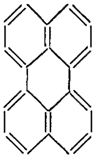
333. *Synthetical Applications of Activated Metal Catalysts. Part IX.* A Comparison of the Desulphurising Abilities of Some Transition Metals.*

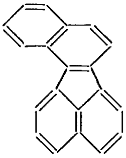
By G. M. Badger, N. Kowanko, and W. H. F. Sasse.

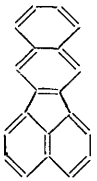
A direct comparison has been obtained between the desulphurising abilities of certain transition metals towards di-1-naphthyl sulphide and dihexyl sulphide. Untreated metals such as copper bronze, zinc dust, precipitated silver, reduced iron, and nickel were inactive towards di-1-naphthyl sulphide at 200°. Raney nickel, cobalt, iron, and copper acted as desulphurising agents, but not all equally effectively. Raney tungsten was inactive towards di-1-naphthyl sulphide at 200°, but it effected some desulphurisation of dihexyl sulphide; Raney nickel, cobalt, iron, and copper were similarly active. Increase in the temperature and presence of external hydrogen facilitate the desulphurisation.

The ability of Raney nickel to remove sulphur has been extensively investigated, not only for the degradation of naturally occurring compounds, but also for organic syntheses,[1,2] and recently Raney cobalt has been used.[3] Desulphurisation with copper and with zinc at elevated temperatures was observed as early as 1886,[4] and was recently studied in connection with the synthesis of derivatives of phenanthrene, phenanthridine, and other nitrogen polycycles.[5] Hauptmann [6] also observed desulphurisation by strongly degassed Raney iron, Raney copper, and Raney cobalt at high temperatures. In view of the increasing interest in desulphurisation with transition metals, a direct comparison between the various metals under varying conditions has been undertaken.

Desulphurisation of di-1-naphthyl sulphide was found to require a highly active catalyst. Copper bronze was without effect on the sulphide up to 300°, and reaction could not be promoted in ethyl benzoate or diethyl phthalate. Reduced iron, reduced nickel, zinc dust, and precipitated silver were inactive at 200°. However a small amount of desulphurisation occurred when this sulphide was fused with zinc dust at 400°: naphthalene, perylene (I), benzo[*j*]fluoranthene (II), and an unidentified hydrocarbon were isolated in very small amounts. A small amount of desulphurisation also occurred on using copper bronze which had been activated with iodine in acetone.[7]


(I)


(II)


(III)

Raney metals were found to be much more effective. Freshly prepared W7 Raney nickel [8] in boiling methanol completely desulphurised di-1-naphthyl sulphide and also effected some hydrogenation to tetralin. Raney nickel contains a large volume of hydrogen,[9] so the hydrogenation is clearly a secondary effect, for naphthalene was

---

* Part VIII, *J.*, 1960, 526.

[1] Badger, *Austral. J. Sci.*, 1958, **21**, 45.

[2] Venkataraman, *J. Indian Chem. Soc.*, 1958, **35**, 1.

[3] Aller, *J. Appl. Chem.*, 1957, **7**, 130; 1958, **8**, 163; Badger, Kowanko, and Sasse, *J.*, 1959, 440.

[4] Ris, *Ber.*, 1886, **19**, 224; Goske, *Ber.*, 1887, **20**, 232; Kym, *Ber.*, 1890, **23**, 2458.

[5] Loudon *et al.*, *J.*, 1957, 3814, 3818; 1958, 1588; 1959, 885.

[6] Hauptmann, *Angew. Chem.*, 1958, **70**, 168; and personal communication.

[7] Kleiderer and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 4225.

[8] Billica and Adkins, *Org. Synth.*, Coll. Vol. III, p. 176.

[9] Mozingo, Wolf, Harris, and Folkers, *J. Amer. Chem. Soc.*, 1943, **65**, 1013.

hydrogenated to tetralin under the same experimental conditions. On the other hand, an aged W7 Raney nickel gave only naphthalene and a trace of 1,1′-binaphthyl; and a W7 Raney nickel which had been deprived of most of its hydrogen (W7-J) [10] at 100°/12 mm. was inactive as a desulphurising agent in boiling methanol. However, this degassed nickel was effective at higher temperatures, in boiling xylene and in diethyl phthalate at 220°, and gave mixtures of naphthalene and 1,1′-binaphthyl, together with small amounts of 2,2′-binaphthyl, perylene (I), and benzo-[*j*]- and -[*k*]-fluoranthene (II and III).

The formation of 1,1′-binaphthyl and the other condensed hydrocarbons is consistent with the view that desulphurisation gives naphthyl radicals which then react with hydrogen (to give naphthalene) or with similar radicals (to give the dimeric and condensed products). Catalytic cyclodehydrogenation of 1,1′-binaphthyl at the temperature of the reaction would give the benzo[*j*]fluoranthene (II) and perylene (I) observed.

