bamates were found to be active in controlling mold on ripening oranges.

SULFUR REMOVAL FROM HYDROCARBONS. It has been revealed that free sulfur may be removed from hydrocarbons by treat-ment with aqueous solutions of hydrocarbon substituted ammonium sulfites (18). The theory of the treatment is that free sulfur reacts with the sulfite solution to form a thiosulfate solution. A reduced nitrogen base sulfite solution was found to be effective for copper strip correction of both aviation gasoline and Stoddard solvent.

DEWAXING SOLVENT. A hydrogenated fraction of pyridine bases boiling between 240° and 500° F. has been suggested for use as a dewaxing solvent (14). The hydrogenated petroleum bases discussed in this paper fit this classification and, therefore, should be useful for this purpose.

EXTRACTION OF ACIDIC COMPOUNDS FROM GASES. A mixture of hydrogenated nitrogen bases with water has been suggested for extraction of weakly acidic compounds from gaseous mixtures (6)

INSECTICIDE. The benzenesulfonic acid amide of hydrogenated petroleum nitrogen bases has been found to enhance the action of insecticides based on pyrethrum (9).

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Hydrogenolysis of Thiophene over Vanadium Oxide

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ANADIUM oxides are widely used as oxidation catalysts. They are also active for catalytic dehydrogenation (5), dehydrocyclization (6), and most recently for hydrogenation and hydrogenolysis.

It has been demonstrated (9) that pure reduced vanadium oxide and vanadium oxide supported on alumina catalysts effect the hydrogenolysis of aliphatic alcohols to the corresponding paraffinic hydrocarbons at temperatures of 380° to 400° C. and atmospheric pressure. Under similar conditions a coprecipitated vanadia-alumina catalyst (35 and 65%, respectively) was shown (?) It has been demonstrated that vanadium oxide is an effective hydrogenation catalyst whose hydrogenating activity is not poisoned by organic sulfur compounds. This investigation was undertaken to determine the action of a pure vanadium oxide catalyst on pure organic sulfur compounds under hydrogenating conditions, with particular emphasis on the hydrogenolysis of thiophene and the mechanism of this reaction.

The experimental results have established that the hydrogenation of thiophene represents a true stepwise hydrodesulfurization process.

A study of the geometric relation between the thiophene molecule and the catalyst suggests that a two-point absorption reaction mechanism is involved. As an indication of what might be expected in terms of a practical hydrodesulfurization process, a 5 weight % solution of thiophene in benzene was desulfurized at 400° C. and atmospheric pressure to an extent of 74%, representing a sulfur reduction of from 1.9 to 0.6%.

to be effective for the hydrogenation of unsaturated aliphatic hydrocarbons to the corresponding paraffins. By x-ray diffraction study (8), the hydrogenating activity of vanadium oxide has been correlated with the presence of trioxide (V_2O_3) , so that the active catalyst for the hydrogenation of olefins at 400 ° C., or for any other reaction in the presence of hydrogen, is considered to be the trioxide.

During the study of the hydrogenation of olefins previously cited (7), the addition of 1% by weight of tert-amyl mercaptan to 1octene did not produce a noticeable decrease in the hydrogenating activity of the vanadia-alumina catalyst. The sulfur resistance of this hydrogenation catalyst was similarly demonstrated by the addition of 1% by weight of thiophene to 1-hexene. In these experiments it was noted that considerable sulfur was converted into hydrogen sulfide.

This investigation was undertaken to determine the action of a pure vanadium oxide catalyst on pure organic sulfur compounds under hydrogenating conditions at atmospheric pressure. Most of the work was directed toward the study of the hydrogenolysis of thiophene, and to the mechanism of the reaction.

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Figure 1. Apparatus for Study of Catalytic Hydrogenation of Organic Sulfur Compounds at Atmospheric Pressure

CATALYST PREPARATION

The catalyst was prepared by a precipition method involving the dropwise addition of concentrated nitric acid to a hot saturated solution of ammonium meta vanadate (approximately 5% concentration). The resulting gel was filtered, washed a total of ten times to remove traces of nitrates, and dried at 110°C. This material was carefully screened and the 8- to 10-mesh granules were selected for this investigation. The catalyst was activated in the catalyst tube by raising the temperature stepwise to 400°C. over a period of several days, while slowly passing hydrogen over the catalyst.

