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SYNTHESIS AND THERMOCHEMICAL PROPERTIES OF SOME

FLUORINE-CONTAINING FORMALS

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Fluorination of bis(2-fluoro-2,2-dinitroethyl) and bis(2,2,2-trinitroethyl) thionocarbonates by elemental fluorine gave bis(2-fluoro-2,2-dinitroethyl) and bis(2,2,2-trinitroethyl) difluoroformals. The reaction of 2,2,2-trinitroethyl nitrate with 2-fluoro-2,2-dinitroethyl chloromethyl ether gave 2-fluoro-2,2-dinitroethyl 2',2',2'-trinitroethyl formal. The standard heats of combustion and formation of the synthesized formals were determined by combustion in a calorimetric bomb. Increments of substitution of the trinitromethyl group by the fluorodinitromethyl group and of the H atom by F in the methylene group for formals were calculated and recommended for rough calculations. It was shown that it is possible to evaluate $\Delta H_{\rm f}^{0}$ of the formals by the method of increments and group contributions.

In a thermochemical sense, fluorine-containing formals are an insufficiently studied class of compounds. The standard heat of formation has been determined for only one compound from this class of substances, namely, bis(2-fluoro-2,2-dinitroethy1) formal [1]. As of the present time, representatives of a new class of formals, in particular difluoroformals ($RCH_2OCF_2OCH_2R'$), have appeared as a result of the development of synthesis methods. The thermochemical study of such compounds is of special interest because the fluorine in them is shielded by two oxygen atoms.

Few difluoroformals have been synthesized thus far because of the significant difficulties encountered in their synthesis by fluorination of carbonates of substituted alcohols by sulfur tetrafluoride [2]: the process is carried out in autoclaves and takes a long time and, because the reaction material contains sulfurous compounds, purification of the final synthesis products is a complex problem whose solution is not always possible. No less complex is the purification of liquid mixed formals of fluoro polynitro alcohols if they are obtained by existing methods.

In our opinion, the following circumstances are the main factors explaining the insufficient study of the thermochemical properties of difluoroformals: only the calculated thermochemical parameters of some of the synthesized substances of this class have been presented, and they are known to only a very few specialists from summary reports or non-Soviet patents [2, 3].

In 1986 we found a simple and convenient method for preparation of diflucroformals by fluorination of thionocarbonates of substituted alcohols by various fluorinating agents [4, 5], which enabled synthesis of a series of compounds from the class of difluoroformals with a sufficiently high content of the main substance. In addition, we were able to find and carry out the preparation of mixed formals. These methods have opened up new possi-

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TABLE 1.	Physicochemical	Characteristics	of	Compounds	(I)-(III)
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Compound	Bp, °C (p, mm Hg) Mp, °C	Density d ₄ (t°)	Content of main component, %
$\begin{array}{l} F(NO_2)_{3}CCH_2OCF_2OCH_2C(NO_2)_{2}F(1iq.)(I)\\ (NO_2)_{3}CCH_2OCF_2OCH_2C(NO_2)_{3}(1iq.)(II)\\ (NO_2)_{3}CCH_2OCH_2OCH_2C(NO_2)_{2}F(1iq.)(III) \end{array}$	98-100,2	1,686 (20)	99,80
	24,0-25,5	1,710 (25)	99,85
	22,0-22,5	1,620 (23)	98,00

bilities for investigation of thermochemical properties of fluorine-containing formals.

EXPERIMENTAL

We chose and synthesized the following three formals to carry out the thermochemical investigations: bis(2-fluoro-2,2-dinitroethyl) difluoroformal (I), bis(2,2,2-trinitroethyl) difluoroformal (II), and 2-fluoro-2,2-dinitroethyl 2',2',2'-trinitroethyl formal (III). The purity and individuality of the compounds were characterized by analyses for elemental composition, and the content of the main component was determined by GLC using a Chrom-4 instrument.

Some properties of compounds (I)-(III) are given in Table 1.