The formation of small amounts of 2,2′-binaphthyl with degassed Raney nickel is surprising. The quantity was too large to have arisen from impurity in the di-1-naphthyl sulphide and, as 1,1′-binaphthyl does not rearrange to 2,2′-binaphthyl under the conditions of the experiment, it seems that the intermediate 2-naphthyl radicals must arise by rearrangement of 1-naphthyl radicals. No 1,2′-dinaphthyl was detected, but this substance could undergo catalytic cyclodehydrogenation at the temperature of the reaction to benzo-[*j*]- and -[*k*]-fluoranthene, both of which were observed (benzo[*j*]fluoranthene could also be formed by cyclodehydrogenation of 1,1′-binaphthyl).

Desulphurisation with Raney cobalt was similar to that with W7-J Raney nickel in that, although little reaction occurred in boiling methanol, it was complete in diethyl phthalate at 220°. However the yields of the different products obtained with the two catalysts were by no means the same, for cobalt produced mainly naphthalene, with very little binaphthyl and only traces of condensed products. The dimerisation of radical intermediates probably occurs on the catalyst surface; but the alternative reaction with hydrogen, to form naphthalene, could conceivably occur either on the catalyst or in solution. The difference in the monomer : dimer ratio could then be a measure of the difference between the abilities of the metals to chemisorb the radicals.

The effect of temperature was also observed with both Raney copper and Raney iron. These metals were almost inactive as desulphurising agents in boiling methanol, and produced reasonable yields of desulphurised products at higher temperatures. Raney tungsten was inactive even at 200°.

The degassing of W7 Raney nickel may result in a decrease in the surface area of the catalyst, and the amount of chemisorbed hydrogen is said to be directly related to the surface area.[11] In the circumstances it would be unwise to conclude from a comparison of W7 Raney nickel and the degassed nickel that hydrogen plays a direct part in the desulphurisation. Its participation has, however, been conclusively demonstrated with both Raney copper and Raney iron: in both cases reaction in a hydrogen atmosphere increased the yields of desulphurised products.

As the removal of the loosely bound hydrogen by degassing renders Raney nickel inactive as a desulphurising agent, it must be this hydrogen which facilitates desulphurisation. A higher reaction temperature evidently releases hydrogen from the interstitial positions in the metal, and desulphurisation is again facilitated. Hauptmann *et al.*[12] suggested that the function of the hydrogen is to assist scission of the C–S bond, perhaps by displacing the radicals from the sulphur, and our results are not inconsistent with this view. Nevertheless Hauptmann and his colleagues showed that desulphurisation can be effected with nickel practically free from hydrogen provided the temperature is sufficiently high.

Further experiments were carried out with dihexyl sulphide. The Raney metals were

[10] Badger and Sasse, *J.*, 1956, 616.

[11] Smith, Chadwell, and Kirslis, *J. Phys. Chem.*, 1955, **59**, 820.

[12] Hauptmann, Walter, and Marino, *J. Amer. Chem. Soc.*, 1958, **80**, 5832.

all obtained in a hydrogen atmosphere, and the desulphurisations were effected at 220° in the presence of external hydrogen. Under these conditions nickel, cobalt, and iron gave complete desulphurisation, but copper gave only 22%. It is also noteworthy that Raney tungsten (which did not react with di-1-naphthyl sulphide at 200°) reacted to an appreciable extent with dihexyl sulphide; and even reduced nickel showed some activity.

No dodecane was detected in any experiment; but this is not surprising as the reactions were carried out in a hydrogen atmosphere, and the reduction of the intermediate hexyl radical would be greatly facilitated. Moreover, it is known that alkyl radicals readily disproportionate to alkane and alkene.[6,13] The latter would be readily hydrogenated under the conditions used.

EXPERIMENTAL

Di-1-naphthyl Sulphide.—This was prepared from 1-naphthylmagnesium bromide and thionyl chloride by Courtot and Paivar's method,[14] except that the intermediate sulphoxide was not isolated. After repeated recrystallisation from ethanol, chromatography in light petroleum on alumina, and further recrystallisation, the sulphide formed colourless needles, m. p. 110° (Found: C, 84·1; H, 5·0; S, 11·4. Calc. for $C_{20}H_{14}S$: C, 83·9; H, 4·9; S, 11·2%).

Desulphurisation with "Inactive" Metals.—Copper bronze, zinc dust, and reduced iron powder were commercial products (B.D.H.). The silver was precipitated with zinc dust from silver chloride in aqueous suspension. Reduced nickel was prepared by heating nickel oxide in a stream of hydrogen at 500°.

