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STEREOCHEMICAL EFFECTS IN THE GAS-PHASE PINACOL REARRANGEMENT OF CIS- AND TRANS-1-METHYLCYCLOHEXANE-1,2-DIOL.

Patrizio CECCHI,[§] Romano CIPOLLINI,[†] Adriano PIZZABIOCCA,[§] Gabriele RENZI,[§] and Maurizio SPERANZA.*[∫]

[§] Dipartimento di Scienze Chimiche, Università di Camerino, I-62032 Camerino (MC),Italy.
[†] Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università di Roma "La Sapienza", I-00185 Roma, Italy.
[∫] Dipartimento di Agrobiologia ed Agrochimica, Università della Tuscia, I-01100 Viterbo, Italy.

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ABSTRACT

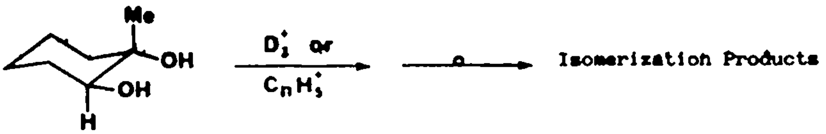
The gas-phase pinacol rearrangement of cis and trans-1-methyl-1,2-cyclohexanediols, promoted by D_3^+ *and* $C_nH_5^+$ *(n = 1,2), was studied by the radiolytic method in the pressure range 100-760 Torr. Under all conditions, 2-methyl-cyclohexanone is the predominant product, arising from both substrates via different pinacol rearrangements and successive fast isomerization of the corresponding primary intermediates, e.g. O-protonated 1-methyl-1-cyclopentanecarboxaldehyde. This conclusion is based from kinetic analysis of competition experiments with pinacol as reference substrate, carried out at high pressure (760 Torr) with or without added base* (NMe_3, *3 Torr), showing that the pinacol rearrangement rates are markedly dependent on the stereochemical features of the diol. Accordingly, the trans diol rearranges more rapidly than the cis isomer, which in turn isomerizes faster than pinacol, indicating that anti-periplanar* CH_2 *migration to the vicinal tertiary* $C\text{-}OH_2^+$ *center in trans (k2) is over five times faster than H migration in cis (k3). Analysis of the relative migrating ability of the different* CH_2 *moieties in trans (k2 > k1) allowed exclusion of appreciable anchimeric assistance in these gas-phase pinacol rearrangements. The results are compared with relevant gas-phase data and with those concerning the same substrates in acidic solution.*

INTRODUCTION

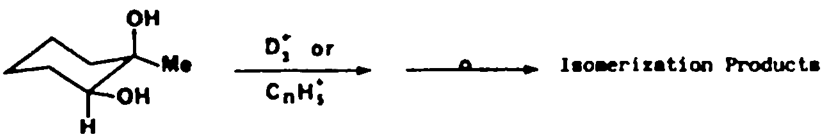
Kinetic evaluation of the stereochemical factors involved in pinacol rearrangements in solution invariably meets with some difficulties mainly due to changes in reaction mechanism and to competitive isomerization processes promoted by interaction with the medium. In the gas-phase, i.e. in a reaction environment essentially free from the complicating effects of solvation and ion pairing, an integrated mass spectrometric and radiolytic approach was recently exploited, which allowed to evaluate the structural effects on the rates of acid-induced pinacol rearrangement in cis- and trans-1,2-dimethylcyclopentane-1,2-diols[1] and -1,2-dimethylcyclohexane-1,2-diols.[2]

The relevant kinetic data demonstrated that, while restricted rotation and strain effects in 1,2-dimethylcyclopentane-1,2-diols favor methyl migration in the cis with respect to trans, in the freely rotating and virtually strainless 1,2-dimethylcyclohexane-1,2-diols, anti-periplanar assistance to the leaving water molecule increases in the order $CH_3 < CH_2 < OH$. As a consequence, the trans isomer is found to rearrange faster than the cis one. However, from such limited data, it could not be decided whether water loss in these systems is accelerated by anchimeric assistance by the participating vicinal groups. To obtain this piece of information as well as to gain further insight into the relative participating ability of other neighbouring groups, such as hydrogen, we extended the investigation to closely related, but asymmetric, cyclic diols, such as cis- and trans-1-methylcyclohexane-1,2-diols 1 (eq. 1).
The present paper is aimed at investigating the course of the pinacol rearrangement of 1 in the 100 - 760 Torr pressure range, using different γ-radiolytic Brönsted acids, i.e. D_3^+ and $C_nH_5^+$ (n = 1,2), and evaluating the stereochemical factors affecting the corresponding isomerization rates.

