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Investigation of molecular carbonium ion rearrangements by the molecular mechanics method

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ABSTRACT. The review considers problems of the application of the molecular mechanics method in the prediction of the conversion reactions of hydrocarbon carbonium ions with a localised charge. The methods for the estimation of the heights of the activation barriers to the 1,2-shift of the migrating species, the possibilities of the method for the prediction of the transannular cyclisation of carbonium ions, and certain examples of the influence of the acidity of the medium are discussed.

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I. Introduction

The foundations of the method of molecular mechanics (MM) [1] or the method of atom–atom potentials[2,3] were laid in Hill's study in 1946.[4] At the present time, this method has been widely used in a wide variety of chemical fields. This review deals with only a narrow range of applications of the method, namely the possibilities of the MM method in the study of complex multistage carbonium ion rearrangements involving carbocyclic cations (excluding π-delocalised ions, ions with a heteroatom in the α-position relative to the carbonium ion centre, and ions with the charge on a heteroatom).

The MM method deals with an isolated molecule (unless otherwise stipulated) and its results can be compared directly only with certain gas-phase data. On the other hand, carbonium ion reactions are investigated in media of different acidity, frequently under the so called long life conditions.[5] In general, the influence of the medium, for example, on the heat of formation, is enormous. Thus the heats of formation of the t-butyl cation in the gas phase and in the SO_2FCl system differ by 239 kcal mol^{-1}.[6] Direct allowance for the interaction of carbonium ions with the medium is very difficult. However, it has been shown by Arnett and Pienta,[6] who compared the enthalpies of formation in the gas phase and in SO_2FCl, that there is a satisfactory correlation (with a slope of 0.973 and $r = 0.986$) between the values of $\Delta H_f^\circ(R^+$, gas) and $\Delta H_f^\circ(R^+, SO_2FCl)$. Thus the absence of specific solvation of the cations by the medium was demonstrated in this instance, so that we can use directly the results of calculations by the MM and quantum-chemical methods.

II. Calculation of the stabilities and geometries of carbonium ions

In the early studies,[7] the MM method was used to predict the preferred carbonium ion reaction pathways, but, in order to estimate the stabilities of different cations, the values of ΔH_f° were calculated in these investigations for neutral hydrocarbons on the basis of the idea of the parallel nature of the stability series of carbonium ions and the corresponding neutral hydrocarbons. The MM method was first used directly for calculations involving carbonium ions in the study of Gleicher and Schleyer.[8] They found the parameters of the force field by the MM method and successfully compared the solvolysis rate constants and the differences between the steric energies of the carbonium ions and the corresponding hydrocarbons.

The next important step in the establishment of the MM method in the chemistry of carbonium ions was the introduction of an additive scheme for the calculation of gas-phase heats of formation,[9] which made it possible to compare quantitatively the stabilities of secondary and tertiary ions. As a result, it became possible to carry out calculations for the energetics of carbonium ion reactions, i.e. to establish whether the given process proceeds "uphill" or leads to more stable final ions.

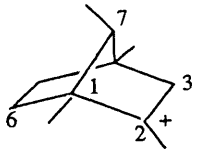
A study[10] in which the conformational analysis was carried out for tertiary (C_6, C_7, and C_8) cycloalkyl carbonium ions by the NMR method is noteworthy. The authors observed the unexpected preference (to the extent of 0.5 kcal mol^{-1}) for the twist conformation of the methylcyclohexyl cation compared with the chair conformation. This investigation was followed by a study[11] on the conformational analysis of the above tertiary carbonium ions by the MM method. According to the authors' calculations, the twist conformation of the methylcyclohexyl cation is less stable than the chair conformation by only 0.14 kcal mol^{-1} and, if account is taken of the known fact[12] that the MM method overestimates the stability of the chair form by ~0.3 kcal mol^{-1}, then the result obtained agrees well with experimental data.

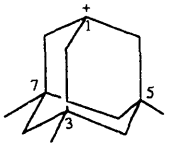
The study of Olah, et al.[13] on 1,4-bicyclo[2.2.2]octyl dication—a new pseudoaromatic system—is of interest. The causes of the surprising stability of this cation were discovered with the aid of the MM and MINDO/3 methods.

After the publication of calculations in which the force field and Allinger's MM2 method[14] were resorted to, it was natural to expect the extension of this version of the MM method also to carbonium ions, which was in fact achieved by Muller and co-workers,[15–18]

who found the necessary parameters of the MM method from kinetic data for the solvolysis of secondary[15] and tertiary[16,17] alcohols and obtained the enthalpy parameters from the experimental gas-phase heats of formation.[18] It is noteworthy that the parametrisation of the MM method for carbonium ions in the MMX program is different from that proposed by Muller.

