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# A STUDY OF THE DESULPHURIZATION OF ORGANIC SULPHUR COMPOUNDS ON RANEY NICKEL BY MEANS OF REACTION GAS CHROMATOGRAPHY

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## SUMMARY

The qualitative and quantitative course of the reactions of sulphur compounds on a Raney nickel containing 0-5% w/w of sulphur is described. In the arrangement usual in reaction gas chromatography, the course of the reaction is reproducible and characteristic for the individual types of sulphur compounds, so that the method can be used for analytical purposes. The desulphurization on Raney nickel has been used successfully for the determination of trace amounts of diphenyl sulphide in hydrocarbons, the relative error amounting to 3%.

## INTRODUCTION

The fact that hydrogenation catalysts have a high affinity towards sulphur and sulphur compounds is generally known. Sulphur compounds generally act as poisons of hydrogenation catalysts and reduce their hydrogenation activity significantly.

The above phenomenon was used by MOZINGO *et al.*<sup>1</sup> for the desulphurization of organic sulphur compounds on Raney nickel, in which the organic sulphur forms a modification of nickel sulphide that is soluble in acids, and the moieties formed react, in a suitable solvent, with the hydrogen bound on the Raney-nickel surface:



Many papers have been published on the use of the above reaction for preparative purposes as well as for the qualitative<sup>2-4</sup> and quantitative<sup>5-8</sup> analysis of organic sulphur compounds.

Gas chromatography (GC) has made it possible to determine quickly and conveniently the carbon skeleton of the desulphurization products.

THOMPSON and coworkers<sup>9-15</sup> applied the classical desulphurization reaction on hydrogenation catalysts in reaction GC and used palladium deposited on alumina for desulphurization. BEROZA and coworkers<sup>16-23</sup> simplified the experimental arrangement and gave the method the name "carbon skeleton chromatography" of organic compounds.

The desulphurization of aliphatic and aromatic sulphides, in the classical method described by MOZINGO<sup>1</sup>, was carried out in reaction GC by FRANC *et al.*<sup>24</sup>. STASZEWSKI *et al.*<sup>6</sup> used Raney nickel deposited on glass beads for hydrogenolysis and followed the course of the desulphurization of butyl mercaptan, isobutyl mercaptan, diisobutyl sulphide and thiophene in a flow-through reactor. They also applied the above version of hydrogenolysis to the determination of low concentrations of thionaphthene in technical-grade naphthalene<sup>8</sup>.

In the use of the Raney nickel<sup>3,6</sup>, the sulphur remains bound in the catalyst bed. It should be emphasized that the sulphur content in the desulphurization packing increases gradually in this case and that the hydrogenation and desulphurization activities of the packing are changed accordingly. For a correct analytical account of the products of the hydrogenolysis of sulphur compounds to be made, it is necessary to know the basic hydrogenation, dehydrogenation and hydrogenolysis properties of the catalytic bed so that one may choose the desulphurization conditions under which only the hydrogenation of the carbon skeleton of the parent substance will take place, besides the cleavage of the C-S bonds, while preventing its dehydrogenation or hydrogenolysis. Otherwise the isomers of unsaturated aliphatic and alicyclic hydrocarbons and their lower homologues extend the chromatogram of the reaction products so much that the study of the latter becomes complicated. At the same time, however, it is necessary to know the characteristic factors that control the course of the secondary dehydrogenation and hydrogenolysis reactions of hydrocarbon moieties in the catalyst bed to avoid false conclusions being drawn from the chromatograms of the desulphurization products.

The objective of the present paper is therefore to characterize in detail Raney nickel on glass beads as a desulphurization packing in reaction GC and to describe the course of the desulphurization of the basic types of sulphur compounds on the desulphurization packings containing 0-5% w/w of sulphur.

## EXPERIMENTAL

All the GC analyses were carried out on a Shimadzu 4A-PTF apparatus, equipped with thermal conductivity (TCD) and flame-ionization (FID) detectors. The maximum sample amounts corresponded to 0.1  $\mu$ l of pure substances, injected as such or in mixtures or solutions. All the reactions described took place in the reaction bed of a home-made reactor installed ahead of the chromatographic column. The reaction products were purged into the chromatographic column by the carrier gas and separated. The columns were 3 m long and 0.3 cm I.D., made of stainless steel, and packed with 25% w/w of squalane on Chromosorb W, 60-80 mesh. With both detection systems, hydrogen was used as the carrier gas at a flow-rate of 60 ml/min (unless stated otherwise). The hydrogen served as the reaction medium in the reactions on the Raney nickel. The analyses were carried out at a column temperature of about 80° (unless stated otherwise). In the analyses with flame-ionization detection, nitrogen was added to the flame so as to provide for the usual proportions of air, nitrogen and hydrogen in the flame<sup>25</sup>.

### Arrangement of the reactor

The reactor mouth led into the chromatographic column via a stainless-steel

injection needle in such a way that it was possible also to inject a sample directly into the column. The reaction tube was of brass, the inner diameter and the length of the desulphurization packing being 0.4 and 5 cm, respectively. The reaction tube was inserted into a heating element as used in soldering tools and the whole apparatus was thermally isolated. It was ascertained by direct measurement that the temperature of the outside wall of the reaction tube was approximately the same as the temperature inside the tube. Therefore, the temperature of the outside wall of the reaction tube was measured with a thermocouple and the value obtained was taken as the approximate temperature of the reaction bed,  $T_R$ ; the value of  $T_R$  is quoted for individual measurements as the temperature at which the reaction in question took place. The hydrogen, the control of which was carried out by the system used for the carrier gas flow control, was led into the reactor via a copper capillary. A schematic diagram of the reactor and its coupling with the column is shown in Fig. 1.

