METHODS OF ANALYSIS OF SULPHUR COMPOUNDS IN HYDROCARBON MIXTURES

III. STUDY OF LIQUID PHASE HYDROGENOLYSIS OF THIONAPHTHENE OVER RANEY NICKEL AT ROOM TEMPERATURE; DETERMINATION OF THIONAPHTHENE ADMIXTURES IN TECHNICAL GRADE NAPHTHALENE BY GAS CHROMATOGRAPHY

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SUMMARY

The hydrogenolysis of thionaphthene by Raney nickel in the medium of benzene at room temperature leads to ethylbenzene, which is the only quantitatively significant reaction product. The degree of conversion of 0.01–2.0% thionaphthene solutions in benzene amounts to approximately 80%. However, both the qualitative and quantitative course of the desulphurization is reproducible even in the presence of a large excess of naphthalene. The reaction can be utilized for the routine determination of 0.05–2.0% thionaphthene contents in technical-grade naphthalenes, the relative error of the analysis being not higher than ± 5%.

INTRODUCTION

The by now classical desulphurization of sulphur compounds with Raney nickel by MOZINGO *et al.*[1] has been much used in organic syntheses and, particularly, in studying the structure of various types of organic sulphur compounds[2].

The desulphurization proper by Raney nickel is not a catalytic reaction; organic sulphur is fixed to the nickel and forms an acid-soluble modification of NiS (ref. 3). Raney nickel contains fixed hydrogen, so that the elimination of the sulphur is accompanied by hydrogenation of the desulphurized hydrocarbon remainder, if the latter is unsaturated and amenable to hydrogenation under the conditions of the reaction.

If the desulphurization of the organic sulphur compound proceeds perfectly according to the scheme quoted in the initial paper by MOZINGO *et al.*[1] (the author mentioned did not notice the combination of radicals produced transitorily),

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$$R\text{--}S\text{--}R' + Ni(H) \rightarrow \underbrace{NiS}_{A} + \underbrace{R\text{--}H + R'\text{--}H,}_{B}$$
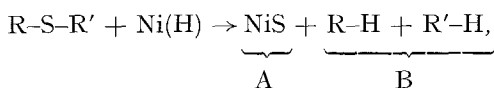
and if the experimental conditions are chosen such that quantitative conversion of organically bound sulphur to NiS is guaranteed, then the above reaction can be made use of in two ways:

(a) determination of the amount of NiS

(b) determination of the amount of the hydrocarbon (R = R'), or of a mixture of hydrocarbons (R ≠ R').

Deviations from the presupposed ideal scheme may occur in the course of desulphurization, but, if the reaction is reproducible under a given set of experimental conditions, it is possible to carry out a direct calibration of the tare of the organic sulphur compound *vs.* the amount of the reaction product A or B.

A method based on the determination of the product A, *i.e.* on the determination of the amount of NiS produced, has been developed by TRIFONOV et al.[4] and by GRANATELLI[5]. TRIFONOV and co-workers determined thiophenic, sulphidic, disulphidic, and elementary sulphur up to total sulphur contents of 2%. The sulphur content in NiS was determined polarographically with the use of calibration curves for the determination of the individual compounds. According to GRANATELLI[5], it is possible to determine both elemental and organically bound sulphur in concentrations within 10^{-4}–10^{-2}% with a relative accuracy of ±1.6%. The amount of NiS is determined as H_2S by titrating it with a mercury acetate solution, whose titre has been determined empirically on elementary sulphur, as the degree of conversion to NiS is approximately 95%. With the use of the empirical sulphur titre, the apparent recovery was 99%.

Up till now, the identification of the desulphurization product B has only been used for the qualitative analysis of the initial sulphur compound[1,6-8]. Quantitative investigation of the desulphurization product B was launched recently by STASZEWSKI et al.[9]. They performed the hydrogenolytic reaction at ambient temperature in the medium of an aprotic solvent (isooctane, benzene), and ascertained that the majority of the hydrocarbon was formed in 3–5 min, the degree of conversion being about 90%. It was still questionable, however, whether the desulphurization would proceed in a similar way with more complicated molecules as well.

