ISOMERIZATION OF HYDROCARBONS

EDITH WILSON[1]
Chicago, Illinois

Received April 10, 1937

Isomerization of hydrocarbons affords a study of intramolecular rearrangements in molecules which have only two different atoms. This type of reaction provides systems inducive to fundamental theoretical research, since the variable factors may be reduced to a minimum. Furthermore, it may play an important part in the petroleum industry, owing to the superior qualities of branched-chain to straight-chain isomers in gasoline, the many isomers present in the naphthene fractions, and the possibility of making available to industry many hydrocarbons which in the form of their less desirable isomers find little market. If the laws and conditions that govern isomerization become known, they should find wide application in the industrial field. An attempt has been made here to assemble the information relative to the isomerization of hydrocarbons.

GENERAL DISCUSSION

Thermodynamic data

It is only within the last few years that sufficient thermodynamic data have been accumulated to make the application of thermodynamic laws an important tool for hydrocarbon reactions. For the lower members of the paraffin and olefin series, very accurate values are now available, but other data involve uncertainties that allow only for an indication of the trends of reactions. These uncertainties arise largely from insufficient knowledge of the heat capacities and of accurate values for the heats of combustion. Isomerization reactions in the gaseous phase are important for many hydrocarbons, and heat capacity data in the gaseous state are known accurately in most cases only up to room temperatures. But even the accurate values often involved an extrapolation from 90° to 0°K., and this may make a contribution of from 10 to 15% of the total entropy. It is probable that this does introduce an appreciable error in some values. For hydrocarbons that are liquid at ordinary temperatures, the heat capacity data may be known experimentally for the liquid state, but for the gaseous state the data available are generally estimated values. Al-

---

[1] *Present address:* 416 East Seminary Avenue, Wheaton, Illinois.

though, in general, thermodynamic data serve to indicate the trend in a particular reaction of hydrocarbons, the significance to be attributed to these uncertainties is an open question in the case of isomerization. For instance, are the differences in the free energies of the isomeric butanes, butenes, or heptanes real, and what are the limits of error?

Differences in the behavior of the isomeric hydrocarbons will depend on the distribution of energy in the rotational and vibrational states. The energy of a polyatomic molecule may be represented as the sum of the translational, rotational, vibrational, and electronic energies. Distribution of the energy in each form may be determined by the partition function, and since the entropy is proportional to the logarithm of the partition function, the entropy becomes an interesting property. Eidnioff and Aston (23) have developed a method for calculating the classical partition function for the rotational energy. Kassel (64) has further refined the calculation of the determinant occurring in this partition function and has calculated the entropies of the isomeric butanes and butenes. The calculated entropies for the translational and rotational energies show that the vibrational energy contributes only a small part to the total entropy, but the exact amount has not been calculated. Moreover, the calculated translational and rotational entropies raise some question as to the accuracy of the experimental values, the correctness of the assumptions used for the statistical entropies, and a fundamental error in the third law.

Equilibrium and velocity constants

Relatively few equilibrium constants have been determined experimentally for isomerization reactions. Information about the equilibrium constant may be obtained from the thermodynamic properties. But since

$$\frac{\Delta H}{T} - \Delta S = R \ln K$$

the calculation for the equilibrium constant is concerned with the same thermodynamic properties as those considered above and encounters the same uncertainties. For a reaction with favorable thermodynamic properties and equilibrium constant, the desirability of a rate constant is obvious. From the kinetic viewpoint little is known about the isomerization of hydrocarbons. With only a few rate constant measurements available, there is need of a simple method of calculating the rate constant. Rice and Gershinowitz (100, 101) have used the statistical method for such a calculation where the collision factor in the reaction velocity constant contains the entropies for the different forms of energy. They have applied this method to the cyclopropane–propylene reaction and have found fair agreement if the shift of a hydrogen atom rather than the breaking of a carbon–carbon bond is the rate-determining step. Eyring (25) has used potential energy surfaces and the activating complex to calculate specific rate constants. This method holds much promise. For the *cis–trans* isomerization of β-cyanostyrene, however, the method appears to give a too small frequency for the torsional vibration around the double bond, according to Kistiakowsky and Smith (72). As yet both methods have not been tested sufficiently for us to know their real value for isomerization reactions. Kinetic measurements, particularly the *cis–trans* type, have been found difficult to interpret and to fit into the theories.

Catalytic action

From experimental evidence the reasonable assumption may be made that isomerization reactions are slow reactions. This is logical, since in this type of reaction atoms shift their position in the molecule from one atom to another atom. If the action were energetic, the atom in this migrating process might travel to such a distance that instead of linking again to another atom it would leave the molecule and cause dissociation. It follows that for isomerization reactions to be of technical value, catalysts must be found to speed up the rate of transformation. Two types of catalysts have proven effective: namely, the solid and the liquid catalyst.

The solid catalyst is usually a metal, a metallic oxide, mixtures of metallic oxides, carbon, or silica. The reaction occurs on the surface of the solid and is related to the phenomenon of adsorption. Since solubility and surface in themselves can not explain adsorption, Taylor (121) has proposed the concept of activation energy as a theory of catalytic action. Experimental evidence of Taylor and coworkers supports this theory, for they found definite activation energies for the various reactions of hydrocarbons. For example, Turkewich and Taylor (128), working with magnesium oxide–chromium oxide and ethylene, found that there was a rapid reversible adsorption at 0°C. due to van der Waals forces; at 110°C. some activated adsorption occurred; at 184°C. decomposition accompanied the activated adsorption and ethylene was hydrogenated as well as decomposed; at 444°C. no hydrogenation occurred, as ethylene was decomposed rapidly. Methane, ethane, and propane showed the same type of adsorption, but the initial activation adsorption occurred at higher temperatures. It has been shown by Howard and Taylor (47), who have listed the activation energy for the van der Waals and hydrogen adsorption for the various metallic oxides and ethylene, that the activation energy varied for each catalyst. These authors have concluded for the hydrogenation of ethylene that the activity of the oxides will depend on the rate of activated adsorption.

Morikawa, Benedict, and Taylor (85) have studied the exchange reactions of deuteromethanes and deuteroethanes and the reactions of methane and ethane with a nickel catalyst; Farkas, Farkas, and Rideal (26) have studied deuteroethylenes; and Polanyi and coworkers (45, 46) have worked with deuterobenzenes. All these studies indicate definite temperatures for activated adsorption which are characteristic for each type of reaction that the hydrocarbon undergoes. To account for these phenomena, Taylor has assumed activated dissociative adsorption of the hydrocarbon into fragments on the surface of the catalyst.

Good catalysts for isomerization reactions will cause only this type of reaction to occur, and for hydrocarbons this will involve either the carbon-carbon bond, the carbon-hydrogen bond, or both bonds. Presumably, the activation energy for isomerization reactions will be lower than for the other reactions of the hydrocarbons. Moreover, this activation energy will be characteristic of each hydrocarbon and each catalyst. If, then, the isomerization reactions are to occur to the exclusion of other reactions, such as replacement and decomposition reactions, there should be an appreciable difference between the activation energies of these reactions and the activation energies for other types of reaction. It would be expected that effective catalysts would fall into two classes: namely, those effective for the carbon-carbon bonds only, and those effective for the carbon-hydrogen bond only. Before the advent of the idea of activated energy, Lazier and Vaughan (76) applied the term "specific catalyst" to the catalyst which appeared to effect only one type of reaction. This use of specificity should not be confused with the above selective action of catalysts, for the above refers only to a specificity in a small range of the total activated adsorption. The application of the term "specificity" for this particular activated adsorption would lead only to confusion. Through the experimental data certain catalysts seem consistently to effect the shifting of a carbon atom or a hydrogen atom. These will be referred to as carbon-carbon or carbon-hydrogen isomerization catalysts. This is not a finely drawn distinction, for it should be remembered that in many cases the shifting of a carbon atom necessitates the shifting of a hydrogen atom as well. The above terms apply to catalysts where the rearrangement is determined by the initial shift of a carbon atom or a hydrogen atom. For rearrangements where the initial shift may be either atom, both types of catalysts should prove effective. The methylcyclopentane-cyclohexane conversion is an example of the latter.

For the liquid catalyst, where adsorption no longer holds, the forces between the catalyst and the hydrocarbon will have different characteristics from those of the solid catalyst, but the catalytic action may still be attributed to dissociation of the hydrocarbon into fragments under the influence of the catalyst. It might be pointed out that the average life of these fragments has not been specified. For isomerization these shifts may take place almost instantaneously. With the solid catalyst in the liquid phase, such as aluminum chloride, which may or may not dissolve and has unshared electrons, the intermediate compound formation between the catalyst and hydrocarbon has been the popular theory. Olefins are known to form such addition compounds, but an attempt to carry the theory over to a general one for all hydrocarbons meets with difficulty. In the case of liquids, such as acids, many workers have for years accepted the formation of esters as intermediate compounds for the mechanism of the formation of olefins. An example of this is the reaction of phosphoric acid with ethylene. This reaction shows various activating steps, for at low temperatures ethylene may be driven off; at somewhat higher temperatures, higher olefins are formed; and at still higher temperatures, paraffins, naphthenes, and aromatics are formed. These steps correspond to the activation adsorption for particular reactions of a hydrocarbon with the solid catalyst. The theory of an intermediate compound necessitates the assumption of very short life for the ester during the ordinary reaction period. More recently, it has seemed to some workers that the assumption of catalytic dissociation into fragments is the simplest mechanism. This mechanism has advantages in that it is applicable to any type of hydrocarbon, that no assumption about the intermediate compound is necessary, that it is only a slight modification of the theory for thermal reactions, and that it is closely related to catalytic action of solids. This theory does not exclude the formation of esters or intermediate compounds, but it makes the formation of these a side reaction which will depend on the particular experimental conditions.

In the experimental data that follow, many references are to cases where isomerization is but one of several reactions occurring. These have been included not because the catalyst was considered a good catalyst, but because isomerization occurred under particular conditions. It is quite possible that under other conditions these poor catalysts might become good catalysts.

EXPERIMENTAL DATA

Molecules with three carbon atoms

The redistribution of energy in the simplest system of hydrocarbons is found in the cyclopropane–propylene isomerization. Accurate values for the thermodynamic quantities of propylene are available, but the values of cyclopropane involve estimated quantities. These data are given in table 1. The ΔH^0_{298} value for propylene is taken from the value of Rossini and coworkers (103) for the heat of combustion of propane and the value of Kistiakowsky and coworkers (68) for the heat of hydrogenation of propylene. The entropy value was obtained by Parks and Huffman (93) from the third law. The heat of combustion for the ΔH^0_{298} value of cyclopropane is taken from Thomsen's value (123). This is somewhat higher than the value given by Kharasch (66) and is preferred, since Thomsen's values for propane and propylene are very close to the new values for these hydrocarbons. The entropy value is one estimated by Parks and Huffman (93). For the process cyclopropane→propylene, ΔH^0_{298} is equal to -6865 cal. and ΔF^0_{298} to -9275 cal. This gives for the equilibrium constants at 298° and 773°K. the values 5.83×10^6 and 4.88×10^3. These values can not be far from the true values in the order of magnitude even with the estimated quantities.

Assuming for temperatures around 500°C. that the only reaction taking place was cyclopropane→propylene,—an assumption supported by the lack of a trend in the rate constants at constant pressure,—Chambers and Kistiakowsky (12) found that the thermal reaction was unimolecular and dependent on pressure. By extrapolation to infinite pressure, the high pressure constants or values of K_∞ at the temperatures 469.6°, 499.5°, and 518.6°C. were 1.14, 6.08, and 17.8×10^{-4} sec.$^{-1}$, respectively. The energy of activation was 65,000 cal., a value in good agreement with 63,900 cal., or that obtained by Trautz and Winkler (126). The value for the collision factor for the rate velocity constant differed by more than a power of 10 in the two experiments, and Chambers and Kistiakowsky attributed this to uncertainties in the temperatures used by Trautz and Winkler.

