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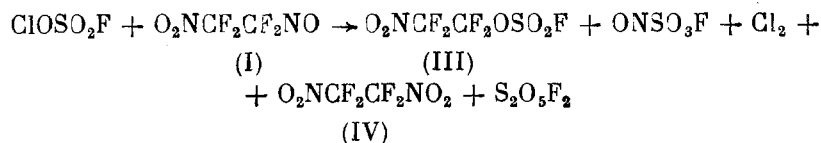10. B. L. Dyatkin and I. L. Knunyants, Zh. Vses. Khim. Obshch. im. D. I. Mendeleeva, 15, 5 (1970).

REACTION OF CHLORINE FLUOROSULFATE AND PEROXYDISULFURYL

DIFLUORIDE WITH PERFLUORONITROSOALKANES

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It is known that highly electrophilic chlorine fluorosulfate ($ClOSO_2F$) easily replaces with fluorosulfate groups the halogen atoms in haloalkanes [1, 2] and even the Cl atoms in Freons [3, 4]. Unlike $ClOSO_2F$, under mild conditions peroxydisulfuryl difluoride ($S_2O_6F_2$) which is a radical agent, replaces with the fluorosulfate group only the Br [5] and I [6] atoms in Freons, i.e., the comparatively easily oxidizable halogens.

Therefore, the study of the reaction of perfluoronitroso compounds with such strong oxidizing agents as $ClOSO_2F$ and $S_2O_6F_2$ seemed of definite interest. Previously we noted that 1-chloro-2-nitrotetrafluoroethane (II) is formed in the reaction of $ClOSO_2F$ with 1-nitroso-2-nitrotetrafluoroethane (I) [7]. In the present paper, we have determined that (II) is formed only under very mild conditions (<−50°C, dilution with an inert solvent) with obligatory addition of $ClOSO_2F$ to a large molar excess of (I). In the absence of a solvent or in sufficiently concentrated solutions, even at low temperature (≤−50°C), the main direction of the reaction is replacement of the nitroso group not by Cl, but by the fluorosulfate group with the formation of 2-nitrotetrafluoroethyl fluorosulfate (III), nitrosyl fluorosulfate, and Cl_2. 1,2-Dinitrotetrafluoroethane (IV) and pyrosulfuryl difluoride ($S_2O_5F_2$) were also isolated as byproducts.

$$ClOSO_2F + O_2NCF_2CF_2NO \rightarrow O_2NCF_2CF_2OSO_2F + ONSO_3F + Cl_2 +$$
$$\text{(I)} \qquad \text{(III)}$$
$$+ O_2NCF_2CF_2NO_2 + S_2O_5F_2$$
$$\text{(IV)}$$

In the considered process, about 2 moles of $ClOSO_2F$ is consumed per 1 mole of (I). Increasing the temperature to between −30 and −20°C leads to some decrease of the yield of (III) and $ONSO_3SF$ and to a simultaneous increase of the yield of (IV) and $S_2O_5F_2$.

At −60°C, $ClOSO_2F$ also reacts easily with trifluoronitrosomethane (CF_3NO)

$$ClOSO_2F + CF_3NO \rightarrow CF_3OSO_2F + CF_3Cl + ONSO_3F + Cl_2 + CF_3NO_2 + S_2O_5F_2$$
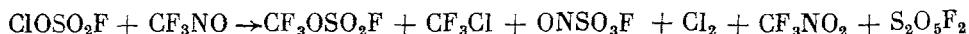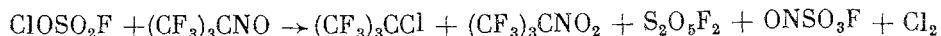
Unlike in the case of the reaction involving (I), in this case, despite the reverse order of mixing of the reagents, not only the product of replacement of the nitroso group by fluorosulfate, trifluoromethyl fluorosulfate (CF_3OSO_2F), is formed, but also the product of its replacement by Cl—CF_3Cl.

