JOURNAL OF CATALYSIS 30, 21-29 (1973)

Effect of High Pressure on the $AlBr_3$ Catalyzed Isomerization of Saturated Hydrocarbons

RICHARD K. LYON

Corporate Research Laboratories, Esso Research and Engineering Company,
Linden, New Jersey 07036

Received December 19, 1972

The effect of hydrostatic pressure up to 6800 atm on the $AlBr_3$ catalyzed isomerization of saturated paraffins in homogeneous reaction media has been observed. The rate of isomerization of nC_8H_{18} as a function of pressure shows a pronounced maximum; this maximum is less pronounced for nC_6H_{14}, still less pronounced for nC_5H_{12} and does not occur for nC_4H_{10} isomerization. Experiments with mixtures indicate that the isomerization rate versus pressure curve is a characteristic of the hydrocarbon, independent of the presence or absence of other hydrocarbons. Isotopic mixing and other experiments suggest that the chief effect of pressure is on the concentration of the carbonium ions (which are the chain carriers of the reaction) rather than on the rate constants with which they react. It was also observed that pressure is very effective for enhancing catalyst life and surpressing degradation reactions during the isomerization of the trimethylpentanes. The effect is in accord with mechanism of the degradation reaction proposed by previous workers.

INTRODUCTION

The Lewis acid catalyzed isomerization of saturated hydrocarbons is a process of academic interest as well as importance to the petroleum industry. Hence, the process has been studied by a wide variety of methods but there has been no study on the effect of high pressure on isomerization rate in a homogeneous reaction media. Gonikberg and co-workers (*1, 2*) have reported brief studies on the effect of pressure on the isomerization rates of methylcyclopentane and *n*-hexane catalyzed by 10 wt % $AlCl_3$, but, since this system is grossly inhomogeneous, it is not clear whether the observed rate decreases are due to the effect of pressure on chemical processes or on mass transport processes. Accordingly the author undertook the present study, in the hope of obtaining a new insight into the reaction mechanism.

EXPERIMENTAL METHODS

The homogeneous reaction medium used in most of these experiments was ⅓ by volume hydrocarbon, ⅔ catalyst solution. The nominal catalyst solution composition was 0.5 *M* $AlBr_3$, 0.1 *M* H_2O, and 0.02 *M* methyl *t*-amyl ether in 1,2,4-trichlorobenzene solution. As demonstrated by Kramer, Skomoroski and Hinlicky (*3*) this reaction medium is homogeneous both immediately after preparation and after appreciable reaction. The catalyst has an isomerization activity suitable for the measurement of isomerization rates in which the branching of the carbon chain is altered, i.e., most of the present experiments. The more rapid process, methyl migration along the chain, is too fast to conveniently observe with this catalyst. Hence, during the experiments with 2,3,4-trimethylpentane (2,3,4-TMP) in which methyl migration is a process of interest, the catalyst solution used was 0.5 $AlBr_3$ in trichlorobenzene, deactivated with benzene.

The Kramer catalyst has a low cracking activity toward all of the hydrocarbons used in this research except the trimethylpentane. The cracking reaction is associated with loss of isomerization activity. It was observed that within the precision of the present measurements, isomerization activity was constant within the reaction times normally used, for all hydrocarbons except the trimethylpentanes.

Solutions were prepared in fairly large amounts so that one catalyst preparation could be used for several batches of samples. When necessary, experiments were rerun so that comparisons could be made among runs done with the same catalyst preparation.

The hydrocarbons used were obtained from Chemical Samples Co. and Matheson Coleman and Bell. They were 99+% stated purity. At the start of this research, hydrocarbons were further purified by vacuum distillation out of $AlBr_3$. This appeared to have little, if any, effect on the experimental results and the practice was discontinued. The deuterocarbons were obtained from Merck, Sharp and Dohme of Canada and were used without further purification.

The $AlBr_3$ was also obtained from Matheson Coleman and Bell. It was purified by double vacuum sublimation. The methyl *t*-amyl ether used was prepared by the method of Evans and Edlund (*4*). The product was proven pure by GC. The 1,2,4-trichlorobenzene was obtained from Matheson Coleman and Bell and was dried by allowing it to stand in contact with molecular sieves.

