

Selenium Dioxide as an Oxidant

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The investigations of Riley, Morley, and Friend² established the fact that selenium dioxide oxidizes a number of types of organic compounds and at times exhibits marked specificity, yielding aldehydes and ketones which are difficult to prepare by ordinary methods. Later Riley and co-workers extended the study to include olefines,³ alcohols, esters,⁴ dibenzyl, stilbene, and phenyl-substituted aliphatic esters.⁵

The reactions of selenium dioxide with compounds containing the group $-\text{CH}=\text{CH}-\text{CH}_2-$ were investigated by Schwenk and Borgwardt;⁶ with ethyl acetoacetate by Müller;⁷ with poly-nitrotoluenes by Fisher;⁸ and with several substances containing double bonds by Postowsky and Lugowkin.⁹

The purpose of the work described in this paper has been to extend the use of selenium dioxide as an oxidizing agent and also to elaborate and verify some of the previous work in this field.

Experimental

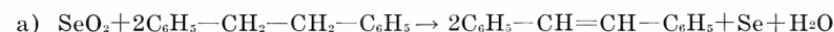
Reaction of Propionic Acid with Selenium Dioxide. Propionic acid when boiled with selenium dioxide yields pyruvic acid and amorphous black selenium.

Mixture of 10 g. propionic acid and 2 g. selenium dioxide were maintained at boiling temperature under reflux for periods of 4 to 24 hours and subjected to distillation under reduced pressure, and the pyruvic acid was determined in aliquot portions of the distillates by the method of Wieland,¹⁰ as described by Wendel,¹¹ with results as follows:

Heating Period, Hours.....	4	6	8	10	24
Pyruvic acid, Milligrams.....	88.5	160.9	94.9	69.97	57.0

The decrease in yields for heating periods beyond 6 hrs., the indicated optimum, could be due either to decomposition of the acid or to its polymerization. Since tests for carbon dioxide were negative, it was probably the latter.

Reaction of Dibenzyl with Selenium Dioxide. Dibenzyl when heated with selenium dioxide at 300°C. yields stilbene and benzil.



Mixtures of varied molar quantities of the reactants, contained in sealed Pyrex tubes, were placed in an electrically heated tube furnace and

¹Compiled from a thesis presented in partial fulfillment of the requirements for the degree Ph.D.

²H. L. Riley, J. F. Morley, and N. Friend, 1932. *Jour. Chem. Soc.* 1932:1875.

³H. L. Riley and N. Friend, 1932. *Jour. Chem. Soc.* 1932:2342

⁴S. Astin, A. Neuman, and H. L. Riley, 1933. *Jour. Chem. Soc.* 1933:391. Astin and Riley, 1934. *Jour. Chem. Soc.* 1934:844.

⁵S. Astin, L. deV. Moules, and H. L. Riley, 1935. *Jour. Chem. Soc.* 1935:901.

⁶E. Schwenk and E. Borgwardt, 1932. *Ber.* 65:1601.

⁷R. Müller, 1933. *Ber.* 66:1668.

⁸C. H. Fisher, 1934. *Jour. Amer. Chem. Soc.* 56:2056.

⁹J. J. Postowsky and B. P. Lugowkin, 1935. *Ber.* 68:852.

¹⁰H. Wieland, 1924. *Ann. d. Chem.* 436:229.

¹¹W. B. Wendel, 1932. *Jour. Biol. Chem.* 94:719.

maintained at the reaction temperature for periods of 1.5 to 18 hours. The constituents of the reaction mixture, stilbene, benzil and dibenzyl, were separated and quantitatively determined by an especially devised method,¹² as follows: The reaction mixture was dissolved in methanol and the volume brought to 500 ml. To 100 ml. of this solution were added 5 g. of hydroxylamine hydrochloride and 5 drops of concentrated hydrochloric acid. The mixture, after heating for one hour on a water bath to complete the formation of benzil oxime,¹³ was distilled with steam, until 2000 ml. of distillate were collected, to carry over the stilbene and dibenzyl. The combined weight of these substances was obtained by ether extractions of the distillate, evaporation of the ether and weighing the dry residue. The weight of the benzil was obtained by difference.

Another aliquot portion, 100 ml., of the methanol solution was evaporated to dryness and the residue dissolved in carbon disulphide. To this solution was added a solution of bromine in carbon disulphide, and after 24 hours the insoluble di-brom stilbene was collected on a filter, washed with absolute alcohol, dried, and weighed and the weight of stilbene calculated.

The yields of benzil and stilbene, expressed as percentages of the selenium dioxide and of the dibenzyl used, are given in Table I.

TABLE I.

