

CARBON SUBOXIDE

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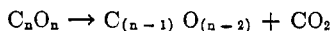
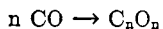
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Oxides of carbon other than carbon dioxide and carbon monoxide have received very little mention in American chemical literature. This review of carbon suboxide, C_3O_2 , and its properties will attempt to bring up to date the information available on this interesting substance, which is now being investigated in the chemical laboratory of the University of Minnesota.

HISTORICAL

Brodie (1) in 1873 submitted carbon monoxide to the action of the electric current and found that the volume of gas contracted with the formation of carbon dioxide and of a transparent red-brown film on the walls of the tube. This film dissolved completely in water to give a strongly colored solution with an intensely acid reaction. Analysis showed the substance to be an oxide of carbon, but samples from different experiments did not have the same composition. Brodie reported two oxides, C_4O_3 and C_5O_4 . He suggested that a series of "oxycarbons" existed which would be analogous to the series of hydrocarbons of the acetylene series. On this basis C_4O_3 was analogous to C_4H_6 or crotonylene, and C_5O_4 analogous to C_5H_8 or valerylene.

Berthelot (2) repeated the work of Brodie and found that this brown oxide when heated decomposed to form carbon dioxide, carbon monoxide and a new oxide $C_{16}O_6$. He believed that a series of carbon suboxides (3) were formed from the reactions:



He reported (4) the possibility of the first member of the series, C_2O .

The splitting and dehydration of esters of carbamic acid by phosphorus pentoxide was well known, such as the formation of phenyl isocyanate from the ethyl ester of carbanilic acid:

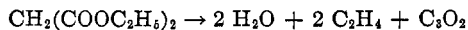


Diels and Wolf (5) tried this reaction on nitrogen-free esters in the hope of preparing a new class of compounds. When diethyl malonate was treated in this manner they obtained ethylene, water and a gas with a highly pungent odor, which on analysis was found to have the formula C_3O_2 . A vapor density determination confirmed this as the molecular formula. This substance they named carbon suboxide.

Berthelot (4) objected to the use of the name "carbon suboxide" for this compound on the basis that the name "suboxide of carbon" represented a whole family of compounds and no one member in particular. Micheal (11) also stated that the name "carbon suboxide" was not fortunately chosen since it did not express the composition of the compound and was also suitable for the compound C_2O . He suggested the name "tricarbodioxide." Otto Diels (12) replied that other names, as "dicarbonylmethane" or "dioxoallene," were also correct, but that they had tried to give the compound a simple name that showed that it consisted only of carbon and oxygen, as is emphasized in the names "carbon dioxide" and "carbon monoxide." From this viewpoint the name chosen seemed appropriate, and as it had already gone into the scientific literature no attempt was made to change it.

PREPARATION OF CARBON SUBOXIDE

Diels and Wolf (5) prepared the suboxide by treating diethyl malonate with a large excess of phosphorus pentoxide and heating the mixture to $300^\circ C$. The reaction took place as follows:

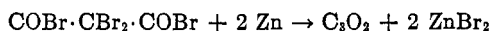


The products were drawn by a vacuum through a receiver cooled in ice to remove any ester which was carried over, and then into a

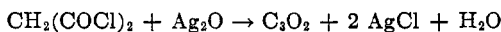
receiver cooled with liquid air where the ethylene and carbon suboxide were condensed. After the reaction was over, the latter flask was connected to a U-tube with a small bulb in the center. This was cooled with a liquid air-alcohol mixture at -60° to -70° , and the receiver which contained the mixed product was removed from the liquid air. The ethylene passed off while the carbon suboxide was condensed in the small bulb. No yield was reported by these authors.

Diels and Meyerheim (8) found that other esters of malonic acid, such as the dimethyl, dibenzyl, and diphenyl esters, yielded carbon suboxide when treated with an excess of phosphorus pentoxide. Other compounds, such as oxalacetic ester, $C_2H_5OOC \cdot CO \cdot CH_2COOC_2H_5$, and methenyltricarboxylic ester, $CH(COOC_2H_5)_3$, also gave carbon suboxide when treated with phosphorus pentoxide. Free malonic acid yielded carbon suboxide when heated with phosphorus pentoxide, but the yields were low (about 10 to 12 per cent) because of the splitting of the malonic acid into acetic acid and carbon dioxide. Stock and Stoltzenberg (18) showed that the low yield by this method was due not to the decomposition of malonic acid into acetic acid and carbon dioxide, but to the polymerization of the carbon suboxide formed. They devised a new apparatus in which they were able to increase the yield to 25 per cent. However Diels (19) considered the apparatus too elaborate for use in this preparation.