Synthesis of Difluoroformals (I)-(II). Compounds (I) and (II) were obtained by the general method of [4].

A fluorine-nitrogen mixture (1:10) was passed at velocity 1.5-2 liters/min into a solution containing 0.01 mole of the thionocarbonate in 15 ml of absolute CH_3CN at -20 to -15°C with intense stirring for 30-40 min, after which the reaction mixture was diluted with water and the product was separated and purified.

<u>Difluoroformal (I).</u> This compound was purified by distillation, with a fraction boiling at 96-100°C (2 mm Hg) being withdrawn in the first operation and a fraction boiling at 98-100°C (2 mm Hg) being withdrawn during repeated distillation. Identification was carried out according to PMR and NMR spectra and also according to the results of analyses for the elemental composition. PMR spectra (σ , ppm): 5.15 doublet (CH₂, J = 15.5 Hz); ¹⁹F NMR (σ , ppm): -34.78 singlet (CF); 13.37 triplet (OCF₂O; J = 3.85 Hz). Found, %: C 16.9, H 1.2, N 15.8, F 21.3. C₅H₄N₄O₁₀F₄. Calculated, %: C 16.86, H 1.13, N 15.73, F 21.34.

<u>Formal (III)</u>. Into a reactor equipped with a magnetic stirring device, thermometer, and dropping funnel was poured 5.0 g of 2,2,2-trinitroethyl nitrate at 0-2°C. A solution of 0.97 g of iron chloride in 3 ml of nitromethane was added with vigorous stirring. The pressure in the reactor, connected to a vacuum system, was decreased to 5-10 mm Hg, and 4.1 g of 2-fluoro-2,2-dinitroethyl chloromethyl ether was added at 0-2°C for 30 min. Then, 10 min after completion of the additon of the chloromethyl ether, the pressure in the reactor was increased to atmospheric, and the reaction material was washed with water.

The organic layer was combined with 20 ml of 20% HNO_3 at 80-90°C and then, after cooling, was extracted with CH_2Cl_2 . The extract was washed three times with 20-ml portions of a 3% aqueous NaOH solution and dried with $MgSO_4$ and, after removal of the solvent, 6.4 g of (III) was recovered. After drying, (III) was additionally purified by recrystallization from CCl_4 . Found, %: C 17.1, H 1.7, N 20.3, F 5.6. $C_5H_6N_5O_{12}F$. Calculated, %: C 17.3, H 1.74, N 20.16, F 5.47.

<u>Thermochemical Study of Compounds (I)-(III)</u>. For a thermochemical study of formals (I)-(III), we used standard calorimeter B-06-II with a fixed platinized bomb. We used this instrument several times previously in investigating fluoronitro organic substances [6, 7] by their combustion in oxygen. Experiments on determination of the heats of combustion of substances (I)-(III) were carried out under conditions accepted as standard in thermochemistry: $P_{0_2} = 3.04$ MPa, T = 298.15 K, and V = const. The method for carrying out the experiments, the analytical procedures, the notation of the main and auxiliary quantities, and the energy values used for their calculation were identical to those described and accepted in [6, 7]. For calculation of ΔH_f^0 of formals (I)-(III), we used the ΔH_f^0 values of CO₂ (gas) and H₂O (liquid) from [8], and the ΔH_f^0 value of HF·nH₂O (solution) was taken from the data of [9].

TABLE 2. Standard Heats of Combustion (ΔH_c^0) of Formals (I)-(III) (act, actual; im, impurities; f, fiber)

