

THE CHEMISTRY OF CARBONYL SULFIDE

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I. INTRODUCTION

The existence of carbonyl sulfide, also known as carbon oxysulfide, was overlooked until 1867, when it was prepared by Than (156). Previous investigators had mistaken it for a mixture of carbon dioxide and hydrogen sulfide.

Carbonyl sulfide has a boiling point near that of propane and is found in a variety of industrial and natural gases. Increasing use of liquefied petroleum gas—mainly propane and butane fractions—as a household and automotive fuel makes timely a review of the literature of this sulfur compound. An article dealing in general with the sulfides of carbon was published twenty-five years ago (86), but no summary of the chemistry of carbonyl sulfide has appeared. The present review includes information cited in *Chemical Abstracts* through Volume 49 (1955).

II. PREPARATION

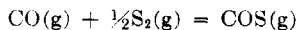
Such industrial gases as coal gas, water gas, carbureted water gas, and producer gas contain concentrations of carbonyl sulfide varying from 3 to 10 grains per hundred cubic feet, measured at 60°F. and 30 in. of mercury (14, 57, 79, 92). It is the predominant sulfur compound in synthesis gas (127). Hydrogen produced from coal contains both carbonyl sulfide and carbon disulfide. Meta-ligneous coal yields more carbonyl sulfide than does bituminous coal (45).

Carbonyl sulfide does not occur in virgin petroleum fractions, but it is formed during thermal and catalytic conversion processes (73).

Carbonyl sulfide was obtained as early as 1841 by Couerbe as a decomposition product from the distillation of alkali xanthates; however, he believed it to be

COSH, which he called xanthin (30). Fleischer and Hanke later showed that xanthin was actually carbonyl sulfide contaminated with hydrogen sulfide and mercaptans (49). Besides sodium and potassium xanthates (30, 49), many organic xanthic esters yield carbonyl sulfide upon dry distillation (95, 158). It is a decomposition product formed during the ripening of viscose (64, 65).

The true identity of carbonyl sulfide was first established by Than, who obtained this compound by the reaction between carbon monoxide and sulfur vapors at a dull red heat (155). Equilibrium conditions for the reaction have been studied.

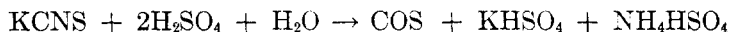


$$K_p = P_{\text{COS}}/P_{\text{CO}}P_{\text{S}_2}^{1/2}$$

K_p	$^{\circ}\text{K.}$	References
4.7×10^4	533	(88, 89, 123)
9.0×10^3	575	(88, 89, 123)
1.5×10^3	873	(122, 123)
3.09	1073	(123, 153)
0.488	1223	(123, 153)

This reaction is used to prepare carbonyl sulfide in the isotopic forms C^{14}OS , CO^{18}S , and COS^{33} (96).

Carbonyl sulfide is obtained by the action of oxidizing agents on carbon disulfide (1, 87) and as a by-product during the preparation of carbon disulfide from carbonaceous matter and sulfur dioxide (22, 38). It may be formed by heating amides and carbon disulfide together in a sealed tube (24, 61), by heating oxides of carbon with sulfides (16, 22, 52, 159), by the action of carbonyl chloride on sulfides (12, 103), or by the action of concentrated sulfuric acid on allyl thiocyanates (66). The best method for making carbonyl sulfide in the laboratory is the hydrolysis of metallic thiocyanates with mineral acids (80, 85, 151).



Methods for preparing carbonyl sulfide are summarized in table 1.

Carbonyl sulfide is conveniently purified by converting it to a thiocarbonate (125) or thiocarbamate (114, 151) and then hydrolyzing the product. Cylinders of carbonyl sulfide have recently become available for laboratory use.

III. GENERAL PROPERTIES

Purified carbonyl sulfide is a colorless, odorless, tasteless gas. Many of its properties are midway between those of carbon disulfide and carbon dioxide (69, 86). At 1 atm. and 25°C. it has a vapor density of 2.485 (76, 85). A critical temperature of 105°C. and a critical pressure of 61 atm. have been reported (86). The gas condenses to a highly refractive liquid with a boiling point of -50.2°C. (1, 63, 76, 151); however, it forms maximum-boiling azeotropes in hydrocarbon