#### *Preparation of the desulphurization packing*

The desulphurization packing was Raney nickel deposited on glass beads (RaNi)<sup>6</sup>. The glass beads, of 120–140 mesh (Carlo Erba), were boiled in dilute sulphuric acid, washed with water until neutral and dried. The GRANATELLI<sup>5</sup> method for the preparation of RaNi was slightly modified:

0.1 g of Raney alloy (42% of Ni and 58% of Al; Johnson Matthey, London)

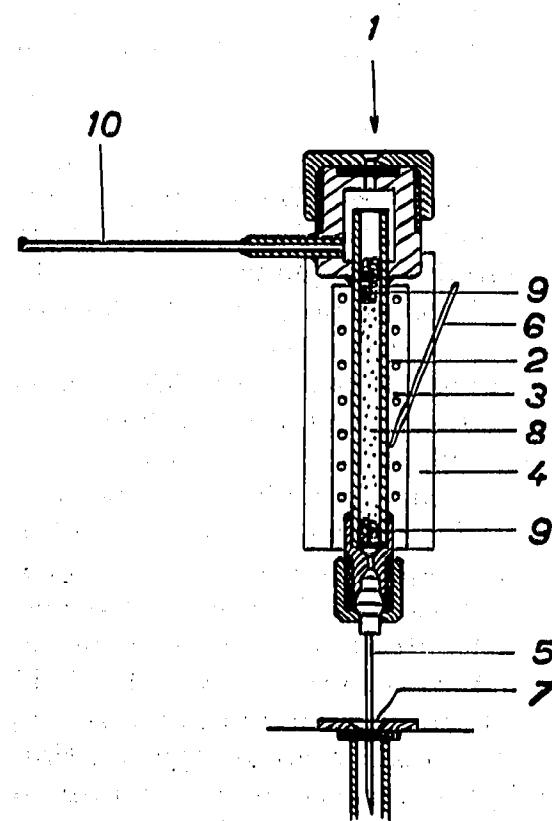


Fig. 1. Reactor scheme. 1 = injection port of the reactor; 2 = reaction tube (0.4 × 7.5 cm); 3 = electrical heater; 4 = thermal insulation; 5 = injection needle; 6 = thermocouple (iron-constantan); 7 = injection port of the gas chromatograph; 8 = desulphurization packing (reaction bed); 9 = quartz wool; 10 = carrier gas inlet.

was added to 2 ml of 2.5 N sodium hydroxide solution heated to 60°. After the evolution of hydrogen had finished, the precipitated nickel was washed with distilled water until neutral and then decanted five times with 2 ml of isoctane. The glass beads and the suspension of RaNi in isoctane were added to a solution of Apiezon M in isoctane, and the solvent was then evaporated under reduced pressure by the procedure used for preparing column packings by the slurry technique. The loose desulphurization packing was kept in sealed-glass ampoules (RaNi-I: 5% of Ni, 3% of Apiezon M and 92% of glass beads; RaNi-II: 10% of Ni, 2% of Apiezon M and 88% of glass beads).

*Preparation of the desulphurization packing with a defined content of bound sulphur*

The activated nickel prepared by the above method reacted with a defined amount of diphenyl sulphide (DPS) in isopropanol under conditions suitable for the quantitative liquid-phase desulphurization of sulphur compounds<sup>5</sup>. In this reaction, part of the nickel is changed into nickel sulphide while the DPS produces benzene and cyclohexane. The suspension of nickel and nickel sulphide was freed of the reaction medium, washed several times with isoctane, and deposited with Apiezon M (isoctane solution) on glass beads. The portion of the unchanged DPS in the reaction medium was determined by the method of GRANATELLI<sup>5</sup>, and was not significant. The dry, loose packing was kept in sealed glass ampoules (RaNi-III: 10% of Ni containing 2% of sulphur as NiS, 2% of Apiezon M and 88% of glass beads; RaNi-IV: 10% of Ni containing 4% of sulphur as NiS, 2% of Apiezon M and 88% of glass beads; RaNi-V: 10% of Ni containing 5% of sulphur as NiS, 2% of Apiezon M and 88% of glass beads).

*Procedures used for the evaluation of the experimental data*

*Identification of the reaction products of sulphur compounds.* The analysed compounds were mercaptans (hexyl mercaptan, cyclohexyl mercaptan, benzyl mercaptan, thiophenol and *p*-thiocresol), sulphides (di(2-methylbutyl) sulphide, dihexyl disulphide, diheptyl sulphide, dioctyl sulphide, dioctyl disulphide, di(2-ethylhexyl) sulphide; 2-thiaproplcyclohexane, 2-thiabutylcyclohexane, 2-thiapentylcyclohexane, 2-thiahexylcyclohexane, dicyclohexyl sulphide, propyl phenyl sulphide, butyl phenyl sulphide, *tert*-butyl phenyl sulphide, diphenyl sulphide and dibenzyl sulphide) and cyclic sulphides (thiacyclopentane, 2-ethylthiacyclopentane, 2-propylthiacyclopentane, 2-ethylthiacyclohexane, 2-propylthiacyclohexane, thiophene, 2-methylthiophene, 2,5-dimethylthiophene and thionaphthene). The purity of the low-boiling sulphur compounds was checked by GC analysis using squalane as the stationary phase, while Apiezon L was used in testing the purity of the high-boiling substances.

The compounds analysed were injected repeatedly in amounts corresponding to within  $10^{-6}$  g of sulphur into the reaction bed packed, consecutively, with RaNi-II and RaNi-IV and maintained at the optimum desulphurization temperature,  $T_0$  (140° for RaNi-II and 160° for RaNi-IV), at which no degradation of the reaction products took place. Hydrogen was passed through the reactor at a flow-rate of 60 ml/min. In order to arrange that the desulphurization proceeded in a packing with optimally uniform sulphur content, the desulphurization packing was always exchanged after about twenty injections of the sulphur compounds.

In addition to the desulphurization of the sulphur compounds in the reaction

bed, side reactions accompanying the desulphurization on hydrogenation catalysts, *viz.*, the hydrogenation and dehydrogenation of the desulphurization fragments, also took place. The reaction products were analysed on squalane at 80° and characterized from their relative retention data and retention indices. In order to make the relative retention data comparable, heptane was chosen as a single internal standard for the whole range of reaction products. The retention indices of the substances analysed within the range 500–900 *I* were calculated by interpolation between two neighbouring alkanes, while the other retention indices were calculated by extrapolation from the nearest pair of alkanes. The data pertaining to the substances that occur only in trace amounts in the reaction products are given in parentheses.

