KINETICS OF THE FORMATION OF N'-(PERFLUOROACYLIMIDOYL)PERFLUOROALKYLAMIDINES FROM PERFLUORONITRILES AND PERFLUOROAMIDINES

G. M. Tolmacheva, S. P. Krukovskii,
E. L. Berman, and V. A. Ponomarenko

UDC 541.127:542.91:547.298.5'161

Considerable work has already been devoted to a study of the synthesis and properties of the N'-(perfluoroacylimidoyl)perfluoroalkylamidines (imidoylamidines) [1, 2]. There has, however, been no study of the kinetics of the formation of the perfluoroimidoylamidines from perfluoroamidines and perfluoronitriles, and this despite the fact that such study might well give interesting information concerning the formation of polyimidoylamidines, intermediates in the synthesis of polyperfluorotriazines.

EXPERIMENTAL

The nitriles and amidines of perfluoro-2-methyl-3-oxahexane carboxylic acid served as starting materials for synthesizing the compounds used in this work.

Nitrile of Perfluoro-2-methyl-3-oxahexane Carboxylic Acid. A 500-ml Favorskii flask equipped with a herring-bone head was loaded with 71 g of the amide of perfluoro-2-methyl-3-oxahexane carboxylic acid and 200 g of P_2O_5 and the mixture was heated to 200°C for 2-3 h, the nitrile being condensed in a spiral trap cooled with a mixture of acetone and solid CO_2 as it distilled off. Redistillation at 49°C gave 51.4 g (77%) of the nitrile of perfluoro-2-methyl-3-oxahexane carboxylic acid. Found: C 23.12; F 67.10; N 4.75%. $C_6F_{11}NO$. Calculated: C 23.15; F 67.20; N 4.50%.

TABLE 1. Properties of Perfluoronitriles and Perfluoroamidines

Compound	bP, °C (p, mm Hg)	Found, %				Empirical formula	Calculated, %			
		C	H	F	N		C	H	F	N
Nitrile of perfluoroenanthic acid	78—80	34,00	—	59,80	5,65	$C_7F_{13}N$	34,28	—	60,00	5,75
Nitrile of perfluorocyclohexane carboxylic acid	50	27,40	—	68,00	4,60	$C_7F_{11}N$	27,36	—	68,07	4,56
Nitrile of 3,3,3-trifluoro-2-trifluoromethyl-2'(alloxy)propionic acid	89—90	36,02	2,23	49,40	5,94	$C_7H_5F_6NO$	36,10	2,15	49,80	6,00
Nitrile of perfluoro-2-methyl-3-oxahexane carboxylic acid	49	23,12	—	67,10	4,75	$C_6F_{11}NO$	23,15	—	67,20	4,50
Nitrile of perflouro-2,5-dimethyl-3,6-dioxanonane carboxylic acid	112—114	22,45	—	67,58	2,96	$C_9F_{17}NO_2$	22,60	—	67,71	2,94
Nitrile of perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecane carboxylic acid	164—166	22,40	—	67,91	2,35	$C_{12}F_{23}NO_3$	22,40	—	67,96	2,40
Nitrile of perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecane carboxylic acid	96—99 (20)	22,30	—	68,10	1,80	$C_{15}F_{29}NO_4$	22,25	—	68,11	1,73
Amidine of methoxypropionic acid	48 (3)	21,12	1,05	58,15	11,20	$C_4H_3F_7N_2O$	21,05	1,31	58,05	12,28
Amidine of perfluorobutyric acid	—	22,40	1,32	62,50	13,35	$C_4H_3F_7N_2$	22,6	1,36	62,74	13,40
Amidine of perfluoroenanthic acid	—	23,28	0,78	68,00	7,85	$C_7H_3F_{13}N_2$	23,20	0,80	68,30	7,70
Amidine of perfluoro-2-methyl-3-oxahexane carboxylic acid	35 (2)	22,86	0,89	63,70	8,37	$C_6H_3F_{11}N_2O$	21,95	0,95	63,72	8,54
Amidine of perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecane carboxylic acid	—	22,45	0,40	65,50	4,26	$C_{12}H_3FN_2O_3$	21,80	0,45	66,40	4,24

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 1963-1968, September, 1976. Original article submitted August 5, 1975.