TABLE 1
Formation of carbonyl sulfide

Reactants	Conditions	References
CO + S	Gases through a tube at 300°C.	(88, 96, 111, 122, 123, 155)
CO ₂ + S	Boiling sulfur	(29)
CO + FeS	600-1700°C.	(159)
CO ₂ + FeS	600-1700°C.	(159)
CO + MgSO ₄	Heated	(119)
CS ₂ + H ₂ SO ₄	Palladium catalyst; 200°C.	(98)
CS ₂ + SO ₂ ClOH	Sealed tube at 100°C.	(40)
CS ₂ + O ₂	Heated kaolin	(52)
CS ₂ + CO ₂	Platinized asbestos; heated	(168)
CS ₂ + CO ₂	Heated magnesia	(119)
CS ₂ + SO ₃	Sealed tube at 100°C.	(1)
CS ₂ + CrO ₃	Sealed tube at 180°C.	(87)
CS ₂ + CO(NH ₂) ₂	Sealed tube at 110°C.	(24)
CS ₂ + (CONH ₂) ₂	Sealed tube at 200°C.	(61)
CS ₂ + CH ₃ CONH ₂	Sealed tube at 210°C.	(87)
CS ₂ + C ₂ H ₅ OH	Red-hot copper	(24)
CS ₂ + C ₂ H ₅ COOH + (C ₂ H ₅) ₃ P	Heated	(61)
CS ₂ + CH ₃ COOH ₂	Cold aqueous solution	(9)
SO ₂ + C + O ₂	S, H ₂ S, CS ₂ also formed	(22, 38, 52)
H ₂ S + CO	Clay in a heated porcelain tube	(16, 22, 52)
H ₂ S + COCl ₂	Pressure; 200°C.	(12)
CdS + COCl ₂	Pulverized CdS; 260-280°C.	(103)
C ₆ H ₁₁ OCSNHC ₆ H ₅	220-240°C.; nitrogen atmosphere	(28)
C ₂ H ₅ OH + CSCl ₂	CSClOC ₂ H ₅ also formed	(81)
KCNS + H ₂ SO ₄	50 weight per cent H ₂ SO ₄ ; 20°C.	(80, 85, 151)
C ₂ H ₅ OCOSK + HCl	Sulfuric acid may be used	(69, 125)
NH ₂ COSNH ₂ + HCl	Dilute HCl	(114, 151)

mixtures (135). Its specific gravity at -87°C . is 1.25 (150). The vapor pressure of the liquid follows the equation:

$$\log P = \frac{-1318.260}{T} + 10.15309 - 0.0147784T + 0.000018838T^2$$

where P is the vapor pressure in centimeters of mercury and T is the temperature in $^{\circ}\text{K}$. for the range 162-224 $^{\circ}\text{K}$. (76).

Carbonyl sulfide crystallizes as extremely fine needles (164) which have a melting point of -138.8°C . (76, 151). It has a heat of fusion of 1130 cal. per mole and a heat of vaporization of 4420 cal. per mole at 760 mm. (76).

An equation has been given (35) for the gas imperfection, β , of carbonyl sulfide in terms of its heat of vaporization, ΔH ; vapor pressure, P ; temperature, T ; vapor molal volume, V ; liquid molal volume, V_l ; and the gas constant, R .

$$\frac{PV}{RT} = -\frac{\Delta H}{R(1 - V_l/V) [d \ln P/d(1/T)]} = 1 + \frac{\beta}{V}$$

The value of β is -565 at 222.8 $^{\circ}\text{K}$. and -470 at 214.0 $^{\circ}\text{K}$.

The empirical heat-capacity equation for carbonyl sulfide gas has been derived (75, 147) from spectroscopic data (33).

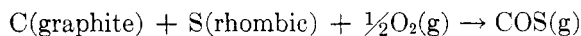
$$C_p^0 = 6.554 + 13.880 \times 10^{-5}T - 88.18 \times 10^{-7}T^2 + 1.964 \times 10^{-9}T^3$$

TABLE 2
Heat capacity of carbonyl sulfide

Solid		Liquid	
Temperature	Heat capacity	Temperature	Heat capacity
°K.	cal./degree/mole	°K.	cal./degrees/mole
20	2.63	140	17.46
30	4.84	150	17.26
40	6.62	160	17.11
50	7.70	170	17.00
60	8.48	180	16.96
70	9.08	190	16.93
80	9.62	200	16.95
90	10.09	210	16.98
100	10.53	220	17.03
110	10.95		
120	11.40		
130	11.85		

This equation gives a maximum deviation from the theoretical of 1.19 per cent in the range 298.1–1800°K. Another equation (20), also from spectroscopic work (6), has a 2 per cent maximum deviation between 400 and 2000°K. Heat capacities determined from calorimetric measurements for liquid and solid carbonyl sulfide (19, 76) are tabulated in table 2.

The free energy of formation of carbonyl sulfide, $\Delta F_{298.1}^0$.



calculated from molecular constants obtained by electron diffraction and Raman and infrared spectra is -40.48 kcal. per mole (33, 75). A value of -39.80 is obtained (106) from thermal data (88, 153). The heat of formation, $\Delta H_{298.1}$, is calculated as -34.07 kcal. per mole. This compares with a value of -32.7 kcal. per mole, which involves amorphous carbon (75). The entropy change accompanying this reaction, $\Delta S_{298.1}$, is 21.83 kcal. per degree per mole (75).

The entropy of carbonyl sulfide at its boiling point, calculated as an ideal gas from calorimetric data, is 52.56 cal. per degree per mole. This is in agreement with a value of 52.66, calculated from electron diffraction and spectroscopic data (76).