Whilst recognising the advantages of the MM method (compared with quantum-chemical and semi-empirical methods) such as speed and reliability of the results for carbonium ions which fall within the sphere of the existing parametrisation, its disadvantages should also be noted. Firstly, at the present time the MM method cannot take into account explicitly the stabilisation of certain carbonium ions owing to the σ-delocalisation of the positive charge. The underestimation of the stability of ions with σ-delocalisation is therefore to be expected. For example, in the case of 2-norbornyl cations the underestimate is by 5 kcal mol^{-1},[9] 6 kcal mol^{-1},[19] or 7.6 kcal mol^{-1}.[20] However, it is difficult to say *a priori* for which cations such a correction should be applied, except for the thoroughly investigated 2-norbornyl cations. (We may note that there is no reliable parametrisation of the MM method for π-delocalised carbonium ions.) Secondly, X-ray diffraction studies on the salts of the 1,2,4,7-*anti*-tetramethyl-2-norbornyl[21] and 3,5,7-trimethyl-1-adamantyl[22] cations revealed an appreciable deviation of the bond lengths from the values used as a basis for the parametrisation of the MM method for carbonium ions. Thus the C(1)–C(2), C(2)–C(3), C(2)–CH_3, and C(1)–C(6) bond lengths in the norbornyl ion are 1.48, 1.48, 1.48, and 1.54 Å respectively according to the calculation by the MM2 method using Muller's parameters, while the experimental bond lengths are 1.44(2), 1.50(1), 1.47(2), and 1.74(2) Å.





In the adamantyl ion, the calculated C^+–C and (C^+)C–C bond lengths are 1.48 and 1.54 Å respectively, while the experimental values are 1.42–1.47 and 1.61–1.62 Å, i.e. the real interaction of the unoccupied orbital of the carbonium ion centre with the nearest valence bonds has not so far been incorporated with adequate accuracy in the MM method. However, it is only fair to note that the MM method reproduces the enthalpies of formation fairly reliably.[18]

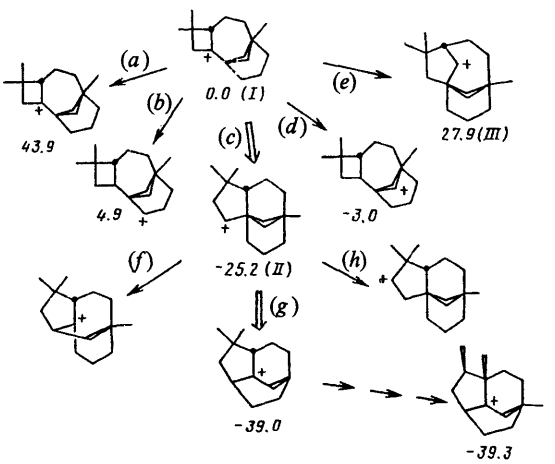
III. Estimation of the heights of the activation barriers to 1,2-shifts

One of the important problems of the chemistry of carbonium ions is that of the prediction of the heights of the activation barriers to intramolecular rearrangements. The direct procedure for the solution of this problem involves non-empirical quantum-chemical calculations (the semi-empirical method yields heats of formation for the transition states in 1,2-shifts which differ very greatly and the best results for hydrocarbon carbonium ions can be obtained with the aid of the MINDO/3 method[23]). In view of the laborious nature of these methods, the search for other approaches has been stimulated. The principal factors determining the activation barriers to the rearrangement of carbonium ions are the size of the positive charge on the carbon atom to which the migrating species moves and the difference between the thermodynamic stabilities of the rearranging and final ions.[5] If carbonium ions with π-delocalisation are disregarded, then the thermodynamic factor becomes one of the decisive ones. For example, the most probable pathway leading to the conversion of 2,3-tetramethylenebicyclo[2.2.1]heptane into adamantane has been refined[9] on the basis of the heats of formation of the carbonium ions calculated by the MM method.

However, the height of the activation barrier to the 1,2-shift of the migrating species may be influenced by specific structural factors responsible for the increased strain in the transition state. In particular, this may be the unfavourable orientation of the unoccupied orbital of the carbonium ion centre relative to the orbital of the carbon–migrating species bond (the orbital factor characterised by the torsional angle Φ between the specified orbitals). Indeed, it has been shown in relation to the solvolysis of *exo*-twistbrendan-2-ol[24] that both factors—the thermodynamic and orbital factors—are important for the prediction of the direction of the 1,2-shift. The attempt to incorporate both factors simultaneously at a qualitative level was undertaken[25] in the analysis of the mechanism of the acid-catalysed reactions of 2- and 4-homoprotoadamantanes. In this case, the pathways leading to the most stable ions and having at the same time the most favourable interorbital angles for the corresponding 1,2-shifts were recognised as the most probable.

In a later study of the rearrangement of 1-substituted caryolanes in superacids,[26] the authors encountered the situation where the pathway to the most stable ion (II) is associated with an extremely unfavourable[7] interorbital angle (Φ = 69°, Scheme 1). The heats of formation ($\Delta\Delta H_f^\circ$, kcal mol^{-1}) of the corresponding ions relative to the initial carbonium ion are indicated in Schemes 1–3 under the structural formulae.

