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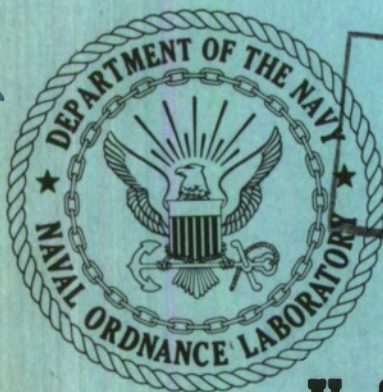
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COMPOUNDS CONTAINING THE TERMINAL FLUORODINITROMETHYL
GROUP, II, A NEW CLASS OF ORGANIC HIGH EXPLOSIVES

By

Mortimer J. Kamlet

Approved by: DARRELL V. SICKMAN
Chief, Organic Chemistry Division

ABSTRACT: As a result of a theoretical study of the factors which affect impact sensitivity it was concluded that the entropy of activation in the decomposition process is a quantity strongly influencing sensitivity. On this basis such entropic factors as the steric conformation about the bond most readily broken should be important considerations in attempts at designing insensitive high explosive molecules.

From such steric considerations it was predicted that compounds containing the $\text{FC}(\text{NO}_2)_2^-$ grouping would comprise a class in which reduced sensitivity to impact and improved thermal stability could be achieved without excessive sacrifice of explosive power. A number of examples containing this linkage have been synthesized by the reactions of the corresponding potassium dinitro salts with perchloryl fluoride. These in turn have served as intermediates in the synthesis of a family of fluorodinitro high explosives for which the prediction of reduced sensitivity and improved thermal stability with relatively little loss in explosive power appears to have been borne out. Of particular interest are fluorodinitroethyl fluorodinitrobutyrate, bis-fluorodinitroethyl carbonate and fluorodinitroethyl orthocarbonate.

CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, SILVER SPRING, MARYLAND

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NAVORD Report 6207

14 February 1959

This report describes the preparation and properties of compounds containing the fluorodinitromethyl group, a promising new family of high explosives in which it appears that reduced sensitivity to impact is achieved without excessive sacrifice of explosive power. The work was done under Task No. FR-44.

MELL A. PETERSON
Captain, USN
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Albert Lightbody
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By direction

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COMPOUNDS CONTAINING THE TERMINAL FLUORODINITROMETHYL GROUP, II, A NEW CLASS OF ORGANIC HIGH EXPLOSIVES

INTRODUCTION

Proposed syntheses and utilization of fluorine-containing compounds for high energy applications have generally had as their purpose the realization of additional energy in the decomposition-recombination process. As a consequence of the high heats of formation of the metal fluorides the calculated heat of detonation of perfluorohydrazine with the stoichiometric amount of aluminum, for example, is 3,000 - 3,500 cal/g. Teflon might yield as much as 2,000 cal/g if the reaction with aluminum or boron could be made to go quantitatively.

While such additional heat of detonation would not be unwelcome, it was not for this purpose that the synthesis and study of fluorodinitro compounds was undertaken. The investigation herein described had as its basis the expectation that these compounds might comprise a class in which reduced sensitivity to impact could be achieved without excessive sacrifice of either oxidant balance or performance. The theoretical background for this expectation is given in detail in the first paper of this series (1).

In the literature dealing with polynitroaliphatic chemistry there are described many reactions of the type,



Bromations, $X = Y = Br$, (2), alkaline nitrations with tetranitromethane, $X = NO_2$, $Y = C(NO_2)_3$ (3), and alkylations, $X = CH_3$, $Y = I$ or CH_3SO_4 (4), all fall into this category and probably conform with the same general mechanism, the S_N2 displacement on X of Y^- by $R-C(NO_2)_2^-$. A mechanistic requirement of the typical reaction is that Y^- be a weaker nucleophile (generally speaking, the conjugate base of a stronger acid) than $RC(NO_2)_2^-$.

An interesting example recently described involved nitryl chloride as $X-Y$. With most dinitromethyl anions this reagent effected chlorination, $X = Cl$, $Y = NO_2$. With the dinitroethylamine zwitterion, however, nitration occurred, $X = NO_2$, $Y = Cl$. The end product was bis-trinitroethylamine (5).

It was felt that for the preparation of fluorodinitromethyl compounds a reaction of this general type gave the best promise of success. At the inception of the study several specific reactions were considered. Fluorination with elementary fluorine seemed to stand a poor chance because of the known proclivity of this reagent to break carbon-carbon and carbon-hydrogen bonds almost indiscriminately in heterogeneous systems and because of the paucity of suitable solvents for homogeneous reactions. However, Dr. D. V. Sickman of these laboratories has pointed out to us the little known fact that fluorine forms a stable complex with 2-fluoropyridine (6). This seemed a potential method of controlling the reaction.

A somewhat better possibility involved nitryl fluoride, $X-Y = NO_2F$. By analogy with the nitryl chloride reactions this might be expected to give either the desired fluorodinitro compound or the terminal trinitro compound, depending on which moiety was displaced. Either alternative seemed attractive since methods available for building up a terminal dinitro to a trinitro compound are not general and any new route is worth investigation.

