value).[10] The lower pK'_D value of glutathione may be caused by the close vicinity of the sulfhydryl group to the peptide linkage. Analogous to observations on the carboxyl group in peptides,[11] this tends to ease the splitting off of the proton. Apparently the peptide linkage has a similar effect on the dissociation of the mercury in the mercaptide of glutathione as it has on the dissociation of hydrogen from the sulfhydryl group. This may largely account for the fact that pK_{III} of glutathione is markedly smaller than pK_{III} of cysteine (see Table III).

Heats and entropies of formation of the mercaptides of TSH, RSH and GSH are about of the same order of magnitude. The ΔH values increase in magnitude from the I to the III species while the ΔS values decrease in the same direction.

Comparison of the three thiol compounds indicates that the stability of the mercuric mercaptides is determined mainly by the strength of the mercury–sulfur bonds while uncharged amino and carboxyl groups, either charged or uncharged, have but little effect on the stability of these mercaptides.

Acknowledgment.—This investigation was supported by a research grant from the National Cancer Institute, U. S. Public Health Service.

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[10] E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943.

[11] M. Zief and J. T. Edsall, THIS JOURNAL, **59**, 2245 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRIGHAM YOUNG UNIVERSITY]

Rhenium Sulfides as Liquid-Phase Hydrogenation Catalysts. A Comparison with Molybdenum Sulfide and Cobalt Polysulfide

BY H. SMITH BROADBENT, LYNN H. SLAUGH[1a] AND N. LYNN JARVIS[1b]

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Rhenium heptasulfide and rhenium disulfide hydrogenation catalysts have been prepared and examined for catalytic activity toward a variety of substrates in comparison with the well-known molybdenum sulfide and cobalt polysulfide catalysts. In these experiments rhenium heptasulfide was most active, rhenium disulfide less so, and molybdenum and cobalt sulfides much less so. Some advantages enjoyed by the rhenium heptasulfide hydrogenation catalyst are as follows: Consistent and easy reproducibility, activity maintained indefinitely by simple storage in a closed bottle, stability to hydrogenative decomposition at high temperatures, extreme resistance to "poisoning," insolubility in strong, non-oxidizing acids, and ability to saturate multiple bond systems without accompanying hydrogenolysis of carbon–sulfur bonds. Its chief disadvantages are its relatively high cost, due in considerable part to the lack of established demand for rhenium compounds, and the fact that it is not as active toward most non-sulfur containing compounds as some nickel, platinum and palladium catalysts.

Introduction

A good hydrogenation catalyst should be active toward a variety of substrates at relatively low temperatures and should be resistant to "poisoning"; moreover, a useful degree of specificity of catalytic activity toward different reducible groups is highly desirable. The metal sulfide catalysts[2] as a group are outstanding in their resistance to "poisoning," but they show very little specificity of action, in large part due to the relatively high temperatures (250–500°) required for their use, which often results in considerable pyrolysis of the substrate(s).

In connection with a general investigation on the catalytic properties of rhenium and its compounds in organic reactions being carried out in these laboratories, preparations of rhenium disulfide and rhenium heptasulfide have been obtained which appear to be significantly superior in some reactions to sulfide catalysts heretofore reported. In the highly empirical science of contact catalysis comparisons are difficult because of differences in experimental conditions. In an effort to achieve valid comparisons two of the most widely employed sulfide catalysts, molybdenum sulfide,[3] and cobalt polysulfide,[4] were prepared and studied along with the rhenium sulfides under closely similar conditions. It is recognized, of course, that cobalt polysulfide catalysts exhibit a rather specialized kind of activity but, since this activity is great, it seemed desirable to include it in the study.

The only specific references to the activity of rhenium sulfides as hydrogenation catalysts report that rhenium disulfide is a superior catalyst for the dehydrogenation of alcohols at 400–550°, but that the reverse reaction is little affected,[5] that rhenium heptasulfide hydrogenates cresol in part to gasoline at 450° and 1400 p.s.i.[6] and that coal, lignin, as-

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[1] (a) Performed work on rhenium sulfides and cobalt polysulfide. (b) Performed work on the molybdenum sulfide.

