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## METHODS OF ANALYSIS OF SULFUR COMPOUNDS IN HYDROCARBON MIXTURES

## I. STUDY OF THE HYDROGENOLYSIS OF THIOPHENE AND SIMPLE ACYCLIC SULFUR COMPOUNDS ON RANEY NICKEL

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SUMMARY

The analytical application of the hydrogenolysis of sulfur compounds over Raney nickel has been studied in some detail. These compounds have been analyzed quantitatively determining the hydrocarbons produced by the reaction.

The reaction carried out in the liquid phase (in solutions of hydrocarbons) was found to be completed in 3–5 minutes at room temperature (in the case of thiophene).

The reaction time of hydrogenolysis in the vapour phase was less than one second under the experimental conditions employed. The Raney nickel must be modified with a small amount of high boiling substance (squalane, Apiezon L, etc.) in order to reduce the adsorptivity.

The appropriate analytical procedures have been worked out for the estimation of the structure and content of the sulfur compounds present in narrow crude oil or coal tar cuts.

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## INTRODUCTION

For some time, the increasing tonnages of crude oil high in sulfur content, being processed have created a need for appropriate analytical methods in petrochemistry.

Classical analysis of the sulfur constituents in crude oil necessitates, as a rule, preliminary, and sometimes repeated, concentration of the sulfur compounds present in small or even trace amounts. The compounds are isolated from the concentrates usually in groups dependent on the functional group present; the individual pure components are only rarely isolated.

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Some time ago, THOMPSON *et al.*<sup>1</sup> utilized the possibilities offered by gas chromatography to characterize the sulfur compounds in Texas crude oil. The sulfur compounds isolated from the crude oil were subjected to hydrogenolysis on Pd deposited on alumina. The original sulfur compounds were identified by the structure of the resulting hydrocarbons. By using this technique they were able to prove the presence of thionaphthene and its methyl homologues among other compounds. Among the hydrogenolysis products, ethylcyclohexane or the methylethylcyclohexanes, if present, have been assayed, depending on the site of attachment of the alkyl substituent. However, the quantitative aspects were not studied.

There also are other well-known hydrogenation catalysts in addition to palladium. Among them Raney nickel occupies a special position, since in addition to its ability to bring about hydrogenation reactions<sup>2</sup>, it displays high affinity towards sulfur. This fact has been utilized by MOZINGO *et al.*<sup>3</sup> who were the first to employ Raney nickel for structural investigations. In this way they were able to elucidate the structure of biotin.

The procedure adopted by MOZINGO *et al.*<sup>3</sup> can be traced in the work of THOMPSON *et al.*<sup>4</sup> or STREIBL<sup>5</sup> who derived the structure of sulfur compounds from the hydrocarbons obtained from the hydrogenolysis, *e.g.* thiaindanes in Texas crude oil and alkylsulfides in the so-called low-temperature spirit.

It has been stated in a monograph<sup>6</sup> that the C-S bond in thiols, organic sulfides and disulfides, sulfo compounds, sulfonic acids and several other compounds, will break upon heating alcoholic solutions of these compounds in the presence of Raney nickel to yield nickel sulfide, while the substituents attached to sulfur give new compounds. The high reactivity of Raney nickel has already been used to determine the sulfur content in sulfur compounds<sup>7</sup> or total sulfur<sup>8</sup> in crude oil or coke oven plant products. The fact, however, that hydrogenolysis of sulfur compounds leads to well defined hydrocarbons, has not yet been made the subject of a critical investigation.

The above facts induced us therefore to study the possibility of employing Raney-nickel hydrogenolysis for the quantitative determination of sulfur compounds, based on the determination of the amount of hydrocarbons resulting from this reaction. Basic experiments were undertaken in an attempt to find out the rate and yields of the hydrogenolysis reaction depending on the conditions used to effect this reaction. The model compounds of choice were simple aliphatic and heterocyclic sulfur derivatives in such solutions and at such concentrations that are encountered in crude oil products.

The hydrogenolysis reaction was checked by gas chromatography in two ways: the reaction was carried out in the liquid phase, thus reproducing the procedure adopted by MOZINGO *et al.*<sup>3</sup> with the only exception that the reaction was carried out at room temperature, and secondly in the gaseous phase in such an arrangement as is usual in reaction gas chromatography (*cf.* ref. 9).