Scheme 1



Pathway	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
Φ, deg	54	59	69	55	2	50	4	30
$\Delta G^{\neq}$, kcal mol^{-1}	44	24	8	17	28	20	4	12

On the other hand, the pathway which is very favourable as regards the orbital factor (Φ = 2°) leads to the highly strained cation (III). Since both these factors are important for the prediction of the rearrangements, the authors put forward the empirical hypothesis that the internal barrier (Λ) to the 1,2-shift in a degenerate

rearrangement depends on the interorbital angle in the following manner:

$$\Lambda = \Lambda_0 / \cos\Phi \,. \qquad (1)$$

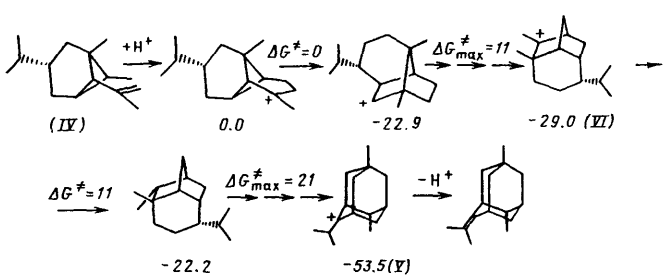
The thermodynamic factor for non-degenerate processes was taken into account with the aid of the Marcus equation, which assumes the following form for isentropic reactions:

$$\Delta G^{\neq} = \Lambda(1 + \Delta\Delta H_f/4\Lambda)^2 , \qquad (2)$$

where $\Delta\Delta H_f$ is the difference between the values of ΔH_f° for the product ion and the rearranging ion. The free energies of activation ($\Delta G^{\neq}$, kcal mol^{-1}), estimated with the aid of Eqns. (1) and (2), are presented in Schemes 1–3. They permit an unambiguous choice between the modes of rearrangement of the initial ion (I). Thus the possibility of predicting the reaction pathway, leading to the conversion of the ion (I) into the final cation with a relative heat of formation of −39.3 kcal mol^{-1} and a length equivalent to seven different 1,2-shifts, was demonstrated in the above study.

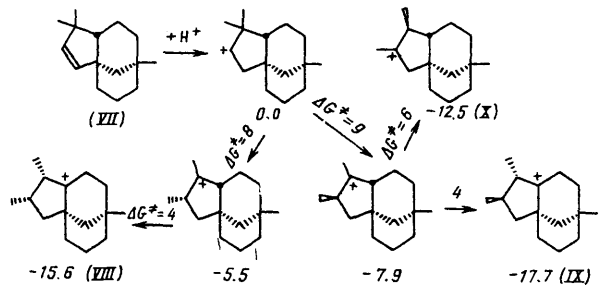
The method for the estimation of the activation barriers to 1,2-shifts examined above has been used[27] to predict the most probable reaction pathways of the sesquiterpene α-copaene (IV). The authors[27] obtained for the first time tricyclic compounds of the adamantane type from α-copaene in superacid media. About 100 structures of different carbonium ions were examined for the purpose of this prediction. Scheme 2 illustrates the fragments of the most probable pathway, consisting of 19 consecutive 1,2-shifts, leading to the rearrangement of the α-copayl ion to the adamantyl ion (V) via the intermediate isosativyl cation (VI).

Scheme 2



The above examples of the reactions of ions generated from 1-substituted caryolanes and α-copaene have in common the feature that the initial carbonium ion is converted into a much more stable ion. A different situation was observed[28] when a "map" of the possible pathways leading to the rearrangement of the cation generated from clovene (VII) was drawn on the basis of Eqns. (1) and (2). According to the prediction, the acid solution should contain in this case a mixture of the two most stable ions (VIII) and (IX) (Scheme 3). In conformity with these data, signals due to two tertiary ions were noted in the ^{13}C NMR spectrum of the reaction mixture, while olefins corresponding to the cations (VIII)–(X) were found among the products of the neutralisation of the mixture.

Scheme 3



Naturally, the simplified method for the estimation of activation barriers by Eqn. (1) has disadvantages (apart from the empirical form of the dependence on the angle Φ). Thus it has been noted in a recent study[29] that, according to the data of Bushmelev et al.,[30] the interorbital angle is not an unambiguous characteristic of the strain in the transition state due to the need for the sp^3-hybrid node of the $C(R_m)-C^+$ fragment to readjust rotationally relative to the unoccupied orbital of the carbonium ion centre, which should depend on the rigidity of the molecule. Little "tricks" such as the search for conformers with a more favourable interorbital angle Φ and the employment of the principle of microscopic reversibility cannot eliminate this disadvantage. Furthermore, the internal barriers Λ_0 to the 1,2-shifts were estimated[26] from Sorensen's kinetic data[31,32] (which include approximate and estimated quantities) for the rearrangements of δ-delocalised 2-norbornyl ions, which are specific models. The neglect of specificity leads to unduly high calculated data in the case of monocyclic and open-chain ions. It is necessary to note the very limited amount of experimental kinetic data for the rearrangements of non-arenium ions. For example, the Wagner–Meerwein rearrangement of the ions under consideration has been scarcely investigated quantitatively. This situation hinders the search for approaches to the description of the rates of the 1,2-shifts.