Nitryl fluoride has the drawback of an extremely low boiling point, ca- 140° , is corrosive to glass and is therefore hard to handle. An investigation of its reactions would involve the construction of a closed system with adequate provision for venting and destroying this dangerous reagent. This, nevertheless, seemed a preferred route*.

Still a third reagent considered was perchloryl fluoride, $FClO_3$, which appeared to fulfill the mechanistic requirement of the reaction in that ClO_3^- is a weaker nucleophile than the dinitroalkyl anion. A preliminary announcement by the Pennsalt Chemicals Corporation (7) first aroused our interest in this unusual reagent. Its price, \$15.00 per pound in experimental quantities, properties, Appendix I, and reactions were interesting, but the feature which caused us to investigate it first was its relative ease of handling. It does not etch glass, corrode metals or attack common gasketing materials at room temperature; toxicologically it is relatively innocuous.

* In order to get an indication of whether it would be worth while doing all this plumbing and pipefitting we had planned to bring some of our potassium dinitro compounds to one of the laboratories already equipped for such reactions to run some preliminary experiments. Although we never availed ourselves of the opportunity, we should like to thank Dr. Marvin Gold of the Aerojet-General Corporation for the invitation.

Among the reactions described in the Pennsalt announcement were those of perchloryl fluoride with sodium salts of such active methylene compounds as malonic and acetoacetic esters to form the dialkyl difluoromalonates and alkyl difluoroacetates respectively. Use of the C-monoalkyl malonates led to monofluorinated derivatives.



Mechanistically these reactions seemed to parallel the desired reactions of dinitroalkane anions.

RESULTS

Thirteen new fluorodinitro compounds prepared in the present investigation are listed in Table I. Of these, four were prepared by fluorination of the potassium salts with perchloryl fluoride and served as intermediates in the preparation of the others by methods analogous to such as have already been described for the corresponding trinitro compounds. Compounds XI, XII and XIII, prepared by the ferric chloride catalysis method, will be discussed in greater detail in a separate NAVORD report (8).

Fluorination with Perchloryl Fluoride

In three instances the reaction of the salt of the dinitro compound with perchloryl fluoride was straightforward. From potassium dinitromethylbenzene was obtained fluorodinitromethylbenzene, I, in 95% yield; potassium dinitroethane yielded 54% of pure fluorodinitroethane, III; potassium methyl dinitrobutyrate gave 93% of the theoretical amount of methyl fluorodinitrobutyrate, IV. Potassium chlorate separated in all three cases in substantially theoretical yields and no other product was isolated. The reactions, therefore, appeared to resemble those reported by the Pennsalt group (7) with the exception only that nitro groups were substituted for the acyl or carbalkoxy.



TABLE I
NEW FLUORODINITRO COMPOUNDS

Compound	m.p., (b.p.) °C	Yield/d (based on)	Calc'd			Found		
			C	H	N	C	H	N
I. Fluorodinitromethyl-benzene	(11q. at -10)	95% (K salt)			not purified			
II. Fluorodinitromethyl-m-nitrobenzene	31-32	73% (I)	34.29	1.63	17.15	34.31	1.81	17.00
III. Fluorodinitroethane	(40.5/20 mm)	54% (K salt)	17.38	2.17	20.25	17.58	2.18	17.12
IV. Methyl Fluorodinitro-butyrate	2-3	93% (K salt)			not purified	17.61	2.16	19.74
V. Fluorodinitrobutyric Acid	37.2-38.6	77% (IV)	24.48	2.55	14.28	24.89	2.76	13.29
VI. Trinitroethyl Fluoro-dinitrobutyrate	42.6-43.8	84% (V)	20.04	1.67	19.50	24.57	3.02	13.87
VII. Fluorodinitroethanol	9-10	25% (K salt)			not purified	19.95	1.92	19.06
VIII. Fluorodinitroethyl Trinitrobutyrate	(56/1.7 mm)	25% (VII)	20.04	1.67	19.50	20.19	2.08	19.36
IX. Fluorodinitroethyl Fluorodinitrobutyrate	53.5-54.5	41% (V+VII)	21.69	1.81	16.86	19.81	2.06	18.99
X. Fluorodinitroethyl 3,5-Dinitrobenzoate	41.4-42.2	78% (VII)	31.05	1.44	16.08	20.40	2.36	16.00
XI. bis-Fluorodinitroethyl Carbonate ^b	133.2-134.2	60% (VII)	17.95	1.20	16.80	22.38	2.13	16.50
XII. Fluorodinitroethyl Orthocarbonate ^b	43.0-43.5	85% (VII) ^c	17.31	1.28	17.95	31.43	1.60	15.50
XIII. Fluorodinitroethyl Orthoformate ^b	136	65% (VII)				31.24	1.55	15.75
	111					17.76	1.51	15.44
						18.09	1.27	15.74
						17.74	1.55	16.99
						17.56	1.85	16.74

^a $n_D^{24.5}$ 1.3961.

^b These compounds will be described in greater detail in a separate NAVORD Report (8).

