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DECAY KINETICS OF BRANCHED FLUORINE-CONTAINING RADICALS

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The distribution of unpaired electrons in active radicals is, as a rule, anisotropic. Consequently, their recombination takes place at certain favorable mutual orientations. In gas-phase reactions a steric factor is usually introduced in order to take into account the anisotropy of reactivity, which is equal to the statistical weight of the orientations of the partners which are favorable for a reaction. A peculiar feature of liquid-phase reactions is the presence of a "cage" effect which, in particular, lengthens the contact time of the reagents in comparison with the gas phase; rotation of the radicals offers the possibility of averaging the anisotropy of the reactivity of the radicals [1].

In the theory [2, 3], which takes into account these characteristics of liquid-phase reactions, the rate constant of the diffusion-controlled reaction depends on the frequency of encounters of the reacting radicals as well as on the probability of a reaction occuring in the radical pair which, in turn, depends on the competition between the rotary and translatory mobility of the radicals [4]. The dependence of the reaction rate constant on the mutual orientation of the reacting particles is described by the "black spot" model, according to which the reacting particle represents a sphere, while the reaction center occupies only a small space on its surface (black spot) [3]. For the particles to react, alignment (coincidence) of the black spots must occur due to rotating diffusion in the cage. Data are available which support this model [5]. For instance, it has been shown in [6] that the ratio of yields of products of disproportionation and recombination of cumyl radicals depends strongly on the viscosity of the solvent. This ratio is equal to 0.054, 1.00, and 1.48, respectively, at 20-60, –8, and –9.5°. In order to explain this large difference between the yields in the liquid and solid phases it is assumed that, due to retardation of the rotary movement of the radical in the cage, the probability of recombination decreases, while a significantly wider selection of orientation is available for disproportionation. Similarly, the yield ratio of products of disproportionation and recombination of tert-butyl radicals decreases with increasing temperature and decreasing viscosity [7], while the frequency of rotation and the probability of contacts between the black spots increases, resulting in a higher recombination rate in comparison with the disproportionation rate.

Thus, the reaction mechanism of cumyl and tert-butyl radicals depends on the molecular mobility of the radicals. It was considered of interest to study the influence of steric

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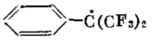
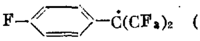
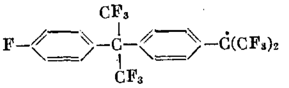
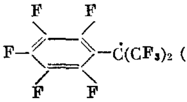
TABLE 1. Recombination Rates of Some Fluorine-Containing Radicals

Radical	$K_{rec}^{20°}$, liter/mole·sec
 (I)	$2{,}5 \cdot 10^8$
 (II)	10^7
 (III)	$5{,}6 \cdot 10^5$
 (IV)	Stable (does not recombine)
$(CF_3)_3\dot{C}$ (V)	$4 \cdot 10^9$

factors and molecular mobility on the recombination reaction alone. For this purpose we have investigated in [8, 9] and in the present work the kinetics of decay of different fluorine-containing radicals which represent isostructures to those mentioned above but which do not enter into disproportionation reactions. Thus, the rate constant for the decay of the fluorine-containing radicals represents only the recombination, not the summary constants of the disproportionation and recombination rates as in the case of the hydrogen-containing radicals.

It has been established earlier that the mechanism of decay of fluorine-containing cumyl radicals, formed in the photolysis of the corresponding dimers of the type $[p\text{-}RC_6H_4\text{-}C(CF_3)_2]_2$ depends on the type of the substituent R. When R = F, the cumyl radical (II) recombines in the para position with the formation of a quinoid dimer [9]; an increase in the volume of the substituent [R = $p\text{-}FC_6H_4C(CF_3)_2$, radical (III)], leads to a change in the direction of the reaction and recombination of the radicals according to the "head-to-head" mechanism [9]. In the present work we have studied the decay rate of the cumyl radical when R = H (I), the fully fluorinated radical (IV), and of the perfluoro-tert-butyl radical (V) (Table 1). The observed retardation of the decay rate of radical (II) by a factor of 25 in comparison with (I) is close to the difference between the recombination rates of p-bromocumyl and cumyl radicals [10]. It can be assumed that this retardation is connected to a decrease in the size of the black spot and slowed-down rotation in the cage. The black-spot model is in agreement with the data obtained for the radical (III). The reduction in its decay rate by a factor of 500 in comparison with (I) is due to the fact that recombination following the "head-to-head" mechanism is sterically hindered much more than the reaction according to the "head-to-tail" mechanism. In other words, the size of the black spot for the recombination of radical (III) is much smaller.