APPARATUS AND PROCEDURE

The apparatus employed in most of these experiments is shown in Figure 1. A unique method has been developed by the authors for introducing liquid compounds into a gas stream at predetermined constant rates, with the provision for varying the addition rate over a wide range.

The principle involves introducing the liquid into the gas stream by means of borosilicate glass hypodermic syringe, the barrel of which is mechanically moved by means of a variable-speed motor whose speed has been reduced appropriately. The syringe is provided with a standard-taper joint, such that the syringe can be easily removed for loading and weighing. The liquid compound is ejected from the syringe through a capillary impinging on the walls of a vaporizer maintained at a temperature above the liquid's boiling point, so that it is flash-vaporized into the gas stream.

The rate of addition of liquid into the vaporizer was varied by two means: (1) by regulating the speed of the motor on the addition apparatus, and (2) by the use of syringes of different sizes. The syringes employed in this study were 10-, 30-, and 50ml. sizes, thus affording addition rates of 1 to 20 ml. per hour. Electrolytic hydrogen was used in all experiments. The cata-

Electrolytic hydrogen was used in all experiments. The catalyst tube was a borosilicate glass tube 34 inches long having an inside diameter of 13 mm. and was charged with 50 ml. of catalyst. The catalyst was maintained at constant temperature by means of a vertical furnace electrically heated and thermostatically controlled.

The reaction vapors were stripped of liquid products by passing the effluent gas, first through a water condensing spiral where the water condensables were collected in liquid receiver 1 (see Figure 1), and secondly through a spiral trap immersed in a Dewar flask kept at about -5° C. where further condensables were collected in liquid receiver 2. Hydrogen sulfide was next removed from the gas by passage through two Drexel-type scrubbers containing 10% sodium hydroxide. Condensable and noncondensable gases were collected in the conventional manner.

Were contended in the conventional number. Prior to each experimental run, the catalyst was brought to 400° C. in a hydrogen atmosphere. The hypodermic syringe was charged, weighed, and clamped into position. The sulfur compound was then ejected into the hydrogen stream at the desired flow rate by adjusting the speed of the motor on the liquid addition apparatus. Addition rates were varied from 1 to 10 ml per hour, which gave a corresponding liquid hourly space velocity of 0.02 and 0.20, respectively. All experiments were made at atmospheric pressure. The hydrogen flow rate was adjusted to obtain a flow rate corresponding to a mole ratio of hydrogen to thiophene of approximately 8 to 1. After the addition of a suitable volume of liquid organic sulfur compound, which required from 2.5 to 8.0 hours, hydrogen was allowed to sweep through the apparatus for 1 hour. The liquid receivers and adsorbers were then disconnected and subjected to the various analytical procedures.

In one experiment the apparatus was modified to allow for a continuous run by replacing the syringe addition device with a Mulligan-type gas saturator. A uniform liquid addition rate

temperature bath, so that the vapor pressure of the liquid at a selected temperature determined the ratio of the liquid to hydrogen.

ORGANIC SULFUR COMPOUNDS

A sample of thiophene with a reported purity of over 99% was obtained from the Socony-Vacuum Oil Co., and was used without further purification.



Velocity and Conversion

The n-butyl mercaptan used in this study was a product of the Eastman Kodak Laboratories, and was distilled in a Vigreux column just prior to being used (boiling range 97–98° C.).

ANALYSIS OF PRODUCTS

The liquid products collected in receivers 1 and 2 were combined, dried over anhydrous sodium sulfate, and subjected to distillation.

The condensable gases were analyzed by the Gockel method (14). Butadiene was determined in the condensable gases by the maleic anhydride method (13).