In the present paper, we have investigated the feasibility of determining quantitatively condensed sulphur-containing heterocyclics by desulphurizing them and subsequently determining the hydrocarbon produced. The model substances used were thionaphthene and mixtures of thionaphthene and naphthalene in the ratios usually found in technical grade naphthalenes produced by the coal-tar and petrochemical industries. Thionaphthene represents an important impurity in the above products; the aim of the present work was to develop an analytical method for its routine determination.

In this respect, the findings by NIGAM et al.[10] on the utilization of gas phase hydrogenolysis of thionaphthene by Raney nickel for the determination of minute contents of thionaphthene in technical grade naphthalenes were complemented, using the experimental arrangement appropriate to reaction gas chromatography.

Materials and instrumentation

The purity of the chemicals used (analytically pure benzene, chromatographically pure *n*-octane, pure ethylbenzene) and of the standard compounds (pure thionaphthene, Gesellschaft für Teerverwertung mbH, Duisburg, Germany; zone refined naphthalene, Lachema, N.E., Czechoslovakia) was checked by gas chromatography employing packed columns with two stationary phases of different polarity (Apiezon L and polyethyleneglycol adipate), and a 50 m long squalane coated capillary column with 0.25 mm I.D. The thionaphthene was subjected to elementary analysis; the zone refined naphthalene was found to contain 0.0016% of sulphur[5].

The chromatographic analyses were performed on a Chrom 2 apparatus (Laboratory Equipment, N.E., Prague, Czechoslovakia) fitted with a flame ionization detector. The reaction mixtures, produced from more concentrated model solutions of thionaphthene in benzene (1.0–2.0%), were analysed on a stainless steel column (length 85 cm, I.D. 0.6 cm) packed with 10% Apiezon L-on-Chromosorb W 80/100 mesh packing at a temperature of 90°. Nitrogen was used as the carrier gas at a flow rate of 30 ml/min. The reaction mixtures coming from the other model solutions were analysed on a column of the same dimensions, packed with Celite, 60/80 mesh, coated with 20% of squalane, the column temperature and carrier gas flow rate being kept at 70° and 50 ml/min, respectively.

Solutions of model substances and samples of technical grade naphthalene

Benzene was chosen as both a solvent and reaction medium as more than 25 wt.% of naphthalene[11] could be dissolved in it even at ambient temperature. Model solutions of thionaphthene in benzene of approximate thionaphthene concentrations of 0.05–2.0% (Table Ia) were prepared by weighing. Model solutions in benzene were also prepared of thionaphthene-zone melted naphthalene mixtures, approximate thionaphthene concentrations in naphthalene 0.05–1.9% (Table IIa), the corresponding thionaphthene concentrations in the benzene varying between 0.01 and 0.5%.

The samples of the technical naphthalenes (A = distilled naphthalene; B = sublimed naphthalene; C = hot-pressed naphthalene), together with pure naphthalene (D = analytical grade naphthalene, Lachema, N.E., Czechoslovakia), were analysed in the form of approximately 25% solutions in benzene. All the solutions contained *n*-octane, which served as an internal standard for the quantitative determination of the ethylbenzene produced as a result of the desulphurization of the thionaphthene.

Procedure

An appropriate amount of Raney nickel suspension[9] in isopropyl alcohol is transferred into a ground-stoppered vessel, the isopropyl alcohol is poured off, the solution of the mixture to be analysed and *n*-octane (internal standard) are added, in an amount of 0.5–1.0 ml, to the catalyst, and the vessel is closed. After two hours reaction at room temperature, the reaction mixture is decanted off the Ni–NiS suspension and kept for GC analysis in a bottle with a rubber septum closure, which permits sampling with an injection microsyringe (Hamilton Co., Whittier, U.S.A.).

The ethylbenzene in the reaction mixture, produced by the desulphurization of thionaphthene, is determined by the internal standard technique. The percentage of

TABLE I

MODEL SOLUTIONS OF THIONAPHTHENE IN BENZENE

n = Number of determinations; T = thionaphthene content in the solution in benzene (wt. %); T^x = percentage of thionaphthene in the solution, corresponding to the portion of thionaphthene reacted (calculated by relation (1), as the average of at least three GC determinations, for $W_{(t)}$ denoting the weight of solution to be mixed with standard; $\bar{T}^x$ = average of two parallel determinations; T' = calculated thionaphthene content in the solution in benzene; d = absolute bias of the determination ($d = T - T'$); e = relative bias of the determination ($e = 100(T - T')/T$ (%)).