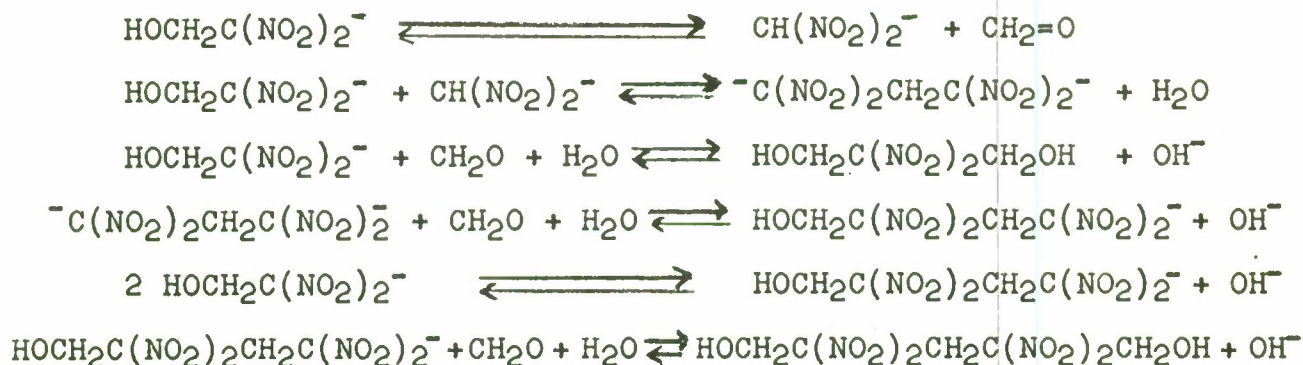
^c A small amount of XI also isolated.

^d Yields of crude products are given.

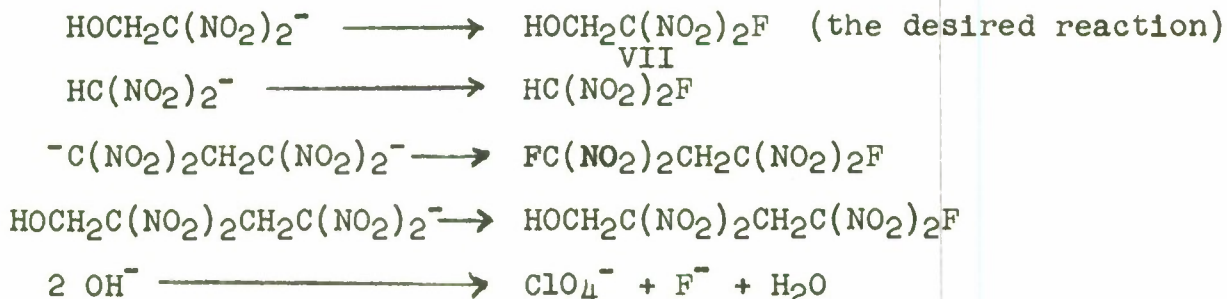
Fluorodinitroethane, III, was a relatively low boiling liquid and readily purified by fractionation. No purification was attempted in the cases of the higher boiling I and IV, however, since they could easily be converted to solid derivatives.

With potassium or sodium dinitroethanol the fluorination reaction was very much more complex. Under a variety of conditions the best yields of fluorodinitroethanol, VII, ranged from 20-25%. There were always obtained appreciable amounts of 2,2-dinitropropandiol-1,3 and potassium perchlorate. By contrast with the previous examples which appeared to go quite cleanly, the reaction mixtures in these cases always discolored badly. In one instance a fume-off occurred during the attempt to isolate the fluoroalcohol by fractionation. While no method has yet been devised to circumvent this unfortunate behavior, its reasons are easily understood.

Of the solvents tried, only in aqueous methanol or in dimethylformamide, in which the salts are somewhat soluble, did reaction take place at a reasonable rate. In such solvents the dinitroethanol anion participates in a series of complex equilibria (9).



With perchloryl fluoride a number of reactions may take place involving the participants in these equilibria.



In the face of these multifold reactions and the additional deformylation equilibria involving VII and $\text{HOCH}_2\text{C}(\text{NO}_2)_2\text{-CH}_2\text{C}(\text{NO}_2)_2\text{F}$ and considering also that potassium fluorodinitromethane as a solid or in solution rapidly decomposes to as yet unidentified products, it is not surprising that yields of VII were low. Attempts to improve these yields by fluorinating more rapidly, varying the temperature, buffering the solution with acetic acid, etc., were unsuccessful. That some of the contaminants boiled in the same range with fluorodinitroethanol was evidenced by the fact that we were unable to obtain an analytically pure sample by refractionation. On the other hand, the high yields of X, XI and XII based on VII indicated that our once fractionated product was at least 90 weight percent pure.

Unsuccessful attempts to fluorinate polynitroaliphatic salts with perchloryl fluoride involved dinitroethylamine zwitterion (5) in a methanol-water-ether mixture, dipotassium tetranitroethane in methanol and DMF and potassium nitroform in methanol, in water and in dimethylformamide. The failure of the latter to react was anticipated on the basis that nitroform anion is a weaker nucleophile than chlorate anion.

