could make no conclusion as to the nature of the thiocyanate bonding involved.

It should be pointed out that N-bonding is the normal bonding mode for cobalt(III) and chromium(III) thiocyanate complexes. Indeed, it is believed that the preparation of $K_3[Co(CN)_5SCN]$ represents the first isolation of a thiocyanate-containing complex of cobalt(III) wherein the thiocyanate is bonded through the sulfur atom. It is evidently the stable form of the complex, for heating the complex at 118° *in vacuo* for several hours did not result in any spectral changes. The stability of the Co–SCN bond in this case is undoubtedly due to the presence of the cyanide ions in the coordination sphere, although a rationale for this effect is, as yet, not available. The opposite effect, *i.e.*, a change from the normal S-bonded mode to one of N-bonding, has been found[3b,4] for platinum(II) and palladium(II) thiocyanate-containing complexes wherein strong π-bonding ligands, *e.g.*, trialkylphosphines, triphenylarsine, and 2,2′-bipyridine, are included in the coordination sphere. Since cyanide ion is believed to be a strong π-bonding ligand, one can obviously not apply the explanation given for the bonding in the platinum(II) and palladium(II) complexes to the cobalt(III) complex discussed above.

The cobalt(III)–cyanide–selenocyanate system is currently being studied.

Acknowledgments.—The author wishes to thank Professors F. Basolo, W. K. Wilmarth, and J. Halpern for helpful discussions.

CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.,
EMERYVILLE, CALIFORNIA

Rhenium Heptasulfide-Catalyzed Hydrogenation of Nitric Oxide to Nitrous Oxide or Nitrogen and Sulfur Dioxide to Hydrogen Sulfide

BY LYNN H. SLAUGH

Received January 13, 1964

Rhenium heptasulfide, Re_2S_7, is a stable hydrogenation catalyst for a variety of organic substrates and is not readily poisoned by sulfur- or nitrogen-containing compounds.[1] Furthermore, it is apparently more active for unsaturated organic substrates than other poison-resistant metal sulfides.[1,2] These observations prompted us to test this catalyst for the hydrogenation of nitric oxide, nitrous oxide, and sulfur dioxide. Several interesting qualitative results were obtained.

Experimental

Unsupported rhenium heptasulfide was prepared as described previously[1] by bubbling hydrogen sulfide through a 6 *N* hydrochloric acid solution of ammonium perrhenate (A. D. Mackay, Inc.).

The catalyst (<0.5 g.) and 20 ml. of *n*-dodecane were sealed in an 80-ml., magnetically-stirred autoclave and the gas (50–100 mmoles) to be reduced was injected. The autoclave was heated to the desired temperature and hydrogen introduced (10–30 atm.). After stirring was initiated, the decrease in hydrogen pressure was recorded continuously throughout the length of the experiments (2–100 min.).

The products were analyzed by a combination of mass spectrometry and gas–liquid chromatography. The hydrogen sulfide obtained in the reduction of sulfur dioxide also was determined gravimetrically by the precipitation of lead sulfide from a lead sulfate solution. The ammonia from nitric oxide reductions was determined by acid titration.

The nitric oxide consisted of N_2, 4.9%; N_2O, 6.3%; and NO, 88.8%. The nitrous oxide analyzed: N_2, 2.0%; NO, 0%; N_2O, 98%. A reactant mixture of the two nitrogen oxides employed in one experiment analyzed: N_2, 2.7%; NO, 26.5%; N_2O, 70.8%.

Results and Discussion

While rhenium heptasulfide is capable of catalyzing the hydrogenation of nitric oxide even at room temperature, the product was dependent upon the reaction temperature. At 200° mainly nitrogen and a small amount of ammonia were formed. However, at 100° nitrous oxide was almost the exclusive product. In fact, the hydrogenation of a mixture of nitric oxide and nitrous oxide ceased abruptly when all of the nitric oxide had been converted to nitrous oxide. To our knowledge, this degree of selectivity in the reduction of nitric oxide has not been achieved previously in significant yields. Other catalysts promote the formation of either ammonia, hydroxylamine, or nitrogen[4] at elevated temperatures (usually >200°). Cooke[4a,4h] did find that a small amount of hydrogen occluded on platinum reduced nitric oxide to nitrous oxide, but with more hydrogen, ammonia and hydroxylamine were also produced.