Staudinger and Klever (10) applied methods used for ketenes to the preparation of carbon suboxide. Upon the treatment of dibromomalonyl bromide in ether solution with metallic zinc the following reaction occurred:

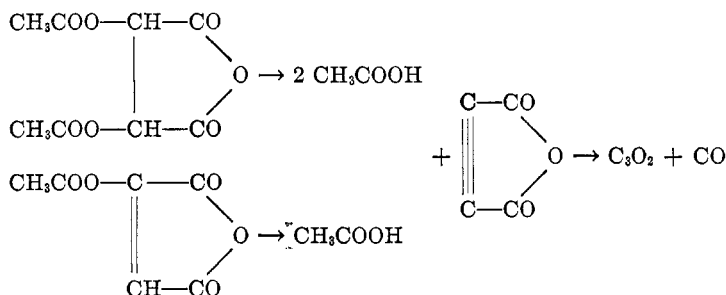


The ether was distilled off, giving an ethereal solution of carbon suboxide. Staudinger and Bereza (14), by treating malonyl chloride with various oxides and salts, such as silver oxide, lead oxide, zinc oxide, silver oxalate and silver malonate, prepared carbon suboxide in yields of from 5 to 10 per cent.

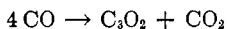


Acid chlorides were found to react with silver malonate to give carbon suboxide in yields of 1 or 2 per cent. It was also found that dibromomalonyl chloride in ether solution reacted with zinc dust, so that by dropping the solution of the acid chloride on the zinc dust at such a rate that the ether boiled vigorously, and by condensing the vapors in a cooled receiver, an ethereal solution of carbon suboxide was obtained which corresponded to an 80 per cent yield.

Ott (17) found that carbon suboxide could be prepared in good yields by the pyrogenic decomposition of diacetyltartaric anhydride or acetoxymaleic anhydride.

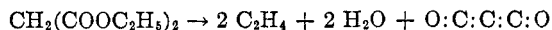


Ott believed that the course of the reaction was the splitting off of acetic acid, which he isolated to the extent of 90 per cent of the theoretical value, and the formation of the anhydride of acetylene diacid, which decomposed into carbon suboxide and carbon monoxide. The diacetyltartaric anhydride may be easily prepared from acetic anhydride and tartaric acid. Using this method Ott (21) obtained a yield of 42.5 per cent of carbon suboxide. Ott and Schmidt (22) designed an apparatus for the carrying out of this reaction in which the vapors of the diacetyltartaric anhydride are passed over a heated platinum filament and the decomposition products are then collected and separated much as in the method of Diels. Using this apparatus they were able to prepare 31.5 grams of diacetyltartaric anhydride, or a yield of 41 per cent of the theoretical amount. Ott (31) reported that carbon monoxide reacted in an ozonizer to give the suboxide.

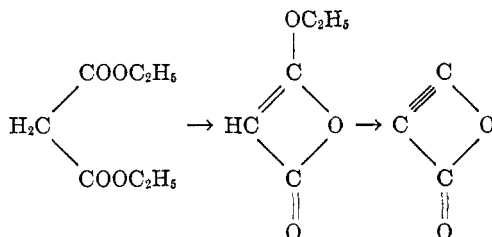


CONSTITUTION OF CARBON SUBOXIDE

The constitution of carbon suboxide has given rise to controversy. Diels and Wolf (5) considered that carbon suboxide had the constitution $O=C=C=C=O$, and gave the following equation for its formation:

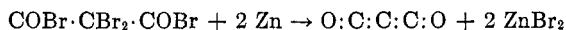


It was shown that carbon suboxide gave reactions similar to those of the ketenes, so they considered it to possess the diketene structure. Micheal (6), however, thought that it would be possible to split off ethylene and water in such a way as to leave a cyclic compound.



Thus carbon suboxide would be the lactone of β -hydroxypropionic acid. Diels attempted to show, on the basis of the boiling point (8) and the molecular refraction (9) of carbon suboxide, that the constitution which he had suggested for this compound was the correct one. His arguments were refuted by Micheal (11), but again stated by Diels and Blumberg (12).

