THE FLUORO-NITRATO-HYDROGENATE(I) ANION, $[F \cdots H \cdots ONO_2]^-$

NABILA AL-ZAMIL, BRIAN W. DELF and R. D. GILLARD*

Departments of Chemistry (N.A-Z. and R. D. G.) and Physics (B.W.D.), University College, P.O. Box 78, Cardiff, CF1 IXL, Wales

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Abstract—The products of reaction of dry nitric acid and the fluorides of sodium and caesium are characterised. In the case of caesium fluoride, one product is an unstable hydrogen-bonded species, containing the $(FHONO_2)^-$ anion, losing HF readily.

INTRODUCTION

In structural studies of the so-called hydrogen dinitrate anion, " $[H(NO_3)_2]^{-}$ ", first characterised [1] as its salt with *trans*-[Rh(C₅H₅N)₄Cl₂]⁺ some years ago, there has been a difference of opinion between those favouring the simple linear hydrogen-bond suggested by the original spectroscopic work [1] and those supporting the apparently tetrahedral structure, suggested by the original diffraction work using X-rays on [2] CsNO₃ HNO₃ and [3a] the [Rh(C₅H₅N)₄Cl₂]⁺ salt. This argument has been resolved recently, in favour of the linear hydrogen bond, by detailed work [4] on the caesium salt using neutron diffraction, by a new and fuller study, using X-rays, on [3b] the rhodium complex salt and its isomorphous ruthenium congener, and by a neutron study [3c] of the rhodium salt.

However, in the interim, it seemed of interest to evaluate the stereochemistry around hydrogen of the unknown ion $(FHONO_2)^-$. This report describes our approaches to its synthesis.

While species of the type HX_2^{-} are quite numerous [5] (for example, where $X = RCOO^{-}$, chloride, bromide, iodide, cyanide, isothiocyanate, carbonate, nitrate), the mixed anions with formula XHY⁻ have not received so much attention. Anions with such hydrogen bonds as $(F \cdots H \cdots OR)^{-}$ are rare; this is attributed to the high stability of the hydrogen difluoride anion, which makes it difficult for any other salt to exist in hydrofluoric acid. However, Emsley recently found [6a] that solutions of potassium fluoride in glacial acetic acid gave extra bands in the IR spectra, arising from hydrogen-bonded species. One of these bands was attributed to the species shown as I below, and Emsley made [6a] a rather stable potassium salt KF CH₃CO₂H, which he formulated as containing the ion, II, with a linear hydrogen bond, as opposed to the earlier proposal [6c] of a three coordinated hydrogen atom in the analogous formato-





hydrogen fluoride (III). Emsley suggested [6a] that this species would involve one of the strongest hydrogen bonds known, with a bond energy around 120 kJ per mole. Further, on the basis of *ab initio* LCAO-MO-SCF calculations, the fluoride-formic acid species would have [6b] the strongest hydrogen bond known, at about 250 kJ mol^{-1} .



While the hydrogen nitrate fluoride ion seems not to have been prepared, there are several indications that it may well exist. First, the nitrate ion is isoelectronic with the acetate ion, so that the species fluoride hydrogen nitrate would be similar to the allegedly extremely stable fluoride hydrogen formate. Secondly, Caesar and Goldfrank showed [7] that nitric acid could be extracted from organic media by shaking with sodium fluoride. In the nitration of starches with dinitrogen pentoxide in chloroform, the nitric acid formed seemed to affect the yield of product, and so they wished to remove it. This was achieved by adding sodium fluoride to the reaction medium. They implied that the efficacy of the sodium fluoride was because it formed a hydrogen bond with the nitric acid, as shown



Thirdly, the analogous chloro-species $(Cl \cdot H-ONO_2)^-$ was prepared and thoroughly characterised [8] by Salthouse and Waddington.

The aim of our work was therefore to prepare and characterise the species $(FHONO_2)^-$, by repeating the

work [7] of Caesar and Goldfrank, (preliminary experiments in aqueous media having been unpromising).