TABLE 1

Thermodynamic data for isomeric hydrocarbons with three carbon atoms

SUBSTANCE	ΔH^0_{298}	S^0_{298}	ΔS^0_{298}	ΔF^0_{298}
	15°-calories	*E.U.*	*E.U.*	*15°-calories*
Propylene	4,475	63.1	−34.7	14,820
Cyclopropane	11,340	55.0	−42.8	24,095

Rice and Gershinowitz (101) have found good agreement with the above rate constants for the calculated value obtained when using their statistical method, if the shifting of a hydrogen atom is assumed the rate-determining step. This does not tell the mechanism. These authors have pointed out that a carbon-carbon bond might break first. This might be followed by the establishing of an equilibrium between the activated molecules formed and the normal molecules. Finally, there might be a rearrangement into a propylene molecule or the rate-determining step. Since the calculated value depends on the assumed mechanism of the reaction, the usefulness of this method of calculation is considerably restricted, and no definite conclusion may be drawn as to the mechanism of this simple isomerization reaction.

Thermal and catalytic studies, shown in table 2, have been made on the cyclopropane reaction with the one exception of the thermal experiment for the reverse reaction made by Engler and Rogowski (24). This is open to question. The thermal studies show that cyclopropane changes to propylene very slowly at as low as 20°C., but the rate increases with an increase in temperature. Catalysts increase the rate so that more than a 65 per cent conversion has been obtained. Platinum black, aluminum oxide, caustic potash, and zinc chloride have been used as catalysts. If the shifting of the hydrogen atom is the rate-determining step, experimental work for platinum black and aluminum oxide is sufficient to suggest that these might be termed carbon-hydrogen isomerization catalysts, a suggestion that finds support throughout the following work.

TABLE 2

Experimental data for isomeric hydrocarbons with three carbon atoms

SUBSTANCE	TEMPERATURE	TIME	CATALYST	PRODUCTS	REFERENCE
	°C.				
Cyclopropane..	550	20 min.	$ZnCl_2$	Propylene (30%)	(6)
Cyclopropane..	Room	5 months	Sunlight	No change	(118, 119)
Cyclopropane..	100		KOH	Propylene (50–70%)	(53)
Cyclopropane..	200–315	90 min.	Pt black	Propylene (4.5–29%)	(57)
Cyclopropane..	350–360	105 min.	Al_2O_3	Propylene (15%)	(57)
Cyclopropane..	370–385	105 min.	Al_2O_3	Propylene (20%)	(57)
Cyclopropane..	360–370	195 min.		Propylene (1–2%)	(57)
Cyclopropane..	100	120 hrs.	Pt black	Propylene (45%)	(118, 119)
Cyclopropane..	20	5 months	Pt black	Propylene (19–30%)	(118, 119)
Cyclopropane..	100	120 hrs.		Propylene (15–18%)	(118, 119)
Cyclopropane..	500	12–30 min.		Propylene (25–65%) (kinetic study)	(12)
Propylene......	400		(a)	Cyclopropane (50%)	(24)

(a) Sealed tube.

Molecules with four carbon atoms

Thermodynamic data for the four-carbon atom hydrocarbons are the most accurate available for any group of isomeric hydrocarbons. These data are given in table 3. The data for butane have been obtained from the heat of combustion value of Rossini and coworkers (103) and from the entropy value of Parks and Huffman (93); those for isobutane have been taken from Rossini's data (104) for the conversion of *n*-butane to isobutane, the data for butane, and Parks and Huffman's (93) predicted value for the entropy change. Parks and coworkers (96a) have made a recent recalculation of the entropy with a more careful extrapolation of the heat capacities and obtained slightly different values for the entropy of butane and isobutane. From the heats of hydrogenation obtained by Kistiakowsky and coworkers (68) and the entropy values of Todd and Parks (125), the data for the olefins have been obtained. The second series of values for isobutene were given by Parks and Huffman (93), and have been reproduced to emphasize how the more accurate values may completely reverse the information about the nature of a reaction.

TABLE 3

Thermodynamic data for hydrocarbons with four carbon atoms

SUBSTANCE	ΔH^0_{298}	S^0_{298}	ΔS°_{298}	ΔF^0_{298}	ΔS°_{298} ‡
	15°-calories	*E.U.*	*E.U.*	*15°-calories*	*E.U.*
Butane (g)	−30,570	74.5†	−87.2	−4,580	75.37
Butane (g)*		75.8	−85.8	−5,000	
Isobutane (g)	−32,200	69.4	−92.2	−4,720	71.25
Isobutane (g)*		70.0	−91.6	−4,900	
Butene-1 (g)	−480	72.5	−57.9	16,780	72.47
cis-Butene-2 (g)	−2,250	73.0	−57.4	14,860	68.22
trans-Butene-2 (g)	−3,200	71.2	−59.2	14,450	67.61
Isobutene (g)	−4,060	69.0	−61.4	14,240	68.21
Isobutene (g)§	−200	67.3	−62.8	18,500	

* Recent recalculated values.

† See ref. 96a.

‡ Calculated translational and rotational entropy.

§ Old data.

In the last column appear the calculated values for the entropy due to translation and rotation as obtained by Kassel (64). Comparing the calculated and experimental values, Kassel concluded that since the estimated value for the vibrational contribution for normal butane is 2.79 E.U., giving a total entropy of 78.16 E.U., the experimental value obtained by Parks and Huffman appears to be too low. If the vibrational entropy for *n*-butane and isobutane is taken as approximately the same, the experimental value for isobutane is too low. Likewise, the experimental values of the entropy for butene-1 and isobutene are too low, and while the difference between the calculated values for *cis*-butene-2 and *trans*-butene-2 is of the right order of magnitude, the difference between the experimental values is too large. The differences between the experimental values and the calculated values may arise from the extrapolation from 90° to 0°K., from an incorrect assumption of free rotation about the carbon–carbon bond in the statistical calculation, or from a finite entropy in the crystalline hydrocarbon at absolute zero. However, Parks and coworkers (96a) from their recent calculations rule out the possibility of error in the extrapolation from 90° to 0°K. for *n*-butane and isobutane, and believe that the difference in values is due to a fundamental error in the third law or to the statistical entropies.

From the data in table 3 the free energy, entropy change, and equilibrium constant have been calculated for the various isomerization reactions of these hydrocarbons and are given in table 4. At 298°K. the isomerization reactions listed in table 4 are spontaneous reactions. If the free energy is considered a linear function of the temperature, all the isomerization reactions 1 to 6, with the exception of reaction 3, which has a positive entropy change, will exhibit a limiting temperature for the spontaneous reaction. Limiting temperatures for these reactions are 53°, 750°, 1819°, 255°, and 180°C., respectively.

TABLE 4

Thermodynamic quantities for isomerization reactions of hydrocarbons with four carbon atoms

REACTIONS	ΔF^0_{298}	ΔS^0_{298}	K_{298}	
	15°-calories	*E.U.*		
n-Butane ⇌ Isobutane	−140	−5.0	1.26	(1)
Butene-1 ⇌ Isobutene	−2,540	−3.5	71.3	(2)
Butene-1 ⇌ *cis*-Butene-2	−1,920	+0.5	25.2	(3)
Butene-1 ⇌ *trans*-Butene-2	−2,330	−1.3	50.1	(4)
cis-Butene-2 ⇌ *trans*-Butene-2	−410	−1.8	1.99	(5)
cis-Butene-2 ⇌ Isobutene	−620	−4.0	2.83	(6)

For the isomerization of *n*-butane to isobutane the limit of error is of the same magnitude as the absolute value, and the older data indicate merely a spontaneous reaction at 298°K. The new recalculated data give the conversion of isobutane to *n*-butane as the spontaneous reaction. This reaction has not been studied directly. Ipatieff and Grosse (56) obtained isobutane in the presence of aluminum chloride and hydrogen chloride under pressure. Egloff and Parrish (19) have shown that the experimental data on stability favor isobutane as slightly more stable in the temperature range of 550–1100°C. If the entropy values at 298°K. are considered valid at the higher temperatures, the calculated order of stability is reversed at 53°C.; therefore it would appear that there is a slight error in the entropy values or that the specific heat may vary appreciably with higher temperatures. However, the new recalculated data give *n*-butane as slightly more stable than isobutane at 298°K., with the stability of *n*-butane increasing rapidly with an increase in temperature. When the pressure was increased to 48.5 atm. at 555°C., the stability was doubled. The data at 48.5 atm. can not be used in strict comparison, since the thermodynamic data are for a constant pressure of 1 atm.

According to the thermal data of Hurd and Goldsby (50), the conversion of butene-1 to butene-2 occurred at 600–650°C. with a yield of 21 to 16 per cent, and that of butene-2 to butene-1 at 650–700°C. with a yield of 16 to 30 per cent. In both cases decomposition accompanied isomerization. Frey and Huppke (32) obtained an equilibrium mixture for butene-1, *cis*-butene-2, and *trans*-butene-2 of 25:40:30 at 350°C. From the thermal reaction of butane they obtained a 67:16:33 mixture at 375°C., and they believed that this was due to two end methyl groups in butane.

Catalysts have been found to speed up the conversion, as shown in table 5. In this connection it might be recalled that the butenes formed from butanol and the butyl halides (54, 80, 81, 99) vary in composition depending on the catalyst used. From the dehydrogenation of butanol, butene-1 was formed with the use of neutral or alkaline catalysts, and butene-2 with acid catalysts. Gillet (35) believed that in the case of the formation of butene-2, it was a result of the isomerization of butene-1 to butene-2. Matignon, Moureu, and Dole (80, 81) favor this view, and believe that they have shown experimentally that exceptions to this rule are due to traces of acid on the catalysts. Recently, Young and coworkers (134, 135) have pointed out that information favors the rearrangement of crotyl and methylvinylcarbinyl bromides when they are treated with the Grignard reagent or zinc in alcohol before the formation of the butenes. They rule out the possibility of isomerization of the butenes after their formation on the basis of the thermal experiments of Hurd and Goldsby and of Frey and Huppke. Since catalysts have a profound effect on the isomerization of the butenes, and since magnesium and zinc bromides, which are catalysts, were present during these reactions, the thermal data are not truly applicable in this case.

The isomerization of *n*-butene to isobutene is feasible up to 750°C., with an equilibrium constant of 71.2 at 298°C. Ipatieff and Pines (59) with phosphoric acid in the presence of hydrogen gas obtained small amounts of isobutane from butene-1. They believed that the isobutane obtained from butane in the work of Ipatieff and Grosse (56) resulted from the formation of butene-1 and its isomerization to isobutene, followed by hydrogenation to isobutane. The fact that isobutane was not obtained from *n*-butane with phosphoric acid as the catalyst, supported this contention. In the experimental data it is seen that when phosphoric

TABLE 5

Experimental data for hydrocarbons with four carbon atoms

SUBSTANCES	TEMPERATURE	TIME	CATALYSTS	PRODUCTS	REFERENCES
	°C.				
n-Butane			H_3PO_4	No change	(59)
n-Butane	175	3-4 hrs.(a)	$AlCl_3 + HCl$	Isobutane	(56)
Butene-1	500-650	40 sec.		Butene-2 (0-10.5%)	(50)
Butene-2	650-700	48-97 sec.		Butene-1 (11.7-7.5%)	(50)
Butene-1	249	206 sec.	H_3PO_4(b)	Butene-2 (100%)	(60)
Butene-1	21		$HClO_4$ (7%)	Butene-2 (21%)	(60)
Butene-1	76		$C_6H_5SO_2H$ (75% aq.)	Butene-2 (13%)	(60)
Butene-1	100		$ZnCl_2$ (75% aq.)	Butene-2 (5%)	(60)
Butene-1	427		$H_3PO_4 + Al_2O_3$	Butene-2 (70-80%)	(60)
trans-Butene-2	100		H_3PO_4 (100%)	Butene-1 (6.6%); *cis*-butene-2 (6%); *trans*-butene-2 (87.4%)	(60)
Butene-1	330	12 hrs.	$H_3PO_4 + H_2$(c)	Isobutane (6%)	(59)
Butene-1	400-600		CaO	Butene-2 (87%)	(107)
Butene-1	420		$AlPO_4$ + pumice	Butene-2 (92%)	(107)
cis-Butene-2	490-520	4.5-11.9 hrs.		*trans*-Butene-2 (kinetic study)	(71)
Methylcyclopropane	340-360	1.5-3.5 hrs.	Al_2O_3	Butene-2 (large); isobutene (small); propane (large); *tert*-butyl-1,1-dimethylethylene	(17)
Methylenecyclopropane	350		Al_2O_3	Butadiene	(83)

(a) 35 atm. (b) 7.18 atm. with impregnated diatomaceous earth. (c) 100 atm.

acid is a catalyst, a shift of a hydrogen atom occurs. If catalysts may be selective for the different types of bonds in isomerization reactions, phosphoric acid is probably a carbon–hydrogen isomerization catalyst. At 298°K. the order of increasing stability of the butenes is butene-1, *cis*-butene-2, *trans*-butene-2, and isobutene. If it is assumed that there is no appreciable change in the entropy at higher temperatures, this order is changed around 973°K. with the order of *cis*-butene-2 and isobutene reversed. For the butenes the experimental thermal data are not in complete agreement, as shown by Egloff and Parrish (19), but the data favor the order of stability given by the thermodynamic data at 298°K. However, in the work of Tropsch, Parrish, and Egloff (127), isobutene was found to be less stable than butene-1 at 1100°C. and 55 mm. pressure. According to the thermodynamic data at 1100°C., the free energies of butene-1 and isobutene are 79,016 and 80,242 cal., or, isobutene is less stable than butene-1.