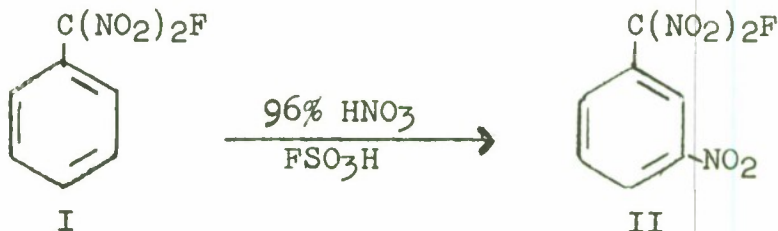
Several trials were made at the synthesis of N-fluoro compounds by this method. Potassium hexanitrodiphenylamine in DMF failed to react as did disodium ethylenedinitramine in methanol-water or in ethylene glycol. With potassium 4-nitrophthalimide in DMF extensive decomposition took place and only 4-nitrophthalimide could be isolated. With potassium phthalimide in methanol-water and with sodium phthalimide in methanol, reaction took place as evidenced by the rapid uptake of perchloryl fluoride. The only products isolated, however, were potassium (or sodium) perchlorate, potassium fluoride, phthalimide and in about 3% yield a compound which analysis later showed to be N-methylphthalimide. Evidently the following sequence of reactions had taken place.



Reactions of perchloryl fluoride with sodium alkoxides to form sodium fluoride, sodium perchlorate and the dialkyl ether have already been described with the alkyl perchlorate suggested as a probable intermediate (7).

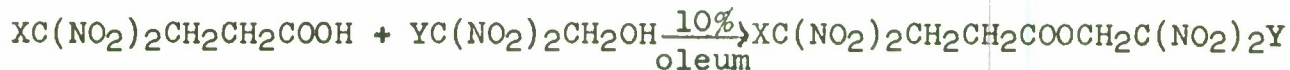
Reactions of Fluorodinitro Compounds:

Treatment of fluorodinitromethylbenzene with a mixture of equal volumes of 96% nitric and fluosulfonic acids at 0° gave fluorodinitromethyl-m-nitrobenzene, II, in 73% yield. The above mixture is believed to be a new nitrating system. It is convenient to use and appears to be quite powerful since it remains anhydrous due to the reaction $\text{FSO}_3\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{HF}$. There is ample reason to assume that nitration took place in the meta position as indicated (10).



Hydrolysis of methyl 4-fluoro-4,4-dinitrobutyrate, IV, to the carboxylic acid V was readily accomplished by refluxing with constant boiling hydrochloric acid. The high yield of fluorodinitrobutyric acid indicated that, like the trinitromethyl group (11), the fluorodinitromethyl group is unaffected by such treatment.

Three analogs of TNETB with fluorine atoms replacing nitro groups on either end and on both were prepared by direct esterification in oleum according to the procedure of Hill (12).



VI, X = F, Y = NO₂

VIII, X = NO₂, Y = F

IX, X = Y = F

Only in the case of trinitroethyl fluorodinitrobutyrate, VI, did the product separate as a second phase from the reaction mixture and it was with this compound that the best yield was obtained. All three fluoronitro esters melted below 55° compared with 94° for TNETB. This low-melting behavior compared with the corresponding trinitro analog is characteristic of all fluorodinitro compounds thus far studied.

Some question arose as to whether the fluorodinitromethyl grouping would remain unaffected during the course of attempted metal halide catalyzed reactions, i.e., whether it would take part in halide exchange or other modes of decomposition. For this reason the reaction with 3,5-dinitrobenzoyl chloride was carried out. On the addition of slightly less than the theoretical amount of aluminum chloride to a saturated solution of fluorodinitroethanol in chloroform-carbon tetrachloride, complete solution occurred with the evolution of hydrogen chloride. Presumably formation of fluorodinitroethyl dichloroaluminate took place with reactivity and solubility properties resembling those of the known trinitroethyldichloroaluminate (13). Addition of the acid chloride and a short reflux gave an ester-aluminum chloride complex from which, on decomposition with 20% sulfuric acid, fluorodinitroethyl 3,5-dinitrobenzoate, X, was obtained in excellent yield.



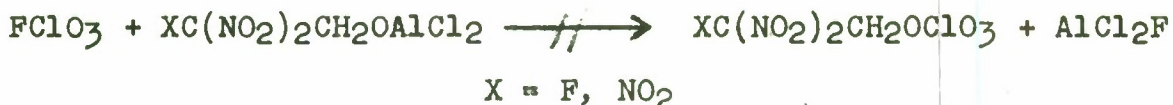
Fears about possible side reactions were evidently unfounded.

Fluorodinitroethyl orthocarbonate, XII and bis-fluorodinitroethyl carbonate, XI, prepared by ferric chloride catalyzed reactions of fluorodinitroethanol with dry and wet carbon tetrachloride and fluorodinitroethyl orthoformate, XIII, from the reaction with chloroform will be described in greater detail in a separate NAVORD report. It suffices to say here that fluorodinitroethanol is the only compound other than trinitroethanol which has yet been found to undergo these interesting types of reaction.

