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Reviews

ESR and quantum chemical studies of the structures and thermal transformations of the radical cations of vinylcyclopropane in irradiated frozen Freon matrices. Simulation of radical processes in solids

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Thermal transformations of vinylcyclopropane radical cations ($VCP^{\cdot+}$) in X-ray-irradiated frozen Freon matrices ($CFCl_2CF_2Cl$ and $CFCl_3$) were studied by ESR; radical processes involving $VCP^{\cdot+}$ in solid VCP were simulated. *Gauche*- and *anti*-$VCP^{\cdot+}$ were found to be the primary radical cations, however, the former, unlike the latter, is stable only under "gas-phase" conditions. The thermodynamic equilibrium between *anti*-$VCP^{\cdot+}$ and its less stable distonic form, *dist*(90,0)-$C_5H_8^{\cdot+}$, is established in frozen Freon matrices and the VCP host matrix; the structure of *dist*(90,0)-$C_5H_8^{\cdot+}$ is stabilized by a molecule of *anti*-VCP. In $CFCl_3$, along with *dist*(90,0)-$C_5H_8^{\cdot+}$, π-dimeric resonance [*anti*-VCP]$_2^{\cdot+}$ complex was detected. A general scheme of the transformations of $VCP^{\cdot+}$ in the solid phase has been proposed.

Key words: radiolysis, Freon matrices; vinylcyclopropane, primary radical cations, distonic radical cation, dimeric radical cation; thermal rearrangement; solid phase; ESR; quantum chemical analysis.

Introduction

Compounds containing a cyclopropane ring are used extensively in synthesis[1] and are often used as models for investigating problems of theoretical organic chemistry.[2] Considerable attention has been attracted by diamagnetic and paramagnetic intermediates of numerous rearrangements of cyclopropane derivatives: carbocations,[3] carbanions,[4] and neutral[5,6] and charged[7,8] free radicals. In particular, it is customarily believed that

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radical cations (RC) are the main intermediates in oxidation processes occurring in both the gaseous and condensed phases.[9]

According to a rather well established opinion,[10] in the gas phase and in the condensed phase hydrocarbon RC behave in a similar way. This statement leads one to believe that the behavior established for the transformations of RC under the conditions of mass spectrometry also holds for the more complex processes occurring during the radiolysis of hydrocarbons in condensed states.[10] However, there are strong reasons to believe that the chemical behavior of the hydrocarbon RC depends essentially on the physical state of the substance. Among the examples which demonstrate this dependence are RC of the vinylcyclopropane series, which isomerize in the gas phase to give linear diene structures,[11] but only undergo rapid *cis-trans* rearrangement in the liquid state.[12]

Hydrocarbon RC possess high reactivity and are therefore only stable in the "separate" state, *i.e.*, when they are far enough removed from each other and from the starting neutral molecules. If only one neutral molecule is present in the nearest environment of an RC, it participates efficiently in ion-molecular processes. This means that, in contrast to the gas phase, the hydrocarbon RC, short-lived in a solid, cannot as a rule be detected in the condensed host matrix. Therefore, a direct comparison of the pathways of the transformations of hydrocarbon RC in the condensed and gas phases is impossible, since reliable data for the condensed phase are lacking. In addition, the reactions of RC in different media are usually studied by different physicochemical methods, which also hampers the direct comparison of the results obtained.

In order to overcome the above-mentioned difficulties, the ESR method was used to register the hydrocarbon RC in Freon matrices frozen at low temperatures. The matrices were preliminarily subjected to γ- or X-ray irradiation at 77 K.[13] Freon-113 ($CFCl_2CF_2Cl$) is widely used for simulating radical reactions of RC in condensed media. When the concentration of the additive is increased from 1.0 to 20.0 mol. %, the probability that a starting neutral molecule will be present in the local environment of the RC increases; in the limiting case (~98 mol. %) this corresponds to a hydrocarbon host matrix. Increasing the temperature also results in an increase in the efficiency of the ion-molecular reactions which occur, as a rule, near the temperature of the "glass—semicrystal" type phase transition (110±5 K), owing to the defrosting of the diffusive mobility of molecules and RC. The fact that it is possible to obtain well-resolved structurally-informative spectra of the RC and neutral radicals in some cases allows a detailed study of the mechanisms of these processes to be carried out.

On the other hand, the Freon-11 ($CFCl_3$) matrix remains polycrystalline and "diffusionally rigid" over the whole temperature interval used (77—160 K). At the same time the rotary mobility of the RC in this matrix increases as the temperature is increased. For these reasons Freon-11 is widely used for simulating thermal transformations of RC in the gas phase. For this purpose dilute solutions (< 1.0 mol. %) are used.

Experimental studies of the temperature, concentration, and other dependences of the ESR spectra do not always allow one to judge with confidence the electron structure, spin distribution, and the structural peculiarities of the transformations of the RC under consideration in a particular matrix. Substantial assistance may be provided by the corresponding quantum chemical calculations[14,15] which, as a rule, considerably increase the structural information content of the ESR spectra.

Using precisely this unified approach we have simulated thermal transformations of the $VCP^{\cdot+}$ RC in the gas and condensed phases. The radiospectroscopic and quantum chemical data obtained allowed us to consider in detail the most probable mechanisms of the formation, stabilization, and transformation of these RC. In the present work, we generalize the peculiarities of the behavior of $VCP^{\cdot+}$ in a solid.

The procedure for simulation of thermal transformations of hydrocarbon RC in solids

Vinylcyclopropane was synthesized and purified according to the procedures described previously.[16] The method for the purification of $CFCl_2CF_2Cl$ and $CFCl_3$ (Freon-113 and Freon-11, respectively) is given in the literature.[17] Solutions of VCP in Freons (concentration varying from 1.0 to 20.0 mol. %) in ampules of SK-4B glass (which does not exhibit an ESR signal upon irradiation) were evacuated to 10^{-4} Torr and X-irradiated at 77 K (a dose of 0.5 Mrad). The ESR spectra were recorded at temperatures between 77 and 160 K. The field was calibrated using the Mn^{2+} lines in MgO. The computer simulation of the isotropic ESR spectra was carried out by means of an original program.[9]

The peculiarities of using glass-like (Freon-113) and polycrystalline (Freon-11) matrices have been comprehensively described previously.[18] The action of γ- or X-ray radiation leads initially to ionization of the Freon molecules (Eq. (1)). Then the positive charge is transferred to molecules of the additive having a lower ionization potential (indirect ionization, Eq. (2)). The resulting hydrocarbon RC are stabilized in the frozen Freon environment.

In this work the simulation of the ion-molecular reactions of the hydrocarbon RC in their own condensed medium was carried out using Freon-113. As the concentration of the additive in the Freon solution is increased (from 1.0 to 20.0 mol. %) or the solution is heated to 110±5 K (the temperature at which the local (10—20 Å) diffusive mobility of molecules and their RC defrost), the proportion of RC, containing at least one starting molecule in their local environment, increases. In this case the ion-molecular reactions which cause the corresponding changes in the ESR spectra occur efficiently.