The kinetics for the *cis–trans* thermal reaction has been investigated by Kistiakowsky and Smith (71), who found that the rate was dependent on pressure. With less than 1 atm. the conversion appeared to be a first-order homogeneous reaction. For pressures greater than 1 atm., the results were erratic and, in general, could not be satisfactorily explained. Their results confirmed the work of Hurd and Goldsby (50) at 650°C., in that the rate was slow with a rate constant of 1.0 to 1.7×10^{-6} $\mathrm{sec.}^{-1}$ at 663–620°K. The equilibrium constant was 1.12, corresponding to 52.8 per cent of the *trans*-isomer (low-boiling). According to the thermodynamic data at 298°K., the equilibrium constant is 1.99, corresponding to 66.7 per cent of the *trans*-isomer. From the calculated entropy values for the translational and rotational entropy, Kassel obtained an equilibrium constant at 298.1°K. of 1.97, with a lower value predicted for the additional vibrational entropy. In the work of Hurd and Goldsby on the thermal reaction at 923° and 973°K., butene-2 was found to consist of 62 per cent of the *trans*-isomer (low-boiling) before pyrolysis and 61 per cent after pyrolysis. Also, butene-2 formed from butene-1 at the same temperatures showed 62 per cent of the *trans*-isomer. The entropy change for the conversion given by the work of Kistiakowsky and Smith was -1.2 E.U. at 663°K., as compared with -1.8 E.U. given by the work of Todd and Parks. From Kassel's calculated values the translational and rotational entropy would contribute -0.6 E.U. to the total entropy change for the reaction. An additional -0.6 E.U. for the vibrational entropy is plausible, but an additional -1.2 E.U., which would be necessary for a total change of -1.8 E.U., is out of line with the calculated or experimental data.

Effective catalysts for the isomerization of the butenes, where the rearrangement is due to a shift of a hydrogen atom, are catalysts of the acid or neutral type, as shown in table 5. Whether aluminum chloride actually caused the shift of a carbon atom in the paraffin is not known, but isobutane was obtained from butane when it was used. For the break in a three-membered ring, as in methylcyclopropane or methylenecyclopropane, aluminum oxide was effective. This same catalyst was used for the cyclopropane–propylene isomerization, where evidence favors the hydrogen shift as the rate-determining step.

Molecules with five carbon atoms

Although thermodynamic data are known for several hydrocarbons with five carbon atoms, uncertainties in some of the data and the lack of information on other isomers leave the thermodynamic picture incomplete. These data are given in table 6. The source of the new data for *n*-pentane is the value of Rossini and coworkers (103) for the heat of combustion, and that of Parks, Huffman, and Thomas (96) for the entropy. The free energy of gaseous pentane was calculated by Parks (92). The heat of combustion values for the old data of *n*-pentane and 2-methylbutane are from Kharasch's value (66), and the entropy for 2-methylbutane from the data of Parks, Huffman, and Thomas (96). For neopentane the International Critical Tables (62) and Kharasch (66) give the same value for the heat of combustion. The molal entropy for the ideal gas at the boiling point, 286.6°K., has been determined by Aston and Messerly (3). This value of 71.7 E.U. is to be compared with 78.89 E.U. calculated from the Raman spectrum and moments of inertia. These authors believe that the discrepancy is real, and is due either to rotation of the methyl groups or to arrangements in the crystal. The value of

TABLE 6

Thermodynamic data for hydrocarbons with five carbon atoms

SUBSTANCE	ΔH°_{298}	S°_{298}	ΔS°_{298}	ΔF°_{298}
	15°-calories	*E.U.*	*E.U.*	*15°-calories*
n-Pentane (g)				−2,570
n-Pentane (l)	−42,230	62.0	−132.2	−2,820
n-Pentane (l)*	−47,960	62.0	−131.9	−8,600
2-Methylbutane (l)	−43,060	59.5	−134.7	−2,920
Neopentane (g)	−38,460	72.9	−122.5	−2,300
Trimethylethylene (l)	−17,050	59.5	−103.2	13,700
Methyl-1,4-butadiene (l)	18,060	58.2	−73.5	39,970
Cyclopentane (l)	−37,088	47.0	−116.0	3,235

* Old data.

72.94 E.U. at 298°K. has been used to calculate the free energy. The data for trimethylethylene are from the estimated value of Parks and Huffman (93) for the heat of combustion and from their experimental value (94) for the entropy: those for methyl-1,4-butadiene are from the recent data for pentane, the value of Kistiakowsky and coworkers (69) for the heat of hydrogenation, and that of Parks, Todd, and Shomate (97) for the entropy. The data for cyclopentane are from the value for the heat of combustion given in the International Critical Tables (62) and from Parks and Huffman's estimated value (93) for the entropy.

Data for the isomeric pentanes are difficult to compare. Kharasch's value for the heat of combustion of *n*-pentane is definitely incorrect, and in view of this it is not safe to predict what changes more accurate data would give to those of other isomers. The magnitude of the correction made by the new data may be seen by comparing isobutene in table 3 and *n*-pentane in table 6. With the exception of the paraffins, the data for the hydrocarbons with more than four carbon atoms must not be taken too seriously. Where differences are involved in different types of hydrocarbons, the older figures may give a fairly accurate value, provided older figures are compared. As the interest here is often in small differences between the same type of isomeric hydrocarbons, the exact value of the data must be borne in mind.

The experimental data for these hydrocarbons are given in table 7. The isomerization of *n*-pentane to isopentane in the presence of catalysts, as carried out by Glasebrook, Phillips, and Lowell (36), suggests a greater thermodynamic stability for isopentane. This is in line with the data on the butanes. These investigators found that aluminum bromide, activated by small amounts of hydrogen bromide or hydrogen chloride, proved to be the best catalyst, being 11.4 times more active than aluminum chloride. Pentane gas streamed over aluminum chloride activated with hydrogen bromide gave a lower yield of isopentane but a higher yield of isobutane. Apparently aluminum chloride caused the *n*-pentane to split into smaller molecules to a greater extent than aluminum bromide. Egloff and Wilson (21) have pointed out that dry aluminum chloride or bromide has always been found an ineffective catalyst, but that traces of water, alkyl halide, or hydrated aluminum chloride were sufficient to start the reaction. The work of Glasebrook, Phillips, and Lowell agreed with these facts. Anhydrous aluminum oxide produced no action, but on the addition of hydrogen chloride the reaction started.

Hurd, Goodyear and Goldsby (51) found that the thermal reaction of pentene-1 yielded at 580–600°C. small amounts of pentene-2,trimethylethylene, *n*-butane, isobutane, and larger amounts of isopropylethylene. These workers found that pentene-2 underwent decomposition at 525–

TABLE 7

Experimental data for hydrocarbons with five carbon atoms

SUBSTANCES	TEMPERATURE	TIME	CATALYST	PRODUCTS	REFERENCES
	°C.				
n-Pentane	Room		$AlBr_3$; HBr; HCl	Isopentane (56%); butanes (5%); high-boiling products	(36)
n-Pentane	40		$AlCl_3$; HBr	Isopentane (13.4%); butane (4-11%); isobutane (23-29%)	(36)
Pentene-1	550-600	8-13 sec.		Pentene-2 (small); decomposition	(51)
Pentene-2	550-600	12-19 sec.		Pentene-1 (small); decomposition	(51)
Pentene-2	350-450		Al_2O_3; H_3PO_4; $Al_2(SO_4)_3$	No action	(91)
Pentene-2	70-80	65 hrs.		Pentene-2 (transformed)	(110)
Isopropylethylene	450	16 sec.	Al_2O_3	Trimethylethylene (10%)	(91)
Isopropylethylene	500	14 sec.	H_3PO_4	Trimethylethylene (29%)	(91)
Isopropylethylene	425	16 sec.	$Al_2(SO_4)_3$	Trimethylethylene (47%)	(91)
Isopropylethylene	400-500	1 hr.		Trimethylethylene (traces)	(54)
Isopropylethylene	525-535	2 hrs.	Al_2O_3	Trimethylethylene (80%)	(54)
Isopropylethylene	400-500		Al_2O_3	Trimethylethylene (65%)	(54)
Isopropylethylene	500-505		Silica	Trimethylethylene (45%)	(54)
Trimethylethylene	520-530	70 min.	Al_2O_3	No action	(54)
Trimethylethylene	450	21 sec.	Al_2O_3	No isomers; polymers	(91)
	500	20 sec.	H_3PO_4		
Cyclopentane	60	8 hrs.	$AlCl_3$	No action	(15)
Dimethylcyclopropane	340-345	1.1 hrs.	Al_2O_3	Trimethylethylene	(57)
Ethylcyclopropane	300-310		Al_2O_3	Methylethylethylene	(105)
Methylcyclobutane	300-350	2 hrs.	Al_2O_3	*s*-Methylethyl-, isopropyl-, and *as*-methylethyl-ethylene	(106)
Methylenecyclobutane			HX	Methylcyclobutene	(31)
Methylenecyclobutane	300		Al_2O_3	Methylcyclobutene	(30)
Methylenecyclobutane	395-405	30 min.	Al_2O_3	Isopropylacetylene	(117)
Methylenecyclobutane	410-430	45 min.	Al_2O_3	Isoprene; polymers	(17)
Methylenecyclobutane			H_2SO_4; HBr; alkali	Methylcyclobutene	(40)
Methylenecyclobutane	180-185		Sodium	Methylcyclobutene	(142)
Methylenecyclobutane	300		Al_2O_3	Methylcyclobutene	(61)

560°C., while Norris and Reuter (91) obtained no reaction at 350–425°C. in the presence of aluminum oxide, phosphoric acid, or aluminum sulfate. These catalysts were effective for the isomerization of isopropylethylene to trimethylethylene with yields as high as 65 per cent. The reverse process was not obtained with the same catalysts.

Sherrill, Ott, and Pickett (110) obtained a rearrangement of pentene-2 into another pentene-2 which they believed represented isomeric electromers, as postulated by Kharasch (67). The same transformation was effected by sunlight or ultra-violet light. When treated with hydrogen bromide the initial pentene gave 15 per cent of 3-bromopentane and 85 per cent of 2-bromopentane, while the transformed pentene gave 78 per cent of 3-bromopentane and 22 per cent of 2-bromopentane. They found no evidence of *cis–trans* isomerization and no shift of the double bond, and suggested that the halide derivatives may be a racemic or meso form of *cis–trans* isomers. Sherrill, Baldwin, and Haas (109) showed that pentene-2 made from 3-bromopentane was transformed by ultra-violet light but not that made from 2-bromopentane. Absorption spectrum evidence favored the existence of electromers and not *cis–trans* isomers, according to Carr (11). Sherrill (108a) believes now that this observed difference in the behavior of pentene-2 may be due to mixtures of *cis-* and *trans*-isomers of various compositions.

