Russian Journal of Applied Chemistry, Vol. 75, No. 6, 2002, pp. 959–961. Translated from Zhurnal Prikladnoi Khimii, Vol. 75, No. 6, 2002, pp. 976–978.

ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

Fluorination of Organic Compounds with Cobalt Trifluoride and Elemental Fluorine in the Presence of Cobalt Trifluoride[1]

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Received January 17, 2002

Abstract—Fluorination of organic compounds with cobalt trifluoride and elemental fluorine in the presence of cobalt trifluoride was studied. Fluorination with elemental fluorine proceeds under external-kinetic control at a constant rate. Examples of fluorination with elemental fluorine of certain fluorinated olefins and polyfluorinated paraffins in the presence of CoF_3 are presented.

Cobalt trifluoride is a common fluorinating agent for synthesis (including commercial production) of perfluorinated organic compounds (paraffins, ethers, etc.) form hydrocarbon and unsaturated analogue [1, 2]. In the reaction, cobalt trifluoride is reduced to difluoride:

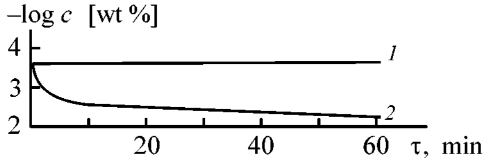
$$CoF_3 + C_nH_{2n+2} \rightarrow CoF_2 + C_nF_{2n+2} + HF.$$

Fluorination with cobalt trifluoride is characterized by low yield (30–40%) of target products, limited productivity because of the low content of available fluorine (16.30 wt %; the actual consumption is lower by a factor of 1.2–3), and noticeable amount of residual hydrogen-containing and unsaturated compounds (up to 1 wt %), instead of 1×10^{-3}–5×10^{-4} wt % required in medicine, electronics, and other branches of industry. Therefore, other synthesis methods should be searched for. One of them is catalytic fluorination of fluorine-containing organic compounds with elemental fluorine. Higher fluorides of metals with variable oxidation state, including nickel, copper, and cobalt fluorides [3–5], are usually used as such catalysts. In this work, we studied fluorination of monohydroperfluorotripropylamine $C_3F_6HN(C_3F_7)_2$ (**I**) and monohydroperfluorotributylamine $C_4F_8HN(C_4F_9)_2$ (**II**) with cobalt trifluoride and with elemental fluorine in the presence of cobalt trifluoride. Compounds **I** and **II** are the main process impurities in electrochemical synthesis of perfluorotripropylamine $(C_3F_7)_3N$ and perfluorotributylamine $(C_4F_9)_3N$, respectively. Their content in crude products reaches 30 wt %.

Fluorination was performed in a reactor packed with CoF_3. In the first case, a mixture of vapors of a compound to be fluorinated and fluorine was supplied, and in the second case, nitrogen was introduced instead of fluorine at the same flow rate. The figure shows the kinetics of fluorination of monohydroperfluorotributylamime (**II**).

Curve *2* describing the rate of fluorination with CoF_3 is characteristic for reactions whose initial stage proceeds on the surface of a solid reactant (CoF_3 in this case) under external-kinetic control. Since CoF_3 is consumed in the surface layer, the reaction becomes diffusion-controlled, which accounts for the observed decrease in the reaction rate [6]. It should be noted that the initial section of curve *2* is rather difficult for analysis, and the majority of papers on CoF_3 fluorination kinetics contain only data for the diffusion region, in which the decrease in the reaction rate is neglected and the rate is considered to be constant [6, 7]. Studies of fluorination of fluorinated methanes [7] and hexafluoropropane [8] have shown that the fluorination reaction is first-order.

Fluorination with elemental fluorine in the presence of CoF_3 (curve *1*) proceeds under external-kinetic control since the CoF_3 concentration in the surface



Relative rate of fluorination of **II**: (*c*) concentration of **II** and (τ) time. Fluorination with (*1*) CoF_3–F_2 and (*2*) CoF_3.

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[1] Reported at the 3th International Conference "Chemistry, Technology, and Application of Fluorinated Compounds," St. Petesrburg, June 6–9, 2001.

