

## LETTERS TO THE EDITOR

### ETCHING OF ANTIMONY SINGLE CRYSTALS

In continuation of our work on studies of etched surface of bismuth single crystals,<sup>1</sup> we report here our results on the etch phenomenon on single crystals of antimony. The experimental procedure was the same as described in our earlier work.<sup>1</sup>

The freshly cleaved specimen was chemically etched in a solution containing 3 parts  $\text{HNO}_3$  + 9 parts tartaric acid + 1 part water, for one to several seconds. In the initial stage of etching triangular etch pits distributed at random were observed. Moreover, there were two distinct types of pits, viz., sharp triangles and rounded triangles. Rows of closely packed triangular etch pits with branching at some places (Fig. 1)



FIG. 1

were observed and with the increase in time of etching the pits became large and deep but the site of pits remained the same. The cleavage plane of the crystal was scratched quickly with a sharp needle and then subsequently etched in the above etchant. An array of triangular etch pits, lined up on many straight lines in a particular specified direction near the scratch, was observed. Dislocation etch pits have been observed on the cleavage plane of antimony produced by 3 parts HF, 5 parts  $\text{HNO}_3$ , 3 parts  $\text{CH}_3\text{COOH}$  and 1 part  $\text{Br}_2$  (Lovell and Wernick)<sup>1,2</sup> and by 10 gm.  $\text{FeCl}_3$ , 30 ml. HCl and 120 ml. water (Shigeta and Hiramastu).<sup>3</sup> Among the different etchants tried by the authors the present etchant was found to be more suitable; in this case with the increase in etching

time the surface did not become tarnished and progressively dull as was the case with the other etchants used. One cleavage face was etched with one etchant and its counterpart was etched with another etchant and it was found that there was a close correspondence between the etch pits on both the faces. The etch pits obtained by the present etchant on cleavage (111) face of single crystal of antimony were similar to those obtained by earlier workers.<sup>2,3</sup> Considering their orientation and density of distribution it seems that the etch pits are formed at dislocation sites.

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### FLUORIDE COMPLEXES OF URANIUM (IV) AND THORIUM WITH HYDRAZINE AND HYDROXYLAMINE

HYDRAZINE fluoride complex of uranium  $\text{UF}_4\text{N}_2\text{H}_4\text{HF}$  has been isolated in this laboratory and will be reported.<sup>1</sup> The compound can be recommended as a suitable intermediate for the production of anhydrous uranium tetrafluoride. Though there is a close similarity between the physical behaviour of ammonia, hydrazine and hydroxylamine salts, so far no attempt has been made to prepare the corresponding hydroxylamine complex. The present note describes such an attempt for the preparation of the compound. When a mixture of uranyl-nitrate, hydroxyl amine, hydrofluoric acid is exposed to sunlight in presence of alcohol a green precipitate is obtained in about 10 to 15 minutes time and on further exposure more of the compound is formed. The compound on analysis has been found to possess the formula  $\text{UF}_4\text{NH}_2\text{OH}\text{HF}$ .



The compound on heating under vacuum at about 300° C. yields partially decomposed uranium tetrafluoride. The analogous hydrazine complex  $UF_4 \cdot N_2H_4 \cdot HF$  on refluxing with formic acid gives uranium tetrafluoride. In this case, however, the hydrated tetrafluoride  $UF_4 \cdot H_2O$  was obtained.

A more expeditious method of preparation, as compared to the photolytic one, of the above mentioned complexes has been achieved, by the use of copper ion as catalyst for the purpose of reduction. With 2 gm. of uranyl nitrate, 1 gm. of hydrazine hydrochloride or hydroxylamine hydrochloride, 20-30 c.c. of 40% hydrofluoric acid and 5 drops N/20 copper sulphate solution, the yield of the product is 95% in about 10 minutes time at 80-90° C. The fluoride complexes are obtained in the pure form as bright-green dense crystals.

Thorium is known to form isomorphous compounds with that of tetravalent uranium, with which it is associated in certain minerals. Attempt was therefore made to isolate the analogous thorium fluoride complexes. When hydrofluoric acid is added to a solution of thorium nitrate in presence of hydrazine or hydroxylamine a flocculent white precipitate is immediately formed. On raising the temperature to 70-80° C. the precipitate settles down in fine crystalline form. The compounds on analysis have been found to be isomorphous with the corresponding uranium (IV) complexes and possess the formulæ  $Th_4N_2H_4HF$  and  $ThF_4 \cdot NH_2OH \cdot HF$  respectively.