In the qualitative assay of the reaction products, practical conclusions were used that were derived from the investigation of the repeatability of measuring retention data in the experimental system used<sup>26</sup>. The possibility of calculating the standard deviation of the absolute retention data of further substances by an, empirically obtained relation saved a significant amount of time in the long-term qualitative analyses of the wide range of hydrocarbons. If the absolute retention data are characterized by the variance  $s_1^2$ , the relative retention data and the retention indices calculated from the above data may be considered to be functions of the variables characterized by a certain variance; their resultant variance may be estimated by using the principle of error propagation<sup>26–28</sup>, thus avoiding the time-consuming empirical determination of the resultant variance of the relative retention data and retention indices.

The retention indices of the reaction products (Tables Ia and IIa) were then compared by means of the *t* test<sup>27</sup> (Tables Ic and IIc) with the retention indices of standard hydrocarbons (supposed reaction products) chromatographed on the same column (Tables Ib and IIb). The values of the retention data of most of the reaction products were consistently higher compared with those of the corresponding standard hydrocarbons. The shifts of the peak maxima are associated with the course of sorption and desulphurization of the sulphur compounds in the reaction bed, since no perceptible shifts of the peak maxima of the reaction products were observed in the reactions of the standard hydrocarbons on the same reaction bed<sup>29</sup>. Generally, it is impossible to identify unequivocally the reaction products from their retention data only, if the values of the latter are systematically higher than those of the standard substances. However, if chromatographically pure model substances were analysed by reaction GC in the given experimental arrangement, after having proved empirically that reaction products with neither a smaller nor larger carbon skeleton originated under the reaction conditions, the enhancement of the retention data may be considered to be characteristic for the substance being analysed and the reaction conditions used, so that it was not necessary to introduce an intermediate step of collecting the reaction products and injecting them again into the chromatographic system. The retention indices of the other desulphurization products were compared with literature values<sup>30,31</sup> for the supposed reaction products. The reaction products identified in the above way are given in square brackets.

*Quantitative course of the reactions of diphenyl sulphide.* The solutions analysed, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, contained, respectively, 4.0, 0.15, and 0.015% w/w of DPS, with heptane (S) as the internal standard. The solvents were toluene (R<sub>1</sub>, R<sub>2</sub>) and *p*-xylene (R<sub>3</sub>). The cyclohexane, cyclohexene and benzene (substances i) which were produced

TABLE I

## RETENTION DATA OF THE REACTION PRODUCTS OBTAINED FROM SULPHUR COMPOUNDS ON RaNi-II

(a)  $R$  is the type of reaction in which the reaction products characterized by the retention indices were produced from the sulphur compound quoted: DS = desulphurization; H = hydrogenation.  $I$  = retention indices of the reaction products of the sulphur compounds ( $I^S_{80^\circ}$ );  $s_E^2$  = variances of the retention indices of the reaction products, calculated by the relations:

$$s_E^2 = [1/(n-1)] \sum_{j=1}^n (I_j - I)^2 \text{ for } n > 10 \text{ and } s_E^2 = k_n R \text{ for } n < 10$$

( $R$  is the range of variation and  $k_n$  is the coefficient for calculating the standard deviation from the range of variation after DEAN AND DIXON<sup>27</sup>);  $n$  = number of measurements, used in calculation of the averages and variances of the retention indices.

(b)  $I$  = retention indices of the standard hydrocarbons ( $I^S_{80^\circ}$ );  $s_E^2$  = variances of the retention indices of the standard hydrocarbons, calculated by the above relations;  $n$  = number of measurements, used in calculation of the averages and variances of the retention indices.

(c)  $t$  = Student  $t$  coefficient calculated from:  $t = (I_A - I_B)/[(n_A + n_B)(n_A s_A^2 + n_B s_B^2)/n_A n_B(n_A + n_B - 2)]^{1/2}$  where  $I_A$  and  $I_B$  are the averages of retention indices of the hydrocarbons under comparison,  $s_A^2$  and  $s_B^2$  are the variances of the retention indices of the above hydrocarbons and  $n_A$  and  $n_B$  are the numbers of measurements, used in calculation of the averages of the retention indices of the hydrocarbons under comparison;  $t_{crit}$  = tabulated value of the Student  $t$  coefficient for  $v = (n_A + n_B - 2)$ .

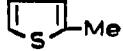
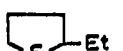
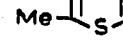
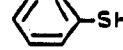
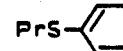
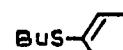
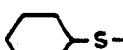
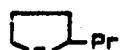
Compound	a				Standard hydrocarbon	I	s_E^2	n	c	
	R	I	s_E^2	n					t	t <sub>crit</sub>
(2MeC <sub>4</sub> ) <sub>2</sub> S	DS	473.0		1	[2MeC <sub>4</sub> ]	475.5 <sup>a</sup>				
	DS, H	502.1	8.73	3	C <sub>5</sub>	500	13.9	15	0.868	2.120
C <sub>6</sub> SH	DS	601.4	0.09	3	C <sub>6</sub>	600	0.39	12	3.518	2.160
(C <sub>6</sub> ) <sub>2</sub> S <sub>2</sub>	DS	604.8	3.23	4					7.407	2.145
	DS	601.2	0.94	4					2.614	2.145
Me 	DS, H	601.3	3.14	3	↓				1.935	2.160
Ph-SH	DS	670.8	0.39	2		670.1	0.13	15	2.188	2.131
	DS, H	671.7	0.46	4					6.038	2.110
PrS- 	DS, H	671.7	0.46	4					6.038	2.110
Bus- 	SD, H	671.4	0.59	3					5.851	2.120
tert-Bus- 	DS, H	671.0	0.12	5					4.706	2.101
	DS	673.2	2.18	3					6.725	2.120
	DS, H	673.3	3.45	6	↓				6.072	2.093
(C <sub>7</sub> ) <sub>2</sub> S	DS	702.2	3.14	3	C <sub>7</sub>	700	0.07	12	3.826	2.160
	DS	702.2	0.67	5					7.801	2.131
	DS	701.5	1.22	4	↓				4.054	2.145