Previously discussed considerations concerning the nature of the rearrangement process apply to this study as well, which traces the formation of the neutral radiolytic products to entirely ionic sequences triggered by attack of the selected Brönsted acids on 1.



trans - 1 (1a)



cis - 1 (1b)

RESULTS

Table I reports the composition of the irradiated mixtures and the yield of the neutral product, i.e. 2-methylcyclohexanone 2, exclusively recovered under all conditions by protonation of the substrates with gaseous radiolytic Brönsted acids.[3] The ionic nature of the reaction product is ensured by the presence of O_2 (5 Torr), an effective radical scavenger, and by the observed strong decrease (from 66 to 79%) of the product yield when 0.4 mol % of NMe_3, an efficient interceptor of gaseous acids, is added to the mixture. The rearrangement reaction is very clean and the absolute yield of 2 is well reproducible within 10% from run to run, no other products traceable to the substrates being recovered. It should be noted that the G(M) values, defined as the number of molecules formed per 100 eV of energy absorbed by the gaseous systems, measured for 2 at 760 Torr accounts for only 3 - 12% of the gaseous Brönsted acids formed, owing to the very low concentration of the substrates (ca. 5 x 10^{-3} mol %) in the systems, limited by their vapour pressures, and to the competition by adventitious nucleophiles, either originally present as impurities or accumulated during the radiolysis. In fact, at lower pressures (100 Torr, a factor of 7.6 in the partial pressure of the bulk gas), the product yields increase by a factor ranging from 3 to over 7.

In order to ascertain the possible occurrence of extensive structural interconvertion among the primary dehydration intermediates involved in eqs. 1a,b, gaseous 2-methylcyclohexanone 2, 1-methyl-1,2-epoxycyclohexane 3, methyl cyclopentyl ketone 4, and 1-methyl-1-cyclopentanecarboxaldehyde 5 were individually submitted to protonation by D_3^+ and $C_nH_5^+$ under the same experimental conditions of Table I.

Table II shows that, while structural rearrangement of $2H^+$ to $4H^+$ is barely detectable (4.7%) only when the very energetic D_3^+ acid is employed, the reverse isomerization reaction $4H^+ \longrightarrow 2H^+$ takes place to a considerable extent (60%). It is worth noting that the latter process is observable only when D_3^+ is used and, therefore, the protonated intermediates involved are highly excited (vide infra). Pronounced isomerization of $5H^+$ to $2H^+$ is instead observed under all conditions, as shown in Table III. Protonation of epoxide 3 by both D_3^+ and $C_nH_5^+$ induces extensive isomerization of the primary excited intermediate $3H^+$ to either $2H^+$ and $4H^+$ (Table IV).

TABLE I. Products from the Protonation of _cis_- and _trans_-1-Methylcyclohexane-1,2-diol (1) by Gaseous Acids.[a]

System Composition (Torr)[b]				Absolute yield of 2[d] (%)[e]
Bulk gas	NMe_3	Substrate	G(M)[c]	
D_2,760	3	_trans_-1, 0.54	0.05	1.6
D_2,760	-	_trans_-1, 0.54	0.15	5.0
D_2,100	-	_trans_-1, 0.50	0.76	25.3
D_2,760	3	_cis_-1, 0.51	0.05	1.6
D_2,760	-	_cis_-1, 0.48	0.19	6.3
D_2,100	-	_cis_-1, 0.51	1.36	45.3
CH_4,760	3	_trans_-1, 0.46	0.03	1.1
CH_4,760	-	_trans_-1, 0.49	0.09	3.2
CH_4,100	-	_trans_-1, 0.48	0.65	23.2
CH_4,760	3	_cis_-1, 0.54	0.07	2.5
CH_4,760	-	_cis_-1, 0.45	0.34	12.1
CH_4,100		_cis_-1, 0.50	1.02	36.4