n	Ia			Ib		
	T (wt. %)	T^x (wt. %)	$\bar{T}^x$ (wt. %)	T' (wt. %)	d (wt. %)	e (%)
1	2.146	1.686	1.704	2.146	0.000	0.0
2	1.077	1.723				
3		0.853	0.852	1.068	+0.009	+0.8
4	0.518	0.852				
5		0.430	0.434	0.538	−0.020	−3.9
6	0.217	0.437				
7		0.187	0.187	0.225	−0.008	−3.7
8	0.082	0.187				
9		0.070	0.070	0.077	+0.005	+6.1
10	0.042	0.070				
11		0.035	0.035	0.032	+0.010	+24.0
12		0.035				

Ic

Statistical evaluation of the relation between the values of T and T^x

Regression line, $Y = b_0 + b_1 x = 0.0096 + 0.7891x$ (2)

$b_0 = 0.0096$
95 % confidence limits of the constant β_0, $-0.0016 \geqq \beta_0 \geqq +0.0208$

$b_1 = 0.7891$
95 % confidence limits of the constant β_1, $0.7780 \geqq \beta_1 \geqq 0.8002$

$s_{yx} = 0.013$

$$T' = \frac{\bar{\bar{T}}^x - 0.0096}{0.7891}$$ (2a)

TABLE II

MODEL SOLUTIONS IN BENZENE OF MIXTURES OF THIONAPHTHENE AND ZONE REFINED NAPHTHALENE

T = Thionaphthene content in the thionaphthene–naphthalene mixture (wt. %); T^x = percentage of thionaphthene in the mixture analysed, corresponding to the portion of thionaphthene reacted (calculated by relation (1), as the average of at least three GC determinations, for $W_{(s)}$ denoting the weight of thionaphthene–naphthalene mixture, in the benzene solution, to be mixed with standard); a = amount of thionaphthene weighed out in the benzene solution; T' = calculated thionaphthene content in naphthalene (as x from regression line (3); cf. relation (3a)). The other constants have the same meaning as in Table I.

n	IIa				IIb			IIc
	T (wt. %)	a	T^x (wt. %)	$\bar{T}^x$ (wt. %)	T' (wt. %)	d (wt. %)	e (%)	Statistical evaluation of the relation between the values of T and T^x
1	1.892	0.506	1.555	1.552	1.892	0.000	0.0	
2			1.550					Regression line, $Y = b_0 + b_1 x = -0.00119 + 0.82097x$ (3)
3	1.578	0.343	1.326	1.332	1.624	−0.046	−2.9	
4			1.339					
5	1.368	0.332	1.085	1.088	1.326	+0.042	+3.1	$b_0 = -0.00119$
6			1.091					95 % Confidence limits of the constant β_0, $-0.02566 \leqq \beta_0 \leqq 0.02328$
7	1.055	0.282	0.861	0.858	1.046	+0.009	+0.8	
8			0.856					
9	0.886	0.212	0.702	0.706	0.861	+0.025	+2.8	$b_1 = 0.82097$
10			0.711					95 % Confidence limits of the constant β_1, $0.80947 \leqq \beta_1 \leqq 0.83247$
11	0.602	0.122	0.506	0.508	0.620	−0.018	−3.0	
12			0.510					$s_{yx} = 0.022$
13	0.094	0.025	**0.079**	0.079	0.097	−0.003	−3.2	
14			0.079					
15	0.054	0.014	0.046	0.046	0.057	−0.003	−5.6	$T' = \dfrac{\bar{T}^x + 0.00119}{0.82097}$ (3a)
16			0.047					

thionaphthene in the sample analysed, T^x, corresponding to the amount of thionaphthene having reacted under the conditions of the reaction, is calculated by the use of relation (1) (ref. 12):

$$T^x \text{ (wt.\%)} = \frac{W_s \ RMR_{sr} \ A'_i \ M_t}{W_{(i)} \ RMR_{ir} \ A'_s \ M_s} \cdot 100 \tag{1}$$

where W_s is the weight of the standard added, $W_{(i)}$ is, when analysing the thionaphthene solutions, the weight of the solution to be mixed with the standard, or, in the case of solutions of the thionaphthene–naphthalene mixtures or technical grade naphthalenes, the weight of the mixture and the naphthalene, respectively, to be mixed with the standard, RMR_{sr} and RMR_{ir} are the relative molar responses of the internal standard (n-octane) and of the substance determined (ethylbenzene), A'_i and A'_s are the ethylbenzene and standard peak areas, and M_t and M_s are the molecular weights of thionaphthene and the internal standard, respectively. The RMR_{sr}/RMR_{ir} ratio was found to have a value of 1.066 by the internal standard technique.