An attempt has been made[29] to model the strain in the transition and ground states of the 1,2-shift of the migrating species by the strains in the neutral hydrocarbons of the cyclopropane and alkane types.[29] However, it was shown that the difference between the steric energies of the components of the cyclopropane–alkane pair reflects with insufficient adequacy the changes in the quantity $\Delta G^{\neq}$ for the 1,2-shift as the molecular skeleton of the ion is altered. Other workers,[33] who investigated the reactions of 6-tricyclo[3.3.0.0^{2,7}]octyl ion, arrived at a similar conclusion. Nevertheless this approach constitutes the next step compared with the approach described by Eqns. (1) and (2) where the strain in the transition state is estimated solely from data for the ground state of the rearranging cation (i.e. an attempt is made to estimate the height of a mountain whilst standing at its base).

Further development of quantitative estimations of the activation barriers to the 1,2-shift of the migrating species in carbonium ions with a localised charge was stimulated by the successfully developing field of the chemistry of arenium ions. Thus the most general approach to the quantitative description of the rates of the 1,2-shifts of the hydrogen atom and the methyl group has been proposed[34] in relation to the degenerate rearrangement of a large series of benzenoid and non-benzenoid arenium ions. The following dependence of the energy barrier to degenerate 1,2-shifts of the

migrating species on the Hückel charge $q_{\pi x}$ on the atom to which the migrating species shifts and on the basicity constant K_i of this centre in the aromatic hydrocarbon formed after the abstraction of the migrating species was then discovered:

$$\Delta G_{\mathrm{H}}^{\neq} = 14.1 - 7.5\ q_{\pi_x} + 0.37\ \lg K_i\ (\text{kcal mol}^{-1}); \quad (3)$$

$$\Delta G_{\mathrm{CH_3}}^{\neq} = 26.5 - 23.4\ q_{\pi_x} + 0.32\ \lg K_i\ (\text{kcal mol}^{-1}). \quad (4)$$

The basicity constants can be calculated by the MM method with the aid of the relations

$$\lg K_i = -108.9 + 0.528\ PA_i\ (\text{kcal mol}^{-1}),\ \text{(Ref.34.)} \quad (5)$$

$$PA = 367.2 + \Delta H_f^0(\text{olefin}) = \Delta H_f^0(\mathrm{R}^+)\ (\text{kcal mol}^{-1}),\ \text{(Ref.35)} \quad (6)$$

where PA is the proton affinity.

Adopting $q_{\pi x} = 1$ for aliphatic and alicyclic carbonium ions, the authors[29] obtained with the aid of Eqns. (3) and (4) the free energies $\Delta G^{\neq}$, which on the whole agree quite well with experimental data. In the case of σ-delocalised carbonium ions, it was suggested that the chemical shifts (δC) of the corresponding carbon atom in the ^{13}C NMR spectrum be used to estimate the charge q^+: $q^+ = (\delta C - 115)/205$ for secondary ions and $q^+ = (\delta C - 123)/212$ for tertiary ions.

Having supplemented the basic set of the ions [for the correlations (3) and (4)] by aliphatic ions, the authors[29] obtained the following better founded relations for degenerate 1,2-shifts:

$$\Delta G_{\mathrm{H}}^{\neq} = 15.33 - 10.79\ q_{\pi_x} + 0.232\ \lg K_i\ (\text{kcal mol}^{-1}), \quad (7)$$

$r = 0.986,\ s = 0.90,\ n = 8;$

$$\Delta G_{\mathrm{CH_3}}^{\neq} = 25.74 - 21.48\ q_{\pi_x} + 0.303\ \lg K_i\ (\text{kcal mol}^{-1}), \quad (8)$$

$r = 0.995,\ s = 0.79,\ n = 7.$

Comparison of the available experimental activation energies $\Delta G^{\neq}$ and the values calculated by Eqns. (7) and (8) demonstrated that the relations are quite effective:

$$\Delta G_{\mathrm{H}}^{\neq}(\text{exp}) = 1.03\ \Delta G_{\mathrm{H}}^{\neq}(\text{calc.}) + 0.4,$$

$r = 0.943,\ s = 1.6,\ n = 23;$

$$\Delta G_{\mathrm{CH_3}}^{\neq}(\text{exp}) = 1.11\ \Delta G_{\mathrm{CH_3}}^{\neq}(\text{calc.}) - 1.2,$$

$r = 0.971,\ s = 1.7,\ n = 14.$

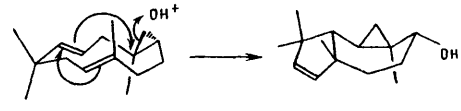
We emphasise the following advantages of this approach: (1) the use of proton affinity, which led to the indirect allowance for the orientation factor; (2) allowance for the "olefin" strain[33] arising from the Dewar representation of the transition state of the 1,2-shift in the form of the π-complex, which proved to be important for the estimation of the stability of the transition state. The "olefin" strain is also involved in the proton affinity.

