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"A New Method for the Preparation of Fluorodisulfate Salts"

By Darryl D. Des Marteau and George H. Cady

University of Washington
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"A New Method for the Preparation of Fluorodisulfate Salts"

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The only reported fluorodisulfate salt is that of potassium. It was prepared by the reaction of potassium fluoride with excess sulfur trioxide.\(^1\)

\[
KF + 2SO_3 = KS_2O_6F = KSO_3F + SO_3
\]


The white crystalline compound was unstable and decomposed completely to potassium fluorosulfate and sulfur trioxide when heated to 100° for 4 hours. Calcium fluorodisulfate has been suggested as an intermediate in the reaction of calcium fluoride with sulfur trioxide.\(^2\)


Potassium, sodium and, probably, ammonium fluorodisulfates have now been produced by reaction of peroxydisulfuryl difluoride with the corresponding peroxydisulfates, the potassium and sodium

\[
M_2S_2O_8 + S_2O_6F_2 = 2MS_2O_6F + O_2 = 2MOSO_2F + 2SO_3 \quad (M = K, Na \text{ or } NH_4)
\]
salts being obtained in high yield. The ammonium salt was impure and was obtained in approximately 15% yield.

Experimental

Reagents.— Peroxydisulfuryl difluoride was prepared and purified by the method of Shreeve and Cady.\(^3\) The peroxydisulfate salts were obtained from commercial sources and were dried by heating in vacuo.

Preparation and Analysis.—The reactions were run in a Pyrex glass bulb fitted with a Fischer-Porter glass valve closed by a Teflon stem. S\(_2\)O\(_6\)F\(_2\) was condensed onto the dried, powdered peroxydisulfate at -183° and the mixture was then allowed to warm to room temperature. A slow reaction took place near room temperature liberating oxygen. An approximate 10:1 mole ratio of S\(_2\)O\(_6\)F\(_2\) to M\(_2\)S\(_2\)O\(_8\) was used in each case. The reactions were very slow and became slower with time, probably due to surface effects. Oxygen was removed periodically by pumping on the reaction vessel at -183°. After no further oxygen was observed to form (21 days for 1.7384g K\(_2\)S\(_2\)O\(_8\), 4 days for 1.033g Na\(_2\)S\(_2\)O\(_8\), 8 days for 1.0356g (NH\(_4\))\(_2\)S\(_2\)O\(_8\)), the excess S\(_2\)O\(_6\)F\(_2\) was removed by pumping at room temperature until the rate of weight loss was only a few mg per hr. The products could not be pumped to constant weight because the unstable fluorodisulfate salts dissociated slowly into SO\(_3\) and MOSO\(_2\)F at room temperature. For the above samples of K\(_2\)S\(_2\)O\(_8\) and Na\(_2\)S\(_2\)O\(_8\) the weights of product were 2.743g and 1.718g respectively (Theory: 2.807g)

and 1.756 g). For the sample of \((NH_4)_2S_2O_8\) the weight of product was 1.169 g (1.789 g theor) and corresponded to approximately 55\% \((NH_4)_2S_2O_8\) mixed with 35\% \(NH_4SO_3F\). The products were then heated to 135\°C maximum and pumped to constant weight. After this treatment the above samples weighed 1.760, 1.073 and 1.035 g, respectively, corresponding closely to the theoretical weights, 1.770, 1.060 and 1.063 g, respectively for KSO_3F, NaSO_3F and NH_4SO_3F.

Cher runs were similar to those just described. The KOSO_2F, NaOSO_2F and NH_4OSO_2F were then hydrolyzed in 1N sodium hydroxide for 10 hours at 100\°C and the resulting solutions were analyzed for sulfur and fluorine. Sulfur was determined gravimetrically as barium sulfate and fluorine volumetrically by the method of Willard and Winter. The sulfur trioxide was identified qualitatively by its physical properties, by tendency to liborate iodine from aqueous potassium iodide and by giving a positive test for sulfate after hydrolysis. Oxygen was identified by its mass spectrum and volatility at -183\°C. The infrared spectrum of the excess peroxydisulfuryl difluoride remaining after reaction corresponded to \(S_2O_6F_2\) containing a trace of SiF_4. Analytical data for the runs given above are summarized in table I.

X-ray powder photographs were taken for samples of KOSO_2F and KS_2O_6F prepared by the method given above and by the method of Lehmann and Kolditz. The two methods gave materials having essentially the same patterns. These are given in the

### Table I

**Analytical Data**

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<th>K⁺</th>
<th>NH₄⁺</th>
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<td>Moles O₂&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>Moles SO₃&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>calc.</td>
<td>26.3</td>
<td>23.2</td>
<td>27.3</td>
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<sup>a</sup> per mole of M₂S₂O₈ consumed

<sup>b</sup> per mole MS₂O₆F decomposed by heating

<sup>c</sup> analysis of MOS₂F
Ph.D. thesis of the junior author.\textsuperscript{5} When the patterns were compared with those reported by Lehmann and Kolditz\textsuperscript{1} the extent of agreement was incomplete. Prof. Dr. Kolditz has also compared the data and powder patterns (private correspondence) and agrees with us that the materials obtained by the two methods must be the same even though the reported powder patterns are not exactly the same.

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Potassium and sodium fluorodisulfates are produced by the reaction of peroxydisulfuryl difluoride with the corresponding peroxodisulfates:

\[ M_2S_2O_8 + S_2O_6F_2 = 2MS_2O_6F + O_2 \quad (M = Na \text{ or } K) \]

When \( M \) is ammonium, some \( NH_4S_2O_6F \) is obtained together with much \( NH_4SO_3F \), apparently formed by the reaction:

\[ NH_4S_2O_6F = NH_4SO_3F + SO_3 \]

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Fluorodisulfate salts