Samples were prepared in batches. The reaction mixture was prepared by standard dry box vacuum line procedures and injected into a length of 0.13 cm o.d. × 0.07 cm i.d. Teflon tubing (22 gauge) with sleeves of annealed stainless steel tubing (0.21 cm o.d. × 0.16 cm i.d.) distributed along it. The first portion of the reaction mixture going through the tubing serves as purge. The steel sleeves were then pinched shut and the Teflon tube was cut into segments, two sleeves per segment. The steel tubing sleeves are quite satisfactory as one-close-one-open valves. The tube segments were stored in a liquid nitrogen refrigerator until used. Care was taken throughout the above procedure so that the reaction mixture was kept cold at all times and contacted only glass, Teflon, and dry nitrogen.

Provided the sample containers were completely full of the liquid reaction mixture, they were quite satisfactory for transmission of an external hydraulic pressure to the reaction mixture, ruptures at compressions up to 7×10^3 kg/cm^2 being rare. The pressure vessel used in this research was a length of 1.27 cm o.d. × 0.32 cm i.d. high pressure tubing, surrounded by a water jacket. Ice water was circulated through this jacket while the cold sample was loaded, the pressure vessel was sealed and the desired hydrostatic pressure was applied. The water jacket was then switched to a constant temperature circulating bath for the desired reaction time, after which it is switched back to ice water and the sample was recovered. This method has the advantage that the sample is never exposed to a temperature at which significant reaction occurs except when it is under the desired pressure. Due to rapid heating and cooling of the narrow pressure vessel reaction times as short as 10 min are well defined. The hydraulic pressure was generated by a hand pump-intensifier combination and measured by a Heise gauge. The merits of the above procedures as general methods for the study of chemical kinetics at high pressure have been discussed elsewhere (*5*).

Experiments were always run at 40°C unless otherwise described. Mixtures of hydrocarbons or hydrocarbon–deuterocarbon were always equivolume mixtures.

Reaction products were analyzed chiefly by a P & E F-11 gas chromatograph with a 300-ft squalane capillary column and flame ionization detector. Peak areas were measured by an Infotronic CRS-100 integrator. The resolution was adequate to provide complete or virtually complete analysis of all hydrocarbon reaction product mixtures. The resolution was also adequate to separate nC_6D_{14} from nC_6H_{14} but inadequate to separate the numerous partially isotopically scrambled isomeric C_6 products. Hence, after GC analysis to determine total iso-C_6 formed, the nC_6 fraction was recovered by prep. GC and subjected to mass spectrometric analysis. In the $nC_4H_{10} + nC_4D_{10}$ experiments, essentially the same procedure was used.

RESULTS

The difficulty of doing reproducible absolute rate measurements with Lewis acid catalysts is well known and the present results are no exception. It is only because the effects of pressure on the reaction rate are large that significant measurements are possible.

The observed extents of reaction as a function of time were used to calculate first order rate constants assuming the isomerization reactions to be irreversible. Since the starting hydrocarbon is in all cases a minor component in the equilibrium isomer distribution, and the conversions used in these experiments were small, this approximation should be better than the data.

In Fig. 1 the pressure dependence of the rate constant of the methyl cyclopentane (MCP) to cyclohexane (CH) isomerization is given for both MCP alone and in equivolume mixture with other hydrocarbons.

Figure 2 gives the pressure dependence of the isomerization rate constants for the reactions $nC_5H_{12} \rightarrow iC_5H_{12}$, $nC_6H_{14} \rightarrow$ all isomeric C_6H_{14}, $nC_8H_{18} \rightarrow$ all isomeric C_8H_{18}, observed with nC_5H_{12} alone, nC_6H_{14} alone,

