layer formed, it was removed in a small separatory funnel, and the amine was redried with fresh sodium hydroxide for eight to ten hours. The filtered amine was then distilled through a short, Vigreux column into an ice-cooled receiver equipped with a soda-lime tube. The yield was 31-34 g. (71-78%), b. p. 44-46°, m. w. 73 by glass electrode titration. Double quantities also were used with no significant change in yields. It is suggested that the procedure, with obvious modifications in details, is probably applicable to the preparation of *t*-amylamine from *t*-amylurea.

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Colored Complexes of Tungsten Hexafluoride with Organic Compounds

BY HOMER F. PRIEST AND WALTER C. SCHUMB

It was observed in the course of a study of the reduction of tungsten hexafluoride by organic compounds that when the hexafluoride was dissolved in certain of these compounds deep colors were produced. Apparatus was devised in which tungsten hexafluoride could be added as liquid to a sample of the organic liquid, an atmosphere of dry air being maintained above the solution. Solutions were also prepared quantitatively by distilling the pure hexafluoride into a known weight of organic solvent contained in weighed cylindrical comparison tubes for a Coleman spectrophotometer (Model 14). The tubes could be sealed off and reweighed so as to obtain the weight of added fluoride. Spectrometric traces were made, all values being obtained by use of the potentiometer drum rather than by direct galvanometer deflection.

TABLE I

EFFECT OF DISSOLVING TUNGSTEN HEXAFLUORIDE IN ORGANIC LIQUIDS

Solvent	Color of solution	Effect of cooling to −78°	Effect of dilution	Remarks
Benzene	Red	White crystals	Orange–yellow	
Toluene	Red	None	Orange–yellow	Color retained when frozen
Acetone	Red	None	Orange	Color intensified on standing
Cyclohexanone	Red	None	Orange	Some intensification on standing
Ethyl alcohol	None	White crystals		
Carbon tetrachloride	None	White crystals		
sym-Tetrachloroethane	None	Solidified		
n-Decane	None	Solidified		
Cyclohexane	None	Solidified		
Diethylcarbitol	Violet–brown	None	Brown	
Diethyl ether	Violet–brown	None	Brown	
Dioxane	Pale red	White solid	Orange	Some crystals deposited

The tungsten hexafluoride had been prepared from metallic tungsten and fluorine, followed by redistillation to eliminate any WOF_4 which might be present. Analysis of the hexafluoride showed it to be better than 99% pure. The organic solvents employed were of carefully selected purity; thus, analytical reagent grade, thiophene-free benzene; reagent grade acetone, toluene, *sym*-tetrachloroethane, ethyl alcohol and diethyl ether; Eastman Kodak Co. pure grade cyclohexane, cyclohexanone, and *n*-decane; dioxane free from unsaturated compounds. Most of the liquids were dried over anhydrous calcium sulfate and redistilled.

A summary of the qualitative observations made on the solution of tungsten hexafluoride in the different organic solvents is shown in Table I.

From these results it appears that the presence of certain functional groups in the solvents employed results in similar colors; thus the colors in benzene and toluene are similar, as are those in diethylcarbitol and diethyl ether. Ketones, such as acetone and cyclohexanone, give similar colors which intensify on standing and may be due to polymerization of the ketone rather than to the formation of a complex with the hexafluoride. Chlorinated solvents and hydrocarbons containing no functional groups give no colors. Alcohol also gives no color, but it is to be expected that alcoholysis of the hexafluoride could interfere with complex formation.

Because of the intense color given by benzene, a quantitative study was made of this solvent. At concentrations above 0.04 molar the color appeared to remain stable for several weeks. Solutions were made up at three concentrations of tungsten hexafluoride, 0.048, 0.118 and 0.121 molar, and the optical densities of these solutions were measured at 520, 550, 560 and 570 μ. A plot of optical density *vs.* concentration of tungsten hexafluoride gave straight lines, indicating that the colored material follows Beer's law, and that the concentration of the colored complex is directly proportional to the tungsten hexafluoride concentration. By absorption measurements carried out on four solutions of tungsten hexafluoride and benzene in carbon tetrachloride, results were obtained which led to the conclusion that the concentration of the colored complex also varies directly as the benzene concentration, from which fact it is concluded that the complex contains one molecule of benzene per molecule of the hexafluoride, $WF_6 \cdot C_6H_6$.

It has been noted previously by others,[1] as well

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[1] See, for example, Fischer, *Z. anorg. Chem.*, **81**, 170 (1930); Kalischer, "Zur Kenntnis der Halogenide des höherwertigen Wolframs und Molybdäns," Berlin, 1902; Roscoe, *Ann.* **162**, 351 (1872).

as by ourselves, that colored solutions are also formed by tungsten hexachloride in various solvents; but we feel that the two cases are not comparable, for the following reasons. (1) Tungsten hexachloride itself has a blood-red color, so that solutions in various solvents showing a red, brown, or yellow color are reasonably to be expected, whereas tungsten hexafluoride itself is colorless. (2) The red solution of the hexafluoride in benzene freezes to a colorless crystalline solid, which on warming regains its color. (3) If the hexafluoride were reduced by solvent to lower valences of tungsten, the solution could not be expected to follow Beer's law, as was found to be the case. Furthermore, the colored solution of the hexafluoride in benzene remained unaltered for weeks, indicating lack of reaction, whereas the hexachloride solutions change gradually, owing to reduction of the tungsten.