The replacement of H atoms by F in the benzene ring has an even stronger effect on the reactivity. The fully fluorinated radical (IV), obtained by reaction of the corresponding bromide with finely dispersed copper without a solvent (in liquid bromine), does not recombine and its stationary concentration is not dependent on the temperature. The sharp increase in the steric hindrance of the reaction center manifests itself by the retarded rotation of CF_3 groups in comparison with the radicals (I)-(III). The changes in the lines of the EPR spectrum of the radical (IV) are analyzed in the experimental part of the work.

It must be pointed out that the activation energy of the decay of radicals (I)-(III) is small (1-2 kcal); however, the rate constants differ considerably from the diffusion constants, particularly in the case of (III). Thus, the change in the decay rate constant by several orders of magnitude as function of structure and the absence of a noticeable activation energy is evidently due to the manifestation of anisotropy of reactivity of the radicals, which does not get averaged due to rotary diffusion in the cage. In order to study further the role of retarded rotation in the decay of the radicals, we have studied the recombination kinetics of the perfluoro-tert-butyl radical (V). It was not possible to determine the recombination rate constant of (V) in pure perfluoropentane, since the radical concentration was lower than the sensitivity (detection limit) of the equipment [due to the high decay rate of (V)]. However, the addition of pyridine to the perfluoropentane reduces significantly the

TABLE 2. Recombination Rate of Radicals $(CF_3)_3\dot{C}$ Radicals (V) as Function of Concentration and the Reciprocal Square of Pyridine Concentration, Added to the Medium $(n\text{-}C_5F_{12})$

C_6H_5N [Py], mole/liter	$1/[Py]^2$	K_2, liter/ mole·sec
0,033	909,0	$2{,}2\cdot10^9$
0,065	236	$2\cdot10^8$
0,11	82,6	$5{,}6\cdot10^7$
0,142	50	$2{,}3\cdot10^7$

recombination rate of (V), symbatically with increasing pyridine concentration which, apparently, forms a weak complex with the radical.

The recombination rate constants, obtained at different pyridine concentrations, are shown in Table 2. Analysis of the kinetic scheme, by assuming complex formation of the radicals with pyridine, leads to the equation

$$K_{ef} = \frac{[R_0]^2}{(1+K_e[Py])^2}(K_{ns} + K_s K_e^2 [Py]^2) \qquad (1)$$

where $[R_0]$ is the total concentration of solvated and nonsolvated (R) radicals; [Py] is the pyridine concentration; K_s is the decay rate constant of the solvated radicals; K_{ns} is the decay rate constant of the nonsolvated radicals. At high pyridine concentrations when $K_e/Py \gg 1$, Eq. (1) takes the form

$$K_{ef} = \frac{K_{ns}}{K_s^2 [Py]^2} + K_s$$

It can be seen that K_{ef} is a linear function of $1/[Py]^2$. The experimental relationship between K_{ef} and $1/[Py]^2$ can therefore be used to determine the equilibrium constant K_e and the recombination rate constant K_s of the complexed radicals, which were 84.5 and $9.1\cdot10^6$ liters/mole·sec respectively.

The value of $K_{rec} = 2.2\cdot10^9$ liters/mole·sec at a pyridine concentration of 33 moles/liter is probably very close to the value of K_{dif} (for perfluoropentane, the viscosity of which is equal to 0.5 cP, according to the equation $K_{dif} \simeq 8RT/3000\eta = 2\cdot10^9$ liters/mole·sec). With account of the experimental error in the determination of K_{dif}, we can take therefore for K_s the value $2\text{-}4\cdot10^9$ liters/mole·sec and for $K_{ns} = 4\cdot10^9$ liters/mole·sec.