Table 1. Fluorination of CoF_2 and hydrogen-containing impurities of perfluorotributylamine [contact time τ = 5 min, $(C_4F_8H)_3N$ initial concentration 17.5 wt %]

T, °C	Content, wt %		T, °C	Content, wt %	
	available fluorine (CoF_3)	hydrogen-containing compounds		available fluorine (CoF_3)	hydrogen-containing compounds
200	13.0 (79.4)	7.5	350	16.0 (97.5)	2.1
250	13.6 (83.0)	4.8	400	16.38 (100)	0
300	15.4 (94.0)	3.2	450	16.38 (100)	0

Table 2. Fluorination of certain hydrogen-containing and unsaturated compounds with elemental fluorine on CoF_3

Compound		T, °C	τ, min	$A^* \times 10^{-4}$, wt %	Yield, mol%
fluorinated	fluorinated				
$C_3F_7CFH–CHF_2$	C_5F_{12}	230–280	5	6	94.4
$C_2F_4HN(C_2F_5)_2$	$(C_2F_5)_3N$	270–330	5	5	95.5
$C_3F_6HN(C_3F_7)_2$	$(C_3F_7)_3N$	320–380	10	6	96.0
$C_4F_8HN(C_4F_9)_2$	$(C_4F_9)_3N$	360–410	13	7	93.2
$C_5F_{10}HN(C_5F_{11})_2$	$(C_5F_{11})_3N$	380–430	16	8	90.1
$C_4F_8HOC_4F_8H$	$(C_4F_9)_2O$	300–350	5	5	96.5
$(C_3F_7)_2CF–CF=CF_3$	C_9F_{20}	320–380	6	5	97.0
cyclo $C_6F_9–C_2F_5$	cyclo $C_6F_{11}–C_2F_5$	300–360	7	5	96.4

* (A) Residual content of hydrogen-containing and unsaturated compounds.

layer is constant owing to timely or even advance supply of fluorine:

$$RH + CoF_3 \rightarrow RF + HF + CoF_2,$$

$$CoF_2 + F_2 \rightarrow CoF_3.$$

This is illustrated by the data on fluorination of CoF_2 and compound **II** at various temperatures presented in Table 1.

It follows from the kinetics of fluorination of **I** that this reaction is second-order. The activation energy amounts to 37.5 kJ mol^{-1}. The equation of the reaction rate is as follows:

$$\log V = \log \text{const} - 4.56 E/RT.$$

It should be noted that the catalytic fluorination is characterized by high yield of the target products and their insignificant degradation.

Data on catalytic fluorination of certain hydrogen-containing and unsaturated compounds are listed in Table 2.

The results make evident the difference between fluorination with CoF_3 and that with fluorine in the presence of CoF_3 as a catalyst.

In the first case, the fluorination rate is low and decreases with time; the process is limited by the content of available fluorine, which prevents its being performed in the continuous mode. The residual content of hydrogen-containing or unsaturated compounds in the resulting products is substantial ($> 1 \times 10^{-3}$ wt %), which requires additional purification. In the second case, the fluorination rate is fairly high and constant; the process has no time limitation, which allows it to be performed in the continuous mode; the residual content of hydrogen-containing compounds is less than 1×10^{-3} wt %.[2]

EXPERIMENTAL

The UV spectra were recorded on a UF-26 spectrophotometer; the fluoride ion was determined with an ET-1 fluoride-selective electrode. In chromatographic analysis, a heat-conductivity detector was used; carrier gas helium, solid phase Silokhrom, liquid phase 20% α,α,α-tri(β-cyanoethyl)acetophenone, 2 m × 3 mm

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[2] The catalytic fluorination process was implemented at the pilot plant of the "Prikladnaya Khimiya" Russian Scientific Center.

column. The GC-MS analysis was performed on a Hewlett-Packard device comprising an HP-5890 gas chromatograph, an HP5972 mass-selective detector, and a Vectra 5/100 working station with software for data processing and Wiley138.L and NBS75K.L database.

Chromatographic separation was performed on a 30 m HP-5MS capillary column in the programmed-heating mode. Chromatograms were recorded by the total ion current within the 35–700 mass range. The impurities were identified by comparing the mass spectra of separated mixture components with those from the Wiley138.L and NBS75K.L databases and by calculation.

The kinetics of fluorination of **I** was studied in a vertical reactor made from a nickel tube (inner diameter 36 mm). The reactor was packed with CoF_3 with bed height of 300 mm. A thermocouple pocket was arranged along the reactor axis. The temperature variation throughout the bed did not exceed 3°C. From a batcher, a mixture of **I** (25 wt %) with $(C_3F_7)_3N$ (75 wt %) and fluorine were supplied at definite and constant rates into a mixer-evaporator, which was a 500-mm nickel tube 36 mm in diameter, equipped with a controllable heater. The fluorine excess did not exceed 20% relative to the stoichiometry. From the evaporator, the reaction mixture passed through a catalyst bed (with particle size of 0.035–0.05 mm) and condensed in a trap cooled with liquid nitrogen. After process completion, the trap was warmed to room temperature and weighed, and the reaction products were analyzed by GLC. Low-boiling products containing fluorine and HF were neutralized in a column with lime and analyzed by GLC. The experiments were performed at 150, 180, 220, and 250°C.

The fluorination rate constants and activation energy [9] were calculated from the concentration-vs.-time plots for 150, 180, 220, and 250°C.

ACKNOWLEDGMENTS

The work was financially supported by ISTC.

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