TABLE I (continued)

Compound	a	b					c				
		R	I	$s_E^2$	n	Standard hydrocarbon	I	$s_E^2$	n	t	$t_{crit}$
<chem>Cc1ccccc1S</chem>	DS, H	735.8	0.42	3		<chem>Cc1ccccc1C</chem>	734.8	0.53	9	1.927	2.228
<chem>Cc1ccccc1S</chem>	DS, H	736.3	0.03	3						3.219	2.228
<chem>CC1(Cc2ccccc2)SC</chem>	DS	735.8	0.06	3						2.128	2.228
<chem>CC1(Cc2ccccc2)SC2</chem>	DS	735.1	0.02	4						0.750	2.201
<chem>CC1(Cc2ccccc2)SC3</chem>	DS	735.5	0.01	2						1.226	2.262
<chem>CC1(Cc2ccccc2)SC4</chem>	DS	735.5	0.03	2						1.220	2.262
<chem>Cc1ccccc1SCc2ccccc2</chem>	DS, H	736.5	0.64	2						2.648	2.262
<chem>C2CC(C)SCC2</chem>	DS	777.0	0.89	3	[2EtC6]	773.3 <sup>a</sup>					
<chem>C2CC(C)SC2</chem>	DS	800.7	0.89	7	C8	800	0.05	12	2.007	2.110	
<chem>C2CC(C)SC2</chem>	DS	802.4	1.06	3						6.897	2.160
<chem>CC1(Cc2ccccc2)SC2</chem>	DS	802.9	0.71	2						9.265	2.179
<chem>C1=CC2=CSC2=C1</chem>	DS, H	843.1	0.79	3	<chem>Cc1ccccc1C</chem>	842.2	0.48	15	1.840	2.120	

<sup>a</sup> Value taken from ref. 30.

by the desulphurization of DPS were analysed quantitatively by GC by the internal standard technique<sup>32</sup>, and the amounts of the former were recalculated for the amounts of DPS that entered the reactor. The substances were again separated on a squalane stationary phase at 80°; thermal conductivity or flame ionization detection was used. The relative molar response,  $RMR_{S,1}$ , values determined experimentally are given in Table III. The small areas of the cyclohexene peaks were evaluated by means of the  $RMR_{S,1}$  measured for cyclohexane. For the sake of objectivity, the weight fractions of the substances analysed have been expressed as percentages.

## RESULTS AND DISCUSSION

### Characterization of the desulphurization packing

In order to define the conditions under which the desulphurization of sulphur compounds proceeds reproducibly and to an optimum degree from the analytical

TABLE II

RETENTION DATA OF THE REACTION PRODUCTS OF THE SULPHUR COMPOUNDS ON RaNi-IV

DH = dehydrogenation; other symbols as in Table I.

Compound	a	b					c				
		R	I	$s_E^a$	n	Standard hydrocarbon	I	$s_E^a$	n	t	$t_{tert}$
<chem>Cc1ccccc1S</chem>	DS, H	648.3	0.17	3		<chem>c1ccccc1</chem>	647.9	0.29	4	0.909	2.571
<chem>Cc1ccccc1S</chem>	DS	648.0	0	2						0.217	2.776
<chem>CC(C)c1ccccc1S</chem>	DS	649.9	0.01	3						5.405	2.571
<chem>CC(C)c1ccccc1S</chem>	DS	650.5	0.29	4						5.909	2.447
<chem>CC(C)c1ccccc1S</chem>	DS	648.3	1.40	3						0.741	2.571
<chem>Cc1ccccc1SCc2ccccc2</chem>	DS, DH	650.7	3.80	2						2.188	2.776
<chem>Cc1ccccc1SCc2ccccc2</chem>	DS	650.3	0.01	4						7.742	2.447
<chem>Cc1ccccc1S</chem>	DS	672.5	0.22	3	<chem>c1ccccc1</chem>	670.1	0.13	15	9.412	2.120	
<chem>Cc1ccccc1S</chem>	DS	673.3	—	1	<chem>c1ccccc1</chem>				—	—	
<chem>Cc1ccccc1S</chem>	DS, DH	680.0	0.35	3	<chem>c1ccccc1</chem>	678.2	0.17	15	6.000	2.120	
<chem>Cc1ccccc1S</chem>	DS, H	677.2	0	2						3.226	2.131
<chem>CC(C)c1ccccc1S</chem>	DS, H	677.5	0	3						2.777	2.120
<chem>CC(C)c1ccccc1S</chem>	DS, H	678.4	0	2						0.645	2.131
<chem>Cc1ccccc1SCc2ccccc2</chem>	DS, DH	681.0	1.54	3						6.604	2.120
<chem>Cc1ccccc1SCc2ccccc2</chem>	DS, H	680.2	0.05	4						5.882	2.110
<chem>Cc1ccccc1CH2S</chem>	DS	752.9	2.36	3	<chem>c1ccccc1Cc2ccccc2</chem>	752.7	0.34	15	0.364	2.120	
<chem>CC(C)c1ccccc1CH2S</chem>	DS	752.9	0.22	3						0.526	2.120
<chem>CC(C)c1ccccc1CH2S</chem>	DS, DH	753.2	0	3						1.389	2.120
<chem>CC(C)c1ccccc1CH2S</chem>	DS, DH	753.5	0.03	3						2.222	2.120
<chem>CC(C)c1ccccc1CH2S</chem>	DS, DH	753.9	0.06	3						3.333	2.120
<chem>CC(C)c1ccccc1CH2S</chem>	DS, DH	753.8	0.09	3						2.973	2.120
<chem>Cc1ccccc1C(C)c2ccccc2S</chem>	DS	753.5	0.28	3						2.051	2.120
<chem>Cc1ccccc1C(C)c2ccccc2S</chem>	DS	842.8	0.01	2	<chem>c1ccccc1Cc2ccccc2</chem>	842.2	0.48	15	1.154	2.131	