## EXPERIMENTAL

### *Reagents and apparatus*

Two brands of Raney alloy (50 % Ni + 50 % Al) were used in the experiments; a specimen from the Research Institute of Metals, Panenské Břežany, Czechoslovakia, and a commercial product of British Drug Houses Ltd., Poole, Great Britain. Both

alloys were powders; their particle size was up to 0.1 mm. Other chemicals, *viz.* 2,2,4-trimethylpentane (isooctane), benzene (for spectrography), isopropanol A.R., and sodium hydroxide A.R. were commercial products of Lachema, N.E., Brno, Czechoslovakia. Of the model substances, thiophene was a commercial chemical of Lachema, N.E., Brno, Czechoslovakia and the other sulfur compounds were synthetic products procured from the Departments of Organic Technology and of Synthetic Fuels and Petroleum, of the Institute of Chemical Technology, Prague, Czechoslovakia.

The analyses were carried out with a commercial gas chromatograph Chrom 2 (Laboratory Instruments, N.E., Prague, Czechoslovakia) equipped with a packed column. The decrease in thiophene content was determined using 25 % by weight of formamide<sup>10</sup> on Sterchamol (particle size 0.125–0.20 mm) packing material, while other analyses were performed on a 80 × 0.6 cm column packed with 30 % by weight of squalane on the same support as above. The column temperature was 40–50°, nitrogen flow-rate was 1–2 ml/sec. The components were detected with a flame ionization detector.

#### PREPARATION OF RANEY NICKEL

The nickel was activated according to GRANATELLI<sup>8</sup>. To 40 ml of 2.5 *N* NaOH kept at about 80°, the requisite amount of Raney alloy (2 g) was added in one portion. After settling (approx. 15 min) and withdrawing the supernatant, the Raney nickel was washed as quickly as possible with three 20 ml portions of distilled water while care was taken to maintain a protective layer of water over the product. The product was subsequently washed twice with 40 ml portions of isopropanol yielding a product in principle ready for use. This slurry was transferred into the reaction flask by using isooctane, and the product in the flask was once more washed with another two 20 ml portions of isooctane.

#### STUDY OF THE LIQUID-PHASE HYDROGENOLYSIS OF SIMPLE SULFUR COMPOUNDS

##### *Investigation of the decomposition of thiophene*

The thiophene solution (1 mg or 5 mg thiophene in 1 g of the respective solvent

TABLE I

INCIPIENT AMOUNT OF SUBSTRATA IN REACTIONS OF RANEY NICKEL WITH THIOPHENE MODEL SOLUTIONS

Model system No.	Raney nickel		Model solutions of thiophene			
	Amount (g)	Origin	Amount (ml)	Concentration mg/g	Solvent	
I	1	Czechoslovakia	20	1	1.355	isooctane
II	1	Great Britain	20	1	1.355	isooctane
III	1	Czechoslovakia	20	1	0.952	benzene
IV	1	Czechoslovakia	20	5	6.78	isooctane
V	1	Great Britain	20	5	6.78	isooctane
VI	1	Czechoslovakia	20	5	4.76	benzene

in accordance with the description in Table I) was added to a freshly prepared portion of nickel immediately after decanting the last volume of isooctane.

After adding the thiophene solution, the contents of the reaction flask were immediately shaken and after the nickel had settled from the upper layer of liquid, 0.1 samples were taken with a microsyringe at regular time intervals. The frequency of sampling was 15 sec in the first minute, then 30 sec, 1 min and 2 min (see Table II); the flask was thoroughly shaken between successive sample withdrawals.

TABLE II

THE COURSE OF THE LIQUID-PHASE REACTION OF THIOPHENE WITH RANEY NICKEL IN HYDROCARBON MEDIA

( $a$  = starting thiophene concentration;  $x$  = reduction in thiophene content after  $t$  sec).