    The values of T^x, expressed as weight percentages, are presented in Tables Ia, IIa, and III. Each result represents the average of at least three determinations. The results of the series of determinations of thionaphthene in the model solutions of thionaphthene in benzene (Table Ia) and the model solutions of thionaphthene and naphthalene in benzene (Table IIa) have been processed by regression analysis, as described by FELIX AND BLÁHA[13]. The straight regression lines were estimated from the values corresponding to the points of the co-ordinates $[T,T^x]$; the meaning of the symbols T and T^x, as well as the respective values are quoted in Tables Ia and IIa. The

TABLE III

DETERMINATION OF THIONAPHTHENE CONTENT IN SAMPLES OF TECHNICAL GRADE NAPHTHALENE

$W_{(i)}$ = Naphthalene weighed out in the benzene solution to be mixed with standard (in grams); T^x = percentage of thionaphthene in the sample analysed, corresponding to the portion of thionaphthene reacted (calculated as the average of at least three GC determinations, for $W_{(i)}$ denoting the weight of naphthalene); T' = calculated thionaphthene content in naphthalene (as x from regression line (3); cf. relation (3a)); T^a = thionaphthene content calculated from the total sulphur content determined according to GRANATELLI[5]; T^b = thionaphthene content in naphthalene determined, in identical samples, by NIGAM et al.[10]; n = number of parallel determinations; e = difference between two parallel determinations expressed in percentage ($e = 100(T_1' - T_2')/\bar{T}'$). A = Distilled naphthalene; B = sublimed naphthalene; C = hot-pressed naphthalene; D = analytical grade naphthalene.

Sample	n	$W_{(i)}$ (g)	T^x (wt. %)	T' (wt. %)	$\bar{T}'$ (wt. %)	e (%)	T^a (wt. %)	T^b (wt. %)
A	1	2.17254	0.943	1.15				
					1.15	0.1	1.12	—
	2		0.944	1.15				
B	1	2.31571	0.681	0.829				
					0.83	1.3	0.87	0.82
	2		0.690	0.840				
C	1	2.14162	1.11	1.35				
					1.36	0.5	1.49	1.25
	2		1.12	1.36				
D	1	0.23182	0.315	0.384				
					0.39	3.1	0.43	—
	2		0.325	0.396				

estimations of regression lines (2) and (3) ($Y = b_0 + b_1 x$), the 95 % confidence limits for the constants β_0 and β_1, and the estimation of the standard deviations, s_{xy}, are summarized for both series investigated, in Tables Ic and IIc. The values of T' ($T' = (T^x - b_0)/b_1$) and the absolute and relative errors of the determinations are summarized in Tables Ib and IIb.

The values of T', expressing the thionaphthene content of the naphthalene samples (Table III), determined by the method suggested, have been calculated by expression (3a), using the regression line (3). Expressions (3) and (3a) are quoted in Table IIc.

Note. (a) The analytical determination proper of thionaphthene in naphthalene was preceded by a GC analysis for the presence of substances in the naphthalene studied which could interfere with the final interpretation of the peak areas A'_s and A'_i due to peak overlapping or incomplete resolution.

