Summary

The gross quantum yield, ϕ_{gross} at 27 ± 2° in molecules of oxalic acid per quantum, in the photolysis of a solution in which $[UO_2SO_4] = 0.01$ and $[H_2C_2O_4] = 0.05$ is 0.48 ± 0.01, $\lambda = 208$ mμ; 0.63 ± 0.03, $\lambda = 253$ mμ; 0.59 ± 0.01, $\lambda = 278$ mμ. After correction for light absorbed by uncombined oxalic acid, and for the unsensitized photolysis of this acid, the quantum yield, when $\lambda = 208$ mμ, is considerably higher than at the lower frequencies. A zinc spark of high constancy was the light source. Elaborate radiometric and analytical precautions were taken.

The various absorption coefficients involved are given.

Owing to accentuation of radiometric difficulties in the region of 208 mμ, the uranyl oxalate actinometer should now be especially valuable for photochemical work in this part of the spectrum. The necessary precautions are emphasized.

ϕ_{253} and ϕ_{278} agree closely with findings of W. G. Leighton and one of us in the same regions. It is thus indicated that the two thermopiles used and the uranyl oxalate actinometer integrate periodically intermittent and constant radiation in equivalent fashion.

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Fluorine Polyhalides of Organic Amines

BY HAROLD SIMMONS BOOTH, WILLIAM C. MORRIS AND G. D. SWARTZEL

In this communication are described the preparation and properties of the compounds formed by the union of iodine trichloride and typical members of the four classes of substituted ammonium fluorides and pyridine fluoride. These prove to be similar in general properties to the corresponding fluorine polyhalides of the alkali metals and ammonium,[1] and the trihalides[2] and pentahalides[3] of substituted ammonium salts.

The salts here described were prepared by one of the methods recently developed[1] for the analogous alkali metal and ammonium salts involving the addition of iodine trichloride to the fluoride of the base.

The fluorides of the organic amines are best made by adding slightly more than an equivalent of aqueous hydrofluoric acid to the amine. Iodine trichloride is conveniently prepared by adding finely powdered iodine to an excess of liquid chlorine cooled by solid carbon dioxide in acetone. On evaporating the excess of chlorine the pure iodine trichloride remains as a fluffy powder which is very easily handled.

A cold saturated aqueous solution of this reagent on addition to a cold, nearly

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(1) Booth, Swinehart and Morris, THIS JOURNAL, **54**, 2561 (1932); *J. Phys. Chem.*, **36**, 2279 (1932).

(2) Cremer and Duncan, *J. Chem. Soc.*, **133**, 1857 (1931).

(3) Chattaway and Hoyle, *ibid.*, **123**, 654 (1923).

saturated, slightly acidified solution of the fluoride of the amine causes the immediate separation of the bright yellow fluorine iodine trichloride salt. The compounds described below all form brilliant yellow needle-like tetragonal prisms which exhibit parallel extinction under crossed nicols in two positions and are isotropic in the third. They were collected on a Jena glass filter and dried centrifugally.

Analysis.—For analysis the sample was dissolved in a slight excess of sodium hydroxide solution and gently boiled until colorless, cooled and a small amount of hydrogen peroxide solution added to reduce any hypochlorite and hypoiodite to the normal halide. Excess hydrogen peroxide was driven off by boiling, the solution again cooled and acidified with dilute sulfuric acid, and a small amount of sulfurous acid added to reduce any free iodine. The excess sulfur dioxide was driven off by boiling, a small amount of nitric acid and a slight excess of one-tenth normal silver nitrate solution added and the solution boiled. The mixed silver iodide and chloride was then filtered, washed, dried and weighed on a Jena glass filter. The excess silver nitrate was then back titrated with one-tenth normal ammonium thiocyanate. The following equations give the percentage of iodine and chlorine

$$\text{Cl} = \frac{[0.091035\,(\text{no. m. e. AgNO}_3) - 0.38771\,(\text{wt. Ag salt})] \times 100\%}{\text{weight of sample}}$$

$$\text{I} = \frac{[1.3878\,(\text{wt. Ag salt}) - 0.19894\,(\text{no. m. e. AgNO}_3)] \times 100\%}{\text{weight of sample}}$$

This method of analysis is just as accurate and much quicker than the method of Gooch previously used. The nitrogen was determined by the Kjeldahl method.

