding in the transition state, without which the reaction would not take place.

An evaluation of the efficiency of the hydride transfer between **1H** and GA^+ = *s*-$C_3H_7^+$ or *t*-$C_4H_9^+$, measured in the radiolytic experiments at 640−700 Torr, with that measured at ca. 1×10^{-8} Torr in the FT-ICR cell can elucidate this latter point. Apart from the limited effect of conservation of total

angular momentum,[24,25] the unreactivity of t-$C_4H_9^+$ ions toward **1H**, observed in the FT-ICR experiments, is due to the inability of the [t-$C_4H_9^+$•**1H**] adduct to dispose readily of its excitation energy by collisions with the rarefied gaseous medium (ca. 1×10^{-8} Torr). Under such high-energy conditions, entropy-favored back-dissociation of the excited [t-$C_4H_9^+$•**1H**] adduct by far predominates over the anchimerically assisted hydride transfer, whose transition state requires a rigorous antiperiplanar alignment between the leaving moiety and the assisting group. In dense gaseous media (640−700 Torr), efficient collisional quenching of the excited [t-$C_4H_9^+$•**1H**] adduct takes place in a time (ca. 10^{-10} s) short relative to its back-dissociation, which suddenly becomes no longer energetically feasible. This enhances the lifetime of the [t-$C_4H_9^+$•**1H**] adduct so as to allow a methyl group of **1H** vicinal to the reaction center to attain the proper alignment relative to the leaving hydride ion and to anchimerically assist its departure.

According to the relevant PKIE and SKIE, a similar pattern is operative in the hydride transfer from **1H** to the s-$C_3H_7^+$ acceptor under high-pressure radiolytic conditions. The fact that, at the low-pressures of the FT-ICR experiments (ca. 1×10^{-8} Torr), the hydride transfer from **1H** to s-$C_3H_7^+$ is a rather efficient process as well suggests that the *excited* [s-$C_3H_7^+$•**1H**] adduct can efficiently overcome the limited activation-barrier leading to [C_3H_8•**V**] prior to its back-dissociation to reactants. Under these conditions, the specific mechanism for the *excited* [s-$C_3H_7^+$•**1H**] conversion to [C_3H_8•**V**], whether concerted or involving the entropy-favored stepwise pathway, remains undefined.

Comparison with Related Solvolytic Studies. Comparison of the present gas-phase results with those concerning strictly related solvolytic studies allows us to discern the intrinsic structural and electronic factors determining the anchimerically assisted mechanism from the perturbing influence of solvation and ion-pairing phenomena.

Solvolysis of 2,2-dimethylcyclopentyl *p*-bromobenzenesulfonate (BsO−**1H**) in media of different nucleophilicity follows a stepwise pattern, whose energy profile is qualitatively similar to those reported in Figures 2 and 3.[9a] In nucleophilic solvents, BsO−**1H** (corresponding to [GA^+•**1H**] in Figures 2 and 3) ionizes to form the intimate ion pair [BsO^-•**IV**] (corresponding to [GAH•**IV**] in Figures 2 and 3), which undergoes internal return (analogous to the fast [GA^+•**1H**] ↔ [GAH•**IV**] preequilibrium). Because it is sterically hindered from nucleophilic attack by the solvent, [BsO^-•**IV**] undergoes rate-determining rearrangement to [BsO^-•**V**] (corresponding to [GAH•**V**] in Figures 2 and 3). The solvent is not involved nucleophilically before and during the rate-determining methyl-migration step, so that the reaction rate is influenced primarily by changes in the ionizing strength of the solvent. Accordingly, almost completely rearranged products (analogous to ethers **2H** and **3H**) are formed from solvolysis of BsO−**1H**, irrespective of the nucleophilicity of the reaction medium. The large SKIE of 1.20, measured in these systems, is consistent with a transition state involving no significant covalent bonding by nucleophile (either the solvent or the migrating methyl moiety) to the reaction center and therefore, according to Hammond postulate, its structure resembles that of the [BsO^-•**IV**] ion pair.

In the gas phase, the occurrence of the [GAH•**IV**] intermediate from intracluster hydride transfer in the [GA^+•**1H**] adduct cannot benefit by stabilizing interaction with the medium and, especially, with the counterion, whose role in these systems is played by the far removed nonnucleophilic neutral hydrocarbon GAH (the $C^+\cdots$GAH distance in the transition state may largely exceed 3 Å).[24] Therefore, the system evolves via a concerted route, through a sort of *internally solvated* transition state characterized by the anchimeric assistance of the methyl groups adjacent to the reaction center.

