Translated from *Uspekhi Khimii*, **61** 523–547 (1992) U.D.C. 54-128.4:547.1:543.53

Vinyl cations

V D Nefedov, E N Sinotova, V P Lebedev
St Petersburg State University

ABSTRACT. Methods of obtaining vinyl cations, which are derivatives of the ethenyl cation $H_2C=C^+H$ and have the high reactivity of intermediate species, are examined. Particular attention is given to the nuclear chemical method of obtaining free vinyl cations. Data on the reaction of vinyl cations (including free cations) with different classes of compounds containing *n*, π, and σ reaction sites have been correlated.

The bibliography includes 138 references.

Contents

I. Introduction 283
II. Methods of generating vinyl cations 283
III. Reaction of vinyl cations with nucleophilic reagents 287
IV. Reactions of free vinyl cations 291
V. Conclusion 294

I. Introduction

Vinyl cations (VCs) are carbocations that form a class of reactive intermediate species whose parent is the ethenyl (or vinyl) cation $H_2C=C^+H$.[1–7]

Vinyl cations are formed in electrophilic addition reactions to alkynes and allenes, and also by heterolysis of the (C=)C–X bond of vinyl compounds.

The electrophilic addition of water to acetylenes and allenes has been known since the 1870's.[5] At first, however, VCs were not regarded as independent species since it was thought that the presence in them of a charge in combination with an unsaturated bond on the central carbon atom made such intermediates extremely unstable. The idea that the reaction occurs via the formation of VCs was apparently first put forward to explain the formation of an alkyl acetate in the hydration of alkoxyacetylenes in an acidic medium.[5a]

The idea that VCs were unstable was based on the extremely low rates of solvolysis of vinyl halides even under conditions that permit the formation of primary alkyl cations. Nevertheless, the first direct evidence for the existence of VCs was actually obtained in the solvolysis of 1-arylvinyl bromides.[8]

The discovery and practical research application of vinyl compounds containing groups that could readily be eliminated—anions of fluoroalkylsulphonic acid, such as triflate (trifluoromethanesulphonate) anion and nonaflate (nonafluorobutanesulphonate) anion—constituted a stage of fundamental importance in the chemistry of VCs. Since the rate of solvolysis of these esters is higher than that of vinyl halides by a factor of 10^6-10^8, it was thus possible to obtain simple alkylvinyl cations and cyclic VCs with small strained rings.[7,9,10]

Recently, after preparing vinyl compounds containing a ferrocene group on the double bond, which has a strong stabilising effect, it was possible to observe directly the formation of VCs by means of ^1H NMR spectroscopy.[11–13]

A number of reviews attesting to the considerable interest in the problem of VCs have appeared.[1–7,14] In these reviews the methods of generating VCs, their stability, rearrangements, and the mechanisms of reactions involving VCs are widely discussed. On the other hand, these studies, which were excellent at the time, no longer reflect the current state of knowledge concerning the chemistry of VCs.

An attempt has been made in the present review to correlate the existing data, including the most recent information about the methods of obtaining VCs (principally photochemical and nuclear chemical methods) and the reactions of VCs, including those occurring in a free state.

II. Methods of generating vinyl cations

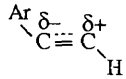
1. Electrophilic addition to alkynes and allenes

a) Alkynes

A study of the mechanism of electrophilic addition to alkynes initiated by Lewis acids showed that initially an ion pair consisting of the anion of the acid and a VC is formed, having a linear or almost linear structure. At the same time the most stable of the possible cations is predominantly formed.[1–7,15–21] The possibility of internal migration in the ion pair and steric separation of the ions predetermine the diversity of products of the alkylation,[16,17] halogenation,[22–24] hydrohalogenation,[1–7] and acylation[25–34] of alkynes.

It was established from a detailed study of the mechanism of hydration of alkynes that the overall rate of this reaction is determined by the rate of the stages involving protonation of the triple bond. This is suggested, in particular, by the substantial kinetic isotope effect that occurs in the hydrolysis of different acetylenic compounds: $k_{H_2O}/k_{D_2O} = 1.7-4.0$.[1–7,35,36]

The results of recent studies of the hydration of substituted alkynes point to the possibility of a considerable acceleration of the addition of a proton to aromatic alkyne molecules under photoexcitation conditions.[37] It is assumed in this case that in its lowest singlet state S_1^* an alkyne molecule acquires a bent structure in which the carbon atoms of the triple bond have an intermediate sp^2-sp character. The bond becomes partially polarised, with the negative charge localised on the β-carbon atom:

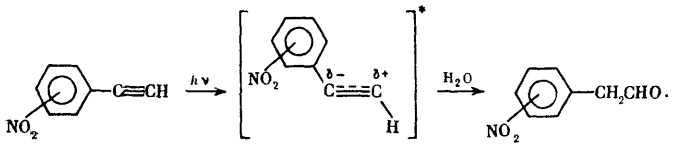


Consequently it is the β-carbon atom that undergoes attack by the proton to form a VC. The activation energy of addition of the proton in this case is much lower than the energy of activation for protonation of alkynes in the ground state. The resulting electronically excited cation rapidly reacts with a water molecule, giving a ketone as the product of photohydration:

$$ArC\equiv CH \xrightarrow{h\nu} [ArC\equiv CH]^{+} \underset{k_{-H}}{\overset{k_H}{\rightleftharpoons}} ArC^{+}=CH_2 \xrightarrow{H_2O} ArCOCH_3 .$$

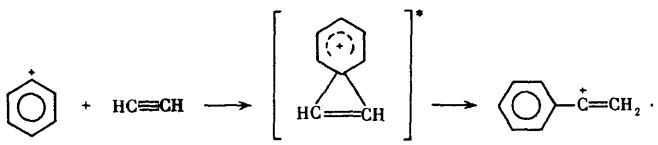
The occurrence of a kinetic isotope effect (k_{H_2O}/k_{D_2O}) indicates that protonation of the acetylene is the rate-limiting stage of photohydration.

In the photohydration of nitrophenylacetylene, an aldehyde rather than a ketone is formed, i.e. protonation does not follow Markownikoff's rule:



This occurs because the nitrophenylacetylene molecule, as a result of the absorption of light (λ = 254 nm), is converted to the T_1 triplet state, in which the distribution of charges on the carbon atoms of the triple bond is the reverse of that in aromatic alkyne molecules in the S_1^* state.[37]

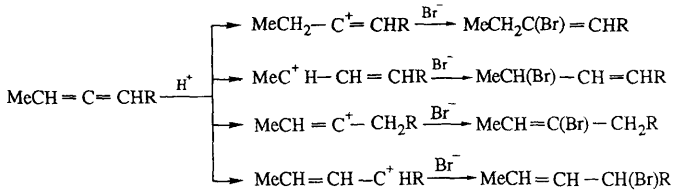
It appears that the alkylation of alkynes in the gas phase also occurs via the formation of VCs. According to the results of Fornarini and Speranza,[38] attack on an acetylene molecule by a free phenyl cation obtained by the nuclear chemical method (see below), yields first an excited bridged phenylvinyl cation, which rapidly isomerises to the more stable 1-phenylvinyl cation:



In a recent study of the kinetics of hydration of acetylene in an acidic medium, results indicating the possible formation of an unsubstituted ethenyl cation in solution were obtained.[39]

b) Allenes

In the addition of electrophilic species to allenes each of the three carbon atoms joined by a cumulated bond can serve as a nucleophilic site. When electrophiles add to the terminal carbon atoms of the cumulated bond, a VC is formed, while attack on the central carbon atoms gives an allylic ion. The direction of attack of electrophiles to allenes is mainly determined by the ability of the substituents to stabilise these ions.[40–44] Thus, in the electrophilic addition of hydrogen bromide to 1,3-dialkylallenes, all possible regioisomers are formed:[45–46]



R= Me, Et, Pr, C_5H_{11}.

In the majority of cases studied the yield of allyl bromides is considerably greater than that of vinyl bromides.

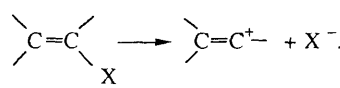
In the photohydration of arylallenes a proton attacks the central atom of the allene group. However, this is due to the presence of a negative charge on the central carbon atom in the allene group of arylallene in an excited state rather than to the effect of the aryl group on the stability.[37]

c) Anchimeric assistance of multiple bonds

Solvolysis of homoallenyl or homopropargyl esters by an S_N1 mechanism is accompanied by the formation of compounds that contain three- or four-membered rings. In the solvolysis of cyclic acetylenic or allenic esters bicyclic compounds are formed.[47–50] According to existing theories,[47–50] as a result of intramolecular attack on a nucleophilic group with a triple or allenic bond by the carbocation centre of the primary cation, cyclic VCs are formed, which participate in the reaction to give the observed cyclic products. In particular, in the solvolysis of homoallenic or homopropargyl esters the formation of a common intermediate, possibly a bicyclobutonium ion, is postulated.[50–52] Stabilisation of cyclic VCs with small rings is achieved through overlap of the vacant orbital of the carbocation centre with the electrons of the C(2)–C(3) σ-bond.[50]

2. Heterolysis of the (C=)C–X bond

Heterolysis of the (C=)C–X bond in vinyl compounds is regarded as an alternative method of obtaining VCs:



This process occurs in the solvolysis of vinyl compounds by an S_N1 mechanism and by the photolysis of vinyl derivatives. Heterolysis of a special type takes place when electron impact and nuclear chemical methods are used.

Reduction of the activation barrier for heterolytic dissociation and formation of intermediate complexes is assisted by those electronic and steric factors that govern the stability of the cations (VCs) and the groups being eliminated. Amongst these are, primarily: different electronegativities of the atoms of the bond to be cleaved; electron-donating effects of the substituents (+*I*, +*C*, anhimeric assistance) that allow delocalisation of the positive charge of the carbocation centre; electron-withdrawing properties of the substituents of the group being eliminated, through which the basicity of X^- is reduced.

The effect of polar properties of the medium which govern the solvation of the ions should be added to those factors already given which assist a reduction in energy of activation of heterolysis of the (C=)C–X bond.

a) Solvolysis of vinyl compounds

As in the case of aliphatic compounds, the rate-limiting stage in S_N1 nucleophilic substitution at an unsaturated carbon atom is cleavage of the (C=)C–X bond.