The other nitriles were prepared in a similar manner (Table 1), their purity (99.9%) being checked by gas – liquid chromatography.

Amidines of Perfluoro-2-methyl-3-oxahexane Carboxylic Acid. Thirty grams of the nitrile of perfluoro-2-methyl-3-oxahexane carboxylic acid were added dropwise to 10 ml of dry NH_3 in a 50-ml ampule cooled by an acetone – solid CO_2 mixture. The ampule temperature was then slowly raised to ~20°C. This procedure gave 29.7 g of the amidine of perfluoro-2-methyl-3-oxahexane carboxylic acid, bp 35°C (3 mm). Found: C 22.86; H 0.89; F 63.70; N 8.37%. $C_6H_3F_{11}N_2O$. Calculated: C 21.95; H 0.92; F 63.72; N 8.54%. The other amidines were prepared in a similar manner (cf. Table 1).

The structure of these compounds were confirmed by the data of NMR, IR, and UV spectroscopies. Each of the compounds showed a characteristic IR absorption band (ν, cm^{-1}): nitriles at 1100-1400 (CF), and 2250-2260 ($C \equiv N$), amidines at 1100-1400 (CF), 1610-1630 (NH def.) 1670-1680 ($C = N$), and 3500-3520 (NH, stretch). The UV spectra of the amidines showed a λ_{max} at 203-205 nm.

Perfluorooctane was used as the solvent. The technical product was boiled over NaOH for 8 h, and then redistilled over $LiAlH_4$, the 104°C fraction being cut out. The product obtained was chromatographically pure, showing no trace of UV absorption in the 200-350-nm range.

Kinetic studies were carried out in a hermetically sealed quartz cell, $10 \times 10 \times 45$ mm with a molybdenum glass junction; this was filled with a previously calculated amount of the perfluoronitrile solution, the perfluoroamidine solution added, the cell cooled with liquid N_2, and the contents then pumped off until there was no further evolution of gases. The cell was then closed off and its temperature rapidly raised to 20°C, following which it was placed in a dense metallic block where its temperature was held constant to within ±0.5°C. The comparison cell contained pure perfluorooctane. Recording of the UV spectrum was begun 2-3 min after introducing the cell into the thermostating block.

Study of the kinetics of perfluoronitrile (PFN) addition to perfluoroamidines (PFA) was made difficult by the high rates of these reactions at ~20°C. In the absence of a solvent imidoylamidine was found to be formed quantitatively over the temperature interval from −75 to 0°C.

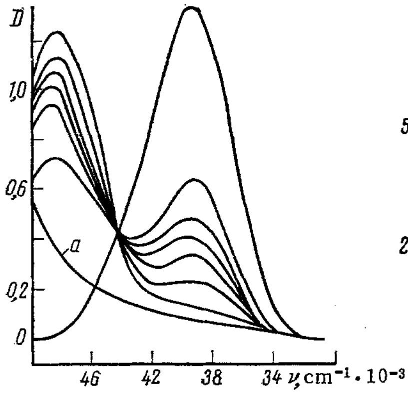


Fig. 1

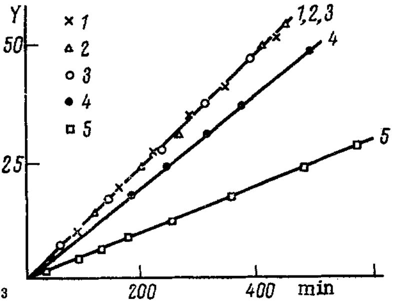


Fig. 2

Fig. 1. Alteration of the UV absorption spectrum of PFA during reaction of the latter with PFN (*a* designates the absorption of the solvent, perfluorooctane).