The sodium hydroxide scrubbing solutions were combined and diluted to 1 liter, and aliquot portions were taken for hydrogen sulfide analysis. High results were obtained by the iodine titration procedure. A sodium peroxide oxidation method followed by a gravimetric barium sulfate analysis was found to give by a gravimetric barium sulfate analysis was found to give. This theoretical recoveries on known hydrogen sulfide samples. This method was employed during the early stages of the investiga-tion. In order to expedite the analytical work, and to determine the presence of mercaptans in addition to hydrogen sulfide, a modified potentiometric silver nitrate titration procedure (11, 15) was utilized for quantitatively determining both hydrogen sulfide and mercaptans individually by a single titration. This procedure was checked on known mixtures.

The noncondensable gases were analyzed by the Gockel method.

Complete experimental data for the hydrogenolysis of thiophene over vanadium oxide are presented in Tables I and II, and portions of the data are graphically illustrated in Figures 2, 3, and 4.

DISCUSSION OF RESULTS

Most of the experiments were conducted at 400° C., which corresponds to the optimum temperature for the activated adsorption of hydrogen on vanadium oxide (4), for the hydrogenolysis of alcohols (9), and for the hydrogenation of olefins(7) over vanadium oxide. The effect of temperature is illustrated in comparable experiments (experiments 5 and 6 of Table I) showing a conversion of thiophene to hydrogen sulfide of 4% at 350° C. as compared to a yield of 49% at 400 ° C.

The decrease of liquid hourly space velocity to 0.02 resulted in increasing the conversion of thiophene to hydrogen sulfide to 67% (see curve, Figure 2).

The experiments on the hydrogenolysis of thiophene have established that a true catalytic process is involved. The sulfur of thiophene (and of other organic sulfur compounds) was eliminated in the form of hydrogen sulfide, without discernible production of vanadium sulfides.

Distillation of the liquid products, and refractive indexes of these distillates, have established that the liquid products represent unreacted thiophene. No evidence was found of possible ring hydrogenation products.

Examination of the sulfur balances obtained in these experiments shows recoveries varying from 78 to 97%, which represent thiophene losses of 1.7 and 0.7 gram, respectively. These losses are readily accountable in terms of mechanical losses inherent in this type of apparatus.

Analysis of the condensable reaction gases by the Gockel method has shown them to consist of a mixture of olefins and paraffins. After absorption of the olefins in bromine water, the residual paraffin gas fraction yielded a paraffin index of 4.0, indicating the paraffin was butane. The butadiene content of the condensable gases was obtained on separate gas samples. From the analysis of the gases, it may be seen that the reaction of the hydrogenolysis of thiophene is a stepwise reaction. At high space velocities, a high percentage of the condensable gases is olefinic,

HYDROGENOLYSIS OF THIOPHENE OVER VANADIUM TABLE I. Oxide Catalyst at Atmospheric Pressure

Experiment No.	6	7	5	-4	8
Temperature, °C. L.H.S.V.4 Thiophene charged, mole/hour Thiophene charged, mole Hydrogen charged, mole/hour	$\begin{array}{r} 350 \\ 0.04 \\ 0.025 \\ 0.12 \\ 0.20 \end{array}$	$\begin{array}{r} 400 \\ 0.02 \\ 0.013 \\ 0.09 \\ 0.10 \end{array}$	$\begin{array}{r} 400 \\ 0.04 \\ 0.025 \\ 0.12 \\ 0.20 \end{array}$	$\begin{array}{r} 400\\ 0,10\\ 0,061\\ 0,27\\ 0,51 \end{array}$	$\begin{array}{r} 400 \\ 0.20 \\ 0.13 \\ 0.30 \\ 0.91 \end{array}$
Liquid products, grams Thiophene converted to H ₂ S, mole % ^b Condensable gases, ml. Conden analysis (venorized sempla)	$\begin{array}{c} 8.8\\ 4\\ 0.0 \end{array}$	$0.8 \\ 67 \\ 3.4$	$3.0 \\ 49 \\ 6.0$	$\begin{smallmatrix}13.1\\40\\9.0\end{smallmatrix}$	$egin{array}{c} 17.6\ 25\ 6.5\end{array}$
Total plefins, volume % Total paraffins, volume % Butadiene, volume % Paraffin index	· · · · · · · ·	$ \begin{array}{r} 12.7 \\ 87.3 \\ 0.7 \\ $	$\begin{array}{c} 22.9\\77.1\\ \ldots\end{array}$	$\begin{array}{c} 37.4\\62.6\\4.0\end{array}$	$53.5 \\ 46.5 \\ 6.0 \\$
Sulfur balance Thiophene accountable, mole Thiophene unaccountable, mole Thiophene unaccountable, mole %	$\begin{smallmatrix}0.11\\0.01\\8\end{smallmatrix}$	$\substack{\begin{array}{c}0.07\\0.02\\22\end{array}}$	$\begin{array}{c} 0.11\\ 0.01\\ 8\end{array}$	$\begin{array}{c} 0.26 \\ 0.01 \\ 4 \end{array}$	$\substack{\substack{0.29\\0.01\\3}}$
^{<i>a</i>} Liquid hourly space velocity.					

