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Study of the decarboxylation mechanism of fluorobenzoic acids by strong N-bases

Błażej Gierczyk,[1] Grzegorz Wojciechowski,[1] Bogumił Brzezinski,[1] Eugeniusz Grech[2] and Grzegorz Schroeder[1]*

[1]Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland
[2]Institute of Chemistry and Environmental Protection, Technical University of Szczecin, Piastów 42, Szczecin 71-065, Poland

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ABSTRACT: The kinetics of the decarboxylation reactions of pentafluorobenzoic and tetrafluorobenzoic acids by various N-bases were studied using ^{19}F NMR spectroscopy. The rate constants of these reactions are dependent on the structure of the fluorinated acid and the pK_a values of the N-bases. Pentafluorobenzoic acid is decarboxylated about two orders of magnitude faster than tetrafluorobenzoic acid. With increasing pK_a values of the protonated N-bases these reactions became much slower. These results suggested that the rate-determining step of the studied reactions is the attack of the conjugated acid (protonated N-base) on carboxylate anion. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: pentafluorobenzoic acid; tetrafluorobenzoic acid; N-bases; kinetics; decarboxylation; ^{19}F NMR; Fourier transform infrared

INTRODUCTION

It is well know that the decarboxylation reactions of carboxylic acids and the interactions between strong N-bases and acids play very essential roles in chemistry and biochemistry.[1–10] In this respect, we have studied many reactions of various acids and strong N-bases.[11–26] In various solvents for these reactions proton transfer from the acid to the N-base was always observed. For some systems a complex equilibrium including ion pairs, free ions and hydrogen-bonded species of different stoichiometry was observed. A very unexpected observation was made in the case of the deprotonation reaction between pentafluorobenzoic acid and 1,8-bis(dimethylamino)-naphthalene (DMAN),[27] where in addition to the proton transfer reaction decarboxylation of the carboxylic acid occurred, as shown in Scheme 1.

In a previous paper,[27] we demonstrated that under infrared spectroscopic conditions the decarboxylation of tetrafluorobenzoic acid by DMAN was not observed. This reaction was similar to other proton transfer reactions from various acids to the DMAN molecule. The formation of the protonated DMAN molecule and homoconjugated anions was very well evidenced in the FTIR spectra independent of the stoichiometry of the substrate, which is shown in Scheme 2.

To explain the decarboxylation mechanism of the pentafluorobenzoic acid by DMAN and the difference between this reaction and that of tetrafluorobenzoic acid with DMAN, we performed kinetic studies of the reaction of the two acids with various N-bases in acetonitrile using ^{19}F NMR spectroscopy.

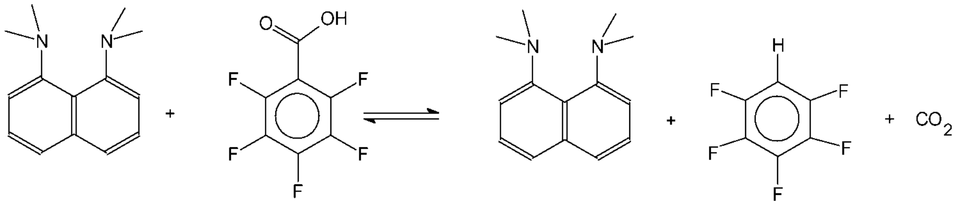
EXPERIMENTAL

Pentafluorobenzoic acid (PFBCOOH) and 2,3,5,6-tetrafluorobenzoic acid (TFBCOOH) were purchased from Aldrich and used without purification. N-bases such as tetramethylguanidine (TMG), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), quinuclidine, phosphazene (P2Et) and DMAN were obtained from Fluka. Quinuclidine was purified by sublimation and DMAN was recrystallized from ethanol.