EXPERIMENTAL

X-Ray powder photographs were taken with either Debye Scherrer or Guinier cameras, with CuK_a radiation in each case. Thermogravimetric analysis was performed using a Stanton Redcroft Balance (TG750). Concentrated nitric acid (d = 1.43)was frozen at -80°C. Then two volumes of concentrated sulphuric acid were added. Distillation was then carried out at 1 mm Hg at 0°C with visible boiling. The colourless crystalline distillate was collected at -80°C. The collected acid was distilled again in the same way after addition of 1.5 volume of H₂SO₄.

The colourless crystalline distillate was collected at -80° . It was then preserved in sealed tubes in the dark at -80° C. It melted to give a colourless liquid, which had the theoretical acid equivalent of nitric acid to within the error of measurement. The IR spectrum of the vapour agreed closely with that [9] in the literature: an extra small band at 1785 cm⁻¹ probably resulted from reaction with the NaCl windows. At temperatures above 0° the material started to decompose rapidly showing brown fumes of NO₂.

Caesium hydrogen dinitrate [2]. Caesium nitrate was added to warm concentrated nitric acid (specific gravity 1.42) until a saturated solution resulted. Cooling to room temperature gave colourless crystals. These were collected and left to dry in the glove-box.

HNO₃ + MF: conditions for equilibrium. 0.42 gm (0.01 mol) of finely ground sodium fluoride was placed in 25 ml dry chloroform. Then 0.84 ml (2 moles) of cold dry nitric acid was added. The mixture was kept at 0°C with continuous stirring. At various time intervals 0.5 ml of CHCl₃/HNO₃ was removed and titrated with 0.5 M NaOH (in 1 ml burette) to determine when equilibrium was established. On plotting the acid content of the organic solvent against time of contact the value decreased rather steadily for some 30 min, then was almost constant, becoming finally steady after 6 hr. We therefore used 30 min as our standard time of shaking, and always left mixtures overnight before analysis.

The molar ratio of reaction for NaF and HNO3 was established as follows.

Eight flasks each containing 0.42 g NaF (0.01 mol) and a known amount of dry nitric acid in 25 cm3 of CHCl3 were shaken for 30 min and then stored cold overnight. From each flask 1 ml of CHCl₃/HNO₃ was taken and titrated with 0.5 M NaOH.

On plotting acid equivalent (titre) against the molar ratio [HNO₃]:[NaF], a sharp break from zero occurred at the ratio 0.5, i.e. $HNO_3 + 2NaF \rightarrow NaNO_3 + Na(FHF)$.

Dry nitric acid (2 mols) was dissolved in dry chloroform and stored at -80°C in a dry box. To this solution, 1 mol of the appropriate alkali fluoride (either sodium or caesium) was added, as a solid. After time for the system to come to equilibrium, the solution was removed, leaving a white powder. These products will be designated A (sodium) and B (caesium).

Dry nitric acid (1 mol) was treated with the alkali fluoride (1 mol) at - 30°C under nitrogen, in chloroform solution, stirring for 30 min. The solid products obtained under these conditions will be called C (sodium) and D (caesium).

Dry nitric acid (1.5 mol) in chloroform solution at -80° C was similarly treated with 1 mol of caesium fluoride. This product will be called E.

The products were characterised by analysis, X-ray powder photography, and thermogravimetric analysis.

As shown in Table 1, A is a mixture of sodium nitrate and sodium hydrogen fluoride, and the analytical results of Table 2 confirm this (at 2NaNO₃: 1NaHF₂).

B was the now well-known [2] caesium hydrogen dinitrate.