Staudinger and Klever (10) considered carbon suboxide to be a diketene, and applied methods of preparation which had been used for the ketenes, such as



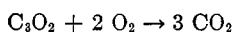
Redgrove (20) calculated the molecular heats of combustion and of formation of the compound according to the two formulas, but no data have ever been given as to these constants.

The diketene formula of Diels is the one usually accepted and written. However, the formula of Micheal has never been proven to be incorrect.

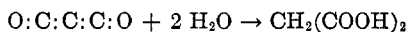
PROPERTIES OF CARBON SUBOXIDE

The physical properties of carbon suboxide are of considerable interest. It is a gas under ordinary conditions, having an unbearable odor like acrolein and mustard oil (5). In small amounts it acts as a lachrymator; in high concentrations it attacks the eyes, nose and breathing organs, giving a feeling of suffocation. The gas is easily condensed to a colorless, refractive, extremely mobile liquid having a boiling point of $+7^\circ$ at 761 mm. pressure (5). Its density at 0° compared to water at 0° is 1.11 (8). It can be solidified to large crystals which melt at -107° to -108° according to Diels and Meyerheim (8), and at -111.3° according to Stock and Stoltzenberg (18). The vapor pressure was measured by Stock and Stoltzenberg (18) over a range from -100° to $+6^\circ$, and by Edwards and Williams (26) from -62° to $+4^\circ$. The latter also calculated the heat of vaporization from their vapor pressure curve. The molecular refraction of the liquid at 0° was found to be 16.6 (9). The refraction and dispersion of the gas were studied at several temperatures (15).

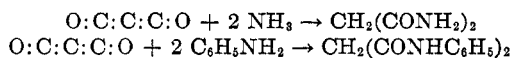
It is in its chemical reactions that carbon suboxide shows its most interesting behavior. Diels and Wolf (5) found that it burns in air to form carbon dioxide.



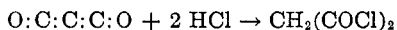
They showed that its reactions with simple substances were those that would be expected from a diketene. It reacts with cold water to form malonic acid.



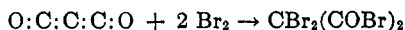
It reacts with ammonia and aniline at temperatures under 0° to form malonamide and malonanilide.



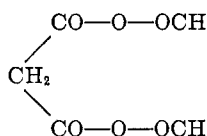
It is reported that the latter reaction may be used for the quantitative determination of carbon suboxide. It reacts with dry hydrogen chloride to form malonyl chloride.



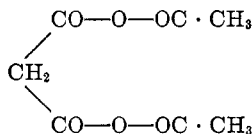
It also reacts with bromine to form dibromomalonyl bromide (10).



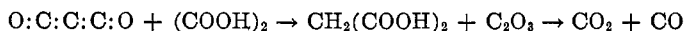
Diels and Lalin (13), using liquid sulfur dioxide at -30° to -40° as solvent, found that carbon suboxide reacted with formic acid giving crystals having the composition $(\text{C}_3\text{O}_2 + 2 \text{HCOOH})$. With water these crystals gave an equivalent amount of formic and malonic acids, so the compound may be a mixed anhydride of malonic and formic acids, having the formula



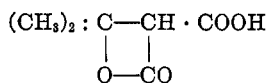
Carbon suboxide and acetic acid also reacted to give a compound having the properties of a mixed anhydride of malonic and acetic acids, whose formula would be



In a succeeding paper (23) the properties of these compounds were discussed. Carbon suboxide split water from anhydrous oxalic acid and gave the oxalic anhydride C_2O_3 , which immediately decomposed into carbon dioxide and carbon monoxide.



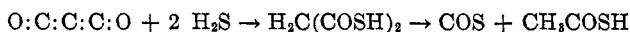
This reaction was carried out in acetone, and there also resulted the lactone of β -hydroxyisopropylmalonic acid.



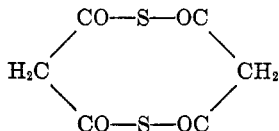
Malonic acid with carbon suboxide gave a product resembling polymerized carbon suboxide.