Hours at 300°C.	% Used for Diphenyl	Benzil SeO ₂	% Used for Diphenyl	Stilbene SeO ₂	Selenium Dioxide % Used
I. SeO ₂ one mole; dibenzyl two moles.					
1.5.....	6.4	22.1	0.0	0.0	22.1
3.0.....	10.5	36.6	13.5	18.9	55.5
6.0.....	14.8	51.6	16.7	23.4	75.0
12.0.....	21.9	76.9	15.3	21.7	98.6
18.0.....	23.0	80.0	13.9	19.5	99.5
II. SeO ₂ two moles; Dibenzyl one mole.					
3.0.....	50.1	43.4	9.5	3.3	46.7
12.0.....	95.6	89.8	4.4	1.6	91.4
III. SeO ₂ one mole; Dibenzyl one mole.					
6.0.....	32.7	55.7	15.3	10.5	56.2
12.0.....	46.1	79.9	21.7	14.5	94.4

From the data in Section I of this table, it is evident that the reaction proceeds more rapidly at first because of greater concentration of reactants. In the period 6 to 12 hrs. the amount of benzil formed corresponds to 25.3% of the selenium used, while in the period 12 to 18 hrs. only 3.1% is formed. The maximum amount of stilbene is attained with the heating period of 6 hrs. The ratio of the starting materials

¹²The error of this method of analysis was found to be less than 0.5% when applied to a mixture of known quantities of the three substances.

¹³H. Grossman and J. Mannheim, 1916. Ber. 50:708.

does not remain constant during the course of the experiment. As the selenium dioxide is depleted, the reaction slows, and a point is finally reached when the dioxide reacts more easily and rapidly with stilbene to produce benzil than with dibenzyl to form the intermediate product stilbene.

The ratio of the reactants in Section II is theoretical for the production of benzil, and the quantities of benzil resulting are larger but not in direct proportion to the length of the heating period.

Reacting equimolecular quantities (Section III), as expected, resulted in a greater yield of benzil than in the first group of experiments. However, the maximum stilbene formation was not attained at 6 hrs.

Reaction of Toluene with Selenium Dioxide. When 15 ml. of toluene was heated with 2.9120 g. selenium dioxide in sealed tube for 12 hrs. at 300° C., 0.5846 g. of benzoic acid was produced. This amount of benzoic acid is 27.4% of the theoretical for the selenium dioxide employed. Reduction of the excess of toluene in the mixture gave decreased quantities of the acid and increased amounts of tar. Theoretical quantities of the reactants, under the above conditions, yielded tar containing no trace of benzoic acid.

Phenols and Polyhydric Alcohols with Selenium Dioxide. Investigation of the effect of selenium dioxide on phenol, o- and p-amino phenol, and o- and p-cresol revealed each of these substances to be susceptible to vigorous attack by selenium dioxide at relatively low temperatures, yielding insoluble tarry resins in which expected or possible oxidation products could not be detected. Efforts to reduce the rapidity and vigor of the oxidation did not lead to more satisfactory results.

Anisole and o-, m-, and p-methyl anisole, when reacted with selenium dioxide at water bath temperatures, suffered loss of the methoxy group and yielded resins comparable to those produced from phenol and the cresols.

Ethylene glycol, glycerol, and an aqueous solution of gluconic acid, when heated at their respective boiling points with selenium dioxide, did not yield aldehyde, ketone, or other evidences of oxidation.

Reaction of Iso-eugenol with Selenium Dioxide. The report of Riley, Morley and Friend,¹⁴ that buchu camphor is formed when menthone is oxidized with selenium dioxide, suggested the possibility of producing vanillin by the oxidation of iso-eugenol with selenium dioxide.

Mixtures of 2 g. acet-iso-eugenol in 25 ml. alcohol, and 1 g. selenium dioxide remained inactive at room temperature, but, at 50°C., selenium mixed with a carbon was rapidly precipitated. Traces of vanillin were recognized by means of the phloroglucinol color reaction applied to the hydrolyzed acetylated reaction product. The discrepancy between the amount of vanillin and the amount of dioxide reduced was thought due to the pronounced susceptibility of the methoxy- group to oxidation at low temperatures by selenium dioxide.

Reaction of Aniline with SeO₂ and the Inhibiting Action of H₂SO₄. Aniline when vigorously stirred with an alcoholic or aqueous solution of selenium dioxide at room temperature was not oxidized; however, at

¹⁴loc. cit.

30°C., aniline black was produced. An aqueous solution of aniline sulphate was not attacked by selenium dioxide at room temperature but yielded aniline black at 40°C. When 5% sulfuric acid was used as a solvent, the aniline sulfate was not attacked until a temperature of 50°C. was attained. The temperature at which the aniline is attacked by selenium dioxide was found to rise 10°C. for each increase of 5% in the concentration of sulfuric acid in the solvent up to 20%.

Summary

The investigation of the action of selenium dioxide on dibenzyl has been extended to include improved experimental technique, method of analysis, and larger yields of oxidation products.

Pyruvic acid is produced in small yield from the reaction of selenium dioxide with propionic acid.

Selenium dioxide attacks the methoxy- group on a benzene ring and burns it off at low temperature but does not attack either the primary or secondary alcohol groups of glycol or glycerol at their respective boiling temperatures.

Sulfuric acid exercises an initial inhibitory effect in the reaction of selenium dioxide on aniline.

Toluene is oxidized to benzoic acid at 300°C. by selenium dioxide.