[2] A valuable summary of the activity of various substances in catalytic hydrogenations and dehydrogenations covering the literature up to 1940 is provided by S. Berkman, J. C. Morrell and Gustav Egloff, "Catalysis," Reinhold Publ. Corp., New York, N. Y., 1940, pp. 809–906.

[3] The following few references are representative of the nearly one hundred references dealing with molybdenum sulfide catalysts: W. H. Jones, U. S. Patent 2,112,292 (Mar. 29, 1938); A. F. Nikolaeva and P. V. Puchkov, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1153 (1938); **9**, 277 (1939); P. C. Condit, *Ind. Eng. Chem.*, **41**, 1704 (1949); B. L. Moldavskii and S. Livshitz, *J. Gen. Chem.*, (*U.S.S.R*), **4**, 948 (1934); V. F. Polozov, *Khim. Tverdogo Topliva*, **6**, 78 (1935) [*C. A.*, **29**, 7294 (1935)]; Lee C. Cheney, British Patent 608,969 (Sept. 23, 1948); E. Krebs, W. Demann and H. Brochers, *Tech. mitl. Krupp. Tech.*, **6**, 59 (1938) [*C. A.*, **33**, 6257 (1939)]; Grant S. Stewart, U. S. Patent 2,490,488 (Dec. 6, 1949); E. I. Prokopetz, *et al.*, *J. Applied Chem.* (*U.S.S.R.*), **11**, 1475 (1938); W. G. Appleby, *et al.*, U. S. Patent 2,429,575 (Oct. 21, 1947); S. Andō, *J. Chem. Ind., Japan*, **41**, suppl. binding, 413 (1938); M. K. D'yakova and A. V. Losovoi, *Compt. rend. acad. sci. U.R.S.S.*, **2**, 254 (1935) [*C. A.*, **29**, 6396 (1935)].

[4] The following are representative of the literature on cobalt polysulfide catalysis: M. W. Farlow, *et al.*, THIS JOURNAL, **70**, 1392 (1948); M. W. Farlow and F. K. Signaigo, U. S. Patent 2,402,613 and U. S. Patent 2,402,614 (June 25, 1946); W. A. Lazier, F. K. Signaigo and L. G. Wise, U. S. Patent 2,402,645 (June 25, 1946); W. A. Lazier and F. K. Signaigo, U. S. Patent 2,402,641 (June 25, 1946); and E. I. du Pont de Nemours, British Patent 577,279 (May 13, 1946).

[5] M. S. Platanov, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 683 (1941) [*C. A.*, **36**, 397 (1942)].

[6] N. v. de Bataafsche Petroleum Maatschappij, British Patent 358,180, July 29, 1930 [Gmelins Handbuch der anorganischen Chemie, 8th Ed., Verlag Chemie, Berlin, No. 70, p. 40].

phalt, etc., are similarly hydrogenated at 1500 p.s.i. and 430°.[7] However, it is also reported that rhenium "partially 'poisoned' " by hydrogen sulfide or arsenic trisulfide dehydrogenates methanol,[8] ethanol,[8] cyclohexanol,[9] isoamyl alcohol,[10] *n*-butyl alcohol[11] and isobutyl alcohol[11] at *ca.* 350–400°. Also rhenium sulfides are listed in the patent literature along with a group of many metallic sulfides as effective in the destructive hydrogenation of oils and other carbonaceous substances at above 400°.[12]

The study herein reported consisted of the preparation of rhenium heptasulfide, rhenium disulfide, molybdenum trisulfide and cobalt polysulfide followed by an investigation of their catalytic activity in the hydrogenation of a rather diverse variety of substrate compounds under minimal conditions of temperature and pressure. The catalysts were easily prepared, and their activity was regularly duplicable. The results given below are representative.

Experimental

Preparation of Catalysts. Rhenium Heptasulfide.—Hydrogen sulfide was bubbled through 3% solutions of potassium perrhenate in 5–6 *N* hydrochloric acid maintained at the boiling point until precipitation was complete. The suspensions were allowed to stand overnight and then filtered through fine sintered glass crucibles. The precipitate was washed with 1:4 hydrochloric acid followed by distilled water, dried for several days over anhydrous calcium chloride in a desiccator, finely powdered with a mortar and pestle, and stored in an ordinary screw cap vial. Catalyst activity did not seem to be adversely affected by occasional exposure to the atmosphere. The lower than theoretical sulfur content is probably due to the presence of moisture and perhaps some conversion of the rhenium to its heptoxide.