The molecular structure of carbonyl sulfide has been a matter of controversy. Data obtained by Raman spectra indicate a nonlinear molecule with a valency angle of 152° (162, 163). Infrared absorption supports the lack of symmetry but does not conclusively indicate the type of structure (5). The results of structure studies presented in table 3 indicate that carbonyl sulfide is a linear molecule with a probable carbon–oxygen distance of 1.16 Å. and a carbon–sulfur distance of about 1.56 Å. These interatomic distances are in agreement with distances calculated from the three resonance structures:

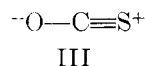
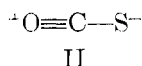
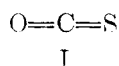


TABLE 3
 Structure of carbonyl sulfide

Method of Investigation	Structure Indicated	Bond Distances		References
		Carbon to oxygen	Carbon to sulfur	
		A.	A.	
Electron diffraction	Linear	1.16 ± 0.02	1.56 ± 0.03	(34)
Electron diffraction	Linear	1.13 ± 0.05	1.58 ± 0.08	(41)
Electron interference	Linear	—	—	(13)
Microwave	—	1.1637	1.5584	(148)
Ultrasonic	Linear	—	—	(43, 129)
X-ray	Linear	1.10	1.96	(161)
Viscosity	Linear	1.30	1.68	(117)
Dielectric constant and electric moment	Linear	—	—	(169)
Heat capacity calculations	Linear	—	—	(19)
Calorimetric entropy	Linear	—	—	(44)
Raman spectra	—	1.04	2.38	(36)
Raman spectra	Nonlinear; valence angle 152°	—	—	(162, 163)

Structure III, containing the triple carbon-sulfur bond, is less important; structures I and II predominate (34, 110). The value observed for the carbon-sulfur separation in carbonyl sulfide is essentially the same as that in carbon disulfide, 1.54 ± 0.03 A. The carbon-oxygen distance agrees with the value, 1.15A., in carbon dioxide (34, 110).

The electronic configuration and force constants of carbonyl sulfide are nearly the same as in carbon dioxide and carbon disulfide, both of which are linear symmetrical molecules. As expected for an unsymmetrical triatomic molecule, carbonyl sulfide has a complicated spectrum with three fundamental frequencies. These frequencies correspond to wave numbers 859, 527, and 2079 cm^{-1} (112). Only the first two frequencies are active at temperatures of a few hundred degrees Centigrade (136). The infrared spectrum of carbonyl sulfide has been measured by several workers. Observed bands in terms of wave numbers are compared in table 4.

Wave numbers corresponding to the fundamental Raman lines for carbonyl sulfide are 524, 859, and 2055 cm^{-1} . Other Raman lines are 678, 862, 1041, 1383, and 2233 cm^{-1} (36).

The ultraviolet absorption spectrum of an ethanol solution of carbonyl sulfide is continuous from 2200 A. to 3100 A. (17). The ultraviolet absorption spectrum of gaseous carbonyl sulfide was first described as continuous from a wavelength of 2550 A. to the far ultraviolet (90). These measurements were made using a hydrogen continuum and pressures of a few tenths of a millimeter of mercury. More recent studies using lower pressures (0.01 mm. of mercury) report continuous absorption starting at 1600 A. (50). A rounded absorption maximum occurs at 2250 A. and a sharp maximum at 2080 A. (115).

In microwave spectroscopy carbonyl sulfide is a useful secondary standard, particularly at high frequencies. Its lines are harmonic except for a known

TABLE 4
Infrared spectrum of carbonyl sulfide

Wave Number of Absorption Maxima*	References	Wave Number of Absorption Maxima*	References
<i>cm.</i> ⁻¹		<i>cm.</i> ⁻¹	
4952	(23)	2010	(23)
4153	(23)	1898	(6)
4114	(23)	1894	(23)
4101	(7)	1892	(7)
4084	(6)	1718	(6)†
4002	(23)	1710	(7, 23)
3942	(23)	1559	(7)
3768	(23)	1530	(7)
3742	(6)	1051	(6)†
3739	(7)	1048	(23)
3096	(7)	1047	(7)
3095	(6)	859	(6, 7, 23, 112)†
2919	(7)	530	(23)
2918	(23)	527	(7, 112)
2904	(6)	527	(6)†
2862	(23)	524	(23)
2576	(23)	522	(7)
2575	(7)	517	(23)
2107	(23)	514	(7)
2079	(6, 112)		
2064	(23)		
2051	(7)		

* The sets grouped together represent values for the same maximum from different sources.

† Absorption maximum shown graphically in this region.

centrifugal distortion effect. The absence of quadrupole splittings and the small value of the line-breadth parameter, $\Delta\nu = 6$ Mc. per millimeter, also make carbonyl sulfide lines important (46, 54).

Carbonyl sulfide was the first molecule whose microwave Stark effect was investigated. The dipole moment based on measurements of the Stark effect is 0.72 Debye unit (37). This is in agreement with infrared measurements (167) and a value of 0.720 ± 0.005 Debye units, obtained by observing the temperature dependence of the polarization of gaseous carbonyl sulfide (72).

The viscosity of gaseous carbonyl sulfide in micropoises is 119.0 at 15°C. and 154.1 at 100°C. (145). The refraction and dispersion of gaseous carbonyl sulfide are given for the 5790 and 4040 Å. wavelength range (68).

