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# Catalytic Dehydrocyclization of Hydrocarbons in the Presence of Sulfur Dioxide

Catalytic processes are relatively new. As new processes there are many avenues that must be investigated to provide optimum processing conditions. Dehydrogenation and dehydrocyclization of hydrocarbons over chromia-alumina catalyst have received wide attention because of their importance to the chemical process industries. Here is the story of a group of researchers looking at a possible avenue for improving the process. Conclusions drawn from their studies eliminate another approach to the problem

DISCREPANCIES appear in the literature on the use of sulfur dioxide for dehydrogenation and dehydrocyclization of hydrocarbons. Teplitz and others (*20*) have reported enhanced aromatic yields when olefins and paraffins having six-carbon linear chains are processed with added sulfur dioxide over catalysts such as chromia-alumina, alumina, and activated carbon. Another report does not mention aromatic formation; thiophenes production is described as the major reaction when 1-hexene or *n*-hexane is allowed to react with sulfur dioxide under similar conditions (*1*). Patents (*4*, *8–11*, *14*, *17*) report the synthesis of thiophenes in this way.

Other investigators (*2*, *3*) showed that the dehydrogenation of cyclohexanes over activated carbon was improved by the use of sulfur dioxide as a hydrogen acceptor, and that selective dehydrogenation of methylcyclohexane occurred when

Table I. Sulfur Dioxide in Dehydrocyclization of *n*-Hexane and 1-Hexene Did Not Improve Benzene Efficiency

(With and without $SO_2$)

| | $Cr_2O_3$-$Al_2O_3$,[a] | | $Cr_2O_3$-$Al_2O_3$[b] | | |
|---|---|---|---|---|---|
| | *n*-Hexane | | *n*-Hexane | 1-Hexene | |
| **Added gas** | $H_2$ | $SO_2$ | $H_2$ | $H_2$ | $SO_2$ |
| **Moles/mole hydrocarbon** | 0.9 | 1.5 | 0.9 | 0.9 | 1.5 |
| **Conditions** | | | | | |
| **LHSV, vol./vol./hr.** | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| **Temp., ° C.** | 550 | 550 | 550 | 550 | 550 |
| **Throughput, vol./vol.** | 4.0 | 3.0 | 4.0 | 4.0 | 2.75 |
| **Products, wt. % liquid feed** | | | | | |
| **Benzene** | 20.5 | 19.1 | 37.6 | 21.7 | 27.0 |
| **Toluene** | 0 | 0 | 0 | 0 | 0.3 |
| **Thiophene** | 0 | 6.5 | 0 | 0 | 11.1 |
| **Methylthiophene** | 0 | 1.7 | 0 | 0 | 2.0 |
| **Dimethylthiophenes** | 0 | 2.6 | 0 | 0 | 0.9 |
| **Ethylthiophenes** | 0 | 4.3 | 0 | 0 | 1.9 |
| **Total aromatics, wt. % liquid feed** | 20.5 | 19.1 | 37.6 | 21.7 | 27.3 |
| **Total thiophenes, wt. % liquid feed** | 0 | 15.1 | 0 | 0 | 15.9 |
| **Efficiency of conversion to benzene, mole %** | 58.4 | 31.4 | 80.7 | 48.5 | 32.1 |
| **Conversion of feed, mole %** | 37.8 | 67.1 | 51.2 | 48.2 | 91.3 |

[a] 12% chromia impregnated on H-42 alumina. [b] Coprecipitated chromia-alumina containing 27% chromia.

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a mixture of *n*-hexane and methylcyclohexane was passed over activated carbon in the presence of sulfur dioxide. This behavior is not entirely unexpected, as Sanford and Friedman (*18*) have shown that the dehydrocyclization of *n*-heptane proceeds with more difficulty than the dehydrogenation of methylcyclohexane over activated carbon catalysts in the absence of sulfur dioxide.

Following completion of the present work, Murray (*13*) reported that in the aromatization of paraffins over a variety of catalysts in the presence of sulfur dioxide, the sole function of sulfur dioxide is as an oxidizing agent. The oxidation of hydrocarbons by sulfur dioxide presumably causes higher actual temperatures than those measured in the reaction system, and thus effects higher conversions to aromatics. No mention was made of formation of thiophenes, although the data indicate that sulfur combined with hydrocarbons to some extent during the reaction.

