- 4. M. V. Galakhov, V. A. Petrov, G. G. Belen'kii, L. S. German, É. I. Fedin, V. F. Snegirev, and V. I. Bakhmutov, Izv. Akad. Nauk SSSR, 1063 (1986).
- 5. G. A. Olah and R. J. Spear, J. Am. Chem. Soc., <u>97</u>, 1539 (1975).
- 6. G. A. Olah, G. Liang, and Y. K. Mo, J. Org. Chem., <u>39</u>, 2394 (1974).
- 7. R. W. Taft, R. H. Martin, and F. W. Lampe, J. Am. Chem. Soc., 87, 2490 (1965).
- 8. V. V. Tyuleneva, L. A. Rozov, Yu. V. Zeifman, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1136 (1975).
- 9. S. A. Postovoi, Yu. V. Zeifman, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2826 (1982).
- I. L. Knunyants, L. S. German, and B. L. Dyatkin, Izv. Akad. Nauk SSSR, Ser. Khim., 1353 (1956).

INFLUENCE OF A SUBSTITUENT AT THE 2 POSITION ON THE STABILITY OF FLUORINE-CONTAINING ALLYL CATIONS ACCORDING TO ¹⁹F NMR SPECTROSCOPY DATA

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Allyl cations have been well investigated by NMR spectroscopy [1]. Exceptions are polyfluorinated allyl cations, for example the perfluoroallyl cation, which up to now could not be recorded by this method on the ¹⁹F nuclei [2, 3]. Recently, we have unequivocally proved the formation of the perfluoroallyl cation and its analogs (Ia-e) from the corresponding fluoroolefins (Scheme 1), using antimony pentafluoride as a fluoride ion acceptor [4, 5].

$$CF_{3} - C(X) = CF_{2} \xrightarrow{SbF_{3}} [CF_{2} = C(X) = CF_{2}]^{+}$$

$$X = CF_{3}(Ia), F(Ib), CI(Ic), Br(Id), H(Ie)$$
(1)

A complete analysis of the ¹⁹F and ¹³C NMR spectra of both cations and their predecessors, the fluoroolefins, showed that, in the formation of cations, a sharp shifting to the weak field of the resonance signals of the ¹³C^{1,3} and ¹⁹F nuclei is observed at these carbon atoms (with reference to the predecessors), while the C² signal practically does not change its position [4, 5]. This order of change in the chemical shifts (CSs) corresponds to the generally accepted concepts on the localization of the positive charge at the 1,3 positions of the allyl cation, and to the experimental data obtained for hydrocarbon allyl cations [1]. It should be noted that in all the cases studied, the resonance signals of the C¹ and C³ nuclei carrying a main positive charge are present in a somewhat stronger field than are the same signals in hydrocarbon allyl cations [1]. This can be explained by partial quenching of the positive charge in cations (Ia)-(Ie) due to reversed transfer of the electronic density from the F atoms directly bound to C¹, C³ atoms. The sharp shift to the weak field of just these F nuclei in cations (Ia)-(Ie) confirms this supposition [4, 5].

As a result of charge localization on C^1 and C^3 , it could be expected that the substituents at C^2 in fluorine-containing allyl cations (Ia)-(Ie) will not noticeably influence the stability of these moieties. However, as has already been mentioned in [4, 5], cations (Ia) $(X = CF_3)$ and (Ib) (X = F) could be recorded only in a mixture with the corresponding olefins and at low temperatures in a SO₂FCl medium. But cations (Ic)-(Ie) are observed already at about 25°C, while signals of the initial olefins are not present in the ¹⁹F and ¹³C NMR spectra. These preliminary data indicate a noticeable influence of the substituent at the 2 position on the stability of fluorine-containing allyl cations. The present work is devoted to the study of this problem.