An increase in stability of the VC and the group being eliminated leads to an increase in the rate of unimolecular substitution in vinyl compounds. The values of log k correlated with the σ^+ constants of the substituents on the double bond in virtually all of the reported cases for this reaction. In terms of its absolute magnitude, the reaction parameter ρ^+ has quite a high negative value, and for arylvinyl derivatives it varies from -6.6 to -2.0 (for aliphatic systems it varies from -7.7 to 0).[53] This phenomenon demonstrates, on the one hand, that a strongly polarised intermediate (vinyl cation) is formed at the intermediate stage of the reaction, and on the other hand, that special stabilisation is required for VCs, which are less stable than their saturated analogues.

Stabilisation of VCs is considerably assisted by groups that have donor properties, including ferrocenyl, aryl, cyclopropyl, vinyl, and allyl. The greatest effect for the stabilisation of VCs occurs when such a group is introduced into an α-position conjugated with the carbocation centre. Quantum-chemical calculations show that an increase in stability of α-arylvinyl cations results from overlap of the HOMO of the π-electron system of the aromatic ring with the vacant 2*p* orbital of the carbocation centre. In this case a shift in electron density from the ring to the carbocation centre is recorded, which gives rise to positive charges on the carbon atoms at the *ortho* and *para* positions of the aryl group.[54–58]

There has been comparatively little study of ethynylvinyl systems as π-electron systems. An ethynyl group, when it is conjugated with carbocation centre, can destabilise a VC through its electron-withdrawing inductive effect ($-I$ effect). At the same time this group can participate in resonance delocalisation of the positively charged ion, which overall stabilises the cation. According to calculations, ethynyl and methyl groups have comparable stabilising effects.[55] It is assumed that in the 1-ethynylvinyl cation, these effects due to the presence of a triple bond balance each other out. In a study of the solvolysis of ethynylvinyl systems it was established that the response to the question as to whether the electron-withdrawing effect or resonance stabilisation of charge predominates depends on the nature of the substituent on the α-carbon atom of the triple bond.[59–61]

Alkylvinyl halides usually do not undergo an S_N1 type of solvolysis; the solvolysis of brosylates and tosylates takes place very slowly.[1–7] For this reason a study of the effect of alkyl substituents on the rate of reaction has only been possible with the use of the trifluoromethanesulphonate or nonafluorobutanesulphonate ions, which have sufficiently high stability as a result of significant charge delocalisation through the $-I$ effect of the fluorine atoms. The low reactivity of alkylvinyl compounds indicates that stabilisation of VCs by alkyl groups (hyperconjugation effect) is not sufficiently effective. Thus, a study of the effect of alkyl groups at the double bond on the rate of S_N1 solvolysis of alkylvinyl triflates showed that replacement of a methyl group by an ethyl group causes a slight increase in the rate of reaction, which is of a similar magnitude when R = iso-Pr and when R = t-Bu.[62]

Solvolysis of vinyl compounds which are mono- and di-substituted at the β-position but unsubstituted at the α-position, occurs at a low rate and usually gives rearrangement products even when aryl or cyclopropyl groups are used as substituents. At the present time it is thought that the most probable mechanism for solvolysis of compounds of this type is a mechanism involving successive elimination and addition and not involving the formation of a VC.[1–7]

The steric effects of the β-substituents are exhibited most clearly in the solvolysis of α,β-disubstituted vinyl compounds, although it is not always possible to distinguish them from the inductive effect. In a VC the carbocation carbon atom is *sp*-hybridised and the σ-bonds to it have a linear configuration. In the initial vinyl compound, the carbon atom attached to the substituent and the leaving group (α-atom) is sp^2-hybridised. Hence an increase in the size of the substituent on this atom must give rise to considerable steric repulsion between the substituents on the α- and β-atoms of the vinyl group. This undoubtedly assists the formation of a VC; the rate of solvolysis of the vinyl compound should also increase. In fact, the rate of solvolysis of (*E*)-1-anisyl-2-alkylvinyl bromides increases in the series

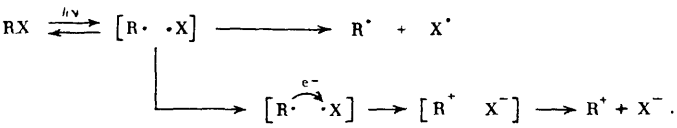
$$H < MeM < p\text{-}MeOC_6H_4 < t\text{-}Bu$$

approximately by a factor of 10^3. At the same time the rate of solvolysis of the (*Z*)-isomers remains virtually unchanged.[63]

As has already been mentioned, one of the factors in the stabilisation of VCs is anchimeric assistance of substituents due to the presence in the initial molecule of a centre of nucleophilicity that is not conjugated with the reaction site. When β-mercapto groups are present in vinyl compounds, acceleration of solvolysis occurs. It may be assumed from the formation of a considerable number of cyclic products (thiophenes) that S_N1 solvolysis of β-arylmercapto-vinyl derivatives takes place as a result of anchimeric assistance from the sulphur atom to form an intermediate thiirenium ion, which has greater stability than a linear VC.[1–7]

b) Photochemical methods for obtaining vinyl cations

The photolysis of vinyl compounds can result in the formation of VCs. According to Kropp and McNeely,[64,65] the formation of VCs is due to electron transfer in the primary radical pair formed on excitation of a vinyl halide molecule:



It is evident that heterolytic cleavage of the bond between the atoms requires a greater consumption of energy than the homolytic cleavage that accompanies the formation of a radical pair. Therefore, ionic products are generally formed with lower yields.[66–68]

A considerable increase in yield of the products of the reactions between photogenerated VCs and nucleophiles can be achieved through oxidation of vinyl radicals by reacting the latter with Cu(II) salts.[69]

Cu(II) salts are capable of almost completely suppressing the formation of products of the photolysis of vinyl halides by a radical mechanism. It is assumed[69] that oxidation with Cu(II) salts is most likely to occur via the formation of an intermediate complex between a vinyl radical and Cu(II), which is supported by the formation of vinyl ethers with a nonrearranged skeleton during photolysis.

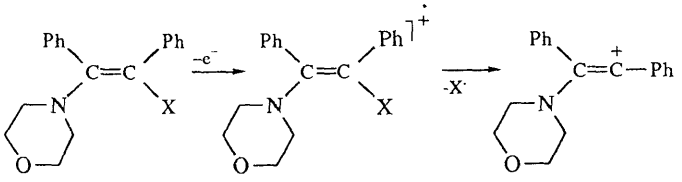
An undoubted advantage of the photochemical method of generating VCs is the possibility of obtaining cations, including primary cations,[65] in a greater variety of nucleophilic media and under milder conditions (absence of strong acids, lower

temperatures) than in the case of solvolysis. However, the reactivity of the cations obtained by this method is higher than that of the cations formed as a result of solvolysis, which may be due to a difference in their energy states. The results of four studies,[14,70–72] according to which the extent of degenerate rearrangements of photogenerated triarylvinyl cations is substantially lower than in species of this type obtained by solvolysis, may be cited as an example. One of the most likely explanations for this phenomenon is that photoexcited VCs evidently have a greater reactivity and the rate of their reaction with nucleophiles is substantially higher than the rate of their isomerisation.

c) Electron impact method

Electron impact, which involves the formation of cations as a result of the fragmentation of the initial vinyl compound on exposure to an electron beam, has found extensive application in research into the thermodynamic properties of simple VCs and in the study of molecular ion reactions.[73–79]

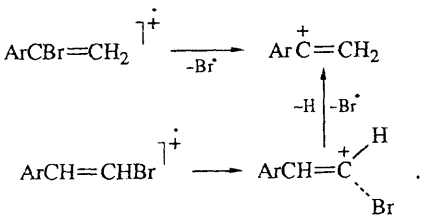
Vinyl cations with a relatively complex structure were obtained by fragmentation of 2-morpholino-*cis*-stilbenyl halide on exposure to a beam of accelerated electrons:[6]



X = Br, Cl.

From a comparison of the relative yields of the VCs in this case it was possible to conclude that atomic chlorine is eliminated with greater difficulty than atomic bromine.

A study of the dissociative ionisation of α- and β-aryl-substituted vinyl bromides showed that monomolecular loss of a Br· radical by the radical cation of the β-bromo derivative is accompanied in the transition state by a rapid 1,2-shift of hydride ion via the double bond to form the more stable secondary 1-arylvinyl cation:[56]

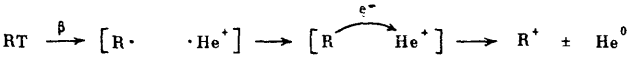


A study of the structures of the species obtained by impact activation with the use of labelled ^{13}C bromine derivatives made it possible to conclude that primary cations are not formed by electron impact.[56]

d) Nuclear chemical method of obtaining vinyl cations

The nuclear chemical method (NCM) occupies a special place amongst those methods used to generate carbocations.[80–83]

On β-decay of a covalently bonded tritium atom that forms part of a hydrocarbon and its conversion to helium, positively charged RHe^+ molecular ions are formed in different energy states and in which the charge is localised on the helium atom. The large difference in ionisation potential between the helium atom and radical R· (approximately 14 eV) causes the positive charge to migrate to the organic fragment. At the same time the neutral helium atom and charged R^+ fragment separate. At the final stage spatial separation of these species occurs, resulting in the formation of free R+ carbocations:



It has been established experimentally that as a result of the β-decay of tritium that is contained in hydrocarbons, singly charged R^+ ions are formed with a yield of the order of 70–80%†, most of which occur in the ground state or in energy levels close to it.[80,81]

During β-decay of tritium there is a marked (twofold) relative change in charge on the nucleus of the daughter He atom—the highest for nuclei undergoing β-decay. However, additional ionisation of the daughter atom as a result of perturbation of the electron shell does not occur, since as a result of the doubling of charge on the nucleus, the electrostatic interaction between the electron and nucleus increases accordingly. This leads to a sharp decrease in yield of species with a charge greater than +1. It should also be stressed that there are no daughter ions having higher charges, because of the impossibility of a cascade of vacancies (the Auger effect) occurring in this case. The latter favourably distinguishes the β-decay of tritium from the decay of radionuclides of other elements such as halogens, whose decay in the form of halogen derivatives of hydrocarbons can also lead to the formation of carbocations.[80,81]

The carbocation nature of the R^+ species obtained by NCM has been demonstrated by numerous experiments, in which their reactions with various nucleophiles were studied (aromatic compounds, ethers and esters, alcohols, etc.).[80–83]

The nature of the processes that occur in molecular systems during β-decay of tritium governs a number of unique features of NCM.