When all of the C—H bonds in the molecule are of the C(sp^3)—H type (as is the case, for example, with normal and branched alkanes),[19] then a RC eliminates the proton that bears the highest positive spin density. The final products of this ion-molecular reaction (Eq. (3)) are a neutral radical and a protonated molecule. If all of the C—H bonds in the starting molecule are of the C(sp^2)—H or C(sp)—H type (as, for example, in ethylene, benzene, or acetylene),[20—24] then the π-dimeric RC, π-$[RH]_2^{\cdot+}$, is formed, which can be further converted to a σ-bonded structure, σ-$["RH"]_2^{\cdot+}$ (Eqs. (4) and (5)). When there are C—H bonds of both types (C(sp^3)—H and C(sp^2)—H or C(sp)—H) in the molecule, deprotonation (3) is preceded by the formation of the π-$[RH]_2^{\cdot+}$ π-dimeric RC (see Refs. 21, 24).

$$\text{Freon} \rightsquigarrow \text{Freon}^{\cdot+} \qquad (1)$$

$$\text{Freon}^{\cdot+} \longrightarrow \text{RH}^{\cdot+} \qquad (2)$$

$$\text{RH}^{\cdot+} + \text{RH} \longrightarrow \text{R}^{\cdot} + \text{RH}_2^{+} \qquad (3)$$

$$\text{RH}^{\cdot+} + \text{RH} \longrightarrow \pi\text{-}[\text{RH}]_2^{\cdot+} \longrightarrow \sigma\text{-}[\text{"RH"}]_2^{\cdot+} \qquad (4), (5)$$

For the investigation of the conformational peculiarities of the chemical behavior of hydrocarbon RC we used Freon-11. The concentration of the additive was 1.0—20.0 mol. %. In contrast to the Freon-113 matrix, the Freon-11 matrix allows the RC to adopt a conformation closer to that existing in the gas phase and retains the ratio between monomeric, dimeric, and cluster structural forms during heating of the sample. This makes it possible to study the thermal transformations of each of the forms independently.

The ESR spectra of X-irradiated concentrated solutions of VCP in $CFCl_2CF_2Cl$

Figure 1 presents the ESR spectra recorded at 77 K of solutions of VCP in Freon-113 at three different concentrations irradiated with X rays at 77 K. As the concentration of VCP increases, the spectra change substantially. However, they are not resolved enough for reliable interpretation to be carried out.

Well-resolved ESR spectra are recorded for samples heated to 100—113 K (Fig. 2). The spectrum at 113 K is a triplet of triplets with the following absolute values of the constants: $|a_1(2\ H(\alpha))| = 22.7$ Oe, $|a_2(2\ H(\beta))| = 30.4$ Oe (see Fig. 2, *c*) which are typical of *n*-alkyl radicals of the type $^{\cdot}CH_2CH_2Z$ (where Z is any neutral or charged substituent), provided the β-protons are equivalent and $\theta_1 = \theta_2 = 30°$ (where θ_i is the angle between the axis of the unpaired electron π-orbital and the C—H(β) bond). However, the hyperfine coupling constants (HFC) with the β-protons are somewhat lower than would be expected from the known relationship, $a(H(\beta)) = B\rho < \cos^2\theta >$ at the $B\rho$ product values typical of *n*-alkyl radicals,[25] *i.e.*, about 46—50 Oe, which may be explained by kinetic effects caused by the momentary nonequivalence of the β-protons. In particular, it is known[26] that a decrease in the effective HFC constants at the H(β) proton caused by the moderate frequency of this molecular motion is accompanied by a characteristic change in the widths (ΔH) and relative intensities of the components of the spectrum.

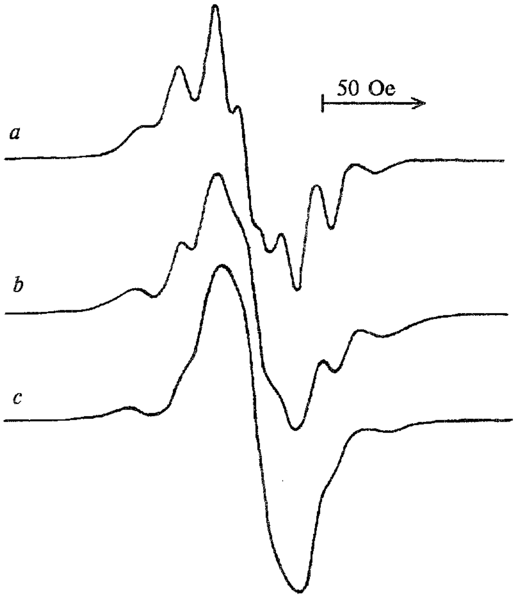


Fig. 1. The ESR spectra of X-irradiated (0.5 Mrad) solutions of VCP in $CFCl_2CF_2Cl$ recorded at 77 K. Concentration (mol. %): 98.5 (*a*); 10.0 (*b*); 1.0 (*c*).

In fact, the ratio between the intensities of the components of triplets with great splitting deviates from binomial (1 : 2 : 1) and amounts to 1 : 1 : 1. When the temperature is decreased from 113 to 100 K, $a_2(2\ H(\beta))$ increases to 32.4 Oe, while $a_1(2\ H(\alpha))$ decreases to 20.7 Oe. Such a temperature dependence of the constants of the HFC with the H(β) nuclei, together with the deviation of the line intensities from the binomial ratio, are well known for $^{\cdot}CH_2CH_2Z$-type radicals[27] and result from the dynamic broadening of the central component of the triplet for 2 H(β) owing to the "rocking" of the C(β)H_2 group in relation to the C(α)H_2 group. A decrease in the spin density at the H(α) proton means that this intramolecular motion is accompanied by delocalization of the spin density over the p-orbitals of the β- and γ-carbon atoms in the C(α)C(β)C(γ) plane. The total length of the spectrum does not change, which is in agreement with the opposite signs of the a_1(H) and a_2(H) constants. Since the absolute value of a_2(H) is far more than 23 Oe, we should ascribe to it the positive sign.[14]

