335. *Selenium Dioxide, a New Oxidising Agent. Part II. Its Reaction with some Unsaturated Hydrocarbons.*

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The study of the specific oxidising action of selenium dioxide has now been extended to ethylene, propylene, acetylene, certain higher olefines, and ethane.

Reaction with Ethylene.—SeO_2 (40 g.) was placed in a flask, which was connected, on the one hand, through a drying train of KOH and $CaCl_2$, to a 10-l. gas-holder, and, on the other, to a receiver surrounded by a freezing mixture. The apparatus was swept out with dry C_2H_4, and the gas-holder filled. At room temp., the SeO_2 soon developed a faint pinkish tint, indicating reduction. At 45—55° the C_2H_4 was absorbed with appreciable velocity, indicated by a manometer attached to the side tube of the receiver: the reaction was sufficiently exothermic to proceed without further heating, and its velocity (as roughly judged by the rate of passage of the C_2H_4 through the bubbler necessary to keep the pressure constant) became a max. at 120—150°. The temp. finally rose to approx. 200°. When the loss of heat through radiation is not too great, once the reduction of SeO_2 has started, it will spread through the whole mass without further heating. The reduction of the SeO_2 under the above conditions was far from complete, owing to the Se formed on the surface preventing further access of C_2H_4. A contraction in vol. of approx. 1 l. occurred.

Apart from a little H_2O, there was no condensate in the receiver; the walls of the flask were, however, covered with a sticky colourless liquid, and when it was washed out with H_2O or MeOH the extract was found to contain unreduced SeO_2 and glyoxal (phenylhydrazone, m. p. 173°).

The glyoxal produced was in the trimeric form (cf. Harries and Temme, *Ber.*, 1907, **40**, 165; Debus, *Phil. Mag.*, 1857, **13**, 39, 66). Monomeric glyoxal was prepared by a slight modification of the above method: SeO_2 was ground with an equal bulk of P_2O_5, and the mixture rapidly introduced into the flask. Replacement of the air by C_2H_4 and gentle warming caused the white mixture to darken, C_2H_4 was absorbed, and the flask gradually filled with the yellowish-green vapour of monomeric glyoxal. Yellowish-white feathery crystals were deposited on the walls of the receiver, and on removal of the freezing mixture these gave the yellowish-green vapour, which disappeared in an hour, a white mist, probably one of the polymerides of glyoxal, having been deposited on the walls of the flask. The yield of glyoxal was small, for considerable charring occurred. Monomeric glyoxal is, however, of particular interest, being the simplest coloured substance possessing a conjugated system of valencies, and the above expt. makes a convenient lecture demonstration.

It was shown by the following expt. that this reaction can be represented, almost completely, by the equation $3SeO_2 + 2C_2H_4 = 2(CHO)_2 + 3Se + 2H_2O$.

Finely powdered SeO_2 (5 g.) was heated in an atmosphere of C_2H_4 in a hard-glass reaction tube, the temp. being kept at 110—120°: the absorption of C_2H_4 ceased after about 200 c.c. (less than 1/3 theoretical) had reacted. The temp. was gradually raised to 220—240°, whereupon the unreduced SeO_2 sublimed through the molten Se and then reacted with the C_2H_4 (cf. expts. with $CH_3{\cdot}CHO$; Part I, this vol., p. 1875). All the glyoxal remained in the reaction tube, which was extracted with H_2O and the diphenylhydrazone pptd. and weighed in the usual manner. The contraction in vol. was 523 c.c. (78·4% of the theoretical) and a yield of 82·4% of glyoxal was obtained. Some CO_2 was also formed, and this probably accounted for the remaining 17·6%. The heating at the higher temp. must be carried out carefully, as there is a great tendency for the C_2H_4 to burn in the SeO_2 vapour, with a characteristic moonlight-like flame, at temps. a little higher than the above. This phenomenon will be described more fully later.