1. During β-decay of tritium that is contained in hydrocarbons, carbocations of a given structure are formed with a strictly determined initial localisation of charge, including that which does not correspond to the most stable state of the ion. The structure of the carbocations is determined by the structure of the initial hydrocarbon and the position in it of the decaying tritium atom

2. The carbocations being generated occur in a free state, i.e. they do not have a counterion or equilibrium solvent cage. The released β-particle (nuclear electron), which provides electrical neutrality to the system as a whole, cannot be regarded as a counterion since it is separated by a distance such that its Coulomb interaction with the carbocation is negligible.

3. With the use of NCM it is possible to obtain carbocations and study their reactions in media of all compositions in the gas, liquid, and solid states. The rate of formation of carbocations in the system is determined by the number of molecules of the tritiated compound (the ion source) and the number of tritium atoms in a molecule of the compound, and it does not depend on external conditions

† The remaining percentage is made up by a large number of ionic and neutral fragments of a different nature. Since the individual contribution of each does not exceed 2–3% and they have a very variable nature, the yields of their reaction products are small.

(temperature, pressure, state of aggregation), since the method is based on radioactive decay processes:

$$dN_{R+}/dt = kq\lambda N_{RT},$$

where dN_{R+}/dt is the rate of formation of carbocations; k is the number of tritium atoms in the molecule (ion source); $q = 0.7-0.8$, a coefficient representing the proportion of effective conversions leading to the formation of a carbocation during tritium decay; λ is the decay constant of tritium, equal to 1.8×10^{-9} s^{-1}; N_{RT} is the number of molecules of the tritiated compound in the system.

4. Reactions in free cation–molecule systems are in best agreement with models used in quantum-chemical calculations of the reaction route (see Section IV).

5. This method presents excellent opportunities for obtaining various reactive species (carbocations, their silicon and germanium analogues, nitronium and nitrenium ions, etc., and halogen ions formed during decay of tritium contained in HHal) in order to study their reactions.

Tritiated hydrocarbons serve as sources of carbocations. In a special case these may be hydrocarbons containing a single tritium atom. However, it is then impossible to monitor the behaviour of cations since the concentration of the reaction products of these ions with given substrates is extremely small. Thus, with an initial activity of the carbocation source of 4×10^7 Bq, about 10^{13} ions are formed over 10–30 days, which corresponds to about 10^{-10} mol of their reaction products. The only method used for determining such small quantities of products is a radiochemical method that is based on the use of hydrocarbons containing at least two tritium atoms as an ion source. The decay of one of these atoms results in the formation of a cation, while the other atom, remaining in the product molecule, can be used for identification of this product chromatographically with detection of its radioactivity‡. We should stress that in contrast to mass spectrometry and ion cyclotron resonance, the radiochemical method can be used to record neutral compounds and, what is very important, distinguish their isomeric forms.

Recently the possibility of using β-decay to obtain reactive species including the case where one radioactive atom forms part of the initial molecule and gives a stable isotope of a neighbouring element, for example, $^{14}CO_2 \xrightarrow{\beta} {}^{14}NO_2^+$, was demonstrated. The yield of products of the reactions that occur with the participation of NO_2^+ can be determined by high-performance liquid chromatographic (HPLC) methods.[84]

NCM was successfully used to generate a number of aliphatic and aromatic C_1-C_{10} carbocations and for studying their reactions with various types of nucleophilic reagents.[80–83,85,86] Subsequently, vinyl[87,88] and ethynyl[89] cations were obtained by the same method. To date the ethenyl cation[88] and 1- and 2-phenylvinyl cations[87] have been obtained. Doubly tritiated ethylene THC=CHT and styrene PhTC=CHT have been used as sources of VCs. β-Decay of tritium in the alkene leads to the formation of free VCs as a result of heterolysis of the C–He bond in the primary molecular ion:

$$RTC{=}CHT \xrightarrow{\beta} R\overset{+}{C}{=}CHT \text{ (or } RTC{=}\overset{+}{C}H)$$

R = H, Ph.

‡ The probability of simultaneous decay of two tritium atoms is negligible, being dependent on the square of the decay constant of tritium.

The ethenyl cation has low thermodynamic stability. Therefore previously it was only possible to detect its formation and reactions through the use of electron impact in the gas phase at low pressures.[77–79] With the application of NCM it was possible to study the reactions of this ion with benzene and methanol in the liquid phase,[88,90] hydrogen and methanol in the gas phase,[91] and with a number of arenes in the gas and liquid phases.[92]

As a result of the nonequivalence of the positions of the tritium atoms in the side chain of the styrene-T_2 molecule, the cations formed through processes initiated by β-decay have different structures and the positive charge on them is localised at different positions. Since decay of each of the tritium atoms is equally probable, the initial number of isomeric 1- and 2-phenylvinyl cations must be the same.

According to quantum-chemical calculations, the heat of formation of 2-$C_8H_7^+$ is higher than that of 1-$C_8H_7^+$.[60,62] Consequently, the 2-$C_8H_7^+$ ion is more reactive. Moreover, its isomerisation to 1-$C_8H_7^+$ by a hydride 1,2-shift is to be expected. The possibility of this isomerisation was examined in the case where generation of 1- and 2-phenylvinyl cations was achieved by dissociative ionisation of the corresponding bromides through electron impact.[56] However, it was shown by MNDO calculations that the isomeric forms of a phenylvinyl cation are separated by a potential barrier of 80 kJ mol^{-1}. As according to theory the vast majority of cations obtained by NCM occur in ground energy states, it is clear that isomerisation of the 2-$C_8H_7^+$ ion to 1-$C_8H_7^+$ must be a difficult process. Hence the difference between the yields of products obtained by reaction of each of the cations with given nucleophilic reagents may be solely dependent on their different reactivities (see Section IV).

III. Reaction of vinyl cations with nucleophilic reagents

According to their definition, VCs constitute a type of carbocation. The carbon atom of the carbocation centre of a VC is formally trivalent and has a vacant orbital§. Therefore VCs, like aliphatic cations, can attack those parts of molecules with increased electron density, namely, atoms with an unshared electron pair (*n*-donors), multiple bonds (π-donors), and σ-bonds. Moreover, VCs can exhibit the properties of Brønsted acids, having the ability to transfer a proton to a specific nucleophile.

1. Reactions of vinyl cations with *n*-donors

The main products of an S_N1 reaction involving the solvolysis of vinyl compounds in oxygen-containing solvents are vinyl ethers and ketones. A number of authors explain the formation of these products by the fact that intermediate oxonium ions are formed during reaction (by analogy with aliphatic ions) as a result of the addition of the VC to the oxygen atom of the solvent. The route of the subsequent decomposition of the oxonium ions depends on the composition of the medium and on steric factors.[94–101]

For the solvolysis of vinyl compounds in alcohols or acids the most typical reaction is formation of vinyl ethers as products of the deprotonation of oxonium ions. The alternative possibility for

§ When considering the structure of the parent cation of this class — the ethenyl cation — nonempirical calculations[93] have shown that it probably possesses a bridged structure, which is estimated to be 12 kJ mol^{-1} more stable than a linear structure.

decomposition of oxonium ions with elimination of R groups and formation of an alcohol (ketone) virtually never occurs. Such selectivity in the course of the reactions of VCs with HOR molecules is evidently due to the impossibility of forming a stable intermediate involving an R group in a nucleophilic medium. This is caused, firstly, by the considerable steric hindrance which arises during the formation of a complex between an eliminated R group and the solvent (or buffer base) compared to similar complexes involving a proton. Secondly, according to the principle of hard and soft acids and bases (HSAB), interaction of the protonised hydrogen atom of an oxonium ion with the oxygen or nitrogen atoms of a nucleophile (solvent, buffer base) is energetically more favourable.

In the solvolysis of 1-anisyl-2-methylpropene-1-yl bromide or tosylate in trifluoroethanol (TFE), the sole product formed is an ether, which is consistent with the idea that an oxonium ion is formed, transferring a proton to a solvent molecule:

$$AnCX{=}CMe_2 \longrightarrow An\overset{+}{C}{=}CMe_2 \xrightarrow{TFE} AnC(OCH_2CF_3){=}CMe_2$$

An – anisil, X = OTs, Br.

The solvolysis of vinyl compounds on treatment with acids sometimes results in the formation of ketones. For example, in the acetolysis of 1-anisyl-2-methylpropen-1-yl bromide in the presence of sodium acetate as a buffer base, a ketone was identified amongst the reaction products:[94,95]

$$AnCBr{=}CMe_2 \longrightarrow An\overset{+}{C}{=}CMe_2 \xrightarrow[-H^+]{HOAc} AnC(OAc){=}CMe_2 \xrightarrow{HOAc} AnCOCHMe_2.$$

However, it was established that formation of the ketone is not due to decomposition of the oxonium ion through separation of the R group but results from a side reaction in which an initially formed ether is converted to the ketone on treatment with the acid.

In a study of the solvolysis of halogen derivatives of *p*-methoxystyrenes in 80% aqueous ethanol, it was established that when there are no substituents at the β-position, a ketone is the sole product, whereas both a ketone and an ether are formed from the β,β-dimethyl derivative.[95] The authors specially noted the fact that the reaction conditions excluded the possible occurrence of a side reaction involving hydrolysis of the resulting ether and its conversion to a ketone.

The effect of a buffer base on the reactions of VCs was studied by Grob and Nussbaumer.[102] The ratio of the yields of ether to ketone as solvolysis products of the *cis*- and *trans*-isomers of 1-anisyl-propen-1-yl bromide in 80% ethanol increases with an increase in concentration of triethylamine:

$$(E)\text{- or } (Z)\text{-}AnC(Br){=}CHCH_3 \xrightarrow[H_2O]{EtOH} AnCOC_2H_5 + \; + \; AnC(OEt){=}CHCH_3. \qquad (1)$$

The buffer bases are used to suppress processes competing with the S_N1-type monomolecular nucleophilic substitution which result in the formation of similar products. An $Ad_E{-}E$ process that takes place with an electrophilic addition–elimination mechanism may be examined in this connection. At the first stage protonation of the vinyl compound and formation of a trisubstituted carbocation occur. The ion is then attacked by the nucleophile, resulting in the elimination of HX and the formation of a substitution product. The introduction of a buffer base can suppress the development of an $Ad_E{-}E$ mechanism since the base reacts with the proton.