## Apparatus and Materials

All experiments were made at atmospheric pressure in a glass reactor consisting of a borosilicate glass tube of 1 inch in inside diameter with central thermowell 8 mm. in outside diameter. The catalyst bed (90 cc.) was 6 inches long, preceded by a preheater section, about 12 inches long, containing borosilicate glass chips. The preheater and catalyst sections were heated by an electric furnace equipped with three heaters. Two heaters were controlled manually by Variacs, and one was automatically controlled. Temperatures were measured by five thermocouples placed in the preheater and reaction sections; a separate thermocouple measured the furnace temperature.

The reactor was equipped with an inlet system for introduction of hydrogen, sulfur dioxide, nitrogen, and air. The rate of introduction was measured by calibrated rotameters and controlled by needle valves. The liquid feed was pumped at a constant rate from a water-cooled buret by a bellows pump. The temperature was determined by an immersed thermocouple.

The effluent from the reactor could be diverted by a three-way stopcock to either of two identical receiver systems, each consisting of a water condenser, a liquid receiver, a dry ice–acetone reflux condenser, a dry ice–acetone trap, a gas sampling bulb, and a wet-test meter.

**Materials.** Commercial grade sulfur dioxide (99.9 mole %), Matheson Co. Pure grade *n*-hexane (99 mole %), technical grade *n*-octane (95 mole %), and technical grade 1-hexene (analyzed as 98.1 mole %), Phillips Petroleum Co. Ethylbenzene (analyzed as 95 mole %), Matheson, Coleman, and Bell, Inc. Cyclohexane (analyzed as 100 mole %), Eastman Kodak.

Chromia-alumina catalysts, prepared in this laboratory and used as 1/8-inch pellets. Activated carbon catalyst, Columbia activated carbon, Grade CXLC, 4/6 mesh.

## Procedure

Preceding the runs, fresh catalysts were purged with nitrogen and reduced with hydrogen for 3 hours at 550° C. The system was then purged with nitrogen at run temperature. At the start the liquid hydrocarbon was pumped downward through the reaction tube; shortly thereafter the sulfur dioxide flow was begun. When sulfur dioxide was used instead of hydrogen, the reaction was exothermic rather than endothermic; and a reaction front, evident as a high-temperature zone, proceeded through the catalyst bed from top to bottom. When the high-temperature zone reached the end of the catalyst bed, free sulfur and sulfur-containing tars were formed in the condensing system. The high temperature zone

### Table II. Product Distribution Typical Experiment

With hydrogen as added gas, degradation to olefinic and paraffinic liquid and gaseous products was extensive

| Feed | *n*-Hexane |
|---|---|
| Added gas | $H_2$ |
| Moles gas/mole hydrocarbon | 0.9 |
| Conditions | |
| LHSV, vol./vol./hr. | 1.0 |
| Temp., ° C. | 550 |
| Throughput, vol./vol. | 4.0 |
| Total liquid product wt. %, liquid feed | 89.86 |
| Distribution of hydrogenated product,[a] wt. % liquid product | |
| Butanes | 0.7 |
| Pentanes | 2.0 |
| $C_6$ isoparaffins | 6.5 |
| Cyclopentane | 0.3 |
| Methylcyclopentane | 1.3 |
| *n*-Hexane | 65.4 |
| Cyclohexane[b] | 23.8 |
| Dry gas, wt. % liquid feed | 5.85 |
| Distribution, wt. % | |
| Methane | 12.4 |
| Ethane | 27.3 |
| Ethylene | 0.3 |
| Propane | 27.8 |
| Propylene | 8.3 |
| Butanes | 2.8 |
| Butenes | 3.5 |
| Isopentane | 15.2 |
| Hydrogen, wt. % liquid feed | 3.01 |
| Carbon, wt. % liquid feed | 0.38 |
| Loss, wt. % liquid feed | 0.90 |