The absence of a temperature dependence of K_{ef} indicates a low value of ΔH for complex formation; the retardation of the recombination rate of solvated radicals can therefore be connected to retardation of rotational diffusion and, as a result of this, to the increased role of anisotropy of reactivity. The data obtained lead to the conclusion that the anisotropy of reactivity of radicals (I)-(III) is due to retarded diffusion rotation. The cause of this retardation or slow-down could be the association of radicals and recombination products with the solvent. In the case of equal heats of association it will manifest itself only through slowing-down of rotational diffusion, but not in the activation enery of the recombination reaction.

Thus, in the case of the cumyl and tert-butyl radicals, slow-down of rotation in the cage increases the probability of disproportionation, while, in the case of fluorinated analogs, it leads to a decrease in the decay rate constant.

EXPERIMENTAL

The EPR spectra were recorded on a Varian E-12 A spectrometer. Rapid reactions were investigated by the intermittent irradiation method. The kinetic curves were recorded by means of an S-1024 storing device, by using the synchronization system described in [11].

The radical (IV) was generated by photolysis of a mixture of 1 M $(CF_3)_3CI$ and 0.5 M $[(CF_3)_3C]_2Hg$ in $n\text{-}C_5F_{12}$. The formation of the dimerization product $(CF_3)_3CC(CF_3)_3$ in the

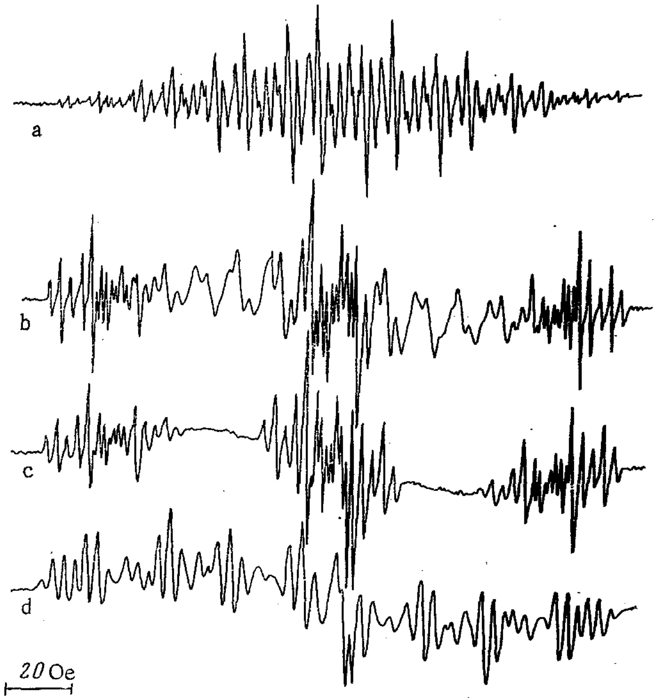


Fig. 1. EPR spectrum of radical (IV) as function of temperature: a) 30°; b) −40°; c) −80°; d) −125°C.

reaction was confirmed by ^{19}F NMR of the mixture after 10 h of photolysis (singlet at 21.83 ppm, compare [12]). Radicals (I) and (III) were generated from the corresponding dimers according to [8, 9]; the radicals (II), from the bromide, the synthesis of which has been described in [10]. The following reaction, carried out in pentane, was used to investigate the retarded rotation of CF₃ groups in the radical (V) at low temperature:

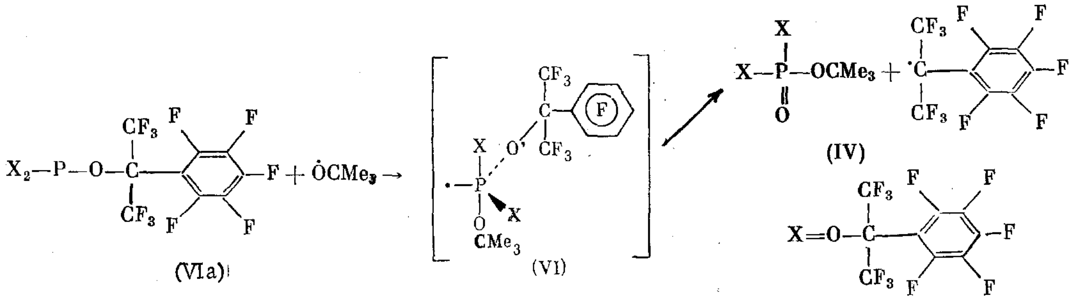


Figure 1 shows the EPR spectra of the perfluorocumyl radical at different temperatures. At 20° the EPR spectrum is characterized by the following hfi constants: a_{CF} = 17.1, a_{p-F} = 10, a_{o-F} = 7, a_{m-F} = 2, $a_{^{13}C}$ = 34.6 Oe (−70°). At −125° the fluorine atoms of the CF₃ group are not equivalent, and the hfi in the radical is described by the constants: a_{CF_1} = 31.3, a_{CF_2} = 17, a_{CF_3} = 3, a_{p-F} = 12.1, a_{o-F} = 7, a_{m-F} = 3 Oe. The reaction with the β-atoms of F is described by the equation $a_F = Q_{CF_3} \cos\theta$, where Q = 34.2 Oe, θ is the dihedral angle between the C—F bond and the 2p orbital of the unpaired electron, equal to θ^1 = 17°, θ^2 = 137°, and θ^3 = 257° (Fig. 2). The broadening of the lines was used to determine the frequencies and the barrier or rotation of the CF₃ groups, $K_{rot} = 3\cdot10^{12}$ exp (2700 + 500/RT) sec^{-1}.

An investigation of the kinetics of radical decay in pentane showed that the reaction is of the first order with respect to the radical and that it proceeds at a constant rate $K = 2\cdot10^8$ (exp(11000)/RT) sec^{-1}. The first order of the reaction is due to the fact that the radical (IV) decays in an H removal reaction. The phosphite (VIa) was prepared *in situ* from 3 eq of the corresponding alcoholate and PCl₃. The radical (V) splits off at a high rate from the metastable phosphoranyl radical (synchronous substitution of tert-butoxy by the radical). The proposed mechanism of radical formation is confirmed by the detection of the phosphoranyl radical in the reaction

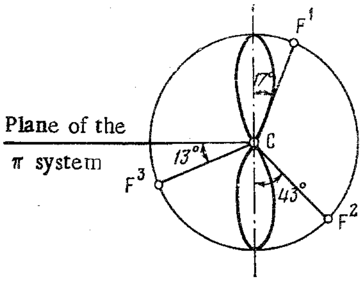
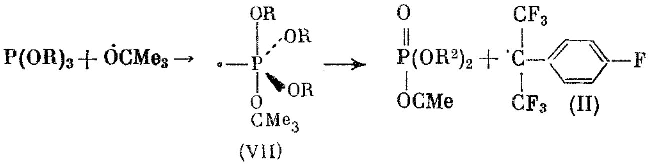
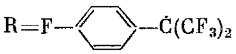


Fig. 2. Distribution of the F atoms of the CF_3 groups with respect to the orbital of the unpaired electron in the "frozen" structure of radical (IV) (−125°).



$a_P = 1070$ Oe



$$Me_3CO{-}OCMe_3 \xrightarrow{h\nu} 2Me_3C\dot{O}$$

The higher decay rate of the radical (VI) in comparison with (VII) is probably due to the influence of steric factors of the CF_3 groups on the strength of the O—C bond. The phosphite (VII) was prepared as described above; its structure was confirmed by the EPR spectrum of the phosphoranyl radical (VII). The bromide $C_6F_5(CF_3)_2CBr$ was used to investigate the recombination of the radicals (IV) which is not obtained following the typical procedure given in [13]. It can be synthesized by the reaction of the corresponding alcoholate with PBr_3 and Br_2. It must be pointed out that, when using ethanol as the solvent, by-products are formed based on the EtO group by p-F.