However, the effect of the buffer bases is evidently more complex, since solvolysis of the vinyl compounds can occur by an electrophilic addition–elimination mechanism even when a buffer is present in the system.[103] It is to be expected that buffer bases not only create favourable conditions for S_N1 solvolysis but are also capable of reacting with the primary products of the reactions between VCs and HOR molecules, namely, oxonium ions. This explains the increase in yield of enol ethers and the decrease in yield of ketone in reaction (1), with an increase in concentration of triethylamine.[103]

The reaction of VCs with anions leads directly to the formation of neutral products. These processes occur most frequently in the electrophilic addition to acetylenes or allenes.

In the electrophilic addition to substituted acetylenes the direction of attack of the anion on the double bond of the VC at the first stage depends to a considerable extent on the size of the substituents at the α- and β-positions of the cation. This occurs because steric strain in the developing vinyl system increases as a result of the relative steric effect of the substituents.[104–107]

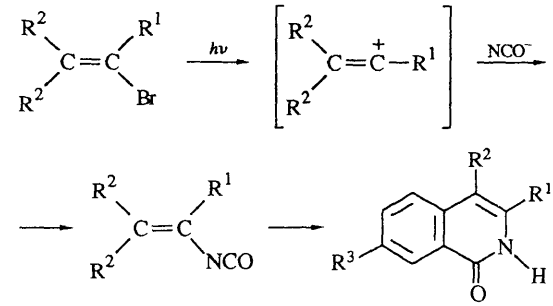
The reaction of VCs with anions during solvolysis has been examined in a number of studies.[6,108,109] In solvolytic systems reactions of VCs may be regarded solely as competing processes for the interaction of cations with the eliminated X^- group and solvent and/or with an added conjugate base $(OR')^-$ and solvent:

$$RX \longrightarrow X^- + R^+ \begin{cases} \xrightarrow{(OR')^-} ROR' \\ \xrightarrow{HOR'} ROR' + H^+. \end{cases}$$

From a study of the effect of additions of a common ion on the rate of solvolysis it was possible to derive a series of reactivity of certain anions that act as *n*-donors towards the 1,2-dianisyl-2-phenylvinyl cation:

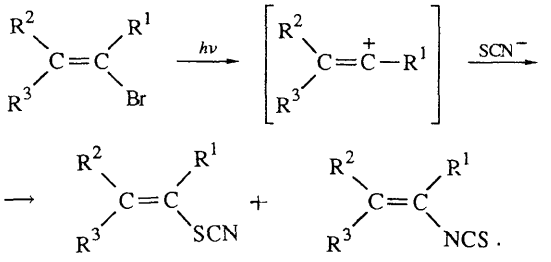
$$Br^- > Cl^- > AcO^- > CH_3SO_2O^- > AcOH.$$

Studies were conducted on the reactions of triarylvinyl cations obtained by photolysis of the corresponding bromides with ambident nucleophiles such as cyanate and thiocyanate anions.[70] The main products of the reaction between the cations and cyanate ion proved to be isoquinolones:



$R^1 = An$; $R^2 = Ph$, *p*-An; $R^3 = H$(when $R^2 = Ph$), OMe(when $R^2 = p$-An).

The reaction with thiocyanate anion occurs by two routes, which is caused by the presence of the two reaction sites on the anion—the sulphur atom and the nitrogen atom:



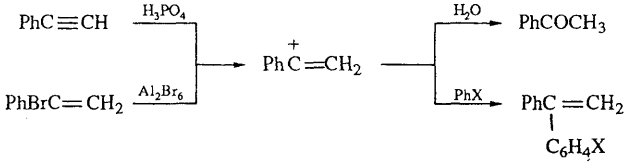
It should be noted that the VC mainly attacks the sulphur atom of the thiocyanate anion. This is due to the fact that the sulphur atom is a softer reaction site than the nitrogen atom and, according to the HSAB principle, attack by a soft reactant such as triarylvinyl cation is energetically more favourable on the sulphur atom.

2. Reactions of vinyl cations with π-electron systems

a) Aromatic compounds

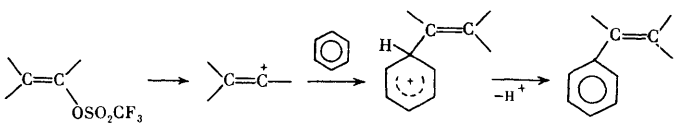
Although they are of undoubted practical interest, the reactions of VCs with π-electron systems have received very little study. This is primarily related to the question of using vinyl and acetylenic compounds as vinylating agents in electrophilic substitution reactions in aromatic systems.

In a study of the reaction between toluene and α-bromostyrene or phenylacetylene in the presence of Al_2Br_6 or H_3PO_4 it was found[110] that products derived from the replacement of a hydrogen atom at the *ortho* and *para* positions of the benzene ring of toluene and also acetophenone are mainly formed in this reaction. Vinylation of anisole with phenylacetylene in H_3PO_4 also results in the formation of the *ortho* and *para* derivatives. These results are consistent with the proposed formation of an intermediate of a 1-phenylvinyl cation:



Trisubstituted vinyl bromides in the presence of silver tetrafluoroborate as a catalyst were used as the vinylating agent in substitution reactions in a series of aromatic compounds, making it possible to obtain vinyl-substituted arenes in high yield.[69]

When alkylsulphonates are used it is possible to carry out the alkylation in the absence of Friedel–Crafts catalysts.[111] Vinyl triflates were very promising in this respect. The results are consistent with the assumption that the reaction takes place by a mechanism whose first stage is elimination of the $CF_3SO_2O^-$ anion from vinyl triflate to give a VC. The subsequent reaction with arene results in the formation of a phenonium ion (σ-complex), which is converted to the substitution product after elimination of a proton:



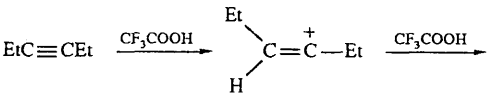
The σ^+ constants of Brown are the most suitable for a determination of the effect of a substituent on the rate of vinylation with vinyl triflates. The value of $\rho = -2.57$ obtained for the reaction parameter indicates that a positive charge develops on the reaction site.

On the other hand, the absence of a kinetic isotope effect in this reaction suggests that vinylation of arenes by vinyl triflates occurs by an electrophilic substitution mechanism. The ratio of the rate constants of reactions involving normal and perdeuterated benzenes ($k_H/k_D = 0.98$) is consistent with the ratios $k_H/k_D = 0.90$ for nitration and $k_H/k_D = 1.13$ for benzylation.

The absolute value of the reaction parameter ρ for alkylation of vinyl triflates is one of the lowest in a series of electrophilic substitution reactions of aromatic compounds.[111] This is due to the high reactivity of the alkylating agent—a vinyl cation—and hence indicates its lack of selectivity towards different monosubstituted arenes containing both electron-donating and electron-withdrawing substituents.

b) Alkenes and alkynes

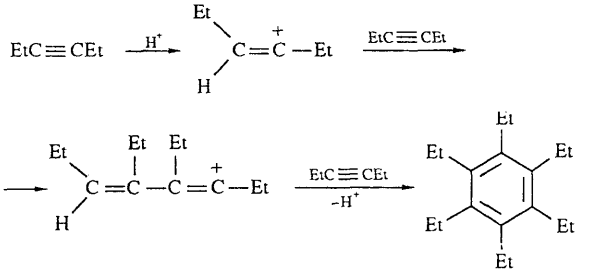
In the reaction between hex-3-yne and trifluoroacetic acid, isomeric vinyl trifluoroacetates are formed in almost equal quantities and are stable under the reaction conditions:[112]



$\longrightarrow$ (*E*)- or (*Z*)-EtHc=C(OCOCF$_3$)Et +

+ MeCOCH$_2$CH$_2$CF$_3$ + C$_6$Et$_6$.

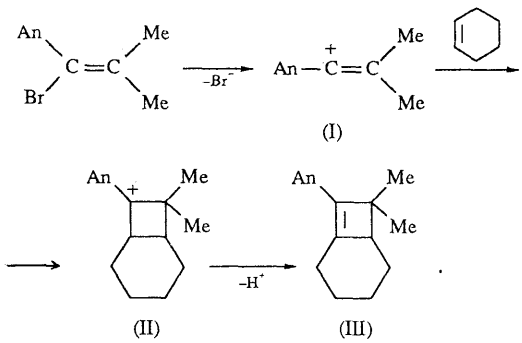
These products are formed as a result of the nonstereospecific addition of trifluoroacetic acid to the linear hexene-3-yl cation. On increasing the concentration of hex-3-yne, hexaethylbenzene is formed. This product most probably occurs as a result of the reaction of the hexen-3-yl cation with an alkyne molecule, which leads to the formation of a homoallylic ion[31–34] and then to trimerisation:



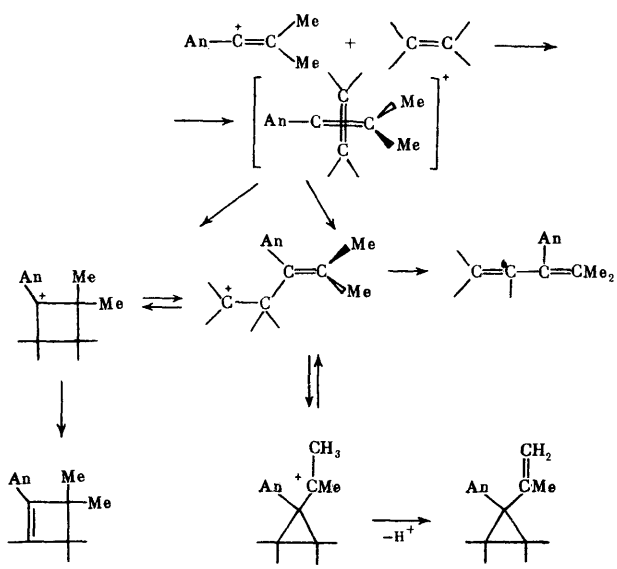
The mechanism of cycloaddition of VCs to olefins was studied in detail by Hanack, et al.[113–117]

On treatment of 1-anisyl-2-methylpropen-1-yl bromide with silver tetrafluoroborate in cyclohexene, compound (III) was obtained in 60% yield. It is evidently formed through the involvement of cation

(II), which occurs as a result of the concerted or stepwise cycloaddition of VC (I) to cyclohexene:



In the reaction between VCs and certain olefins, cyclopropane derivatives were isolated together with cyclobutene derivatives:[116,117]



The formation of cyclobutenes is apparently due to the presence of silver ions in the reaction medium. Silver very readily forms complexes with unsaturated organic compounds and may serve as a catalyst for the process that leads to the formation of cyclobutene derivatives. If VCs are obtained by solvolysis of triflates in the absence of silver ions, cyclopropane derivatives are mainly formed, as a result of [2 + 1] cycloaddition. When silver salts are introduced, the formation of cyclobutenes occurs again. The results obtained suggest that cycloaddition of VCs to olefins occurs by a successive addition mechanism.