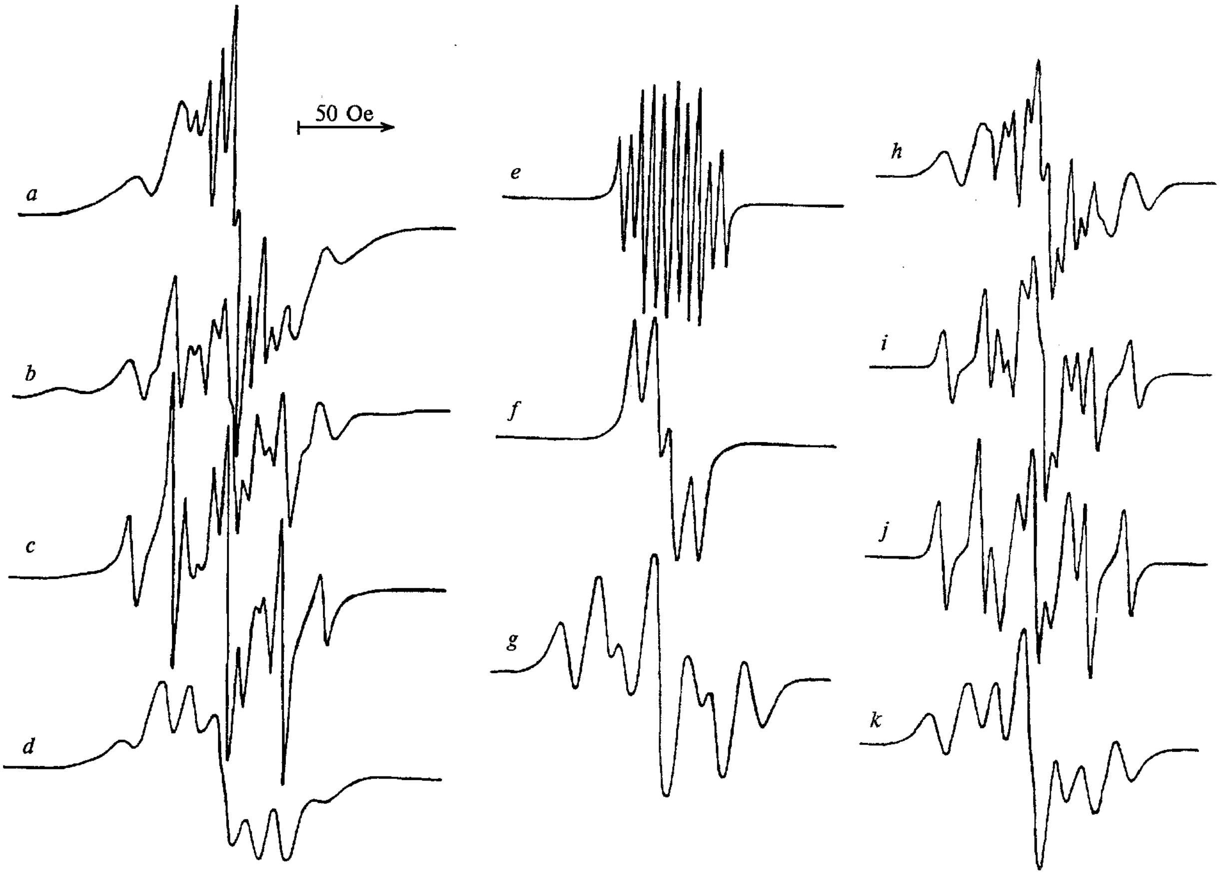


Fig. 2. The ESR spectra of a solution of VCP in $CFCl_2CF_2Cl$ (1.0 mol. %) X-irradiated (0.5 Mrad) at 77 K, recorded at 100 K (*a*), 110 K (*b*), 113 K (*c*), at 100 K after heating to 113 K (*d*). The individual simulated ESR spectra of *gauche*-$VCP^{\cdot +}$ (*e*): a_1(2 H) = 13.0 Oe, a_2(1 H) = 7.3 Oe, a_3(1 H) = 26.0 Oe, ΔH = 3.0 Oe (with Lorentzian contribution, L = 0.2); *anti*-$VCP^{\cdot +}$ (*f*): a_1(2 H) = 13.0 Oe, a_2(1 H) = 7.3 Oe, a_3(1 H) = 2.7 Oe, ΔH = 6.0 Oe (with L = 0.2); *dist*(90,0)-$C_5H_8^{\cdot +}$ (*g*): a_1(2 H) = 20.7 Oe, a_2(2 H) = 32.4 Oe, a_3(1 H) = 3.0 Oe, ΔH = 10.0 Oe (with L = 0.3); *dist*(90,0)-$C_5H_8^{\cdot +}$ (*j*): a_1(2 H) = 22.7 Oe, a_2(2 H) = 30.4 Oe, ΔH = 5.0 Oe (with L = 0.2) and ΔH = 6.3 Oe (with L = 0.2) for the central and outer components of the triplets with great splitting, respectively. Simulated spectra *h*—*k* correspond to experimental spectra *a*—*d*. The ratio of the fractions of *gauche*- (*e*) : *anti*- (*f*) : *dist*(90,0)- (*g*) $VCP^{\cdot +}$ is 0.040 : 0.192 : 0.768 (*h*), 0.0 : 0.4 : 0.6 (*i*), and 0.0 : 0.2 : 0.8 (*k*).

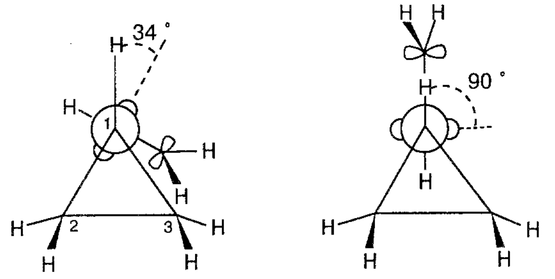
At the same time, in the central part of the spectrum recorded at 100 K after heating the sample to 113 K (see Fig. 2, *d*), a symmetrically located doublet appears, instead of a series of narrow lines. After the above-noted irreversible transformation of the ESR spectra (see Fig. 2, *a, d*) caused by heating the sample to 113 K (see Fig. 2, *c*), the subsequent changes in the spectra occurring in the temperature range 77—113 K (see Fig. 2, *c, d*) are completely reversible. Lowering the temperature results in the broadening of the lines for both types of radicals present in the system, and the portion of the *n*-alkyl radical $^{\cdot}CH_2CH_2Z$ reversibly decreases. This indicates a reversible reaction occurring between the two types of radicals.

The ESR spectra of solutions of VCP in Freon-113 recorded at 77 K and X-irradiated at 77 K, are poorly resolved (see Fig. 1). As the concentration of VCP decreases from 98.5 to 1.0 mol. %, the portion of the extended septet component sharply decreases, while the contribution from the unresolved broad singlet located in the central part of the spectrum increases. This means that the former component is caused by radicals produced from VCP clusters or dimers, and the latter is associated with radicals of monomolecular origin. However, due to low resolution, the ESR spectra under consideration cannot be directly identified, and become informative only in combination with the results of the analysis of ESR spectra recorded at higher temperatures (see Fig. 2).

At 100 K, instead of the central broad singlet (see Fig. 1, *c*), a series of narrow lines appear in the ESR spectrum of an X-irradiated solution of VCP (1.0 mol. %) in Freon-113 (see Fig. 2, *a*) and there is a simultaneous increase in the intensity of broader lines which correspond, according to their shape and position, to the two terminal components of the septet constituent (see Fig. 1, *a*) of the spectrum. This series of lines, which irreversibly disappears when the sample is heated to 105 K, has the following set of a_{iso}(H) constants: 13.0 Oe (2 H), 7.3 Oe (1 H), and 26.0 Oe

(1 H) and is associated with the monomeric VCP$^{\cdot +}$. The constants a_{iso}(H) = 13.0 Oe (2 H) and 7.3 Oe (1 H) are characteristic of HFC with α-protons when the single-occupied MO is localized at the π-system of the planar vinyl group (Table 1, radicals **1—7**, **13**), while a_{iso}(H) = 26.0 Oe (1 H) points to the prevalence of the delocalization mechanism in the formation of the spin density ρ_sH(β) > 0 at the β-proton.[14,15] Such distribution of the spin density occurs in the *gauche*-VCP$^{\cdot +}$ (**7**) which forms upon ionization of a *gauche*-VCP molecule. The orientation of the C(1)—H chemical bond in the cyclopropane moiety with respect to the p-AO axis of the neighboring carbon atom of the vinyl group in the *gauche*- and *anti*-conformations of the starting VCP molecules (34° and 90°, respectively)[40] is presented in Scheme 1.

Scheme 1



The series of narrow lines has a considerably lower integral intensity than the broad septet spectrum. Since for the separate broad singlet the intensity is markedly higher, *gauche*-VCP$^{\cdot +}$ cannot be the prevailing monomeric RC. Under the experimental conditions considered, only *anti*-VCP$^{\cdot +}$ (**6**) can act as the major primary RC. In fact, in the crystalline state VCP exists exclusively as the more stable *anti*-conformer.[39,40] Even after increasing the temperature to 293 K and transition to the gaseous phase, the portion of *gauche*-VCP is still considerably lower than that of *anti*-VCP (0.25 and 0.75, respectively).[40] Thus, in a frozen Freon matrix that fixes the conformational composition of VCP, the vast majority of the molecules have the *anti*-conformation. Since at temperatures < 105 K the glass-like Freon-113 matrix rigidly prevents internal molecular rotations,[18] at 100 K the matrix imposes the conformation of the molecular precursor, VCP, on the primary RC. Therefore, in a Freon-113 matrix at 100 K (see Fig. 1, *a*) *anti*-VCP$^{\cdot +}$ should predominate, and only a minor admixture of *gauche*-VCP$^{\cdot +}$ is possible.

When the sample is heated above 105 K, the loss of the *gauche*-VCP$^{\cdot +}$ admixture occurs. As a result, additional doublet constituents appear in the central part of the spectrum, instead of the series of narrow lines corresponding to *gauche*-VCP$^{\cdot +}$. The shapes of the ESR spectra recorded at 110 K (see Fig. 2, *b*) and at 100 K after heating the sample to 113 K (see Fig. 2, *d*) are the most characteristic. In the latter case the spectrum is the combination of the former triplet of triplets (the $^{\cdot}CH_2CH_2Z$ radical with two equivalent β-protons, at $\theta_1 = \theta_2 = 30°$, see Fig. 2, *c*) and a new equally broadened doublet which we assign to *anti*-VCP$^{\cdot +}$.