Anal. Calcd. for Re_2S_7: S, 37.63. Found: S, 35.92.

Rhenium Disulfide.—Rhenium heptasulfide prepared as indicated above was heated for 16 hours at 350–400° in a tube furnace under a stream of carbon dioxide to sweep out the sulfur vapor leaving the disulfide behind. After cooling in a desiccator, the catalyst was stored in an ordinary screw cap vial. The lower than theoretical sulfur content is probably due to some oxidation of the catalyst.

Anal. Calcd. for ReS_2: S, 25.61. Found: S, 23.31.

Molybdenum Sulfide.—A 13% solution of ammonium molybdate in 0.3 *N* hydrochloric acid was heated to boiling while a rapid stream of hydrogen sulfide was bubbled in until precipitation was complete. After standing overnight the blue-black suspension was filtered, dried, ground, and stored as indicated for rhenium heptasulfide. While the catalyst was not analyzed, it was assumed to be predominately molybdenum trisulfide.[13]

Cobalt polysulfide was prepared according to published directions.[14]

Hydrogenation Procedure.—The compound to be reduced (usually 0.2 mole), a solvent or diluent (usually ethanol), and the catalyst (usually 2.5 g./mole of substrate) were placed in the hydrogenation bomb, which was then charged with hydrogen under pressures varying from 800 to 4400 p.s.i. depending on the difficulty of reduction. In most cases an Aminco rocking type bomb was used which operated at the fixed rocking speed of 37 cycles per minute. In a few cases, a Magne-dash (Autoclave Engineers, Inc.) apparatus, which has variable agitation, was employed. It was operated at *ca.* 35–40 cycles per minute. The usual procedure was to maintain the temperature at a fairly low value initially, and if no appreciable reduction was observed (pressure change was the criterion), successively higher temperatures were employed until reduction proceeded at an appreciable rate, if at all. In this way approximately minimal temperatures were obtained, in many cases, for reduction of a given substrate. In most cases more than one reduction was run in order to check results. Duplicability was good. In those cases where a given compound was reduced both directly in contact with the walls of the type 316 stainless steel bomb and with the use of a glass liner, while maintaining all other known factors identical, no detectable difference could be discerned in the course of the reaction.

Analysis of Reaction Product.—The solvent was removed by distillation and the residue analyzed by fractional distillation, chemical extraction, or in the case of binary mixtures, refractometrically.

Discussion of Results

Rhenium Heptasulfide.—Repeated preparations of this catalyst did not vary significantly in activity, moreover, they retained their activity indefinitely when stored in the dry powdered form in an ordinary vial. The catalyst was insoluble in concentrated non-oxidizing acids; it was easily prepared, and it was extremely stable under all conditions of hydrogenation in which it was employed, *i.e.*, it was not reduced to form hydrogen sulfide. As anticipated, it was remarkably resistant to "poisoning." For instance, large amounts of sulfur compounds (hydrogen sulfide, thiols, etc.) were added to nitrobenzene and styrene without significantly affecting their course of reduction.

Attention may be called to several conclusions evident from Table I.

The carbon–carbon double bond conjugated with a benzene ring in styrene or a carboxyl group in maleic acid was much more easily reduced than the isolated double bond in cyclohexene, whereas the isolated double bond in allyl phenyl sulfide was nearly as easily reduced as that in styrene. Dimethylphenylcarbinol was easily dehydrated and reduced in a single step.

The carbon–oxygen double bond (acetophenone) was more difficultly reduced than the carbon–carbon double bond (styrene) as expected.

The reduction of acetophenone to the carbinol was accompanied by considerable catalytic debenzylation at *ca.* 100°, and at the higher temperatures the latter became predominant.

The conjugated system of unsaturation presented by cinnamic aldehyde was not selectively reduced.

The nitro group was easily reduced at room temperatures or slightly higher without accompanying hydrogenolysis of ring bound halogen. Indeed, ring bound halogen was extremely resistant to hydrogenolysis by this catalyst (*cf.* no. 17, 18, 19).