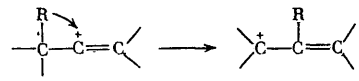
3. Reactions of vinyl cations with the electrons of σ-bonds

Reactions of this type include the conversions of VCs in which the carbocation centre of the cation makes its vacant orbital available to the pair of electrons participating in the formation of a σ-bond between atoms, such as C–H or C–C. There is only a limited number of such reactions, but of these the rearrangement of VCs and the deprotonation of VCs with the formation of acetylenes may be singled out.

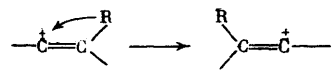
a) Rearrangements of vinyl cations

Rearrangement of VCs takes place as a result of 1,2-shifts of groups of atoms:

1) transfer of groups to a double bond with the formation of allylic cations:



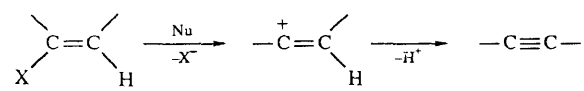
2) displacement of groups between carbon atoms forming a double bond, with the result that one VC is isomerised to another



Comprehensive information on the rearrangements of VCS and essential examples can be obtained from a monograph[4] and two reviews;[6,14] therefore they are not included in this review.

b) Deprotonation of vinyl cations

In the solvolysis of β-unsaturated vinyl compounds, in many cases acetylenes are formed together with ketones and/or ethers:



From a study of the mechanism of elimination reactions in a series of vinyl compounds undergoing solvolysis it was possible to establish that the ratio of the yield of products of an S_N1 reaction to that of products of $E1$ deprotonation depends to a considerable extent on the structure of the VC, the nature of the solvent in which solvolysis is occurring, and the basicity of the reaction medium.

As was mentioned in the examination of solvolytic methods for generating VCs, a decrease in steric strain in the initial vinyl compound through the formation of a VC with an *sp*-hybridised carbocation centre assists heterolysis of the (C=)C–X bond. In this case the yield of alkynes must increase with increased size of the substituents; elimination of a proton from the cation reduces the steric strain to an even greater extent. On the other hand attack by a nucleophile on the carbocation centre has the reverse effect.[8,63,98,118,119]

In addition to steric factors, the basicity of the reaction medium has a considerable effect on the ratio of substitution to elimination products. This can be illustrated in the case of the hydrolysis of *p*-aminobromostyrene in ethanol at different pH values.[120] With an increase in pH from 3.8 to 13.1 the yield of *p*-aminophenylacetylene increases from 16 to 85%, which on the whole is consistent with the HSAB principle. The carbocation centre of the cation is classed as a soft reaction site, whereas a hydrogen atom which has a partial positive charge is a hard reaction site. Since interactions between centres of the same type are energetically more favourable, the use of hard strongly basic nucleophiles favours the removal of a proton from the vinyl cation, which is reflected in an increased yield of alkynes.

IV. Reactions of free vinyl cations

As was mentioned in our description of the nuclear chemical method of generating carbocations, these cations occur in the free state, i.e. they do not have a counterion or equilibrium solvent cage and their reactions are classed as ion–molecule reactions (IMRs).

The rate of the reactions between ions and molecules is extremely high; in the majority of known cases the rate constants of IMRs are $10^{-12}-10^{-8}$ cm^3 mol^{-1} s^{-1}, which are many orders higher than the constants for reactions between neutral molecules. The low of zero values of the energy of activation and the high collision cross-sections account for this. As a consequence the cross-sections of IMRs (10^{-14} cm^2) match the cross-sections for collisions between ions and species of the medium.[80–84]

In the interaction between a thermolysed molecule and ion, an associated state, or "long-lived complex", develops, in which a statistical exchange of energy between different vibrational degrees of freedom occurs. In this case excitation of the internal degrees of freedom of the reacting species occurs and the complex is converted to a vibrationally excited state. Further conversion of the "long-lived complex" depends on the nature of the distribution of its internal energy and the degree of complexity of its transformation to the corresponding activated complex and then to the reaction products.

In the gas phase species have a long mean free path and in the intervals between collisions they may be regarded as free. At low densities when there is no interaction between the species, the distribution of the latter is random and the activation barrier for unimolecular decomposition or isomerisation of the activated complex in the gas phase may be surmounted through the energy of its collisions with species of the medium.

A completely different pattern occurs in the reaction between free cations and molecules in condensed phases (liquid phase and solid vitreous phase, which occurs as a result of a marked cooling of the liquid below the freezing point)¶.

A short mean free path is typical of the species in a condensed phase. Each molecule of liquid is surrounded by a given number of its immediate neighbours, but thermal movement results in disruption of the order arising on interaction between the species themselves.

Let us examine which processes occur in a liquid with the "instantaneous" formation in it of a carbocation as a result of the β-decay of tritium forming part of a hydrocarbon molecule.

A carbocation is formed at the concluding stage of nuclear chemical processes on cleavage of the C^+-He bond in the initial RHe^+ ion. Cleavage of this bond occurs over a period of $10^{-14}-10^{-13}$ s, which is of the same order of magnitude of time for atomic vibrations in a molecule.[80–84] It is evident that over approximately the same period of time the initial structure of the ion is transformed to an equilibrium state through vibrational relaxation.

The ion inherits the solvent cage of the mother molecule, which is not in equilibrium with the ion. In order for this cage to be reorganised, the following must change:[121]

a) the average radius of the cage, if it is assumed to be spherical;

b) the coordination number;

c) the symmetry of the quasi-crystalline structure of the cage, i.e. its shape;

d) the position of molecules with a permanent dipole;

e) the magnitude of the induced dipole moment and the induction energy, which change as a result of a charge developing;

f) the energy of the dispersion interaction, related to the polarisability of the ion.

The rate of these changes accompanying the formation of a carbocation is variable, $10^{-15}-10^{-10}$ s being required to accomplish them. The most rapid are the electronic forms of polarisation (10^{-15} s) and dispersion interactions (10^{-13} s). Orientational polarisation occurs more slowly (10^{-11} s) and the reorganisation of complexes of molecules fixed by hydrogen bonding is even slower (10^{-10} s). Hence, as a result of the very rapid redistribution of charges when a carbocation is suddenly formed, inductive polarisation of the medium by the field of the charge mainly occurs without any change in the spatial distribution of the species. In this sense a carbocation obtained by the nuclear chemical method can be regarded as being in a free state and the formation of the ion as a special Franck–Condon transition. It is clear that in condensed phases the excess energy of a "long-lived complex" is dispersed extremely rapidly by collisions with the surrounding species of the medium. The existence of an ion-dipole interaction between the complex and molecules of the medium increases the probability of such a transfer of energy to an even greater extent. For these reasons the reactions of a "long-lived complex" in solution are determined almost exclusively by the lowest vibrational energy level of this complex.

One of the most fruitful concepts that relates the electronic structure of molecules and ions to their behaviour in chemical reactions has been the frontier orbital theory of Fukui.[122] According to this approach, the frontier orbitals of reacting species play a decisive role in chemical interactions. It was shown by the PMO method that the interaction of the HOMO of one of the reactants (electron donor) with the LUMO of the other reactant (acceptor) makes a predominant contribution to the attractive energy.[123–125] In this case a reaction which results in the formation of a bond between atoms with the maximum charge densities in their frontier orbitals (reaction sites) becomes the most probable. This does not exclude a different coordination of the reactants with respect to each other and a reaction occurring by an alternative route involving other atoms and other reaction sites.[126]

It should be noted that the use of quantum-chemical methods of determining reactivity is most justified for free species, such as in gas-phase reactions (the "isolated molecule" approximation).

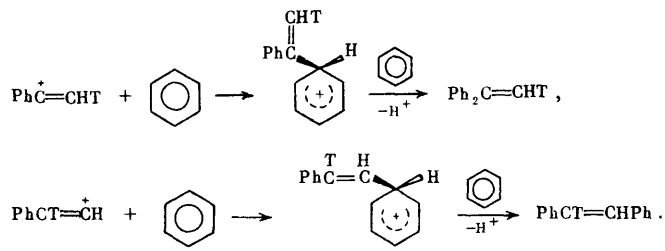
Since low or zero energies of activation and high rates are typical of ion-molecule reactions, the interaction between free cations and molecules in condensed phases may be regarded to the first approximation as the interaction of two free species which also results in the formation of a vibrationally excited "long-lived complex" or a polarised capture complex. Assuming a rapid transfer of energy to molecules of the surrounding medium, this phenomenon makes it sufficiently valid to use different quantum-chemical models, including PMO theory, for predicting the reactivity of free cations generated by the nuclear chemical method.

1. Reaction of free vinyl cations with aromatic and oxygen-containing compounds

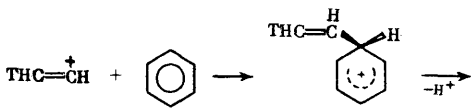
The reactions of free ethenyl and phenylvinyl cations obtained as a result of decomposition of the tritium atoms in doubly tritiated ethylene and styrene (see Section II.4) have been investigated in several studies.[85,87,88,90–92,126,127] Ethenyl cations were generated in benzene and methanol in the liquid state. Phenylvinyl cations were

¶ At the present time the state of a supercooled liquid in which the structure of the initial liquid is preserved is usually regarded as a solid vitreous state.

obtained in the presence of benzene and oxygen-containing compounds with the general formula ROR′ (R, R′ = H, Et) in the gas, liquid, and solid states. It was established in this case that the state of aggregation of the reaction system affects the route of the reactions between free vinyl cations and nucleophiles. The main products of the reaction between free phenylvinyl cations and benzene were 1,1-diphenylethylene, *trans*-stilbene, and isomers of phenylstyrene (see Section IV.2):



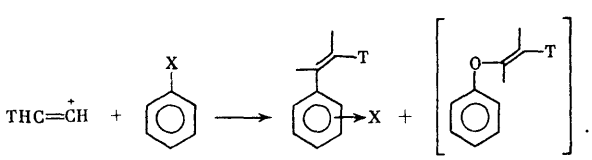
Attack on a benzene molecule by an ethenyl cation results in the formation of styrene:



The formation of diphenylethylene, stilbene, and styrene is consistent with the idea that arenonium ions (σ-complexes) are formed at an intermediate stage of the reaction.