TABLE III

EXPERIMENTALLY DETERMINED VALUES OF  $RMR_{S,i}$ 

$RMR_{S,i}$  = relative molar response calculated by the relation  $RMR_{S,i} = W_i M_S A_S / W_S M_i A_i$  where  $W_i$  is the weight of the analysed substance,  $i$ ,  $W_S$  is the weight of the internal standard,  $S$ , (heptane),  $M_i$  and  $M_S$  are the molecular weights of substances  $i$  and  $S$ , and  $A_i$  and  $A_S$  are the areas of the chromatographic curves pertaining to the analysed substances ( $i$ ) and the internal standard  $S$ ;  $i$  = the substance analysed by the internal standard method;  $n$  = number of measurements, used in calculation of the average value and the variance of  $RMR_{S,i}$ ;  $s_E^2$  = variances of  $RMR_{S,i}$ , calculated from:

$$s_E^2 = [1/(n-1)] \sum_{i=1}^n (RMR_{S,i} - \bar{RMR}_{S,i})^2$$

where  $h$  = peak height;  $w_{1/2}$  = peak width at the half-height.

$i$	Detector	Evaluation of peak areas	$RMR_{S,i}$	$n$	$s_E^2 \times 10^4$
Benzene	TCD	$A = h \times w_{1/2}$	1.354	28	0.93
	FID	$A = h \times w_{1/2}$	1.032	20	0.84
	FID	Planimetrically	1.009	20	2.72
Cyclohexane	TCD	$A = h \times w_{1/2}$	1.301	31	0.88

viewpoint, DPS was used as a model sulphur compound. The desulphurization of DPS results in benzene and, if the RaNi is sufficiently active, cyclohexane is also produced, the proportion of which is a measure of the hydrogenation activity of the desulphurization packing. The organic sulphur remains bound in the catalyst bed since hydrogen sulphide never appears amongst the reaction products.

*Effect of temperature on the course of the desulphurization of diphenyl sulphide.* The dependence of the quantitative course of the desulphurization of DPS on the temperature of the reaction bed filled, consecutively, with RaNi-I, RaNi-II, RaNi-III and RaNi-IV is apparent from the results summarized in Table IV. The amount of desulphurized DPS increases with increasing temperature up to a certain value attained at temperature  $T_O$ , which may be called the optimum temperature, although the conversion of DPS is not complete at this temperature. Further increase in the temperature results in no significant increase in the amount of DPS converted. At temperature  $T_D$ , which may be called the degradation temperature, partial degradation of the individual components of the reaction mixture occurs. The actual values of  $T_O$  and  $T_D$  depend on the degree of activity of the desulphurization packing used and, with fresh desulphurization packings, increase when the content of the nickel sulphide increases.

It is important, in respect of the analytical utilization of the Raney nickel, that the conversion of the test substance on desulphurization packings of different activity should be approximately the same at the temperature  $T_O$ , which applies even for the RaNi-I packing whose properties may be considered to be very unfavourable (prepared 6 months before the testing and kept in a bottle with a ground-glass stopper).

*Effect of the hydrogen flow-rate on the course of the desulphurization of diphenyl sulphide.* It is apparent from the results in Table V that the degree of the desulphurization of DPS on RaNi-I is nearly independent of the flow-rate within the specified limits.

TABLE IV

## EFFECT OF TEMPERATURE ON THE COURSE OF THE DESULPHURIZATION OF DPS

$T_R$  = temperature of the reaction bed ( $^{\circ}\text{C}$ );  $T_O$  = optimum temperature for desulphurization;  $T_D$  = temperature at which the degradation of the reaction products and of the solvent occurs;  $\bar{g}_{DPS}$  = degree of the conversion of DPS to the products of the desulphurization (%) (the average was calculated from at least 10 measurements); sample charge size, 1.0-1.8  $\mu\text{l}$  of RI; hydrogen flow-rate through the reactor, 60 ml/min; detector, katharometer.

Desulphurization packing	$T_R$ ( $^{\circ}\text{C}$ )	Desulphurization products	$\bar{g}_{DPS}$ (%)
RaNi-I	180		7.9
	250		80.2
	280 ( $T_O$ )		92.6
	300 ( $T_D$ )	 slight degradation	93.6
RaNi-II	120	(  ), 	80.9
	140 ( $T_O$ )	(  ), 	93.9
	160 ( $T_D$ )	Extensive degradation	
RaNi-III	140	 ) 	87.9
	160 ( $T_O$ )	 ) 	92.3
	180 ( $T_D$ )	 )  , slight degradation	90.7
RaNi-IV	140	 , (  )	89.0
	180 ( $T_O$ )	 , (  )	95.0
	200 ( $T_D$ )	 , (  ), slight degradation	92.5
	240	 , (  ), slight degradation	89.4
	270	 , (  ), slight degradation	84.0

*Absolute amounts of components desulphurized in the charge and the degree of conversion.* It follows from the results in Table VI, that there is a certain limiting amount of a sulphur compound, the desulphurization of which will still proceed to the optimum degree in the given experimental arrangement. The empirically determined limiting amount of a sulphur compound in a charge must either be adhered to or any lower sulphur content in a single charge can be chosen when carrying out the desulphurization in practice.

TABLE V

## EFFECT OF THE HYDROGEN FLOW-RATE ON THE COURSE OF THE DESULPHURIZATION OF DPS

Sample charge size, 1.4  $\mu$ l of RI;  $T_R = 280^\circ$ ; detector, katharometer. The desulphurization product was benzene.

Desulphurization packing	Flow-rate of $H_2$ (ml/min)	$\bar{g}_{DPS}$ (%)
RaNi-I	44	93.6
	60	93.3
	92	94.7

TABLE VI

## ABSOLUTE AMOUNT OF DPS IN THE SAMPLE CHARGE AND ITS DEGREE OF CONVERSION

$T_R = 280^\circ$ ; detector, katharometer. The desulphurization product was benzene.