Time (sec)	Model system No.					
	I $a - x$ (mmole/mole)	II $a - x$ (mmole/mole)	III $a - x$ (mmole/mole)	IV $a - x$ (mmole/mole)	V $a - x$ (mmole/mole)	VI $a - x$ (mmole/mole)
0	1.355	1.355	0.952	6.78	6.78	4.76
15	0.474	0.745	0.609	3.18	3.61	3.90
30	0.217	0.474	0.476	1.925	2.92	3.04
45	0.108	0.271	0.362	1.490	2.44	2.48
60	0.041	0.163	0.200	1.423	2.31	2.31
90	0.014	0.068	0.105	1.151	1.76	1.83
120	—	—	0.076	0.921	1.18	1.40
180	—	—	0.029	0.555	0.746	1.03
240	—	—	—	0.298	0.542	0.60
300	—	—	—	0.163	0.474	0.552
420	—	—	—	0.041	0.217	0.428
540	—	—	—	—	0.136	0.314
660	—	—	—	—	0.068	0.257
780	—	—	—	—	0.027	0.200
900	—	—	—	—	—	0.162
1020	—	—	—	—	—	0.133

The concentration of thiophene in the sample was determined by gas chromatography using calibration graphs prepared by carrying out analyses of standard thiophene solutions in isooctane or benzene, where thiophene was present in concentrations ranging from 5 to 0.25 mg thiophene per g of the solution. The results obtained are listed in Table II and plotted after transformation of the data to mole units (see Fig. 1).

#### Determination of the hydrocarbon formed from model sulfur compounds

The reaction was carried out in reaction flasks of known volume, in all cases with 10 ml of the standard solution containing a known amount of sulfur compound according to the description in Table III. Each standard solution also contained *n*-pentane admixed as an internal standard for quantitative determinations. The concentrations of sulfur compounds listed in Table III are in milligrams of the respective model substance per ml of solution without the internal standard. On the other hand, the separately listed amounts of the internal standard are in mg of *n*-pentane added to 1 ml of the respective model solution.

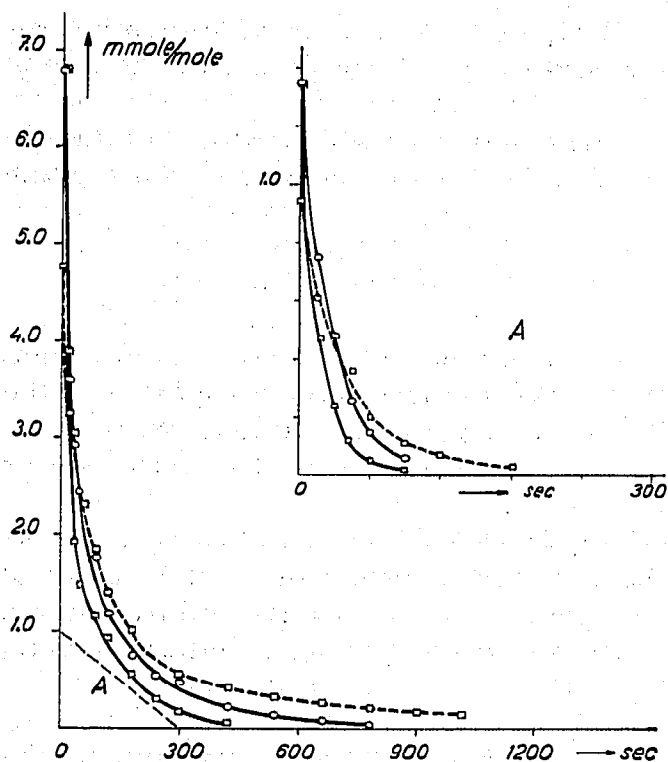


Fig. 1. The course of the liquid phase reaction of thiophene on Raney nickel in isooctane solution (—) and in benzene solution (---), respectively. (□) Raney alloy (Czechoslovakia); (○) Raney alloy (Great Britain).

The flasks were stoppered with silicone rubber wrapped in tin foil and their contents were mechanically shaken for 1 h at room temperature; the liquid and gaseous contents of the flasks were then subjected to qualitative and quantitative analyses. The injected volumes were 1  $\mu$ l of liquid and 1 ml of vapour in each case. The results are summarized in Table III.