The side reactions leading to secondary and tertiary amines which accompany the reduction of nitriles to primary amines can sometimes be minimized by operating under acidic conditions. Since rhenium sulfides are not attacked by rather high concentrations of non-oxidizing acids, the use of that catalyst was indicated in such cases; the data shown were not encouraging, however.

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[7] N. v. de Bataafsche Petroleum Maatschappij, British Patent 362,354 (1930) ["Gmelin," ref. 6].

[8] M. S. Platanov, *et al.*, *J. Gen. Chem. U.S.S.R.*, **7**, 1803 (1937) [*C. A.*, **31**, 8341 (1937)].

[9] E. V. Tur, S. B. Anisimov and M. S. Platanov, *ibid.*, **7**, 2895 (1937) [*C. A.*, **32**, 5383 (1938)].

[10] M. S. Platanov, *ibid.*, **11**, 590 (1941) [*C. A.*, **35**, 6924 (1941)].

[11] M. S. Platanov and S. B. Anisimov, *ibid.*, **7**, 1350 (1937) [*C. A.*, **31**, 8503 (1937)].

[12] International Hydrogenation Patents, French 793,227 (Jan. 20, 1936); French 793,799 (Jan. 31, 1936); French 765,923 (June 18, 1934); British 427,435 (May 23, 1935) [S. Berkman, *et al.*, ref. 2, pp. 866, 876].

[13] *Cf.* W. H. Jones, ref. 3.

[14] See the first reference listed under ref. 4.

TABLE I

HIGH PRESSURE HYDROGENATION WITH RHENIUM HEPTASULFIDE CATALYST

No.	Substrate reduced	Amt. cat. (g./mole) substrate	Solvent	Ave.[a] pressure, p.s.i.	Ave. temp., °C.	Time, hr.	Yields,[b] %,	product
1	Styrene	0.5	Ethanol	1500	25	20	3.5	Ethylbenzene
2	Styrene	2.5	Ethanol	1700	100–135	1	100	Ethylbenzene
3	Phenylacetylene	2.5	Ethanol	1900	106–135	1.75	70	Ethylbenzene
4	Dimethylphenylcarbinol	2.5	Ethanol	2000	130	0.33	100	Cumene
5	Cyclohexene	0.5	Ethanol	2000	240	3	92	Cyclohexane
6	Cyclohexene	0.5	None	2000	180	5	40	Cyclohexane
7	Benzene	2.5	None	4400	225	7	5.5	Cyclohexane
							94.5	Benzene
8	Benzene	2.5	None	3400	300	9	57	Cyclohexane
							43	Benzene
9	Naphthalene	2.5	Ethanol	3000	300	4	0	Reduction
10	Maleic acid	1.0	Water	1300	150	<5	100	Succinic acid
11	Cinnamic aldehyde	0.5	Ethanol	2000	180–200	<7.5	15	Hydrocinnamic aldehydes
							29	Hydrocinnamyl alcohol
							12	*n*-Propylbenzene
12	Acetophenone	2.5	Ethanol	2300	216–230	0.17	85	Ethylbenzene
							15	Methylphenylcarbinol
13	Acetophenone	2.5	Ethanol	2000	105–125	1.66	26	Ethylbenzene
							22	Methylphenylcarbinol
14	Nitrobenzene	2.5	Ethanol	900	25	7	65	Aniline
15	Nitrobenzene	2.5	Ethanol	1900	25	6	100	Aniline
16	Nitrobenzene	2.5	Ethanol	1900	60–100	0.5	100	Aniline
17	*p*-Nitrobromobenzene	2.5	Methylcellosolve	1900	60	0.5	100	*p*-Bromoaniline
18	Bromobenzene	2.5	Methylcellosolve	2700	225–250	3	89	Bromobenzene
							11	Benzene
19	Bromobenzene	2.5	Methylcellosolve	3500	320–335	2.5	30	Benzene
							70	Cyclohexane
20	Benzonitrile	2.5	Ethanol	3000	180–210	0.5	22	Benzylamine
							58	Dibenzylamine
21	Benzonitrile	2.5	Acetic acid	2200	125–170	1	6	Benzylamine
							51	Dibenzylamine
							16	Tribenzylamine
22	Benzonitrile	2.5	Acetic acid + HCl	2600	170–260	1.33		No reduction
							100	Benzoic acid
23	Allyl phenyl sulfide	2.5	Ethanol	1900	100–110	2	23.5	*n*-Propyl phenyl sulfide
24	Allyl phenyl sulfide	2.5	Ethanol	1900	150–160	0.5	100	*n*-Propyl phenyl sulfide
25	Diphenyl sulfide	2.5	None	2300	280–300	2	94	Benzene
26	Diphenyl disulfide	2.5	Methylcellosolve	2200	165–195	1	100	Thiophenol
27	Thiophenol	2.5	Ethanol	3600	300	9	60–65	Benzene
							35–40	Cyclohexane
28	Thiophene	2.5	None	2000	230–260	3.75	70	Thiophane
							0	Butyl mercaptan