	Table 1. d-spacings for product A			
A	NaNO ₃	NaHF ₂	NaF	
4.5482		4.593		
4.4357				
3.8635	3,8635			
3.2995				
3.0253	3.0253			
2.9283		2.935		
2.7945	2.7945			
2,7525		2.753		
			2.6727	
2,5265	2.5266			
2.3074			2.3074	
2.2794				
2.1252	2.1252			
2.0256		2.029		
1.9316	1,9513			
1.8937	1.8937			
1.8754	1.8754			
1,7891				
1.7263		1.7345		
1.6407		1.653		
			1.3955	
			1.3346	

	Na ⁺ (b)	F (c)	H+(q)
Observed ^a	29.79	16.34	0.47
NaF	54.75	45.25	0
Na FHONO2	21.89	18.14	0.95
Na H(ONO2)2	15.52	0.0	0.67
NaNO ₃	27.05	0.0	0.0
NaHF ₂	37.08	61.29	0.68
NaNO ₃ + NaHF ₂	31.28	25.85	0.69
$2NaNO_3 + NaHF_2^e$	29.73	16.38	0.43
Observed ^a	29.79	16.34	0.47

Table 2. Analyses^a of product A

^aThe identical top and bottom sets are values found: the remainder are those calculated for the substance(s) given.

^bBy atomic absorption; ^cusing calcium chloride; ^dby titration.

Consistent with the X-ray results; the product of a 1:1 reaction of NaF+HNO₃ is NaNO₃+HF, and of a 2:1 reaction is NaNO₃+NaHF₂. The solid analyzed here has a composition between these extremes.

Product C	NaNO ₃	Product D	CsN03
3.8969	3.89	4.4577	4.47
3.0354	3.03	3.1508	3.15
2.8029	2.81		2.996
2.5265	2.53		2.583
2.3074	2.311	2.5615	2.573
2.1252	2.125		2.483
1.9513	1.947		2.453
1.8937	1.898	2.2254	2.232
1.8754	1.830		1.999
1.6543	1.652	1.9918	1.996
1.6273	1.629	1.8226	1.826
1.5359	1.544		1.580
		1.5764	1.576
			1.488
		1.4847	1,485

Table 3. Identification of C + D

Found F, 0.0; HNO₃ 24.3 \pm 0.5; Calc for Cs[H(ONO₂)₂]: F, 0.0; HNO₃ 24.5%. M.p. 100° (lit.¹⁰ 100°). It was extremely hygroscopic. We comment elsewhere on the properties of this and some newly synthesized hydrogen dinitrates.

C was high-melting, showed zero acidity and was identified as sodium nitrate by its powder photographs (Table 3); D was (similarly) caesium nitrate; E: From thermogravimetric analysis, E loses 10% at 46°C to give CsNO₃ (whose further TGA curve runs exactly parallel 120–950°C with that of an authentic sample of CsNO₃. [Calc for Cs(FHONO₂) \rightarrow Cs(NO₃) + HF↑; 9%). However, although the analyses for H⁺, NO₃⁻, F⁻, and Cs⁺ (given in Table 4) all lie between the values calculated for CsNO₃HF and CsNO₃, the analyses were done on samples of differing ages, and using methods of differing reliability. For instance, after an attempt to analyse for caesium in CsNO₃ using sodium tetraphenylborate gave very inconsistent results, atomic flame emission analysis for Na and Cs used a Varian Techtron emission spectrometer AA6. The nitron method applied to caesium nitrate gave results with error $\pm 4\%$. The lead chlorofluoride method was checked against pure NaF and gave results only within $\pm 1\%$ of the calculated, whereas results for the calculated chloride method were only within $\pm 2\%$ of the calculated.

RESULTS

The detailed course of the reaction of sodium fluoride with dry nitric acid in chloroform depends upon the mole ratio. Under 1:1 conditions, the reaction seemed to stop at the stage shown:

$NaF + HNO_3 \rightarrow NaNO_3 + HF.$

This corresponds to the solid product C, described in the experimental section, where the X-ray powder pho-

Method	Cs ⁺	н+	NO3	F
·	AA	acid/base	Nitron	PbC1F
Found	67.1	0.35	29.9	3.5
CsN03	68.2	-	31.81	-
CsF	87.5	-	-	12.5
Cs(FHONO2)	61.84	0.46	28.85	8. 83
CsH(NO3)2	51.51	0.38	48.07	-
CsHF ₂	77.31	0.58	-	22.09
CsF.2HNO3	47.82	0.72	44.62	6.83
CsF.CsHFNO3	72.46	0.27	16.9	10.35