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TABLE 1. Thermodynamic Parameters of Equilibrium (2)

Cation	x	Range				AC ²⁹⁸
		T., °C	K _{eq} • 10 ²	ΔH , kcal/mole	<u>Д</u> 8, е.u.	kcal/mole
(Ia) (Ib)	CF₃ F	$ \begin{array}{ c c } -60 \div -3 \\ -40 \div 10 \end{array} $	$ \begin{array}{r} 30-3 \\ 40-7,5 \end{array} $	$-4,6\pm0,1$ $-5,9\pm0,5$	$-23,9\pm0,8$ $-26,1\pm1,8$	$2,5\pm0,1$ $1,8\pm0,4$

The stability of cations (Ia)-(Ie) can be determined according to the position of equilibrium (2) from the ratio of integral intensities of the cations and the corresponding olefins in the ¹⁹F NMR spectra.

$$CF_{3} - C(X) = CF_{2} + SbF_{5} \rightleftharpoons [CF_{2} - C(X) - CF_{2}]^{+} + SbF_{6}^{-}$$
(2)

The NMR spectra of mixtures of olefins (IIa) and (IIb) with SbF_5 (molar ratio 1:2, based on the SbF_5 monomer) were recorded in a SO_2FC1 medium to prevent freezing of the sample at low temperatures. In the temperature studied, signals of both cations (Ia), (Ib) and their predecessors (IIa), (IIb) were simultaneously observed in the spectra, while signals corresponding to the reaction products of the cations with olefins were not detected. Variation in the temperature of the solutions causes a change in the relative integral intensities of olefins and cations. In the case of the perfluoromethallyl cation (Ia), the relative molar content of the cation decreases from 0.50 to 0.16 with increase in temperature from -61 to -3°C. For the perfluoroallyl cation (Ib), this ratio changes from 3.8 to 1.5 in the temperature range from -43 to -4°C. The ¹⁹F NMR spectra can thus be used to calculate the equilibrium constants Keq of formation of cation (2) according to Eq. (3) and then to obtain

$$K_{p} = \frac{\left[\operatorname{Cat}\right]_{eq}^{2}}{\left[\operatorname{Olefl}_{eq}\left(\left[\operatorname{SbF}_{5}\right]_{0} - \left[\operatorname{Cat}\right]_{eq}\right)\right]}$$
(3)

the thermodynamic parameters of this equilibrium. The parameters obtained for (IIa, b) \neq (Ia, b) are given in Table 1. Verification of the reproducibility of the data in Table 1 showed a satisfactory coincidence of the values of the angular B (±5%) and free (±8%) terms in Eq. (4)

$$K_{eq} = A + B \cdot T^{-1}$$

$$A = \Delta S - 23.76; \quad B = \frac{\Delta H}{R} \quad . \tag{4}$$

It should be noted that in the case X = F, to improve the signal/noise ratio, the ¹⁹F NMR spectra were recorded with a "boxcar" integrator. Therefore, to evaluate the influence of the relaxation times of ¹⁹F of the cation and olefin on the experimental value of K_{eq}, we determined the ratio of the intensities of the fluorine signal at C² during a change in the duration of the base pulse (10-90°) and lag between the pulses (0-50 sec). The results of these experiments showed that the relative integral intensities are practically independent of the above-enumerated parameters, and hence indicated an equality of the relaxation times of the F nuclei at the 2 position in both the cation and the olefin at different temperatures.

The data in Table 1 show that the formation of cations (Ia, b) according to Scheme (2) is energetically favorable, since the value $\Delta H = H_{cat} - H_{olef} < 0$. The predominance of olefin (IIa) in the temperature range studied is due to a decrease in the value of the entropy factor during the formation of cations (Ia, b). The negative values of $\Delta S = S_{cat} - S_{olef}$ indicate an increase in the orderliness in the system as a result of solvation by the solvent molecules of the charged centers formed. It is interesting to note that the ΔS values obtained are practically the same in both cases. Cation (Ib) (X = F) is 1.3 kcal/mole energetically more favorable than (Ia) with X = CF₃. Since in the allyl cations the positive charge is concentrated mainly at the 1,3 positions, substituent at C² should apparently influence the stability of these cations only at the expense of its inductive effect, which in both cases is negative. Based on the values of the Taft constants [6], it could be expected that the F atom at C² in the allyl cation will be destabilized to a greater extent than the CF₃ group present at the same position or, in other words, cation (Ia) should be more stable than cation (Ib). Hence, the decrease in the stability of perfluoroallyl cations on transition from X = F to X = CF₃

cannot be explained by electronic effects. It is possible that the difference in the stability of these cations is due to an increase in the steric hindrances when the F atom is replaced by the CF_3 group. Construction of molecular models showed that in the case of (Ia) appreciable deformations arise, leading to partial deviations of the fluorine atoms at C¹ and C³ from the plane, and thus deterioration in the stabilization of the positive charge