Fig. 2. Kinetics of the interaction of the amidine of perfluorobutyric acid with perfluoronitriles at 25°C; $[PFA] = 2 \cdot 10^{-3}$, $[PFN] = 2 \cdot 10^{-2}$ mole/liter: 1) nitrile of perfluoro-2,5-dimethyl-3,6-dioxanonane carboxylic acid; 2) nitrile of perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecane carboxylic acid; 3) nitrile of perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecane carboxylic acid; 4) nitrile of perfluoro-2-methyl-3-oxahexane carboxylic acid; 5) nitrile of cyclohexane carboxylic acid

$$Y = \frac{1}{[H]_0 - [A]_0} \ln \frac{[A]_0([H]_0 - [U])}{[H]_0([A]_0 - [U])}$$

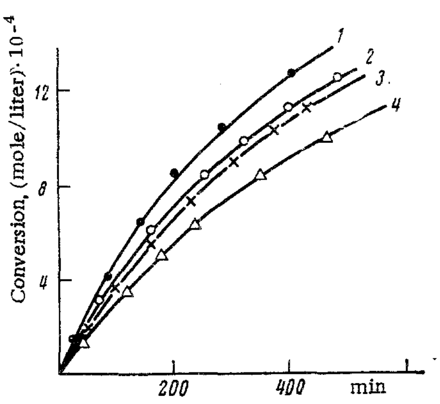


Fig. 3

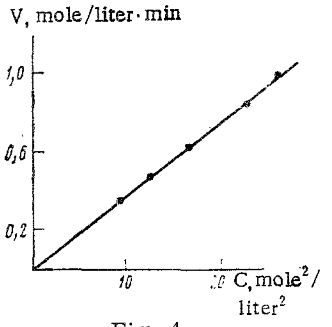


Fig. 4

Fig. 3. Kinetic curves for the reactions of the amidine of perfluorobutyric acid with perfluoronitriles at 25°C; $[PFA] = 2 \cdot 10^{-2}$, $[PFN] = 2 \cdot 10^{-2}$ mole/liter: 1) nitrile of perfluoroenanthic acid; 2) nitrile of perfluoro-2,5-dimethyl-3,6-dioxanonane carboxylic acid; 3) nitrile of perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecane carboxylic acid; 4) nitrile of perfluoro-2-methyl-3-oxahexane carboxylic acid.

Fig. 4. Variation of the initial reaction rate with the product of the initial concentrations of the amidine of perfluorobutyric acid and the nitrile of perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecane carboxylic acid.

A rather considerable dilution of the system solutions was required when working at controlled reaction rates over the 20 to 70°C temperature range. Perfluoronitriles do not absorb in the 200-350-nm range. It was found that the optical density increased linearly with the component concentrations, over the entire concentration range. For perfluoroimidoylamidine (PFIA), and the PFA, the extinction coefficients were close to 7700 (λ_{max} 253 nm) and equal to 5500 (λ_{max} 205 nm) $mole^{-1} \cdot cm^{-1}$, respectively.

In the course of the PFN – PFA interaction, the optical density diminished at 205 nm and, starting from zero, steadily increased at 253 nm (Fig. 1). The various imidoylamidines were synthesized and their UV spectra obtained $[(1\text{-}2) \cdot 10^{-2}$ liter/mole$]$ as a preliminary to determining the extent of PFA conversion to PFIA. The limiting spectral diagram proved to be adequate for complete conversion of PFA to PFIA and further concentration changes in the components could not be detected. The appearance of a clearly defined isobestic point was further confirmation of the absence of side reactions.