Weighed amount of substance	Weight of fiber.	W. Atact	q _{HNO3}	q _{im}	qf	$\tilde{m}_{CO_2}^{expt}$	$-\Delta U_B$	$-\Delta \overline{H}_{c}^{\circ}$ (average)
under vacuum, g	g			Ţ		m ^{theo} CO ₂	kJ/m	ole
	F(NC) ₂) ₂ CCH ₂ O(CF₂OCH	[2C (NO	2)2F(I)	(1 mole - 3	356.101 g)
1,48511 1,91219 1,76434 1,34782	$\begin{array}{c} 0.00342 \\ 0.00292 \\ 0.00340 \\ 0.00377 \end{array}$	8373,5 10780,3 9940,8 7640,9	53,8 70,7 76,0 45,9	1,84 2,26 2,34 5,0	58,8 50,2 58,5 64,8	100,12 100,08 100,18	1980,3 1984,6 1978,7 1988,2	1958,9±6 , 7
						1	$982,9\pm6,7$	
(NO ₂) ₃ CCH ₂ OCF ₂ OCH ₂ C(NO ₂) ₃ (II) (1 mole - 410.116 g)								
1,06063 0,99371 1,19487 1,71666	0,00614 0,00316 0,00434 0,00532	5535,9 5136,6 6187,9 8888,5	64,9 72,6 97,7 104,8	1,7 10,4 2,6 2,7	105,7 54,4 74,7 91,4	100,0 99,82 100,01	2073,9 2063,2 2063,8 2075,9	2038,4±10,3
)]				$2069,2\pm10,$	3
	(NO ₂))₃CCH₂OCH	I2OCH2	C(NO₂)	2F(III)	(1 mole -	347.128	g)
0.65486 1,21739 0.96697 1,16440	$\begin{array}{c} 0.00125\\ 0.00180\\ 0.00148\\ 0.00125\end{array}$	4628,4 8556,4 6813,1 8195,2	$\begin{array}{c c} 32.2 \\ 56.1 \\ 46.0 \\ 53.7 \end{array}$	$\begin{array}{c c} 8,2 \\ 4,1 \\ 4,4 \\ 2,9 \end{array}$	$\begin{array}{c c} 21,5 \\ 20,4 \\ 25,4 \\ 19,3 \end{array}$	99,92 99,89 -	$2420,6 \\ 2416,8 \\ 2418,6 \\ 2420,5$	2394,5±2,9
]				1	2419,1±2,	9

Table 2 gives the results of experiments on determination of the heats of combustion of compounds (I)-(III) in oxygen to CO_2 (gas), H_2O (liquid), and $HF \cdot nH_2O$ (solution).

RESULTS AND DISCUSSION

As was already mentioned above, the preparation of highly pure formals is a complex problem. Despite repeated attempts to use recrystallization and distillation to achieve a high content of the main substance for formal (III), we were unable to obtain a product containing more than 98% of (III). In the impurities we detected 1.5% $F(NO_2)_2CCH_2OCH_2OCH_2-C(NO_2)_2F$, water, and traces of CCl₄. Formals (I) and (II) contained 0.2 and 0.15% impurities, respectively, the nature of which could not be determined. For compound (III) a correction factor taking into account the presence of impurities in it was calculated on the basis of the heat of combustion of the main impurity substance $[FC(NO_2)_2CH_2O]_2CH_2$ known from [1] and the assumption of thermal inertness of the remaining impurities in the amount of 0.5%.

As a result, a correction factor equal to 10.0 kJ/mole was introduced into the experimental values of ΔH_c^0 of (III), and the error of the final value of ΔH_c^0 of (JII) was corrected appropriately. For formals (I) and (II), the impurity content of which was significantly less than in (III), the experimental values of ΔH_c^0 were not corrected. Taking into account what has been presented for the standard heats of formation of formals (I)-(III), we obtained the following values: ΔH_f^0 (liq.) of (I) = -1297.9 ± 6.7; ΔH_f^0 (liq.) of (II) = -642.3 ± 12.9 (in kJ/mole).

Because the experimental derivation of the ΔH_{f}° values of the fluorinated formals is laborious, it seemed appropriate, for practical purposes, to evaluate increments of the substitution of $C(NO_2)_3$ and CH_2 groups by $FC(NO_2)_2$ and CF_2 groups, respectively. Knowledge of these values enables calculation of ΔH_{f}° of compounds containing fluorine if the ΔH_{f}° values of unfluorinated or incompletely fluorinated analogs are known. Table 3 gives the results of such an evaluation for some formals whose values are known from the results of the present paper, compounds (I)-(III), and for other formals whose values were taken from published sources [1], compounds $(NO_2)_3CCH_2OCH_2OCH_2C(NO_2)_3$ (IV) and $F(NO_2)_2CCH_2OCH_2OCH_2C(NO_2)_2F$ (V).