Identification of the products from hydrogenolysis was effected by comparing

TABLE III

THE COURSE OF HYDROGENOLYSIS OF SEVERAL SIMPLE SULFUR COMPOUNDS ON RANEY NICKEL

Amount of catalyst (g)	Model solution		Sulfur compound	Orig. concn. of the sulfur compd. (mg/ml)	After hydrogenolysis		Internal standard	
	Vol. (ml)	Solvent			Hydrocarbon produced	Estimated concn. of the sulfur compd. (mg/ml)	Compound	Concn. (mg/ml)
0.5	10	Isooctane	<i>n</i> -Butyl thiol	2	<i>n</i> -Butane	1.82	<i>n</i> -Pentane	2
0.5	10	Benzene	<i>n</i> -Butyl thiol	2	<i>n</i> -Butane	1.80	<i>n</i> -Pentane	2
0.5	10	Isooctane	Isobutyl thiol	4	Isobutane	3.76	<i>n</i> -Pentane	4
0.5	10	Benzene	Isobutyl thiol	4	Isobutane	3.78	<i>n</i> -Pentane	4
0.5	10	Isooctane	Di-isobutyl sulfide	4	Isobutane	3.88	<i>n</i> -Pentane	4
0.5	10	Benzene	Thiophene	4	<i>n</i> -Butane	3.75	<i>n</i> -Pentane	4
0.5	10	Isooctane	Thiophene	2	<i>n</i> -Butane	1.85	<i>n</i> -Pentane	4

the retention times of the reaction products with the retention times of known hydrocarbons. This procedure was deemed sufficient because of the simplicity of the model solutions used in this study.

The content of the sulfur compound was arrived at, from the products of liquid-phase hydrogenolysis determined by internal standardization (*cf.* ref. 11), using the relation

$$g_x' = g_s' \frac{A_t'}{A_s'} \cdot \frac{RMR_{sr}}{RMR_{tr}} \cdot \frac{M_x}{M_s} \text{ (mg/ml)}$$

where  $g_s'$  is the weight of the internal standard in unit volume of the original solution under analysis,  $A_t'$  is the peak area and  $RMR_{tr}$  the relative molar response of the resultant product from hydrogenolysis;  $A_s'$  and  $RMR_{sr}$  are the same quantities for the internal standard used; and  $M_x$  and  $M_s$  are molecular weights of the sulfur compound and of the internal standard, respectively.

The content of the hydrogenolysis products from the gaseous phase was determined by comparison with calibration graphs. After transformation to the weight of the respective sulfur compounds, the results obtained above were corrected by adding, per 1 ml of the liquid phase, such amount of the sulfur compound as determined by calculation.

### Discussion

From the data in Fig. 1 it follows that the hydrogenolysis of thiophene over Raney nickel is a process leading to the comparatively rapid disappearance of this sulfur compound from its solution, when concentrations in the same range as are encountered in various hydrocarbon materials and the above amounts of Raney nickel are used. In contrast to MOZINGO *et al.*<sup>3</sup>, we found that the reaction proceeds to the desired degree even at room temperature, and thus it is well suited for analytical purposes.

A comparison of the shape of plots for the rate of thiophene depletion in reactions carried out in isooctane or benzene showed (Fig. 1.) that at comparable starting concentrations the behaviour of thiophene in these solvents differs to some extent. In spite of both solvents pertaining to the same type of so-called aprotic solvents, the rate of thiophene depletion is higher in isooctane than in benzene. Previous opinion on the influence of the solvent on the course of hydrogenolysis reactions<sup>2</sup> was that the reaction proceeded better in protic solvents (*e.g.* alcohols), but differences have also been indicated, however, in the behaviour of aprotic solvents. The experimental finding<sup>7,12</sup> that the presence of unsaturated hydrocarbons has a negative influence on the course of hydrogenolysis should be mentioned here. The cause of a lower reaction rate in benzene can also be the higher tendency of this hydrocarbon to adsorb on a metal surface; it would seem that this factor plays a greater role in our case.

From what has been said above it follows that opinion on this point is far from being clear-cut and unanimous. An exact picture of the transformations occurring can be best obtained by determining the order and rate constant of the reaction. However, the mechanism of a heterogeneous reaction and particularly the mechanism of a catalytic reaction taking place on a surface possessing chemisorptive properties, is intricate and not easily understood. This is also the reason why no kinetic equation involving the rates of all subsequent processes can be derived.

Since thiophene, a compound very resistant in contrast to thiols, sulfides, and similar sulfur compounds, readily undergoes hydrogenolysis on Raney nickel, it would be expected that other sulfur compounds would react more readily in this way. This expectation has been confirmed. Both the thiols and sulfides studied (Table III) undergo hydrogenolysis to produce the respective hydrocarbons in yields confirming an unequivocal and quantitative reaction course. Occurrence of other compounds in addition to the expected hydrocarbons has not been observed as can be illustrated by the hydrogenolysis of di-isobutylsulfide (Fig. 2).