Desulphurization packing	Amount of DPS in the sample charge ( $\mu$ g)	Flow-rate of $H_2$ (ml/min)	$\bar{g}_{DPS}$ (%)
RaNi-I	10	60	93.3
RaNi-I	20	60	87.3
RaNi-I	40	60	74.1
RaNi-I	10	92	94.7
RaNi-I	20	92	69.4

*Effect of the sulphur content in the Raney nickel on its desulphurization properties.* The sulphur content in the packing increases with every desulphurization of a sulphur compound. This will lead to changes in the desulphurization and catalytic properties of the packing, which may result in the irreproducibility of the analytical data obtained. This problem may be obviated by exchanging the desulphurization packing in the reactor before every successive injection<sup>9</sup>, but such a procedure is inconvenient and substantially increases the time required for analysis.

In analytical practice, it would be much more advantageous to carry out a larger series of desulphurizations of sulphur compounds on the same desulphurization bed. When comparing the amount of sulphur in a single charge of a sulphur compound (*ca.*  $10^{-6}$  g) and the total amount of the active component of the desulphurization packing in the reactor (*ca.*  $10^{-1}$  g of nickel in the experimental arrangement described), the above concept seemed to be realistic despite the fact that only part of the total amount of nickel was effective in desulphurization.

The measurements carried out verified the above presumption. On the RaNi-I packing 260 desulphurizations were carried out. Assuming, for the sake of simplicity, that all the charges contained a constant amount of 10  $\mu$ g of sulphur, 0.0026 g of sulphur reacted with 0.05 g of nickel in the desulphurization bed, which means that nickel containing 5% of sulphur still retained the capability of desulphurizing DPS. The degrees of the conversion of DPS on RaNi-I without any sulphur, on RaNi-I with 5% of sulphur (after 260 desulphurizations) and on RaNi-V also containing 5% of sulphur are given in Table VII, and are almost the same.

TABLE VII

## EFFECT OF THE SULPHUR CONTENT IN RaNi ON ITS DESULPHURIZATION PROPERTIES

Sample charge size, 1.4  $\mu$ l of RI; hydrogen flow-rate, 60 ml/min; detector, katharometer;  $T_R$  = temperature of the reaction bed ( $^{\circ}$ C).

Desulphurization packing	Sulphur content (% w/w)	$T_R$	Desulphurization products	$\bar{g}_{DPS}$ (%)
RaNi-I	0	280		93.6
	5	280		92.5
RaNi-V	5	180	 , 	94.2

*Effect of ageing of the Raney nickel on its desulphurization properties.* The desulphurization packing RaNi-I had been aged for 6 months in an evacuated bottle having a ground-glass stopper. The desulphurization activity of the packing towards DPS remained unaltered. The hydrogenation activity of RaNi-I was very low and disappeared completely at a sulphur content as low as 0.5%. Some degradation and isomerization properties of the packing became perceptible at a temperature as high as 300° ( $T_D$ ). The desulphurization of sulphur compounds had to be carried out at a temperature of 280° ( $T_O$ ) on this packing.

The ageing of RaNi-II proceeded much more slowly in a sealed ampoule and manifested itself mainly by a gradual decrease in the hydrogenation activity of the packing and a slight increase in the values of  $T_O$  and  $T_D$ . At the optimum desulphurization temperature, total hydrogenation of unsaturated desulphurization fragments took place on a fresh packing, while an older one (aged a year or more) brought about partial hydrogenation. Degradation and isomerization properties of the packing became evident at temperatures as low as 160–180°.

The results of the comparison of the properties of desulphurization packings are given in Table VIII.

TABLE VIII

## EFFECT OF THE AGEING OF RaNi ON ITS DESULPHURIZATION PROPERTIES

$T_O$  = optimum desulphurization temperature;  $T_D$  = temperature at which the degradation occurs; sample charge size, 1.4  $\mu$ l of RI; hydrogen flow-rate, 60 ml/min; detector, katharometer.

Desulphurization packing	$T_O$ ( $^{\circ}$ C)	Desulphurization products	$\bar{g}_{DPS}$ (%)	$T_D$ ( $^{\circ}$ C)
RaNi-I	280		93.3	300
RaNi-II	140	 , 	93.9	160
RaNi-II (after 6 months)	150	 , 	93.1	180

*Qualitative course of the reactions on Raney nickel*

Organic sulphur compounds that do not contain any other hetero-atoms give only hydrocarbon moieties on desulphurization, which react further according to the type and activity of the reaction bed. In order to guess the structure of the original sulphur compound from the hydrocarbons produced by desulphurization, it is necessary to know the conditions under which the hydrocarbon moieties are stabilized without any changes in their carbon skeletons. A first step towards defining the above conditions is the knowledge of the qualitative course of the reactions of the basic types of hydrocarbons on desulphurization packings with different sulphur contents and at different temperatures.

*Qualitative course of the reactions of hydrocarbons*<sup>20</sup>. As model hydrocarbons were chosen those with basic structural types that occur as the most frequent products of the desulphurization of organic sulphur compounds, and also cyclopentane and cyclopentene. The hydrogenation of aromatic hydrocarbons was considered in studying the hydrogenation capability of the desulphurization packing, while the dehydrogenation of alicyclic hydrocarbons was used in studying the dehydrogenation capability of the packing. If the carbon skeleton of the five-membered carbon ring remained preserved, it was possible to state that the reaction bed displayed no destructive properties.

When the temperature of the reaction bed did not reach the temperature  $T_D$ , at which the degradation of hydrocarbons and further side reactions begin, the carbon skeleton of the parent hydrocarbon remained unchanged.

*Qualitative course of the reactions of sulphur compounds*. The sulphur compounds were chosen in such a way that compounds of different functional types yielded the same carbon skeletons, the latter being identical with the skeletons of some of the model hydrocarbons.