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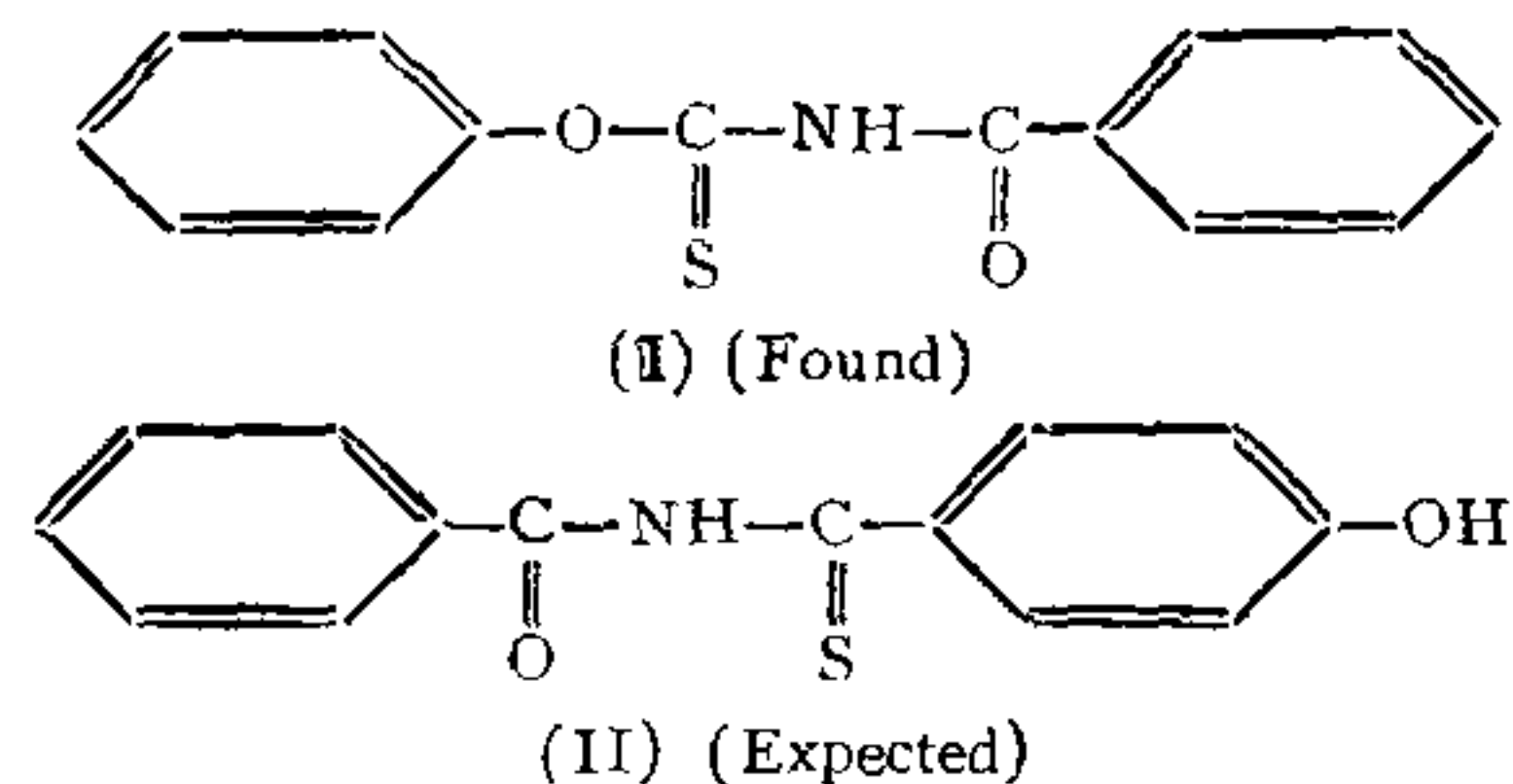
### ACYL ISOTHIOCYANATES: FRIEDEL-CRAFT REACTION OF PHENOLS WITH BENZOYL ISOTHIOCYANATES

ISOTHIOCYANATES have been known to condense with phenols in presence of a Lewis acid. Thus Karrer and Weiss<sup>1</sup> studied the action of isothiocyanates and hydrogen chloride upon polyhydric phenols. They obtained in all cases substituted amides of the corresponding thioacids. For example, ethyl isothiocyanate with resorcinol afforded ethylamide of thioresorcylic acid. Rivier and Kunz<sup>2</sup> studied action of isothiocyanates on phenols in presence of anhydrous aluminium chloride. They reported that phenyl isothiocyanate when condensed with phenol gave thioanilide of *p*-Hydroxybenzoic acid

*p*-PhNHCSC<sub>6</sub>H<sub>4</sub>OH structure of which was also proved by these authors.

Acyl isothiocyanates have not apparently been studied. Benzoyl isothiocyanate was therefore selected for the present study, which was prepared according to Ambelang and Johnson.<sup>3</sup> This was then condensed with phenol according to details described in the experimental. The product contains nitrogen and sulphur and was proved to be *N*-benzoyl-phenyl-thiocarbamate (I) and not the expected *N*-benzoyl-thioamide of *p*-Hydroxybenzoic acid (II) since the hydrolysis of the final product gave only benzoic acid and no trace of *p*-Hydroxythiobenzamide or *p*-Hydroxybenzamide or *p*-Hydroxythiobenzoic acid.

Resorcinol is found to behave analogously. Condensation of other polyhydric phenols is under investigation and a detailed paper will be presented in future. It can be concluded from results that acyl isothiocyanates behave differently from alkyl isothiocyanates and undergo addition reaction with phenols in presence of a Lewis acid. This is probably because there is a strong additional electromeric shift due to keto group in acyl isothiocyanates.



#### EXPERIMENTAL

**Condensation.**—Phenol (4 g.) was mixed with finely pulverised anhydrous aluminium chloride (8 g.) and benzoyl isothiocyanate (6.6 g.) was added dropwise with efficient cooling. The reaction becomes vigorous and the colour of the mixture changes to red. It was left overnight at room temperature and decomposed with ice-water next day. The semi-solid red mass solidified when chilled in ice-bath. It was crystallised from ethanol and finally with petroleum ether (80°) when pale-yellow, orange needles were obtained. It melted at 66° C. Yield 2.5 g.

$C_{14}H_{11}N.SO_2$  requires N, 5.83% ; S, 12.45% (Found N, 5.61% ; S, 12.40%).

The product was insoluble in alkali or dilute acid in cold. It did not give any colouration with alcoholic ferric chloride.

**Hydrolysis.**—Above product (1.0 g.) was refluxed with 10 ml. of 10% sodium hydroxide