It is necessary to say a few words about the disadvantages characteristic of the method under discussion. The method is unsuitable for the calculation of the free energies $\Delta G^{\neq}$ for the Wagner–Meerwein rearrangement, because in such cases it is impossible to abstract the migrating species from the skeleton in order to calculate the basicity of the corresponding olefin. Furthermore, in sterically hindered carbonium ions no account is taken of the repulsion of the migrating species (particularly the methyl group) from any other group which arises solely in the transition state of the 1,2-shift of the migrating species. Finally, this approach does not distinguish between the *exo*- and *endo*-shifts of the migrating species in 2-norbornyl cations, the difference between the $\Delta G_{\mathrm{CH_3}}^{\neq}$ for which reaches 10.6 kcal mol^{-1}.[36] We may note that semi-empirical quantum-chemical methods distinguish only imperfectly between the 2,3-*exo*- and 2,3-*endo*-shifts in the 2-norbornyl ion.[37]

IV. Transannular cyclisation of carbonium ions

The transannular cyclisation in the carbonium ion reactions of bifunctional and polyfunctional compounds, particularly of the terpene series, is fairly common. It is responsible for the possibility of the mutual approach in space of the carbonium ion centre and the double bond to a distance sufficient for effective interaction. Modelling of this process by the MM method is so far impossible owing to the lack of the corresponding parametrisation. Nevertheless, the MM method can already provide significant assistance in this case also.

The necessary mutual approach of the potential carbonium ion centre and the double bond is possible even in the ground state (or in the less stable conformer) of the neutral precursor. In this case, the appearance of the cationic centre may be accompanied by cyclisation. Such a phenomenon has been observed for the humulene 6,7-epoxide.[38] When the humulene epoxide is treated with HSO_3F, the concerted opening of the epoxide ring and transannular cyclisation are observed.

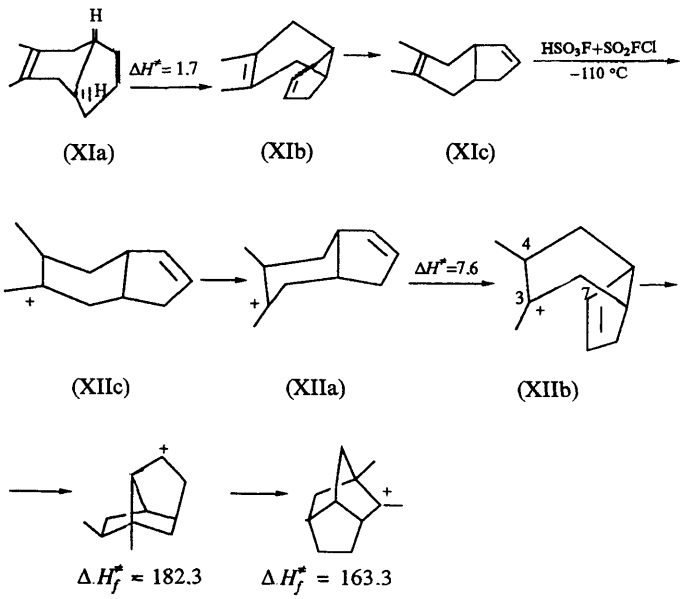


The initial protonation or opening of the epoxide ring provides an additional degree of freedom in the cation formed and hence may promote the mutual approach to the centres required for transannular cyclisation. The following method for the application of the MM method arises from these considerations: conformational analysis of the neutral precursor and of the cation formed initially and allowance for the heat of the possible cyclisation reaction.

We shall consider several examples. In a study[39] of the mechanism of the superacid transannular cyclisation of the bicyclic 1,5-diene (XI), an explanation was found for the experimental finding that the diene (XI) cyclises (Scheme 4), while the allyl ion (XIV) is formed in α-myrolene (XIII) (Scheme 5) under identical

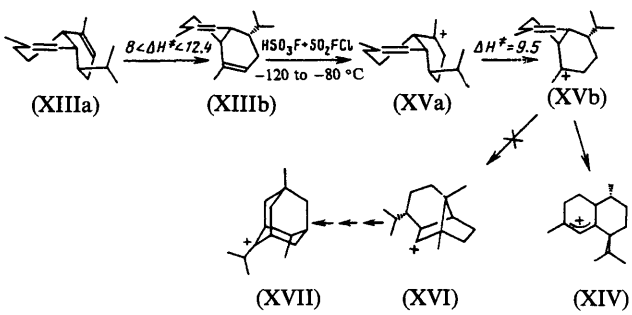
conditions. The fractions of the principal conformers (N, %) at 25 °C are indicated in Schemes 4 and 5.