Recently the reactivity and selectivity of free ethenyl cations towards substituted arenes such as toluene, anisole, fluoro-, chloro-, and bromo-benzene in the liquid and gas phases were studied by the method of competing reactions.[92]

In liquid-phase systems the predominant route was exothermic attack by an ethenyl cation on the π-electron system of an aromatic compound. As a result of this attack, an excited arenonium ion (σ-complex) is formed, being deactivated by collisions with molecules of the surrounding medium and undergoing deprotonation to form substituted styrenes. Anisole acts as an ambidentate nucleophile in reactions with an ethenyl cation since, in addition to the phenyl group, the unshared electron pair of the oxygen atom of the methoxy group also undergoes electrophilic attack, resulting in the formation of an oxonium ion. It is converted to phenyl vinyl ether as a result of reaction with another molecule of substrate. However, the efficiency of this process is very low. In reactions with halobenzenes the ethenyl cation exclusively attacks the phenyl group:



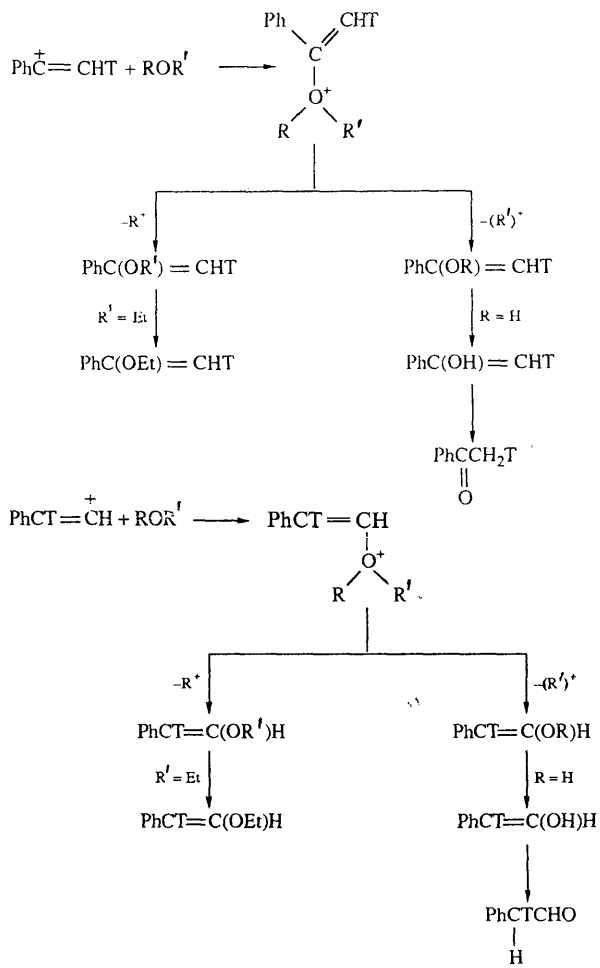
X = Me, OMe, F, Cl, Br X = OMe

The nucleophilic reagents that have been studied can be arranged in the following series of reactivity towards the ethenyl cation in the liquid phase: PhOMe > PhCl > PhMe.

The results obtained from studies on gas-phase reactions of free ethenyl cations with arenes are consistent with the hypothesis that isomeric conversions of their primary reaction products—arenonium or onium ions—take place. In this case the latter occur in an excited state for a considerable time as a result of the difficulty or impossibility of their deactivation through collisions.[80–81,128] Therefore, in contrast to liquid-phase reactions, the isomeric composition of substituted styrenes in gas-phase reactions approximates to the thermodynamically stable composition with a predominance of *meta* isomers. Similar results were obtained in a radiochemical study of ion-molecule reactions of free methyl and phenyl cations with certain alkylbenzenes.

Oxonium ions are known to act as adducts in electrophilic addition reactions of aliphatic carbocations to molecules with the general formula ROR′ (R, R′ = H, Alk).[80,81] The results of four studies[92,124,125,129] are also consistent with the idea that these intermediates are formed as a result of attack by free ethenyl and phenylvinyl cations on the unshared electron pair of the oxygen atom of an ROR′ molecule.

From a quantitative determination of the yields of products formed in the liquid phase it was possible to conclude that the oxonium ions decompose preferentially with the detachment of an alkyl group Et^+ (or Me^+). Thus, in the case of 1- and 2-phenylvinyl cations the yields of acetophenone or phenylethanol were approximately ten times higher than the yields of 1- or 2-ethoxystyrenes respectively:[129]



Formation of an ion by an S_N1 mechanism is accompanied by a substantial reorganisation of the surrounding medium with a change in the orientation of the molecules of the medium and their relative configuration. The cation is in thermodynamic equilibrium with the medium.

In contrast to this, when cations are generated by NCM in condensed phases, the molecules of the medium hardly change their spatial configuration at all relative to the ion formed because of the high rates of nuclear chemical processes. Since for IMRs extremely high reaction cross-sections are typical and virtually every collision of the reacting species results in reaction, the excited intermediate complex between an ion and molecule (an oxonium ion in this case) appears to be isolated from the surrounding medium. As a result, the transfer of excitation energy from the complex to the medium is difficult. Therefore, the complex mainly decomposes by a unimolecular mechanism with formation of the thermodynamically most stable species (an alkyl cation), while elimination of a proton is forbidden. To a certain extent this resembles the reaction of carbocations in the gas phase, such as the reaction of free methyl cations with alcohols and ethers.[80–81] The presence of ethers amongst the products of reactions between free phenylvinyl cations and ethanol in the liquid phase is an indication of the contribution of a bimolecular mechanism for decomposition of the oxonium ion through the transfer of a proton to a substrate molecule. This is due to the occurrence of hydrogen bonding in alcohols.

In competing reactions of free phenylvinyl cations with ethanol and water in equimolar quantities, the ratio of yields of ether to ketone was approximately 0.1 : 1, which indicated the higher reactivity of ethanol relative to water.[129] This is consistent with results on the solvolysis of anisylvinyl halides in 80% aqueous ethanol,[130] which is also supported by a study of reactions involving free triarylvinyl cations produced by flash photolysis.[131] In the latter study it was established that the nucleophilicity of alcohols decreases in the series: MeOH > EtOH > iso-PrOH > (H_2O) > t-BuOH. The ratio of rate constants of reactions between the 2,2-diphenyl-1-anisylvinyl cation and methanol and t-butanol is 12 : 1, while in the case of reactions of the trianisylvinyl cation it is 21 : 1. This variation in reactivity is evidently due to an increase in steric hindrance in the intermediate complex. The low reactivity of water is probably due to the fact that its molecules and the molecules of the solvent — acetonitrile — in which flash photolysis was conducted from clusters via hydrogen bonds, and this makes water less nucleophilic. However, the question as to whether this series of reactivity of alcohols and water is retained when the composition of solution is changed was not discussed by Kobayashi, et al.[131]

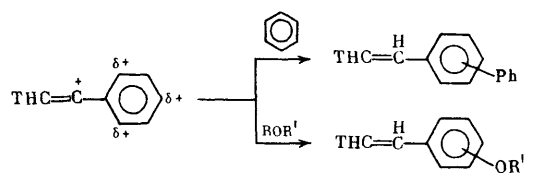
Free VCs of the type $R^1R^2C{=}C^+R^3$ ($R^1{-}R^3$ = Ph, An, Me) which are obtained by flash photolysis of the corresponding bromides in acetonitrile have a characteristic band (λ = 355 nm) in their absorption spectrum and a lifetime of 1–20 μs.[132] The rate constants of reactions between nucleophilic reagents (*N*-methyl and *N*-vinyl-2-pyrrolidone styrene, *n*-butyl vinyl ether, α-methylstyrene, methyl methacrylate, tetrahydrofuran, ethers, and aliphatic alcohols) and cations are 10^5-10^8 litre mol^{-1} s^{-1}. The composition of the products has not been studied. The highest reactivity of the 1-(*p*-anisyl)-2,2-dimethylvinyl cation has been attributed to the high positive charge on its carbocation centre and low steric hindrance (in the series of VCs studied).

2. Participation of aryl groups in reactions of free substituted vinyl cations

As was demonstrated by quantum-chemical calculations of the electron densities on the atoms of phenylvinyl cations, the 1-phenylvinyl cation is stabilised through overlap of the vacant 2*p* orbital of the carbocation centre and the HOMO of the phenyl group, occurring as a result of the Ph group rotating through 90°. This causes the carbon atoms at the *ortho* and *para* positions of the phenyl group to be activated. The $2p_y$ orbitals of these atoms participate in the formation of the LUMO of the cation, which results in a positive charge developing at these positions.

