Compound	G. of solute per 100 g. of solvent
Trinitro-methylphenylnitramine (tetryl)	14
Trinitro-resorcinol	13
Hexamethylene-triperoxide-diamine, less than	0.9
Normal lead trinitro-resorcinolate, less than	.1
Cyanuric triazide, less than	.9

It was noted that when trinitrotoluene was dissolved in warm glycol diacetate and allowed to cool slowly to air temperature, extremely large and nearly white crystals were obtained, while the quick cooling of such a solution yielded small crystals. This is important when the control of the crystal size of explosive compounds is desired.

Summary

The most important physical properties of glycol diacetate have been studied and found to be such that its application as a solvent in the purification and crystallization of explosives may prove of value. It is neutral, stable, has a high boiling point and solvent power, is practically non-volatile under ordinary conditions and will permit control of the crystal size of a solute.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE B. F. GOODRICH COMPANY]

RUBBER DI(HYDROXYPHENYL) AND ITS DIMETHYL ETHER[1]

BY HARRY L. FISHER, HAROLD GRAY AND EUGENE M. MCCOLM

RECEIVED OCTOBER 19, 1925 PUBLISHED MAY 5, 1926

Twenty-five years ago C. O. Weber[2] showed that rubber "tetrabromide" and melted phenol react with the evolution of hydrogen bromide and the formation of a compound, $C_{34}H_{36}O_4$, in accordance with the following equation: $C_{10}H_{16}Br_4 + 4C_6H_5OH = C_{10}H_{16}(O.C_6H_5)_4 + 4HBr$. He considered it an ether, as indicated, and named it "tetroxyphenyl-polyprene." Other phenols reacted similarly, but thiophenol gave a different reaction, although hydrogen bromide was evolved, and phenol ethers like anisole did not react at all. The phenol product was found to form dark brown solutions in alcohol, acetone, ether, ethyl acetate and aqueous alkalies, and to be insoluble in benzene, chloroform, carbon disulfide, turpentine, and petroleum ether. Since the reaction was different with thiophenol and since there was no reaction with anisole, Weber concluded that "this is almost conclusive evidence that it is the hydroxyl hydrogen of the phenol which forms the point of attack in the reaction in question, and this fact is at the same time the reason why, in the above formula, the oxygen appears

---

[1] Presented in part under the title "The Tetra-hydroxyphenyl Derivative of Rubber and Its Tetra-methyl Ether," at the 62nd meeting of the American Chemical Society, New York, Sept. 6–10, 1921.

[2] Weber, *Ber.*, **33**, 791 (1900).

as ether oxygen and not as hydroxyl oxygen." Also, "the solubility of this substance in alkali is apparently in contradistinction with this constitution, but at the same time this circumstance is hardly sufficient to vitiate the significance of the reaction behavior described." Gottlob[3] states that the formula "should possibly be accepted somewhat with caution."

We have studied this reaction and verified Weber's work, but we believe that he was in error when he assigned the ether formula to the phenol reaction product. The substance is readily soluble in cold aqueous alkalies and, therefore, it must contain phenolic hydroxyl groups. Furthermore, we have found that it is very easily methylated with dimethyl sulfate in the presence of alkali at the ordinary temperature, and that this methylated product is soluble in benzene and insoluble in aqueous alkalies, these solubilities being just the opposite of those of the "tetroxyphenyl" compound. The position of the linkage between the rubber carbon and the phenyl carbon in each case is still in doubt, although it is presumably *para* to the methoxyl group. It is expected that this point will be cleared up later.

The name of the new compound must be based upon the fundamental grouping involved since the molecular weight of the substance cannot be determined. The phenol compound must also be renamed and the same basis used in each case. Recent work has shown that the fundamental grouping in rubber is[4] C_5H_8, and accordingly, the three compounds used and discussed should be represented and named as follows: $(C_5H_8Br_2)_x$, rubber dibromide; $(C_5H_8(C_6H_4OH)_2)_x$, rubber di(hydroxyphenyl); and $(C_5H_8(C_6H_4OCH_3)_2)_x$, rubber di(methoxyphenyl).