At the inception of the project it was our hope that potassium fluorodinitromethane might be prepared and used in the synthesis of a variety of fluorodinitro compounds in much

the same way as potassium nitroform serves as the prime intermediate in the preparation of the trinitro analogs. An attempt to prepare this material by deformylation of fluorodinitroethanol with KOH in aqueous methanol resulted in the expected precipitation of an orange salt whose ultraviolet absorption, $\lambda_{\max} = 382 \text{ m}\mu$, was consistent with $\text{KC}(\text{NO}_2)_2\text{F}$. On filtering and washing, however, violent decomposition always took place as the last of the solvent was being drawn off. The material also decomposed when dissolved, the rate being rapid in alkaline solution and slower in neutral or mildly acidic media. This behavior does not preclude synthetic methods whereby the potassium salt may be filtered off, kept wet with additional solvent, rapidly neutralized with acid and caused immediately to react as desired. No such methods have yet been investigated.

A number of unsuccessful trials involved Mannich reactions of fluorodinitroethanol. No products were obtained from this compound on fusion with urea or with trinitrobutyramide nor from reaction with ammonium acetate under a variety of conditions. Also unsuccessful were attempts at reacting fluorodinitroethyl dichloroaluminate and trinitroethyl dichloroaluminate with perchloryl fluoride in chloroform. It was hoped that the perchlorate esters might thus be obtained and that these, being esters of quite acidic alcohols, might prove to be stable compounds. Even at reflux, however, there were no signs of reaction.



Physical Properties

Additional physical properties of selected fluorodinitro compounds are listed in Table II. Several of these deserve further discussion. The basis for this project lay in the prediction that this family of compounds would be less sensitive than other polynitroaliphatics at equivalent values of OB/100 (see Part I) (1). This expectation was partially borne out in that of the six fluorodinitro compounds containing no additional trinitromethyl group, 50% impact heights of V, X, XI and XII were substantially higher than predicted for compounds of similar oxygen balance from the equation describing the "true trend for polynitroaliphatics" (14). The impact height of IX was only slightly higher while that of XIII was slightly lower. No explanation can yet be advanced for the anomalous behavior of XIII nor for the fact that compounds VI and VIII

TABLE II
ADDITIONAL PROPERTIES OF SELECTED FLUORODINITRO COMPOUNDS

Compound	Heat of Formation/a Kcal/mole	Detonation/b Cal/g	Xtal Density	Vacuum Stability/c	Actual/d(sigma)	Impact Sensitivity Predicted/e	OB/100/f
V. Fluorodinitrobutyric Acid	170	830/g	-	r	320	95	-1.02
VI. Trinitroethyl Fluoro- dinitrobutyrate	163	1220	1.71	1.02	13 (0.05)	28	+1.40
VIII. Fluorodinitroethyl Trinitrobutyrate	163	1220	1.71	1.27	19 (0.07)	28	+1.40
IX. Fluorodinitroethyl Fluorodinitrobutyrate	211	990	1.69	<0.1	52 (0.05)	43	+0.60
X. Fluorodinitroethyl 3,5-Dinitrobenzoate	-	-	1.78	<0.1	140 (0.13)	105	-1.14
XI. bis-Fluorodinitroethyl Carbonate	235	1260	1.79	<0.1	42 (0.12)	17	+2.38
XII. Fluorodinitroethyl Orthocarbonate	327	1425	1.71	0.13	21 (0.07)/h	13	+2.90
XIII. Fluorodinitroethyl Orthoformate	-	-	1.76	0.11	31 (0.11)/h 13 (0.15)/i	16	+2.55
TNETB	118	1440					
DNPTB	125	1020					
RDX	-15	1230			23.5		
TNT	18	960			160		

/a Heat of sublimation of 16 Kcal/mole assumed for all compounds.

/b See text for discussion of accuracy of these values.

/c At 100°C, cc of gas/g/24 hr.

/d ERL machine, type 12 tools.

/e See text.

/f Equivalents of oxidant per 100 g above the amount necessary to oxidize all carbon to carbon monoxide and all hydrogen to water.

/g Calculated on the assumption that the carboxyl group remains intact and ends up as a mole of CO₂ in the detonation products. If this assumption is not made the heat of detonation is 560 cal/g.

/h This and all other results are for 25 shot tests unless otherwise noted.

/i 13 shot tests.

containing both the trinitromethyl and the fluorodinitromethyl groups are more sensitive than would be predicted for compounds containing only the former grouping. The relative insensitivity of XI and XII casts an attractive light upon the possibility of further development involving these compounds although the lower melting point of XI limits its potential utilization to special applications such as explosive plasticizer. The relative unreliability of any single impact result is emphasized by the two values listed for Compound XII on the basis of two separate series of trials.

The arguments in Part I (1) upon which the prediction of improved impact sensitivity was based would also lead to the expectation of enhanced thermal stability for fluorodinitro compounds as compared with other polynitroaliphatics. Like impact sensitivity, the thermal stability of a molecule is in effect a measure of the ease of breaking of its weakest bond. For comparison, most trinitromethyl compounds show thermal stabilities of more than 1 cc/g/24 hr with 2 cc/g considered the limit of acceptability and 5 to 10 cc/g not unusual. Thermal stability in the melt is almost invariably poorer than that of the solid. Five fluorodinitro compounds containing no trinitromethyl group were tested, the test temperature being more than 55° above the melting point in the cases of IX and XI. That all showed unusually good thermal stabilities serves as further evidence that the theoretical background for this undertaking had some basis in fact.