Carbonyl sulfide is less soluble in water than carbon dioxide. However, some reduction in the total organic sulfur content of water gas, coal gas, or coke-oven

TABLE 5
Solubility of carbonyl sulfide
 (Volume per 100 volumes of solvent at 1 atm.)

Solvent	Temperature	Solubility	References
	°C.		
Water	13.5	50	(63)
Alcohol	22.0	800	(151)
Alcoholic potassium hydroxide*	13.5	7200	(63)
Cuprous chloride in HCl	13.5	20	(63)
Toluene	22.0	1500	(151, 166)
Nitrobenzene	13.5	12	(63)
Pyridine	13.5	4.4	(63)

* 1 g. of potassium hydroxide dissolved in 2 ml. of water and 2 ml. of alcohol.

gas has been obtained by treatment with water at temperatures of 5 to 10°C. and pressures of 15 to 50 atm. (14). It dissolves readily in alcohol and toluene (151, 166). Liquid carbonyl sulfide is claimed not to be associated (111). Solubility data for carbonyl sulfide in various solvents are summarized in table 5.

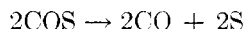
In physiological action, carbonyl sulfide resembles carbon disulfide except that it acts faster. Like nitrous oxide, it first affects the nervous system (80). Cold-blooded animals show more resistance to carbonyl sulfide than do warm-blooded animals. Mice and rabbits die quickly when they are exposed to air containing more than 0.3 per cent carbonyl sulfide (48, 63, 83).

IV. CHEMICAL REACTIONS

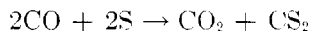
Carbonyl sulfide is stable, but it can undergo decomposition, hydrolysis, oxidation, and reduction to produce reactive compounds such as hydrogen sulfide and elemental sulfur. These reactions as well as reactions with ammonia and amines are important in the removal of carbonyl sulfide from other gases.

A. Dissociation

Carbonyl sulfide undergoes thermal decomposition by either of two reactions:



Dissociation by the first reaction is rapid and reaches a maximum of 64 per cent at 900°C.; that by the second reaction is slow and reaches a maximum at 600°C. (109, 152, 153). The second reaction is catalyzed by quartz (109) and charcoal (153) and may be due to the reaction:



The extent of dissociation of carbonyl sulfide is independent of the amounts of carbon dioxide or carbon disulfide present (153). Dissociation of carbonyl sulfide present in furnace gases from iron and steel manufacture is reported (122, 123).

TABLE 6
Hydrolysis of carbonyl sulfide in gases

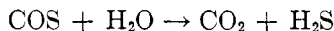
Gas	Catalyst	Temperature	Pressure	Reference
Gas obtained by the action of steam on coke or from thermal cracking	Caustic solution containing sodium aluminate	°C. 24	atm. 10	(126)
C ₂ -C ₄ liquefied petroleum gas	Soluble cadmium salt* †; suspension of insoluble cadmium hydroxide, oxide, or carbonate	0 to 43	4 to 35	(133)
C ₁ -C ₄ liquefied petroleum gas	Alkaline solution or suspension of a cupric compound †	0 to 43	4 to 35	(133)
C ₂ -C ₄ liquefied petroleum gas	Sodium plumbite †	0 to 43	4 to 35	(131)
Gaseous mixtures of low-boiling hydrocarbons	Alkaline solution or suspension of copper, zinc, iron, or nickel compound †	90 to 370	1 to 15	(132)

* Chloride, acetate, or sulfate.

† On an adsorbent.

B. Hydrolysis

The reaction of carbonyl sulfide with water closely follows a unimolecular order and is catalyzed by many substances and ions, especially the hydroxyl ion (156). Carbonyl sulfide and water react slowly:



Because both hydrogen sulfide and carbon dioxide are acidic, carbonyl sulfide is relatively stable toward acids. It exists indefinitely in an aqueous solution containing 50 weight per cent sulfuric acid (80, 132). In carbonated mineral waters it decomposes to hydrogen sulfide after long storage in closed containers (40). Although hydrolysis is accelerated by alkaline material, carbonyl sulfide is still only slowly hydrolyzed by strongly alkaline reagents, such as sodium hydroxide (11). Washing a propane-butane mixture with a 10-20 weight per cent sodium hydroxide solution hydrolyzes only 20-30 per cent of the carbonyl sulfide present (135).

Several methods have been devised for carrying the hydrolysis of carbonyl sulfide to completion. Alkaline solutions or moist suspensions of heavy metal salts impregnated on solid adsorbents hydrolyze 85-100 per cent of the carbonyl sulfide present. Four processes based on this reaction are summarized in table 6. Although this type of process permits counter-current operations, one disadvantage is the necessity of periodically cleaning out and replacing the solid reagent.

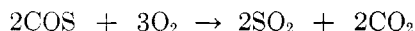
Solutions containing 0.8 per cent of sodium aluminate and 3 per cent of sodium hydroxide catalyze the hydrolysis of 85-90 per cent of the carbonyl sulfide present in a gas (126). Carbonyl sulfide present in a petroleum naphtha is hydrolyzed to hydrogen sulfide by contact with activated bauxite at 370°C. (62). Liquefied petroleum gas containing carbonyl sulfide may be dried without affecting the carbonyl sulfide if silica gel is used as a dehydrating agent instead of alumina (47).