^b Thiophene conversion based on H₂S analysis of caustic scrubbing solution.

TABLE II. HYDROGENOLYSIS OF THIOPHENE OVER VANADIUM OXIDE CATALYST AT 400° C. and Atmospheric Pressure^a

(Study of catalyst activity with time)

			Continuous H ₂ S		Intermittent H ₂ S Adsorption Analysis				
Time, Hours	Total Thiophene Charged, Moles	Caled. Av. ^b Thiophene Charged, Mole/Hour	<u>Adsorpti</u> Sample	on Analysis ^c Thiophene converted to H ₂ S, moles	Sample	Sampling time, hours	Thio Converte Mole	phene ed to H ₂ S Mole/ hour	Calcd. con- version of thiophene to H ₂ S, mole % ^d
$\begin{array}{c} 0 \\ 1.00 \\ 2.00 \\ 3.00 \\ 21.67 \\ 42.08 \\ 51.08 \\ 65.49 \end{array}$	0.56 1.26 1.57	0.026 0.024 0.022	· · · · · · · · · · · · · · · · · · ·	$\begin{array}{c} & & & \\ & & & \\ & & & \\ 0.41 \\ & & & \\ 0.38 \\ & & & \\ 0.17 \\ & & & \\ 0.23 \end{array}$	$ \begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \end{array} $	$\begin{array}{c} 0.25 \\ 0.25 \\ 0.25 \\ 0.50 \\ 0.83 \\ 0.33 \\ 0.25 \end{array}$	$\begin{array}{c} 0.003\\ 0.006\\ 0.005\\ 0.009\\ 0.006\\ 0.006\\ 0.006\\ 0.006\\ 0.004 \end{array}$	$\begin{array}{c} 0.012\\ 0.022\\ 0.021\\ 0.019\\ 0.019\\ 0.018\\ 0.018\\ 0.018\\ \end{array}$	50 92 88 79 79 75 75
65.49	1.57	0.024 (av.)		1.19			0.039		79 (a v.)

^a L.H.S.V. of 0.04; mole ratio of hydrogen to thiophene 10.5:1; fresh catalyst used.
 ^b Average thiophene added during designated time increments.
 ^c Analysis of caustic scrubbers which were continuously "on stream," except during intermittent sampling per-

iods. $\overset{a}{}$ Calculation based o over-all average thiophene addition rate of 0.024 mole/hour.



Figure 3. Composition of Condensable Gases at Varying Liquid Hourly Space Velocities

and the percentage of total olefins decreases with decrease in space velocity. A corresponding increase in total paraffins is observable (see Figure 3).

A continuous 65.5-hour experiment was performed in which a constant hydrogen-thiophene feed rate was maintained (see Table II). Continuous, as well as intermittent, sampling and analyzing of the effluent gas stream for hydrogen sulfide were designed to show the variation of catalyst activity with time. Fresh catalyst was used in the experiment, and the catalyst was activated just prior to the run. A total of 132.7 grams of thiophene was added during the 65.5-hour run; 103.0 grams of thiophene were found converted to hydrogen sulfide. An over-all yield of 79% was obtained for this experiment. The vanadium oxide catalyst exhibited a typical catalyst activity curve (see Figure 4). After reaching a maximum point during the first 3 hours, the curve leveled off, indicating practically constant activity thereafter for the duration of the test.