[a] D_3^+ from the radiolysis of D_2 and $C_nH_5^+$ (n = 1,2) from CH_4.
[b] O_2 (5 Torr) was present in all systems as radical scavenger.
[c] Number of molecules formed per 100 eV absorbed energy. Standard deviation of data ca. 10%.
[d] Other plausible pinacol-rearrangement products (i.e. 3 - 5) below detection limit (G(M) $\leq 1 \times 10^{-4}$).
[e] Absolute yields are calculated from the ratio of the G(M) value of 2 to the G(D_3^+) and G($C_nH_5^+$) formation values (see refs. 4,5).

TABLE II. Products from the Protonation of 2-Methylcyclohexanone (2) and Methyl cyclopentyl ketone (4) by Gaseous Acids.[a]

System Composition (Torr)[b]			Absolute yield of Products (%)[e]	
Bulk gas	Substrate	G(M)[c]	2	4
D_2,760	2 , 0.53	0.14	-	4.7
CH_4,760	2 , 0.58	f	-	f
D_2,760	4 , 0.60	1.80	60.0	-
CH_4,760	4 , 0.60	f	f	-

[a,b,c,e] See footnotes of Table I.
[f] Below detection limit (G(M) $\leq 1 \times 10^{-4}$).

TABLE III. Products from the Protonation of 1-Methyl-1-cyclopentanecarboxaldehyde (5) by Gaseous Acids.[a]

System Composition (Torr)[b]				Absolute yield of Products (%)[e]	
Bulk gas	NMe_3	Substrate	G(M)[c]	2	4
D_2,760	3	5 , 0.56	0.08	3	f
D_2,760	-	5 , 0.71	1.89	63	Traces[g]
CH_4,760	3	5 , 0.45	0.27	10	Traces
CH_4,760	-	5 , 0.63	1.06	38	Traces

[a,b,c,e] See footnotes of Table I.
[f] See footnote of Table II.
[g] $1 \times 10^{-4} < G(M) < 1 \times 10^{-3}$.

TABLE IV. Products from the Protonation of 1-Methyl-1,2-Epoxycyclohexane (3) by Gaseous Acids.[a]

System Composition (Torr)[b]			Relative yield of Products (%)		Total Absolute yield	
Bulk gas	NMe_3	Substrate	2	4	G(M)[c]	%[c]
D_2,760	3	3 , 0.57	100	f	0.05	1.7
D_2,760	-	3 , 0.53	81.3	18.7	0.91	30.3
D_2,100	-	3 , 0.48	79.6	20.4	2.99	100
CH_4,760	3	3 , 0.55	100	f	0.14	5.0
CH_4,760	-	3 , 0.55	90.8	9.2	1.52	54.3
CH_4,100	-	3 , 0.47	95.2	4.8	2.73	97.5

[a,b,c,e] See footnotes of Table I.
[f] See footnote of Table II.

However, while at 760 Torr and in the presence of NMe_3 only $2H^+$ is formed, in the absence of added bases formation of $2H^+$ is accompanied by minor amounts of $4H^+$. Irradiation of systems containing either cis-1 or trans-1, 760 Torr D_2 or CH_4 and up to 20 Torr of H_2O, did not show any cis-trans epimerization occuring in competition with the pinacol rearrangements. Furthermore, GLC/MS analysis of the irradiation product 2 showed no deuterium incorporation into the ketone from all reactions with D_3^+ ions.

The relative reactivity of isomeric 1 was measured by competition experiments of each substrate vs. pinacol, taken as a standard compound, in complete analogy with the previous studies.[1,2] The composition of the competition systems and the relative yields of the radiolytic products are summarized in Table V.