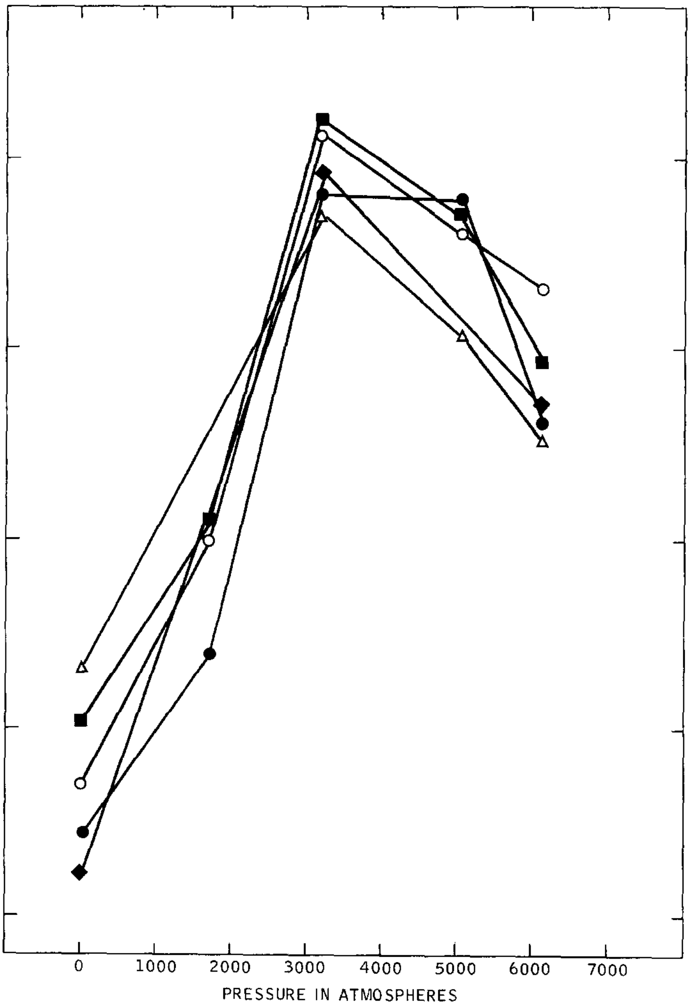

FIG. 1. Dependence of $k_{MCP \rightarrow CH}$ on pressure. MCP alone (●), MCP mixed with nC_8H_{18} (○), MCP mixed with nC_8H_{18}, second series (■), MCP mixed with 2,3-dimethylhexane (◆), MCP mixed with nC_4H_{10} and nC_6H_{14} (△).

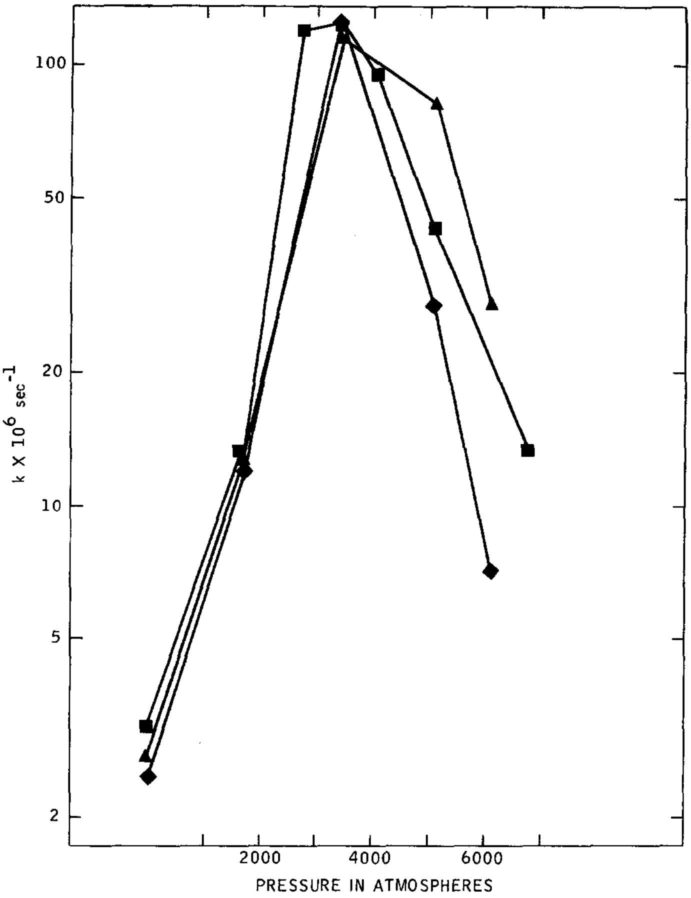

FIG. 2. Pressure dependence of: $k_{nC_5H_{12}}$ (▲), $k_{nC_6H_{12}}$ (■), and $k_{nC_8H_{18}}$ (◆).