Unlike the ESR spectra of *gauche*-VCP$^{\cdot +}$ and $^{\cdot}CH_2CH_2Z$, the spectrum of *anti*-VCP$^{\cdot +}$ is poorly resolved and does not appear individually. We take the $|a_{iso}(H)|$ constants to be 13.0 Oe (2 H) and 7.3 Oe (1 H), *i.e.*, the same as those for *gauche*-VCP$^{\cdot +}$. The $|a_{iso}(H)|$ constant for the proton at the C(1) atom of the cyclopropane ring was chosen to be 2.7 Oe (1 H), which corresponds to the average value for similar protons in the RC of butadiene (see Table 1, radical **3**) and in the cyclopropylmethyl radical (see Table 1, radical **8**).

Individual simulated ESR spectra of the isomeric VCP$^{\cdot +}$ are given in Fig. 2, *e—g, j*. A superposition of these spectra (see Fig. 2, *h, i, k*) gives a good reproduction of the experimental ESR spectra including the position and shape of lines associated with *anti*-VCP$^{\cdot +}$ (see Fig. 2, *a—d*). The imperfect correspondence between the experimental (see Fig. 2, *d*) and the simulated (see Fig. 2, *k*) spectrum may be explained by an admixture of the broad component from the matrix radicals, which is present in the experimental spectrum and was not taken into account in the simulation.

The a_{iso}(H) constants calculated for *anti*-VCP$^{\cdot +}$ (−12.4 Oe (2 H), −5.2 Oe (1 H), and −1.1 Oe (1 H)) and *gauche*-VCP$^{\cdot +}$ (−12.2 Oe (2 H), −7.6 Oe (1 H), and 26.0 Oe (1 H)) by the MNDO-UHF method are close to the corresponding experimental a_{iso}(H) presented above. The results of quantum chemical calculations will be considered in more detail in the next work devoted to the simulation of radical reactions in the gaseous phase.

Over the temperature range 77—113 K the radical $^{\cdot}CH_2CH_2Z$ is in equilibrium with the radical corresponding to the doublet in the ESR spectrum, *i.e.*, with *anti*-VCP$^{\cdot +}$. Therefore, $^{\cdot}CH_2CH_2Z$ is also a radical cation. We identify it as the distonic form of VCP$^{\cdot +}$ (**12**), *i.e.*, assume Z to be $CHCHCH_2^+$ (Scheme 2).* Radical

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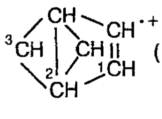
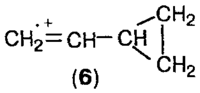
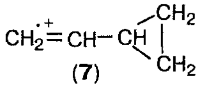
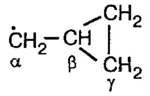
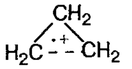
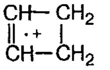
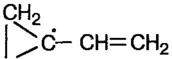
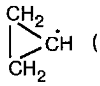
* For distonic RC **12** (the radical and cation sites are separated by a chain of methylene groups $(CH_2)_n$)[41] we write *dist*(90,0)-$C_5H_8^{\cdot +}$ where the dihedral angles are given in parentheses (see Ref. 42): $\tau_r = 90°$ between the plane normal to the H(α)C(α)H(α) plane and the C(β)—C(γ) chemical bond in the C(α)—C(β)—C(γ) "cyclopropane—trimethylene" moiety with the radical site at the terminal methylene group,[43] and $\tau_c = 0°$ for the cation moiety of the allyl system Z = C(γ)HC(δ)HC(ε)H_2^+. With this designation, normals to the H(α)C(α)H(α) and H(γ)C(γ)C(δ) planes coincide with the p-AO axes of the sp^2-hybridized C(α) and C(β) carbon atoms in **12**, and the rotation angles of the C(α)H_2 group and the allyl fragment Z with respect to their original positions in the cyclic form are τ_r and τ_c, respectively.

Table 1. Parameters of the ESR spectra of radical cations VCP$^{\cdot +}$ and related radicals

Radical	Matrix	Temperature /K	g-Factor	$\lvert a_{iso}(H)\rvert$ constants/Oe	Literature
$CH_2{=}CH_2{}^{\cdot +}$ (**1**)	—	—	—	3.0 (4 H)[b]	28
$CH_2{=}CH{-}CH_3{}^{\cdot +}$ (**2**)	$CFCl_3$	77	2.0033(3)	23.0, 12.0 ($CH_2{=}$); 7.0 ($CH{=}$); 24.0 (CH_3)	27—29
	$CFCl_3$	130	—	16.0, 9.0 ($CH_2{=}$); 9.0 ($CH{=}$); 24.0 (CH_3)	27,29
	$CFCl_2CF_2Cl$	77	—	23.5, 11.0 ($CH_2{=}$); 6.0 ($CH{=}$); 23.5 (CH_3)	27,30
$CH_2{=}CH{-}CH{=}CH_2{}^{\cdot +}$ (**3**)	$CFCl_3$	130	2.0029(2)	11.2 (2 H(*exo*)); 10.5 (2 H(*endo*)); 2.8 (2 H)	31
$CH_2{=}CH{-}Ph^{\cdot +}$ (**4**)	$CFCl_3$	77	—	10.0 ($CH_2{=}$); 10.0 (1 H(*p*-H))	32
 (**5**)	CF_3CCl_3	115	2.0029(1)	8.4 (2 H(1)); 1.6 (2 H(2)); 27.9 (2 H(3))	33
 *anti*- (**6**)	$CFCl_2CF_2Cl$[a]	100	2.0034(4)	13.0 ($CH_2{=}$); 7.3 ($CH{=}$); 2.7 (1 H)[c]	e
	$CFCl_3$	150	2.0034(4)		
 *gauche*- (**7**)	$CFCl_2CF_2Cl$	100	2.0034(4)	13.0 ($CH_2{=}$); 7.3 ($CH{=}$); 26.0 (1 H)	e
	$CFCl_3$	150	2.0034(4)	10.7 ($CH_2{=}$); 6.4 ($CH{=}$); 26.8 (1 H)	e
 (**8**)	*cyclo*-C_3H_5Me	123	—	20.7 (2 H(α)); 2.6 (1 H(β)); 3.0 (2 H(γ), *anti*-); 2.0 (2 H(γ), *syn*-)	34
$^{\cdot}CH_2{-}CH_2{-}CH{=}CH_2$ (**9**)	*cyclo*-C_3H_6	168	—	22.2 (2 H(α)); 28.5 (2 H(β))[d]	34
 (**10**)	$CFCl_2CF_2Cl$	4.2	2.0040	12.5 (4 H(α)); 21.0 (2 H(β))	35,36
	$CFCl_3$	4.2	2.0040	11.0 (4 H(α)); 21.0 (2 H(β))	35,36
$^{\cdot}CH_2{-}CH_2{-}CH_2{}^{+}$ (**11**)	$CFCl_2CF_2Cl$	108	2.0028	22.7 (2 H(α)); 30.2 (2 H(β))	7,37
$\dot{C}H_2{-}CH_2{-}CHCH\overset{+}{C}H_2$ (*dist*(90,0)-$C_5H_8^{\cdot +}$) (**12**)	$CFCl_2CF_2Cl$	113	2.0034(4)	22.7 (2 H(α)); 30.4 (2 H(β))	e
 (**13**)	$CFCl_3$	130	2.0030(2)	11.1 (2 H(α)); 28.0 (4 H(β))	38
 (**14**)	$CFCl_3$	77	—	24.7 (4 H(β)); 12.1 (1 H(β))	e
 (**15**)	SF_6	4.2	—	23.5 (4 H(β)); 7.0 (1 H(α))	35
	cyclo-C_3H_6	193	—	23.4 (4 H(β)); 6.5 (1 H(α))	44