(b) After ten subsequent analyses of the reaction mixture, it is necessary to wait for complete elution of the accumulated naphthalene and nonconverted thio-
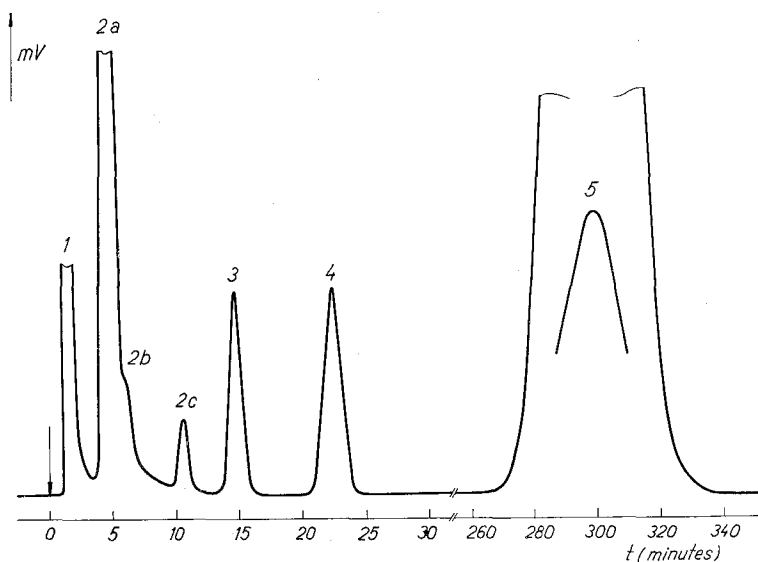

Fig. 1. Chromatographic record of an ordinary analysis of naphthalene for its thionaphthene content. 1 = Isopropyl alcohol (coming from the preparation of Raney nickel); 2a = solvent (benzene); 2b = cyclohexane; 2c = impurity in the solvent (toluene); 3 = *n*-octane; 4 = ethyl-benzene; 5 = naphthalene and unreacted thionaphthene.

naphthene from the column (Fig. 1). When employing the method for routine analysis a precolumn is recommended to use for retaining the high-boiling components which can be eluted from the precolumn by back flushing or by bypass during analysis.

DISCUSSION

Starting from the basic mechanism of the hydrogenation–desulphurization by Raney nickel of organic sulphur compounds, as has been quoted by MOZINGO *et al.*[1],

and reckoning the amount of the hydrogen fixed to Raney nickel to be 25–150 ml/g (ref. 14), we can assume the hydrogenolysis of thionaphthene to proceed as follows:
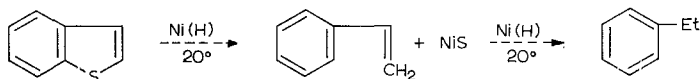

Easy hydrogenation of the conjugated double bond in styrene, the intermediate in the reaction of thionaphthene hydrogenolysis, is known[3], as is the fact that the aromatic core of styrene remains intact under such mild conditions of hydrogenation[7,15]. The quantitativeness of the course of styrene hydrogenation under the conditions employed was checked by capillary gas chromatography on a squalane stationary phase. Not even trace amounts of styrene remained in the reaction mixture after the reaction of styrene with Raney nickel was finished, and only traces of cyclohexane and of the respective alkyl derivatives resulted from the reaction of benzene, toluene, and n-propylbenzene. The action of Raney nickel upon ethylbenzene yielded no trace of compounds of lower molecular weight, which would have indicated a contingent consecutive cleavage of ethylbenzene.

     Hence, it is possible to conclude the quantitative part of the present study by saying that ethylbenzene is the sole product of the hydrogenation–desulphurization of thionaphthene by Raney nickel at room temperature. Our findings are in agreement with the qualitative results of the investigation by BLICKE AND SHEETS[15], and, more recently, by THOMPSON et. al.[7] who followed the original MOZINGO procedure[1] and performed the hydrogenolysis at the temperature of the reaction medium's boiling point. BLICKE AND SHEETS only isolated products of the type
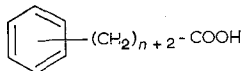
after the desulphurization of substituted carboxylic acids of the type
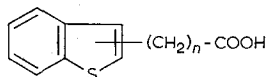
THOMPSON et al. have proved by infrared spectroscopy that the products of the desulphurization of thiaindanes consist only of the respective alkylbenzenes.

     It was found that the hydrogenolysis by Raney nickel of thionaphthene in a benzene medium does not proceed quantitatively at room temperature. Therefore, we investigated the progress of thionaphthene hydrogenolysis with two model solutions of thionaphthene in benzene (thionaphthene contents were 0.1 and 1.0 wt.%) in the presence of Raney nickel charges prepared from 0.2 and 0.8 g of the alloy per 1 ml of the model solution. In 60–80 min, the portion of thionaphthene reacted had reached a limit of approximately 80%, and, over four days, it neither rose nor fell. The results of the analyses of samples taken sequentially from the model solutions within the first 4 h are depicted in Fig. 2.