In the identification of the alkyl bromides, the refractive indices were used. Another method of identification has been developed by Lauer and Stodola (74), in which the halides were converted to the anilides and the percentage composition determined by the comparison of mixed melting points for known mixtures. By this method hydrogen bromide was found to add to pentene-2 to give equal amounts of 2-bromopentane and 3-bromopentane, where the method of preparation of pentene-2 made no difference in the products formed. Hence Lauer and Stoddard believe that there is no evidence to support the formation of electromers.

Derivatives of cyclopropane and cyclobutane have been shown to isomerize readily in the presence of a catalyst. With the three-membered carbon ring the ring was broken; with the four-membered carbon ring either the ring was broken, or a shift of the hydrogen between the side chain and the ring occurred when a double bond was present. Conditions which caused the breaking of the three-membered carbon ring often caused only a shift of the hydrogen atom in the four-membered ring.

The dehydration of isoamyl alcohol (91) gives the various pentenes with different experimental conditions and in line with the above data for the isomerization reactions. The same is true for tertiary-amyl alcohol (8, 111, 122), even though this necessitates a rearrangement of the carbon structure.

If the shift of the hydrogen atom is assumed to be the rate-determining step in the isomerization of the pentenes, the experimental data may readily be understood. Starting with pentene-1, the hydrogen atoms on the third carbon atom are the important ones, for if one hydrogen atom moves to the first carbon atom in the direction of the double bond, pentene-2 results. A shift of the same hydrogen atom in the other direction, to the fourth carbon atom, would give two methyl groups, which presumably may readily rearrange to give the isopropyl group or isopropylethylene. Since the chances for a hydrogen atom to move to the adjacent carbon atom are greater than its chances to move to the first carbon atom, isomerization to isopropylethylene should occur more readily than to pentene-2. In the experimental data there is little evidence for the formation of pentene-2. If the second hydrogen atom on the third carbon atom shifted, it would move only in one direction or toward the double bond, as in the conversion of isopropylethylene to trimethylethylene. This change occurs readily, as the experimental data show. Hence the experimental data support the following arrangement for the order of increasing thermodynamic stability: pentene-1, pentene-2, isopropylethylene, pentane, and isopentane.

The data suggest also that the stability of cyclo derivatives should be intermediate between that of the pentenes and the pentanes. No direct evidence is available for this, but the work of Cox (15) may be cited for indirect evidence. In the cracking of nonane in the presence of aluminum chloride for eight hours at 110–120°C., butane and cyclopentane were obtained. The author claimed experimental support for the formation of the latter from pentene. The above order of stability is in agreement with the order of thermal stability for the pentenes, according to Egloff and Parrish (19), but not for the pentanes. In the last instance, the thermal data are meagre.

In the isomerization of the pentenes, the effective catalysts were the type for carbon–hydrogen bonds, as shown in the case of the butenes. For the formation of isopropylethylene it is true that a carbon–carbon bond is broken, but in this case it appears to be a result of the initial shift of a hydrogen atom. For the isomerization of pentane to isopentane, since there is no point of unsaturation, the rate-determining step was probably the shifting of a carbon atom, and the effective catalysts were aluminum chloride or bromide. These catalysts appear to be carbon–carbon isomerization catalysts.

Molecules with six carbon atoms

The isomeric hexanes and hexenes have been used in very few investigations. Only thermodynamic data are available for *n*-hexane, hexene-1, cyclohexane, and methylcyclopentane. These are given in table 8. The values in the International Critical Tables (62) for the heat of combustion of hexane, cyclohexane, and methylcyclopentane, the value of Huffman, Parks, and Barmore (48) for the entropy of hexane and methylcyclopentane, and the value of Parks, Huffman, and Thomas (96) for the entropy of cyclohexane have been used. The heat of combustion and entropy data for hexene-1 are values estimated by Parks and Huffman (93). Again, the order of increasing stability for the various types of hydrocarbons is olefin, cycloparaffin, and paraffin.

Nenitzescu and Dragen (90) and Ipatieff and Grosse (56) have recorded experiments in which isomeric hexanes have been obtained from *n*-hexane with aluminum chloride as the catalyst. Of the possible isomers only 2-methylpentane or 3-methylpentane were identified. Petrow, Meschitcherjakow, and Andrewjew (98) found that hexene-1 isomerized into hexene-2 and hexene-3 with molybdenum sulfide as a catalyst. From the experimental and thermodynamic data on the butenes and the pentenes, hexene-1 would be expected to form a number of isomeric hexenes.

TABLE 8

Thermodynamic data for hydrocarbons with six carbon atoms

SUBSTANCE	ΔH^0_{298}	S^0_{298}	ΔS^0_{298}	ΔF^0_{298}
	15°-calories	*E.U.*	*E.U.*	*15°-calories*
n-Hexane (l)	−32,110	70.6	−155.6	−7,000
n-Hexene (l)	−23,000	68.1	−127.1	14,900
n-Hexene (g)				15,780
Cyclohexane (l)	−36,700	49.2	−146.0	6,800
Cyclohexane (g)				8,030
Methylcyclopentane (l)	−37,800	59.2	−136.0	2,700

TABLE 9

Thermodynamic quantities for isomerization reactions of hydrocarbons with six carbon atoms

REACTIONS	ΔF^0_{298}	ΔS^0_{298}	K_{298}	K_{973}
	15°-calories	*E.U.*		
Hexene-1 $\rightleftharpoons$ Cyclohexane	−8,100	−18.9	5.25×10^4	2.15×10^2
Hexene-1 $\rightleftharpoons$ Methylcyclopentane	−12,200	−8.9	1.29×10^7	3.23×10^3
Cyclohexane $\rightleftharpoons$ Methylcyclopentane	−4,100	−10.0	2.45×10^2	1.51×10^1

Laughlin, Nash, and Whitmore (75) have shown that an equilibrium mixture of tetramethylethylene, *as*-methylisopropylethylene and tertiary-butylethylene in the ratio of 61:31:3 was obtained from any one of the

TABLE 10

Experimental data for hydrocarbons with six carbon atoms

SUBSTANCES	TEMPERATURE	TIME	CATALYSTS	PRODUCTS	REFERENCES
	°C.	hours			
n-Hexane	100	7.5	AlCl$_3$	2- or 3-Methylpentane	(90)
n-Hexane	69–72	3	AlCl$_3$(a)	Gases; isobutane (90%); pentane (9%); isomeric hexanes; paraffins	(56)
Hexene-1	350–400	1	MoS$_3$(b)	Hexene-2; hexene-3	(98)
Hexenes*	300	5–8	P$_2$O$_5$; silica gel	Tetramethylethylene (61%); *as*-methylisopropylethylene (31%); *tert*-butylethylene (3%)	(75)
Cyclohexane	300–330	5–8	HI	Methylcyclopentane	(2)
Cyclohexane	250–260		HI; P	No change	(79)
Cyclohexane	740–750	1	Al$_2$O$_3$	Methylcyclopentane	(55)
Cyclohexane	500–510	4	Al$_2$O$_3$(c)	Methylcyclopentane; aromatics; naphthenes; olefins; methane	(55)
Cyclohexane	750	1		No change	(55)
Cyclohexane	135–145	6–8	AlCl$_3$	No change	(37)
Cyclohexane	Low	48	AlCl$_3$; HCl	Methylcyclopentane	(2)
Cyclohexane	65–70	3	AlCl$_3$; 0.6% H$_2$O	Methylcyclopentane (22.8%)	(89)
Methylcyclopentane	65–70	30	AlCl$_3$	Methylcyclopentane (77.2%)	(89)
Cyclohexane	150	24	AlCl$_3$; HCl	Isobutane; methylcyclopentane; *m*-dimethylcyclopentane; dicyclohexyl; dimethylcyclopentyl	(58)
Cyclohexane	100	24	AlBr$_3$	*cis*- and *trans*-Cyclohexane; methylcyclopentane; dimethylcyclobutane	(146, 149)

* Each isomer gives same mixture.

(a) 35 atm. (b) 40 atm. (c) 110–112 atm.

isomers with phosphorus pentoxide on silica gel as the catalyst. The same equilibrium mixture was obtained with the same catalyst and tertiary-butylcarbinol (pinacolyl alcohol) by Whitmore and Meunier (132). Tetramethylethylene is symmetrical, while the other isomers are asymmetrical, and it would be expected that the latter would isomerize to tetramethylethylene. Moreover, tetramethylethylene will be the first product of isomerization from either *as*-methylisopropylethylene or tertiary-butylethylene. From the equilibrium ratio tertiary-butylethylene appears to have a highly unbalanced structure.

Thermodynamic data in table 8 predict that hexene-1 should form cyclohexane and methylcyclopentane. For these isomerizations and for the conversion of cyclohexane to methylcyclopentane, the thermodynamic quantities are given in table 9. For ΔF^0_{298} the free energies for the liquid state have been used. These values for hexene-1 and cyclohexane are increased by 880 and 1230 cal., respectively, for the gaseous state. This might make a change in ΔF^0_{298}, for the reaction in the gaseous state, of not more than 400 cal. as a reasonable estimate. Although there are no direct measurements for the change of hexene-1 to cyclohexane, Egloff and Wilson (20) have shown that there is much evidence to support this isomerization in the reactions of the gaseous olefins. There are several studies of the change of cyclohexane to methylcyclopentane, and these are given in table 10. Even up to 750°C. the thermal conversion was not obtained, according to Ipatieff and Dowgelewitsch (55), but Nenitzescu and Cantuniari (89) claimed an equilibrium from both directions with 22.8 per cent methylcyclopentane at 70°C. in the presence of aluminum chloride. This does not agree with the equilibrium constants given by the thermodynamic data in the liquid state.

With the exception of hexene-1, in the experimental reactions of this group, both the carbon–carbon and the carbon–hydrogen bonds are involved. Aluminum oxide and aluminum chloride or bromide have been found good catalysts. The temperature range of reaction for aluminum oxide was 500–750°C., while for aluminum chloride or bromide the temperature range was 65–150°C. With aluminum chloride and the cyclohexane–cyclomethylpentane isomerization the isomer was the product at 65–100°C., but at 150°C. decomposition and alkylation accompanied isomerization. This would indicate that the shift of either a carbon atom or a hydrogen atom can be the rate-determining step in the mechanism.

Molecules with seven carbon atoms

The isomeric heptanes have been favored in that the thermodynamic data have been determined experimentally for all the isomers. These are given in table 11. The heat of combustion data for the group were determined at the U. S. Bureau of Standards (66), and the molal entropies were made on the same samples by Parks, Huffman, and Thomas (96). The differences between the experimental values for the heats of combustion are not more than 1200 cal. This is the same as the magnitude of error for each value. At the time of the determinations Parks and Huffman assumed that there were no real differences in these values. The recent accurate data for the heat of combustion of *n*-heptane as determined by Rossini and coworkers (103) give a value for the free energy that is lower by an amount as great as or greater than the differences between the various isomers. With the recent data favoring a definite variation in the heats of combustion of the same type of isomeric hydrocarbons, it is quite possible that more accurate values for the heats of combustion might alter appreciably the information on some of the isomerization reactions, since the small differences in the free energies are highly significant for these reactions.