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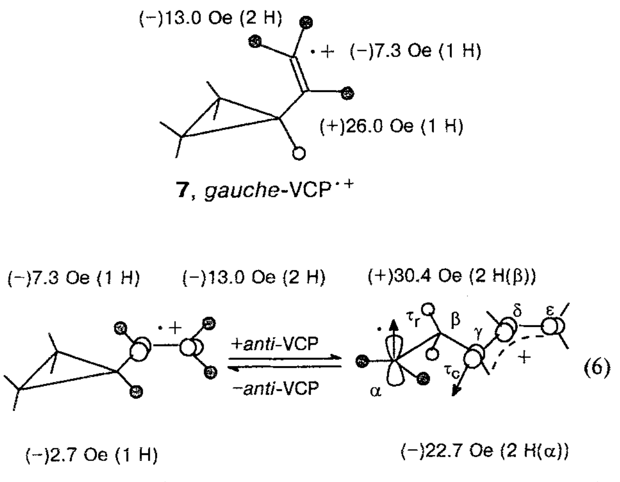
[a] Solutions of VCP in Freons were subjected to X-ray irradiation in a dose of 0.5 Mrad at 77 K, the concentration of VCP in Freon $CFCl_2CF_2Cl$ was 1.0 mol. % (for radicals **6**, **7**, **12**), that in $CFCl_3$ was 0.1 mol. % (for **7**). [b] The twist angle for the C=C double bond is 25° for **1**, 17.2° for **2** (see Ref. 28) and 0° in the remaining cases. [c] The estimated parameters. [d] The $\theta_1 = \theta_2$ angles in the relationship $a_{iso}(H(\beta)) = B\rho\langle\cos^2\theta\rangle$ are close to 30° for radicals **9**, **11**—**13**. [e] The present work.

cation **12** has the same configuration of β-protons ($\theta_1 = \theta_2 = 30°$) as the distonic RC of cyclopropane, the homoallyl radical, and RC of cyclobutene (see Table 1, radicals **11**, **9**, and **13**, respectively). We denote the distonic VCP$^{\cdot +}$ with $\theta_1 = \theta_2 = 30°$ by *dist*(90,0)-$C_5H_8{}^{\cdot +}$. The septet spectrum of an X-irradiated solution of VCP in Freon (see Fig. 2, *d*), which is a combination of the lines from *dist*(90,0)-$C_5H_8{}^{\cdot +}$ and *anti*-VCP$^{\cdot +}$, is qualitatively analogous to the spectrum of X-irradiated VCP containing 1.5 mol % of Freon-113 (see Fig. 1, *a*). This means that in both Freon-113 and the host VCP matrix, process (6) (see Scheme 2) occurs either in an ionized cluster of VCP molecules or at least in the complex of *anti*-VCP$^{\cdot +}$ with a neutral *anti*-VCP molecule. The bimolecular character of the formation of the *dist*(90,0)-$C_5H_8{}^{\cdot +}$ RC is indicated by the fact that its content increases when the starting concentration of the solution of VCP in Freon-113 is increased. The portion of *anti*-VCP, which, as Figure 1, *a* indicates, is stable at 77 K in the host VCP matrix, increases simultaneously.

Scheme 2



7, *gauche*-VCP$^{\cdot +}$

(6)

6, *anti*-VCP$^{\cdot +}$

12, *dist* (90,0)-$C_5H_8{}^{\cdot +}$

Thermodynamic equilibrium (6) depends on the temperature of the sample. The simulation of the ESR spectra recorded at 105, 100, and 77 K for a solution of VCP in Freon-113 (1.0 mol. %), X-irradiated at 77 K and heated to 113 K, gives *dist*(90,0)-$C_5H_8{}^{\cdot +}$/ *anti*-VCP$^{\cdot +}$ ratios equal to 4.88, 4.00, and 2.57, respectively. When the spectra of *anti*-VCP$^{\cdot +}$ (see Fig. 2, *f*) and *dist*(90,0)-$C_5H_8{}^{\cdot +}$ (see Fig. 2, *g*) are combined, their mutual contributions to the intensities of the lines between the central and terminal components of the resulting spectra (see Fig. 2, *d, k*) are negligibly small. These lines were used for determining the portions of *anti*-VCP$^{\cdot +}$ and *dist*(90,0)-$C_5H_8{}^{\cdot +}$ in the mixture of radicals.

The shift of equilibrium (6) over the temperature range 77—105 K is properly described by the Boltzmann dependence of the equilibrium constant, $K = [dist(90,0)\text{-}C_5H_8{}^{\cdot +}]/[anti\text{-}VCP^{\cdot +}]$, on the temperature. In ln K *vs* T^{-1} coordinates, the experimental points fall on a straight line, whose slope implies that *anti*-VCP$^{\cdot +}$ is more stable than *dist*(90,0)-$C_5H_8{}^{\cdot +}$ by 0.35 kcal mol^{-1}.

The ESR spectra of X-irradiated concentrated solutions of VCP in $CFCl_3$

Figure 3 presents the ESR spectra of a frozen solution of VCP in $CFCl_3$ (20.0 mol. %) irradiated with X-rays. The ESR spectra recorded at 77 K, immediately after the irradiation of the solutions, do not vary qualitatively over a wide concentration region (0.01—20.0 mol. %) and are caused by a mixture of the radicals present in the sample. As the concentration of VCP in Freon-11 increases, like in Freon-113, the portion of *dist*(90,0)-$C_5H_8{}^{\cdot +}$ in an equilibrium with *anti*-VCP$^{\cdot +}$ increases (see Figs. 1 and 3, *a*), together with that of the radical represented by a multiplet with small splitting (3.5 Oe) in the central part of the spectrum. Heating the sample to 100 K results in an irreversible increase in the resolution of this multiplet, which consists of no less than nine equidistant lines (see Fig. 3, *c*). The increase in the resolution of the central multiplet occurs against the background of the irreversible transformation of the lines from *dist*(90,0)-$C_5H_8{}^{\cdot +}$ into a new spectrum which may be interpreted as a quintet of doublets with splittings: a_1(4 H) = 24.7 Oe and a_2(1 H) = 12.1 Oe (see Fig. 3, *b*). The high-field part of the spectrum is poorly resolved and is not shown in Fig. 3, *b*. The subsequent changes in the ESR spectra of the samples in the temperature range 100—160 K are completely reversible.

We assign the multiplet of equidistant lines (no less than 9) with the splitting of 3.5 Oe to the resonance π-dimeric RC, [*anti*-VCP]$_2{}^{\cdot +}$, (**16**) having "head—tail" (HT) coordination (Scheme 3), because assuming multiple splittings a_1(4 H) = 7.0 Oe and a_2(2 H) = 3.5 Oe, the spectrum is presented by eleven lines (see Fig. 3, *d*), and the splitting itself is half as great as those for monomeric *anti*-VCP$^{\cdot +}$ [a_1(2 H) = 13.6 Oe and a_2(1 H) = 7.3 Oe (see Table 1)]. This ratio between the splitting for the monomeric and dimeric RC of alkenes[21] and alkynes[24] is rather typical and reliably established. The simulated spectrum (see Fig. 3, *e*) of the system which contains, along with *gauche*- and *anti*-VCP$^{\cdot +}$, an admixed portion (0.006) of [*anti*-VCP]$_2{}^{\cdot +}$, corresponds qualitatively (only a portion of the radicals of the mixture has been taken into account) to the ESR spectra of the irradiated solutions of VCP in Freon-11 at 77—100 K. As the temperature of the sample is increased from 100 to 150 K, reversible broadening of the lines from [*anti*-VCP]$_2{}^{\cdot +}$ occurs, which may be explained by an increase in the concentration of "monomeric" *anti*-VCP$^{\cdot+}$ in equilibrium with the dimer (see Scheme 3, HT).