Typical Dehydrocyclization Experiment

| Feed | *n*-Hexane |
|---|---|
| Total feed, g. | 175.46 |
| Added gas | $SO_2$ |
| Total gas, g. | 195.84 |
| Moles gas/mole hydrocarbon | 1.5 |
| Conditions | |
| LHSV, vol./vol./hr. | 1.0 |
| Temp., ° C. | 550 |
| Throughput, vol./vol. | 3.0 |
| Products, g. | |
| Liquid organic compounds | 117.58 |
| Dry gas | 13.40 |
| Carbon (coke) | 7.01 |
| CO | 4.29 |
| $CO_2$ | 81.79 |
| COS | 1.10 |
| $CS_2$ | 0.44 |
| Sulfur (solids) | 30.20 |
| $H_2$ | 0.74 |
| $H_2S$ | 66.14 |
| $H_2O$ | 44.31 |
| Loss | 4.30 |
| Product distribution, wt. % | |
| Liquid organic compounds (of *n*-hexane feed) | 67.0 |
| Liquid distribution (of liquid product) | |
| Benzene | 28.5 |
| Thiophene | 9.7 |
| Methylthiophene | 2.5 |
| Dimethylthiophene | 3.9 |
| Ethylthiophene | 6.4 |
| Hexanes | 43.5 |
| Hexenes | 5.5 |
| Product distribution, wt. % | |
| Dry gas (of *n*-hexane feed) | 7.7 |
| Distribution (of dry gas) | |
| Methane | 7.9 |
| Ethane | 9.8 |
| Ethylene | 16.9 |
| Propane | 3.4 |
| Propylene | 30.1 |
| Butanes | 11.2 |
| Butenes | 7.8 |
| Pentanes | 2.6 |
| Pentenes | 10.3 |
| Hydrogen (of *n*-hexane feed) | 5.1 |
| Distribution (excluding hydrogen in hydrocarbons) | |
| Hydrogen (free) | 7.8 |
| Hydrogen ($H_2O$) | 54.9 |
| Hydrogen ($H_2S$) | 37.3 |
| Carbon (of *n*-hexane feed) | 18.0 |
| Distribution (excluding carbon in hydrocarbons) | |
| Coke | 22.3 |
| CO | 5.9 |
| $CO_2$ | 70.9 |
| COS | 0.7 |
| $CS_2$ | 0.2 |

[a] Before hydrogenation, liquid product contained 24.9 wt. % olefins, calculated from bromine number. [b] Before hydrogenation, liquid product contained 22.2 wt. % benzene, calculated from ultraviolet analysis.

was followed through the bed, and the reactant flow was stopped when the zone reached the end of the catalyst bed. The flow of sulfur dioxide was stopped first, then the flow of hydrocarbon; and the system was purged with nitrogen.

Normal operation was divided into 1-hour periods. At the end of each period, the product stream was diverted to the second receiving system; the dry ice–acetone reflux condenser was emptied and warmed to remove solidified benzene. The liquid product receiver was then removed; the hydrocarbon layer was separated from the water and weighed.

## Analytical

The refractive index, density, and bromine number of the liquid samples from each period were immediately determined. As preliminary experiments showed no significant change in product distribution as a function of throughput, in later runs the liquid samples were composited and flash-distilled to remove heavy tars. An aliquot of the flash distillate was then analyzed by mass spectrometer. Another aliquot was hydrogenated at atmospheric pressure and 157° C. over 90 cc. of Harshaw 0101 nickel catalyst, previously treated with a thiophene-containing stock. This pretreatment enabled the catalyst to saturate the olefins selectively and desulfurize the sulfur compounds without saturating the aromatics. The effluent was analyzed for paraffin isomers by gas elution chromatography, for aromatics by ultraviolet spectrophotometry. Back calculation from the mass spectrometric analysis permitted determination of the amount of paraffins formed by desulfurization and accurate determination of paraffins suitable for recycle. Only paraffins and olefins containing a linear six-carbon chain were used in calculating efficiencies.

## Results

Initially, the dehydrocyclization of *n*-hexane was carried out over an impregnated chromia-alumina catalyst with and without added sulfur dioxide under otherwise similar conditions to determine the nature of the products. Early in this work chemical analysis showed that the liquid products in the presence of sulfur dioxide contained considerable quantities of sulfur. These sulfur compounds, examined by mass spectrometric analysis, consisted primarily of thiophene and substituted thiophenes. It was significant that chemical and spectrometric sulfur analyses were in quantitative agreement. Considerable quantities of aromatics were also formed.

Although increased conversions of *n*-hexane were obtained in the presence of sulfur dioxide, a considerable part was used to make mixed thiophenes (Table I). Thus, benzene yield was not improved.

Weight-balanced product distributions for the first two experiments of Table I are listed in Table II. With hydrogen as the added gas, degradation of *n*-hexane to olefinic and paraffinic liquid and gaseous products was extensive.

Table II also presents the weight-balanced results of a similar experiment using sulfur dioxide; because of the complexity of the products, product distribution in grams is also given. Considerable *n*-hexane was degraded by oxidation reactions, large quantities of carbon dioxide and water being obtained as major nonhydrocarbon by-products. Large quantities of coke and free sulfur were also obtained.