Table 4. Analysis of product E

Table 5. d-spacings for Cs[FHONO₂]

CsF ^a	Cs(HF ₂) ^b	CB (FHONO2) ^C	$Cs[H(ONO_2)_2]^d$
			5.72
			4.52
		4.5026	
	4.37		
			4.99
			3.99
	3.88		
		3.8144	
			3.73
			3.65
			3.59
			3.51
3,469			
			3.245
			3.21
			3.19
		3.1399	3.14
	3.10		
		3.0354	
3.003			
		2.9283	
	2.91		
			2.86
		2,7200	
	2.60		
		2.5265	
	2.43		
			2.42
			2.38

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CsF ·	Cs(HF ₂)	Cs(FHONO2)	$C_{B}[H(ONO_{2})_{2}]$
······		2.3074	·····
		2.1445	
2.125	2.13		
		2.0429	
		1.9876	
		1.9552	
	1.935		
	1.894		
		1.8682	
	1.854		
1.8131			
	1.757		
1.7366		1.7385	
		1.6407	
		1.5405	
1.5036			
		1.4890	
		1.4699	
1.3798			
1.3446			
1.2278			

Table	5.	(Contd)

*From ASTM X-ray powder diffraction file.

^bFrom R. Konh, K. Fuwa and T. E. McEver, J. Am. Chem. Soc. 78, 4256 (1956).

'In sealed Lindemann tube: exposure time 2.3 hr.

^dFrom Ref. [2].

tograph (Table 3) shows the lines of sodium nitrate only. In this case, the glass of the reaction vessel was distinctly etched, confirming the production of hydrofluoric acid.

The reaction takes time to come to equilibrium, clearly because of solubility problems. However, after equilibration, it is possible to titrate any residual unconsumed nitric acid, as a function of the molar ratio of nitric acid to sodium fluoride. Below the value of 0.5 for this ratio, there is no free acid present at equilibrium in the organic solvent. Above the value 0.5, the acid concentration becomes finite, so that the reaction, in the presence of excess of sodium fluoride is

$$2NaF + HNO_3 \rightarrow Na(HF_2) + NaNO_3$$
.

With caesium fluoride, the situation is different. The now well-known caesium hydrogen dinitrate [2] is the product under some conditions, but, using a molar ratio of 3:2 (nitric acid: caesium fluoride), the product appears, at least initially, to contain the desired caesium fluoride hydrogen nitrate.

It rather readily decomposes, losing hydrogen fluoride on standing. This pathway of decomposition, giving HF and caesium nitrate, would agree well with expectation, since based on the scheme used by Salthouse and Waddington to explain [8] the decomposition of tetramethylammonium chloronitratohydrogenate(I) to the nitrate and hydrogen chloride gas, the decomposition of $C_{s}(FHONO_{2})$ to $C_{s}NO_{3(s)} + HF_{(g)}$ should be favoured by about 100 kJ mol⁻¹ over decomposition to $C_{s}F_{(s)} + HONO_{2(g)}$.

Finally, it is possible to comment on the old and ingenious suggestion [7] of Caesar and Goldfrank. They decided that the alkali fluoride which was most effective in removing nitric acid from organic media was the sodium salt. Although, from our present work, caesium fluoride would look more effective from the quantitative point of view (because one mole of caesium fluoride reacted with two moles of nitric acid to give caesium hydrogen dinitrate, whereas for sodium fluoride, only one half mole of nitric acid was absorbed), the reaction products from sodium fluoride were much more stable, settling as solids in the reaction vessel. The reaction using caesium gave rise to hydrofluoric acid, which, of course, generates its own problems.

The X-ray powder photograph of caesium fluoronitratohydrogenate, E, Cs[F-H-ONO₂], is described in Table 5. Work on the characterization of the novel hydrogenbonded species continues. However, it is clearly not so stable to decomposition as the analogous $(F...H...OCOCH_3)^-$, since the potassium salt of that anion was obtained after treatment at 100°C in vacuo.

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