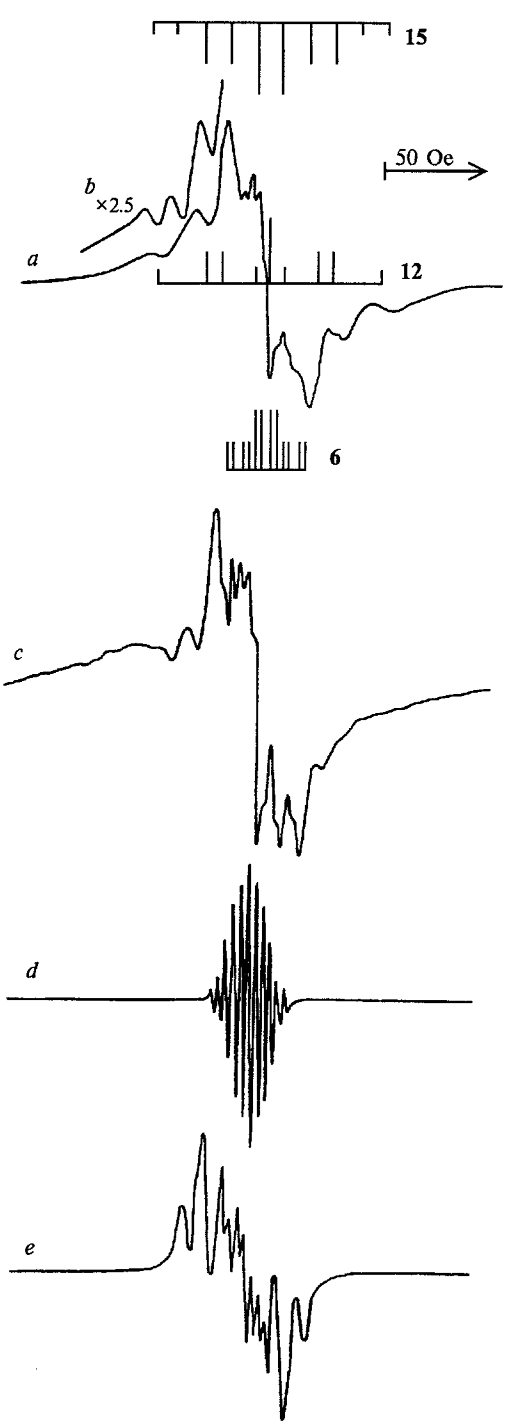


Fig. 3. The ESR spectra of a solution of VCP in $CFCl_3$ (20.0 mol. %) X-irradiated (0.5 Mrad) at 77 K, recorded at 77 K (*a*); at 77 K after heating to 135 K (*b*); at 100 K (heating from 77 K) (*c*). Simulated spectra of π-[*anti*-VCP]$_2^{\cdot+}$ (*d*): a_1(4 H) = 7.0 Oe, a_2(2 H) = 3.5 Oe, ΔH = 1.0 Oe (with L = 0.2); a mixture of *gauche*-, *anti*-, dimeric-VCP$^{\cdot+}$ in a ratio of 0.497 : 0.497 : 0.006 (*e*). For the parameters see spectra 2, *e*, *f* and 3, *d*.

We assign the quintet of doublets with splittings a_1(4 H) = 24.7 Oe and a_2(1 H) = 12.1 Oe (see Fig. 3, *b*) formed when the temperature of the sample is increased to 100 K to the 1-vinylcyclopropyl radical (**14**) (Scheme 4), because the value of 24.7 Oe for the four equivalent protons is close to the value (23.4—23.5 Oe)[35,44] known for the analogous four β-protons in cyclopropyl radical **15**. Since the formation of radical **14** is associated with the decay of *dist*(90,0)-$C_5H_8^{\cdot+}$ (see Fig. 3, *a*, *b*) we believe that when the temperature of the sample is increased to 100 K, radical substitution in the "dimeric" complex [*dist*(90,0)-$C_5H_8^{\cdot+}$...*anti*-VCP] (see Scheme 3) or in the cluster of molecules occurs, which consists of the transfer of a hydrogen atom from *anti*-VCP to the radical site of *dist*(90,0)-$C_5H_8^{\cdot+}$ (see Scheme 4, Eq. (7)).

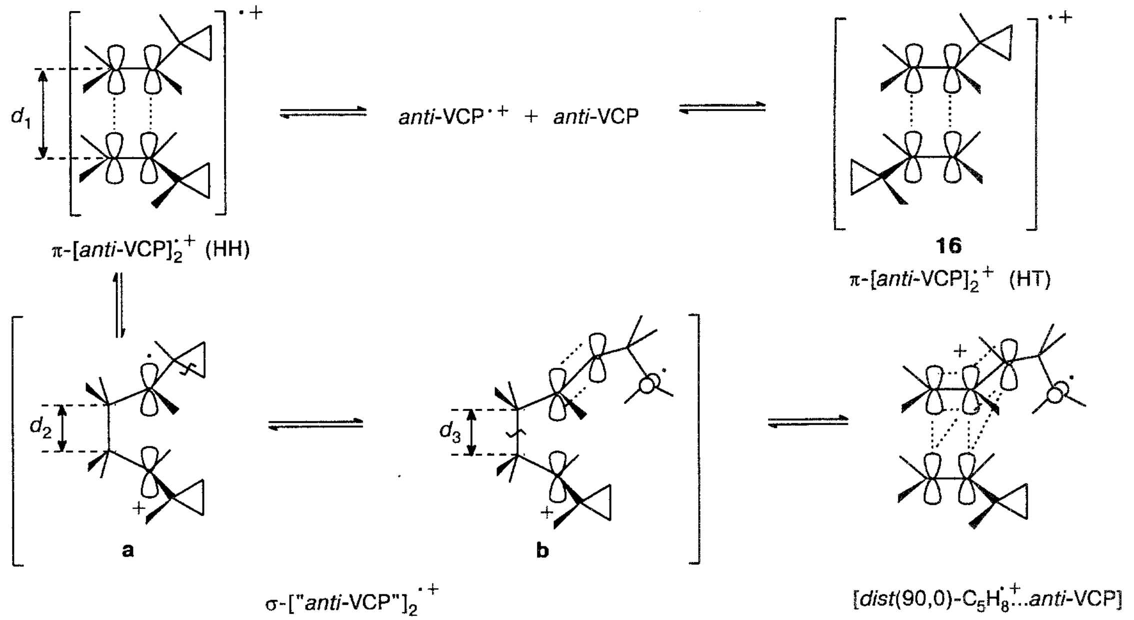
Primary *gauche*- and *anti*-VCP$^{\cdot+}$

The primary RC are *gauche*- and *anti*-VCP$^{\cdot+}$, however, their behavior in frozen Freon solutions is quite different. The *gauche*-VCP$^{\cdot+}$ radical is only stable under the "gas-phase" conditions (the peculiarities of its transformations will be described in another communication). When radical processes in condensed media are simulated (either the concentration of VCP in Freons-11 and -113 is increased or the temperature of the solution is increased to 105 K), *gauche*-VCP$^{\cdot+}$ is rapidly lost in ion-molecular reactions. On the other hand, *anti*-VCP$^{\cdot+}$ is stable even in its own matrix. This inertness of *anti*-VCP$^{\cdot+}$ in relation to the main types of ion-molecular transformations of RC (deprotonation (3), dimerization with the starting molecule (4), (5)) is rather unusual and is probably due to the relatively high strength of all of the C—H bonds in the VCP molecule and in its *anti*-VCP$^{\cdot+}$ RC, on one hand, and to thermodynamic equilibrium (6) between *anti*-VCP$^{\cdot+}$ and *dist*(90,0)-$C_5H_8^{\cdot+}$, on the other hand.