TABLE V. Competitive Rearrangement of 1-Methylcyclohexane-1,2-diols (1) and Pinacol in the Gas Phase.[a]

System Composition (Torr)[b]				G(M)[c]			Total Absolute yield (%)[e]	Apparent Reactivity Ratio
Bulk gas	NMe_3	1	Pinacol	2	4	Pinacone		(k/k_p)[h]
D_2,760	-	cis, 0.04	0.44	0.18	g	1.69	62	1.1
D_2,760	3	cis, 0.05	0.54	0.16	f	0.37	18	4.3
D_2,760	-	trans, 0.05	0.47	0.06	g	1.90	65	0.3
D_2,760	3	trans, 0.05	0.53	0.04	f	0.20	8	2.0
CH_4,760	-	cis, 0.04	0.48	0.20	g	1.79	71	1.1
CH_4,760	3	cis, 0.04	0.42	0.04	f	0.16	7	2.5
CH_4,760	-	trans, 0.04	0.42	0.08	g	1.53	58	0.5
CH_4,760	3	trans, 0.05	0.45	0.07	f	0.17	9	4.1

[a,b,c,e] See footnotes of Table I.
[f] See footnote of Table II.
[g] See footnote of Table III.
[h] Calculated by correcting the yields of rearranged products for the concentration ratio of the competing substrates.

DISCUSSION

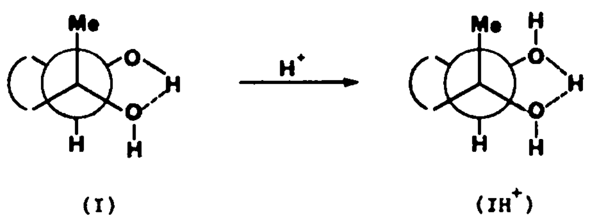
The Gas-Phase Protonation Reaction

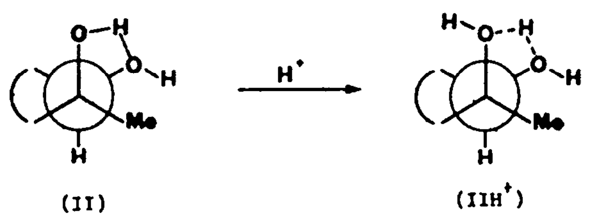
The gaseous acids used in the present study, i.e. D_3^+ and $C_nH_5^+$ (n = 1,2), are formed in known yields from the γ-radiolysis of the corresponding neutral bulk gas, i.e. D_2[4] and CH_4,[5] respectively, and thermalyzed by a large number of unreactive collisions with the parent molecules before reacting with the selected substrates 1. Thermal D_3^+ and $C_nH_5^+$ ions may act as Brönsted acids by protonating a n-type center (an O atom) of the substrate.

Althoug the gas-phase basicities (GB) of 1 are not yet available from the literature, a rough estimate based on the known GB's of their unsubstituted analogues[6,7] suggests that all the substrates, i.e. isomeric 1 as well as pinacol, should have very close $\Delta G°$ values for the O-protonation reaction by D_3^+ and $C_nH_5^+$. Thus, $-\Delta G°$ is estimated to fall within 97-98 Kcal mol^{-1} for D_3^+, 65-67 Kcal mol^{-1} for CH_5^+, and 36-37 Kcal mol^{-1} for $C_2H_5^+$. These values refers to model compounds with a H atom instead of the CH_3 substituent on the C1 bearing the OH group. The actual $-\Delta G°$ values might be very close to the estimated ones and anyhow well within their uncertainty range, taking into account the very close basicity values of 1,2-ethanediol (GB= 191.7 Kcal mol^{-1}), 1,2-propanediol (GB = 191.6 Kcal mol^{-1}), and 2,3-butanediol (GB = 192.4 Kcal mol^{-1}).[7] On the same grounds, it is plausible that the basicity difference between the two OH moieties of each individual 1-methyl-1,2-cyclohexanediol isomer is vanishingly small. Therefore, it is expected that the highly exothermic protonation of 1 by D_3^+ and $C_nH_5^+$ ions will occur indiscriminately on either the OH group at C1 and the OH group at the C2.