and nC_8H_{18} in the presence of MCP. The isomerization rate constant of nC_6H_{14} in the presence of MCP and in presence of nC_4H_{10} has also been observed and is the same function of pressure within experimental error as is observed for nC_6H_{14} alone. A brief series of experiments established that for nC_6H_{14} isomerization the maximum in the rate constant against pressure plot was also present at 60°C.

The rate constant for $nC_4H_{10} \rightarrow iC_4H_{10}$ was measured as a function of pressure at 40 and 60°C and in the presence of MCP at 60°C. These data are given in Fig. 3 relative to the rate constant observed in each series of experiments at 6190 atm.

Experiments were also performed with 2,3-dimethylhexane mixed with MCP. During sample preparation and handling the starting octane isomer came to equilibrium with the isomers, 2,4-dimethylhexane, 2,5-dimethylhexane, and 3,4-dimethylhexane, however reaction rate measurements as a function of pressure were made for the rates at which this equilibrium mixture of doubly branched nonquaternary octanes (DBNO) formed 2,2-dimethylhexane and the equilibrium mixture of singly branched octanes. Both these processes showed pronounced maxima at or about 3300 atm but the ratio of the rate constants for these reactions was independent of pressure within an average deviation of 20%.

The rate of the isotopic mixing reaction, $nC_4H_{10} + nC_4D_{10} \rightarrow nC_4H_9D + nC_4D_9H$, increased monotonically with pressure to 6600 atm, while the rate of $nC_6H_{14} + nC_6D_{14} \rightarrow nC_6H_{13}D + nC_6D_{13}H$ showed a maximum

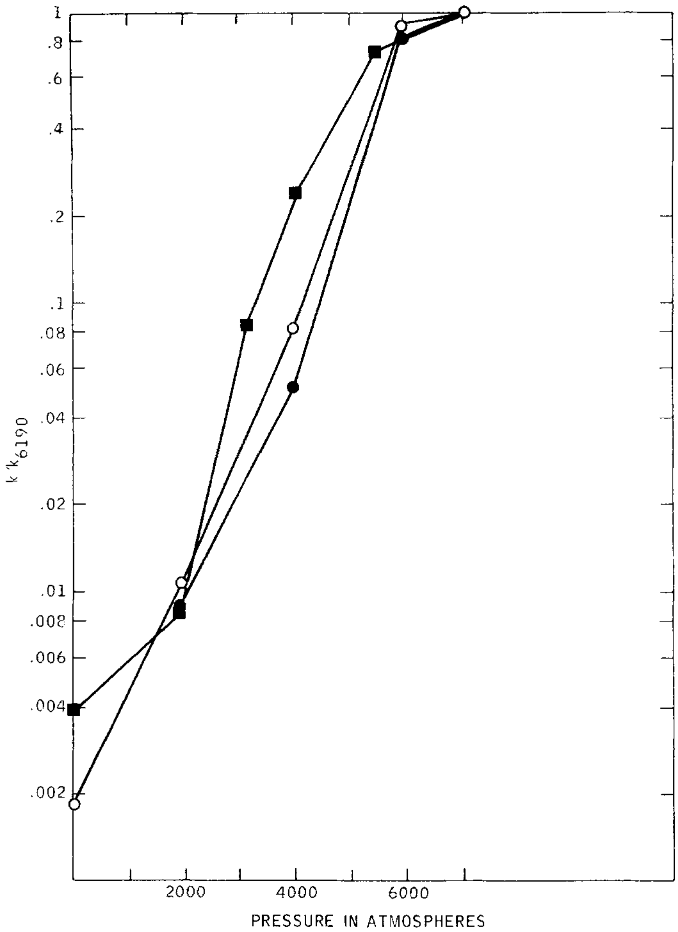

FIG. 3. Pressure dependence of: $k_{nC_4H_{10}\rightarrow iC_4H_{10}}$ alone at 40°C (■), alone at 60°C (○), and in mixture with MCP at 60°C (●).