The range of reactant concentrations was so selected that the whole reaction process could be completed in less than 24 h. By treating the spectra data in terms of the change in optical density at an arbitrarily chosen wavelength on the long-wave side of the PFIA absorption band where the PFA absorption was negligible, the reaction could be carried out with an excess of nitrile. The nitrile and amidine were used in perfluorooctane solution, working at concentrations in the $(1\text{-}2) \cdot 10^{-2}$ to $1 \cdot 10^{-3}$ mole/liter range. The UV spectra were recorded with a double-beam Specord recording spectrophotometer. The IR spectra were obtained with a UR-10 spectrophotometer. Chromatographic analysis was carried out with an LKhM-8-MD chromatograph, using a column packed with Chromaton + 10% SKTF.

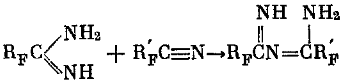
DISCUSSION OF RESULTS

The kinetic curves covering the interaction of PFA with excess PFN were treated by the method of least squares, using the second-order rate equation

$$\frac{1}{[PFN]_0[PFA]_0} \ln \frac{[PFA]_0([PFN]_0-[PFIA])}{[PFN]_0([PFA]_0-[PFIA])} = kt$$

optical densities being recalculated to concentrations in moles/liter. In each case the experimentally developed relation was linear up to a high degree of advancement of the reaction (Fig. 2). Kinetic curves for reactions with equimolar concentrations of PFA and PFN are shown in Fig. 3. These curves are readily rectified by plotting in the coordinates of the equation $1/[PFIA] = (1/[PFA]) + (1/[PFA]_0^2kt)$. The initial reaction rate varied

TABLE 2. Rate Constants for the Interaction of Perfluoroamidines and Perfluoronitriles



$$R_FC\genfrac{}{}{0pt}{}{\nearrow NH_2}{\searrow NH} + R'_FC{\equiv}N \rightarrow R_F\overset{NH}{\overset{\|}{C}}N{=}\overset{NH_2}{\overset{|}{C}}R'_F$$

[PFA] = $1\cdot10^{-3}$, [PFN] = $1\cdot10^{-2}$, mole/liter, 25°C

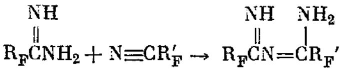
Expt. No.	R_F	R'_F	$k^*\cdot10^3$, liters/mole·sec
1	$CF_3CF_2CF_2$	$CF_3CF_2CF_2O(\underset{CF_3}{CF}CF_2O)_2\underset{CF_3}{CF}$	1,85
2	$CF_3(CF_2)_5$		1,59
3	$CF_3OCF_2CF_2$		2,13
4	$CF_3CF_2CF_2O\underset{CF_3}{CF}$		1,69
5	$CF_3CF_2CF_2O(\underset{CF_3}{CF}CF_2O)_2\underset{CF_3}{CF}$		1,96
6	$CF_3CF_2CF_2$	$CF_3CF_2CF_2O\underset{CF_3}{CF}$	1,91
7		$CF_3CF_2CF_2O\underset{CF_3}{CF}CF_2O\underset{CF_3}{CF}$	1,97
8		$CF_3CF_2CF_2O(\underset{CF_3}{CF}CF_2O)_3\underset{CF_3}{CF}$	2,10
9		$CF_3(CF_2)_6$	2,74
10		$\underbrace{CF_2CF_2CF_2CF_2CF_2CF}$	0,84
11		$CH_2{=}CHCH_2O\underset{(CF_3)_2}{C}$	0,0064 †

*Reliability of determination no more than $8\cdot10^{-5}$, with a correlation coefficient of 0.999.

†Values of k (25°C) calculated by extrapolating the Arrhenius plot for the interval from 50 to 70°C.

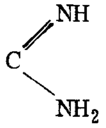
linearly with the product of the concentration of the reacting components over the entire concentration range (Fig. 4).