Di-1-naphthyl sulphide (2 g.) was heated with the metal (5 g. of nickel or an equivalent amount of other metal) at 200° for 4 hr. The melt was then extracted with benzene–hexane, and the solution chromatographed on alumina in light petroleum. In each case (copper bronze, zinc dust, iron, silver, nickel) 91—99% of unchanged sulphide was recovered, and $\not>$0·1% of naphthalene could be detected except in the silver experiment. No naphthalene was obtained on attempted desulphurisations with copper bronze in boiling ethyl benzoate or in diethyl phthalate. Heating the sulphide with zinc dust at 400° gave a mixture from which dinaphthyl sulphide (87·5%) and naphthalene (3·95%) were isolated. Traces of perylene, benzo[*j*]fluoranthene, and an unknown substance (m. p. 298—300°) were also obtained. Perylene and benzofluoranthene were identified by chromatography on acetylated paper and by their ultraviolet spectra. Heating with iodine-activated copper bronze[7] at 290° gave unchanged dinaphthyl sulphide (87·8%), naphthalene (3·14%), and a trace of perylene.

Comparison of Raney Metals by using Di-1-naphthyl Sulphide.—W7 Raney nickel was prepared by the method of Billica and Adkins.[8] Aged W7 Raney nickel had been kept for 3 months under methanol. W7-J Raney nickel was obtained by the method already described.[10] W7 Raney cobalt was prepared from 3 : 7 cobalt–aluminium alloy (Lights) by the procedure used for nickel;[8] Raney iron was obtained from 1 : 1 iron–aluminium alloy (Fluka) by the method of Johnston *et al.*[15] except that hydrogen or nitrogen was used instead of argon to supply the inert atmosphere, and the catalyst was washed with methanol instead of pyridine. Raney copper was similarly prepared[15] from 1 : 1 copper–aluminium alloy (Fluka); and W7 Raney copper was prepared by the method used for nickel.[8] W7 Raney tungsten was prepared from 3 : 7 tungsten–aluminium alloy (obtained by igniting a mixture of tungsten trioxide and aluminium bronze), the procedure for nickel being used.

(i) *Desulphurisations in diethyl phthalate.* Freshly prepared catalyst (5 g.) was washed by decantation with methanol, transferred quickly to the reaction flask, and diethyl phthalate (5 ml.) and di-1-naphthyl sulphide (2 g.) were added. The mixture was cautiously distilled to remove water and methanol, and then heated in a metal-bath under hydrogen or nitrogen at 220° for the specified time. The cooled mixture was heated with potassium hydroxide solution under reflux, to saponify the ester, and then extracted with ether, and the ether extract was dried and evaporated to give a residue which was sublimed at 100°/15 mm. to remove any naphthalene. The residue was recrystallised from light petroleum (b. p. <40°), weighed, and identified by a mixed m. p. The residue left after sublimation was chromatographed on alumina in light petroleum, and eluted with benzene–hexane. The fractions obtained were concentrated

---

[13] Kharasch, Hambling, and Rudy, *J. Org. Chem.*, 1959, **24**, 303.

[14] Courtot and Paivar, *Chimie et Industrie*, 1941, **45**, 80; *Chem. Abs.*, 1943, **37**, 2366.

[15] Johnston, Heikes, and Petrolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5388.

and chromatographed on partially acetylated paper in ethanol–toluene–water or in ether–methanol–water. Identical, homogeneous, fractions were combined, recrystallised, and identified by mixed m. p. and infrared or ultraviolet spectra, and the final separation of mixed fractions was carried out by rechromatographing on alumina or by chromatography on a column of partially acetylated cellulose.

(ii) *Desulphurisations in methanol.* A mixture of catalyst, dinaphthyl sulphide, and methanol was refluxed for the specified time, and the cooled mixture transferred to the thimble of a Soxhlet extractor and extracted with methanol for 8—10 hr. (Prolonged extraction was necessary to remove unchanged sulphide in the case of Raney cobalt.) The extracts were concentrated to small volume through a fractionating column, and then allowed to crystallise. The mother-liquors were evaporated, and the residue was sublimed at 100°/15 mm. and worked up as above. The crystalline material was chromatographed on alumina in low-boiling petroleum–benzene, and worked up as usual.

The results are summarised in Table 1.

