[CONTRIBUTION FROM THE LABORATORIES OF UNIVERSAL OIL PRODUCTS COMPANY]

Isomerization of Certain Olefins by Silica Gel at Room Temperature

BY W. S. GALLAWAY AND M. J. MURRAY

Silica gel adsorption techniques for the analysis and separation of hydrocarbon types have, in recent years, found wide application.[1] There has, however, been little published on the effect of the gel upon olefins although difficulty with this type of hydrocarbon has been mentioned by Mair.[2]

The present authors have made use of silica gel techniques together with infrared spectroscopy in a study of the composition of the various fractions of thermally cracked gasolines. The comparisons of the infrared spectra of these hydrocarbon mixtures before and after contact with the silica gel showed, in general, that the intensities of the absorption bands characteristic of olefin types were as expected. There were, however, two very striking exceptions. The strength of the 890 cm.$^{-1}$ band (normally associated with the structure $RR'C{=}CH_2$) in the spectrum of the starting material was always much greater than that found by summation over the cuts from the silica adsorption column. At the same time, the bands near 825 cm.$^{-1}$ (usually found in the spectra of tri-alkylethylenes) became stronger in the cuts than was anticipated. Such a change in double bond position might be caused either by polymerization or by isomerization.

The effect of silica gel upon two olefins of the type $RR'C{=}CH_2$ and one of the type $RCH{=}CR'R''$ was then investigated. All these olefins were found to isomerize rapidly at room temperature. 2-Ethyl-1-hexene isomerizes almost completely (90%) when passed through a silica gel column at 25° whereas 20% of 2,4,4-trimethyl-1-pentene is converted to the -2 isomer. The latter case was shown to have closely approached thermodynamic equilibrium by an experiment wherein 2,4,4-trimethyl-2-pentene was passed through the silica tower. A conversion of 80% was realized yielding an effluent found, by infrared, to be almost identical with that obtained on charging the 2,4,4-trimethyl-1-pentene. It appears probable that the composition of the effluent when 2-ethyl-1-hexene was charged also approximates the equilibrium mixture. 1-Hexene was not detectably isomerized under similar conditions.

The isomerization of the tertiary olefins which were studied occurs so readily at room temperature by contact with silica that the reaction was easily followed by an infrared examination of samples decanted from a vial containing the hydrocarbon and the gel. The results of this semiquantitative study are given in Fig. 1a and 1b wherein the intensity of a characteristic band of each of the 2,4,4-trimethylpentene isomers is shown as a function of contact time.

As is to be expected, the rate of isomerization is dependent upon the ratio of gel to olefin. In the experiment just cited, in which there was a low gel to olefin ratio, only 29% of the 2,4,4-trimethyl-2-pentene was found to isomerize in two hours. However, in a silica gel adsorption column where the ratio was many times larger, the equilibrium composition was approached in a comparable time.

An infrared analysis of the effluent from the silica gel runs with the two diisobutylenes showed that, for these olefins, polymerization exerts a very minor effect compared to isomerization. As may be seen from Fig. 2, only 2,4,4-trimethylpentenes are present in measurable amounts in the main portion of the effluent. The last portion of the effluent was found to contain minor amounts of other materials, either polymers or oxidation products, which can account for no more than 3 or 4% of the total. A similar conclusion was reached in the case of 2-ethyl-1-hexene wherein by infrared study and by distillation of the effluent from the gel column, only minor amounts of higher boiling material were shown to be present.

The effect of temperature upon the degree of isomerization is very striking. When a C_7 fraction of a thermally cracked gasoline was passed through a silica gel adsorption column at room temperature, only 20 to 25% of the material having an 890 cm.$^{-1}$ infrared absorption band was recovered in the effluent. However, when the column was cooled to $-20°$, there was, within experimental error, no loss of this type of olefin.

In another test of the temperature effect, 2-ethyl-1-hexene was added to an excess of gel in each of two tubes which were held at $-24°$ and $+24°$, respectively, for one hour. Infrared analyses of the recovered hydrocarbons showed that only 5% of this olefin isomerized at the lower temperature while 65% was converted at the higher temperature. The product recovered from the low temperature test had an odor similar to the charge, whereas the product obtained from the room temperature experiment had an odor suggesting contamination with oxygenated compounds. The infrared spectrum, however, showed only weak OH bands at 3300 cm.$^{-1}$ and no $C{=}O$ absorption at 1725 cm.$^{-1}$.

The authors feel that the above-reported results though somewhat qualitative in nature, emphasize the necessity of carrying out the adsorption at low temperatures when certain types of olefinic hydrocarbons are present.

Experimental

The silica gel used in these experiments was from the

---

[1] A number of references on the use of silica gel may be found in a recent article by Mair, Gaboriault and Rossini, *Ind. Eng. Chem.*, **39**, 1072 (1947).

[2] B. J. Mair, *J. Research, Natl. Bur. Standards*, **34**, 435 (1945).