However, the above statement only concerns compounds that have been studied in this paper. The question of unequivocal hydrogenolysis of such sulfur compounds that would produce radicals which would persist as independent entities or would further react in one way or other, can be solved only after carrying out further basic studies.

#### STUDY OF THE VAPOUR-PHASE HYDROGENOLYSIS OF SIMPLE SULFUR COMPOUNDS

The results obtained in the liquid-phase reaction have confirmed that hydrogenolysis could in practice be used for quantitative determination of sulfur compounds. The only difficulty is that sometimes the liquid and the gaseous phase of the reaction mixture must be analyzed separately. The difficulties tend to grow in such cases, where highly volatile hydrocarbons are produced, e.g. methane or ethane.

It seemed expedient to study hydrogenolysis in such a set-up as would allow the hydrogenolysis products to enter immediately the analytical column of a gas chromatograph. The principle of reaction gas chromatography, developed by DRAWERT *et al.*<sup>9</sup>, can be used for such a purpose.

#### The reactor

The reactor is shaped as a pre-column of a gas chromatograph; it is illustrated in Fig. 3. It has its own injection port and hydrogen inlet. It can be electrically heated to a controlled temperature. The pre-column is fitted at the end with an injection needle which allows it to be joined directly to the injection block of a gas chromatograph, by piercing its rubber septum. Such a construction permits easy sampling, both *via* the pre-column and directly, on to the analytical column of the apparatus. Thus, operation conditions in the analytical column can be maintained constant regardless of whether the sample passes through the reactor or the latter is by-passed.

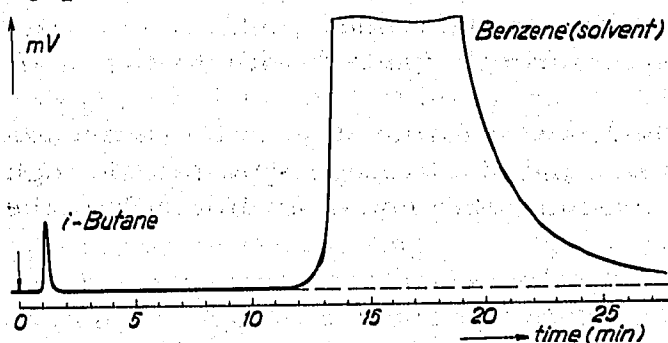


Fig. 2. Chromatogram of di-isobutyl sulfide (4 mg/ml) in benzene model solution after reaction with Raney nickel (squalane, 50°, sample 1  $\mu$ l).

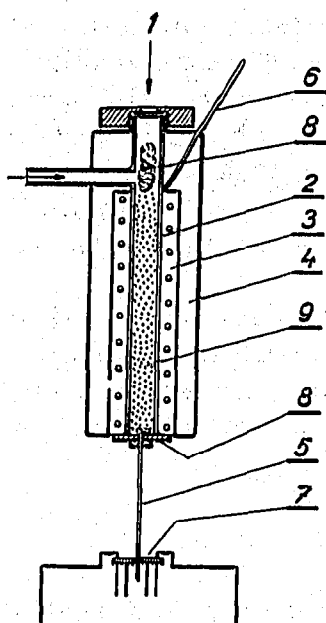


Fig. 3. Reactor layout: 1 = injection port (silicone rubber septum); 2 = reactor tube (90 × 6 mm); 3 = electric heating; 4 = thermal insulation (asbestos cord); 5 = injection needle; 6 = mercury thermometer in contact with the outer reactor tube wall; 7 = sampling port of the connected gas chromatograph (silicone rubber septum); 8 = quartz wool; 9 = catalyst bed in reactor (Raney nickel and stationary liquid applied to glass beads).

#### Preparation of Raney nickel

The nickel was prepared and activated in the same way as has been described in the section Experimental. After decanting the last portion of isooctane, 5 ml of a solution of *n*-hexadecane in isooctane (1.5 mg *n*-hexadecane/100 ml isooctane) was added. To this slurry, 10 g of acid-washed glass beads (size 0.25–0.315 mm) were added. The solvent level is maintained so that the beads are continuously covered. After "homogenization" the isooctane is evaporated. This can be done by heating the flask in warm water. The glass beads serve as an inert support for the Raney nickel and the *n*-hexadecane stationary liquid serves to bind the powdery catalyst to the supporting material and to impair the adsorptivity of the catalyst metal.