TABLE 7
Hydrogenation of carbonyl sulfide in gases

Gas	Catalyst	Temperature	Pressure	References
		°C.	atm.	
Pure carbonyl sulfide	Nickel subsulfide	125-200	1.0	(32)
C ₂ -C ₄ gases from petroleum cracking	Alumina-molybdena	900-1050	3.5-30	(74)
Water gas or coke-oven gas containing at least 20 per cent of hydrogen	Cuprous sulfide, tripotassium phosphate, and potassium carbonate	200-250	1.0	(141, 142, 143, 144)
Industrial gases containing hydrogen	Reduced, pelleted manganese oxide; manganese ore	250-550	1.0	(121)
Water gas or other hydrogen-containing gas	Ferric oxide and anhydrous sodium	Above 300	1.0	(15)

C. Oxidation

Carbonyl sulfide is highly flammable, burning with a slightly luminous blue flame (157).

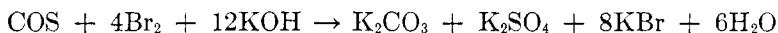


However, it is less readily oxidized than carbon disulfide (57). A mixture of one volume of gaseous carbonyl sulfide and 1.5 volumes of oxygen burns with a small explosion; with 7.5 volumes of oxygen combustion occurs without explosion (63). The critical explosion limits for mixtures of carbonyl sulfide and oxygen at temperatures between 190°C. and 408°C. have been studied in quartz and glass vessels (58). A reaction mechanism has been proposed (8), and kinetic measurements have been made for the oxidation of carbonyl sulfide from room temperature to 100°C. (55).

Such catalysts as palladium promote the oxidation of carbonyl sulfide in concentrated sulfuric acid (97, 99).

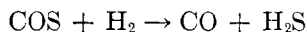
Carbonyl sulfide and other organic sulfur compounds have been separated from gaseous carbon dioxide by treating with oxygen over an active carbon catalyst above the critical temperature of the carbon dioxide and at pressures between 100 and 200 atm. (53). A nickel subsulfide catalyst has been used for the oxidation of traces of carbonyl sulfide in nitrogen (55).

Bromine in alkaline solutions readily oxidizes carbonyl sulfide (157).



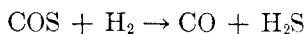
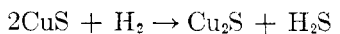
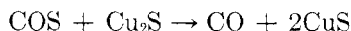
D. Reduction

Carbonyl sulfide is reduced by hydrogen according to the equation:



Processes that combine catalytic reduction with removal of hydrogen sulfide are summarized in table 7. The carbonyl sulfide content of gases from petroleum cracking can be lowered from 1000 ppm. to less than 0.04 ppm. by hydrogenation under pressures slightly greater than the vapor pressure of the hydrocarbon

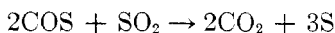
(74). Cuprous sulfide is the essential ingredient in the mixed catalyst; it is believed to function in the following manner (141):



Manganese oxide or manganese ore catalyst is effective so long as a large proportion has not been converted to manganese sulfide (121). The life of a catalyst containing a mixture of iron oxide and sodium carbonate may be increased by pretreatment with hydrogen at 500°C. (15).

E. Reaction with sulfur dioxide

Elemental sulfur is formed when carbonyl sulfide is mixed with an excess of sulfur dioxide and passed over red-hot pumice or brick (22).

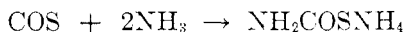


Best results were obtained at 400–425°C. over a catalyst prepared from blast furnace slag containing about 55 per cent aluminum oxide (2). The oxide adds to the mechanical strength of the catalyst but does not improve its activity; the presence of iron decreases both catalyst strength and activity (2). The reaction of carbonyl sulfide with sulfur dioxide was also investigated at 600–800°C. in the presence of oxides of iron, aluminum, or titanium on pumice and porcelain supports (26). It proceeds nearly to completion with iron and titanium catalysts, ceasing when the gas phase contains 0.6 per cent carbonyl sulfide and 0.3 per cent sulfur dioxide (26). Such alkaline compounds as sodium oxide, sodium sulfide, and sodium carbonate function as catalysts at temperatures above 350°C., either in aqueous solution or deposited on a porous support (56, 165).

F. Reaction with ammonia and amines

Ammonia and many amines react readily with carbonyl sulfide. These reactions are of commercial importance in the removal of carbonyl sulfide from gases.

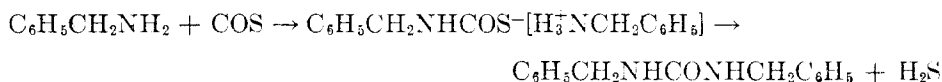
Ammonia gas and ammonia solutions absorb carbonyl sulfide with the formation of ammonium thiocarbamate (18, 130):



If an ammonia solution is used, evaporation decomposes it to urea and hydrogen sulfide (10, 11). The first reaction is fairly slow; decomposition to urea is much more rapid (138). When carbonyl sulfide and ammonia react in the absence of large amounts of water and at temperatures and pressures under which one or both of the reagents are in the liquid state, urea is obtained directly (82, 84).