Scheme 4



Conformer	(XIa)	(XIb)	(XIc)	(XIIa)	(XIIb)	(XIIc)
ΔH_f^0, kcal mol^{-1}	9.2	10.8	9.5	171.8	172.0	172.3
N, %	58.4	4.5	35.2	47.0	32.2	20.3

Scheme 5



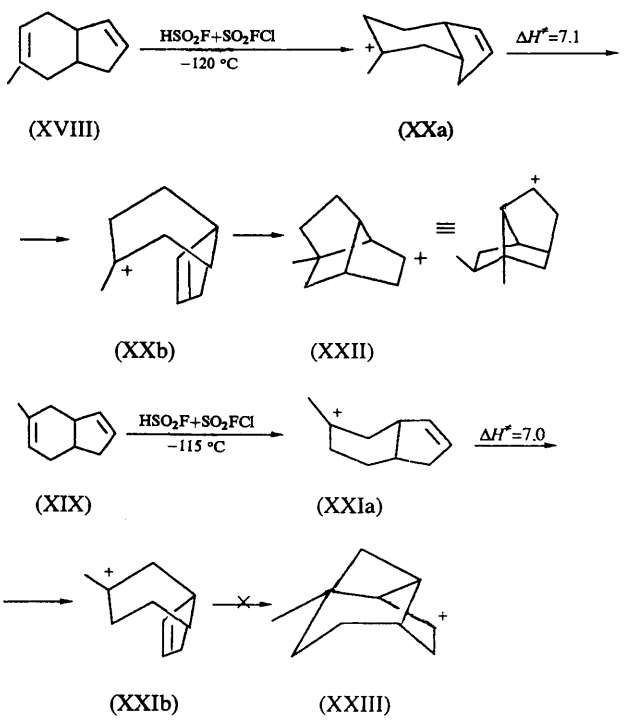
Conformer	(XIIIa)	(XIIIb)	(XVa)	(XVb)	(XVI)	(XVII)
ΔH_f^0, kcal mol^{-1}	−22.2	−20.0	145.7	150.1	150.7 (Ref.27)	102.5 (Ref.27)
N, %	82.4	18.6	99.9	0.06	–	–

Conformational analysis showed that the main conformer (XIa) of the diene (XI) can be very readily converted into the conformer (XIb), which has a geometry favourable for cyclisation. For the diene (XIII), the analogous transition requires an appreciable consumption of energy. Furthermore, one of the main conformers (XIIb), formed initially from the diene (XI), has a disposition of the interacting centres convenient for cyclisation, in contrast to the main conformer (XVa) of the initial cation formed from α-muurolene (XIII). Finally, the competing pathway operates for the ion (XV), involving conversion via the intermediate tertiary cations into the allyl ion (XIV), which constitutes a "potential well".[40]

It follows from the examination of the thermodynamics of the cyclisation of the ion (XIIb) that the quantity ΔH for this process should exceed 10.3 kcal mol^{-1}. At the same time, the cyclisation reaction in the ion (XVb) has a virtually zero heat and apparently not an unduly high activation barrier. This permits the hope that, on raising the reaction temperature, which increases the fraction of the conformer (XIIIb) or (XVb), there is a possibility of the appearance in the reaction mixture of the products of the transannular cyclisation α-muurolene. Indeed, knowing that temperature influences the composition of the ions formed on protonation of α-muurolene, Polovinka et al.[27] increased the temperature of the system (XII) + HSO_3F + SO_2FCl to −30 to −20 ° C and recorded the appearance of the tricyclic adamantyl cation (XVII).

In order to confirm the mechanism of the transannular cyclisation of the diene (XI) proposed by Tatarova et al.,[39] the behaviour of the 3- and 4- monomethyl derivatives of *cis*-bicyclo[4.3.0]nona-3,7-diene (XVIII) and (XIX) was investigated.[41] The conformational compositions of the dienes (XVIII) and (XIX) are almost indistinguishable, while there are differences (Scheme 6), albeit not very pronounced, between the ions (XX) and (XXI) formed from them initially.