The packing material obtained in this manner is immediately poured into the pre-column while passing hydrogen at a moderate rate through the latter. Pre-column conditioning is achieved by heating it in a stream of hydrogen for 4–5 hours at 100°. The pre-column temperature during actual analyses is maintained at 95°.

After use, the pre-column must be continuously purged with hydrogen or else it will rapidly lose its activity.

The analyses were carried out at a column temperature of 50°, at a carrier-gas flow rate (H<sub>2</sub> + N<sub>2</sub> mixture) of up to 1.5 ml/sec, and at a hydrogen flow-rate through the reactor of up to 0.4 ml/sec. On these grounds, the flow of hydrogen into the detector micro-burner was reduced.

#### Discussion

In the initial experiments, Raney nickel was applied to powdered teflon without any liquid stationary phase. The results obtained, however, have shown that



such a packing material readily adsorbs hydrocarbons (Fig. 4a). Raising the pre-column temperature up to 200° was of no help in this problem.

The adsorptivity of Raney nickel was reduced successfully by adding a stationary phase. Higher alkanes (*n*-hexadecane, squalane) or Apiezon L were used for this purpose.

First, it was necessary to find out the necessary amount and type of phase to be used. In suppressing the adsorptivity of the nickel, slowing down of the course of the hydrogenolysis is unavoidable due to the layer of stationary phase prolonging the time necessary for a sulfur compound to diffuse through to the active surface of the catalyst; the restoration of the hydrogen content on the catalyst surface is also hampered in this way.

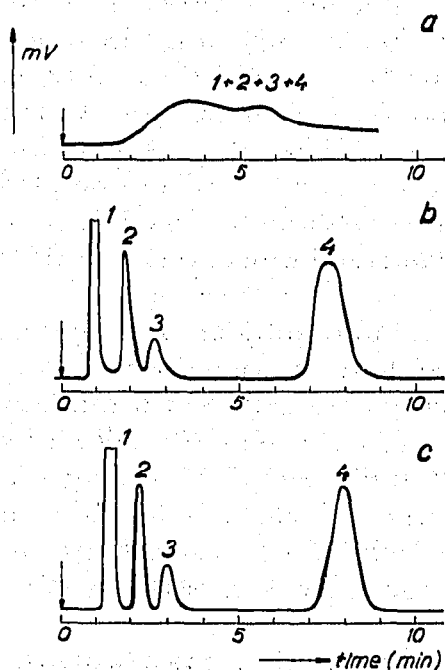


Fig. 4. The influence of Raney nickel modification on the adsorption properties of reactor packing. Injected mixture: propane + iso-butane + *n*-butane + *n*-pentane; chromatographic column: squalane at 30°. (a) Reactor packed with Raney nickel fixed on teflon at 100°. (b) Reactor packed with Raney nickel on glass beads modified with 50 mg *n*-hexadecane (per 1 g Raney nickel and 10 g glass beads) at 100°. (c) Reactor by-passed.

The stationary phases used for this purpose were *n*-hexadecane, squalane, and Apiezon L. The packing material was prepared in such a way that the respective stationary phase was added to a mixture of Raney nickel and glass beads (1:10 by weight) in amounts gradually increasing from 25 to 400 mg. Each of the packing materials prepared in this way was then investigated at temperatures ranging from 20° to 200°.

Even the smallest amount of stationary phase sufficed to reduce the adsorptive properties of the packing, at room temperature; it did not however eliminate them to a sufficient degree. The conditions could be improved by raising the temperature and increasing the amount of stationary phase. Stationary liquid in amounts of 50–150 mg/1 g Raney nickel and 10 g glass beads can be considered sufficient for practically eliminating adsorptive properties of the catalyst (Fig. 4b). An increase in the amount

of stationary phase over 150 mg has no further influence on the state of affairs, except to slow down the rate of hydrogenolysis. Apiezon L, *n*-hexadecane, and squalane give similar results; with *n*-hexadecane or squalane, however, the proportion of stationary phase can be decreased to some extent.