Weber's yields of the dihydroxyphenyl compound were all approximately 50% of those calculated. Our yields were 65–77% and remained the same even when anhydrous aluminum chloride or zinc chloride was used. With anhydrous ferric chloride, however, practically quantitative yields were obtained. The reaction may be like the Friedel and Crafts reaction.

Experimental Part

Rubber Dibromide.—This was prepared according to the general directions given by Weber.[5]

Anal. Calcd. for $C_5H_8Br_2$: Br, 70.13. Found: 70.12, 70.41.

Rubber Di(hydroxyphenyl).—The preparation of this compound is also described by Weber.[6] It is not necessary to use his ether extraction and the yield is almost quantitative if ferric chloride is used, as follows.

---

[3] Gottlob, "Technologie der Kautschukwaren," Vieweg, Braunschweig, **1915**, p. 5.

[4] Pummerer and Burkard, *Ber.*, **55**, 3458 (1922). Pummerer and Koch, *Ann.*, **438**, 294 (1924). Compare Fisher, "Recent Important Investigations in the Chemistry of Rubber, and Substantiation of the C_5H_8 Ratio," *Ind. Eng. Chem.*, **15**, 860 (1923).

[5] Weber, "The Chemistry of India Rubber," Griffin, London, **1902**, p. 32.

[6] Ref. 5, p. 33.

Five g. of rubber bromide powder is added to 50 g. of melted phenol containing 0.5 g. of anhydrous ferric chloride, in a 250cc. beaker or Erlenmeyer flask, on the steam-bath and the mixture is stirred frequently during the initial reaction. Within a few minutes the evolution of hydrogen bromide begins and continues for some time, depending upon the heating and stirring. The liquid is very dark[7] on account of the presence of the ferric chloride. The rubber bromide slowly dissolves and the solution becomes very limpid. After the first hour the vessel is covered with a cover glass to avoid loss of phenol, and the heating continued during occasional stirring for several hours. The warm, purplish liquid is then slowly poured into 2 liters[8] of water containing 30 g. of sodium hydroxide, thoroughly stirred, and then filtered to remove the ferric hydroxide. The clear brownish-black filtrate is then stirred mechanically and 100 cc. of 50% acetic acid carefully added to precipitate the product. Light brown flocks separate and slowly settle. As much of the clear supernatant liquid as possible is decanted or sucked off and the remainder filtered off with suction. The moist brown cake or mush is removed and thoroughly worked up with another 2 liters of water in order to remove soluble salts and phenol, and filtered off again. The filtrations usually are tedious and take several hours. The product is then allowed to dry. It contains a small amount of ash. It is further purified by being dissolved in acetone, the acetone solution is then filtered, the filter paper washed with acetone, and the deeply colored filtrate slowly poured into 2 to 3 liters of water which is stirred mechanically. If a suspension is formed dil. sulfuric acid is added in small amounts during good stirring, until flocculation takes place. The brown flocks are filtered off as described above in a 15cm. Büchner funnel, using a hardened filter paper, and the product dried in a desiccator over solid potassium hydroxide; yield, 5.30 g., or 95% of the calculated amount and 106% on the basis of the bromide used.

The solubilities of the substance are given above. It is amorphous and like other rubber derivatives it gives no definite melting point, shrinking at 190°, melting slowly around 195° and more or less completely at 200–205°. The melting varies, depending possibly upon the physical condition. A small amount of phenol adhering to the product may lower the melting temperature as much as 100°.

Anal. Subs., 0.1661, 0.2032: CO_2, 0.4842, 0.5946; H_2O, 0.1113, 0.1344. Calcd. for $C_{17}H_{18}O_2$: C, 80.27; H, 7.14. Found: C, 79.50, 79.81; H, 7.50, 7.40.