Heats of formation and detonation were calculated following the Brinkley-Wilson convention that all hydrogen is burned to water before carbon is burned to carbon monoxide (15). Values for conventional explosives similarly calculated are given for comparison. The energy of the C-F bond was taken as 107 Kcal/mole but is probably 5-10 Kcal lower in actuality because of the proximity of the two electron-withdrawing nitro groups. Thus, the heat of explosion values of the fluorodinitro compounds are on the conservative side by as much as 50-100 cal/g. It can be seen that if heat of detonation of the self-explosive be the criterion, these compounds show up not at all poorly. In metallized mixtures where the high energy of the metal-fluorine bond can be realized they show up even better by comparison.

EXPERIMENTAL(16)

CAUTION! Many of the procedures described below involve the filtration of potassium chlorate and/or perchlorate from organic mixtures containing both combustible solvents and explosive organic materials. Although no untoward incidents have yet occurred, it should be recognized that during the course of these filtrations one goes through a stage where the perchlorate-fuel-explosive ratio represents a potentially dangerous situation. For this reason the filtration operations are well shielded and the filter cakes are exhaustively washed with additional solvent before being allowed to air dry.

General. Reactions of potassium (or sodium) dinitro compounds with perchloryl fluoride (PF) were carried out by bubbling the gas into a well-stirred suspension of the salt in a solvent in which it was at least partially soluble. Apparatus generally involved a gas inlet tube and stirrer in a three-neck round bottom flask surmounted by a reflux condenser and with bubble counters fore and aft. After introducing the salt and solvent, most of the air was purged from the system by blowing through a rapid stream of PF which was vented to the hood. The rate of input of PF was then cut back until there was a partial vacuum in the system as shown by the liquid level rising in the bubble counter aft, this partial vacuum being due to uptake of the PF by the solvent in forming a saturated solution. Reaction of the salt of the dinitro compound was then evidenced by a rapid input of PF with the partial vacuum being maintained. Generally, where reaction took place the rate was determined by the speed of solution of the gas. Increasing the stirring rate would increase PF uptake, decreasing it would have the opposite effect.

Where reaction took place it was also evidenced by the gradual solution of the yellow dinitro salt and precipitation of white potassium chlorate. Preferred solvents were those in which both PF and the dinitro salt had mutually maximal solubilities (see Appendix I for solubility of PF). Thus, reactions were extremely slow in ether in which the dinitro salt was insoluble and in water in which PF was relatively insoluble. Methanol was a more rapid solvent, aqueous methanol faster still and dimethylformamide the most rapid.

Temperatures were chosen between 0 and 50° to give the most convenient rates and, except in one case, temperature control was easy. The reactions appeared to be slightly exothermic and could be held at the desired temperature by varying the PF input rate and with moderate cooling. A self-sustaining exothermal decomposition took place with potassium methyl dinitrobutyrate in dimethylformamide, but in the slower solvent methanol the reaction was easily controlled.

Fluorodinitromethylbenzene, I. A suspension of 9.7 g potassium dinitromethylbenzene in 200 ml methanol was maintained at 25° while perchloryl fluoride was slowly bubbled in. During

the course of 1-1/2 hour the suspended yellow-orange salt was slowly replaced by a white precipitate as the color of the solution changed to pale chartreuse. Addition of 120 ml ether and filtration yielded 5.10 g potassium chlorate. After stripping off the solvent, adding ether, filtering off an additional 0.20 g potassium chlorate (total 98%) and again evaporating the ether in vacuo, there remained as a yellow oil 8.30 g (95%) of crude I.

m-Nitrophenylfluorodinitromethane, II. Portionwise addition of 3.3 g of the above crude product to a stirred solution of 10 ml 96% nitric acid in 10 ml fluosulfonic acid at 0.50 caused vigorous bubbling, evolution of brown fumes and the eventual formation of a homogeneous pale yellow solution. Pouring over crushed ice gave a yellow oil which on standing slowly solidified. Decantation, trituration with cold methanol and filtration yielded 2.29g of a white solid, m.p. 29-30°. From the combined decantate and washings was obtained an additional 0.69 g (total 73%). Recrystallization of 2.29 g from ether-hexane yielded 1.63 g of II, m.p. 31-32° as feathery ivory-colored platelets; a further recrystallization from methanol-water gave an analytical sample of similar m.p.

Anal: Table I

Fluorodinitroethane, III. A comfortable rate of uptake was achieved by bubbling PF into a suspension of 90 g potassium dinitroethane in 750 ml methanol plus 200 ml water at 40°, about seven hours being required for complete replacement of the insoluble yellow crystals by white potassium chlorate. After filtering off the latter material, the solution was diluted with 500 ml water and extracted with 500 ml ether. The ether phase was washed several times with water to remove most of the methanol, dried over calcium chloride, and the ether evaporated off in vacuo. Fractionation of the residue through a 70 cm jacketed column packed with 1/4 inch glass helices yielded 1/2 g of forerun, b.p. below 40.5°/20 mm, n_D^{24} 1.3968; 42.5 g (54%) of pure III, b.p. 40.5-41.5°/20 mm, $n_D^{24.5}$ 1.3959-1.3961; 1.2 g final cut b.p. rising to 42°/20 mm, then falling, $n_D^{24.5}$ 1.3970. About ten grams of oil remained as a pot residue.