It has been found that, for hydrogenolysis of highly volatile sulfur compounds (b.p. under 120°), there is an advantage in using *n*-hexadecane and keeping the pre-column temperature at less than 100°. For sulfur compounds of medium volatility (b.p. under 200°), squalane is well-suited for temperatures of 120–150°. With low volatile sulfur compounds (b.p. above 200°) the pre-column temperature should be increased to 150–200° and Apiezon L should be used to modify the nickel.

It was also necessary to investigate the influence of the time of residence in the reactor of the sulfur compound on the yield of the hydrogenolysis process. Thiophene was again used as a model substance. In order to have something in hand, the least appropriate phase was chosen (*i.e.* Apiezon L) and this was added in a high, *i.e.* less favourable amount (200 mg/1 g Raney nickel and 10 g glass beads). At the same time, the lower temperature limit (150°) suited for use of this phase was maintained. Thus, the conditions created were the least favourable of those recommended for use. Under these conditions, 0.5 ml saturated thiophene vapour was injected, thus introducing an additional factor which can have a negative influence on catalyst activity, *i.e.* oxygen from air.

The time of residence in the pre-column of the compound subjected to hydrogenolysis is, under otherwise stabilized conditions, dependent on the flow rate of hydrogen through the reactor. This parameter was gradually changed over a range of 0.095–2.87 ml/sec. Up to a hydrogen flow-rate of 2.0 ml/sec, no unreacted thiophene has been found among the hydrogenolysis products. It only occurred among the products at rates higher than 2.87 ml/sec. After reducing the calculations to the time of residence of thiophene in reactor, the lowest time limit found was 0.9 sec. It can be assumed therefore that a time of residence in excess of 1 second will ensure the complete reaction of thiophene.

Vapour phase hydrogenolysis under the conditions of reaction gas chromatography has also been used to analyse the same solutions of model compounds as have been used in the first part of this paper. Identification of the products and quantitative calculations were made by using the procedure described therein. The results obtained do not differ from those summarized in Table III. The procedure adopted for the vapour-phase analyses has proved to be simple, together with their quantitative evaluation, even in such cases where highly volatile hydrocarbons appeared among the products.

Another positive feature is that neither the character of the solvent nor that of the accompanying hydrocarbons have anything like so marked an influence on the course of hydrogenolysis, as has been encountered when carrying out the analysis in the liquid phase. A favourable fact is that the vapour phase hydrogenolysis takes place in a hydrogen atmosphere and also that nickel is present in a large excess over the injected amount of sample.

It can be assumed that the activity of the reaction medium will be higher in the gaseous rather than in the liquid phase. With this in mind, it is also necessary to consider secondary changes in the hydrocarbon backbone formed by the desulfurization of the original sulfur compound. This can occur especially in such cases where this backbone will tend towards further hydrogenation.

## CONCLUSIONS

The aim of the present paper has been to study the hydrogenolysis of sulfur compounds over Raney nickel and to use this reaction for the quantitative determination of these compounds, based on the type and amount of hydrocarbons produced. The study has been performed with model sulfur compounds of simple structure and in presence of hydrocarbons, both in the liquid and gaseous phases.

It has been found that, with thiophene, the rates, direction and yields of reactions carried out in both liquid and gaseous phases permit the use of the procedure for analytical purposes.

The reaction in the liquid phase is complete within 3–5 minutes at room temperature; its course was unequivocal and an equivalent amount of *n*-butane was produced. The only question to be solved yet is whether other sulfur compounds can also be quantitatively determined in this manner.

It is convenient for analytical purposes to carry out the gaseous phase reaction over Raney nickel under the conditions of reaction gas chromatography. It has been found that the time necessary for completion of the reaction of this compound on Raney nickel, in the gaseous phase, is less than one second. The Raney nickel must be modified with a small amount of a stationary liquid (50–150 mg *n*-hexadecane, squalane or Apiezon L/1 g nickel) in order to reduce catalyst adsorptivity.

The results obtained in the present study form a basis for working out appropriate analytical methods for the estimation and determination of sulfur compounds present in narrow crude-oil or coal-tar cuts. The hydrocarbons produced have considerably lower molecular weight relative to that of the original sulfur compound and appear early in the chromatogram which affords an advantage, especially in trace analysis. In some cases, the reactor can be interposed even behind the analytical column or at any location along the column which, undoubtedly, will permit the further extension of the suggested procedure.

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