Preparation of Perfluorocumyl Bromide. A 29-g sample of redistilled PBr_3 was carefully added to the Na alcoholate prepared from 20 g $C_6H_5C(CF_3)OH$. The mixture was carefully heated, which led to a violent reaction; 6 ml dry bromine was then added and the mixture was heated with a reflux condenser. Having stripped off the excess bromine and PBr_3, the liquid was distilled under vacuum which separated into two layers (the bottom layer was PBr_3). The liquid was poured onto ice, washed with water, sodium carbonate, and again with water, and dried with $MgSO_4$. Distillation gave two fractions: 8.7 g with a bp 90-92° (50 mm) and 10.5 g with bp 100-110° (8 mm). The first fraction contains according to GLC data 36% of the initial alcohol; the rest is bromine (yield 24%) which was purified by preparative GLC (20% OG-1 on Shimalin support, 115°), bp 176-177° (according to Sivolobov). ^{19}F NMR spectrum (δ ppm, J, Hz): −9.8 t (CF_3, $J_{CF_3-F-o} = 21.7$), 48.8 m (o-F), 71.8 t.t (p-F, $J_{p-F-F-2} = 2.5$, $J_{p-F-F-m} = 19.8$), 79.2 (m-F, $J_{m-F-F-o} = 13.2$). Found: Br 20.3%. $C_9F_{11}Br$. Calculated: Br 20.62%.

CONCLUSIONS

1. The mechanism and rate of decay of fluorine-containing cumyl radicals depends on the type of substituent in the para position.

2. The dimerization rate of perfluoro-tert-butyl radicals is limited by diffusion and depends on the concentration of pyridine which forms a weak complex with the radical.

3. Perfluorocumyl radicals do not dimerize.

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PREPARATION OF COMPLEXES OF π-ALLYLPALLADIUM CHLORIDE WITH FERROCENYLPHOSPHINE LIGANDS AND INVESTIGATION OF RETARDED ROTATION AROUND Pd—P BOND

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Complexes of bis-π-allylpalladium chloride with tertiary phosphines have been investigated repeatedly by various physical and chemical methods, mainly in connection with the dynamic behavior of the π-allyl ligand. For the most part, the phosphines that have been used are the readily accessible PPh_3 [2], $PPhMe_2$ [3], or PEt_3 [4]. As reported here, we have obtained, for the first time, adducts of bis-π-allylpalladium chloride with phosphines containing ferrocenyl groupings; also, we have investigated their PMR spectra.

The ferrocenylphosphine derivatives of π-allylpalladium chloride were obtained by cleavage of the halogen bridges in the molecule of dimeric bis-π-allyl-μ-dichloropalladium under the influence of an equimolar quantity of the phosphine [5]. The reaction was carried out in THF at approximately 20°C in a stream of Ar. The products were difficult to isolate and purify because of their low solubilities in organic solvents. By washing repeatedly with petroleum ether, we obtained from the original phosphines certain yellow-orange, infusible substances with the general formula $\pi\text{-}C_3H_5Pd(Cl)L$, where $L = PFc_nPh_{3-n}$, $n = 1, 2, 3$, $Fc = C_5H_5FeC_5H_4$. The original triferrocenylphosphines and ferrocenylphenylphosphines were synthesized by methods given in [6, 7].

The composition and structure of the π-allylphosphine derivatives of palladium were confirmed by elemental analysis and PMR. In the PMR spectrum of the free triferrocenylphosphine, from the protons of the substituted cyclopentadienyl ring, two signals appeared downfield from the resonance of the unsubstituted C_5H_5 ligand [8]. It is not possible to assign these signals unambiguously to the α or β protons. Upon coordination with the palladium atom, the downfield signal is clearly separated into two individual signals. This effect is most pronounced at low temperatures (Fig. 1).

On the basis of the picture that has been obtained, we can conclude that the signals in the 4.54-4.46 ppm region pertain to α protons of the substituted cyclopentadienyl ligand, and that the signals at 4.29 ppm pertain to the β protons. Let us note that in the complex $(CO)_5MoPPh_2Fc$, the α protons absorb upfield from the β protons [9]. Apparently the reason for the nonequivalence of the α protons in the complex-bound triferrocenylphosphine is retardation of

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