TABLE 11

Thermodynamic data for hydrocarbons with seven carbon atoms

SUBSTANCE	ΔH^0_{298}	S^0_{298}	ΔS^0_{298}	ΔF^0_{298}
	15°-calories	*E.U.*	*E.U.*	*15°-calories*
n-Heptane (l)*	−55,410	78.5	−180.9	−1,480
n-Heptane (l)	−56,760	78.5	−180.4	−3,000
2-Methylhexane (l)	−57,760	75.3	−183.8	−3,000
3-Methylhexane (l)	−57,760	74.0	−185.1	−2,600
3-Ethylpentane (l)	−56,760	74.6	−184.5	−1,800
2,2-Dimethylpentane (l)	−58,760	68.1	−191.0	−1,800
2,3-Dimethylpentane (l)	−57,760	72.4	−186.7	−2,100
2,4-Dimethylpentane (l)	−57,760	69.7	−189.4	−1,300
3,3-Dimethylpentane (l)	−58,760	70.1	−189.0	−2,400
2,2,3-Trimethylbutane (l)	−58,760	64.8	−194.3	−800
Heptene-1 (l)	−25,520	78.6	−149.5	19,050
Methylcyclohexane (l)	−46,550	59.3	−168.4	3,600
1,2-Dimethylcyclopentane (l)	−47,650	64.5	−163.2	1,000

* New data.

For the data on heptene-1 the value of Rossini and coworkers (103) for the heat of combustion of *n*-heptane with Kistiakowsky and coworkers' value (69) for the heat of hydrogenation and the value of Parks, Todd, and Shomate (97) have been used. The values of the heat of combustion for methylcyclohexane and dimethylcyclopentane are from the International Critical Tables (62), the entropy value for methylcyclohexane from Parks and Huffman (94), and the entropy value for dimethylcyclopentane from Huffman, Parks, and Barmore (40).

TABLE 12

Experimental data for hydrocarbons with seven carbon atoms

SUBSTANCES	TEMPERATURE	TIME	CATALYSTS	PRODUCTS	REFERENCES
	°C.	*hours*			
n-Heptane	100	10	$AlCl_3$; 1% H_2O	1,3-Dimethylcyclopentane; methylcyclohexane; methylcyclopentane; propane; isobutane; bicycloparaffin	(90)
n-Heptane	220	3	$AlCl_3$	Isomers (8%)	(98)
n-Heptane	300–400	6–7	$ZnCl_2$(a)	Isomers (27–18%)	(98)
n-Heptane	400	7	CuO; MoS_3(b)	Isomers (15%)	(98)
n-Heptane	420	3–14	MoS_3(c)	Isomers (4–11%)	(98)
n-Heptane	100	10	$AlCl_3$(d)	*n*-Hexane (1%); 2-methylhexane (4%)	(10)
n-Heptane	96		$AlCl_3$(e)	Isomers (5–6%); pentanes (4.6%); 2-methylpentane (3.4%); 3-methylpentane (2.0%); *n*-hexane (0.4%); 2,4-dimethylpentane (1.5%); 2,2,3-trimethylbutane (0.5%); 3,3-dimethylpentane (0.4%); 2-methylhexane (1.2%); 3-methylhexane (1.6%); polymerization products (24.4%)	(9)
Methylenecyclohexene	140	3	Quinoline hydroiodide; chinolin	Methylcyclohexene-1,2	(29)
Methylenecyclohexene	170–150	6–7	Benzoic acid	Methylcyclohexene-1,2	(29)
Methylenecyclohexene	300		Quinoline hydroiodide(f)	Methylcyclohexene-1,2	(139)

(a) 50–60 atm. (b) 60 atm. (c) 70 atm. (d) Added as 50 per cent initial. (e) 10 g. added every 2 min. (f) Sealed tube.

The data in table 11 are for the liquid state, and it is very probable that the heat of vaporization will contribute further small variations for the gaseous state. However, assuming a linear temperature relationship and using the old data for *n*-heptane, the data for the isomeric heptanes are applicable to the work of Calingaert and Beatty (9) given in table 12. With aluminum chloride as the catalyst, the following heptanes, listed in the order of decreasing yields, were obtained from *n*-heptane: 3-methylhexane, 2,4-dimethylpentane, 2-methylhexane, 2,2,3-trimethylbutane, and 3,3-dimethylpentane. This order would not be predicted from the thermodynamic data. However, Parks, Huffman, and Thomas do not claim accuracy for the molal entropy of 3-methylhexane or of 2,3-dimethylpentane, since these did not crystallize at 70°K. It should be remembered also that the separation of the isomers is a difficult problem, and that the amount of isomerization of heptane was small in order to exclude secondary reactions. Therefore no conclusions are warranted. Other studies on the heptanes have been qualitative in nature and some are open to question. Besides aluminum chloride, zinc chloride, cupric oxide, and molybdenum sulfide have been used as catalysts, but except in the case of aluminum chloride the isomers formed were not identified.

Since the order of thermodynamic stability of this group is heptenes, cyclohexane and cyclopentane derivatives, and heptanes, the formation of the naphthenes in the thermal or catalytic reactions can be accounted for if heptenes are identified. Unfortunately, these reactions have not been investigated. However, Nenitzescu and Dragen (90) have recorded isobutene, cyclohexane, and the methyl derivatives of cyclohexane and cyclopentane as products from *n*-heptane with aluminum chloride as the catalyst. These products speak strongly for the decomposition to olefins and the isomerization of the olefins. Reactions of paraffins in the presence of aluminum chloride are characterized by the formation of higher paraffins and in some cases with small amounts of unsaturates. It has been assumed that this is due either to the olefin adding to the paraffin or to the reaction proceeding largely by way of free radicals (21). Whether the term "free radical" or the term "fragment" is used would depend on how the definition of free radical specifies the average life of a free radical. The non-appearance of olefins may also be due in part to the isomerization to naphthenes. If the conditions under which the reaction is carried out are vigorous, the olefin formation will increase.

A less profound change has been studied in the methylenecyclohexane–methylcyclohexene system, where a hydrogen atom shifts between the ring and the side chain with a change in the position of the double bond. The catalysts for these isomerization reactions in contrast to the isomerization reactions of heptane are large complex organic molecules.

Molecules with eight and more carbon atoms

The thermodynamic information on the isomeric octanes is much the same in character as that for the heptanes, though fewer isomers have been studied. When the older data from the International Critical Tables (62) for the heat of combustion are replaced by the new data of Rossini and coworkers (103), the change in the free energy value amounts to more than the difference between the values for the free energy of the various isomers, as shown in table 13. The heat of combustion data for the other isomeric octanes are from Kharasch's values (66). But here again, as Parks and Huffman (93) have pointed out, the limit of error is of about the same magnitude as the variations between the isomers; in other words, there is no real difference between the ΔH^0_{298} values. The molal entropy for *n*-octane was determined by Huffman, Parks, and Barmore (48) and that for hexamethylethane and 2,2,4-trimethylpentane by Parks, Huffman, and Thomas (96) with a small correction for the latter (97). It is highly probable that more accurate data for the heats of combustion will show significant differences between the isomers. The same prediction can be made for the octenes, although thermodynamic quantities for diisobutylene alone are available. Commercial diisobutylene is really a mixture of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 in the ratio of 4:1. These have been separated into low-boiling and high-boiling fractions, and the thermodynamic data obtained by Parks, Todd, and Shomate (97), where the value of Rossini and coworkers (103) for the heat of combustion of the parent paraffin and the value of Kistiakowsky and coworkers (69) for the heat of hydrogenation have been used.

TABLE 13

Thermodynamic data for isomeric hydrocarbons with eight carbon atoms

SUBSTANCE	H^0_{298}	S^0_{298}	ΔS^0_{298}	F^0_{298}
	15°-calories	*E.U.*	*E.U.*	*15°-calories*
n-Octane (l)*	−62,260	86.0	−206.0	−850
n-Octane (g)*				1,520
n-Octane (l)	−64,210	86.0	−205.5	−3,000
2,2,4-Trimethylpentane (l)	−65,310	75.0	−216.5	−770
Hexamethylethane (s)	−67,410	61.4	−230.1	1,200

* New data.

The experimental data are extremely limited, for the only studies made on *n*-octane are those by Petrow, Meschitcherjakow, and Andrewjew (98); these studies are qualitative in nature, with no attempt made to identify the isomers. The results are given in table 14. Zelinsky and Levina (140) have identified the shifting of the double bond in 2,6-dimethyloctene-7 to the 6-position. For this, palladium in the presence of carbon dioxide was used as the catalyst. Since the temperature for this reaction was 200°C. and the catalyst was palladium, the octenes are undoubtedly sufficiently stable to furnish some very interesting isomerization reactions. However, the work of Whitmore and Stahly (131) on the dehydration of methyl-di-tertiary-butylcarbinol and that of Nasarow (88) on ethylisopropyl-tertiary-butylcarbinol showed that the higher olefins split and rearrange into smaller olefins in line with the experimental equilibrium data for these olefins. This indicates, as would be expected, that the higher olefins are less stable than the lower olefins and in the presence of a catalyst decompose readily. Nasarow (88a) has recently made a detailed study of the effect of structure on the products formed from large olefin molecules in the presence of a catalyst, 1-bromonaphthalene-4-sulfonic acid. All these reactions are accompanied by decomposition of the molecule. Nasarow believes that the initial olefin molecule loses a hydrogen atom; the free radical formed isomerizes and a hydrogen atom is added; finally, decomposition of either one or both isomers occurs. The products are not isomers usually, but olefins with a varying number of carbon atoms. It has not been definitely proven that isomerization actually precedes decomposition. Since this work has been with pure isomerization reactions, the results are not reproduced here.

Grignard and Stratford (37) investigated the action of aluminum chloride on the alkyl derivatives of cyclohexane. These reactions are all characterized by the formation of polymethyl derivatives of cyclohexane. The number of methyl groups which become attached to the ring is dependent on the number of carbon atoms in the original alkyl side chain. For the *o*- and *p*-dimethylcyclohexane and ethylcyclohexane, the meta isomer was obtained. It is rather surprising that aluminum chloride should cause the severing of the carbon–carbon bond in the side chain and apparently not attack the carbon–carbon bonds in the ring, for the paraffin is more stable than the cyclo structure. Since propane, butane, and isobutane were also formed with the propyl, butyl, and isoamyl derivatives, the alkyl group may break from the ring first and these fragments will be very unstable. Perhaps the break in the carbon–carbon bond once removed from the ring is the preferred break, and the released fragment is added to another carbon in the ring. This process might be repeated until the side chain contained only one carbon atom. There can be little doubt that a monoalkyl derivative, where the alkyl group is other than the methyl group, is less stable than the polymethyl derivative and that the differences between the free energies of the isomers will be small. This reaction is distinctly the shifting of the carbon atoms in the side chain and is brought about by aluminum chloride. It is another illustra-

TABLE 14

Experimental data for hydrocarbons with eight or more carbon atoms

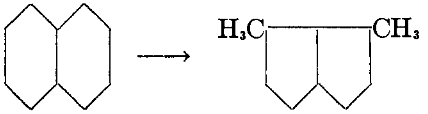
SUBSTANCES	TEMPERATURE	TIME	CATALYSTS	PRODUCTS	REFERENCES
	°C.	*hours*			
n-Octane	405–410	3	$AlCl_3$(a)	Isomers (23%)	(98)
n-Octane	360	3	MoS_3(a)	No change	(98)
n-Octane	440	3	MoS_3(a)	Isomers (23.6%)	(98)
n-Octane	410	3	$ZnCl_2$(a)	Isomers (13.3%)	(98)
2,6-Dimethyloctene-7	200		Pd + CO_2	2,6-Dimethyloctene-6	(140)
o- or *p*-Dimethylcyclohexane	115–120	7	$AlCl_3$	*m*-Dimethylcyclohexane	(37)
Methyl- or dimethylcyclohexane	120–130		$AlCl_3$; $ZnCl_2$	No change	(148)
Ethylcyclohexane	115–120	8	$AlCl_3$	*m*-Dimethylcyclohexane	(37)
cis (*o*- or *p*-)-Dimethylcyclohexane	170–175		$AlCl_3$	*trans* (*o*- or *p*-)-Dimethylcyclohexane	(78)
trans (*o*- or *p*-)-Dimethylcyclohexane	170–175		As + Os	Tetramethylcyclohexane; butane; polymers	(78)
m-Dimethylcyclohexane	120–130	4	Ni + H_2	No *cis*-form	(37)
n-Propylcyclohexane	135–145	7.5	$AlCl_3$	Trimethylcyclohexane; propane	(37)
Isopropylcyclohexane	130–145	7	$AlCl_3$	Trimethylcyclohexane; propane	(37)
n-, *sec*-, *tert*-Butylcyclohexane	150–160	8	$AlCl_3$	Tetramethylcyclohexane; butane	(37)
Amylcyclohexane	130–155	7	$AlCl_3$	Isoamyl-, methyl-, and tetramethylcyclohexane; butane	(37)
Isoamylcyclohexane	130–140	5	$AlCl_3$	Methyl-, pentamethyl-, and tetramethylcyclohexane; *n*-butane and isobutane	(37)
cis-Hydrindan	100	12	$AlCl_3$	*trans*-Hydrindan	(145)
cis-Decalin	Room	22	$AlCl_3$	*trans*-Decalin (only)	(147)
cis-Decalin	100	12	$AlCl_3$	*trans*-Decalin; other products	(147)
cis-Decalin	175–210		$AlCl_3$	Dimethylbicyclo[0.3.3]octane	(150)