FURTHER EXPERIMENTAL WORK

HYDROGENOLYSIS OF *n*-BUTYL MERCAPTAN. In addition to the experimental work on the hydrogenolysis of thiophene, one experiment was performed with n-butyl mercaptan (butanethiol) using the hypodermic syringe addition technique. A 12.2-gram mercaptan sample was added at a liquid hourly space velocity of 0.12. The reaction was carried out at 400° C. with a mole ratio of hydrogen to mercaptan of 5.5 to 1. No liquid products were obtained. Potentiometric analysis of the scrubbing solutions (in the absence of air) showed 78% of the sulfur was converted to hydrogen sulfide, but no unreacted mercaptan could be found in the caustic scrubbing solution. Analysis of the condensable gases indicated a mixture of 80.1% butane and 19.9% butene.

This experiment would seem to indicate that the hydrogenolysis of n-butyl mercaptan under these conditions proceeds by splitting out hydrogen sulfide, yielding butene, which is then hydrogenated to butane. The hydrogenolysis of alcohols over vanadium oxide was shown to follow a similar mechanism (9).

HYDROGENATION OF BUTADIENE. It has been reported (7) that a coprecipitated vanadia-alumina catalyst hydrogenated butadiene directly to butane. The presence of butadiene in the condensable gases obtained on the hydrogenolysis of thiophene suggests that the reaction mechanism proceeds through butadiene, butene, and butane in a stepwise fashion. In order to establish such a stepwise reaction mechanism, it was necessary to demonstrate that butadiene is hydrogenated stepwise over pure reduced vanadium oxide at 400 ° C.

Butadiene was passed over vanadium oxide catalyst at a gaseous hourly space velocity of 24.0, with hydrogen at a 4 to 1 mole ratio. Analysis of the condensable gases yielded 14.6% butadiene, 70.6% butene, and 14.8% butane, thus proving a stepwise hydrogenation.

SULFUR CONTENT OF USED CATALYST. Qualitative tests on the used catalyst failed to show the presence of sulfides. A total sulfur determination was made by subjecting a portion of used catalyst to a fuming nitric acid digestion treatment, and subsequent gravimetric barium sulfate analysis. The total sulfur content of the used catalyst was calculated to be 0.03%.

DESULFURIZATION OF THIOPHENE-BENZENE MIXTURE. IN order to indicate what might be expected in terms of a practical hydrosulfurization process, an experiment was performed using a feed stock of 5% by weight thiophene in benzene. The experiment was run at atmospheric pressure and at 400° C. It had been previously established (γ) that benzene is unaffected by vanadium oxide in the presence of hydrogen at this temperature, except at extremely high pressures. The thiophene-benzene mixture was added by means of the hypodermic syringe technique. A liquid hourly space velocity of 0.20 was employed, and the mole ratios of thiophene-benzene-hydrogen were 1:18:10, respectively.



A total sulfur determination by the A.S.T.M. lamp sulfur method (1) was run on the liquid condensate product after a preliminary caustic wash. The results showed a benzene desulfurization of 74%, which represents a sulfur reduction from 1.9 to 0.58%. Further work on the desulfurization of practical mixtures will be reported in subsequent communications. It is planned to investigate practical hydrosulfurizations at both atmospheric and superatmospheric pressures.

MECHANISM FOR HYDROGENOLYSIS OF THIOPHENE

Evidence has been presented to show that the hydrogenolysis of thiophene over vanadium oxide at 400° C. and atmospheric pressure yields hydrogen sulfide, butadiene, butene, and butane. The reaction may proceed according to the stepwise hydrogenation, as shown in Figure 5.

A potentiometric titration of a sodium hydroxide solution which was used to extract mercaptans and hydrogen sulfide from the unreacted thiophene recovered (experiment 8 using the highest liquid hourly space velocity of 0.20) revealed a trace of mercaptan. A mercaptan odor is detectable in the unreacted thiophene collected from all the experiments on thiophene. While these observations do not prove that mercaptan is an intermediate in the reaction mechanism, the presence of mercaptan suggests this possibility.