The specific properties and analytical results are given in the table. When heated in open melting point tubes the salts undergo decomposition; this appears not to take place in sealed tubes, indicating the phenomenon to be primarily dissociation, analogous to the action of heat on the fluorine polyhalides of the alkali metals.

TABLE I

		M. p., °C.		
	Salt	Open tube	Closed tube	Sp. gr.
1	$CH_3NH_3FICl_3$	25–30 dec.	35–40	1.216 (4°)
2	$(C_2H_5)_2NH_2FICl_3$	50; dec. 85	60–63	1.216 (19°)
3	$(CH_3)_3NHFICl_3$	116, dec. complete at 140	121–145	1.115 (19°)
4	$(CH_3)_4NFICl_3$	265–267 dec. complete at 275	267–270, dec. 310	1.646 (19°)
5	$C_5H_5NHFICl_3$	175–180; darkens 135	187–190; reddens at 147 no decomp.	2.912 (19°)

	Analyses, %					
	Cl		I		N	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	37.15	37.35 37.25	44.33	43.53 43.48	4.89	4.87 4.88
2	32.59	32.61 32.61	38.89	38.82 38.82	4.29	4.34 4.33
3	34.05	34.06 34.02	40.63	40.53 40.60	4.49	4.47 4.48
4	32.59	32.47 32.51	38.89	38.85 38.77	4.29	4.27 4.28
5	32.00	32.04 32.16	38.19	37.76 37.88	4.22	4.21 4.23

Attempts to prepare analogous compounds from the hydrofluorides of aniline, *m*-nitroaniline and *o*-chloroaniline failed; chlorination obviously occurred, with evolution of heat and acid fumes, and only tarry products were obtained.

Summary

Organic amines form fluorine polyhalides, similar to those formed by the alkali metals, on adding a cold saturated solution of iodine trichloride to a cold saturated solution, slightly acidified, of the hydrofluoride of the amine, except in cases where the amine is chlorinated by the iodine trichloride.

The tetramethylammonium fluoride iodine trichloride is the most stable and the monomethylamine salt the least. The pyridine salt is next in stability to the quaternary amine salt and both of them compare favorably with the corresponding alkali metal polyhalides. The thermal decomposition is primarily dissociation as in the case of the alkali metal polyhalides.

All the organic fluoride polyhalides thus far prepared form orange-yellow tetragonal crystals.

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The Sorption of Oxygen by Nickel Catalysts[1]

BY W. WALKER RUSSELL AND LEONARD G. GHERING

In a recent investigation[2] it was found that catalytically active nickel strongly sorbed large amounts of oxygen at 0°. Because evidence of the true nature of a sorption process is probably best obtained by studying it at several temperatures, measurements in the present work have been extended below and somewhat above 0°. Furthermore, sorption measurements have been made on nickel catalysts in several states of activity, in an endeavor to throw further light upon the general problem of the correlation of sorptive behavior with catalytic activity.

Apparatus and Experimental Method

Apparatus.—Although the apparatus shown in Fig. 1 is almost self-explanatory, attention may be called to certain of its features. Catalyst bulb A allowed for successive reductions *in situ*. The manometer M could be used to measure pressures both in the catalyst system A, B, C, D and in the constant volume buret I, J. The by-pass G[3] facilitated the admission of oxygen to the catalyst. Mercury levels were adjusted at the fixed contacts D, E or F by means of a suitably connected radio loud speaker. These settings were reproducible to better than 0.02 mm., the sensitivity of the cathetometer used in the pressure measurements. A diffusion pump backed by a Sprengel pump allowed desorbed gases to be collected. The catalyst was protected by a liquid air trap

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(1) From a thesis submitted in May, 1933, by Leonard G. Ghering to the Graduate School in partial fulfilment of the requirements for the degree of Master of Science.

(2) Russell and Bacon, THIS JOURNAL, **54**, 54 (1932).

(3) Benton and White, *ibid.*, **52**, 2325 (1930).