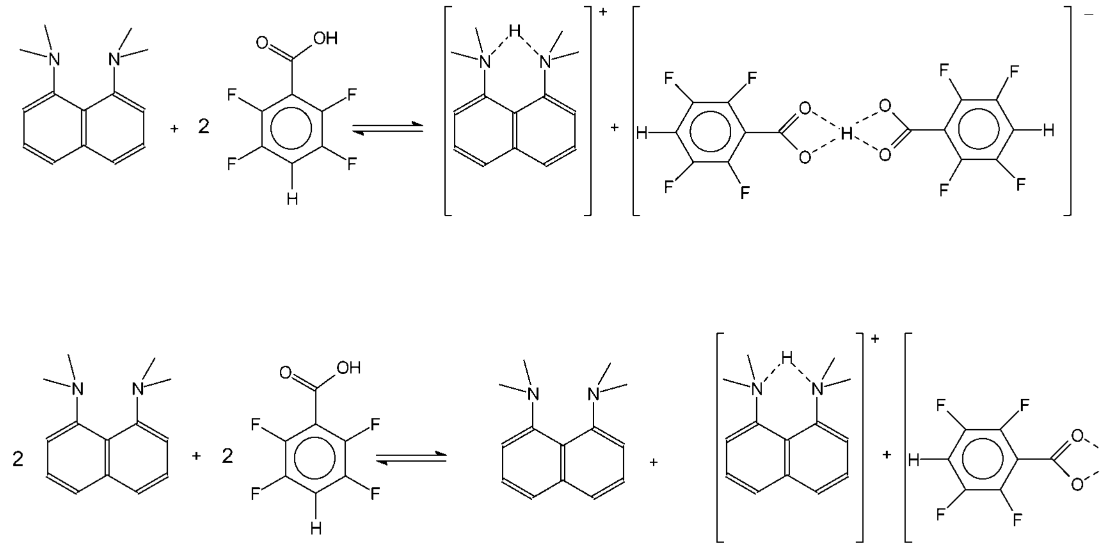
^{19}F NMR spectra were recorded on a Varian-Gemini 300 spectrophotometer at 282.322 MHz in acetonitrile-d_3. The chemical shifts were measured with respect to $CFCl_3$ as an internal standard. The conditions used were spectral width sw = 65 000 Hz, 60° pulse widths and 0.64 s acquisition time.

Kinetic measurements were performed on the basis of the changes of the integration of the ^{19}F signal of fluorine in an *ortho* position to the carboxylic group for substrate and products. The concentration of bases was much higher than that of the fluorinated acids, so a pseudo-first-order method was used. An example of changes in the ^{19}F

**Correspondence to:* G. Schroeder, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland.



Scheme 1



Scheme 2

NMR spectra for the reaction between PFBCOOH and DMAN is shown in Fig. 1.

Second-order rate constants (k) for the reaction were calculated by a linear least-squares fit of the variation of the pseudo-first-order rate constants vs base concentration. The activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) were determined using the Eyring equation [$k = (k_B/h) \exp(\Delta S^{\neq}/R)\exp(-\Delta H^{\neq}/RT)$] by a linear least-squares fit of $\ln k/T$ vs $1/T$. The $\Delta G^{\neq}$ values were calculated using the Gibbs–Helmholtz relation ($\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$) for a temperature of 298 K.

The spectra of the samples were taken with an Fourier transform infrared (FTIR) spectrophotometer (Bruker IFS 113 v) using a cell with Si windows (sample thickness 0.176 mm, detector DTGS, resolution 2 cm^{-1}). The temperature of the samples was 293 K and the concentration of the P_2Et base was 0.1 mol dm^{-3}.

The measurement of the pK_a values of N-bases in acetonitrile was achieved using a published potentiometric procedure.[28]