around 3300 atm. Let k_S/k_I be the ratio of the isotopic scrambling rate to the rate of the concurrent isomerization. For $nC_4H_{10} + nC_4D_{14}$ and $nC_6H_{14} + nC_6D_{14}$ k_S/k_I were 0.241 ± 0.027 and 0.266 ± 0.054, respectively, independent of pressure up to 6600 atm. By combination GC–MS some qualitative information was obtained on the isotopic composition of the $iC_4H_{10-X}D_X$ product formed during the isomerization of $nC_4H_{10} + nC_4D_{10}$. As expected from the mechanism discussed below it consisted almost entirely of iC_4H_{10}, iC_4H_9D, iC_4D_9H and iC_4D_{10}.

A set of experiments was done using 3-methylpentane. During sample preparation the rapid equilibration between 3-methylpentane and 2-methylpentane and 2,3-dimethylbutane occurred. At one atmosphere this equilibrium mixture was observed to form 2,2-dimethylbutane and nC_6H_{14} in the ratio 0.86 ± 0.06 while at 6600 atm the ratio was 3.9 ± 0.4.

During the course of the above described experiments, a variety of blank experiments were performed. Analyses of the sample preparations were always done and sometimes the extent of reaction occurring during sample preparation was a significant correction. Numerous blank experiments were done in which a sample was placed in the pressure vessel, subjected to high pressure, the pressure released and the sample recovered, the pressure vessel being cooled by ice water at all times during this procedure.

TABLE

ISOMERIZATION OF 2,3,4-

Pressure (atm):			1	1	1	1700	3400
	Starting hydrocarbon blend	Blanks av of 4	(hr): 0.5 av of 2	1 av of 2	2 av of 2	1 av of 2	0.5 av of 2
$\frac{iC_4H_{10}}{\text{2,2,3,3-TMB}}$	0	0.199 ± 0.048	0.84 ± 0.10	1.2 ± 0.4	0.78 ± 0.18	0.5 ± 0.2	0.31 ± 0.06
$\frac{\text{MCP + CH}}{\text{2,2,3,3-TMB}}$	10.5	10.3 ± 0.7	10.1 ± 0.3	9.5 ± 0.6	9.3 ± 0.1	10.2 ± 0.1	10.2 ± 0.8
$\frac{C_6H_6}{\text{2,2,3,3-TMB}}$	NM	0.188 ± 0.029	—	—	—	—	0.142
$\frac{\Sigma\text{DMH}}{\text{2,2,3,3-TMB}}$	—	—	—	—	—	—	0.144 ± 0.003
$\frac{\Sigma\text{TMP}}{\text{2,2,3,3-TMB}}$	9.54	9.1 ± 0.5	8.31 ± 0.08	7.5 ± 0.5	8.1 ± 0.2	8.7 ± 0.3	8.6 ± 0.4
$-\ln \frac{\text{MCP}}{\text{MCP + CH}}$	—	—	0.005 ± 0.003	0.03 ± 0.02	0.012 ± 0.008	0.03	0.08 ± 0.01
2,2,3/ΣTMP	—	0.006 ± 0.003	0.012 ± 0.004	0.009 ± 0.009	0.013 ± 0.001	0.04 ± 0.02	0.147 ± 0.006
2,2,4/ΣTMP	—	0.21 ± 0.02	0.384 ± 0.002	0.42 ± 0.02	0.40 ± 0.01	0.45 ± 0.05	0.42 ± 0.02
2,3,3/ΣTMP	—	0.12 ± 0.02	0.152 ± 0.002	0.18 ± 0.02	0.19 ± 0.01	0.28 ± 0.04	0.309 ± 0.005
2,3,4/ΣTMP	1	0.67 ± 0.03	0.472 ± 0.003	0.393 ± 0.003	0.39 ± 0.01	0.2 ± 0.1	0.12 ± 0.01

Blanks treated in this manner never showed significantly different extent of reaction from those taken directly to analysis. A set of experiments was done with nC_6H_{14} and a 0.5 M $AlBr_3$ in trichlorobenzene solution to which no co-catalyst was added. This mixture showed no isomerization at 1, 3300 or 6600 atm.