[a] Figures in this column refer to the average total pressure of the system at the temperature shown. [b] The yields column shows only the reduced product. Unless otherwise specified the remainder of recovered material was unreduced substrate. In most cases the percentage figure given is based on 100% recovery of all products of reaction. The same reservations apply also to the other tables contained in this paper.

The stability of the carbon–sulfur bond to hydrogenolysis by this catalyst was notable (*cf.* Raney nickel). Thus allyl phenyl sulfide yielded only *n*-propyl phenyl sulfide; diphenyl disulfide yielded only thiophenol at 165–195°; thiophene yielded only thiophane at 230–260°; and only under the drastic conditions of *ca.* 300° did carbon–sulfur bond scission occur, *i.e.*, thiophenol to cyclohexane and benzene, and diphenyl sulfide to benzene.

Rhenium Disulfide.—While rhenium disulfide was a more active catalyst in the three cases studied than the molydenum and cobalt catalysts, its activity was parallel to but lower than that of rhenium heptasulfide (see Table II).

Molybdenum Sulfide.—Five different modifications of the method of preparing molybdenum sulfide were employed, but the different preparations did not vary significantly in activity.

The catalyst was assumed to be a mixture of molybdenum trisulfide and molybdenum disulfide under the conditions of use.[15]

Table III shows that the molybdenum sulfide was much less active in general than the rhenium sulfides, although the reduction products were the same except in two cases. Considerable hydrogenolysis of the carbon–sulfur bond in thiophene

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[15] W. Biltz and A. Köcher, *Z. anorg. Chem.*, **248**, 172 (1941) [*C. A.*, **37**, 2674 (1943)].

TABLE II

HIGH PRESSURE HYDROGENATION WITH RHENIUM DISULFIDE CATALYST IN ETHANOL

No.	Substrate reduced	Amt. cat. (g./mole) substrate	Solvent	Ave. pressure, p.s.i.	Ave. temp., °C.	Time, hr.	Yields, %, product	
1	Styrene	1.0	Ethanol	2000	150–180	1	63	Ethylbenzene
							Remainder	Polymerized styrene
2	Nitrobenzene	0.5	Ethanol	1800	110–200	2	94	Aniline
3	Allyl phenyl sulfide	2.5	Ethanol	2300	240–245	1	91	*n*-Propyl phenyl sulfide