Deno and Bollinger [7] observed a similar influence of the volume of the substituent at C^2 on the stability of the hydrocarbon allyl cations of type $[(CH_3)_2C...C(X)...C(CH_3)_2]^+$, where X = H, CH_3 . In this case, replacement of the hydrogen atom by an electron-donor, but a more bulky CH₃ group, led to a decrease in the stability of the corresponding cation. It should be noted that the SSCC through four bonds between the F nuclei, marked in Scheme (5), whose value is strongly influenced by direct steric interaction, changes in the following way for cations (Ia-e) [4]: 150.7 Hz (X = Br) $\stackrel{>}{_{\sim}}$ 149.6 (X = C1) > 140.3 (X = F) > 123.1 Hz (X = H), i.e., the SSCC increases monotonically with an increase in the volume of the substituent at C². However, cation (Ia) with $X = CF_3$, for which ${}^4JF-F = 146.8$ Hz [5], somewhat deviates from this series. It can be assumed that this is due to a rotation around the C^1 ... C^2 and C^1 ...C³ bonds, which leads to a decrease in the steric contact of the F* atoms and simultaneously causes a decrease in the thermodynamic stability of cation (Ia). Unfortunately, we could not obtain the thermodynamic parameters of equilibrium (2) for cations (Ic-e). We found that when olefins (IIc-e) were mixed with SbF_5 under the above conditions, in the ^{19}F NMR spectra only multiplets corresponding to cations (Ic-e) could be recorded. When the concentration of SbF5 was halved, in the spectra signals were observed both the cations and the corresponding olefins (IIc-e) in a ratio of about 1:1. This ratio changes by less than 4% when the temperature changed by 35°C. It was found that the inappreciable temperature dependence of the ratio of the integral intensities of the cation and olefin is due to stratification of the sample at low temperatures. The upper layer, consisting of an olefin solution in SO₂FC1, thus exceeds the limits of the working zone of the NMR spectrometer sensor. A certain increase in the initial concentration of SbF₅ leads to an increase in the relative content of the cation, which is also independent of temperature. The results show that in the case of X = C1, Br, H, the value of Keq >> 1, and indicate that the stability of cations (Ic-e) is much higher than that of cations (Ia, b). Unfortunately, because of this, quantitative information for cations (Ic-e) cannot be obtained by the NMR method.

The decreased order of the C....C bond in allyl cations can ensure rotation around this bond. It could also be expected that the measurement of the intramolecular rotation parameters by the NMR method will supplement information on the relative stability of the fluorinecontaining allyl cations (Ia-e). It was found that when solutions of olefins (IIc, d) are heated in excess SbF₅, containing only cations (Ic, d), the signals of the ¹⁹F^{1,3} nuclei become successively broadened, which may be the result of this rotation. Complete analysis of the form of the line, necessary for calculating the rotation parameters of the cations studied, is very complicated by the presence of strongly bound spin systems [4, 5]. To reveal the possible use in this case of an approximation of a slow position exchange, we studied the temperature dependence of the line width of 1,1,2-trichloro-3,3-difluoroallyl cation (If). The ¹⁹F NMR spectra of this cation represent an AK type spin system with J = 245 Hz and $\Delta v = 1700$ Hz [8]. Heating a solution of (If) in excess SbF₅ causes broadening of the line from 8.3 at 48°C to 16.0 Hz at 68°C. Complete analysis of the line form according to a program composed by formalism [9] leads to the following dependence of the lifetime of magnetically nonequivalent positions (τ) on the temperature in Arrhenius coordinates

$$-\ln \tau = (47.4 \pm 3.8) - (15.0 \pm 1.2) \cdot T^{-1}$$
(6)