It is known[19] that deprotonation of RC usually involves the H(β) proton with the highest positive spin density. This is especially typical of the RC of normal and branched alkanes and of other RC containing such moieties. According to *ab initio* calculations in the extended basis sets of the 6-31 G** type with allowance made for the electron correlation,[45,46] all of the C—H bond lengths in normal and branched alkanes are close to 1.086 Å and are of the C(sp^3)—H type.[45] When the alkane is ionized, those of the C—H bonds whose protons acquire positive spin density in the RC, are substantially lengthened (for example, 0.045 Å in $C_2H_6^{\cdot+}$ (C_{2h}) when a_{iso}(H(β)) = 152.5 Oe)[46] and thus weakened. It is precisely these C—H bonds in the RC that undergo deprotonation in the course of the ion-molecular reaction.

VCP consists of vinyl and cyclopropyl moieties. All of the C—H bonds in cyclopropane and ethylene are shorter than those in normal and branched alkanes by 0.01 Å and are of the C(sp^2)—H type, and the

Scheme 3



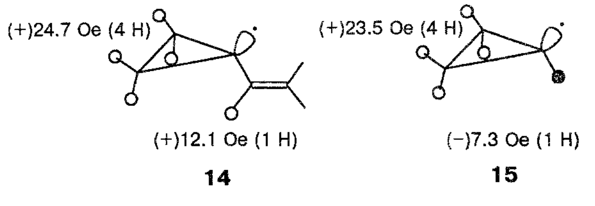
(H—C—H) bond angles between them are 115—117° (see Refs. 47, 48). For this type of C—H bonds located in the nodal plane of the single-occupied MO of *anti*-VCP$^{\cdot+}$, all of the a_{iso}(H) constants corresponding to α-protons should have a negative sign. In line with this, the *ab initio* calculations of a series of RC including the RC of cyclopropane (C_{2v}) have shown[43,46] that such C(sp^2)—H bonds in them are either the same as in the starting molecules or even somewhat shorter (by ~0.005 Å) and therefore stronger.

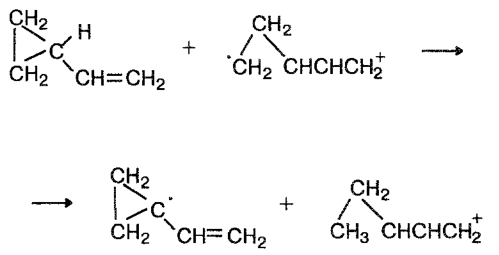
Thus, in *anti*-VCP$^{\cdot+}$, as in the starting molecule, the C—H bonds are not prone to the abstraction of a proton in the course of an ion-molecular reaction. For the same reason, in the case of ethylene[20] and butadiene[49] RC, dimerization with the starting molecule to give σ-bonded structures occurs much more efficiently. The inertness of *anti*-VCP$^{\cdot+}$ in relation to such ion-molecular transformations may be due to the fact that addition at the double bonds in dimer [*anti*-VCP$^{\cdot+}$...*anti*-VCP] or in a similar cluster is associated with the opening of the cyclopropane ring in the RC, *i.e.*, with the formation of *dist*(90,0)-$C_5H_8^{\cdot+}$. The distonic RC is a dimeric complex which, as has already been mentioned, is only 0.35 kcal mol^{-1} less stable than its noninteracting monomeric constituents, *anti*-VCP$^{\cdot+}$ and *anti*-VCP. Owing to the tendency of olefin RC to dimerize with the starting molecule and to the low stability of the [*dist*(90,0)-$C_5H_8^{\cdot+}$...*anti*-VCP] complex, equilibrium (6) is established, instead of the formation of stable σ-bonded dimeric structures.

Secondary *dist*(90,0)-$C_5H_8^{\cdot+}$

The *dist*(90,0)-$C_5H_8^{\cdot+}$ radical is formed through the ion-molecular dimerization of *anti*-VCP$^{\cdot+}$ and *anti*-VCP. Along with *dist*(90,0)-$C_5H_8^{\cdot+}$, we also detected the dimeric RC, π-[*anti*-VCP]$_2^{\cdot+}$ in the Freon-11 matrix. Increasing the temperature of the sample to 100 K results in the decay of *dist*(90,0)-$C_5H_8^{\cdot+}$ according to reaction (7), whereas π-[*anti*-VCP]$^{\cdot+}$ is stable up to 160 K. Over the temperature region 77—100 K the Freon-11 matrix presents substantially greater freedom than the Freon-113 matrix. This suggests that at 77 K in the Freon-11 matrix, which is rigid for macroscopic diffusion, *anti*-VCP molecules in dimeric "workpieces" [*anti*-VCP]$_2$ exist in no less than two considerably different mutual orientations incapable of interconversion. Taking into account the somewhat higher stability of *anti*-VCP$^{\cdot+}$ as compared with *dist*(90,0)-$C_5H_8^{\cdot+}$ and

Scheme 4





(7)

known analogies,[5,6,20,42,50–55] the mentioned peculiarities of the chemical behavior of *dist*(90,0)-$C_5H_8{}^{\cdot +}$ and π-[*anti*-VCP]$_2{}^{\cdot +}$ may be explained in terms of the same scheme of ion-molecular dimerization of *anti*-VCP$^{\cdot +}$ and *anti*-VCP.

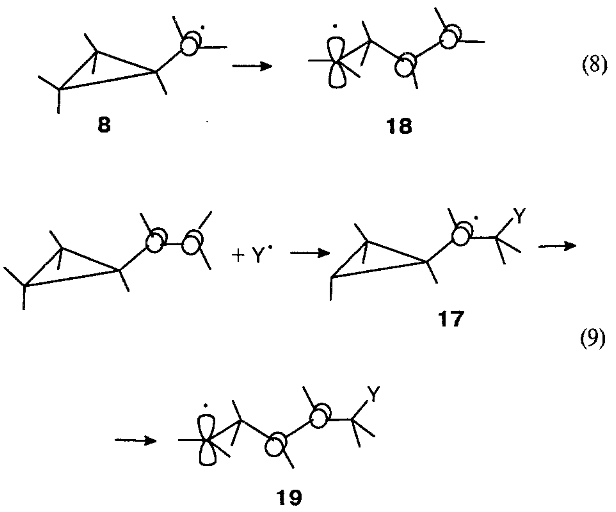
The above-presented Scheme 3 reflects the proposed equilibria between various dimeric structures including *anti*-VCP$^{\cdot +}$ and *anti*-VCP, with HT or "head—head" (HH) "cyclical" coordination. At the first step, the resonance π-dimeric RC π-[*anti*-VCP]$_2{}^{\cdot +}$ is formed [$d_1(CH_2...CH_2) \approx 2.5$ Å].[50] HT-type coordination gives structure **16**, which is not capable of subsequent transformations except for reversible decomposition to give the constituents, and can therefore be detected in Freon-11 by ESR. On the other hand, HH-type interaction leads to the activation of internal rearrangements, ending with the formation of the π-dimeric complex [*dist*(90,0)-$C_5H_8{}^{\cdot +}$...*anti*-VCP] which has also been detected in both Freon matrices by ESR.