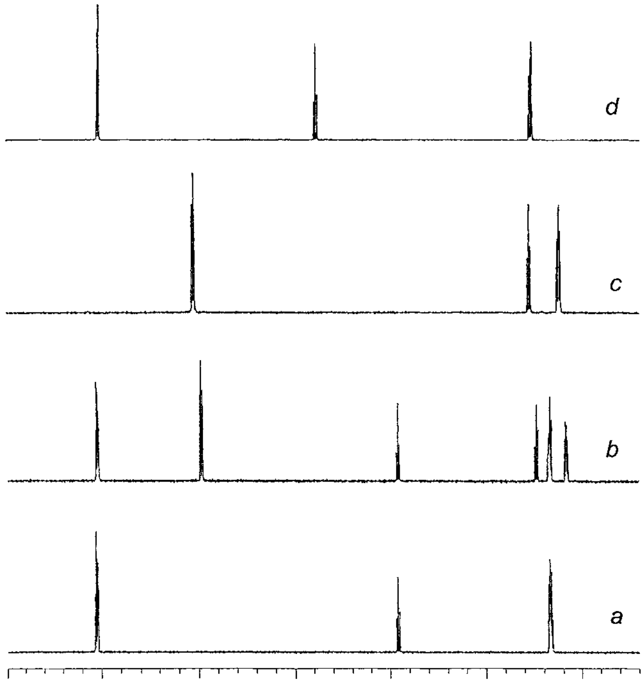
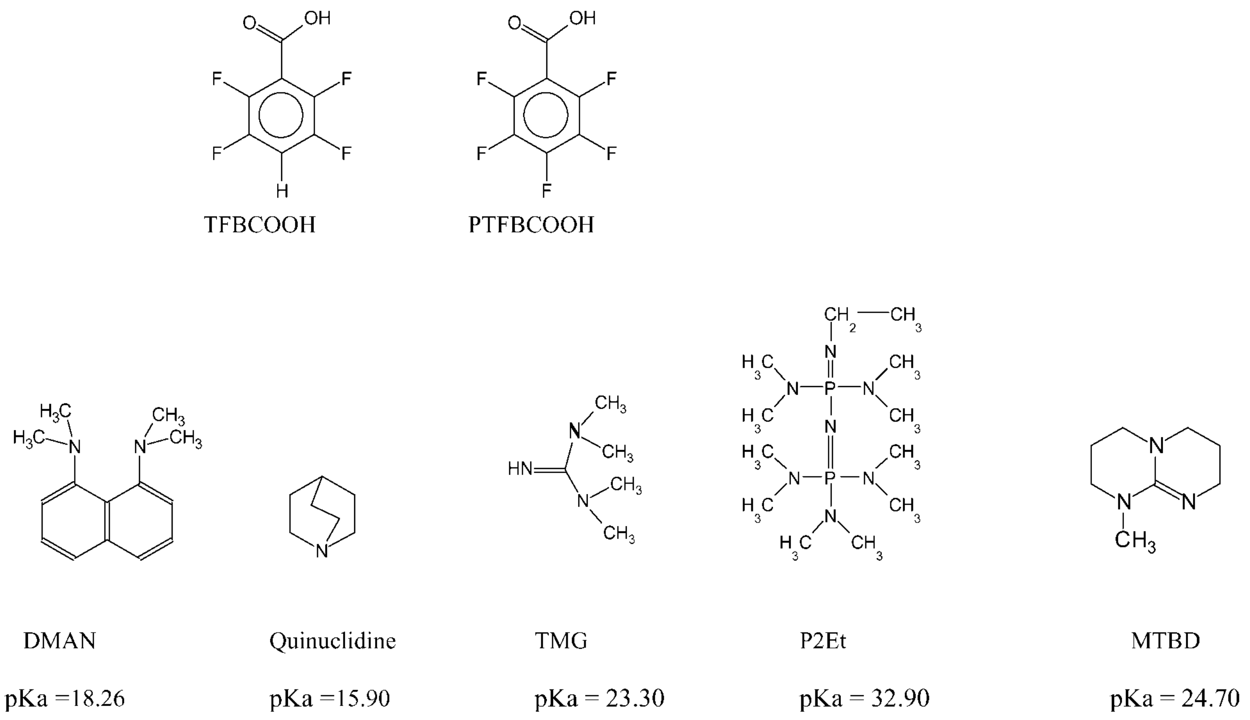


Figure 1. ^{19}F NMR chemical shifts vs time for solutions of PFBCOOH (0.1 mol dm^{-3}) and DMAN (1 mol dm^{-3}) in acetonitrile. (a) PFBCOOH (substrate); (b) PFBCOOH and DMAN immediately after mixing; (c) PFBCOOH and DMAN after 5 h; (d) pentafluorobenzene (product) after 50 h