This dependence, calculated in the slow exchange approximation, is described as

$$-\ln \tau = (44.0 \pm 2.7) - (13.9 \pm 0.9) \cdot T^{-1}$$
(7)

(5)

TABLE 2. Kinetic Parameters of Rotation around the C...C Bond of Allyl Cation in SbF_5 Medium*

Cation	x	ΔE^{\neq} , kcal/mole	AH F , kcal/mole	∆S≠, e.u	$\Delta G^{\neq 298}$, kcal/mole
(1c) (Ie) (If) **	Cl H	$\begin{array}{c c} 12,5\pm0,8\\ 9,4\pm0,3\\ 29,8\pm1,8 \end{array}$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{ c c c } -43,3\pm3,0\\ -34,9\pm2,1\\ 37,2\pm2,7 \end{array}$	$\begin{array}{c} 24,8{\pm}0,8\\ 19,1{\pm}0,3\\ 19,2{\pm}0,9 \end{array}$

*The results were obtained in the 20-70°C range. $+F_2C$CCl....CCl₂.

TABLE 3. Kinetic Parameters of Reaction of Cations with F Anion*

Cation	x	∆E. kcal/mole	ΔH_{\bullet} kcal/mole	ΔS, e.u.	ΔG^{298} , kcal/mole
(Ib)	F	6,2±0,3	$6,9\pm0,3$	$-8,4\pm0,3$	$9,4\pm0,3$
(Ic)	Cl	21,6±1,3	22,2 $\pm1,3$	$-12,1\pm1,5$	$25,5\pm1,3$
(Id)	Br	13,7±0,9	14,2 $\pm0,9$	$-15,0\pm1,0$	$18,7\pm0,9$

*The results were obtained in the range of -10 to +50°C.

The calculation carried out by the two methods thus showed practical equality of the corresponding coefficients obtained, so that further use could be made of the slow exchange approximation in the analysis of the ¹⁹F NMR spectra of cations (Ic, e, f). Table 2 shows the kinetic parameters of the position exchange, from which it is seen that in the series studied the values of $\Delta E^{\#}_{act}$, $\Delta H^{\#}$, and $\Delta S^{\#}$ suspiciously strongly change. Special attention should be paid to the sharp change in the entropy factor [from -43 to +37 e.u. on transition from (Ia) to (If), while for the rotations around the C...C bond, in all the cases studied, the value of $\Delta S^{\#} \sim 0$ e.u. should be expected, since in the transition state of this process the charge does not change. The above shows that the experimental kinetic parameters are apparent. One of the probable reasons for this is the occurrence of the addition-splitting reaction of fluoride anion according to Scheme (2), and not an intramolecular rotation. Since under these conditions the equilibrium concentration of the olefin is low and cannot be taken into account in the calculation, the kinetic parameters obtained for Ic-e may differ with a large scattering of values, and are possibly not real. In this connection, and to measure the kinetics of an intramolecular exchange between cations (Ia-e) and (IIa-e) according to Scheme (2), the experiment had to be carried out under conditions where the ¹⁹F NMR spectra simultaneously contain signals of cations and the corresponding olefins. In the present work, we studied the temperature dependences of the spectra of mixtures of fluoroolefins with SbF_5 in a molar ratio of 1:1 in a SO₂FCl medium, which ensured observations of the cations and olefins at the same time. It was found that an increase in the temperature of the solutions leads to broadening of the lines of both cations and their predecessors. An increase in the Lewis acid concentration decreases the content of olefin in the mixture and changes the line widths of the cation and the olefin (narrowing of the cation lines, and broadening of the olefin lines). These results unequivocally show that in the NMR spectra a pseudorotation around the C....C bond of the cations is observed, i.e., the rotation around this bond is controlled by the addition-splitting of the F anion according to Scheme (2). A similar effect has already been observed in the case of the rotation around the $C_{\dots}C$ bond of enamines; its kinetic control was effected by the proton transfer reaction [10]. Thus, with the observed temperature dependences of the ¹⁹F NMR spectra of mixtures of olefins (II) with SbF_5 in a molar ratio of 1:1 in a SO₂FC1 medium, we can study the kinetics of addition of the F anion to the corresponding cation and obtain the quantitative characteristics of this process, shown in Table 3. By using these parameters, we can arrange the compounds into the following series according to the decrease in the rate of addition of F^- to the cations, depending on the nature of the substituent at the 2 position: (Ib) (X = F) > (Id) (X = Br) > (Ic) (X = C1), which characterizes the kinetic stability of the cations.