In agreement with the conclusions reached in previous investigation on related compounds,[2] pinacol rearrangement in isomeric 1 is expected to occur much faster than cyclohexane ring inversion in the gas phase. Now, according to IR spectra of isomeric 1 taken in apolar aprotic media (CCl_4), the conformers populations of trans- and cis-1 coincide with the most stable structures I and II, respectively, wherein an intramolecular hydrogen-bond interaction is present.[8]

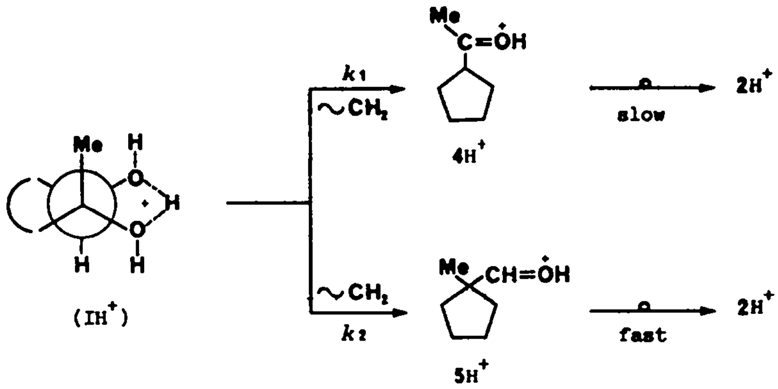
It is likely that, in the gas phase, such conformers are even more favored among all possible structures, especially the less stable not hydrogen-bonded conformer III for trans-1. As a consequence, indiscriminate protonation at the almost equally basic OH groups of I and II by D_3^+ or $C_nH_5^+$ will produce the corresponding O-protonated structures IH^+ and IIH^+, characterized by a quasi-symmetric proton-bound $[HO\cdots H\cdots OH]^+$ interaction (eqs 2).[9]
However, at variance with the data concerning 1,2-dimethylcyclohexane-1,2-diols,[2] protonation of I gives significantly lower yields of the rearranged product 2 with respect of II (see Table I). In view of the similar basicity of I and II of eqs. 2a,b and in analogy with the conclusions reached in previous studies,[1,2] such yield difference cannot be accounted for by a significantly different protonation rates in eqs. 2a,b, but rather to some protonation-induced parasitic processes, e.g. rapid successive elimination of two water molecules, which seems to be especially pronounced in trans epimers of cyclic 1,2-diols.[10]


(2a)


(2b)

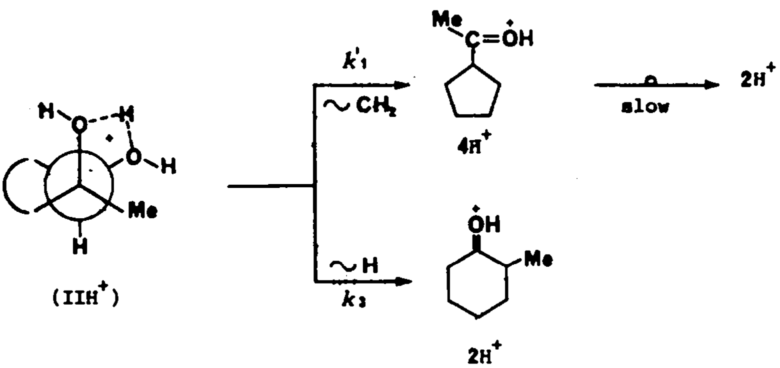
The Gas-Phase Isomerization Process.

In agreement with the behaviour of 1,2-dimethylcyclopentane-1,2-diols[1] and 1,2-dimethylcyclohexane-1,2-diols,[2] no evidence for the intermediacy of a free carbenium ion could be found nor epimerization of the substrates in the presence of water was observed. Accordingly, the dehydration and migration steps in IH^+ and IIH^+ cannot be separated kinetically, and any difference among the rearrangement rates of the substrates can be traced to their stereochemistry and to the different participating ability of the migrating groups which are anti-periplanar to the leaving water molecule. Anti-periplanar CH_2-group participation to the H_2O loss in IH^+ is expected to yield both $4H^+$ and $5H^+$ as primary intermediates (eq. 3), whereas, in IIH^+, anti-periplanar H and CH_2 migration leads to $2H^+$ and $4H^+$, respectively (eq. 4). In this connection, exclusive formation of 2 from both 1 epimers under all experimental conditions (Table I) can be hardly accounted for without assuming the possibility of rapid, extensive isomerization of $4H^+$ and $5H^+$ to $2H^+$, before neutralization.