trans-Decalin	290–340	10–12	HI	Dimethylbicyclo[0.3.3]octane or 2-methylbicyclo[0.3.4]nonane	(144)
trans-Decalin	130	24	$AlBr_3$	Dimethylbicyclo[0.3.3]octane	(63)
cis-Bicyclo[0.3.3]octane	Room	48	$AlCl_3$	Bicyclo[1.2.3]octane	(5)
cis-Decalin	100	12	$AlBr_3$	*trans*-Decalin (best)	(144)
trans-Bicyclo[0.3.3]octane	200		$Pt + H_2$	No change	(147)
Cycloöctane	300	Short time	Pt	Methylcycloheptane; bicyclo[0.3.3]-octane (probably)	(138)
Stilbene	Room	192	Ultraviolet light	Isostilbene	(117)
Isostilbene	170–180	1	$CS_2 + Br_2$ (trace)	Stilbene	(117)
Isostilbene		Few minutes	HNO_3 vapor	Stilbene	(117)
Stilbene	320–341			Isostilbene (6–8%) (kinetic study)	(70)
Isostilbene	320–341			Stilbene (82–83%)	(70)
4-Phenyl-1-butene	550	15 sec.		4-Phenyl-2-butene; 1-phenyl-1-butene	(49)

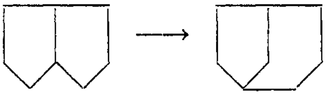
(a) 70 atm.

tion in which aluminum chloride acts as a carbon–carbon isomerization catalyst.

Three bicyclic compounds are known to show isomerization reactions. These are the *cis* to *trans* isomerization of decalin and hydrindan, of decalin to dimethylbicyclo[0.3.3]octane and bicyclo[0.3.3]octane to bicyclo[1.2.3]octane. The latter two are given below. For the isomerization of decalin, the data of Zelinsky and Turowa-Podlak shown in table 14 are sufficiently complete to show the various steps in the activation energies. Thus, with aluminum chloride at room temperature, *trans*-decalin alone is formed; at 100°C. other products appeared with the *trans*-decalin; and at 175–210°C., dimethylbicyclo[0.3.3]octane was formed accompanied by decomposition. This same bicycloöctane was obtained at a somewhat higher temperature, 290–340°C., with hydrogen iodide as the catalyst. Aluminum bromide gave the best conversion of *cis*- to *trans*-decalin at 100°C. Jones and Linstead (63) obtained dimethylbicyclo[0.3.3]octane at 130°C. with aluminum bromide and a long contact time. While *cis*-decalin and *cis*-hydrindan isomerized into the *trans*-form, the *cis–trans* conversion of bicyclo[0.3.3]octane did not occur; instead there was a more deep-seated change to a five- and six-membered bicyclic compound, according to Barrett and Linstead (5). Thus with two six-membered rings, or with one six- and one five-membered ring, the *cis–trans* conversion occurred, but it did not occur with two five-membered rings. Zelinsky and Freeman (138) found also that cycloöctane isomerized and was dehydrogenated with platinum at 300°C.



Decalin Dimethylbicyclo-[0.3.3]octane

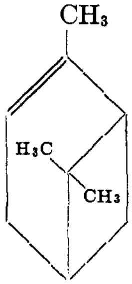


Bicyclo[0.3.3]-octane Bicyclo[1.2.3]-octane

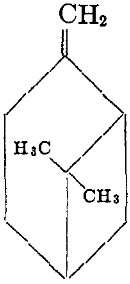
Stilbene–isostilbene thermal isomerization gave an equilibrium of 83 to 94 per cent stilbene depending on the direction of approach, according to Kistiakowsky and Smith (70), who made a kinetic study of the reaction. This is of interest in that it involves rotation around the double bond and is closely related to the *cis*- and *trans*-butenes. Assuming the entropy change for the reaction was equal to zero, the calculated ΔH^0_{320} was 3000 cal. and the velocity constant $6 \times 10^{12}e^{-42,800/RT}$. The kinetic data showed inconsistencies for the *cis*- and *trans*-butenes, so that a comparison of this velocity constant of $e^{-18,000/RT}$ with the above constant is not warranted.

Pinene and its isomers

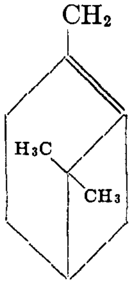
Pinene with a four-carbon atom ring and a six-carbon atom ring in its structure provides for the formation of a number of isomers where the four-carbon atom ring may be broken or a double bond shifted between the side chain and the six-carbon atom ring. These isomers are shown structurally below. There is some confusion in the literature as to the structure of isopinene; hence two forms are given here. Besides the structural isomers, these isomers often contain an asymmetrical carbon atom, so that optical isomers are formed. Of the structural isomers



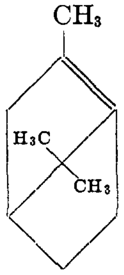
α-Pinene



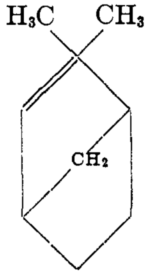
β-Pinene



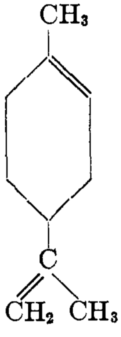
Isopinene
A



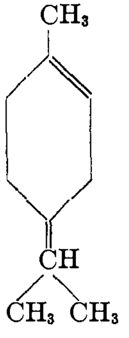
Isopinene
B



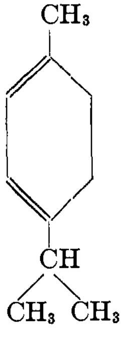
Camphene



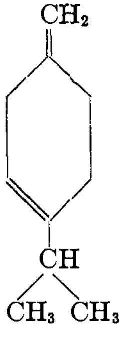
Dipentene
Limonene



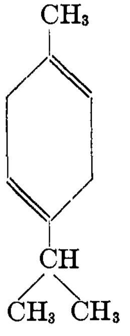
Terpinolene



α-Terpinene



β-Terpinene



γ-Terpinene

TABLE 15

Experimental data for pinene and its isomers

SUBSTANCE	TEMPERATURE	TIME	CATALYSTS	PRODUCTS	REFERENCES
	°*C.*				
Pinene	250–270	Several days		Dipentene; polymers	(130)
Pinene	400	1 day	H_2SO_4	Isomers	(130)
β-Pinene	Room	6 hrs.	Pd(H_2)	α-Pinene	(102)
α-Pinene	Room	1 hr.	Pd(H_2)	Isopinene	(137)
β-Pinene	145–160	30 hrs.	Trichlorophenol	α-Pinene; bornyl ethers	(4)
β-Pinene	150–170	6 hrs.	Pd(H_2)	α-Pinene	(4)
β-Pinene	145		Benzoic acid	Pinene; terpinene; limonene; bornyl ethers	(4)
β-Pinene	160	12–20 hrs.	Salicylic acid	Terpenes larger than with benzoic acid	(4)
β-Pinene	175–180	20 hrs.	Abietic acid	α-Pinene (97.6%)	(4)
d-Pinene	217–237	10–4 hrs.		*dl*-Pinene (believed); dipentene (actually)	(114)
d-Pinene	200	18 hrs.		Dipentene (19–34%)	(14)
Pinene	300	Short	Active carbon + steam	Camphene	(33)
Pinene	200		Active carbon + steam	Dipentene	(33)
α-Pinene	−20–158	4 hrs.	Fuller's earth	Terpinene; dipentene	(129)
Pinene	−20–room		Fuller's earth	Camphene	(39)
α-Pinene	145–150	1.5 hrs.	Activated charcoal	Limonene, dipentene, terpinene (75%); camphene (25%)	(84)
Pinene	200–300	13 hrs.	Al_2O_3	Camphene (traces); terpinene; dipentene; limonene	(86)
α-Pinene	300	Short	Cu chromite	Terpenes (30%)	(1)
α-Pinene	375	Short	Cu chromite	Terpenes (31%); dipentene (42%); allocimene in terpenes	(1)
d-Pinene	380–425	2.75–3.5 hrs.	ThO + pumice	Dipentene (55–65%); camphene	(13)
d-Pinene	65–70		H_2SO_4; H_3PO_4	Terpinolene	(13)
α-Pinene	22–37		H_2SO_4; CH_3COOH	Terpenes	(1)
Pinene	50	24 hrs.	H_3PO_4; H_2SO_4	Camphene; limonene; terpinene; *p*-cymene; 1,4-cineole	(18)
α-Pinene	250	20 hrs.	HgCl + I + Al	Terpinolene	(34)

α-pinene, isopinene, and β-pinene bear the simplest relation, for here a hydrogen atom shifts from a side chain to the six-carbon atom ring, while the four-carbon atom ring remains unchanged. Structure A is assumed for isopinene. As seen in table 15, these changes occur with palladium saturated with hydrogen (102, 137); at a higher temperature, 145–170°C., with trichlorophenol, benzoic acid, or salicylic acid (4); or at a slightly higher temperature, 175–180°C., with abietic acid when almost a complete change from α- to β-pinene occurred (4).

Dipentene was the preferred isomer when experimental conditions which break the four-carbon atom ring were used. The "preferred" isomer may mean the isomer recorded more frequently, for the separation and the identification of the isomeric terpenes is a difficult problem. Du Pont (18) has obtained the most information on these isomers with the use of Raman spectra, and has identified the terpene isomers shown above (p. 157).

For the thermal reaction at 200–237°C., Conant and Carlson (14) obtained dipentene and polymers from *d*-pinene. Smith (114) studied the kinetics of this reaction and thought he had obtained *dl*-pinene, but, as shown by Conant and Carlson, he had in reality obtained dipentene. Kassel (65) has made a correction in the kinetic data of Smith. Arbutzov (1) believed that he obtained the chain isomer, allocimene, but Charlton and Day (13) could find no evidence to support this transformation. In general, high temperatures, 200–400°C., are used with metals, metallic oxides, or mixtures of metallic oxides, while low temperatures, 50–70°C., are sufficient for acid catalysts. It should be pointed out that the acid catalysts in the latter case are either dilute inorganic acids or inorganic acids plus acetic acid or alcohol, while in the former case for the simpler isomerization, large organic acid molecules are catalysts. Of the inorganic acids Charlton and Day (13) found that phosphoric acid was much less effective than sulfuric acid; Austerweil (4) found that the temperature of reaction varied with the strength of the organic acid and that for very long contact times, twelve to twenty hours, the organic acid catalysts also produced a small amount of terpene isomers. Venable (129) found that silica gel, iron gel, and activated charcoal did not bring about the change of pinene to dipentene and terpinene, while fuller's earth did. Gallas and Montanes (33a) claimed that pinene gave dipentene but not camphene at 150–200°C. with silex, activated carbon, kieselguhr, or magnesium oxide.

Pinene and its isomers are a group of isomers that will probably have small differences in their energy values; yet the isomerization reactions among the isomers are real, as is the selective influence which is possible with certain experimental conditions.