The 1-phenylvinyl cation can be regarded as a multicentre electrophile. The 2-phenylvinyl cation is a single-centre electrophile as its LUMO is formed almost completely from $2p_y$ atomic orbitals of the carbocation centre, on which the main positive charge is localised.[55,57,58]

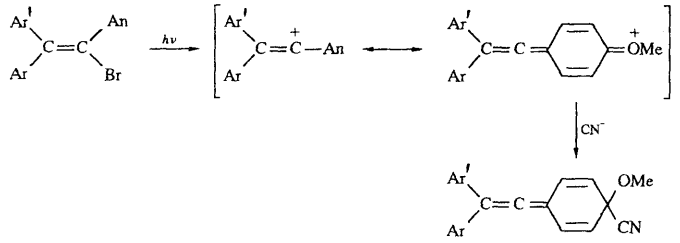
By regarding the interaction between carbocations obtained by NCM and molecules as an interaction between free species whatever their state of aggregation might be, the formation of "long-lived complexes" involving each reaction site may be assumed.[58,87,126–128] This can explain the replacement of a hydrogen atom at the *ortho* and *para* positions of the phenyl group of phenylvinyl cations and the formation of their reaction products with benzene — *o*- and *p*-phenylstyrenes — as well as the formation of hydroxy- and ethoxystyrenes when they react with ROR′ compounds (R, R′ = H, Et):



In a condensed state, in contrast to gas-phase reactions, interaction between phenylvinyl cations and benzene does not lead to the formation of *o*-phenylstyrene. Furthermore, the reaction sites at the *ortho* position of the phenyl group in 1-$C_8H_7^+$ in the addition of this cation to ROR′ molecules had no recorded effect on the process. This is presumably due to the fact that in a condensed state the conversion of *ortho*-oriented complexes to reaction products encounters a number of difficulties caused by electronic repulsion of the vinyl residue in the sterically strained molecule of the *ortho* isomer and the need to disrupt the conjugation between the vacant orbital of the carbocation centre and the HOMO of the phenyl group of 1-$C_8H_7^+$. In the gas phase these barriers are readily surmounted, since the resulting complexes occur in a vibrationally excited state.[58,87,126–128]

A study of the flash photolysis of arylvinyl bromides has supported the idea that α-aryl groups participate in reactions of the resulting VCs.[131–133] Thus, because of the delocalisation of positive charge and the development of additional reaction sites, the addition of cyanide or alkoxide ions becomes possible not only to the carbocation centre of the 1-(*p*-anisyl)-2,2-diarylvinyl cation but also to the α-anisyl substituent, which is accompanied by *ipso*-substitution

of the methoxy group. The intermediate of *ipso*-substitution—diarylmethoxycyanovinylidenecyclohexadiene—was identified by ^{1}H NMR[133–135] and isolated from the reaction mixture.[136,137]



In the photolysis of 1-(*p*-anisyl)-2,2-diarylvinyl bromide in solutions of MeOH, EtOH, and PrOH in the presence of NEt_3, pyridine and $NaHCO_3$, *ipso*-substitution does not take place.[134] Diphenylvinylidenecyclohexadienone acetal—a product of *ipso*-substitution—is stable in neutral and weakly acidic media, while in an acidic medium it decomposes to form a 2,2-diphenyl-1-alkoxyphenylvinyl cation, which made it possible to study the reaction of the latter with methanol, water, anisole, and bromide and thiocyanate ions.[138]

3. Free-cationic polymerisation

One of the most important reactions of carbocations with olefins is cationic polymerisation. The process is initiated by the addition of an ion to an olefin molecule, as a result of which a new carbocation is formed that is also capable of attacking an olefin molecule.

This question has not been studied in relation to VCs except in the specific case of the free-cationic polymerisation of styrene in bulk and also in its solutions in cyclohexane and methylcyclohexane by phenylvinyl cations generated by NCM.[124] The polymers obtained had a high molecular weight—10^6 in the polymerisation of pure styrene and 10^5 in 10% solutions of these solvents. They had a unimodal molecular weight distribution. The latter circumstance provides evidence that polymerisation is initiated by species of the same nature, namely, phenylvinyl cations. On lowering the temperature to −78 °C the molecular weight of the polymer increased, which also pointed to the cationic nature of the processes occurring. However, the possibility of radical cations which may be formed as a result of radiolysis of components of the solution participating in these processes cannot yet be excluded categorically.

V. Conclusion

Vinyl cations, which were discovered more than 25 years ago, have become the subject of intense experimental and theoretical study, and they have currently gained general recognition.

Vinyl cations, as has been convincingly demonstrated in a considerable number of studies, are in many respects similar to the well-studied alkyl and aryl cations. They may be obtained by methods that are similar to those used for generating saturated cations, such as by electrophilic addition to the triple bond of acetylenes and the cumulene bond of allenes, including intramolecular attack on the double bonds of the carbocation centre formed as a result of solvolysis. The method based on heterolysis, in particular solvolysis of the (C=)C−X bond in vinyl compounds, has been used the most extensively.

Unique opportunities are presented by the nuclear chemical method of generating VCs in a free stage. This is related to the application of the β-decay of tritium that is covalently bound in vinyl compounds (a free state is taken to mean a state that is characterised by the absence of a counterion and an equilibrium solvent cage).

According to quantum-chemical calculations that have been confirmed experimentally, VCs mainly have a structure with a linear or quasi-linear configuration of the σ-bonds at the carbocation carbon atom. Cycloalkenyl cations with small rings (C_3-C_6) in which this linear structure does not occur have been theoretically predicted and obtained.

Studies on the rearrangements of VCs using labelled atoms clearly attest to the possibility of bridged VC structures being formed, especially as a result of the migration of aryl groups.

The results collected to date demonstrate that VCs act as typical electrophilic reagents. Because of the presence of a vacant 2*p* orbital, VCs participate in reactions with *n* and π-donors and they are capable of attacking the σ-electrons of C−C or C−H bonds.

The role of the individual groups of substituents in VCs and their saturated analogues appear to be similar in many respects. However, VCs have greater reactivity as intermediates than aliphatic cations. The reactions in which VCs participate take place with lower selectivity. The main characteristics of VCs are governed by the presence of a rigid double bond, which to a considerable extent affects the stereochemistry of many reactions involving VCs.

References

1. G Modena, U Tonellato *Adv. Phys. Org. Chem.*, 1971, **9** 184
2. P J Stang *Prog. Phys. Org. Chem.*, 1973, **10** 205
3. M Hanack *Acc. Chem. Res.*, 1976, **10** 364
4. P J Stang *Acc. Chem. Res.*, 1978, **11** 107
5. P J Stang, Z Rappoport, M Hanack, L B Subramanian *Vinyl Cations*, Academic Press, New York, 1979, p. 684

5a. T L Jacobs, S Searles *J. Am. Chem. Soc.*, 1944, **66** 686

6. M Hanack *Acc. Chem. Res.*, 1970, **3** 209
7. Z Rappoport *React. Intermed.*, 1983, **3** 427
8. C A Grob, G Cseh *Helv. Chim. Acta*, 1964, **47** 194
9. P J Stang, R H Summerville *J. Am. Chem. Soc.*, 1969, **91** 4600
10. L R Subramanian, M Hanack *Chem. Ber.*, 1972, **105** 1465
11. T S Abram, W E Watts *J. Chem. Soc., Perkin Trans. 1*, 1977, 1522
12. L I Zakharkin, V V Kobak *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1919
13. E W Koch, H U Siehl, M Hanack *Tetrahedron Lett.*, 1985, **26** 1493
14. A A Shchegolev, M I Kanishchev *Usp. Khim.*, 1981, **50**(6) 1046 [English translation in *Russ. Chem. Rev.*, 1981(6)]
15. D Kaufman, R Kupper, T Neal *J. Org. Chem.*, 1979, **44** 3076
16. F Marcuzzi, G Melloni, M V Zucca *Gazz. Chim. Ital.*, 1987, **117** 219
17. G Melloni, G Modena, U Tonellato *Acc. Chem. Res.*, 1981, **14** 227
18. H Martens, F Janssens, G Hoornaert *Tetrahedron*, 1975, **31** 177
19. B E McCarry, R L Markezich, W S Johnson *J. Am. Chem. Soc.*, 1973, **95** 4416
20. W S Johnson, T M Yarwell, R F Myer, et al. *Tetrahedron Lett.*, 1978, 2549