(3a)

(3b)



(4a)

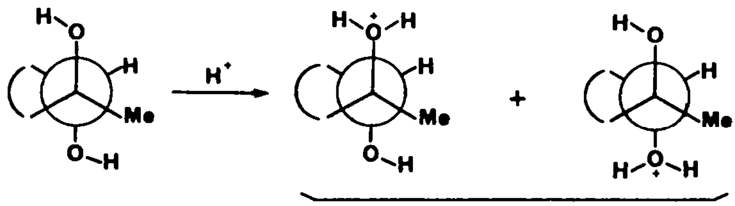
(4b)

The data of Table III appear to substantiate rapid conversion of $5H^+$ into the $2H^+$ structure under all conditions. Concerning the $4H^+ \rightarrow 2H^+$ isomerization, the results reported in Table II seem to indicate an appreciable energy barrier for this process.

The possibility that other protonated rotamers, apart from IH^+ and IIH^+, in particular the axially OH-protonated conformers $IIIH^+$ of trans-1 (eq. 5) where no intramolecular hydrogen bonding is present, be operative in the radiolytic systems is ruled out by the data reported in Table IV.

In $IIIH^+$ structures, in fact, relatively fast anti-periplanar OH participation is expected to take place yielding primarily $3H^+$,[2] which may further rearrange to more stable structures. Accordingly, the results of Table IV indicate that structure $3H^+$ exclusively isomerizes to $2H^+$, at 760 Torr and in the presence of NMe_3. However, in the absence of added bases, formation of $2H^+$ is accompanied by minor, but significant amounts of $4H^+$. The fact that the relative yields of 4 are higher in the D_2 runs with respect to those from the CH_4 experiments, as well as the observation that they increase under conditions favoring isomerization, i.e. in the absence of base and at low pressure (100 Torr), suggest that isomerization of $3H^+$, conceivably formed from $IIIH^+$ by OH participation, would proceed through two essentially independent pathways yielding $2H^+$ and $4H^+$, respectively. Comparatively higher activation barrier is involved in the formation of $4H^+$ with respect to $2H^+$ and, in agreement with previous experimental evidence (Table II), interconversion between $4H^+$ and $2H^+$ is characterized by an appreciable activation energy.

The lack of any detectable amounts of 4 from isomeric 1 under all conditions (Table I) excludes the intermediacy of $3H^+$ and indicates, in agreement with the conclusions of the previous section, that the protonated rotamers IH^+ and IIH^+ are essentially the only structures formed by protonation by gaseous D_3^+ and $C_nH_5^+$ ions of the trans- and cis-1, respectively.



(III) (IIIH$^+$) (5)

Structures IH$^+$ and IIH$^+$, excited by the exothermicity of their formation processes, may undergo the isomerization processes 3 and 4, respectively, in competition with collisional quenching with the batch gas molecules and neutralization by proton transfer to a suitable base. Inspection of Table I, in fact, shows that NMe_3 competes with the substrate for the gaseous acids and, therefore, decreases the overall product yields. Furthermore, NMe_3, having a higher GB (217.3 Kcal mol^{-1})[6] than that of the substrate(s), can also deprotonate the IH$^+$ and IIH$^+$ ions, as well as protonated pinacol in the competitive runs, and therefore define a time window available to them for the rearrangement. This point is particularly evident from the data of Table V, reporting a strong variation of the reactivity ratios of both cis- and trans-1 with respect to pinacol (k/k_P) from the competitive runs with or without the added base. From the same Table, it results that the strong influence of NMe_3 on the k/k_P ratios is not accompanied by appreciable modification of the product distribution, thus indicating that either intermediates 4H$^+$ and 5H$^+$ are not involved in eqs. 3 and 4 or, more likely, the second step of sequences 3a, 3b, and 4a are fast with respect to the collision frequency of the relevant intermediates 4H$^+$ and 5H$^+$ with the added NMe_3 (ca. 2 x 10^8 s^{-1}).[2]

On these grounds, the protonation processes of 1 and pinacol being essentially irreversible, the k/k_P values of Table V, measured in the absence of base, simply reflect the relative rates of formation of the corresponding protonated substrates. With the use of the relative rate of formation of the protonated forms of the competing substrates, as well as of the apparent reactivity ratios k/k_P measured in the presence of NMe_3, and assuming proton transfer efficiency between the protonated intermediates and NMe_3 equal to unit, it is possible to give an estimate of the overall rearrangement rates of IH$^+$ and IIH$^+$ relative to the pinacol rearrangement rate, i.e. $(k_1 + k_2)/k_P$ and $(k'_1 + k_3)/k_P$, respectively. Application of the steady state approximation to the corresponding reaction sequences provides a $(k_1 + k_2)/k_P$ ratio slightly exceeding the value of 11 in both D_2 and CH_4 competition experiments, whereas the $(k'_1 + k_3)/k_P$ value is ca. 4.9 in D_2 and 2.4 in CH_4.