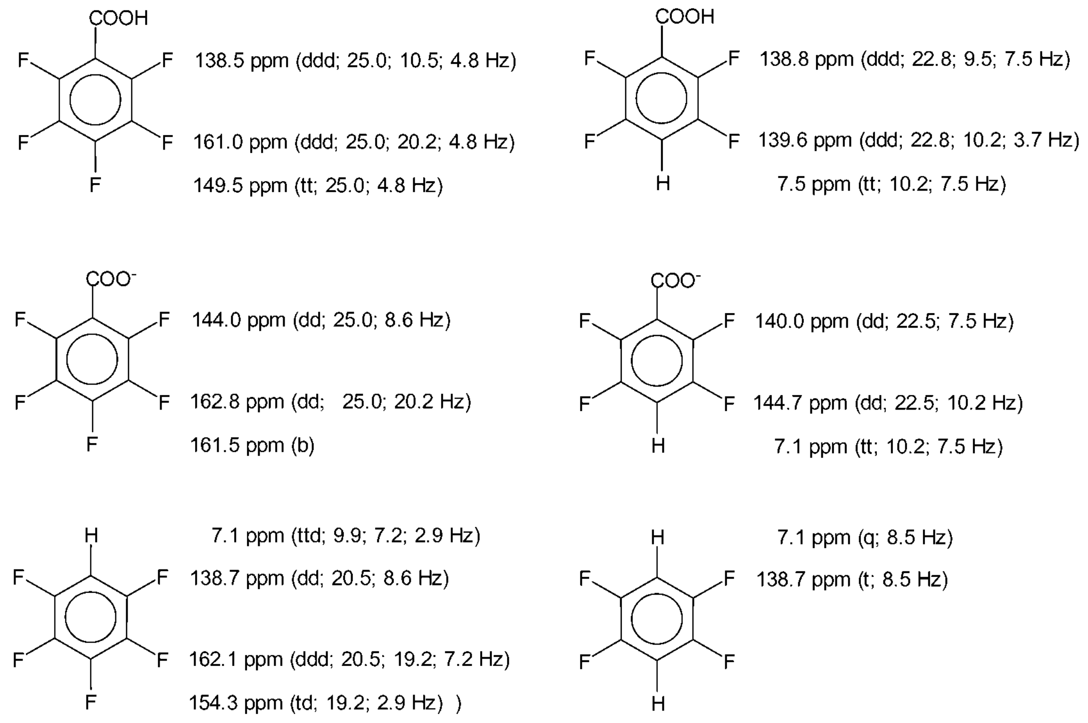
RESULTS AND DISCUSSION

The formulae of the acids and N-bases studied and their pK_a values in acetonitrile are shown in Scheme 3.



Scheme 3

In Scheme 4, the ^{19}F NMR data for PFBCOOH and PTBCOOH acids, their salts (as intermediate products) and the products, i.e. 2,3,4,5,6-pentafluorobenzene and 2,3,5,6-tetrafluorobenzene, in the reaction with DMAN are collected. These data show that the chemical shifts of the ^{19}F signals and the coupling constants $J_{(H-F,F-F)}$ are different for fluorinated acids, their complexes with N-bases (deprotonated species, ion pairs or hydrogen-bonded complexes) and the end products. No other species (i.e. carbanions of decarboxylated acids) were



Scheme 4

Table 1. Second-order rate constants (± standard deviation) for reaction of TFBCOOH or PFBCOOH with N bases in acetonitrile

		k ($dm^3mol^{-1}s^{-1}$)	
N-base	Temperature (K)	TFBCOOH	PFBCOOH
DMAN	293	$(2.83 \pm 0.04) \times 10^{-6}$	$(1.14 \pm 0.04) \times 10^{-4}$
DMAN	298	$(9.10 \pm 0.04) \times 10^{-6}$	$(2.33 \pm 0.04) \times 10^{-4}$
DMAN	308	$(2.86 \pm 0.04) \times 10^{-5}$	$(9.88 \pm 0.05) \times 10^{-4}$
DMAN	313	$(7.61 \pm 0.05) \times 10^{-5}$	$(1.64 \pm 0.04) \times 10^{-3}$
DMAN	318	$(1.29 \pm 0.05) \times 10^{-4}$	$(3.56 \pm 0.04) \times 10^{-3}$
DMAN	333	$(1.25 \pm 0.04) \times 10^{-3}$	
Quinuclidine	298	$(1.06 \pm 0.05) \times 10^{-5}$	$(2.41 \pm 0.04) \times 10^{-4}$
TMG	298	$(7.72 \pm 0.05) \times 10^{-6}$	$(1.73 \pm 0.04) \times 10^{-4}$
MTBD	298	$(6.61 \pm 0.02) \times 10^{-6}$	$(1.57 \pm 0.03) \times 10^{-4}$
P2Et	298	$(9.86 \pm 0.02) \times 10^{-7}$	$(3.60 \pm 0.03) \times 10^{-5}$

observed in the ^{19}F NMR and FTIR spectra of the reaction mixtures. This result suggests that such carbanions are not formed or they are very rapidly protonated.