When similar experiments were made using 1-hexene as feed (Table I), the benzene yield increased about 5% in the sulfur dioxide run, with a 15.9% yield of thiophenes. The efficiency of conversion to benzene was 16% lower than when hydrogen was used. These runs were made with a coprecipitated, rather than an impregnated, chromia-alumina catalyst. The coprecipitated catalyst containing 27% chromia is more effective than the impregnated catalyst containing 12% chromia for the dehydrocyclization of *n*-hexane in the presence of hydrogen.

The conversion of hexane to benzene proceeded more efficiently and completely than the conversion of 1-hexene at the same conditions. These results are contrary to the general belief that olefins aromatize more readily than the corresponding paraffins (7). However, because the objective of this work was to investigate the course of the aromatization reaction when sulfur dioxide was used, this apparent discrepancy was not investigated further.

As the conditions were somewhat different from those of previous investigators, some experiments were made at closely similar conditions to eliminate the possibility that the different products were due to differences in operating conditions.

Table III shows that when sulfur dioxide is used as a hydrogen acceptor in the dehydrocyclization of a paraffin having at least a six-carbon straight chain, formation of aromatics is accompanied by formation of thiophene and substituted thiophenes. Conversely, the synthesis of thiophenes by this reaction results in formation of considerable quantities of

### Table III. Comparative Experiments on *n*-Hexane and *n*-Octane Dehydrocyclization

Both thiophenes and aromatics are formed when $SO_2$ is used

($Cr_2O_3$-$Al_2O_3$ catalyst, with and without $SO_2$)

| | A | B | A | C | D | D |
|---|---|---|---|---|---|---|
| **Feed** | *n*-Hexane | *n*-Hexane | *n*-Hexane | *n*-Hexane | *n*-Octane | *n*-Octane |
| **Added gas** | $SO_2$ | $SO_2$ | $SO_2$ | $SO_2$ | $H_2$ | $SO_2$ |
| **Moles gas/mole hydrocarbon** | 1.5 | $^a$ | 1.1 | 1.0 | 0.6 | 1.5 |
| **Conditions** | | | | | | |
| **LHSV, vol./vol./hr.** | 1.0 | 0.75 | 3.0 | 3.0 | 1.0 | 1.0 |
| **Temp., ° C.** | 500 | 503 | 510 | 510 | 550 | 550 |
| **Throughput, vol./vol.** | 1.0 | $^a$ | 3.0 | 4.5 | 4.0 | 3.0 |
| **Products, wt. % liquid feed** | | | | | | |
| **Benzene** | 18.3 | 35.4 | 10.2 | $^a$ | 3.9 | 4.9 |
| **Toluene** | 0 | $^a$ | 0 | $^a$ | 4.7 | 3.7 |
| **$C_8$ aromatics** | 0 | $^a$ | 0 | $^a$ | 33.2$^b$ | 8.7 |
| **Styrene** | 0 | $^a$ | 0 | $^a$ | 1.3 | 3.4 |
| **$C_9$ aromatics** | 0 | $^a$ | 0 | $^a$ | 0.1 | 0 |
| **Thiophene** | 6.7 | $^a$ | 2.8 | $^a$ | 0 | 2.2 |
| **Methylthiophenes** | 1.7 | $^a$ | 1.0 | 3.1 | 0 | 2.1 |
| **Dimethylthiophenes** | 1.0 | $^a$ | 0.3 | | 0 | 1.0 |
| **Ethylthiophenes** | 0.6 | $^a$ | 0.5 | $^a$ | 0 | 0 |
| **Trimethylthiophenes** | 0 | $^a$ | 0 | $^a$ | 0 | 0.1 |
| ***n*-Butylthiophene** | 0 | $^a$ | 0 | $^a$ | 0 | 1.0 |
| **Benzothiophene** | 0 | $^a$ | 0 | $^a$ | 0 | 0.2 |
| **Total aromatics, wt. % liquid feed** | 18.3 | 35.4 | 10.2 | $^a$ | 43.2 | 20.7 |
| **Total thiophenes, wt. % liquid feed** | 10.0 | $^a$ | 4.6 | 3.1 | 0 | 6.6 |
| **Efficiency of conversion to aromatics, mole %** | 29.8 | $^a$ | 17.4 | $^a$ | 90.2 | 36.6 |
| **Conversion of feed, mole %** | 67.6 | $^a$ | 67.8 | $^a$ | 63.8 | 67.8 |

A. 12% chromia impregnated on H-42 alumina. B. Described merely as chromia-alumina (*20*). C. Described as 10% chromia on alumina (*1*). D. Coprecipitated 27% chromia–73% alumina. [a] Not reported. [b] $C_8$ aromatics were 35.2% ethylbenzene, 53.9% *o*-xylene, 3.3% *m*-xylene, 7.5% *p*-xylene (av. of 6 experiments).

aromatics when the carbon chain length is at least six.