The glyoxal, thus prep., can be isolated conveniently by the addition of a slight excess of satd. $NaHSO_3$ aq. to the aq. extract: the bisulphite compound of glyoxal, which can be purified by recrystn. from H_2O, is slowly pptd. This prep. must be carried out immediately, for within 1—2 hrs. the glyoxal polymerises completely to the non-reactive form.

ββ′-Dichlorodiethyl Selenide Dichloride.—C_2H_4 was bubbled through fuming HCl aq., and the mixture obtained led into a satd. solution of SeO_2 in the same medium. Crystals of ββ′-dichlorodiethyl selenide dichloride soon separated, m. p. 122° after recrystn. from $CHCl_3$ (cf. Bausor, Gibson, and Pope, J., 1920, **117**, 1453; Frick, *J. Amer. Chem. Soc.*, 1923, **45**, 1795; Heath and Semon, *J. Ind. Eng. Chem.*, 1920, **12**, 1100). On resaturating the filtrate with SeO_2 and repeating the process, more of the dichloride was obtained. From the equation $2C_2H_4 + 4HCl + SeO_2 = (CH_2Cl{\cdot}CH_2)_2SeCl_2 + 2H_2O$ it is obvious that the reaction liquid will become gradually more dil. Concn. of this can be effected in vac. at room temp. without decomp. occurring.

$\beta\beta'$-Dibromodiethyl selenide dibromide was even more readily obtained by employing HBr aq. instead of HCl; m. p. 118° (cf. Bell and Gibson, J., 1925, **127**, 1877).

$\beta\beta'$-Dichlorodipropyl selenide dichloride, m. p. 81°, was also prep. similarly, C_3H_6 being used instead of C_2H_4 (cf. Frick, *loc. cit.*; Boord and Cope, *J. Amer. Chem. Soc.*, 1922, **44**, 395).

It is probable that the formation of the above alkyl selenide halides is brought about by the intermediate formation of $SeO_2,2HCl$ or $SeOCl_2,H_2O$, etc., which reacts with the C_2H_4 (see Muehlberger and Lenher, *J. Amer. Chem. Soc.*, 1925, **47**, 1842; Parker and Robinson, J., 1931, 1314).

Reaction with Propylene.—C_3H_6, prep. by the action of H_3PO_4 on $Pr^{\alpha}OH$, which gave a product 88% pure (as indicated by Br absorption), was passed over 5 g. of SeO_2 exactly as described for C_2H_4. Although some yellowish-green vapour was observed during the heating, no appreciable vol. change occurred. Methylglyoxal was identified by means of its diphenylhydrazone, m. p. 145°, and its disemicarbazone, m. p. 254°, as a product of the reaction in 19% yield (on SeO_2 reduced), determined by weighing the disemicarbazone. CO (145 c.c.) was also formed, this accounting for the small vol. change. It is probable that the smaller yield of methylglyoxal, compared to that of glyoxal, is due to the instability of the former, in presence of SeO_2 at elevated temps. (Part I).

Reaction with Acetylene.—Reduction of SeO_2 by means of C_2H_2 commenced at a low temp. (40—50°), but did not proceed so readily as with C_2H_4, the contraction in vol. of the gas being only small. A considerable amount of CO_2 was formed, and the yield of glyoxal was only 6%. C_2H_2 burned in the SeO_2 vapour at the higher temp. in a similar manner to C_2H_4.

Reaction with Ethane.—SeO_2 was not readily reduced by C_2H_6 even at high temps. Of 5 g., heated at 350—400° for about 2 hrs., only 1·5 g. were reduced; a little glyoxal, AcOH, and CO_2 were produced. C_2H_6 also inflames in SeO_2 vapour, but not so readily as C_2H_2 or C_2H_4.

Reaction with Higher Olefins.—SeO_2 is not reduced by β-amylene, trimethylethylene, styrene, crotonaldehyde, and cinnamaldehyde, at their respective b. p.'s, but reduction occurs in sealed vessels at considerably higher temps. The products are, however, complex, and it is hoped to study these reactions later.

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