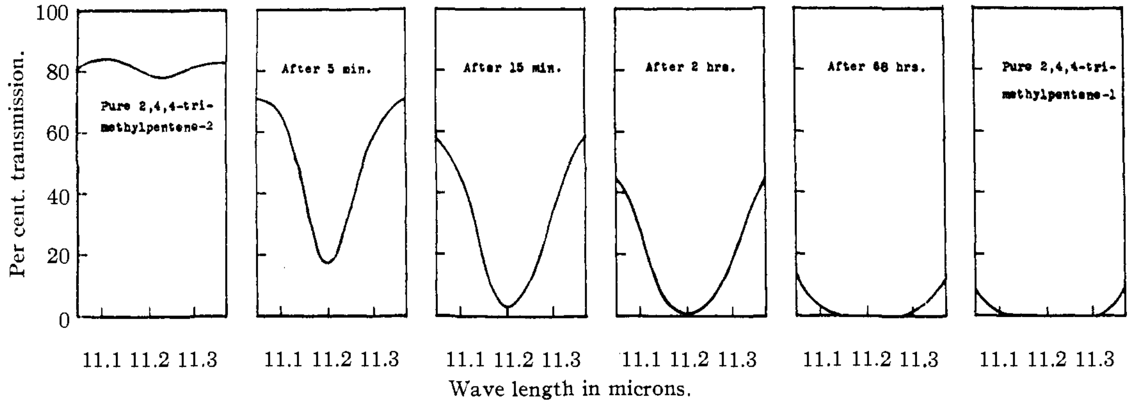

Fig. 1a.—The isomerization of 2,4,4-trimethyl-2-pentene to 2,4,4-trimethyl-1-pentene upon contact with silica gel at room temperature as evidenced by the increase in intensity of the 11.2 μ absorption band of 2,4,4-trimethyl-1-pentene.

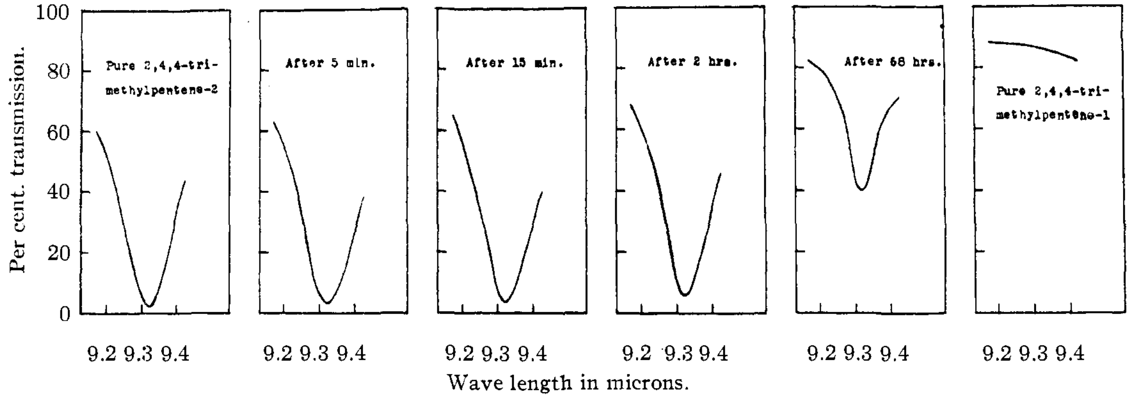

Fig. 1b.—The isomerization of 2,4,4-trimethyl-2-pentene to 2,4,4-trimethyl-1-pentene upon contact with silica gel at room temperature as evidenced by the decrease in intensity of the 9.3 μ absorption band of 2,4,4-trimethyl-2-pentene.

Davison Chemical Corporation. It had a mesh size of 28–200.

The two isomeric 2,4,4-trimethylpentenes were obtained by painstaking fractionation of the product from sulfuric acid polymerization of isobutylene. The infrared absorption spectra of the fractions selected for use followed closely those published by API Project 44. The spectra also showed that the samples of each isomer contained less than 0.5% of the other isomer.

The 2-ethyl-1-hexene was obtained by fractionation of the crude product supplied by the Connecticut Hard Rubber Co. using a Podbielniak Hyper-Cal column. Only the heart cut was used. From the intensity of the characteristic olefin band at 890 cm.$^{-1}$, the spectra of the distillation fractions, and the absence of bands characteristic of other types of olefins, the purity of the sample used is estimated to be of the order of 95%.

The 1-hexene used contained a small amount of other hexenes, both straight chain and of the tri-alkylethylene type. The conclusion drawn as to the non-isomerizing tendency of 1-hexene was based on spectroscopic data which showed no measurable increase in the total amounts of these other olefins.

The technique followed in the silica gel adsorption tests was essentially that described by Mair.[2] The desorbing agent was methanol which was removed from the final fraction of the effluent by water washing. For the low temperature runs, brine at −20° was circulated through the jacket surrounding the adsorption tower.

The semiquantitative experiment involving the rate of isomerization of 2,4,4-trimethyl-2-pentene was performed by shaking intermittently 10 ml. of the olefin with 5 ml. of the gel. At specified times, samples of the hydrocarbon were pipetted out for infrared examination.