Two additional comparative experiments were made using *n*-octane as feed with and without added sulfur dioxide. (Table III). The same general behavior was observed as for *n*-hexane—i.e., formation of both thiophenes and aromatics when sulfur dioxide is used. Quantitatively, however, less sulfur is built into the products.

Further comparison with results obtained with *n*-hexane at similar conditions (Table I) shows additional differences. Whereas the production of benzene from *n*-hexane is not impaired yieldwise when sulfur dioxide is used instead of hydrogen, with *n*-octane the aromatics yield was halved. The sharp reduction in $C_8$ aromatics yield in the sulfur dioxide run, while benzene and toluene formation is not significantly affected, suggests that the intermediate for $C_8$ aromatic formation was more rapidly oxidized by the sulfur dioxide.

The small amounts of benzothiophene in the product probably arose from a secondary reaction of sulfur dioxide with ethylbenzene or styrene. The catalytic synthesis of benzothiophene from styrene (*5, 12*) and from ethylbenzene (*6*) by reaction with hydrogen sulfide has been reported. The patent literature (*9*) reports catalytic synthesis of benzothiophene from ethylbenzene by reaction with sulfur dioxide and synthesis of dibenzothiophene from diphenyl by reaction with hydrogen sulfide (*15*).

The synthesis of benzothiophene from ethylbenzene was reinvestigated (Table IV). Yields compare well with those obtained by other catalytic methods. Noteworthy are the good yield of styrene and the higher yield of benzene than toluene. This latter observation is contrary to the normal by-product distribution obtained in catalytic ethylbenzene dehydrogenation (*22*) and corresponds more closely to by-product distribution in thermal dehydrogenation (*21*).

### Table IV. Dehydrogenation-Dehydrocyclization of Ethylbenzene in the Presence of Sulfur Dioxide

Yield of styrene is good

| | Cat. A | Cat. B |
|---|---|---|
| **Conditions** | | |
| **LHSV, vol./vol./hr.** | 0.9 | 1.0 |
| **Temp., ° C.** | 594 | 594 |
| **Throughput, vol./vol.** | [a] | 1.0 |
| **Products** | | |
| **Liquid product, wt. % liquid feed** | [a] | 59.8 |
| **Benzothiophene yield, mole %** | 6.8 | 12.5 |
| **Styrene yield, mole %** | [a] | 22.4 |
| **Toluene yield, mole %** | [a] | 2.7 |
| **Benzene yield, mole %** | [a] | 15.1 |
| **Ethylbenzene recovery, mole %** | [a] | 8.3 |
| **Efficiency of conversion to benzothiophene, mole %** | [a] | 18.0[b] |

A. Reported as 10% chromia on alumina (*9*). B. Coprecipitated chromia-alumina containing 27% chromia. [a] Not reported. [b] Calculated considering ethylbenzene and styrene both suitable for recycle.

As Danforth (*2, 3*) had reported increased conversions of cyclohexane and methylcyclohexane to benzene and toluene but no conversion to thiophenes, when sulfur dioxide was used as a hydrogen acceptor, an experiment was made under similar conditions to determine whether sulfur builds into the products in this case, as with straight-chain olefins and paraffins. Examination of Table V reveals excellent agreement between these experiments and virtually no conversion to thiophene or substituted thiophenes when cyclohexane was dehydrogenated over activated carbon in the presence of sulfur dioxide.

### Table V. Conversion to Thiophene Is Very Small When Cyclohexane Is Dehydrogenated with Sulfur Dioxide

(Activated carbon catalyst. Cyclohexane feed. 0.29 mole $SO_2$/mole feed. LHSV, 1.33 vol./vol./hr. Temp., 499° C. Throughput 2.66 vol./vol.)

| | A[a] | B |
|---|---|---|
| **Hydrocarbon, wt. % liquid feed** | | |
| **Liquid** | 92.0 | 98.0 |
| **Gas** | 1.7 | 0.2 |
| **Hydrogen (in $H_2O$ and $H_2S$), wt. %** | 2.0 | 1.8 |
| **Coke and unaccounted, wt. %** | 4.3 | <0.1 |
| **Compn. of hydrocarbon product wt. %** | | |
| **Olefins** | 3.5 | 2.5 |
| **Aromatics** | 22.4 | 22.8 |
| **Thiophenes** | [b] | <0.2 |

[a] (*3*). [b] None reported.