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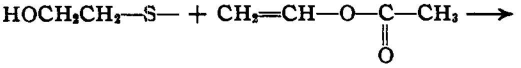
Thiodiglycol Monoacetate by the Photochemical Addition of Mercaptoethanol to Vinyl Acetate

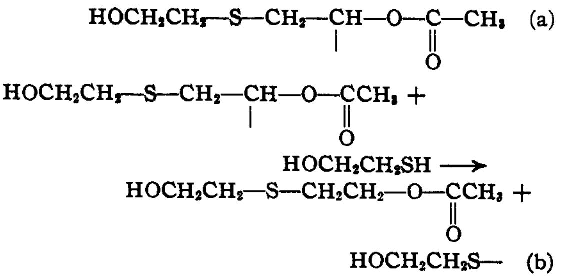
BY WALTER H. C. RUEGGEBERG, JACOB CHERNACK, IRA M. ROSE AND E. EMMET REID

The photochemical addition of mercaptans to olefins has been studied in this Laboratory[1] for several years. Recently, the photoaddition of ethanolmercaptan to vinyl chloride yielding 2-chloroethyl-2-hydroxyethyl sulfide (semi-mustard) was reported by Fuson and Ziegler[2] and from this Laboratory.[3] Inasmuch as the monoacetate of thiodiglycol has not been reported previously in the literature to the best of our knowledge, it appeared worthwhile to synthesize this half-ester through the photochemical addition of ethanolmercaptan to vinyl acetate.

It was soon learned, however, that the reaction rate depended strongly upon the purity of vinyl acetate used. Thus, for example, when freshly distilled vinyl acetate was mixed with mercaptoethanol, the mixture warmed up immediately. Titration of the residual mercaptan with iodine in methanol solution showed that 80% of the mercaptan had reacted after the first hour. On the other hand, if stabilized vinyl acetate (Eastman Kodak Co., practical grade) is employed in the process, no reaction is observed until the mixture is irradiated from an S-4, 100 watt mercury vapor lamp (General Electric Co.) in the presence of 1% of diphenyl disulfide, as catalyst.



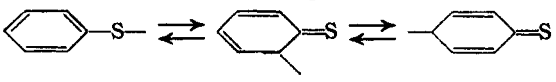
$$\mathrm{HOCH_2CH_2{-}S{-}} + \mathrm{CH_2{=}CH{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_3} \longrightarrow$$



$$\mathrm{HOCH_2CH_2{-}S{-}CH_2{-}\underset{|}{C}H{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_3}\qquad (a)$$

$$\mathrm{HOCH_2CH_2{-}S{-}CH_2{-}\underset{|}{C}H{-}O{-}\underset{\underset{O}{\|}}{C}CH_3} + \mathrm{HOCH_2CH_2SH} \longrightarrow \mathrm{HOCH_2CH_2{-}S{-}CH_2CH_2{-}O{-}\underset{\underset{O}{\|}}{C}CH_3} + \mathrm{HOCH_2CH_2S{-}}\qquad (b)$$

Although disulfides such as diamyl disulfide are known to accelerate the photoaddition of mercaptoethanol to vinyl chloride,[3] it has been shown that diphenyl disulfide is a catalyst superior to aliphatic disulfides in this type of reaction.[1] Two reasons for this behavior may be cited. First, diphenyl disulfide absorbs light more strongly than dialkyl disulfides in the visible and near ultraviolet regions of the spectrum,[1] indicating that free radicals are more easily obtained; secondly, the stabilizing influence of resonance on the thiophenyl radicals should prolong their lives thus increasing reaction probability. The three resonance forms of the thiophenyl radicals may be represented by the following equilibria



In the disulfide-free reaction, the primary dissociation is that of the splitting of the S—H bond

$$\mathrm{HOCH_2CH_2SH} + h\nu \longrightarrow \mathrm{HOCH_2CH_2{-}S{-}} + \mathrm{H{-}}$$

This reaction is then followed by a chain mechanism given by equations (a) and (b), above.

Thiodiglycol monoacetate, so prepared, is a water white liquid resembling thiodiglycol itself in odor and having the physical properties listed in Table I. It is soluble in water, benzene, carbon tetrachloride, chloroform, ethyl ether and acetone but insoluble in hexane or cyclohexane.

TABLE I

SOME PHYSICAL PROPERTIES OF THIODIGLYCOL MONOACETATE[a]

Temp., °C.	Density, g./ml.	Refractive index n_{T_D}	Molar refractivity[b] found	Viscosity, centipoises
9.5	1.1671	....	...	26.96
10	1.1666	1.4916	40.81	...
20	1.1576	1.4879	40.87	...
25	1.1531	....	...	12.43
30	1.1485	1.4841	40.92	...
35.8	1.1433	....	...	8.22
		Mean	40.87	

[a] Surface tension at 28.9°, 41.2 dynes/cm. (du Noüy method). [b] The calculated value of the molecular refractivity is 40.78.

Experimental

Photosynthesis in the Absence of Catalysts.—Mercaptoethanol, 33.2 g., obtained from the Carbide and Carbon Chemicals Corporation was added slowly to 92.4 g. of freshly distilled, unstabilized vinyl acetate, originally obtained from Eastman Kodak Company. Immediately upon mixing, an exothermic reaction ensued. After

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[1] Rueggeberg, *et al.*, reports on file at the Army Chemical Center; not currently available in the published literature.

[2] Fuson and Ziegler, *J. Org. Chem.*, **11**, 510 (1946).

[3] Rueggeberg, Cook and Reid, *ibid.*, **13**, 110 (1948).