A comparison of the results of calculation of increments of substitution of the trinitromethyl group by the fluorodinitromethyl group for formals and difluoroformals (Table

TABLE 3. Increments of Substitution of $C(NO_2)_3$ Group by $FC(NO_2)_2$ Group and of an H atom by F in the Methylene Group for Formals (in kJ/mole)

Compound (with least degree of fluorination)	$-\Delta H_{f}^{\circ}$	Compound for com- parison	$-\Delta H_{f}^{\circ}$	$ \begin{array}{c} \Delta\left(\Delta H_{f}^{\circ}\right) \\ C(\mathrm{NO}_{2})_{5} \rightarrow F(\mathrm{NO}_{2})_{2}C \end{array} $	$\begin{array}{c} \Delta\left(\Delta H_{f}^{\circ}\right) \\ \mathrm{II} \rightarrow \mathrm{F} \end{array}$
(IV) (IV) (II) (III)	402,1 402,1 859,8 640,2	(V) (III) (I) (V)	849,8 642,3 1297,9 849,8	223,9 240,2 219,1 209,6	
			Average:	223,2	
(V) (IV)	849,8 402,1	(I) (II)	1297,9 859,8		224,1 228,9
			Average:	226,5	

TABLE 4. Increment of Substitution of a Hydrogen Atom by F for Some Classes of Compounds (in kJ/mole)

Fluorinated compound	$-\Delta H_{i}^{\circ}$	Unfluorinated compound	$-\Delta H_{j}^{\circ}$	$\begin{vmatrix} \Delta \left(\Delta H_{i}^{\circ} \right) \\ \text{per substitution} \end{vmatrix}$
CF ₃ CH ₂ NH ₂ (liq.) CF ₃ CH ₂ OH (liq.) CF ₃ CH ₂ CH (liq.) CF ₃ CH ₂ CH ₂ OH (liq.) CF ₃ CH ₃ (gas)	740,36 [10] 922,8 [12] 959,9 [11] 734,7 [12]	$\begin{array}{c} CH_{3}CH_{2}NH_{2}(1iq.)\\ CH_{3}CH_{2}OH(1iq.)\\ CH_{3}(CH_{2})_{2}OH(1iq.)\\ C_{2}H_{6} (gas) \end{array}$	74,47 [8] 276,98 [8] 304,6 [13] 84,5 [8]	221,9 215,3 218,4 216,7
			Average:	218,07

3) with those for other classes of compounds [1] shows that the values of these increments do not differ very significantly. This makes it possible to use the method of increments for practical purposes for fluorinated and unfluorinated formals regardless of the nature of the central methylene group. As concerns the increment of substitution of the hydrogen atom in the methylene group by F in formals, its value within the limits of 8 kJ per substitution is the same as that calculated for other classes of compounds, e.g., for fluorinated and unfluorinated alcohols, ethylamine, and ethane (Table 4).

The average values of the increments of substitution of the $C(NO_2)_3$ group by the $FC(NO_2)_2$ group and of the H atom by fluorine that were obtained in this paper for formals can be recommended for rough calculations of ΔH_f^0 of synthesized or still unsynthesized compounds of this type. By using the values that were calculated in [1] for the contributions of various groups and intergroup interactions to ΔH_f^0 of nitro compounds using the ΔH_f^0 value of difluoroformal (II), we obtained for compounds (I) and (III) calculated values of the standard heats of formation satisfactorily agreeing with the experimentally found ΔH_f^0 values of these substances: ΔH_f^0 of (I) (calc.) = -1311.3 kJ/mole and ΔH_f^0 of (III) (calc.) = -630.5 kJ/mole.

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