Scheme 6



Conformer	(XXa)	(XXb)	(XXIa)	(XXIb)	(XXII)	(XXIII)
ΔH_f^0, kcal mol^{-1}	180.5	180.6	180.5	181.4	187.8	199.2
N, %	41.0	34.6	61.6	12.0	–	–

It is noteworthy that the distances between the interaction centres in the cyclisation reaction ($r_{3,7}$ and $r_{4,7}$) are not apparently the main factors determining the course of the reaction. In this case, the

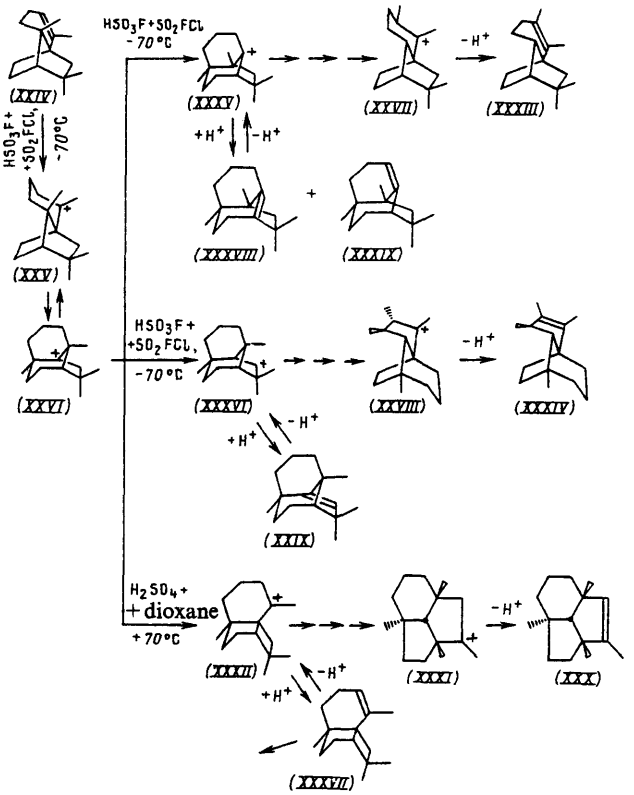
decisive factor is evidently the thermodynamic factor: the heat ΔH of the transannular cyclisation of the cation (XX) is 7.2 kcal mol^{-1}, whereas ΔH for the cyclisation of the ion (XXI) reaches 17.8 kcal mol^{-1}. An attempt may be made to estimate roughly the activation barriers to the cyclisation of the cations (XX) and (XXI) in the following way. We consider the reverse process in the carbonium ions (XXII) and (XXIII)—the dissociation of the corresponding bonds. We assume for simplicity that in the general case the degenernate bond dissociation processes and the Wagner–Meerwein rearrangement begin and proceed similarly, reaching approximately the same transition state as regards energetics. One can then use Eqn. (2) and, having assumed that $\Lambda \simeq 5$ kcal mol^{-1},[26] the values of ΔG^{+} can be obtained for ring opening in the ions (XXII) and (XXIII)—2.0 and 0.1 kcal mol^{-1} respectively. Hence the activation barriers for the reverse transannular cyclisation in the ions (XX) and (XXI) are 9.2 and 17.9 kcal mol^{-1}.

V. The influence of the medium on the rearrangements

This problem is associated with the general problem of the possibility of predicting the preferred pathway in multistep carbonium ion reactions in the usual acids on the basis of the experimentally observed rearrangements of the carbonium ions generated in superacids from the same precursor. Sorensen[31] published previously data on the carbonium ion rearrangements of monoterpenes in various acid media. He found that, firstly, in superacids and under the conditions of acid catalysis, the sequences in which the barriers ΔG^{+} to the "ion into ion" rearrangements increase are the same and "secondly" that the stability of olefins varies in parallel with the stability of the corresponding carbonium ions. Therefore on the basis of direct observations of the rearrangements of carbonium ions in superacids one can predict the reaction pathway also under the conditions of acid catalysis. Several exceptions to this rule were found subsequently. Thus the mode of reaction in different media can be influenced by the site of the cationic centre[42] and by the nature of the internal nucleophile[43] and also by qualitative changes in the relative rates of competing intramolecular 1,2-shifts[44] and the rates of intermolecular processes.[45]

In a study of the conversion of the sesquiterpene neoclovene (XXIV) in media of different acidity, yet another interesting exception to Sorensen's observation was found.[46] When neoclovene was dissolved in the HSO_3F-SO_2FCl system at −120 °C, the authors observed the appearance of an ion, which, as shown by the application of special methods, involves partial σ-delocalisation of the charge and can be represented by two limiting resonance forms (XXV) and (XXVI) (Scheme 7) as required by the MM method in this instance. When an acid solution of the olefin (XXIV) is heated to −70 °C, the above ion is fully converted into a mixture of the new cations (XXVII) and (XXVIII). As can be seen from Scheme 7, the energy gain expected in the intramolecular conversion of the ion (XXV) into the cations (XXVII) and (XXVIII) in a superacid is 10.7 and 13.0 kcal mol^{-1} respectively.