It followed from the study of the reactions of hydrocarbons that the properties of the RaNi changed continuously depending on the amount of bound sulphur present. Therefore, it was expedient to investigate the course of the desulphurization of sulphur compounds on a packing containing no sulphur (RaNi-II) as well as on a packing which contained, from the analytical viewpoint, the maximum amount of sulphur

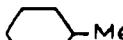
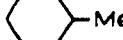
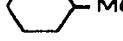
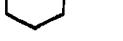
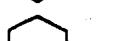
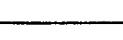
TABLE IX

PRODUCTS OF THE REACTIONS OF MERCAPTANS ON RaNi

Mercaptan	Products	
	RaNi-II	RaNi-IV
C <sub>6</sub> SH	C <sub>6</sub>	[C <sub>6</sub> olefins]
Me-		

TABLE X

PRODUCTS OF THE REACTIONS OF SULPHIDES ON RaNi

Sulphide	Products	
	RaNi-II	RaNi-IV
$(2\text{MeC}_4)_2\text{S}$	$[2\text{MeC}_4]$	$[2\text{MeC}_4, 2\text{MeC}_4 \text{ olefins}]$
$(\text{C}_6)_2\text{S}_2$	$\text{C}_6$	$[\text{C}_6 \text{ olefins}]$
$(\text{C}_7)_2\text{S}$	$\text{C}_7$	$[\text{C}_7 \text{ olefins}]$
$(\text{C}_8)_2\text{S}$	$\text{C}_8$	$[\text{C}_8 \text{ olefins}]$
$(\text{C}_8)_2\text{S}_2$	$\text{C}_8$	$[\text{C}_8 \text{ olefins}]$
$(2\text{EtC}_6)_2\text{S}$	$[2\text{EtC}_6]$	$[2\text{EtC}_6 \text{ olefins}]$
$\text{MeSCH}_2-\text{C}_6\text{H}_5$	+	 +
$\text{EtSCH}_2-\text{C}_6\text{H}_5$	+	 +
$\text{PrSCH}_2-\text{C}_6\text{H}_5$	+	 +
$\text{BuSCH}_2-\text{C}_6\text{H}_5$	$[\text{C}_4]$	 $[\text{C}_4 \text{ olefins}]$
$(\text{C}_6\text{H}_5-\text{CH}_2)_2\text{S}$		
$\text{PrS}-\text{C}_6\text{H}_5$	+	 +
$\text{BuS}-\text{C}_6\text{H}_5$	$[\text{C}_4]$	 $[\text{C}_4 \text{ olefins}]$
$\text{tert-BuS}-\text{C}_6\text{H}_5$	$[2\text{MeC}_3]$	 $[2\text{MeC}_3, 2\text{MeC}_3 \text{ olefins}]$
$\text{C}_6\text{H}_5-\text{S}-\text{C}_6\text{H}_5$		
$\text{C}_6\text{H}_5-\text{S}-\text{C}_6\text{H}_5$		

(RaNi-IV, 4% of S), supposing that the properties of packings with sulphur contents in the range 0-4% might be derived from the results of the measurements. At the high dilution of the reactant substances by the carrier gas used, the recombination of the hydrocarbon moieties was not likely to occur, which was proved empirically. In the desulphurization of methyl propyl sulphide, diethyl sulphide, methyl *sec.*-butyl sulphide, propyl *sec.*-butyl sulphide, isopropyl isobutyl sulphide and isopropyl *sec.*-butyl sulphide, only alkanes and olefins with the presupposed carbon skeleton were produced, while reaction products with larger carbon skeletons did not occur.

The desulphurization activity of the RaNi towards cyclic sulphides, particularly unsaturated ones, falls markedly with an increase in the content of sulphur bound by the nickel. Unsaturated cyclic sulphides were only partially desulphurized on RaNi-IV.

The results of the measurement are summarized in Tables IX-XI (reaction products with retention indices lower than 400 are not given in the tables; their occurrence in the reaction mixture is indicated by a + sign).

TABLE XI

PRODUCTS OF THE REACTIONS OF CYCLIC SULPHIDES ON RaNi

Sulphide	Products	
	RaNi-II	RaNi-IV
	[C <sub>4</sub> ]	[C <sub>4</sub> olefins]
	[C <sub>4</sub> ]	[C <sub>4</sub> , C <sub>4</sub> olefins]
	C <sub>5</sub>	(C <sub>5</sub> )
	C <sub>6</sub>	—
	C <sub>6</sub>	(C <sub>6</sub> )
	C <sub>7</sub>	[C <sub>7</sub> olefins]
	C <sub>7</sub>	—
	C <sub>8</sub>	—

In the desulphurization of thiols, sulphides and cyclic sulphides on the non-sulphurized RaNi-II, which has considerable hydrogenation capability, only alkanes and alicyclic hydrocarbons are produced under optimum conditions, and the quantitative course of the reaction is reproducible. Hydrocarbon moieties having the same carbon skeletons are stabilized in the same way, regardless of having been produced by the desulphurization of sulphur compounds of different functional types. Total hydrogenation of the hydrocarbon moieties takes place during which no rearrangements of the carbon skeletons were observed.

On the desulphurization packing RaNi-IV, which displays negligible hydrogenation properties, the reactive hydrocarbon moieties are stabilized mainly by dehydrogenation. In the desulphurization of alicyclic and aromatic sulphur compounds, the sole reaction products are the aromatic hydrocarbons in which the carbon skeleton of the parent sulphur substance remains preserved. The only exceptions are the reactions of the cyclohexyl moiety, which produce cyclohexane and cyclohexene in addition to benzene, and of the phenyl moiety, in which a small amount of cyclohexene is produced.

The moieties of an aliphatic nature react in a much more varied manner. The stabilization of the hydrocarbon moiety depends on the way in which the latter was bound to the sulphur in the parent compound. For instance, hexane is produced as the sole product in the desulphurization of 2,5-dimethylthiophene, while the desulphurization of dihexyl sulphide results in a mixture of 1-hexene and the isomeric 2-hexenes.