This leads to a $(k_1 + k_2)/(k'_1 + k_3)$ ratio of ca. 2.2 in D_2 and ca. 4.6 in CH_4. If allowance is made for a very similar CH_2 participation rate in eqs. 3a and 4a to a leaving water molecule from a secondary carbon, i.e. $k_1 \simeq k'_1$, it results that H migration in IIH$^+$ (k_3 in eq. 4b) is inherently slower than CH_2 shift in IH$^+$ (k_2 in eq. 3b) under the same experimental conditions. Furthermore, the fact that no detectable amounts of 4 were recovered in both the D_2 and, especially, the CH_4 runs with cis- and trans-1 would suggest that, at least in the CH_4 experiments, the rates of the corresponding channels, i.e. k'_1 and k_1, are much lower than those of the competing paths, i.e. k_3 and k_2. In this view, it results that, in CH_4, $k_2 > k_3 > k_P \geqslant k_1 \simeq k'_1$.

In the D_2 experiments, where a comparatively large excitation energy is maintained in the protonation intermediates, this qualitative order can be slightly modified with the k_1 and k'_1 becoming comparable to k_P. In general, it can be concluded that anti-periplanar participating group effect to a leaving water molecule in pinacol-type rearrangement increases in the gas phase in the order: $CH_3 \leqslant H < CH_2$. In addition, the migratory aptitude of the CH_2 group depends essentially on the nature of the accepting $C\text{-}OH_2^+$ moiety. Thus, in going from a secondary to a tertiary carbon in $C\text{-}OH_2^+$, the participating ability of CH_2 may increase of several orders of magnitude.

CONCLUSIONS

The course of the gas-phase acid-induced pinacol rearrangement of isomeric 1-methyl-1,2-cyclohexanediols 1 was followed by the radiolytic method at various internal energies of the protonated starting substrates, both by varying the nature of the acid catalyst and the pressure of the radiolytic gaseous mixture.

Protonation of cis-1 provides essentially structure IIH^+ completely rearranging to protonated 2-methyl-cyclohexanone $2H^+$. The same product is formed from IH^+ obtained by protonation of trans-1, a process which however is accompanied by secondary parasitic processes. Addition of a powerful base, such as NMe_3, to the radiolytic mixtures realized the experimental conditions suited to exploit the neutralization of the intermediates after a given reaction time and, therefore, allowed us to compare the stereochemical requirements of the pinacol rearrangement in isomeric 1 in the absence of strong solvation interactions. Thereby, it was possible to establish a relative migrating ability order of the CH_2, CH_3, and H groups, as well as of the same group, i.e. CH_2, when migrating to a vicinal secondary or tertiary carbon atom.

The observed trend: $k_2 > k_3 > k_p \geqslant k_1 \simeq k'_1$, shows that anti-periplanar H participation is the major rearrangement process in IIH^+ (k_3), which occurs approximately twice as fast as CH_3 migration in pinacol; it is, however, comparatively slow (over five times slower) with respect to the CH_2 shift to the tertiary $C\text{-}OH_2^+$ moiety, representing the predominant rearrangement pathway in IH^+. In both IH^+ and IIH^+, ring contraction via CH_2 migration to the secondary $C\text{-}OH_2^+$ moiety represent only a very minor, comparatively very slow, isomerization channel. The more pronounced propensity of a tertiary $C\text{-}OH_2^+$ center with respect to a secondary one to undergo vicinal CH_2-group participation implies that a large fraction of positive charge is located on the carbon atom in the relevant transition state. This suggests that the $C\text{-}OH_2^+$ bond is essentially broken, when the interaction between the C atom and the neighbouring participating group becomes operative. In this connection, the observation that the analogous CH_2-group interaction with a secondary $C\text{-}OH_2^+$ center involves a much higher activation barrier spells against any significant anchimeric assistance in this type of neighbouring group participation reactions.