TABLE III

HIGH PRESSURE HYDROGENATION WITH MOLYBDENUM SULFIDE CATALYST

No.	Substrate reduced	Amt. cat. (g./mole) substrate	Solvent	Ave. pressure, p.s.i.	Ave. temp., °C.	Time, hr.	Yields, %, product	
1	Styrene	2.5	Acetone	2000	120	3	8	Ethylbenzene
2	Cyclohexene	2.5	None	2800	250	4	22	Cyclohexane
3	Benzene	2.5	None	3800	250	4.5	0	Reduction
4	Benzene	2.5	None	4100	320	6	0	Reduction
5	Naphthalene	2.5	Ethanol	3650	270	4	0	Reduction
6	Maleic acid	2.5	Water + acetone	2000	120	5	0	Reduction
7	Cinnamic aldehyde	2.5	Ethanol	1900	250	5	11	Cinnamyl alcohol
							23	Hydrocinnamyl alcohol
							12	Hydrocinnamic aldehyde
							18	*n*-Propylbenzene
8	Acetophenone	2.5	Ethanol	2600	200	6	18	Methylphenylcarbinol
							29	Ethylbenzene
9	Nitrobenzene	2.5	Ethanol	1725	65	3.5	0	Aniline (reduction)
10	Nitrobenzene	2.5	Ethanol	2300	120	2.5	0	Reduction
11	*p*-Nitrobromobenzene	2.5	Ethanol	2500	130	3.5	0	Reduction
12	Bromobenzene	2.5	Ethanol	3100	340	4	25	Benzene
13	Benzonitrile	2.5	Ethanol	2800	325	4	85	Toluene (+ NH_3)
							9	Benzylamine
14	Diphenyl sulfide	2.5	Ethanol	3600	300	6.5	40	Benzene
15	Thiophene	2.5	None	2400	300	2.5	7	Thiophane + H_2S evolved
							33	Thiophene recovery

was observed using molybdenum sulfides in contrast to the lack of it using rhenium sulfides. The conditions for reducing benzonitrile using molybdenum sulfides were much more drastic than those employed with the rhenium catalyst; also the reduction products were different as might be expected, being principally toluene and ammonia in the former case and benzylamines in the latter case.

Cobalt Polysulfide.—Perhaps the most interesting of all the sulfide catalysts reported in the literature are the polysulfides of cobalt, particularly, and of various related elements. While they are active under relatively mild conditions (*ca.* 150° and 1000 p.s.i.), they display their activity in a very limited series of reaction types only. In all reported cases thiols are produced either by carbon-sulfur or sulfur-sulfur bond scission or by reducing carbonyl compounds, olefins, nitriles, etc., in the presence of elemental sulfur or hydrogen sulfide.

The catalytic activity of cobalt polysulfide toward several substrates in the absence of added sulfur or hydrogen sulfide is shown in Table IV.

TABLE IV

HIGH PRESSURE HYDROGENATION WITH A COBALT POLYSULFIDE CATALYST[a]

No.	Substrate reduced	Amt. cat. (g./mole) substrate	Solvent	Ave. pressure, p.s.i.	Ave. temp., °C.	Time, hr.	Yield, %, product	
1	Styrene	2.5	Ethanol	2300	160–190	2.5	0	Ethylbenzene
							All	Polymerized styrene[b]
2	Cyclohexene	2.5	Ethanol	3000	275–300	4	17	Cyclohexane
							16	Unidentified by-prod.
3	Benzene	2.5	Ethanol	5000	350	3	0	Cyclohexane
4	Maleic acid	2.5	Water	2700	135–250	2	0	Succinic acid[c]
5	Acetophenone	2.5	Ethanol	3100	270–275	1	8	Ethylbenzene
							20	α-Methylbenzyl alcohol
6	Nitrobenzene	2.5	Ethanol	2000	70–150	0.5	100	Aniline
7	Benzonitrile	2.5	Ethanol	2000	180–220	2.5	7.3	Unidentified, remainder unreduced
8	Allyl phenyl sulfide	2.5	Ethanol	2500	175–200	2	32	Thiophenol
9	Diphenyl sulfide	2.5	Ethanol	3000	250–275	4	4	Unidentified, remainder unreduced

[a] In no case was elemental sulfur added to the reaction mixture. [b] The polymerization of styrene seemed to be catalyzed strongly under these conditions. [c] The catalyst was completely dissolved by the maleic acid.

It will be observed that the catalytic activity of cobalt polysulfide under the conditions of study was even less than that of molybdenum sulfide in every comparable case except toward nitrobenzene. The rate of reduction of the nitro group by cobalt polysulfide was nearly as great as by rhenium heptasulfide.

The most noteworthy difference between the behavior of cobalt polysulfide and rhenium heptasulfide, other than the markedly lower activity of the former in most cases, can be noticed in connection with the hydrogenation of allyl phenyl sulfide. The cobalt catalyst cleaves the carbon–sulfur bond, as reported, to yield thiophenol, whereas rhenium heptasulfide does not, yielding rather *n*-propyl phenyl sulfide. Another difference is a disagreeable formation of hydrogen sulfide from the cobalt catalyst even under mild conditions, but never from the rhenium heptasulfide catalyst even under the most drastic conditions employed. The cobalt catalyst was completely dissolved by maleic acid, whereas the rhenium sulfides were unattacked even by strong, non-oxidizing, mineral acids.