TABLE XII

## QUANTITATIVE COURSE OF THE DESULPHURIZATION OF DPS ON RaNi-IV

a)  $i$  = reaction products analysed by the internal standard technique;  $g_i$  = weight fraction of the substance under determination (i);  $n$  = number of measurements;  $T_R = 180^\circ$ . (b)  $\bar{g}_{DPS}$  = weight fraction of DPS analysed by reaction GC;  $s^2_{DPS}$  = variance of the weight fraction of DPS.

Solution of DPS	Sulphur content (% w/w)	Sample charge size ( $\mu\text{l}$ )	<i>a</i>				<i>b</i>	
				Detector	<i>i</i>	$\bar{g}_i$ (%)	$n$	$\bar{g}_{DPS}$ (%)
R1	0.7	1.4	TCD	benzene	93.743	35	94.679	4.52
R1	0.7	1.4		cyclohexene	0.937			
R2	0.027	0.2	FID	benzene	92.641	35	93.585	6.12
				cyclohexene	0.944			
R3	0.0027	0.3	FID	<sup>a</sup> benzene	94.344	25	96.176	7.27
				<sup>a</sup> (cyclohexene)				
R3	0.0027	0.3	FID	<sup>a</sup> benzene	96.176	25	96.939	4.71
				benzene	96.939			
				(cyclohexene)	+			

<sup>a</sup> The peak areas were evaluated planimetrically (the other peak areas were determined by calculation); hydrogen flow-rate through the reactor, 60 ml/min.

The variation in the stabilization of aliphatic moieties under conditions unfavourable for hydrogenation complicated the analysis of the desulphurization fragments, so that the identification of the latter on a packed column and with a single non-polar stationary phase is only approximate. However, we believe that the agreement of the retention data of the reaction products with those of the isomeric olefins having carbon skeletons identical with those of the parent sulphur compounds was not fortuitous for a number of the compounds analysed, and that the analysis of the desulphurization products on a column of a substantially higher separation efficiency while using stationary phases of different polarity would confirm the results given in Tables IX–XI. It may therefore be very useful in the elucidation of the structure of a parent substance to compare the desulphurization fragments produced by the reaction of that sulphur compound on desulphurization packings with different hydrogenation activities.

#### Quantitative course of the reactions on Raney nickel

It is apparent from the results of the above measurements that it is possible to find the conditions under which the desulphurization of organic sulphur compounds on RaNi will result in qualitatively defined products, the conversion of the sulphur substances to the hydrocarbon products approaching 100%.

*Quantitative course of the reactions of hydrocarbons.* Depending on the hydrogenation activity of the desulphurization bed at a given moment, cyclohexane and benzene in certain proportions are produced by the desulphurization of DPS on RaNi, and in only some cases a small amount of cyclohexene is produced. Therefore, it is expedient to know not only the qualitative behaviour of benzene and cyclohexane in the reaction bed, but also the effect of the hydrogenation activity of the bed on the determination of benzene and cyclohexane when reaction GC is used.

We have since shown<sup>20</sup> from these results that cyclohexane passes through the reactor with RaNi-II and RaNi-IV without any qualitative and quantitative change, while benzene is subjected to total or partial hydrogenation in the reaction bed. The weight fractions of the analysed components determined by reaction chromatography as well as the variances of the former do not differ from the corresponding values obtained by injecting the solutions of benzene and cyclohexane directly into the chromatographic column.

*Quantitative course of the desulphurization of diphenyl sulphide.* Solutions of DPS in toluene (R<sub>1</sub>, R<sub>2</sub>) or *p*-xylene (R<sub>3</sub>), containing 0.0027–0.7% w/w of bound organic sulphur, produce benzene and a small amount of cyclohexene on desulphurization in the reaction bed packed with RaNi-IV and kept at the optimum desulphurization temperature (*T<sub>0</sub>*). The qualitative course of the desulphurization of DPS on RaNi-IV is reproducible, and the conversion of DPS to the hydrocarbon reaction products amounts to 94–97% within the above concentration limits. When calculating the peak areas of the hydrocarbon reaction products, the standard deviation of a single determination was 2.0%, while when the peak areas were measured with a planimeter, the standard deviation was 3.0% and was independent of the concentration of the substance being determined.

In the quantitative analysis of a sulphur compound on RaNi in reaction GC, the empirically determined degree of conversion may be used as a correction factor, and one can analyse, with the precision quoted, samples of as little as 0.1  $\mu$ l of a solution containing  $2.7 \times 10^{-3}$  % w/w of sulphur.

## CONCLUSIONS

It has been shown experimentally that the desulphurization of organic sulphur compounds on RaNi, carried out in reaction GC, may be used successfully for both qualitative and quantitative analysis of liquid and solid sulphur compounds in either the pure state or dissolved in suitable indifferent solvents.

For the analytical utilization of hydrogenolysis, the basic hydrogenation, dehydrogenation and hydrogenolysis properties of the catalytic bed must be known, as well as the dependence of these properties on temperature and on the content of the sulphur, from the preceding desulphurizations, bound in the catalyst bed. If the reaction products are to be analysed on a GC column without carrying out the intermediate collection of the fractions and their re-injection, one must know if the maxima of the peaks of the reaction products are shifted in comparison with the maxima of the peaks of the standard substances. The shifts of the maxima of the peaks of the reaction products may be considered to be characteristic for the individual sulphur compounds. Therefore, it is desirable that the desulphurization be carried out under conditions that permit only the hydrogenation of the carbon skeleton of the parent sulphur substance, in addition to the cleavage of the C–S bonds, while preventing dehydrogenation or further hydrogenolysis. The reproducible results on the structure and amount of the sulphur compound being analysed, obtained quickly and conveniently by reaction GC, are of optimum use only when the above conditions have been met.

The reaction studied may be useful in the desulphurization of mixtures of hydrocarbons and sulphur substances for GC purposes. The same arrangement may

also be used as a monitor in the quantitative analysis of trace amounts of sulphur compounds in the atmosphere and in various organic materials.

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