Although nitrous oxide was not hydrogenated at 100°, it was readily reduced at 200° to mainly nitrogen.

In the absence of a catalyst, the hydrogenation of sulfur dioxide to hydrogen sulfide or sulfur does not readily occur below 500°.[5,6] The few catalysts reported for this reaction also require rather high temperatures. For example, nickel metal (probably converted to the sulfide), cobalt sulfide, and iron sulfide are not active below 300°[4g,6] at atmospheric pressure. Iron group metal oxides pretreated with hy-

---

(1) H. S. Broadbent, L. H. Slaugh, and N. L. Jarvis, *J. Am. Chem. Soc.*, **76**, 1519 (1954).

(2) In the present study, a comparison of Re_2S_7 with tungsten–nickel sulfide[3] indicated the latter to be considerably less active for the hydrogenation (~34 atm.) of α-methylstyrene at 250° than is Re_2S_7 at 120°.

(3) M. D. Abbott, R. C. Archibald, and R. W. Dorn, *Proc. Am. Petrol. Inst.*, **38**, Sect. III, 184 (1958).

(4) (a) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 8, Longmans, Green and Co., New York, N. Y., 1928, pp. 428–429; (b) L. Duparc, P. Wenger, and Ch. Urfer, *Helv. Chim. Acta*, **11**, 337 (1928); (c) *ibid.*, **8**, 609 (1925); (d) M. S. Platonov, S. B. Anisimov, and W. M. Krasheninnrikova, *Ber.*, **68**, 761 (1935); (e) L. Andrussov, *ibid.*, **60**, 536 (1927) [*Chem. Abstr.*, **21**, 1872 (1927)]; (f) R. J. Ayen and M. S. Peters, *Ind. Eng. Chem., Process Design Develop.*, **1**, 204 (1962); (g) P. Neogi and B. B. Adhicary, *Z. anorg. allgem. Chem.*, **69**, 209 (1910); (h) S. Cooke, *Proc. Glasgow Phil Soc.*, **18**, 294 (1887); *Chem. News*, **58**, 103, 135, 155 (1886).

(5) E. Terres, K. Schultze, and H. Forthord, *Angew. Chem.*, **45**, 164 (1932).

(6) M. B. Tomkinson, *Compt. rend.*, **176**, 35 (1923).

drogen and sulfur dioxide are claimed to be catalysts at 273-325° for the hydrogenation of sulfur dioxide to sulfur.[7]

Rhenium heptasulfide catalyzed the hydrogenation of sulfur dioxide at ≦100° (10-30 atm.). Hydrogen sulfide was the major product although some sulfur was formed. Tungsten-nickel sulfide was also tested but found to be ineffective at 360° (10-30 atm.).

Acknowledgment.—Appreciation is expressed to G. W. Schoenthal for technical assistance.

[7] M. C. Boswell, U. S. Patent 1,880,741 (1932).

CONTRIBUTION FROM GENERAL CHEMICAL RESEARCH
LABORATORY, ALLIED CHEMICAL CORPORATION,
MORRISTOWN, NEW JERSEY

Reaction of Oxygen Difluoride with Sulfur Dioxide, Sulfur Trioxide, and Peroxydisulfuryl Difluoride

BY GERHARD FRANZ AND FRANZ NEUMAYR

Received January 23, 1964

Recently Schumacher and co-workers reported the results of their photochemical decomposition studies of oxygen difluoride[1] and of the kinetics of the sulfur trioxide–fluorine interaction.[2] On the basis of their photodecomposition experiments using light of 365 mμ wave length, they postulated an O–F radical species as a reaction intermediate. The subsequent synthesis[3] of peroxysulfuryl difluoride (I) from sulfur trioxide and oxygen difluoride supported the existence of such a radical. In the present work, a gaseous mixture of the reactants was irradiated with light of 365 mμ wave length, giving I in a nearly quantitative yield. Ultraviolet light with a wave length of 365 mμ was used in order to exclude the activation of molecules other than oxygen difluoride.[4]