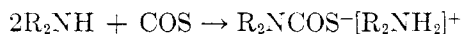
Primary amines react with carbonyl sulfide to form the amines salt of a monothiocarbamic acid. Benzylamine forms a monothiocarbamic salt which,

when heated in the absence of moisture, decomposes to a urea derivative and hydrogen sulfide (59):



Aniline, *o*-toluidine, *p*-anisidine, and *p*-chloroaniline yield diphenylurea derivatives (59).

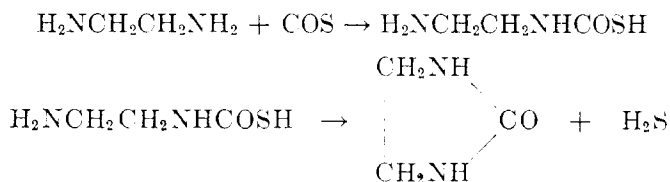
Secondary amines efficiently absorb carbonyl sulfide to yield amine salts of substituted thiocarbamic acids (107).



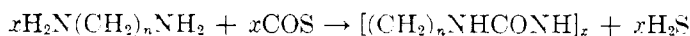
Piperidine, morpholine, and their derivatives have been used, as well as mixtures of these compounds (91, 92). Equilibrium constants for the systems piperidine-carbon dioxide-carbonyl sulfide and morpholine-carbon dioxide-carbonyl sulfide have been determined (57).

Primary alkanolamines react readily with carbonyl sulfide, but many secondary and tertiary ones do not (135). Carbonyl sulfide completely converts monoethanolamine in a heated aqueous solution to diethanolurea, which precipitates on the addition of isopropyl alcohol (78). Carbonyl sulfide will also react with monoethanolamine adsorbed on fuller's earth, activated alumina, charcoal, or silica gel (134, 135); the carbonyl sulfide is converted to an oil-insoluble compound, which is retained on the adsorbent. A 20 per cent solution of monoethanolamine in sodium hydroxide or alcoholic potassium hydroxide absorbs carbonyl sulfide without consuming the amine, which appears to catalyze the reaction of the carbonyl sulfide with the caustic (73).

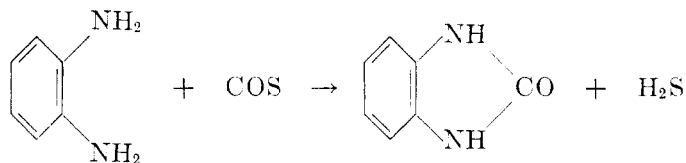
Carbonyl sulfide may react with diamines in several ways. When ethylenediamine dissolved in ethyl alcohol is treated at atmospheric pressure and at room temperature with equimolecular proportions of carbonyl sulfide an intermediate reaction product is formed instantaneously and precipitated from solution. The solid removed by filtration is heated until no more hydrogen sulfide is evolved. The crude melt remaining represents a 93 per cent yield of ethyleneurea (93).



Similar reactions with aliphatic diamines containing amino groups separated by at least three carbon atoms yield hydrogen sulfide and linear condensation products.



The products, when plastic, can be drawn into threads or films (31, 102, 160). When a solution of carbonyl sulfide and phenylenediamine toluene is heated at 225°C., benzimidazoline slowly forms (59):

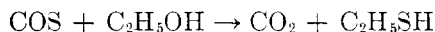


Like monoethanolamines, polyamines impregnated on adsorbents readily react with carbonyl sulfide (134, 135).

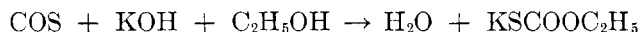
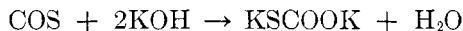
Contact at room temperatures with amines removes carbonyl sulfide from hydrogen, coke-oven gas, water gas, or liquefied propane-butane mixtures. The amines may be dissolved or suspended in a liquid scrubbing medium, which may be water, oil, or a special solvent (104, 139). Polyamine anion-exchange resins remove carbonyl sulfide from gaseous hydrocarbons (124). The effluent from the resins, however, contains carbon dioxide and hydrogen sulfide, hydrolysis products of carbonyl sulfide.

G. Miscellaneous reactions

Carbonyl sulfide reacts extremely slowly with dry alcohol to form a mercaptan:

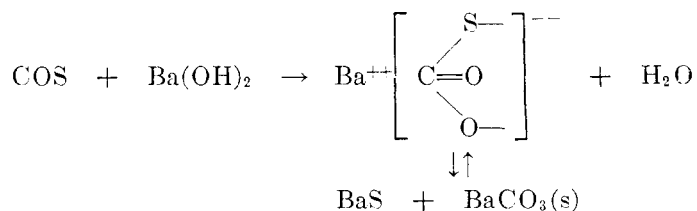


When caustic is added, absorption is rapid and complete (80):

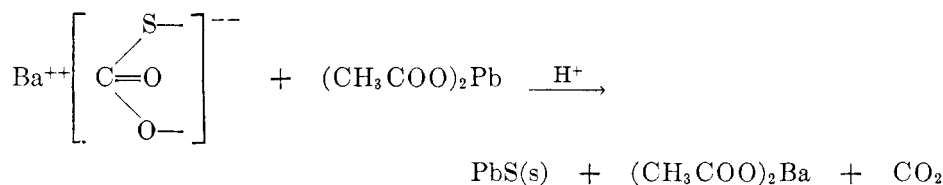


The reaction is so fast that alcoholysis does not occur (156).