Data on the PFIA formation indicated that the PFA + PFN reaction was bimolecular, proceeding according to the scheme



$$R_F\overset{NH}{\overset{\|}{C}}NH_2 + N{\equiv}CR'_F \rightarrow R_F\overset{NH}{\overset{\|}{C}}N{=}\overset{NH_2}{\overset{|}{C}}R_F'$$

It was of interest to follow the alteration in the PFA and PFN reactivities and their relation to the molecular structures (Table 2). Despite differences in polar and steric effects from groups adjacent to the $C{=}N$ bond, there was relatively little difference in the reactivities of most of the compounds studied here (cf. Table 2, Expt. Nos. 1-9). Exceptions here were the nitriles of 3,3,3-trifluoro-2-trifluoromethyl-2-(alloxy)propionic acid and perfluorocyclohexane carboxylic acid. The relatively low reactivity of these nitriles apparently traces back to steric and polar effects from the groups (F, CF_3, etc.) directly adjacent to the $C{\equiv}N$ and



$$C\genfrac{}{}{0pt}{}{\nearrow NH}{\searrow NH_2}$$

reaction centers.

TABLE 3. Activation Parameters for Reactions of the Amidines of Perfluorobutyric Acid with $R'_FC{\equiv}N$

R'_F	k_p, liter/mole·sec (25°C)	A, liters/mole·sec	E, kcal/mole
$CF_3CF_2CF_2O(\underset{CF_3}{CF}CF_2O)_2\underset{CF_3}{CF}$	$1{,}85\cdot10^{-3}$	$5{,}1\cdot10^{5}$	10,8
$CH{=}CHCH_2O\underset{(CF_3)_2}{C}$	$0{,}6\cdot10^{-5}$	$1{,}7\cdot10^{10}$	22,3

TABLE 4. Rate Constants for Reactions of the Amidines of Perfluorobutyric Acid with the Nitriles of Perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecane Carboxylic Acid in the Presence of Certain Additives, at 25°C

Additive	Concentration, mole/liter	$k^{*} \cdot 10^3$ liters/mole·sec ‡
—	—	1,85
H_2O	0,01 †	1,82
$(C_2H_5)_3N$	0,01 †	1,90
C_6F_6	0,001	1,85
$CFCl_2CF_2Cl$	1,0 †	1,89
O_2	0,1 **	1,93

---

* Reliability of determination no more than $5 \cdot 10^{5}$, with a correlation coefficient of 0.999.

† Additive at the limit of the heterogeneity region of the system.

‡ Maximum concentration at which the reaction could be followed spectrally.

** O_2 dosing in the previously evacuated cell at atmospheric pressure; O_2 concentration calculated from the free volume of the loaded cell.

Values of the activation energy, and the pre-exponential factor, for addition of certain nitriles to the amidines of perfluorobutyric acid are shown in Table 3.

Study was also made of the effect on these same reactions of certain additives which did not, by their presence, alter the value of the rate constant. It was obvious that those additives were unable to initiate side reactions (hydrolysis, oxidation, substitution, etc.) in any appreciable degree, during the time required for imidoylamidine formation (Table 4).

The authors wish to thank V. M. Men'shova and S. G. Gurevich for working up the experimental data on a BÉSM-6 computer, and M. G. Deborina for having furnished the nitrile of 3,3,3-trifluoro-2-trifluoromethyl-2-(alloxy)propionic acid.

CONCLUSIONS

1, Study has been made of the kinetics of formation of perfluoroimidoylamidines from amidines and nitriles of the poly- and perfluoro carboxylic acids. There is little difference in the reactivities of the nitriles and amidines of the perfluoro carboxylic and the oxa carboxylic acids.

2. The reaction kinetics are little affected by the addition of water, triethylamine, Freon-113, hexafluorobenzene, or oxygen at the concentrations studied here.

LITERATURE CITED

1. G. B. Fedorova and I. M. Dolgopol'skii, Zh. Obshch. Khim., 39, 2710 (1969).
2. H. C. Brown and P. D. Schuman, J. Org. Chem., 28, 1122 (1963).