     The amount of the Raney nickel used for desulphurization per 1 ml of the sample analysed significantly influences the rate and quantitativeness of the reaction. The minimum amount of Raney alloy (in g per 1 ml of 0.05–2.5% solution) is quoted in Table IV. If higher amounts of Raney nickel are used, the portion of thionaphthene reacted does not rise any higher (Fig. 3).
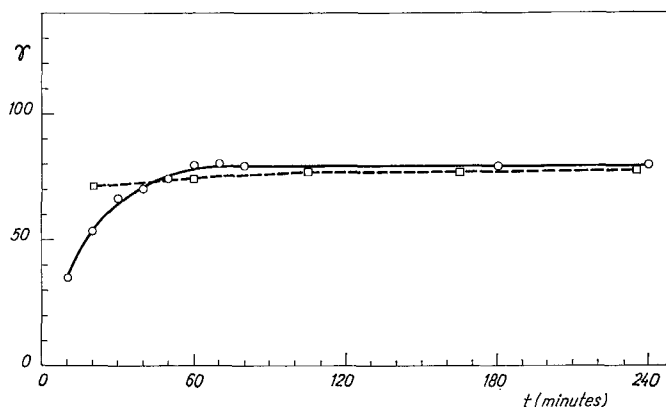
Fig. 2. Progress of the reaction of thionaphthene with Raney nickel. γ = Fraction of thionaphthene having reacted (%); t = time (min); $\bigcirc$ = 1% solution of thionaphthene in benzene; $\square$ = 0.1% solution of thionaphthene in benzene.

On the basis of the above results, it is possible to recommend a standard amount of 0.6 g of Raney nickel per 1 ml of the solution to be analysed and a two hours reaction time for the desulphurization of solutions containing thionaphthene in concentrations within 0.01–0.5%, which corresponds to contents of 0.05–2.0% of thionaphthene in technical grade naphthalenes. Solutions with higher thionaphthene contents have to be diluted so that they contain not more than 2.5% of thionaphthene. At still higher thionaphthene concentrations, the amount of the Raney nickel necessary for reproducible 80% conversion would lead to the formation of a slurry.

The statistical analysis of the results shows that, with both the model series of the solution of thionaphthene in benzene (regression line (2), Table Ic) and the model series of the solutions of the thionaphthene–naphthalene mixtures in benzene (regression line (3), Table IIc), there is a linear relationship between the amount of
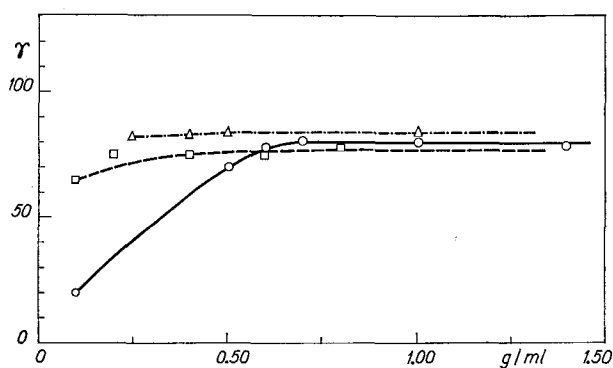

Fig. 3. Effect of the amount of Raney nickel (g/ml) on the quantitativeness of the hydrogenation–desulphurization of thionaphthene. γ = fraction of thionaphthene having reacted; $\bigcirc$ = 1% solution of thionaphthene in benzene; $\square$ = 0.1% solution of thionaphthene in benzene; $\triangle$ = 0.1% solution of thionaphthene in benzene (0.6% of thionaphthene in naphthalene). The individual samples were taken at two hourly intervals.

TABLE IV

MINIMUM AMOUNT OF RANEY ALLOY NECESSARY FOR REPRODUCIBLE CONVERSION OF THIONAPH-THENE TO ETHYLBENZENE

Thionaphthene content in benzene (wt.%)	Amount of Raney alloy (in g per 1 ml of solution)
2.5	1.8
2.0	1.4
1.0	0.8
0.5	0.6
0.25	0.4
0.1	0.2
0.05	0.1

the thionaphthene weighed out into the model solution and the thionaphthene which has reacted. Hence it follows that the presence of naphthalene in the solution has no effect on the character of the course of thionaphthene desulphurization. The systematic error is negligible at the significance level of $\alpha = 0.05$, and the difference between two parallel determinations is also insignificant at the above significance level. The error of the determination displays a so-called concentration dependence, $i.e.$, the error is dependent on the content of the substance under determination in the sample. It is possible therefore to say that hydrogenation–desulphurization of thionaphthene by Raney nickel, under the above conditions, is applicable to the quantitative determination of thionaphthene in naphthalene.