Experiments were done using a hydrocarbon mixture 50.3 wt % MCP, 43.8 wt % 2,3,4-TMP, 4.7 wt % 2,2,3,3-tetramethylbutane (2,2,3,3-TMB) and 1.2 wt % C_6H_6. This hydrocarbon mixture was used in an equivolume mixture with a 0.5 M $AlBr_3$ in trichlorobenzene solution. The 2,2,3,3-TMB is fully inert under reaction conditions. An internal standard is necessary in the set of experiments because the 2,3,4-TMP under some reaction conditions undergoes rapid degradation reactions to iC_4H_{10}, iC_5H_{12} and materials not analyzed, i.e., sludge. The degradation reactions cause catalyst deactivation and meaningful rate constants cannot be calculated. Accordingly the data are given in Table 1 in terms of composition as function of time.

DISCUSSION

The results may appear surprising but there is good evidence to show that they are the effects of pressure on chemical processes rather than artifacts. One of the more common errors in the measurement of reaction rates at high pressure is failure to control the reaction temperature. Temperature differences between the reaction mixture inside the high pressure vessel and the constant temperature bath outside may arise due to exothermic reaction and the nearly adiabatic compression the sample experiences initially. This cannot be the case in the present experiments since the narrow pressure vessel used (1.27 cm o.d. × 0.32 cm i.d.) provides tight thermal coupling between the reaction mixture and the bath. Moreover, the exothermicity of isomerization reactions is very slight and samples are subjected to compression before they were heated to the reaction temperature by the constant temperature bath. Samples which were compressed but not thus heated show no reaction.

There are substances, such as water, which in small amounts activate Lewis acid catalysts but in larger amounts deactivate them, i.e., some co-catalysts are poisons at high concentrations. If high pressure were in some mysterious manner to cause the addition of such a substance to the reaction mixture, this might cause the isomerization rate constant to pass through a maximum

1
TRIMETHYLPENTANE AT 40°C

3400	3400	3400	4762	6120	6120	6120
1 av of 2	2 av of 2	24 av of 2	1 av of 2	0.5 av of 2	1 av of 2	2 av of 2
0.36 ± 0.08	0.5 ± 0.2	0.4 ± 0.2	0.38 ± 0.02	0.25 ± 0.01	0.23 ± 0.06	0.32 ± 0.05
9.6 ± 0.1	9.99 ± 0.01	10.2 ± 0.1	10.0 ± 0.3	9.50 ± 0.04	10.3 ± 0.7	9.6 ± 0.3
0.09 ± 0.04	0.20 ± 0.03	—	0.2 ± 0.2	0.18 ± 0.07	0.17 ± 0.02	0.2 ± 0.1
0.25 ± 0.05	0.99 ± 0.02	3.3 ± 0.1	0.14 ± 0.01	—	0.07	0.07 ± 0.03
8.47 ± 0.03	7.5 ± 0.1	3.9 ± 0.4	8.58 ± 0.01	8.94 ± 0.04	9.03 ± 0.03	8.8 ± 0.1
0.12 ± 0.01	0.382 ± 0.007	1.59 ± 0.06	0.05 ± 0.01	0.0123 ± 0.0001	0.0130 ± 0.0001	0.028 ± 0.008
0.16 ± 0.01	0.238 ± 0.005	0.220 ± 0.008	0.111 ± 0.008	0.071 ± 0.008	0.108 ± 0.008	0.12 ± 0.05
0.422 ± 0.001	0.381 ± 0.003	0.308 ± 0.001	0.384 ± 0.001	0.346 ± 0.009	0.34 ± 0.02	0.35 ± 0.01
0.306 ± 0.002	0.291 ± 0.002	0.40 ± 0.01	0.364 ± 0.001	0.36 ± 0.01	0.388 ± 0.004	0.372 ± 0.005
0.112 ± 0.008	0.094 ± 0.002	0.070 ± 0.006	0.132 ± 0.008	0.217 ± 0.008	0.164 ± 0.008	0.16 ± 0.03

with increasing pressure. This explanation is excluded by the observation that a catalyst solution which is inactive for want of a co-catalyst, remains inactive when subjected to high pressure.