The enhancement of the role of intramolecular factors on the reaction mechanism in the dilute gas state is stressed by a comparison with solution results. In 2M $HClO_4$ at 60 °C, 24% of trans-1 is converted essentially in 2 (80%) and 3 (20%) after 20 h, whereas predominantly 2 (97%) is formed from cis-1 (absolute yield: 30%) together with traces of 3 (3%). Here, the solvent plays a dominating mechanistic role allowing a comparatively very fast chair-to-chair ring inversion in protonated trans-1 to $IIIH^+$, wich undergoes a rapid OH participation to water loss yielding $3H^+$. This, in turn, isomerizes further, but not completely, to $2H^+$. In protonated cis-1, such participation channel is prevented by unfavorable steric requirements, as shown by the very minor yields of 3 (3%). As a consequence, a very effective, in protic polar solvents, 1,2 H-shift[11] takes place in protonated cis-1 to yield directly $2H^+$ in large amounts.

In conclusion, the results of the present work show once more how the interactions with the medium may affect mechanism, and underline the potential of high-pressure gas-phase kinetic approaches as a tool for investigating long-standing solution chemistry problems, including pinacolic rearrangement mechanism, where solvation phenomena determine the evolution of the reaction intermediates involved.

EXPERIMENTAL SECTION

Materials. Deuterium, methane, oxygen, and trimethylamine were high-purity gases from Matheson Co., used without further purification. trans-1-Methyl-1,2-cyclohexanediol (trans-1) and 2-methylcyclohexanone (2) were chemicals from Aldrich and Fluka AG, respectively. A sample of 1-methyl-1,2-epoxycyclohexane(3) was kindly provided by Prof. P.Crotti, University of Pisa (b.p. 140-142°C).[12] cis-1-Methyl-1,2-cyclohexanediol (cis-1) was synthesized from 1-methylcyclohexene (Fluka AG) and osmium tetroxide,[13] the product was purified by three successive crystallizations from ethyl acetate (m.p. 66-67°C). Methyl cyclopentyl ketone (4) was prepared by the method of Witkop and Patric.[14] (b.p.100 95°C; 2,4-dinitrophenylhydrazone m.p. 127°C).[15] 1-Methyl-1-cyclopentanecarboxaldehyde (5) was obtained by the reduction of the corresponding 1-acylaziridine (from 1-methyl-1-cyclopentanecarboxylic acid[16] via acid chloride[17]) with lithium aluminum hydride following the general procedure of Brown and Tsukamoto[18] (b.p.10 31-33°C; semicarbazone m.p. 168°C).[19] All the substrates and products were checked by GLC and NMR spectrometry. The samples used in the radiolytic experiments were assayed by GLC on the same columns subsequently employed for the analysis of the products, and, when required, purified by preparative GLC.

Radiolytic Experiments. The gaseous samples were prepared using a greaseless vacuum line and enclosed in carefully evacuated and outgassed 500-mL Pyrex bulbs, each equipped with a break-seal tip. The irradiations were carried out at 37°C in a 220 Gammacell (Nuclear Canada Ltd.), to a dose of 2 x 10^4 Gy at a rate of 10^4 Gy h^{-1}, as determined by a neopentane dosimeter. The radiolytic products were analyzed by GLC, using HP 5730A cromatograph from Hewlett-Packard, equipped with a FID detector on either a 8 ft x 0.25 in glass column packed with 5% FFAP on Chromosorb G AW-DMCS 80-100 mesh operated at 60-210°C (8°C min^{-1}), or a 50-m long, 0.25 mm. i.d. Carbowax 20M ULTRA performance capillary column, operated at 80-200°C (4°C min^{-1}). The identity of the products was established by comparison of their retention volumes with those of authentic samples and was further confirmed by GLC/MS, using a Hewlett-Packard 5982A quadrupole mass spectrometer. The yields of the products were deduced from the areas of the corresponding elution peaks, using the internal standard calibration method.

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