The acetylenes and diolefins

The alkyl and aryl acetylenes and diolefin molecules are highly unsaturated molecules, and therefore are characterized by the hydrogen atoms shifting readily within the molecule without appreciable decomposition taking place. The free energy of acetylene is approximately 50,640 cal., as compared with 15,280 cal. for ethylene. There are no thermodynamic data for the substituted acetylenes, but there are some for the substituted ethylenes. Thus, the values for the free energy of butene-1 and of heptene-1 are 16,780 and 19,050 cal. These data indicate that the free energy of the straight-chain olefins varies only slightly, but the variation is toward an increase in the free energy with an increase in the length of the chain. The shifting of the double bond from the α- to the β-position lowers the free energy, as shown by butene-2. The branching of the chain also lowers the free energy, as shown by isobutene and 2,4,4-trimethylpentene. From this it may be inferred that the substituted acetylenes would give similar variations, although possibly of greater magnitude. Accordingly, a shift from the alkyl acetylene-1 to the alkyl acetylene-2 would be predicted. Perhaps the unexpected is the ease of the reversibility of this change. The diolefins with adjacent double bonds have not been investigated thermodynamically. Kistiakowsky and coworkers (69) have shown from the heats of hydrogenation that adjacent double bonds exert an unstabilizing effect upon one another. There have been numerous experimental studies on the isomerization of the acetylenes and diolefins. These are given in tables 16 and 17.

Rearrangements take place among the alkyl acetylene-1, the alkyl acetylene-2, and the diolefin where the diolefin is usually considered the form intermediate between the acetylenes. In his early work Favorsky (27) concluded that the preferred structure depended on the nature of the alkyl group adjacent to the unsaturated bond. Thus, for the primary group, the acetylene form resulted, in which case there was assumed an unstable intermediate diolefin form; for the secondary alkyl group, the diolefin resulted; and for the tertiary alkyl group, no reaction occurred. This was extended later (28) to include the diolefin as the only possible form for the tertiary alkyl group, the acetylene as the form from the primary alkyl group, and either the diolefin or the acetylene forms for the secondary alkyl group. Most workers have reported the isomeric substituted acetylenes as the product from the primary alkyl group. There has been some objection to this on the basis of incomplete identification of products. This may be true in some instances, but the experimental conditions probably are a larger factor in determining the form obtained. For the diolefin to form from the acetylene only one hydrogen atom need change its position; and it is reasonable to expect that this

TABLE 16

Experimental data for acetylenes

SUBSTANCE	TEMPERATURE	TIME	CATALYSTS	PRODUCTS	REFERENCES
	°*C.*	*hours*			
Butine-1	170	16	KOH	Butine-2 (100%)	(27, 28)
Pentine-1	170	20	KOH	Pentine-2	(27, 28)
Pentine-2	100	4-5	Na	Pentine-1	(27, 28)
Hexine-2	100-160		Na	Hexine-1	(27, 28)
Isopropylene	170	6	KOH	Dimethylallene	(27, 28)
tert-Butylacetylene	170-200	8-16	KOH	No action	(27, 28)
Butine-1	170	18-20	KOH	Butine-2 (<100%)	(133)
Octine-2	160	2	$NaNH_2$	Octine-1 (80%)	(7)
Octine-3	170	9	$NaNH_2$	Octine-1 (55%)	(7)
Nonine-2	160	2	$NaNH_2$	Nonine-1 (80%)	(7)
Cyclohexylacetylene	140	10	KOH	Cyclohexeneëthylene	(22)
Cyclohexylbutine-2	160	3	$NaNH_2$	Cyclohexylbutine-1 (80%)	(7)
Cyclohexylpentine-2	160	10	$NaNH_2$	Cyclohexylpentine-1 (80%)	(7)
Cyclohexylhexine-2	160	10	$NaNH_2$	Cyclohexylhexine-1 (80%)	(7)
Phenylpropine-2	110	2	$NaNH_2$	Phenylpropine-1 (75%)	(7)
Heptine-1	360-420		Fe tube + soda lime	Heptine-2	(44)
Heptine-1	380		Fe tube + soda lime	Heptine-2 (70%)	(38)
Heptine-1	350		Fe tube + pumice	Heptine-2 (32%)	(38)

TABLE 17

Experimental data on diolefins

SUBSTANCE	TEMPERATURE	TIME	CATALYSTS	PRODUCTS	REFERENCES
	°C.				
Dimethylallene	100	3-4 hrs.	Na	Isopropylacetylene	(27, 28)
Dimethylallene	215-280		Floridin	Isoprene (20%); isopropylacetylene (small)	(112)
Dimethylallene	334		Floridin	Isoprene (20%); isopropylacetylene (60%)	(112)
Methylallene	205-330		Floridin	Bivinyl (20.6%); ethylacetylene (3.4-3.9%)	(113)
Allene	500	86 sec.		Methylacetylene (2%); allene polymers (large)	(82)
Methylallene	400-550	13-20 sec.		Acetylenes (1%)	(52)
Dimethylallene	130-135		Quinoline hydroiodide	Isoprene; isopropylacetylene (small)	(73)
Cyclohexeneëthylene	100		Na	Cyclohexylethylene; cyclohexylacetylene	(22)
Cyclohexeneëthylene	170	10 hrs.	Benzoic acid	1-Vinylcyclohexene-1	(22)
Diallyl	325		Floridin	Diprenpyl; polymers	(77)
Diisobutylene	205		Floridin	Diisoprenpyl; polymers	(77)
Geraniolene	100	4 hrs.	H_2SO_4	α- and β-cyclogeraniolene	(124)

would occur in short contact time thermal reactions, as the work of Hurd and Meinert (52) has shown. On the other hand, for the substituted acetylene-1 to isomerize to the substituted acetylene-2 or the reverse, two hydrogen atoms must shift. This should require more vigorous experimental conditions, such as the presence of a catalyst. This is supported by a number of experiments. The diolefin would be anticipated as the preferred form when the hydrogen atoms are held more tightly by a ring structure, as in the cycloaliphatic compounds. An example of this isomerization is found in the work of Egorova (22) on the conversion of cyclohexylacetylene to cyclohexylidene ethylene.

The work of Marvel and coworkers on the acetylenic ethanes (16, 41, 43, 108, 116, 120) has shown that these rearrange readily into isomeric compounds without catalysts. Although the structure of these rearranged isomeric compounds has not been proven definitely, evidence supports the diolefin structure. Recently, Sparks and Marvel (115) have shown that this rearrangement to diolefins is not limited to hydrocarbons, but occurs readily with the acetylenic halides and carbinols. Zeberg (136) has shown that phenylallene rearranges at once, as methylphenylacetylene was obtained from 1,2-dichloro-3-phenylpropane.

As catalysts for these reactions, sodium, sodium or potassium hydroxide, sodium or potassium ethylate, and sodamide have been used most extensively for the liquid phase. This has led to the popular explanation of intermediate compound formation as a mechanism for the reaction. Hill (44) and Guest (38) extended the work to the vapor phase and found the isomerization occurred readily. Guest attributed Favorsky's failure to obtain a reaction in the vapor phase to the low temperature which he used. Hurd and Meinert (52) obtained rearrangements with the thermal reactions. Besides, such substances as floridin, pumice, benzoic acid, and quinoline hydrobromide are effective catalysts. The only explanation which is inclusive of all these facts is the activated dissociation into fragments under the influence of the catalyst. Again it might be added that the life of these fragments may be extremely short. The process may be likened to a gradual increase in the amplitude of vibration of the atom until its approach to the neighboring atom is so close that it becomes attached to the new atom and does not return to the original atom. From this it follows that intermediate compound formation is not a requisite in the mechanism, but only a side reaction. Sodium salts can be formed and these decomposed to give the isomer, as in the work of Stampfli and Marvel (116), but undoubtedly the actual formation and the extent of the formation of the intermediate compound depend largely on experimental conditions.

It is noteworthy that in all this work the sodium and sodium compounds cause only the shift of the hydrogen atom and not the shift of the carbon atoms. In line with the preceding evidence, these catalysts appear to be carbon–hydrogen isomerization catalysts when there is a point of unsaturation in the molecule.

SUMMARY

The recent thermodynamic data for the isomeric hydrocarbons and the experimental data on the isomerization reactions lend support to small, distinct variations in the free energy of the various isomers for each type of hydrocarbon. The early values for the heat of combustion are not sufficiently accurate to show these small variations. Moreover, it is probable that a small error is introduced into some values for the entropy by extrapolation from 90° to 0°K. in the determination of the heat capacity.

For the various types of hydrocarbons with five or more carbon atoms, the order of increasing thermodynamic stability at 298°K. is olefins, cycloparaffins, and paraffins.

The catalytic data offer several examples of definite activating energies for the various isomerization reactions. These activating energies are dependent on the catalyst used. This suggests that the action for any catalyst may be explained by the concept of activating energies with dissociation of the hydrocarbon into fragments under the influence of the catalyst.

The majority of the isomerization reactions which have been investigated involve the shifting of the hydrogen atom. Few catalysts are known that effect the shifting of the carbon atoms. This is usually a more profound change in the structure. Certain catalysts appear to cause consistently the shifting of a hydrogen atom or a carbon atom. These have been termed carbon–hydrogen and carbon–carbon isomerization catalysts.

The data are too meagre to give the order of stability for any one type of hydrocarbon, but they do indicate that for the olefins at 298°K. the stability is increased for the shifting of the double bond toward the center of the molecule and for a simple branching of the chain. A highly branched chain may cause great instability.

REFERENCES

(1) ARBUTZOV: Ber. **67B**, 563, 569 (1934).
(2) ASCHÂN: Ann. **324**, 12 (1902).
(3) ASTON AND MESSERLY: J. Am. Chem. Soc. **58**, 2354 (1936).
(4) AUSTERWEIL: Bull. soc. chim. [4] **39**, 695 (1926).
(5) BARRETT AND LINSTEAD: J. Chem. Soc. **1936**, 611.
(6) BERTHELOT: Ann. chim. phys. [7] **20**, 27 (1900).
(7) BOURGUEL: Ann. chim. [10] **3**, 191, 325 (1925).
(8) BOURGUEL AND PIAUX: Bull. soc. chim. **51**, 1051 (1932).