21. J Pornet, D Damour, L Miginiac *J. Organomet. Chem.*, 1987, **319** 333
22. K Yates, G H Schmid, T W Regulski, et al. *J. Am. Chem. Soc.*, 1973, **95** 160
23. G Modena, F Rivetti, U Tonellato *J. Org. Chem.*, 1978, **43** 1521
24. M F Ruasse, J E Dubois *J. Org. Chem.*, 1977, **42** 2686
25. Sh O Badanyan, G G Melikyan, G R Mkhitaryan, et al. *Arm. Khim. Zh.*, 1981, **34** 926
26. A V Shastin, E S Balenkova, Yu N Luzikov, et al. *Zh. Org. Khim.*, 1985, **21** 1598
27. I D Gridnev, E S Balenkova, Yu N Luzikov, et al. *Zh. Org. Khim.*, 1988, **24** 1605
28. S V Borodaev, E V Naumova, S M Luk'yanov *Zh. Org. Khim.*, 1986, **22** 1789
29. S V Borodaev, S V Zubkova, S M Luk'yanov *Zh. Org. Khim.*, 1988, **24** 2330
30. D Maniou, M Maniou, G Dinulescu, et al. *Rev. Roum. Chim.*, 1984, **29** 193
31. D Maniou, M Maniou, G Dinulescu, et al. *Rev. Roum. Chim.*, 1984, **29** 201
32. D Maniou, M Maniou, G Dinulescu, et al. *Rev. Roum. Chim.*, 1984, **29** 671
33. D Maniou, M Maniou, G Dinulescu, et al. *Rev. Roum. Chim.*, 1984, **29** 857
34. D Maniou, M Maniou, G Dinulescu, et al. *Rev. Roum. Chim.*, 1985, **30** 223
35. A D Allen, G Angelini, G Paradisi, et al. *Tetrahedron Lett.*, 1989, **30** 1315
36. A D Allen, Y Chiang, A J Kresge, et al. *J. Org. Chem.*, 1982, **47** 775
37. P Wan, K Yates *Rev. Chem. Intermed.*, 1984, **5** 157
38. S Fornarini, M Speranza *J. Chem. Soc., Chem. Commun.*, 1985, 1692
39. V Lucchini, G Modena *J. Am. Chem. Soc.*, 1990, **112** 6291
40. K Grisbaum *Angew. Chem., Int. Ed. Engl.*, 1969, **8** 993
41. F Amar, D R Dalton, G Eisman, et al. *Tetrahedron Lett.*, 1974, 3037
42. T L Jacobs, R N Johnson *J. Am. Chem. Soc.*, 1960, **82** 6397
43. C U Pittman *J. Chem. Soc., Chem. Commun.*, 1969, 122
44. W Smadja *Chem. Rev.*, 1983, **83** 263
45. A V Fedorova *Zh. Obshch. Khim.*, 1963, **33** 3508
46. A V Fedorova, A A Petrov *Zh. Obshch. Khim.*, 1962, **32** 1740
47. M Hanack, A E F Wachtler *Chem. Ber.*, 1987, **180** 727
48. M Hanack, G J Collins, H Stutz, et al. *J. Am. Chem. Soc.*, 1981, **103** 2356
49. M Hanack, G J Collins, H Stutz, et al. *J. Org. Chem.*, 1983, **48** 5260
50. M Hanack, G Auchter *J. Am. Chem. Soc.*, 1985, **107** 5238
51. M Santelli, M Bertrand *Tetrahedron*, 1974, **30** 227
52. Y Apeloig, J B Collins, D Cremer, et al. *J. Org. Chem.*, 1980, **45** 3496
53. P J Stang *Acc. Chem. Res.*, 1978, **11** 107
54. Y Apeloig, P V R Schleyer, J A Pople *J. Am. Chem. Soc.*, 1977, **99** 5901
55. Y Apeloig, P V R Schleyer, J A Pople *J. Org. Chem.*, 1977, **42** 3004
56. Y Apeloig, W Franke, Z Rappoport, et al. *J. Am. Chem. Soc.*, 1981, **103** 2770
57. H Mayr, R Schneider, D Wilhelm, et al. *J. Org. Chem.*, 1981, **46** 5336
58. V P Lebedev, A Yu Shibaev *Zh. Org. Khim.*, 1986, **22** 918
59. J B Hassendenteufel, M Hanack *Tetrahedron Lett.*, 1980, 503
60. M Schiavelli, D M Jung, A K Vaden, et al. *J. Org. Chem.*, 1981, **46** 92
61. H Taniguchi, S Kobayashi, T Nishi, et al. *J. Chem. Soc., Chem. Commun.*, 1980, 103
62. R H Summerville, G A Senkler, P V R Schleyer, et al. *J. Am. Chem. Soc.*, 1974, **96** 1110
63. Z Rappoport, N Pross, Y Apeloig *Tetrahedron Lett.*, 1973, 2015
64. P J Kropp, S A McNeely *J. Am. Chem. Soc.*, 1983, **105** 6907
65. S A McNeely, P J Kropp *J. Am. Chem. Soc.*, 1976, **98** 4319
66. T Suzuki, T Sonoda, S Kobayashi, et al. *J. Chem. Soc., Chem. Commun.*, 1976, 180
67. T Kitamura, S Kobayashi, H Taniguchi *Tetrahedron Lett.*, 1979, 1619
68. W Schnabel, I Naito, T Kitamura, et al. *Tetrahedron*, 1980, **36** 3229
69. T Kitamura, S Kobayashi, H Taniguchi *J. Am. Chem. Soc.*, 1986, **108** 2641
70. T Kitamura, S Kobayashi, H Taniguchi *Chem. Lett.*, 1984, 1526
71. T Kitamura, S Kobayashi, H Taniguchi *J. Org. Chem.*, 1984, **49** 3167
72. T Kitamura, S Kobayashi, H Taniguchi, et al. *J. Org. Chem.*, 1982, **47** 5003
73. F P Lossing *Can. J. Chem.*, 1971, **49** 357
74. F P Lossing, G P Semeluk *Can. J. Chem.*, 1970, **48** 955
75. F P Lossing *Can. J. Chem.*, 1972, **50** 3973
76. D H Aue, W H Davidson, M T Bowers *J. Am. Chem. Soc.*, 1976, **98** 6700
77. G G Freeman, P W Harland, M J McEwan *Mon. Not. R. Astron. Soc.*, 1979, **187** 441
78. F P Lossing, J L Holmes *J. Am. Chem. Soc.*, 1984, **106** 6917
79. S N Senzer, K P Lim, F M Lampe *J. Phys. Chem.*, 1984, **88** 5314
80. V D Nefedov, E N Sinotova, M A Toropova *Khimicheskie Posledstviya Radioaktivnogo Raspada* (Chemical Results of Radioactive Decay), Energoizdat, Moscow, 1981, p. 104
81. V D Nefedov, E N Sinotova, M A Toropova *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk.*, 1980, (3) 35
82. M Speranza *Gazz. Chim. Ital.*, 1983, **113** 37
83. F Cacace *Adv. Chem. Sci.*, 1981, **97** 33
84. V D Nefedov, M A Toropova, T P Simonova, et al. *Zh. Org. Khim.*, 1989, **25** 136
85. M Attina, F Cacace, R Cipollini, et al. *J. Am. Chem. Soc.*, 1985, **107** 4824
86. G Angelini, Y Keheyan, G Lilla, et al. *Gazz. Chim. Ital.*, 1989, **119** 107
87. V D Nefedov, E N Sinotova, V P Lebedev, et al. *Radiokhimiya*, 1985, **27** 144
88. S Fornarini, M Speranza *Tetrahedron Lett.*, 1984, **25** 869
89. G Angelini, M Hanack, J Vermehren, et al. *J. Am. Chem. Soc.*, 1988, **110** 1298
90. S Fornarini, M Speranza *J. Am. Chem. Soc.*, 1985, **107** 5358
91. S Fornarini, M Speranza *J. Phys. Chem.*, 1987, **91** 2154
92. S Fornarini, M Speranza *J. Am. Chem. Soc.*, 1989, **111** 7402
93. L A Curtiss, J A Pople *J. Chem. Phys.*, 1988, **88** 7405
94. Z Rappoport, J Kaspi, Y Apeloig *J. Am. Chem. Soc.*, 1974, **96** 2612
95. Z Rappoport, A Gal *J. Chem. Soc., Perkin Trans. 2*, 1973, 301

96. Z Rappoport, J Kaspi *J. Am. Chem. Soc.*, 1974, **96** 4518
97. Z Rappoport, Y Apeloig *J. Am. Chem. Soc.*, 1975, **97** 836
98. Z Rappoport, A Gal *J. Org. Chem.*, 1972, **37** 1174
99. Z Rappoport, Y Apeloig, J Greenblatt *J. Am. Chem. Soc.*, 1980, **102** 3837
100. Z Rappoport, N Pross *J. Org. Chem.*, 1980, **45** 4309
101. Z Rappoport, J Kaspi, D Tsidoni *J. Org. Chem.*, 1984, **49** 80
102. C A Grob, R Nussbaumer *Helv. Chim. Acta*, 1971, **54** 2528
103. L Eckes, M Hanack *Chem. Ber.*, 1978, **111** 1253
104. F Marcuzzi, G Melloni *J. Am. Chem. Soc.*, 1976, **98** 3295
105. F Marcuzzi, G Melloni *Gazz. Chim. Ital.*, 1975, **105** 495
106. R Maroni, G Melloni, G Modena *J. Chem. Soc., Perkin Trans. 2*, 1974, 353
107. F Marcuzzi, G Melloni *J. Chem. Soc., Perkin Trans. 2*, 1976, 1517
108. Z Rappoport, Y Apeloig *J. Am. Chem. Soc.*, 1975, **97** 821
109. Z Rappoport, M Atidia *J. Chem. Soc., Perkin Trans. 2*, 1972, 2316
110. R M Roberts, M B Abdel-Basset *J. Org. Chem.*, 1976, **41** 1697
111. P J Stang, A G Anderson *J. Am. Chem. Soc.*, 1978, **100** 1520
112. P E Peterson *Acc. Chem. Res.*, 1971, **4** 407
113. G Hammen, M Hanack *Angew. Chem.*, 1979, **91** 649
114. M Hanack *Tetrahedron Lett.*, 1981, **22** 553
115. M Hanack *Pure Appl. Chem.*, 1984, **56** 1819
116. K P Bofinger, M Hanack *Chem. Ber.*, 1985, **118** 2993
117. M Hanck, I Harder *Chem. Ber.*, 1985, **118** 2974
118. Z Rappoport, P Schulman, M Thuval *J. Am. Chem. Soc.*, 1978, **100** 7041
119. K Yates, J Perie *J. Org. Chem.*, 1974, **39** 1902
120. C A Grob, H R Pfaendler *Helv. Chim. Acta*, 1971, **34** 2060
121. S G Entelis, R P Tiger *Kinetika Reaktsii v Zhidkoi Faze. Kolichestvennyi Uchet Vliyaniya Sredy* (Reaction Kinetics in the Liquid Phase. A Quantitative Determination of the Effect of the Medium), Khimiya, Moscow, 1973, p. 416
122. K Fukui *Angew. Chem.*, 1982, **94** 852
123. G Klopman *J. Mol. Struct., Suppl. Theochem.*, 1983, **103** 121
124. G Klopman (Editor) *Reactivity and Reaction Pathways* (Translated into Russian), Mir, Moscow, 1977, p. 384
125. V F Traven' *Elektronnaya Struktura i Svoistva Organicheskikh Molekul* (Electronic Structure and Properties of Organic Molecules), Khimiya, Moscow, 1989, p. 384
126. V P Lebedev, Candidate's Thesis in Chemical Sciences, Leningrad State University, Leningrad, 1986, p. 152
127. V D Nefedov, E N Sinotova, V P Lebedev, et al. *Zh. Org. Khim.*, 1988, **24** 90
128. V A Koptyug *Arenonievye Iony: Stroenie i Reaktionnaya Sposobnost'* (Arenonium Ions: Structure and Reactivity), Nauka, Novosibirsk, 1983, p. 270
129. V D Nefedov, E N Sinotova, V P Lebedev, et al. *Radiokhimiya*, 1987, **29** 73
130. F C Schadt, T W Bentley, P V R Schleyer *J. Am. Chem. Soc.*, 1976, **98** 7667
131. S Kobayashi, T Kitamura, H Taniguchi, et al. *Chem. Lett.*, 1983, 1117
132. S Kobayashi, Q Q Zhu, W Schnabel *Z. Naturforsch., B*, 1988, **43** 825
133. T Kitamura, M Murakami, S Kobayashi, et al. *Tetrahedron Lett.*, 1986, **27** 3885
134. T Kitamura, T Kabashima, S Kobayashi, et al. *Chem. Lett.*, 1988, 1951
135. T Kitamura, T Nakamura, T Kobashima, et al. *J. Chem. Soc., Chem. Commun.*, 1989, 1154
136. T Kitamura, T Kabashima, S Kobayashi, et al. *Tetrahedron Lett.*, 1988, **29** 6141
137. T Kitamura, R Furuki, H Taniguchi, et al. *Tetrahedron Lett.*, 1990, **31** 703
138. T Kitamura, T Nakamura, T Kobashima, et al. *J. Am. Chem. Soc.*, 1990, **112** 6149