As a result of HH-type coordination (see Scheme 3), a σ-dimeric 1,4-distonic RC structure, σ-["*anti*-VCP"]$_2{}^{\cdot +}$ (**a**), is initially formed [$d_2(CH_2—CH_2) \approx 1.6$ Å],[51] in which the $^{\cdot}$C-radical and $^{+}$C-cation sites are spaced ~1.9 Å apart and stabilized by the cyclopropane rings.[52] The formation of this 1,4-distonic structure of the RC is predicted by the theory for asymmetrical [2+1]-cycloaddition of the constituents of the π-dimeric complex $[CH_2{=}CH_2]_2{}^{\cdot +}$ and [2+3]-cycloaddition of ethylene to *cis*-1,3-butadiene RC, since the concerted reaction routes are in both cases forbidden for symmetry reasons.[52,53] It has been suggested[54] that the formation of the distonic RC should be regarded as the first stage of a series of very fast ion-molecular addition processes occurring in clusters, ionized in the gas phase, which incorporate no less than 3—6 molecules of ethylene or propylene. In irradiated Freon ($CFCl_2CFCl_2$, $CFCl_2CF_2Cl$, and CF_2ClCF_2Cl) solutions of ethylene (0.1—0.5 mol. %) the dimerization of its RC and its molecule followed by the 1,3-hydride shift to give the RC of 1-butene was registered[20] when the samples were heated to 100 K.

In the resulting σ-["*anti*-VCP]$_2{}^{\cdot +}$ (1,4-distonic RC) structure **a** the radical and cation sites separated by the two-carbon methylene chain are stabilized by cyclopropane rings to different degrees. The stabilization energies for the cyclopropylmethyl radical and cation are known[6] to be 0—5 and 18 kcal mol^{-1}, respectively. Therefore, at the next step relatively easy opening of the ring at the radical site of σ-["*anti*-VCP"]$_2{}^{\cdot +}$ is possible. On the other hand, similar opening of the cyclopropane ring at the cation site of σ-["*anti*-VCP"]$_2{}^{\cdot +}$ is unlikely, owing to the considerably higher stability of the cyclopropylmethyl cation moiety in the polar Freon-11 and -113 matrices.

The cyclopropylmethyl radical (**8**) and its derivatives (**17**) produced by addition of free radicals Y$^{\cdot}$ to the terminal carbon atom of the vinyl group of VCP (Scheme 5) are known[5,42] to isomerize to give homoallyl structures (**18** and **19**, Eqs. (8) and (9), respectively).

Scheme 5



Taking into account Eqs. (8) and (9), the assumption that in σ-["*anti*-VCP"]$_2{}^{\cdot +}$ a similar **a** $\rightarrow$ **b** radical rearrangement (see Scheme 3) occurs is justified.

Selective conversion of the cyclopropyl radical to the homoallyl radical according to reaction (8) is thermodynamically favorable (by 3.2—5.2 kcal mol^{-1}) and requires an activation energy of 5.9—9.0 kcal mol^{-1} (see Ref. 42). Increasing in the spin density in the p-orbital of the adjacent carbon atom from 0 to 1 lowers the energy of stabilization of the cyclopropane ring by an order of magnitude[6] and, consequently, encourages its opening. Therefore, it may be assumed that the cyclopropane ring is easily opened in σ-["*anti*-VCP"]$_2{}^{\cdot +}$ (**a**) as well as in the homoallyl radical and is opened with much more difficulty in π-[*anti*-VCP]$_2{}^{\cdot +}$ and *anti*-VCP, due to the decrease in the spin density at the adjacent carbon atom to 1/4 and 1/2, respectively.

We believe that at the final step of the series of transformations under consideration the π-dimeric complex [*dist*(90,0)-$C_5H_8{}^{\cdot +}$...*anti*-VCP] is formed. The σ-bond in σ-["*anti*-VCP"]$_2{}^{\cdot +}$ is weakened and lengthened [$d(—CH_2—CH_2—) \sim 1.6$ Å].[51,52] According to the literature data,[51] the cleavage of such σ-bonds is made substantially easier when a functional group that stabilizes the cation site and causes lengthening of the bonds to 1.7—1.8 Å is introduced to the α-position. In the case of the σ-["*anti*-VCP"]$_2{}^{\cdot +}$ (1,4-distonic RC) structure **b**, the central σ-bond cleaves, which is favored by the formation of an allyl cation system in *dist*(90,0)-$C_5H_8{}^{\cdot +}$ **12**. The latter reacts with the vinyl group of *anti*-VCP to form the final π-dimeric complex. The peculiarities of the addition of an alkene to the allyl cation system have been considered previously.[55]

As noted above, under the model conditions corresponding to the occurrence of ion-molecular reactions in a solid (*i.e.*, at 77 K in the host matrix or at 77—113 K in concentrated solutions of VCP in

Freon-113 or at 77—100 K in Freon-11) the VCP molecules have the *anti*-conformation which is retained in the dimeric RC [*anti*-VCP]$_2^{\cdot +}$. Therefore, it is reasonable to assume that VCP, in its dimeric complex with *dist*(90,0)-$C_5H_8^{\cdot +}$, also has this conformation both in the host matrix and in Freon solutions.

* * *

Thermal transformations of VCP$^{\cdot +}$ in Freon-113 ($CFCl_2CF_2Cl$) and Freon-11 ($CFCl_3$) have been studied by ESR over the temperature range 77—113 and 77—160 K, respectively at initial VCP concentrations of 1.0—20.0 mol. %. Under these conditions, which make it possible to simulate radical processes in a solid host matrix of VCP, thermodynamic equilibrium (6) is established between the primary RC, *anti*-VCP$^{\cdot +}$ **6** and the secondary RC, *dist*(90,0)-$C_5H_8^{\cdot +}$ **12** which is incorporated into *anti*-VCP as a moiety. In Freon-113 over the temperature region between 77 and 105 K *anti*-VCP$^{\cdot +}$ is more stable than *dist*(90,0)-$C_5H_8^{\cdot +}$ by 0.35 kcal mol^{-1}.

In Freon-11, along with *dist*(90,0)-$C_5H_8^{\cdot +}$, a resonance π-dimeric RC, [*anti*-VCP]$_2^{\cdot +}$ **16**, was detected by ESR. Unlike *dist*(90,0)-$C_5H_8^{\cdot +}$, which decays when the sample is heated to 100 K to give 1-vinylcyclopropyl radical **14**, dimeric complex [*anti*-VCP]$_2^{\cdot +}$ is stable over the whole temperature interval studied (77—160 K). This distinction between the chemical behavior of *dist*(90,0)-$C_5H_8^{\cdot +}$ and [*anti*-VCP]$_2^{\cdot +}$ is probably due to the initial type of coordination of *anti*-VCP$^{\cdot +}$ and *anti*-VCP, which predetermines the direction of dimerization. The cyclic HH coordination precedes the short-lived complex [*dist*(90,0)-$C_5H_8^{\cdot +}$...*anti*-VCP], HT coordination leads to the stable resonance π-dimeric RC, [*anti*-VCP]$_2^{\cdot +}$ (see Scheme 3).

The *anti*-VCP$^{\cdot +}$ and *dist*(90,0)-$C_5H_8^{\cdot +}$ RC existing in thermodynamic equilibrium (6) are stable not only in frozen Freon matrices but also in the host VCP matrix at 77 K. Such unusual inertness of the primary RC, *anti*-VCP$^{\cdot +}$, with respect to deprotonation or dimerization to give σ-bonded structures can be explained without discrepancies by the high strengths of the C(sp^2)—H bonds in *anti*-VCP and *anti*-VCP$^{\cdot +}$ in combination with the presence of thermodynamic equilibrium (6).

In an X-irradiated solution of VCP in Freon-113 (1.0 mol. %) an admixture of the primary *gauche*-VCP$^{\cdot +}$ RC **7** was detected at 100 K by ESR. However, the conditions for the existence of these RC are close to the gas-phase, and therefore, the RC are rapidly lost in ion-molecular processes when the temperature of the sample is increased to 105 K. On the other hand, in the "diffusionally rigid" Freon-11 matrix, a separate *gauche*-VCP$^{\cdot +}$, along with *anti*-VCP$^{\cdot +}$, is stable up to 160 K.

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