(9) Calingaert and Beatty: J. Am. Chem. Soc. **58**, 51 (1936).
(10) Calingaert and Flood: J. Am. Chem. Soc. **57**, 956 (1935); **58**, 53 (1936).
(11) Carr: J. Am. Chem. Soc. **51**, 3041 (1929).
(12) Chambers and Kistiakowsky: J. Am. Chem. Soc. **56**, 399 (1935).
(13) Charlton and Day: Ind. Eng. Chem. **29**, 92 (1937).
(14) Conant and Carlson: J. Am. Chem. Soc. **51**, 3464 (1929).
(15) Cox: Bull. soc. chim. [4] **37**, 1549 (1925).
(16) Davis and Marvel: J. Am. Chem. Soc. **53**, 3840 (1931).
(17) Dojarenko: Ber. **59**, 2933 (1936).
(18) Du Pont: Bull. soc. chim. [4] **51**, 1579 (1932).
(19) Egloff and Parrish: Chem. Rev. **19**, 145 (1936).
(20) Egloff and Wilson: Ind. Eng. Chem. **27**, 917 (1935).
(21) Egloff and Wilson: Chem. Rev. **20**, 345 (1937).
(22) Egorova: J. Russ. Phys. Chem. Soc. **43**, 1116 (1911).
(23) Eidinoff and Ashton: J. Chem. Physics **3**, 379 (1935).
(24) Engler and Rogowski: In Engler's Neuen Ansichten über die Enstehung des Erdöls, p. 24 (1909).
(25) Eyring: J. Chem. Physics **3**, 107 (1935).
(26) Farkas, Farkas, and Rideal: Proc. Roy. Soc. (London) **A146**, 630 (1934).
(27) Favorsky: J. prakt. Chem. [2] **37**, 328, 417 (1888).
(28) Favorsky: J. Russ. Phys. Chem. Soc. **52**, 507 (1920).
(29) Favorsky and Borgmann: Ber. **40**, 4863 (1907).
(30) Filipov: Bau der Kohlenwasserstoffe von Gustavson gewonnen aus Pentaerythrit, p. 68 (1914).
(31) Filipov: J. Russ. Phys. Chem. Soc. **46**, 1141-99 (1914).
(32) Frey and Huppke: Ind. Eng. Chem. **25**, 441 (1933).
(33) Fujita: J. Chem. Soc. Japan **55**, 1 (1934).
(33a) Gallas and Montanes: Anales soc. españ. fís. quím. **28**, 1163 (1930); Chem. Abstracts **25**, 504 (1931).
(34) Gaponenkov: J. Gen. Chem. (U. S. S. R.) **4**, 1128 (1934).
(35) Gillet: Bull. soc. chim. Belg. **30**, 138 (1921).
(36) Glasebrook, Phillips, and Lovell: J. Am. Chem. Soc. **58**, 1944 (1936).
(37) Grignard and Stratford: Compt. rend. **178**, 2149; Bull. soc. chim. [4] **35**, 931 (1934).
(38) Guest: J. Am. Chem. Soc. **50**, 1744 (1928).
(39) Gurvich: J. Russ. Phys. Chem. Soc. **47**, 827 (1915).
(40) Gustavson: See reference 17.
(41) Halley and Marvel: J. Am. Chem. Soc. **54**, 4450 (1932).
(42) Harkness: J. Am. Chem. Soc. **58**, 1058 (1936).
(43) Harmon and Marvel: J. Am. Chem. Soc. **55**, 1716 (1933).
(44) Hill and Tyson: J. Am. Chem. Soc. **50**, 172 (1928).
(45) Horiuti and Polanyi: Trans. Faraday Soc. **30**, 1164 (1934).
(46) Horiuti, Ogden, and Polanyi: Trans. Faraday Soc. **30**, 663 (1934).
(47) Howard and Taylor: J. Am. Chem. Soc. **56**, 2259 (1934).
(48) Huffman, Parks, and Barmore: J. Am. Chem. Soc. **53**, 3876 (1931).
(49) Hurd: Ind. Eng. Chem. **26**, 51 (1934).
(50) Hurd and Goldsby: J. Am. Chem. Soc. **56**, 1812 (1934).
(51) Hurd, Goodyear, and Goldsby: J. Am. Chem. Soc. **58**, 235 (1936).
(52) Hurd and Meinert: J. Am. Chem. Soc. **53**, 289 (1931).
(53) Ipatieff: Ber. **35**, 1063 (1902).

(54) Ipatieff: Ber. **36**, 2004 (1903).
(55) Ipatieff and Dowgelwitsch: Ber. **44**, 2988 (1911).
(56) Ipatieff and Grosse: Ind. Eng. Chem. **28**, 46 (1936).
(57) Ipatieff and Huhn: Ber. **36**, 2014 (1903).
(58) Ipatieff and Komarewsky: J. Am. Chem. Soc. **57**, 1722 (1934).
(59) Ipatieff and Pines: Ind. Eng. Chem. **27**, 1364 (1935).
(60) Ipatieff, Pines, and Schaad: J. Am. Chem. Soc. **56**, 2696 (1934).
(61) Ipatieff and Tichotsky: J. Russ. Phys. Chem. Soc. **36**, 760 (1904).
(62) International Critical Tables: Vol. V. McGraw-Hill Book Co., New York (1929).
(63) Jones and Linstead: J. Chem. Soc. **1936**, 616.
(64) Kassel: J. Chem. Physics **4**, 276, 435 (1936).
(65) Kassel: J. Am. Chem. Soc. **52**, 1935 (1930).
(66) Kharasch: J. Research Natl. Bur. Standards **2**, 373 (1929).
(67) Kharasch: Chem. Rev. **5**, 571 (1928).
(68) Kistiakowsky, Ruhoff, Smith, and Vaughan: J. Am. Chem. Soc. **57**, 876, (1935).
(69) Kistiakowsky, Ruhoff, Smith, and Vaughan: J. Am. Chem. Soc. **58**, 137, 146 (1936).
(70) Kistiakowsky and Smith: J. Am. Chem. Soc. **56**, 638 (1934).
(71) Kistiakowsky and Smith: J. Am. Chem. Soc. **58**, 766 (1936).
(72) Kistiakowsky and Smith: J. Am. Chem. Soc. **58**, 2428 (1936).
(73) Kucherov: J. Russ. Phys. Chem. Soc. **45**, 1634 (1914).
(74) Lauer and Stodola: J. Am. Chem. Soc. **56**, 1215 (1934).
(75) Laughlin, Nash and Whitmore: J. Am. Chem. Soc. **56**, 1395 (1934).
(76) Lazier and Vaughan: J. Am. Chem. Soc. **54**, 3080 (1932).
(77) Lebedev and Slobodin: J. Gen. Chem. (U. S. S. R.) **4**, 23 (1934).
(78) Margolis: Ber. **69B**, 1710 (1936).
(79) Markownikow: J. Russ. Phys. Chem. Soc. **35**, 1049 (1903).
(80) Matignon, Moureu, and Dole: Compt. rend. **196**, 973, 1560 (1933).
(81) Matignon, Moureu, and Dole: Bull. soc. chim. [5] **2**, 1169 (1934).
(82) Meinert and Hurd: J. Am. Chem. Soc. **52**, 4540 (1930).
(83) Merzhkooskii: J. Russ. Phys. Chem. Soc. **45**, 2072 (1913).
(84) Mochida: J. Pharm. Soc. Japan **53**, 936 (1933).
(85) Morikawa, Benedict, and Taylor: J. Am. Chem. Soc. **58**, 1445, 1795 (1936).
(86) Mulcey: Bull. inst. pin **177**, 201 (1931); Chem. Abstracts **26**, 718 (1932).
(87) Munro and Marvel: J. Am. Chem. Soc. **54**, 4445 (1932).
(88) Nasarow: Ber. **69B**, 21 (1936).
(88a) Nasarow: Ber. **70B**, 606, 617 (1937).
(89) Nenitzescu and Cantuniari: Ber. **66B**, 1097 (1933).
(90) Nenitzescu and Dragen: Ber. **66B**, 1892 (1933).
(91) Norris and Reuter: J. Am. Chem. Soc. **49**, 2626 (1927).
(92) Parks: Chem. Rev. **18**, 315 (1936).
(93) Parks and Huffman: The Free Energies of Some Organic Compounds. The Chemical Catalog Co., Inc., New York (1932).
(94) Parks and Huffman: J. Am. Chem. Soc. **52**, 4387 (1930).
(95) Parks, Huffman, and Barmore: J. Am. Chem. Soc. **53**, 3876 (1931).
(96) Parks, Huffman, and Thomas: J. Am. Chem. Soc. **52**, 1032, 3241 (1930).
(96a) Parks, Shomate, Kennedy, and Crawford: J. Chem. Physics **5**, 359 (1937).
(97) Parks, Todd and Shomate: J. Am. Chem. Soc. **58**, 2507 (1936).
(98) Petrow, Meschitcherjakow, and Andrewjew: Ber. **68B**, 1 (1935).
(99) Pines: J. Am. Chem. Soc. **55**, 3892 (1933).

(100) RICE AND GERSHINOWITZ: J. Chem. Physics **2**, 857 (1934).
(101) RICE AND GERSHINOWITZ: J. Chem. Physics **3**, 479 (1935).
(102) RICHTER AND WOLFF: Ber. **59B**, 1733 (1926).
(103) ROSSINI: J. Research Natl. Bur. Standards **13**, 21 (1934).
(104) ROSSINI: J. Chem. Physics **3**, 438 (1935).
(105) ROZANOV: J. Russ. Phys. Chem. Soc. **48**, 168 (1916).
(106) ROZANOV: J. Russ. Phys. Chem. Soc. **61**, 2291 (1929).
(107) RUNGE AND MUELLER-CUNRADI: U. S. patent 1,914, 674
(108) SALZBERG AND MARVEL: J. Am. Chem. Soc. **50**, 1743 (1931).
(108a) SHERRILL: Private communication.
(109) SHERRILL, BALDWIN, AND HAAS: J. Am. Chem. Soc. **51**, 3034 (1929).
(110) SHERRILL, OTT, AND PICKETT: J. Am. Chem. Soc. **51**, 3023 (1929).
(111) SHERRILL AND WALTER: J. Am. Chem. Soc. **58**, 742 (1936).
(112) SLOBODIN: J. Gen. Chem. (U. S. S. R.) **4**, 778 (1934).
(113) SLOBODIN: J. Gen. Chem. (U. S. S. R.) **5**, 48 (1935).
(114) SMITH: J. Am. Chem. Soc. **49**, 47 (1927).
(115) SPARKS AND MARVEL: J. Am. Chem. Soc. **58**, 742 (1936).
(116) STAMPFLI AND MARVEL: J. Am. Chem. Soc. **53**, 4057 (1931).
(117) STOERMER: Ber. **42**, 4865 (1909).
(118) TANTAR: Ber. **29**, 1297 (1896).
(119) TANTAR: Z. physik. Chem. **41**, 735 (1902).
(120) TASO AND MARVEL: J. Am. Chem. Soc. **55**, 4712 (1933).
(121) TAYLOR: J. Am. Chem. Soc. **53**, 578 (1931).
(122) THOMPSON AND SHERRILL: J. Am. Chem. Soc. **58**, 745 (1936).
(123) THOMSON: Z. physik. Chem. **52**, 543 (1906).
(124) TIEMANN AND SEMMLER: Ber. **26**, 2708 (1893).
(125) TODD AND PARKS: J. Am. Chem. Soc. **58**, 134 (1936).
(126) TRAUTZ AND WINKLER: J. prakt. chem. [2] **104**, 54 (1922).
(127) TROPSCH, PARRISH, AND EGLOFF: Ind. Eng. Chem. **28**, 581 (1936).
(128) TURKEWICH AND TAYLOR: J. Am. Chem. Soc. **56**, 2254 (1934).
(129) VENABLE: J. Am. Chem. Soc. **45**, 728 (1923).
(130) WALLACH: Ann. **227**, 282 (1885).
(131) WHITMORE AND STAHLY: J. Am. Chem. Soc. **55**, 4153 (1933).
(132) WHITMORE AND MEUNIER: J. Am. Chem. Soc. **56**, 3721 (1934).
(133) WISLICENUS AND SCHMIDT: Ann. **315**, 220 (1900).
(134) YOUNG AND WINSTEIN: J. Am. Chem. Soc. **58**, 102, 104 (1936).
(135) YOUNG, WINSTEIN, AND PRATER: J. Am. Chem. Soc. **58**, 289 (1936).
(136) ZEBERG: J. Gen. Chem. (U. S. S. R.) **5**, 1016 (1935).
(137) ZELINSKY: Ber. **44**, 2783 (1911).
(138) ZELINSKY AND FREMAN: Ber. **63B**, 1485 (1930).
(139) ZELINSKY AND GUTT: J. Russ. Phys. Chem. Soc. **38**, 1289 (1906).
(140) ZELINSKY AND LEVINA: Ber. **62B**, 1861 (1929).
(141) ZELINSKY AND LEVINA: Ber. **68B**, 1784 (1935).
(142) ZELINSKY AND STSCHERBAK: J. Russ. Phys. Chem. Soc. **45**, 379 (1913).
(143) ZELINSKY AND TUROWA-POLLAK: Ber. **57B**, 2063 (1924).
(144) ZELINSKY AND TUROWA-POLLAK: Ber. **58B**, 1292 (1925).
(145) ZELINSKY AND TUROWA-POLLAK: Ber. **62B**, 1658 (1929).
(146) ZELINSKY AND TUROWA-POLLAK: Ber. **65B**, 1171 (1932).
(147) ZELINSKY AND TUROWA-POLLAK: Ber. **65B**, 1299 (1932).
(148) ZELINSKY AND TUROWA-POLLAK: Ber. **68B**, 1781 (1935).
(149) ZELINSKY AND TUROWA-POLLAK: J. Gen. Chem. (U. S. S. R.) **2**, 660 (1932).
(150) ZELINSKY AND TUROWA-POLLAK: J. Applied Chem. (U. S. S. R.) **7**, 753 (1934).