Aqueous ethanolysis of (1-methylcyclopentyl)methyl sulfonate esters involves extensive anchimeric assistance by the ring methylene moieties adjacent to the reaction center, in strict analogy with the concerted mechanism observed in the gas-phase hydride transfer from the methyl group of **1H** to the GA^+ acceptor.[9b] In both systems, anchimeric assistance partially compensates for the methyl carbon-leaving group bond dissociation energy (eq 2). Reaction 2 demands a higher extent of anchimeric assistance than that involved in reaction 3, owing to the greater energy of the unrearranged primary cation **I** relative to that of the unrearranged secondary cation **IV**.

Conclusions

The present gas-phase investigation, based upon structural discrimination of the neutral products, deuterium labeling experiments, and kinetic isotope and GA^+-acceptor effects, demonstrates that, in the gas phase, the hydride-transfer reaction from 1,1-dimethylcyclopentane to several ionic acceptors involves significant anchimeric assistance by neighboring alkyl and alkylene groups. This conclusion, which reinforces previous incidental pieces of evidence,[1] outlines the general view of gas-phase hydride-transfer processes, whose occurrence is governed by internal solvation from suitably located groups. This implies that the intention of generating in the gas phase a specific carbocationic structure, especially if secondary or primary, by loss of a hydride ion from suitable hydrocarbons may prove utopian, if the hydride transfer requires the anchimeric assistance from a neighboring group and, therefore, a concerted structural rearrangements.

Irrespective of the GA^+ acceptor employed, the transition state of the concerted hydride transfer reaction from the $C_\alpha H_2$ moiety of 1,1-dimethylcyclopentane is characterized by the extensive cleavage of the C_α−H bond, anchimerically assisted by an adjacent methyl group. The extent of both the C_α−H bond cleavage and the methyl-group anchimeric assistance increases by decreasing the strength of the GA^+ acceptor. Comparatively more pronounced anchimeric assistance by the $C_\alpha H_2$ moiety is observed in the gas-phase hydride-transfer reaction from the CH_3 groups of 1,1-dimethylcyclopentane to GA^+.

Comparison of the gas-phase results with those of strictly related solvolytic reactions, while revealing a substantial mechanistic uniformity, points to some discrepancies between the stepwise mechanism involved in the solvolysis of 2,2-dimethylcyclopentyl brosylate and the concerted one governing the gas-phase hydride-ion transfer from the $C_\alpha H_2$ moiety of 1,1-dimethylcyclopentane, which are attributed to solvation and ion-pairing phenomena.

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(30) In Figure 2, the association enthalpy of any $C_7H_{13}^+$ ion with a propane molecule is taken as equal to that measured for *s*-$C_3H_7^+$ (13.6 kcal mol^{-1}).[23] The ligand exchange leading to [*s*-$C_3H_7^+$•**1H**] + C_3H_8 is estimated to release ca. 13 kcal mol^{-1}, namely, the difference between the association enthalpies of *s*-$C_3H_7^+$ with **1H** (ca. 26.4 kcal mol^{-1}) (see text) and with propane (13.6 kcal mol^{-1})[23] In Figure 3, the association enthalpy of any $C_7H_{13}^+$ isomer with an isobutane molecule is taken as equal to that measured for *t*-$C_4H_9^+$ (7.2 kcal mol^{-1})[23] The ligand exchange leading to [*t*-$C_4H_9^+$•**1H**] + *i*-C_4H_{10} is estimated to release ca. 3 kcal mol^{-1}, namely, the difference between the association enthalpies of *t*-$C_4H_9^+$ with **1H** (ca. 10 kcal mol^{-1}, see text) and with isobutane (7.2 kcal mol^{-1}).[23]

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(36) Isomeric 1,2-dimethylcyclopentanols and 1-methylcyclohexanol display the same mass spectroscopic fragmentation pattern. It is characterized by a distribution of fragment ions paralleling that from ethers **2**−**4**, but shifted by −14 amu (the CH_2 moiety). Thus, the $[MeC(OMe)=CH_2]^+$ fragment (m/z = 72) of ethers **2**−**4** corresponds in the spectra of isomeric 1,2-dimethylcyclopentanols and 1-methylcyclohexanol to a significant m/z = 58 peak, due to the $[MeC(OH)=CH_2]^+$ fragment. A pronounced m/z = 58 peak, but this time due to the $[HC(OMe)=CH_2]^+$ fragment, characterizes the mass spectra of isomers of ethers **2**−**4**, not containing a methyl group geminal to the MeO moiety, i.e., 2,2-dimethyl-1-methoxycyclopentanols.

(37) The deuterium isotope effect of a nonmigrating CHD moiety in the γ position, such as the $C_\alpha'HD$ one in **1D** (third equation of Scheme 2), in the rate determining formation of a carbocation has been measured to fall slightly below 1 (ca. 0.98), see ref 9 and Schubert, W. M.; LeFevre, P. H. *J. Am. Chem. Soc.* **1969**, *91*, 7746).

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