However, the strongest evidence that the observed effects are not artifacts is the mixture experiments. All conceivable causes of artifacts would act equally on both hydrocarbons in a mixture, whereas it is observed that each hydrocarbon has an isomerization rate constant versus pressure curve which is individual to the hydrocarbon and independent of the presence or absence of other hydrocarbons.

Given that the observed maxima are real, an obvious explanation is that the reaction undergoes a change in the rate determining step. The generally accepted mechanism of paraffin isomerization by Lewis acid catalysts is a two-step chain reaction, the chain carriers being carbonium ions formed in equilibrium limited amounts by the Lewis acid (*6*). The two steps of the chain reaction are carbonium ion isomerization and hydride transfer, i.e., a carbonium ion of the same structure as the starting hydrocarbon isomerizes, the isomeric ion thus formed undergoes a hydride transfer with the starting hydrocarbon, forming the isomeric hydrocarbon product and regenerating the starting carbonium ion. If one of these steps is rate controlling and a negative volume of activation while the other has a positive volume of activation, at some pressure a maximum rate will occur. The difficulty with this explanation is that a maximum in the rate versus pressure plot occurs for the isotopic scrambling of $n\mathrm{C}_6\mathrm{H}_{14} + n\mathrm{C}_6\mathrm{D}_{14}$, a process which involves only hydride and deuteride transfer. Since this is effectively a one-step process, a change in rate determining step is not possible.

The initial increase in rate may be attributed to an increase in chain carrier concentration due in increased acidity of the Lewis acid catalyst. Weak acids generally ionize more strongly under high pressure (*7*) due to dielectric contraction, i.e., the volume change associated with formation of the ionic solvation shell. For $n\mathrm{C}_4\mathrm{H}_{10}$, $n\mathrm{C}_5\mathrm{H}_{12}$, $n\mathrm{C}_6\mathrm{H}_{13}$ and $n\mathrm{C}_8\mathrm{H}_{18}$ the observed values of k_{3300}/k_1 were 53 (av) 44, 40, and 54, respectively, corresponding to a volume change of 29–31 ml/mole. Volume changes this large and larger have been reported for the ionization of several weak electrolytes in water and in other solvents (*7*).

The decrease in rate beyond 3300 atm appears to be related to molecular size, since it does not occur for $n\mathrm{C}_4\mathrm{H}_{10}$ and occurs with increasing severity for the sequence $n\mathrm{C}_5\mathrm{H}_{12}$, $n\mathrm{C}_6\mathrm{H}_{14}$, and $n\mathrm{C}_8\mathrm{H}_{18}$. Very tentatively this rate decrease may be attributed to the onset of diffusion control. To the author's knowledge there has been only one previous report of a maxima in rate versus pressure plots, Hamann's (*8*) study of the alkaline etherification of ethyl bromide. In this case the decrease of rate at very high pressures was also attributed to the onset of diffusion control.

One implication of the above explanations is that if the same carbonium ion (or group of closely related ions) may undergo two different reactions to form two different products, the ratio in which these products are formed should be independent of pressure. The isomerization of the doubly branched nonquaternary octanes to methyl heptanes and 2,2-dimethylhexane, and the simultaneous isotopic scrambling and isomerization of $nC_6H_{14} + nC_6D_{14}$ and of $nC_4H_{10} + nC_4D_{10}$ are all processes of this type and as predicted the ratio of rates in all three cases is pressure independent. In a fourth case pressure caused a considerable shift in the ratio in which nC_6H_{14} and 2,2-dimethylbutane are formed by the isomerization of the equilibrium mixture of the other hexane isomers. However, nC_6H_{14} is derived by isomerization of the 2-methylpentyl carbonium ion, while 2,2-dimethylbutane results from the 2,3-dimethylbutyl ion. The proposed explanation does not require that the ratio of these rather different ions be invariant with pressure.