Anal: Table I.

Methyl Fluorodinitrobutyrate, IV. At 37° uptake of PF by a suspension of 73 g potassium methyl dinitrobutyrate in 750 ml methanol was substantially complete in five hours. After cooling the mixture to -10°, 37.5 g of potassium chlorate was filtered off, most of the methanol stripped off in vacuo, an additional 0.8 g potassium chlorate filtered off (98.5% total) and the remaining methanol removed to leave 62 g of crude IV as a pale yellow oil. On standing in the freezer the material solidified and showed m.p. ca. 2-3°.

Fluorodinitrobutyric Acid, V. Fifty-two grams of the above crude material were added to 350 ml constant boiling hydrochloric acid and the mixture heated to reflux. After three hours all but about 1 ml of a tan oil had dissolved. Charcoal was added, refluxing continued for 15 minutes and the mixture filtered hot. During the filtration additional oil separated from the clear pale-green solution but this redissolved on addition of 120 ml water and 130 ml hydrochloric acid. The solution after standing overnight in the freezer deposited as a first crop 22.8 g of crude V, m.p. 35-38°, as chunky white bars. Concentration of the mother liquor yielded in two crops an additional 13.1 g (total 77%) of similar material. Recrystallization of 3.0 g of the crude product from chloroform-carbon tetrachloride afforded 2.7 g of pure fluorodinitrobutyric acid as fine long white needles, m.p. 37.2-38.6°.

Anal: Table I.

Trinitroethyl Fluorodinitrobutyrate, VI. A solution of 9.75 g (0.050 mole) fluorodinitrobutyric acid and 10.0 g (0.055 mole) trinitroethanol in 25 ml 10% oleum was heated to 50° and held for 2-1/4 hr during which time a second phase amounting to about 1/10 the total volume of the solution separated. On cooling to 15°, the second phase solidified. The mixture was poured into a stirred mixture of 150 g ice in 150 ml methanol and 14.9 g (84%) of crude VI filtered off as a white solid, m.p. 34-38°. Recrystallization from methanol-water yielded three crops totaling 12.0 g of VI as clean white feathery needles, m.p. 37.5-40°. A further recrystallization of 5.3 g from hexane-ether afforded 4.8 g of an analytical sample as clusters of tiny white needles, m.p. 42.6-43.8°.

Anal: Table I.

Fluorodinitroethanol, VII. A number of procedures were tried, the following giving the best results. To a cooled, stirred solution of 53.0 g 85% potassium hydroxide (0.80 mole) in 140 ml water and 500 ml methanol was added dropwise 132.8 g 2,2-dinitropropandiol-1,3 in 240 ml methanol, the temperature being kept below 12°. The precipitated potassium dinitroethanol was separated from solvent through the agency of a filter stick and washed, twice with 250 ml portions methanol and once with 350 ml ether; 500 ml dimethylformamide was then added, the mixture cooled to 15° and PF bubbled in at this temperature. The uptake of PF was relatively rapid with the mixture slowly discoloring until, by the time PF uptake was complete, the solution was dark brown. The insoluble material, filtered off and washed with ether (CAUTION) was light yellow, but microscopic examination showed the presence of both white and yellow crystals.

Addition of 2 ml concentrated sulfuric acid to the brown mother liquor caused a color change to bright orange. Most of the dimethylformamide was then distilled off on the vacuum pump at a temperature below 30°/1.5 mm and the residue taken up in 250 ml ether, washed with three 100 ml portions water, the combined aqueous washes reextracted with 250 ml ether and the combined ether phases washed with 100 ml 3% hydrochloric acid. The ether was stripped off and the residual orange oil fractionated in vacuo. After a small forerun the main fraction was taken off at 55-57°/1.7 mm. The yield of VII thus obtained was 30.7 g (25% of theory). The product was colorless, had a slight nitrous odor and froze at 9-10°.

Anal. Calc'd. for $C_2H_3FN_2O_5$: N, 18.20. Found: N, 16.17, 16.44.

The pot residue from the fractionation on cooling set solid. This material, triturated with hexane-benzene and filtered yielded 15.6 g of light tan platelets, m.p. 110-115°. Recrystallization from ether-hexane yielded chunky white prismatic crystals, m.p. 130-132°, no depression in melting point with an authentic sample of 2,2-dinitropropandiol-1,3, m.p. 141-143°.

Refractionation of a portion of the fluorodinitroethanol gave a sample, b.p. 53-54°/1.3 mm, f.p. 9-10°.

Anal. Found: N, 17.28, 16.99.