The reaction of $ClOSO_2F$ with perfluoro-tert-nitrosobutane ($(CF_3)_3CNO$) does not afford perfluoro-tert-butyl fluorosulfate. The formation of perfluoro-tert-butyl chloride, perfluoro-tert-nitrobutane, and $S_2O_5F_2$ was determined by spectral methods and GLC:

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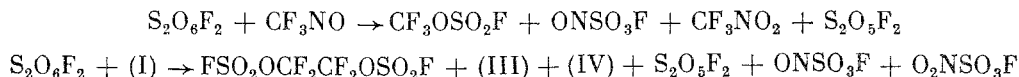
$$ClOSO_2F + (CF_3)_3CNO \rightarrow (CF_3)_3CCl + (CF_3)_3CNO_2 + S_2O_5F_2 + ONSO_3F + Cl_2$$

The $S_2O_6F_2$ is less active than $ClOSO_2F$ and it begins to react with CF_3NO and (I) only above 5-10°C.

Previously, Ginsburg et al. [8] noted replacement of the nitroso group by fluorosulfate in the reaction of $S_2O_6F_2$ with CF_3NO. We isolated not only fluorosulfates, but also products of redox processes, the corresponding perfluoronitroalkanes and $S_2O_5F_2$. In the case of (I), 1,2-bis(fluorosulfonyloxy)tetrafluoroethane (V) was obtained unexpectedly as the main product:

$$S_2O_6F_2 + CF_3NO \rightarrow CF_3OSO_2F + ONSO_3F + CF_3NO_2 + S_2O_5F_2$$

$$S_2O_6F_2 + (I) \rightarrow FSO_2OCF_2CF_2OSO_2F + (III) + (IV) + S_2O_5F_2 + ONSO_3F + O_2NSO_3F$$

The formation of (V) cannot be related to direct replacement of the nitro group by fluorosulfate because it was shown by direct experiments that neither $ClOSO_2F$ nor $S_2O_6F_2$ reacts with such nitro compounds as (III), (IV), fluoronitroform, and tetranitromethane even with prolonged heating in a closed vessel at $\geq 80\text{-}100$°C.

Thus, considering the results of the reactions of $ClOSO_2F$ and $S_2O_6F_2$ with perfluoronitrosoalkanes, we can assume that their mechanism is similar to the mechanism of replacement of I in alkyl iodides in the presence of these same reagents [6, 9]. In the first step, the nitrogen of the nitroso group is oxidized by $ClOSO_2F$ and $S_2O_6F_2$ with the formation of the unstable adducts (A) and (B), respectively.
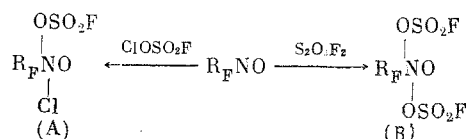
Adduct (A) subsequently either decomposes into perfluoroalkyl chloride and $ONSO_3F$ or reacts with excess $ClOSO_2F$ giving adduct (B). The decomposition of adduct (B) can also occur in two directions with the formation of perfluoronitroalkanes and $S_2O_5F_2$ or the corresponding fluorosulfates and $ONSO_3F$
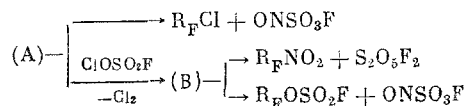
The correlation of these possible reaction routes of adducts (A) and (B) is determined mainly by the structure of the fluoroalkyl group R_F. In addition, the second direction of the decomposition of adduct (B) at a temperature of >0°C, evidently, after elimination of $ONSO_3F$ is related to the intermediate formation of β-nitrotetrafluoroethyl and fluorosulfate radicals, which can lead to tetrafluoroethylene, which, to a certain degree, explains the formation of fluorosulfate (V) in the reaction of $S_2O_6F_2$ with (I):
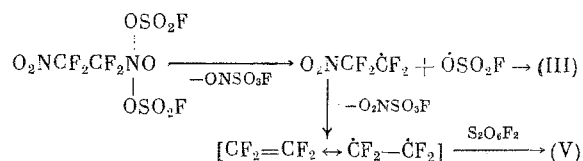
It should be noted that the isolation of tetrafluoroethylene was also observed previously, for example, in the reaction of alkyl mercaptides with 1,2-dibromotetrafluoroethane [10].