The reaction of carbon suboxide with hydrogen sulfide was

also studied (23). With an excess of hydrogen sulfide the following reaction took place:

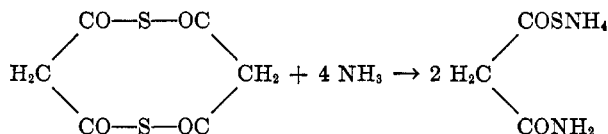


When both were in the proportion of one to one, colorless crystals were formed to which the constitution

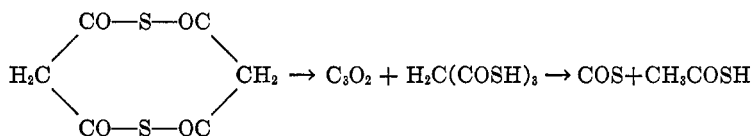


was assigned.

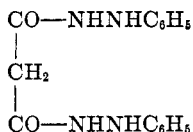
This substance reacted with ammonia according to the equation



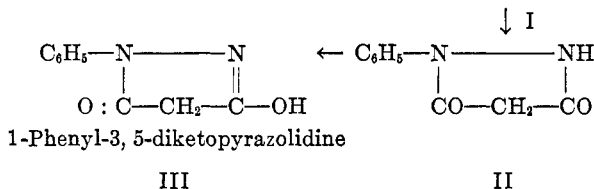
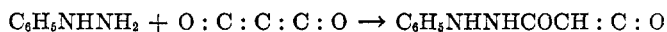
forming the ammonium salt of thiomalonamidic acid. When heated in a high vacuum the substance decomposed.



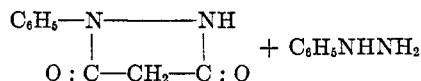
van Alphen (24) studied the action of ketenes, including carbon suboxide, on various hydrazine derivatives, such as phenylhydrazine, phenylhydrazine with substituents in the nucleus and methylhydrazine. From the results with the ketenes, one would have expected from carbon suboxide and phenylhydrazine to obtain malonyl-bis-phenylhydrazide,



However this compound was not obtained. It is probable that phenylhydrazine reacted thus:

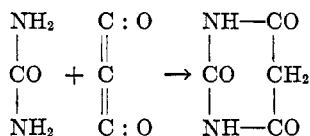


Formula I was ruled out since the compound would not react with aniline to give the expected $\text{C}_6\text{H}_5\text{NHNHCOCH}_2\text{CONHC}_6\text{H}_5$. Compound II was easily changed to its tautomer (III) by heating or allowing to stand. On boiling with water the compound was split to phenylhydrazine and malonic acid. When there were two moles of phenylhydrazine to one of carbon suboxide a molecular compound of structure

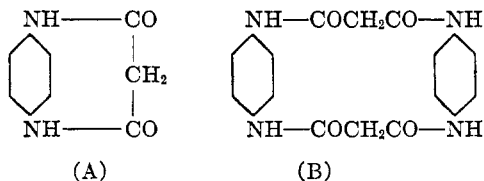


was formed. Similar compounds were formed using *o*-tolyl-, *m*-tolyl-, *o*-nitrophenyl-, *p*-nitrophenyl- and methyl-hydrazines.

With urea a small amount of barbituric acid was formed.



With *p*-phenylene diamine a white compound was obtained which was insoluble in all solvents and which had not melted at 320°. The constitution assigned to it is represented by either (A) or (B).



Similar compounds were formed with *m*- and *o*-phenylene diamine, and the structures (C) and (D) were assigned to these compounds.

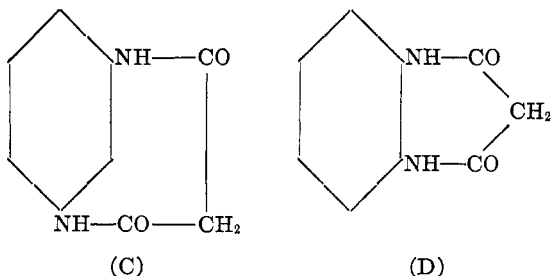
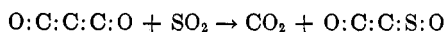


TABLE 1

Addition compounds formed by carbon suboxide and tertiary bases

BASE	PROPORTION OF BASE TO C ₃ O ₂
Isoquinoline.....	1:1
Quinoline.....	1:2
Quinaldine.....	1:2
Nicotine.....	1:3
Codeine.....	1:5
Atropine.....	1:5
Quinine.....	1:7

Diels and Hansen (25) studied the reaction of carbon suboxide with sulfur dioxide and suggested the reaction



followed by the polymerization of the latter compound. They found that tertiary bases formed addition compounds with carbon suboxide and prepared a series of these compounds. (See table 1.)