As discussed by Condon (*9*) paraffin isomerization is generally accompanied by degradation reactions (cracking) which form lighter paraffins and an ill-defined tarry material, sludge. This set of reactions is noncatalytic in that the Lewis acid is consumed by sludge formation and after a time all reaction, both isomerization and cracking, cease. For most hydrocarbons the cracking reaction can be nearly eliminated by controlling the carbonium ion concentration through judicious catalyst preparation; however, for the trimethylpentanes degradation rather than isomerization is the major process and all efforts to chemically inhibit the degradation process are ineffective. The isomerization stops before the isomeric trimethylpentanes can approach mutual equilibrium. The latter process is a methyl migration, observed to be facile in many systems. The isomerization of trimethylpentanes to dimethylhexanes has never been reported.

The generally accepted explanation of this is that for most hydrocarbons degradation occurs via a complex chain process which may be inhibited but in the trimethylpentane case there is also a second degradation mechanism which may not be inhibited because it involves the same reactive intermediates as does the isomerization. Specifically the degradation is attributed to the beta scission of the 2,2,4-trimethylpentyl ion. Since this ion is tertiary it is favored by thermodynamic equilibrium, but its beta scission yields the *t*-butyl ion, and it is plausible that the beta scission of a tertiary ion to yield a tertiary ion would be a facile reaction. Following this reaction the *t*-butyl ion undergoes hydride transfer to form isobutane and the isobutylene further reacts to form sludge. Since beta scission is a dissociation process it should have a positive volume of activation and be inhibited by pressure. The data in Table 1 are fully in accord with this expectation. At 3300 atm the hitherto unknown isomerization of the trimethylpentanes to dimethylhexanes occurs and goes to substantial conversion. The observed first order decays of methylcyclopentane to cyclohexane and trimethylpentanes to dimethylhexanes at 24 hr are, respectively, 41 and 77% of values predicted by extrapolating the initial rates. Hence, under pressure the catalyst lifetime is substantial. In contrast without pressure after 0.5 hr very little reaction occurs.

The equilibrium distribution of the trimethylpentanes may be calculated from API project 44 data (*10*). At 40°C the predicted distribution in the liquid is 2,2,3-TMP = 21.3%; 2,2,4-TMP, 52.9%; 2,3,3-TMP = 13.1% and 2,3,4-TMP = 12.7%. The observed distribution in Table 1 is in only rough accord with this prediction.

CONCLUSIONS

The overall rates of homogeneous Lewis acid catalyzes hydrocarbon isomerization and isotopic scrambling show pronounced maxima as functions of pressure. The initial increase in rate may be attributed to an increase in catalyst activity, while the subsequent decrease could be due to the onset of diffusion controlled reaction. High pressure was also observed to be an effective means of suppressing the beta scission of carbonium ions.

REFERENCES

1. Gonikberg, M. G., Plate, A. F., and Gavrilova, A. E., *Dokl. Akad. Nauk SSSR* **83,** 81 (1952).
2. Gonikberg, M. G., Gavrilova, A. E., and Kazanskii, B. A., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 157 (1952).
3. Kramer, G. M., Skomoroski, R. M., and Hinlicky, J. A., *Amer. Chem. Soc. Div. Petrol. Chem., Prepr.* **7,** 207 (1962).
4. Evans, T. W., and Edlund, K. R., *Ind. Eng. Chem.* **28,** 1186 (1936).
5. Lyon, R. K., *Rev. Sci. Instrum.* **42,** 278 (1971).
6. Condon, F. E., *Catalysis* **6,** 43 (1958).
7. Weale, K. E., "Chemical Reactions at High Pressures," pp. 123–126. E&FN Spon, London, 1967.
8. Hamann, S. D., *Trans. Faraday Soc.* **54,** 507 (1958).
9. Condon, F. E., *J. Amer. Chem. Soc.* **73,** 3938 (1951).
10. "Selected Values of Properties of Hydrocarbons and Related Compounds," Amer. Petrol. Inst. Proj. 44, College Station, TX 1963.