In order to study the effect of temperature upon the rate of isomerization of 2-ethyl-1-hexene, two tubes, each containing 15 ml. of silica gel, were cooled to −80°. To each was added 5 ml. of the olefin cooled to nearly the same temperature to minimize the effect of the heat of adsorption. One tube was then placed in iced hydrochloric acid at −24° while the other was immersed in water at +24°. After one hour, ethanol cooled to about −80° was added to each sample. Following the addition of water, the upper layer was removed, dried and examined by infrared.

The infrared spectra were obtained on a large Gaertner spectrometer equipped with automatic recording. The samples were examined in a rock-salt cell which provided a 0.10-mm. liquid film and allowed no contact with sealing compounds or waxes. The compositions of the mixtures of the 2,4,4-trimethylpentenes were calculated by standard methods[3] since all the components present were identified and reliable spectra of the pure hydrocarbons were at hand. However, in the case of the 2-ethyl-1-hexene samples, wherein the spectra of the other isomers were not available, it was not possible to allow for the interference of the other components. The results reported were calculated by direct comparison of the absorption intensities for the original material and the products, and therefore represent maximum amounts of 2-ethyl-1-hexene present.

---

(3) G. M. Webb and W. S. Gallaway, *Petroleum Processing*, **2**, 365 (1947).

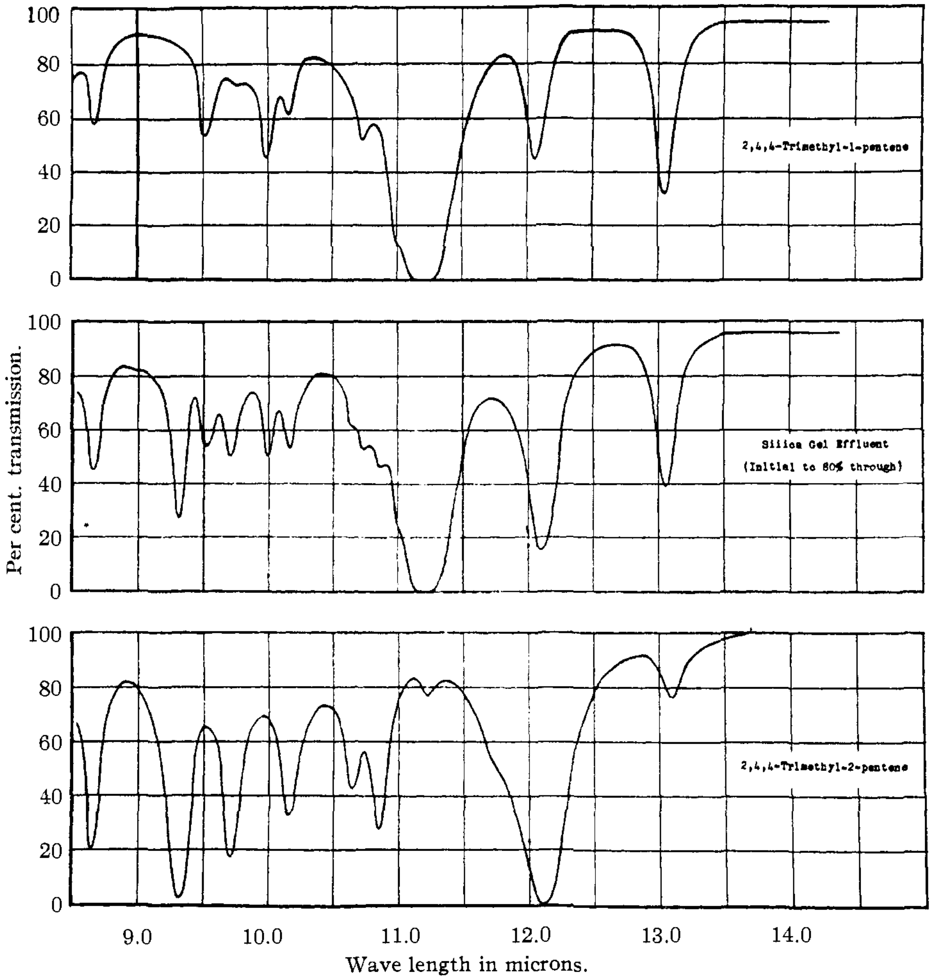

Fig. 2.—Comparison of the spectra of the 2,4,4-trimethylpentenes with the spectrum of the major portion of the effluent from a silica gel adsorption column to which the 2-isomer was charged.

Acknowledgment.—The authors wish to thank Mr. M. J. Stross for his coöperation in running the silica gel adsorption tests and Drs. Louis Schmerling and C. B. Linn for supplying the pure 2,4,4-trimethylpentenes.

Summary

1. At room temperature, each of the 2,4,4-trimethylpentenes is isomerized approximately to the equilibrium mixture of these olefins during passage through a silica gel adsorption column. Under the same conditions, 2-ethyl-1-hexene is almost completely isomerized, probably also to the equilibrium concentration.

2. Olefins of the RR'C=CH_2 type which are present in thermally cracked gasoline are also isomerized. The isomerization of hexene-1 is not appreciable.

3. Reduction of the temperature of the adsorption column to about −20° nearly halts the isomerization of the olefins studied.

Riverside, Illinois Received February 26, 1948