A brief tabular comparison of the catalysts is presented by Table V.

TABLE V

COMPARISON OF CATALYTIC ACTIVITY OF SULFIDE CATALYSTS UNDER COMPARABLE CONDITIONS

		Yield of reduction product(s), %		
No.	Substrate	Rhenium hepta-sulfide	Molyb-denum sulfide	Cobalt poly-sulfide
1	Styrene	100	8	0
2	Cyclohexene	92	22	17
3	Benzene	57		0
4	Naphthalene	0	0	..
5	Maleic acid	100	0	0
6	Nitrobenzene	100	0	100[a]
7	Bromobenzene	100[b]	25[c]	..
8	*p*-Nitrobromobenzene	100	0	..
9	Diphenyl sulfide	94	40	4

[a] Conditions considerably more drastic than for rhenium heptasulfide. [b] 30% benzene, 70% cyclohexane. [c] Benzene only.

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PROVO, UTAH

[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

The Oxidation of Carbon Monoxide in the Presence of Ozone[1]

BY DAVID GARVIN

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The rate and mechanism of the oxidation of carbon monoxide in mixtures of CO, O_2, N_2 and small amounts of ozone have been studied at atmospheric pressure in the temperature range 430–565°K. The production of carbon dioxide is slight and can best be explained by the reaction (III): $CO + O + M \rightarrow CO_2 + M$, which has no activation energy and occurs every 10^3 three body collisions.

Introduction

A direct reaction between carbon monoxide and ozone has been considered in photochemical and combustion studies. In the former all carbon dioxide production has been attributed to reaction (III).[2-4] Lewis and von Elbe[5] analyzed the high pressure explosion limit of carbon monoxide–oxygen mixtures in terms of the chain breaking and branching steps

$$M + CO + O_3 \longrightarrow CO_2 + O_2 + M \qquad (IV)$$

$$CO + O_3 \longrightarrow CO_2 + O + O \qquad (V)$$

and deduced an activation energy difference $E^*_5 - E^*_4 = 35$ kcal.

Trautz[6] and Kondrateev[7] have studied the radiation emitted by heated carbon monoxide–ozone–oxygen mixtures. Both found the radiation intensity to vary approximately with the first power of the CO and O_3 concentrations. The latter reported that the spectrum of the radiation was identical with that of CO–O_2 flames and that reaction IV with an activation energy of 8.8 kcal. was necessary to account for the carbon dioxide production.

The unimportance of ozone in photochemical studies and its instability at moderate temperature (half life less than 5 sec. at 200°) made it questionable whether or not it could be an important intermediate at the explosion temperature. Therefore a study of the rate and mechanism of the oxidation of carbon monoxide by traces of ozone at moderate temperatures has been carried out.

Experimental

The oxidation of carbon monoxide is slower than the thermal decomposition of ozone. Both processes were studied in the temperature range 430 to 565°K. by a conventional flow method in the same apparatus.

1. **Reagents.**—Carbon monoxide was produced in a continuous generator[8] from 90% formic acid and tech. acetic anhydride containing a trace of sulfuric acid as catalyst.[9] The gas was scrubbed with 30% sodium hydroxide in a 30 inch column packed with broken unglazed porcelain, dried by calcium chloride, Drierite and magnesium perchlorate and then metered into the reaction system. Tank oxygen and prepurified nitrogen (American Oxygen Service Corp.) were used after drying with magnesium perchlorate. The

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[1] This research was supported in whole or in part by the United States Air Force under Contract No. AF33(038)-23976 monitored by the Office of Scientific Research.

[2] P. Harteck and U. Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

[3] W. Groth and P. Harteck, *Z. Elektrochem.*, **44**, 621 (1938); W. Groth, *Z. physik. Chem.*, **B37**, 315 (1937).

[4] W. F. Jackson, THIS JOURNAL, **56**, 2631 (1934).

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