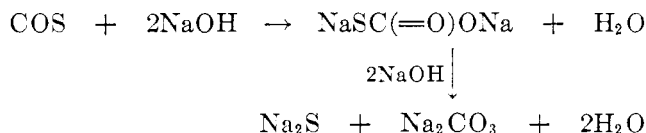
The reaction of carbonyl sulfide with metal salts sometimes involves an induction period. When carbonyl sulfide is passed into a barium hydroxide solution, cloudiness occurs after a brief delay.



Upon treatment of barium thiolcarbonate with an acidic solution of lead acetate, lead sulfide precipitates after several minutes.

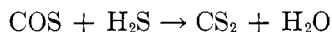


Lead sulfide will precipitate instantly when carbonyl sulfide is added to a more strongly alkaline solution of a lead salt (157).

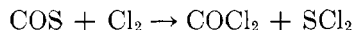


The sodium hydroxide produces sulfide ion, which is instantly precipitated by the metal (157). Ammoniacal solutions of silver or zinc (157) and aqueous solutions of cuprous (11) or palladous chloride (39) react rapidly with carbonyl sulfide to form the corresponding metal sulfides.

At high temperatures, carbonyl sulfide reacts with carbon, hydrogen sulfide, and halogens. With carbon it forms carbon disulfide (25). With hydrogen sulfide at temperatures between 350°C. and 900°C. (154) carbon disulfide is formed.



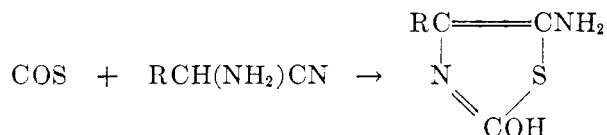
Although carbonyl sulfide does not react appreciably with chlorine at ordinary temperatures, sulfur chloride and carbonyl chloride are formed from it at a red heat (42).



Carbonyl chloride is also obtained with boiling or cold antimony pentachloride. Carbonyl sulfide is fluorinated by a large excess of cobalt trifluoride at 200°C. (140).



Carbonyl sulfide condenses with α -aminonitriles to yield 5-amino-2-hydroxy-thiazoles.

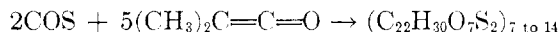


Aliphatic α -aminonitriles have been used where R is CH_3 , C_2H_5 , C_3H_7 , and C_6H_{13} (108). The thiazole yield is 96 per cent when R is COOC_2H_5 and 87 per cent when R is C_6H_5 (27).

TABLE 8
 Reaction of carbonyl sulfide with Grignard reagents

Grignard Reagent	Products			
	Acid	Yield	Alcohol	Yield
		<i>per cent</i>		<i>per cent</i>
C ₂ H ₅ MgBr	C ₂ H ₅ COSH	9	(C ₂ H ₅) ₂ COH	38
C ₆ H ₅ MgBr	C ₆ H ₅ COSH	40	(C ₆ H ₅) ₂ COH	52
<i>o</i> -CH ₃ C ₆ H ₄ MgBr	<i>o</i> -CH ₃ C ₆ H ₄ COSH	73	—	—
<i>p</i> -CH ₃ C ₆ H ₄ MgBr	<i>p</i> -CH ₃ C ₆ H ₄ COSH	50	(<i>p</i> -CH ₃ C ₆ H ₄) ₂ in place of an alcohol	22

An amorphous powder, with a molecular weight between 3000 and 6000, results from the addition of carbonyl sulfide to dimethylketene (149).



Alkyl- and arylmagnesium bromides react with carbonyl sulfide to form thio acids and trisubstituted alcohols in varying proportions, as listed in table 8 (166).

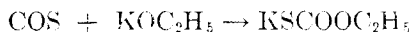
Because carbonyl sulfide occurs as a contaminant in many gases, its corrosive properties are of interest. Liquefied petroleum gas containing as much as 58 ppm. of carbonyl sulfide does not corrode polished copper (100). However, contamination by as little as 1 ppm. of elemental sulfur or hydrogen sulfide causes discoloration of copper. Information is not available on the action of carbonyl sulfide toward other metals. It is corrosive toward concrete (51).

Special carbons have been prepared to mitigate corrosion arising from carbonyl sulfide. An activated carbon that will remove carbonyl sulfide from flue gas has been obtained by carbonizing coals in the presence of salts of nickel, cobalt, or chromium; the salts deposit a residue of catalytically active metal, oxide, or sulfide (101). Carbon kept alkaline by ammonia or ammonium salts has also been used (4, 71). Activated carbon has been used to remove carbonyl sulfide from synthesis gas (127). Carbonyl sulfide is distinguished from carbon disulfide by differences in their adsorption on activated carbon. The carbon first becomes saturated with carbonyl sulfide and then with carbon disulfide (128).