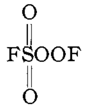
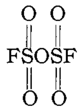
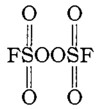
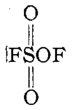
We studied the reaction of sulfur trioxide, sulfur dioxide, and peroxydisulfuryl difluoride (IV) with oxygen difluoride by irradiating the gaseous reaction mixtures with unfiltered ultraviolet light, permitting the excitation of sulfur trioxide, sulfur dioxide, and peroxydisulfuryl difluoride molecules also.

When sulfur trioxide and oxygen difluoride were allowed to react under these conditions only traces of compound I could be detected. The major reaction products were pyrosulfuryl fluoride (II) and sulfuryl fluoride (III). When ordinary window glass was used as a filter, compound I was obtained in a good yield. This glass absorbs below 350 mμ thus preventing the activation of sulfur trioxide.

Infrared and F^{19} n.m.r. analyses proved to be the best methods for differentiating compounds I, II, and III. The F^{19} n.m.r. spectrum of I indicated two different types of fluorine (see Table I) which interact with each other giving rise to spin–spin splitting. Multiplicity, intensity, chemical shift, and coupling constant data strongly support the structure given for compound I. A new synthesis for I was found by irradiating a gaseous mixture of peroxydisulfuryl difluoride (IV) and oxygen difluoride in a Pyrex vessel.

TABLE I

F^{19} CHEMICAL SHIFTS OF SOME S–O–F COMPOUNDS

No.	Structure	Name	Shift, p.p.m.[a]
I	 $\mathrm{FSO_2OOF}$	Peroxysulfuryl difluoride	−291, −43.0
II	 $\mathrm{FSO_2OSO_2F}$	Pyrosulfuryl fluoride	−48.5
III	 $\mathrm{FSO_2F}$	Sulfuryl fluoride	−33.5
IV	 $\mathrm{FSO_2OOSO_2F}$	Peroxysulfuryl difluoride	−40.4
V	 $\mathrm{FSO_2OF}$	Fluorine fluorosulfonate	−249, −37

[a] Measured relative to $CFCl_3$.

Even at room temperature, peroxydisulfuryl difluoride is known to be in equilibrium with its radical form.[5] Irradiation of compound IV and oxygen difluoride yielded peroxysulfuryl difluoride and fluorine fluorosulfonate (V) in accordance with Schumacher's proposed mechanism involving the activation of oxygen difluoride.

The photolysis of a sulfur dioxide–oxygen difluoride reaction mixture yielded compounds II and III only. Fluorine fluorosulfonate, the expected reaction product, could not be found.

Experimental

Preparation of Peroxysulfuryl Difluoride.—A previously reported[3,6] method was modified by substitution of a filter combination by ordinary window glass. Approximately 100 mm. (0.95 g., 0.012 mole) of SO_3, which was distilled from 60% oleum, and 600 mm. of OF_2 (General Chemical Division, Allied Chemical Corp.) were added to a 2-l. Pyrex flask, covered partially with aluminum foil to reflect the radiation.

A plate of window glass large enough to shield the entire flask was placed between a 360-watt high pressure mercury ultraviolet

---

[1] R. Gatti, E. Staricco, J. E. Sicre, and H. J. Schumacher, *Z. physik. Chem.* (Frankfurt), **35**, 343 (1962).

[2] E. Staricco, J. E. Sicre, and H. J. Schumacher, *ibid.*, **35**, 122 (1962).

[3] R. Gatti, E. H. Staricco, J. E. Sicre, and H. J. Schumacher, *Angew. Chem.*, **75**, 137 (1963).

[4] A. Glissmann and H. J. Schumacher, *Z. physik. Chem.*, **24**, 328 (1934).

[5] F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **85**, 3375 (1963).

[6] H. J. Schumacher, private communication.