The thionaphthene content in naphthalene, T', determined according to the method suggested, can be calculated as the quantity x from straight regression line (3) and is given by expression (3a) ($cf.$ Table IIc). The thionaphthene contents determined in the samples available of technical grade naphthalene are summarized in Table III. With regard to the inherent inhomogeneity of the samples of technical grade naphthalene, the data may be considered to agree well with the results of the checking analysis, carried out according to GRANATELLI[5] for the total sulphur content. Very close results were found for the thionaphthene contents also when analysing identical samples of technical grade naphthalenes B and C by hydrogenation in gaseous phase on Raney nickel[10].

CONCLUSIONS

Thionaphthene can be converted to ethylbenzene by hydrogenolysis with Raney nickel at room temperature in a benzene solution, ethylbenzene being the only quantitatively significant product of the reaction. The conversion of 0.01–2.0% solutions of thionaphthene in benzene is not complete (about 80%), however, it has been proved that both the qualitative and quantitative course of the desulphurization is reproducible even in the presence of a high excess of naphthalene. Thus, the feasibility has been demonstrated of using the hydrogenolytic reaction for routine determination of minute contents of thionaphthene (0.05–2.0%) in technical grade naphthalene. One

analysis, inclusive of the evaluation, takes about $2\frac{1}{2}$ h, 2 h of this time being taken by the desulphurization proper. The relative error of the determination does not exceed $\pm 5\%$ (Table II). The maximum attainable sensitivity of the determination is limited by the sensitivity of the GC detector used, as well as by the GC system chosen for the determination of the trace amounts of the hydrocarbon in the presence of a many-fold solvent excess.

REFERENCES

1 R. MOZINGO, D. E. WOLF, S. A. HARRIS AND K. FOLKERS, *J. Am. Chem. Soc.*, 65 (1943) 1013.
2 G. R. PETTIT AND E. E. VAN TAMELEN, *Org. Reactions*, 12 (1962) 356.
3 M. HUDLICKÝ AND J. TROJÁNEK, *Preparativní reakce v organické chemii. Vol. I, Redukce a oxydace*, NČSAV, Praha, 1953, p. 76.
4 A. TRIFONOV, Č. IVANOV AND D. PAVLOV, *Dokl. Bolgar. Akad. Nauk*, 7 (1954) 1.
5 L. GRANATELLI, *Anal. Chem.*, 31 (1959) 434.
6 S. F. BIRCH, *J. Inst. Petrol.*, 39 (1953) 185.
7 C. J. THOMPSON, H. J. COLEMAN, R. L. HOPKINS AND H. T. RALL, *Anal. Chem.*, 38 (1966) 1562.
8 M. STREIBL, *Chem. Průmysl*, 14 (1964) 630; *ibid.*, 15 (1965) 15.
9 R. STASZEWSKI, J. JANÁK AND T. WOJDAŁA, *J. Chromatog.*, 36 (1968) 429.
10 R. N. NIGAM, M. HŘIVNÁČ, R. STASZEWSKI AND J. JANÁK, *J. Chromatog.*, 36 (1968) 440.
11 *The Coal Tar Data Book*, 2nd Ed., The Coal Tar Research Association, Gomersal, 1965, p. B2–63.
12 J. NOVÁK, in J. C. GIDDINGS AND R. A. KELLER (Editors), *Advances in Chromatography*, Vol. 7, M. Dekker, New York, in press.
13 M. FELIX AND K. BLÁHA, *Matematickostatistické metody v chemickém průmyslu*, SNTL, Praha, 1962, p. 289.
14 R. L. AUGUSTINE, *Catalytic Hydrogenation*, M. Dekker, New York, 1965, p. 26.
15 F. F. BLICKE AND D. G. SHEETS, *J. Am. Chem. Soc.*, 70 (1948) 3768.