The second-order rate constants and the activation parameters for the reactions between the fluorinated acids and DMAN are summarized in Tables 1 and 2.

The comparison of the rate constants obtained indicates that the decarboxylation of PFBCOOH is much faster than that of TFBCOOH. The very slow decarboxylation process in the latter case explains why in previous FTIR studies only the intermediate products were observed (see Scheme 2)

The dependence of the rate constants at 25° C on the pK_a values of N-bases is shown in Fig. 2, which indicates that with increasing pK_a values of the N-bases the rate constants of the decarboxylation reaction decrease significantly. In the case of very strong N-bases such as P2Et the decarboxylation of both fluorinated acids is very slow. In the ^{19}F NMR spectra of fluorinated acids with P2Et in acetonitrile, relatively stable free ions of the protonated P2Et molecule and deprotonated fluorinated acids are observed. This result is also confirmed by the FTIR spectrum of a 1:1 mixture of PFBCOOH and P2Et in acetonitrile [Fig. 3(a)]. In this spectrum instead of the ν(C=O) band, observed in the spectrum of free acid at 1745 cm^{-1},[29] a band assigned to $\nu_{as}(COO^-)$ is observed at 1651 cm^{-1}. The $\nu(N\text{–}H^+)$ vibrations of free protonated P2Et molecule are observed at 3334 cm^{-1} and of hydrogen-bonded species to the carboxylate groups at about 3150 cm^{-1}. Furthermore, a sharp band of low intensity is observed at 2339 cm^{-1}, assigned to $\nu(CO_2)$

Table 2. Activation parameters (± standard deviation) for reaction of TFBCOOH or PFBCOOH with DMAN in acetonitrile

Activation parameter	TFBCOOH	PFBCOOH
$\Delta H^{\neq}$ (kJ mol^{-1})	120.9 ± 3.2	103.0 ± 2.6
$\Delta S^{\neq}$ (J K^{-1} *mol^{-1})	61 ± 10	30 ± 8
$\Delta G^{\neq}$ (kJ mol^{-1})	102.8 ± 3.2	93.8 ± 2.6

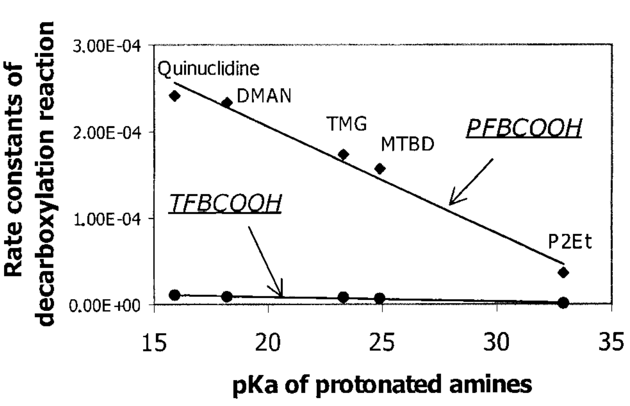


Figure 2. Plot of rate constants of reaction for PFBCOOH or TFBCOOH with various N-bases in acetonitrile at 25 °C