EXPERIMENTAL

The ^{19}F NMR spectra were recorded in ppm on a Hitachi R-20 instrument (56.45 MHz) from CF_3COOH.

Reaction of $ClOSO_2F$ with 1-Nitroso-2-nitrotetrafluoroethane (I). To 10 g (0.057 mole) of (I), 15.3 g (0.114 mole) of $ClOSO_2F$ was added dropwise at −60°C with stirring during 1.5 h, and the whole was stirred for 1 h at between −60 and −40°C and gradually heated to 20°C (∼3 g of Cl_2 was evolved into a trap). The reaction mixture was kept for 2.5 h at 20-40°C under a vacuum of 1 mm, while the volatile products were collected in a trap (−78°C), after

which 7.3 g (99.5%) of $ONSO_3F$ remained. By fractionation of the trap contents, we obtained: a) 8.5 g (60.8%) of 2-nitrotetrafluoroethyl fluorosulfate (III) with bp 76-78°C, d_4^{20} 1.697, n_D^{20} 1.3193 (cf. [11]). Fluorine-19 NMR spectrum: 24.22 t (O_2NCF_2), 6.83 d (CF_2O), -127.42 t (SF), $J_{N-F} = 10.7$, $J_{CF_2O-SF} = 8.5$ Hz (cf. [11]): b) 4 g of the liquid with bp 50-55°C, consisting of a mixture of 1,2-dinitrotetrafluoroethane (IV) and $S_2O_5F_2$ in a ratio of ∿2:1, according to the data of GLC with known samples and ^{19}F NMR: -125.37 s ($S_2O_5F_2$) (cf. [12]), 20.53 t (CF_2NO_2), $J_{F-N} = 11.8$ Hz.

Reaction of $ClOSO_2F$ with Trifluoronitrosomethane. Through 25 g (0.186 mole) of $ClOSO_2F$ placed in a reactor with a reflux condenser (-78°C), 8.3 g (0.083 mole) of CF_3NO was bubbled at between -70 and -60°C and stirred for 3 h, and the whole was stirred for 1 h at -50°C. The evolved gas was collected in a gas container, then it was passed through 10% aqueous NaOH and through a trap (-78°C), and it was condensed in a trap (-110°C). We obtained 2.1 g (24.4%) of CF_3Cl, bp between -81 and -79°C, mol. wt.: found 103.5°C; calculated 104.5°C (cf. [13]). The reaction mixture was heated gradually to -20°C, the temperature in the reflux condenser was brought to between -25 and -20°C, the evolved gases (∿4 g of a mixture of Cl_2 and CF_3NO_2) were collected in a trap (-78°C) and passed through 10% NaOH, and ∿0.9 g (9.4%) of CF_3NO_2 was obtained with bp -30°C (cf. [14]); ^{19}F NMR: -3.88 t, $J_{F-N} = 14.1$ Hz.

The reaction mixture was heated gradually to 20°C, with the volatile products being collected in a trap, and fractionated. We obtained 8.1 g (57.8%) of trifluoromethyl fluorosulfate with bp between -3 and -5°C, ^{19}F NMR (ppm, CF_3COOH); -122.84 q (SF), -19.95 d (CF_3), $J = 7.3$ (cf. [6]). The reaction mixture was kept at 30°C under a vacuum of 50 mm, with the products being collected in a trap. In the residue, 9.9 g (91.7%) of $ONSO_3F$ was obtained. The trap contents (0.8 g) were $S_2O_5F_2$, ^{19}F NMR: -125.18 s (SF) (cf. [12]).