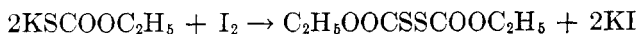
V. ANALYTICAL DETERMINATION

Carbonyl sulfide in gases must often be determined by indirect methods. Absorption of such organic sulfur compounds as thiophene, carbon disulfide, mercaptans, and hydrogen sulfide leaves a residual content which is assumed to be due to carbonyl sulfide (94, 118). One empirical procedure involves determining the proportion of organic sulfur transferred from gas to oil by scrubbing under specified conditions (77). However, several direct methods are available for determining carbonyl sulfide in gases.

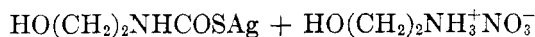
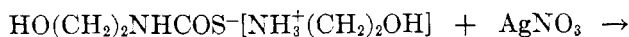
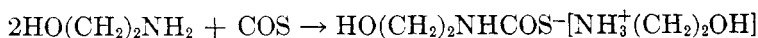
A well-known method is based on the absorption of carbonyl sulfide at 0°C. in an alcoholic potassium hydroxide solution.



The solution is made slightly acidic with acetic acid, and titrated with iodine (18, 60):



In a convenient and reliable method, the gases are passed successively through a 30 per cent sodium hydroxide solution and a 5 per cent solution of monoethanolamine in ethyl alcohol. The first solution removes mercaptans and hydrogen sulfide; the second removes carbonyl sulfide. The second solution is titrated with a standard silver nitrate solution (21).



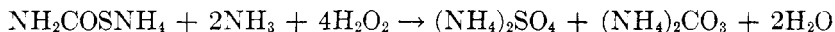
Carbonyl sulfide is quantitatively extracted from gases by piperidine in alcoholic solution.



The amine salt of the piperidine oxythiocarbamate formed absorbs ultraviolet light at 2300 Å. Carbon disulfide forms piperidine dithiocarbamate, which absorbs at 2900 Å, where the oxythiocarbamate is transparent (16, 146). A piperidine-chlorobenzene reagent also absorbs carbonyl sulfide and carbon disulfide. The proportions of each are resolved colorimetrically (120).

An ethanol solution of diethylamine absorbs carbonyl sulfide to yield diethylmonothiocarbamic acid, the amount of which may be determined polarographically. It gives an anodic wave at -0.32 v. (137). An ammoniacal solution of calcium chloride may also be used to absorb carbonyl sulfide for polarographic analysis. This method makes possible the determination of 0.1 mg. of carbonyl sulfide (113). Carbon disulfide does not interfere.

Ammonium thiocarbamate formed when carbonyl sulfide is passed through a bubbler containing an ammoniacal solution of calcium chloride may be oxidized with hydrogen peroxide to ammonium sulfate and ammonium carbonate (3, 157).



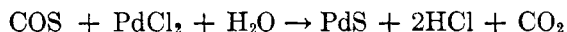
The quantity of carbonyl sulfide present is calculated from the amount of sulfate formed.

The sulfur formed from carbonyl sulfide may be used to determine this compound analytically. Air containing carbonyl sulfide is passed over an electrically heated platinum wire. The sulfur formed by thermal decomposition is oxidized to sulfur dioxide, which may be determined by absorption in caustic solution (70).

The formation of hydrogen sulfide by the hydrolysis of carbonyl sulfide is also used for analysis. The gas to be tested is stored for several weeks, so that the carbonyl sulfide present will be completely hydrolyzed, and is then passed over

silver-coated beads at about 150°C.; the darkening of the beads is compared with that obtained with a gas of known carbonyl sulfide content (67, 73). Carbonyl sulfide may be hydrolyzed by a dilute base and the resulting hydrogen sulfide determined with methylene blue (116).

Traces of carbonyl sulfide in a gas may be determined by passing it through a heated solution of a heavy metal salt, such as palladous chloride:



The palladous sulfide is oxidized and determined as barium sulfate (157).

The concentration of carbonyl sulfide in gases may be determined by reduction at 900°C. with hydrogen over an aluminum oxide catalyst to form hydrogen sulfide (105). Again, a reaction product, rather than carbonyl sulfide itself, is used for determination.

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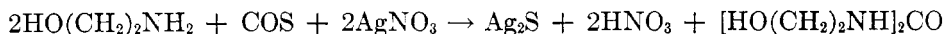
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ADDENDUM

Additional information has recently been published (170) on one of the methods for determining carbonyl sulfide. Burke, Starr, and Tuemmler (21) state that when carbonyl sulfide is absorbed in alcoholic monoethanolamine, ethylthiocarbamic acid forms and is precipitated as the silver salt during the subsequent electrometric titration with silver nitrate. Silver sulfide has now been shown to be the final product. Thus titration of the absorbing solution requires two moles of silver nitrate per mole of carbonyl sulfide as shown by the equation:



This revision in stoichiometry is in agreement with lamp sulfur determinations for total sulfur and mass spectrometer analysis for carbonyl sulfide.

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