Fluorodinitroethyl Trinitrobutyrate, VIII. A solution of 9.0 g crude fluorodinitroethanol and 8.92 g (0.04 mole) trinitrobutyric acid in 30 ml 10% oleum was held at 55° for one hour during which time there was no separation of a second phase. On pouring the solution onto 100 g ice a yellow oil separated. The mixture was extracted with 200 ml ether and the ether solution washed successively with 100 ml water, 200 ml 1% potassium carbonate solution, 100 ml 2% potassium carbonate solution and 100 ml water, and dried over calcium chloride. Evaporation of the ether left a solid which was taken up in hexane-ether and chilled in the freezer whereupon two crops, totaling 3.52 g of white needles, m.p. 53.5-54.0° separated. Recrystallization of 1.26 g of this material from carbon tetrachloride yielded 1.15 g of an analytical sample of VIII as feathery white needles, m.p. 53.5-54.5°.

Anal: Table I

Fluorodinitroethyl Fluorodinitrobutyrate, IX. A solution of 3.90 g (0.020 mole) of fluorodinitrobutyric acid and 4.5 g of crude fluorodinitroethanol in 15 ml 10% oleum, maintained 2-1/2 hr. at 50° and poured over 100 g crushed ice, yielded 2.7 g (dry) of a gummy white solid, m.p. 38-41°. A single recrystallization of 2.2 g of this material from ether-hexane yielded 1.8 g of an analytical sample of IX as feathery needles, m.p. 41.4-42.2°.

Anal: Table I

Fluorodinitroethyl 3,5-Dinitrobenzoate, X. To 4.13 g (0.0268 mole) of crude fluorodinitroethanol in 25 ml chloroform and 25 ml carbon tetrachloride was added 3.35 g (0.025 mole) anhydrous aluminum chloride. The latter material dissolved completely with vigorous evolution of hydrogen chloride. After slight heating to drive off the last of the hydrogen chloride, a solution of 5.75 g (0.025 mole) recrystallized 3,5-dinitrobenzoyl chloride in 20 ml chloroform and 20 ml carbon tetrachloride was added, and the total heated to reflux for 90 minutes. During this time there separated a gummy brown solid, probably an ester-aluminum chloride complex. The mixture was then allowed to stand for several days during which time clusters of white crystals precipitated over the brown solid.

Decomposition of the complex was effected by adding to the mixture 100 ml chloroform, 500 ml ether and 200 ml 20% sulfuric acid and shaking vigorously. The material still insoluble after this treatment, filtered off and vacuum dried, amounted to 4.50 g and melted at 130-132°. The organic phase of the mother liquor, washed with 100 ml water, dried over anhydrous calcium chloride and concentrated, yielded two crops, totaling 2.31 g of material melting over the same range (total yield 78% of theory). Recrystallization of 5.65 g of the combined product from ether-benzene afforded 5.15 g of pure X as pale yellow diamond-shaped platlets, m.p. 133.4-134.2°. A further recrystallization from benzene did not change the melting point.

Anal: Table I

Fluorination of Potassium Phthalimide. A solution of 37.0 g potassium phthalimide in 500 ml 80% methanol-water rapidly took up PF at 32-36°. The precipitated product, mainly potassium perchlorate, 9.1 g, was filtered off and the

solution concentrated whereupon successive crops, totaling 20.8 g of a mixture of products were collected. This mixture extracted with hot acetone to separate from additional potassium perchlorate and the acetone solution concentrated yielded as a first crop 15.8 g of crude phthalimide, m.p. 190-215°, after recrystallization from ethanol fine needles, m.p. 225-228°.

Further concentration of the acetone solution yielded 3.4 g of an extremely soluble fraction melting below 100°. Fractional crystallization of this material from benzene furnished an additional 0.5 g of phthalimide and 1.0 g of a white product m.p. 123-126°. Recrystallization of the latter from ether-hexane afforded an analytical sample of N-methylphthalimide, m.p. 131.6-132.4° (lit. 132°) as cottony conglomerates of beautiful white needles.

Anal: Calc'd. for $C_9H_7NO_2$: C, 67.10; H, 4.34; N, 8.70.
Found: C, 66.78, 66.35; H, 4.26, 4.54; N, 8.90, 9.17.

ACKNOWLEDGMENTS

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APPENDIX I

SELECTED PROPERTIES OF PERCHLORYL FLUORIDE(1)

1. Does not attack glass, corrode metals or attack common gasketing material at ordinary temperatures.
2. Resistant to hydrolysis. Water at 250-300°C gives only slow hydrolysis.
3. Storable in liquid form.
4. Thermally stable to 500°C.
5. Soluble without reaction in

<u>Solvent</u>	<u>Solubility (g/l. at 25°, 760 mm)</u>
water	0.6
ethanol	2.5
methanol	2.6
dioxane	5.0
dimethylformamide	4.7
benzene	2.7
chloroform	4.3

6. Boiling point -46.8°C.
7. Critical temperature 95.17 ± 0.10°C.
8. Critical pressure 53 Atm.
9. Density: Gas at $T_c:P_c$ 0.637 g/ml.
Liquid, 20°C. 1.434 g/ml.
10. Vapor Pressure,

0°C.	86.12 psia
25°C.	176.06 psia
50°C.	322.03 psia
11. Toxicity: Detectable by sweetish odor well below toxic levels.
LD/50 = 630 ppm (4 hrs. exposure) on mice.

Bibliography for Appendix I

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