We were unable to characterize in the same way cation (Ie) (X = H), since under the above conditions heating a solution containing cation (Ie) and olefin (IIe) causes an electrophilic



dimerization of the olefin [11]. Therefore, for a qualitative evaluation of the relative stability of cation (Ie), we obtained a ¹⁹F NMR spectrum of a mixture of olefins (IIe) and (IIc) and SbF_5 in a molar ratio of 1:1:2 in a SO_2FC1 medium at a temperature of 20°C. An analysis of this spectrum showed the presence of multiplets corresponding to cation (Ie) and olefin (IIc) (see Fig. 1). The lines of (IIc) are strongly broadened because of position exchange with cation (Ic) that gives broad signals at -10°C only. This result indicates that cation (Ie) has the highest thermodynamic stability and the lowest ability to react with F⁻.

By summing up the results obtained in the present work, viz., 1) quantitative data on change in the thermodynamic stability of allyl cations (I) in the series (Ia) $(X = CF_3) < (Ib)$ (X = F) << (Ic) (X = C1), (Id) (X = Br), (Ie) (X = H), and (Ic) (X = C1) < (Ie) (X = H); 2)quantitative and qualitative data on change in the ability of cations (I) to accept fluoride anion in the series (Ib) (X = F) > (Id) (X = Br) > (Ic) (X = C1) and (Ic) (X = C1) > (Ie)(X = H), we can construct the following overall series for changes in the thermodynamic stability of fluorine-containing allyl cations: (Ia) $(X = CF_3) < (Ib) (X = F) << (Id) (X = Br) <$ (Ic) (X = C1) < (Ie) (X = H). This series can be interpreted in terms of the competing influence of the electronic and steric properties of the substituent at C², i.e., the stability of the cations increases with decrease in the electron-acceptor ability and steric requirements of this substituent.

EXPERIMENTAL

2-Hydroperfluoropropylene (IIe) was obtained by the method in [11]. 2-Chloro- and 2bromoperfluoropropylenes (IIc) and (IId) were prepared by chlorination or bromination of (IIe) under UV radiation, followed by dehydrohalogenation of the saturated compound formed by solid NaOH. Fluorosulfonyl chloride SO_2FC1 was purified by distillation over SbF_5 . Antimony pentafluoride SbF_5 was distilled directly before use in an inert-gas current.

A weighed sample of SbF_5 was placed in an ampule for taking NMR spectra, and then SO_2FC1 (80-95 ml of gas) and calculated amounts of the corresponding olefin were measured from a gas burette through H_2SO_4 . In the case of 2-bromoperfluoropropylene, the olefin sample was added to the ampule with SbF_5 , and the solvent was condensed. The ampule was sealed, heated to about 20°C, and thoroughly shaken until a homogeneous solution formed.

The NMR spectra were obtained on a Bruker WP-200SY spectrometer (working frequency on 19 F nuclei 188.3 MHz) from one single 90° pulse (except for one specific case). In all the experiments, the memory volume per spectrum was 16K words. The temperature was measured on an STS-1 adapter (Special Design Bureau of the Institute of Organic Chemistry of the Academy of Sciences of the USSR). The temperature in the spectrometer sensor was determined according to the 1H signals of CH₃OH. The complete calculation in an AB system and the calculation of the parameters of the temperature dependences by the method of least squares were carried out on a PDP-12 computer.