Recently considerable attention has been given the geometric relation between the dimensions of organic molecules and the catalysts which are effective in their conversions (3). Twigg and Rideal (12) first showed that ethylene could be adsorbed on nickel atoms spaced at their closest spacing of 2.47 A. on the crystal lattice. They calculated that only a slight distortion of the normal valence angles would be necessary to affect the

ethylene-nickel complex. Further work has shown that metal catalysts, having interatomic spacings between 2.4 and 2.8 A., can effect two-point adsorption of ethylene. This group included nickel, cobalt, copper, platinum, and palladium, all of which can be used for the hydrogenation of olefinic double bonds. Additional evidence in support of the importance of geometric factors in determining catalytic activity may be found in the



Figure 5. Mechanism for Hydrogenolysis of Thiophene

work of Beeck et al. (2). They showed that nickel crystallites oriented according to a specific axis gave a 5-fold increased catalytic activity towards the hydrogenation of ethylene over that of an unoriented nickel catalyst. One of the authors of this paper has applied the geometric reasoning to vanadium trioxide crystals (8). A vanadium-ethylene complex may be effected on adjacent vanadium atoms at their closest spacing of 2.78 A. on the 011 plane. The angle subtended was found to be 108°4' as compared to the normal tetrahedral valence angle of 109° 28'. With regard to the present investigation it was of interest to see if the hydrogenolysis of thiophene is explainable on the basis of two-point contact between the catalyst and the thiophene molecule.

The absence of any ring hydrogenation products would seem to exclude a multiple-point contact in which the thiophene molecule is adsorbed and held flat on the catalyst surface. It seems probable that two-point contact occurs between the thiophene molecule and the vanadium oxide catalyst.

The geometric relation between vanadium trioxide and the thiophene molecule will now be considered. It has been shown (8) that the distance between vanadium atoms of the vanadium trioxide molecule on the crystal surface of the 011 plane is 2.78 A., and that the closest distance of approach of vanadium atoms in the neighboring molecules is 2.98 A. Taking the distances of carbon-sulfur equal to 1.74 A. for the thiophene molecule (10), and vanadium-carbon equal to 2.03 A. (8), the angles subtended were found to be 104° 51' for the short spacings, and 107° 47' for the long spacings. Thus the formation of the vanadium-carbon-sulfur complex may be effected on both spacings with little distortion of the tetrahedral valence angles. Similar calculations were made for the possible two-point contact between the thiophene carbon-carbon double bond and adjacent vanadium atoms. Using the value of 1.35 A. (10) for the distance between carbon atoms in the carbon-carbon double bond of the thiophene molecule, the angles subtended were calculated to be 110° 37' and 113° 40' for the short and long spacings, respectively.

These calculations show that the thiophene molecule could be adsorbed by two-point contact with adjacent vanadium atoms, either by the double bond, or by a carbon-sulfur linkage, as shown in Figure 6. While it is possible to explain the experimental results by either of the proposed two-point adsorptions, the results



Two-Point Adsorption of Thiophene on Figure 6. Vanadium Atoms of Vanadia Catalyst

are more readily explainable on the basis of a two-point adsorption involving the vanadium-carbon-sulfur complex. The experimental evidence indicates that cleavage of the carbon-sulfur linkage is the initial step in the reaction, which could be most easily accomplished if the thiophene molecule contacted adjacent vanadium atoms across the carbon-sulfur bond.

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Hydrodynamics of Liquid-Vapor Flow in Packed Distillation Columns-Correction

In the article on Hydrodynamics of Liquid-Vapor Flow in Packed Distillation Columns [Reed, T. M., III, and Fenske, M. R., IND. ENG. CHEM., 42, 654 (1950)], the fourth and eighth columns of Table IV should read as follows:

Pa, Mm. Hg	$\overset{ hoa}{ imes} 10^3$	Pa, Mm. Hg	$\overset{ hoa/ hol}{ imes 10^3}$
138	0.93	135	0.91
749	5.0	282	1.95
3700	22.0	760	5.0
757	5.0		
775	5.0	37	0.45
		90	1.07
		135	1.56
		285	3.55

Figure 5 is based on the data of Table IV and accordingly should be replotted, using the correct figures given above for T. M. REED ρ_a/ρ_l .