TABLE 1. *Comparison of Raney metals for di-*1*-naphthyl sulphide.*

Raney metal (g.)	Solvent (ml.) *	Temp.	Un-changed sulphide (%)	Tetralin (%)	$C_{10}H_8$ (%)	1,1′-Bi-naphthyl (%)	2,2′-Bi-naphthyl (%)	Peryl-ene	Benzo[*j*]-fluor-anthene (%)
W7 Ni (5)	MeOH (400)	64°	—	*a*	*a*				
W7 Ni (30)	,, (150)	64	—	74	—	—	—	—	—
W7 Ni aged (5)	,, (25) [b]	64	—	—	88·5	1·6	—	—	—
W7–J Ni (5)	,, (25)	64	99·9	—	—	—	—	Trace	—
W7–J Ni (5)	Xylene (5)	140	0·2	—	61·3	15·2	0·4	0·2	Trace
W7–J Ni (5)	Et_2 Ph (5)	220	—	—	69	19·8	0·8	0·3 [f]	
W7 Co (5)	MeOH (25)	64	86·8	—	4·5	—	—	—	—
W7 Co/N_2 (5)	Et_2 Ph (4) [c]	220	—	—	97	0·73	—	Trace	Trace
W7 Cu (5·4)	MeOH (25)	64	83·9	—	1·4	?	—	—	—
Johnston Cu–N_2 (5·4)	Et_2 Ph (4)	220	74·6	—	22·3	Trace	—	Trace	Trace
Johnston Cu–H_2 (5·4)	,, (4)	220	29·5	—	43·7	—	—	0·1	Trace
Fe (5)	MeOH (25) [d]	64	88·9	—	—	0·2	—	—	—
Fe–N_2 (5)	Et_2 Ph (4)	220	82·1	—	4·25	Trace	—	—	—
Fe–H_2 (5)	,, (4)	220	48·7	—	32	Trace	—	Trace	Trace
W (1) [e]	None	200	95	—	—	—	—	—	—

* Et_2 Ph = Et phthalate.

[a] A mixture of naphthalene and tetralin was obtained; this was not separated. [b] Refluxed for 22 hr. [c] Heated for 15 hr. in nitrogen. [d] Refluxed for 24 hr. [e] 0·15 g. of dinaphthyl sulphide. [f] A mixture of perylene and 0·2% of benzo[*k*]fluoranthene was also obtained.

Tetralin was identified by its b. p., retention time in a gas–liquid chromatogram, and infrared spectrum. Naphthalene, 1,1′- and 2,2′-binaphthyl were identified by mixed m. p., and in the case of the binaphthyls by infrared spectra. Perylene, benzo-[*j*]- and -[*k*]-fluoranthene were identified by comparison with authentic specimens on acetylated paper. Perylene was also identified by its ultraviolet and fluorescence spectra, benzo-[*j*]-fluoranthene [16] by its ultraviolet spectrum ($\lambda_{max.}$ 226, 242, 281, 292, 308, 318, 332, 349, 365, 376, 383 mμ), and benzo-[*k*]-fluoranthene [16] likewise ($\lambda_{max.}$ 240, 269, 282, 296, 308, 361, 380, 400 mμ).

Comparison of Raney metals for Dihexyl Sulphide.—Raney metals were prepared under hydrogen from their aluminium alloys, essentially by the method of Johnston *et al.*[15] However, the metal was washed free from water with ethanol and then freed from ethanol and the last traces of water by azeotropic distillation with toluene. The reduced nickel used was prepared by heating the oxide in hydrogen at 500°, and before use was moistened with a little toluene.

Dihexyl sulphide (2 g.) was added to the metal (5 g.) and heated in a slow stream of hydrogen at 220—230° for 15 hr. The low-boiling material was separated in a small fractionating column during the course of the experiment, collected in solid carbon dioxide, and examined by gas–liquid chromatography at 85° in a Griffin and George apparatus modified for the collection of samples.[17] The cooled reaction mixture was extracted with toluene, and the extract analysed by gas–liquid chromatography. Yields of unchanged sulphide and of hexane were calculated

[16] Clar, " Aromatische Kohlenwasserstoffe," 2nd edn., Springer, Berlin, 1952.
[17] Napier and Rodda, *Chem. and Ind.*, 1958, 1319.

from the weights of crude material and the areas under the peaks (to eliminate toluene). No dodecane could be detected in any experiment. The results are summarised in Table 2.

TABLE 2. *Comparison of Raney metals for dihexyl sulphide.*

Metal	Unchanged sulphide (%)	Hexane (%)	Metal	Unchanged sulphide (%)	Hexane (%)
Raney W	72·3 [a]	13·6	Raney Co	—	82
Raney Cu	70	22·4	Raney Ni	—	82·5
Raney Fe	—	84·2	Reduced Ni	89 [a]	0·82

[a] Yield obtained by distillation and isolation.

Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory, Melbourne. This research was supported by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the said fund.

UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA. [*Received, November 2nd,* 1959.]