Scheme 7



Ion/olefin	(XXIV)	(XXV)	(XXVI)	(XXVII)
$\Delta\Delta H_f^0/\Delta H_f^0$, kcal mol^{-1}	−15.6	0.0	3.9	−10.7
s, kcal mol^{-1}	39.0	43.2	52.0	32.9
Ion/olefin	(XXVIII)	(XXIX)	(XXX)	(XXXI)
$\Delta\Delta H_f^0/\Delta H_f^0$, kcal mol^{-1}	−13.0	8.4	−19.7	−2.4
s, kcal mol^{-1}	30.6	63.1	34.9	40.8
Ion/olefin	(XXXII)	(XXXIII)	(XXXIV)	(XXXV)
$\Delta\Delta H_f^0/\Delta H_f^0$, kcal mol^{-1}	6.6	−24.9	−29.8	−11.6
s, kcal mol^{-1}	49.7	30.7	25.8	36.1
Ion/olefin	(XXXVI)	(XXXVII)	(XXXVIII)	(XXXIX)
$\Delta\Delta H_f^0/\Delta H_f^0$, kcal mol^{-1}	2.7	−8.2	8.7	11.4
s, kcal mol^{-1}	38.6	46.6	65.2	45.9

It was shown in the same study[46] that neoclovene (XXIV) is almost fully converted into the olefin (XXX) in a H_2SO_4–dioxane mixture at 70 °C. It is seen from Scheme 7 that the olefin (XXX) is more stable than the initial neoclovene by 4.1 kcal mol^{-1}. The barrier to the conversion of the ion (XXV) into (XXXI) is 18.1 kcal mol^{-1}, the latter being more stable than the initial ion (XXV) to the extent of 2.4-kcal mol^{-1}. [However, experiment showed the opposite situation to be true: at −80 °C in a superacid, the ion (XXXI) is fully converted into the initial ion (XXV)]. It is noteworthy that the pathway leading to the formation of the olefin

(XXX) proceeds via the carbonium ion (XXXII) containing a four-membered ring. This fact conflicts with the postulate[47] that such iosmers be excluded from consideration since they would be very strained.

Thus the pathways in the molecular rearrangements of neoclovene in media of different acidity are completely different. The pathway (XXV)→(XXXI) does not occur in a superacid, because it would lead to a less stable ion. However, it is not clear why the reactions observed in a superacid, which could lead both to more stable ions and more stable olefins (XXXIII) and (XXXIV) than the ion (XXXI) and the corresponding olefin (XXX) actually obtained, do not occur in a usual acid.

If the rearrangements occurred intramolecularly in the usual acids, one would have to expect the same mode of rearrangement in both types of media in conformity with the relative stabilities of the intermediate and final ions. Consequently the process in a usual acid proceeds via the intermolecular protonation–deprotonation pathway. This hypothesis is confirmed by the fact that the reformation of the ion (XXV) from the olefin (XXX), obtained in usual acid, is observed in a superacid (i.e. via an intramolecular pathway). If one considers the "fork" in the rearrangements in different media [Scheme 7, the ion (XXVI)] and attention is turned to the stability of the olefins (XXIX) and (XXXVII)–(XXXIX), whose appearance is possible on deprotonation of the cations (XXXII), (XXXV), and (XXXVI), then it is readily seen that the "normal acid" olefin (XXXVII) is significantly more stable (to the extent of 1.6–19.6 kcal mol^{-1}) than the "superacid", anti-Bredt olefins (XXIX), (XXXVIII), and (XXXIX). Hence one may postulate that the mode of the rearrangements of neoclovene in a usual acid is determined by the relative stabilities of the intermediate olefins. It also follows from Scheme 7 that the principle of the parallel variation of the relative stabilities of carbonium ions and the corresponding olefins, put forward by Sorensen, breaks down in the given instance and the extent to which the variation is antiparallel may exceed 20 kcal mol^{-1}.

In the general case, the rearrangements of carbonium ions in a usual acid are regulated by the competition between several possible intramolecular 1,2-shifts and the protonation–deprotonation reaction. The methods for the estimation of the activation barriers to the intramolecular 1,2-shifts were considered above (see Section III). We shall now examine the protonation–deprotonation equilibrium under the conditions of acid catalysis where the enthalpies of formation of ions and olefins are apparently similar. In this situation, the gas-phase heats of formation calculated by the MM method are unsuitable and we attempted to resort to the concept of the intrinsic strain of the molecule (S) [1] (Scheme 7). It is seen from the values of S that the deprotonation reactions of the carbonium ions (XXVII), (XXVIII), (XXXI), and (XXXII), leading to Bredt olefins, are accompanied by the partial removal of the intrinsic strain (to the extent of 2–6 kcal mol^{-1}). On the other hand, the deprotonation of the ions (XXXV) and (XXXVI) with formation of anti-Bredt olefins increases the intrinsic strain by 10–30 kcal mol^{-1}.

Thus one may expect that the deprotonation processes in a usual acid, accompanied by an appreciable growth of the intrinsic strain in the molecule, would be difficult.

Thus the MM method makes it possible to calculate fairly reliably the stability of carbonium ions with a localised change and to estimate the heights of the activation barriers to the 1,2-shifts of the migrating species. The fruitfulness of the use of the MM method has been demonstrated in predictions of the most probable pathways in the acid-catalysed reactions of terpenoids in media of different acidity.

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