POLYMERIZATION OF CARBON SUBOXIDE

The highly unsaturated character of carbon suboxide causes it to polymerize very readily. Diels and Wolf (5) found that the liquid at room temperature changed in the course of a day into a solid, amorphous, dark red substance which was completely

soluble in water giving a red-brown or eosin-red solution. At a higher temperature (37°) the polymer loses carbon dioxide, leaving a product which contains less oxygen and is but partially soluble in water. The action of heat on the polymerized carbon suboxide thus explains the series of oxycarbons observed by Brodie and by Berthelot. The polymer when heated gave off carbon dioxide, carbon monoxide, and also carbon suboxide in fairly considerable amounts. The residue even when heated to glowing was not carbon, but a carbon oxide very poor in oxygen (8). The polymer resembled the monomolecular form in its anhydride properties. It rapidly took up water from the air and dissolved in water with the simultaneous evolution of carbon dioxide.

Jones and Robinson (16) found that large quantities of a red solid having the properties of polymerized carbon suboxide were formed when they attempted to purify diamyl and diethyl thiomalonates.

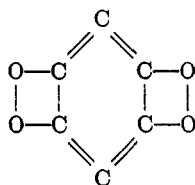
Stock and Stoltzenberg (18) believed the polymerization to be decidedly autocatalytic. The speed of reaction depended upon the nature of the surface of the vessel. The presence of phosphorus pentoxide accelerated the polymerization extraordinarily. Ott and Schmidt (22) found that carbon suboxide prepared from diacetyltartaric anhydride did not polymerize over phosphorus pentoxide, and attribute the results of Stock and Stoltzenberg to traces of volatile phosphorus compounds in the carbon suboxide prepared from malonic acid and phosphorus pentoxide. They also reported keeping pure carbon suboxide in sealed glass tubes for a quarter of a year without polymerization. Diels, Beckmann and Tonnie (23) reported that this result was wrong and that the carbon suboxide prepared by this method polymerized with the same rapidity as that used in the earlier investigations.

Edwards and Williams (26) found that the oxide in the gaseous state was very stable, even at room temperature, when dry and contained in a glass vessel the surface of which had not been previously contaminated with the polymerized product. It could not be stored over mercury for any length of time or in the presence of moisture without the occurrence of polymerization. The

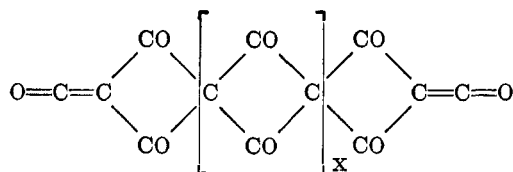
dried gas was not appreciably affected by exposure to ultraviolet light. The polymerization occurred on the surface of the containing vessel and the decrease in pressure was measured. The values of the velocity coefficient were calculated from the change in pressure on the assumption that from one to six molecules might be taking part in the reaction. The values so calculated fell off with the time, which led the authors to state that the reaction was probably a catalytic surface reaction.

The decomposition of carbon monoxide in the corona discharge due to alternating electric fields was carried out by Lunt and his coworkers (27), who studied the kinetics of the formation of the red polymer and its properties.

Some guesses have been made as to the probable structure of the polymerized carbon suboxide. Hartley (7) assigned to it the formula:



From its anhydride properties Diels, Beckmann and Tonnie (23) believe it to be:



CARBON SUBSULFIDE

The sulfur analog of carbon suboxide was known long before carbon suboxide. It was prepared in 1893 by von Lengyel (28) who passed an electric arc through the vapors from boiling carbon disulfide and obtained a few grams of a deep red liquid whose composition corresponded to the formula C_3S_2 . It was also

prepared by passing carbon disulfide vapors through a heated tube (29).

It is an oily, evil-smelling liquid at room temperature. It melts at -0.5° , but on heating it changes to a hard black mass; however, it can be distilled at 60° to 70° in a vacuum with but a small amount of polymerization.

von Lengyel named the compound tricarbonium disulfide. Stock and Praeterius (30) assigned to it the constitution S:C:C:C:S and called it carbon subsulfide. They showed that it was similar to carbon suboxide in its chemical reactions, such as its reaction with aniline to form thiomalonanilide. Although more stable than carbon suboxide, it polymerized slowly at room temperature and in a few minutes at 100° to a black solid which was insoluble in water, sodium hydroxide solution and hydrochloric acid.

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