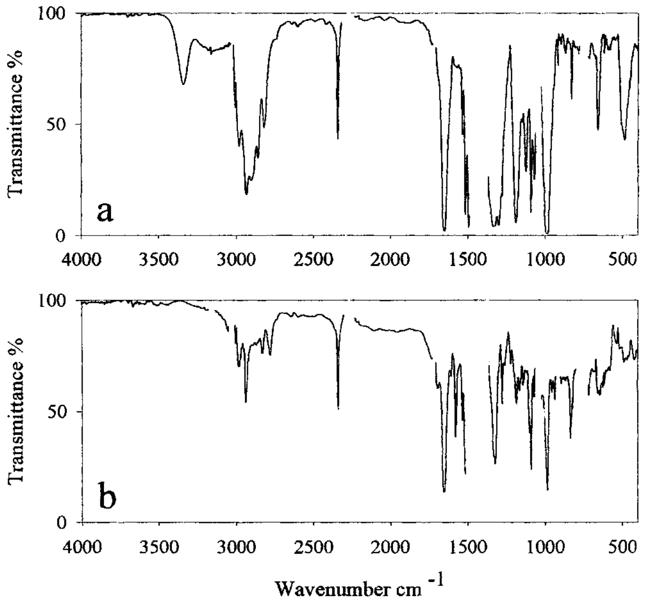
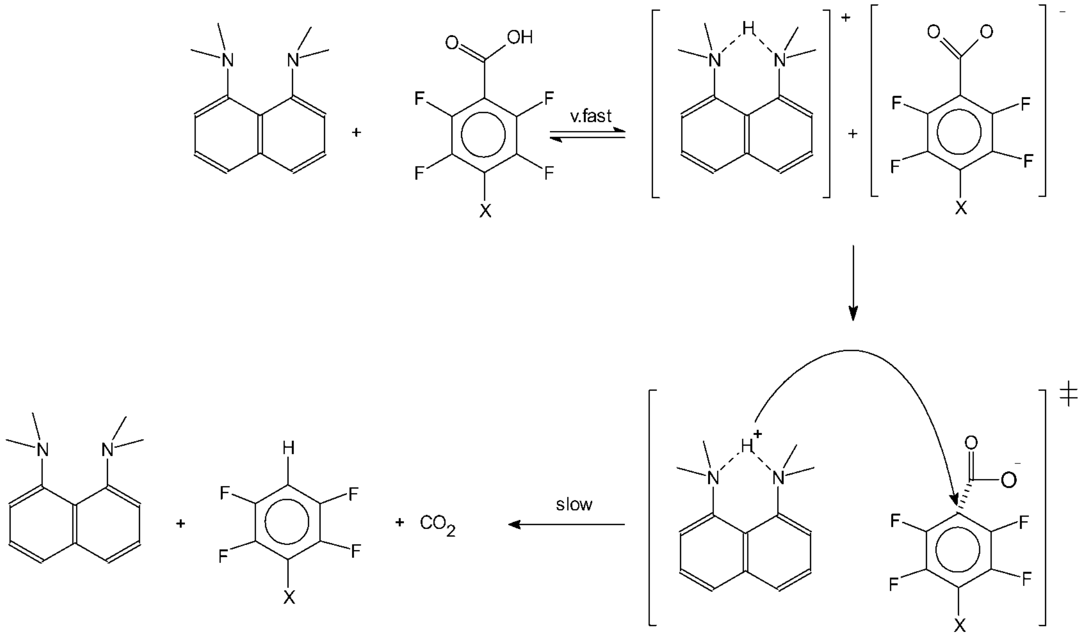


Figure 3. FTIR spectra of a 1:1 mixture of PFBCOOH with N-base immediately after mixing. (a) P2Et phosphazene; (b) DMAN



Scheme 5

vibrations, indicating the beginning of the decarboxylation of the TFBCOO$^-$ anion. A similar situation is observed in the spectrum of a 1:1 mixture of PFBCOOH with DMAN [Fig. 3(b)]. Immediately after mixing, the protonated DMAN molecule forms, as shown by the continuous absorption in the region 1600–400 cm^{-1} as discussed previously.[14–20] The ν_{as}(COO$^-$) band is shown at 1647 cm^{-1}. Furthermore, the so-called Bohlmann bands of low intensity observed at 2780 and 2831 cm^{-1} and the band assigned to the ν(CO$_2$) vibrations at 2339 cm^{-1} indicate the beginning of the decarboxylation of the reaction mixture.

These observations and the result that after the decarboxylation of the fluorinated acids the non-protonated bases occur (see spectra in Ref. 27) demonstrate that the decarboxylation rate of fluorinated carboxylates is determined by the acidity of the protonated bases. With increasing pK_a value of the N-bases the acidity of their conjugated acids decreases and therefore the decarboxylation reaction becomes slower. The proposed mechanism of the decarboxylation of fluorinated acids is given in Scheme 5.

As shown in Scheme 5, in the rate-determining step the transfer of the proton from the protonated N-base and the cleavage of the C—CO$_2^-$ bond are simultaneous processes. The positive $\Delta S^{\neq}$ values (Table 2) show that the decarboxylation reaction is characterized by the desolvatation process because the polar structure of the initial form changes to a neutral transition state and neutral product. The transition state is product-like. This process has a relatively high potential barrier as indicated by the $\Delta H^{\neq}$ values. Such high values are not observed for the proton transfer reactions studied earlier.[28–32]

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