These results, coupled with reports of enhanced paraffin dehydrogenation in the presence of sulfur dioxide (*16, 19*), indicate that sulfur dioxide apparently aids paraffin and naphthene dehydrogenation, but does not help the cyclization reaction as far as production of benzene or other aromatics is concerned. It increases the total yield of cyclic compounds from straight-chain olefins and paraffins if the formation of both aromatic hydrocarbons and heterocyclic thiophenes is considered.

Probably ethylcyclohexane feed, in the presence of sulfur dioxide, would produce some benzothiophene, although Danforth did not report this product.

## Conclusion

Dehydrocyclization of olefins and paraffins having at least a six-carbon linear chain over chromia-alumina catalysts in the presence of sulfur dioxide gives both aromatic hydrocarbons and mixed thiophenes. With a cycloparaffin, sulfur dioxide, and an activated carbon catalyst, however, the reaction is straightforward naphthene dehydrogenation. The conflicting literature reports are thus resolved through application of more complete analytical techniques.

There seems to be no practical advantage in the use of sulfur dioxide to dehydrocyclize straight-chain paraffins and olefins. The desired aromatic hydrocarbons are contaminated with thiophenes, and the efficiencies of conversion to aromatics are considerably lower than when hydrogen is used.

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## Literature Cited

(1) Conary, R. E., Devaney, L. W., Ruidisch, L. E., McCleary, R. F., Kreuz, K. L., Ind. Eng. Chem. **42,** 467–71 (1950).

(2) Danforth, J. D. (to Trustees of Iowa College), U. S. Patent **2,720,550** (Aug. 9, 1952).

(3) Danforth, J. D., Bender, M. J., Ind. Eng. Chem. **46,** 1701–3 (1954).

(4) Devaney, L. W., Clarke, J. T., Culnane, C. H. (to Texas Co.), U. S. Patent **2,558,716** (July 3, 1951).

(5) Greensfelder, B. S., Moore, R. J. (to Shell Development Co.), *Ibid.*, **2,478,914** (Aug. 16, 1948).

(6) Hansch, C., Hawthorne, F., *J. Am. Chem. Soc.* **70,** 2495–6 (1948).

(7) Hoog, H., Verheus, J., Zuiderweg, F. J., *Trans. Faraday Soc.* **35,** 993–1006 (1939).

(8) Kreuz, K. L. (to Texas Co.), U. S. Patent **2,531,279** (Nov. 21, 1950).

(9) *Ibid.*, **2,557,664** (June 19, 1951).

(10) *Ibid.*, **2,557,665** (June 19, 1951).

(11) *Ibid.*, **2,557,666** (June 19, 1951).

(12) Moore, R. J., Greensfelder, B. S., *J. Am. Chem. Soc.* **69,** 2008–9 (1947).

(13) Murray, P. B., Division of Petroleum Chemistry, 131st Meeting, ACS, Miami, Fla., April 1957.

(14) Neuhaus, M., Conary, R. E., Devaney, L. W. (to Texas Co.), U. S. Patent **2,557,678** (June 19, 1951).

(15) Patterson, J. A., Culnane, C. H. (to Texas Co.), *Ibid.*, **2,509,938** (May 30, 1950).

(16) Rosen, R. (to Standard Oil Development Co.), *Ibid.*, **2,126,817** (Aug. 16, 1938).

(17) Sager, W. F. (to Texas Co.), *Ibid.*, **2,570,722** (Oct. 9, 1951).

(18) Sanford, R. A., Friedman, B. S., Ind. Eng. Chem. **46,** 2568–71 (1954).

(19) Stone, C. M. (to Texas Co.), U. S. Patent **2,423,418** (July 1, 1947).

(20) Teplitz, M., Maloney, J. O., Reed, R. L., Division of Petroleum Chemistry, 125th Meeting, ACS, Kansas City, Mo., March 1954.

(21) Webb, G. A., Corson, B. B., Ind. Eng. Chem. **39,** 1153–6 (1947).

(22) Werner, R. R., Dybdol, E. C., *Chem. Eng. Progr.* **44,** 275–86 (1948).

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Division of Petroleum Chemistry, 132nd Meeting, ACS, New York, N. Y., September 1957.