Reaction of $S_2O_6F_2$ with 1-Nitroso-2-nitrotetrafluoroethane (I). To 7 g (0.04 mole) of (I), 9.9 g (0.05 mole) of $S_2O_6F_2$ was added at 5-10°C with stirring, and the reaction mixture was heated gradually to 20°C, stirred for 1 h at 20°C, and kept for 2 h at 40°C under a vacuum of 10 mm, with the volatile products being collected in a trap (-78°C). In the residue, 7.2 g of a mixture of $ONSO_3F$ and O_2NSO_3F was obtained. By fractionation of the trap contents, 1.7 g (17.3%) of 2-nitrotetrafluoroethyl fluorosulfate was obtained, with bp 75-78°C, d_4^{20} 1.702, n_D^{20} 1.3190 (cf. experiment run 1). The ^{19}F NMR spectrum was identical to the spectrum of the product isolated in experiment run 1. We also obtained 5.8 g (52%) of bis(fluorosulfonyloxy)tetrafluoroethane with bp 98-100°C, d_4^{20} 1.809, n_D^{20} 1.3152 (cf. [15]): ^{19}F NMR; 10.13 d (CF_2), -127.4 t (SF), $J = 9.6$ Hz, and 1.5 g of a liquid with bp 50-56°C, consisting of a mixture of (IV) and $S_2O_5F_2$ in a ratio of ∿2:1 (GLC data with known samples), and the ^{19}F NMR spectrum was identical to the spectra of the analogous mixture obtained above.

Reaction of $S_2O_6F_2$ with Trifluoronitrosomethane. Through a mixture of 9.9 g (0.05 mole of $S_2O_6F_2$ and 20 ml of perfluorodecalin, 4.9 g (0.05 mole) of CF_3NO was bubbled with stirring at 5°C for 1 h, the whole was stirred for 1.5 h at 5-20°C and heated gradually to 40°C, with the volatile products being collected in a trap (-78°C). By fractionation of the trap contents, 0.8 g (12.5%) of CF_3NO_2 and 5.2 g (61.9%) of CF_2OSO_2F were isolated. From the reaction mixture, ∿0.7 g (7.7%) of $S_2O_5F_2$ were isolated. The constants and the data of the ^{19}F NMR spectra of CF_3NO_2, CF_3OSO_2F, and $S_2O_5F_2$ were identical to the constants and spectra of the analogous compounds obtained in the first experiment run.

CONCLUSIONS

The replacement of the nitroso group in perfluoronitrosoalkanes in the presence of chlorine fluorosulfate and peroxydisulfuryl difluoride was studied. A hypothesis concerning the possible reaction mechanism was stated.

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SYNTHESIS AND STUDY OF A NEW COMPLEXONE — N,N',N''-TRIS-(DIHYDROXYPHOSPHORYLMETHYL)-1,4,7-TRIAZACYCLONONANE*

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One of the ways to improve the complex-forming selectivity of organic phosphorus polydentate ligands is to limit their conformational mobility. This has been achieved by introducing into the molecule "rigid" segments that hinder the free rotation of the individual components and fix the relative orientations of the donor atoms.

The effect of these factors was studied using the tertiary diphosphine dioxides as model compounds in which the P atoms are separated by vinylene, vinylidene, norbornylene, and xylylene bridges [1-6].

The inclusion of the donor atoms of the ligand in the ring system should also decrease the conformational mobility of the ligand and correspondingly increase the entropy of complex formation. Furthermore in a cyclic polydentate ligand the distances between donor atoms are determined more rigorously than in a saturated linear ligand; this should also favor an increase in the selectivity of complex formation.

The first example of such a series is the change from the linear complexone I

$$(HO)_2P-CH_2 \cdot NHCH_2CH_2 \cdot NHCH_2-P(OH)_2 \qquad (I)$$
$$\overset{\parallel}{O} \qquad\qquad\qquad \overset{\parallel}{O}$$

to the cyclic piperazine derivative II, which is the simplest member of the series II—III—IV, etc.,

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*Previous communication, [1].