Rubber Di(methoxyphenyl) is prepared as follows.

Two g. of rubber di(hydroxyphenyl) is dissolved in 35 cc. of *N* sodium hydroxide solution in a small flask, and 2 cc. of dimethyl sulfate added. The flask is stoppered and shaken vigorously. The reaction soon begins, the mixture sets to a yellow-brown mass which then "breaks," and the liquid becomes *colorless*[9] and filled with yellow-brown flocks. A slight pressure develops in the flask, due probably to a rise of a few degrees in temperature. More alkali is added, if necessary, to keep the liquid alkaline. After an hour or two it is diluted with an equal volume of water and filtered with suction. The moist residue is worked up with water and filtered again. It is dried in a desiccator, dissolved in about 75 cc. of benzene, filtered, the benzene evaporated on the steam-bath and the product dried at 85–90°; yield, 85–95%. It is a yellow-brown, amorphous, ash-free powder, giving dark brown solutions in acetone, ethyl acetate, benzene, chloroform, carbon disulfide and turpentine. It is somewhat soluble in ether and glacial

---

[7] When no ferric chloride is used the particles turn gray as soon as they are "wet" with the phenol and in a few minutes they become deep maroon and the entire mixture takes on the same color as the reaction progresses.

[8] When a small amount of water is used, such as 500 cc., the precipitate comes down like molasses and contains a considerable amount of phenol.

[9] Indicating complete absence of the rubber di(hydroxyphenyl).

acetic acid and insoluble in methyl alcohol, ethyl alcohol, ligroin and aqueous alkalies. It gave no depression of the freezing point in benzene. The substance slowly melts at 151–156° (corr.) without decomposition.

Anal. Subs., 0.2021, 0.2209, 0.1939: CO_2, 0.6028, 0.6591, 0.5743; H_2O, 0.1392, 0.1496, 0.1320. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.86. Found: C, 81.32, 81.37, 80.78; H, 7.70, 7.58, 7.52.

Some other work bearing on the question discussed in this paper is in progress and will be given later.

We extend our thanks to Dr. W. C. Geer, Vice-President of the B. F. Goodrich Company, for his interest in this work and for permission to publish this paper.

Summary

1. Weber's "tetroxyphenyl-polyprene," formed by the action of phenol on rubber "tetrabromide," is shown not to have the ether structure, $R(OC_6H_5)_2$, but the hydroxy structure, $R(C_6H_4OH)_2$. The name is changed to rubber di(hydroxyphenyl).

2. The rubber di(hydroxyphenyl) has been methylated, forming rubber di(methoxyphenyl) and its properties have been studied. The formation of this compound verifies the new structure assigned to the first compound.

AKRON, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 509]

DOES CHROMIUM COMBINE WITH THE BASIC OR ACIDIC GROUPS OF HIDE PROTEIN?[1]

BY ARTHUR W. THOMAS AND MARGARET W. KELLY

RECEIVED NOVEMBER 5, 1925 PUBLISHED MAY 5, 1926

The chemical mechanism of the union between hide protein and chromium in the production of chrome leather is in doubt. Wilson[2] has suggested the possibility of the interaction of the carboxyl radicals of the protein with the chromium cations. Since chrome tanning occurs in solutions which are decidedly on the acid side of the iso-electric point of collagen, the amount of ionized carboxyl groups would be exceedingly slight while the degree of ionized amino groups would be correspondingly great. This would point to the possibility of chrome fixation involving the nitrogen-containing radicals of the protein. It must be conceded, however,

---

[1] From data reported to the Division of Leather Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wisconsin, September 10–14, 1923, and at the 67th Meeting, Washington, D. C., April 21–26, 1924, under the titles "Combination of Chrome with Vegetable-Tanned Leathers" and "Chrome Tanning of Quinone-Collagen."

[2] Wilson, *J. Am. Leather Chem. Assoc.*, **12**, 108 (1917).