CONCLUSIONS

1. It was shown for the first time that the thermodynamic stability of fluorine-containing cations depends on the substituent at the 2 position.

2. In the series studied, the 2-hydroperfluoroallyl cation has the highest thermodynamic stability, and the perfluoromethallyl cation the lowest.

LITERATURE CITED

- 1. J. A. Olah and R. J. Spear, J. Am. Chem. Soc., <u>97</u>, 1539 (1975).
- 2. J. A. Olah and Y. K. Mo, Adv. Fluor. Chem., 7, 109 (1973).
- 3. R. Chambers, A. Porkin, and R. S. Matthews, J. Chem. Soc., Perkin Trans., No. 1, 2107 (1976).
- 4. M. V. Galakhov, V. A. Petrov, V. I. Bakhmutov, G. G. Belen'kii, B. A. Kvasov, L. S. German, and E. I. Fedin, Izv. Akad. Nauk SSSR, Ser. Khim., 306 (1985).
- 5. V. A. Petrov, G. G. Belen'kii, M. V. Galakhov, V. I. Bakhmutov, L. S. German, and É. I. Fedin, Izv. Akad. Nauk SSSR, Ser. Khim., 2811 (1985).
- 6. Tables of NMR Technical and Application Bulletin (Tesla), 10, 27 (1976).
- 7. N. C. Deno and H. G. Bollinger, J. Am. Chem. Soc., <u>85</u>, 2998 (1963).
- 8. V. A. Petrov, G. G. Belen'kii, and L. S. German, Izv. Akad. Nauk SSSR, Ser. Khim., 438 (1984).
- 9. G. Binsch, Top. Stereochem., <u>3</u>, 37 (1968).
- 10. V. I. Bakhmutov and V. A. Burmistrov, Org. Magn. Reson., <u>12</u>, 185 (1979).
- I. L. Knunyants and Yu. A. Cheburkov, Inventor's Certificate No. 130895 (USSR); Byull. Izobret., No. 16, 11 (1960).

STRUCTURE AND ¹³C AND ¹⁹F NMR SPECTRA OF 1-SUBSTITUTED ANALOGS

OF PERFLUOROMETHALLYL CATION

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A study of the influence of substituents on the structure and stability of fluorine-containing allyl cations and on the distribution of the positive charge in them is an urgent problem in the chemistry of fluoroolefins. Many of their reactions proceed through these intermediate moieties. The existence of the perfluoroallyl cation and its 2-substituted analogs has already been shown by the NMR method [1, 2], and the influence of a substituent at the 2 position on their thermodynamic stability was studied in [3]. The present work is devoted to a study of the structure of 1-substituted analogs of the perfluoromethallyl cation by the 19 F and 13 C NMR methods.

 $\begin{array}{c} \stackrel{4}{\overset{CF_{3}}{\underset{|2|1}{\overset{TF_{3}}{\longrightarrow}}}} F^{X} \xrightarrow{SbF_{5}} F^{B} \stackrel{4}{\overset{2}{\underset{3|2|1}{\overset{TF_{3}}{\longrightarrow}}}} F^{X} + F^{B} \stackrel{4}{\overset{3|2|1}{\overset{3|2|1}{\xrightarrow{X}}}} X$ $F_{3}C \stackrel{|1}{\underset{|X|}{\overset{|1}{\xrightarrow{F^{A}}}} F^{X} \stackrel{|1}{\underset{|F^{A}}{\xrightarrow{F^{A}}}} F^{X} + F^{B} \stackrel{|1}{\overset{|2|1}{\xrightarrow{F^{A}}}} (1)$ (1) $E_{-(II)} \qquad Z_{-(II)}$

Mixing fluorolefins (I) with the parameters listed in Tables 1 and 2, with an excess of SbF_5 (see the Experimental section) is accompanied by the disappearance of signals of the initial compounds in the ¹⁹F and ¹³C NMR spectra and the appearance of three groups of new signals; their positions indicate, according to [1, 2], the formation of allyl cations (II) (Tables 3

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