Hydrocarbon Conversion with Special Reference to the Thermodynamical Calculations for the Isomerization Reactions. II.

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Introduction. In the previous paper⁽¹⁾, we have called attention to the fact that the vital importance of the study of hydrocarbon conversion, especially of isomerization, alkylation and aromatization processes etc., must be borne in mind in the field of liquid fuel synthesis; furthermore the vital significance of the investigation of the isomerization reaction not only from the industrial point of view but also from the view of theoretical research should be realized due to the fact that the isomerization reaction which may be utilized for the study of intramolecular rearrangement occurring for the variable factors which influence the reaction can easily be reduced to the minimum.

This paper is a similar investigation to Part I of this series, and is concerned with the thermodynamical calculations and discussions for the unsaturated hydrocarbons with special reference to the isomerization reactions. The procedure of the calculation is similar to the first report. We have derived simple free energy equations as a function of temperature for some eighty isomerization reactions of unsaturated hydrocarbons (C_4–C_8) and calculated ΔF's at 0°, 25°, 100°, 200° and 300°C. Table 1 shows the free energy equations as a function of temperature, and compiles ΔF's as calculated by our derived equations.

Discussion of the Results. As we have already stated in the previous paper⁽¹⁾, the magnitude of ΔF's of isomerization reactions is small as compared with those of ordinary chemical reactions. This is also found true in the case of unsaturated hydrocarbons. It is also found that, the lower the temperature, thermodynamically the more favourable the reaction is. As observed in the table, the majority of the reactions as written is found to be thermodynamically favourable, in all the range from 0°–300°C, except a few, changing the sign of ΔF's at certain temperature. Some thirty reactions as written have been found to be positive ΔF, i.e. thermodynamically not favourable, as in the case of 2-methyl-2-butede=2-methyl-1-butene, i.e., the shift of the position of a double bond from 2 to 1. Similarly with 2-methyl-2-butene=3-methyl-1-butene and 2-methyl-1-butene=3-methyl-1-butene, involving the shift of the position of a methyl group from 2 to 3 position.

2-methyl-2-butene = 2-*trans*-pentene
2-methyl-2-butene = 2-*cis*-pentene
2-methyl-1-butene = 2-*trans*-pentene
2-methyl-1-butene = 2-*cis*-pentene

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(1) S. Hamai, this Bulletin, **18** (1943), 376.

As already mentioned, all of these reactions which show positive ΔF (0°–300°C.), are, with a few exceptions, the more favourable the higher the temperature. Besides these, those which change the sign of ΔF in this range also have been found to be the more favourable when the temperature is higher.

$$\text{3,3-dimethyl-1-butene} = \begin{cases} \text{3-methyl-1-pentene} \\ \text{4-methyl-1-pentene} \end{cases}$$

$$\text{3,3-dimethyl-1-butene} = \begin{cases} \text{3-}\textit{cis}\text{-hexene} \\ \text{2-}\textit{cis}\text{-hexene} \end{cases}$$

Those reactions which are favoured thermodynamically are some thirty-six reactions (0°–300C.°). However, even if the reactions are not thermodynamically possible, it should be remembered that this does not mean there are no reactions, but the thermodynamical possibility only indicates that the reactions proceed to "Conveniently Usable Extent" and no more. But in such a case it is safe to state that a search for the catalyst for such an unfavourable reaction is useless and meaningless. Examining these isomerization reactions closely, we may be able to classify them into, at least, four types, i.e., those which involve merely a double bond shift, as 2-methyl-2-butene=2-methyl-1-butene; those which involve the shift of methyl or ethyl radical as 2-methyl-1-butene=3-methyl-1-butene; those which involve both the double bond and the radical shift as 2-methyl-2-butene=3-methyl-1-butene; and those which involve the transformation or structural change of trans-cis-forms as 2-methyl-2-butene=2-*trans*-pentene. Furthermore, they may be classified into such changes as those in which the carbon-carbod bond, the carbon-hydrogen bond or both bonds are responsible for these isomerization reactions. As regards the effect of catalysts on the isomerization reactions, these will be referred to as carbon-carbon or carbon-hydrogen isomerization catalysts.

As already concluded in the case of the saturated hydrocarbons, the structure which is more complicated and branched seems to be thermodynamically favourable; and moreover those structures which have a double bond at the inner part rather than outer position seem to be thermodynamically favourable. These general trends are very fortunate for us, for these types of structure have been found to give a superior quality of liquid fuel as far as octane values are concerned⁽²⁾.

We have so far presented some correlations of the structure with respect to the thermodynamical possibility; however, it is not necessary to take up here every one of them, because they are self-obvious if we examine the table. Hence we shall not mention it any further. Lastly we shall also indicate that Rossini's conclusion that the isomeric form is thermodynamically more stable than the normal form is amply supported by our calculations.

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(2) *J. Inst. Petroleum Tech.*, April No. (1941); Yamamoto, *Petroleum Bulletin* (Japan), (1942) 327.

Table 1. Equations for Free Energies of Isomerization Reactions as a Function of Temperature and ΔF's at Various Temperature.

Reactions	Free Energy Equations $\Delta F^\circ = A+BT$		ΔF° cal./mol.				
	A	B	0°	25°	100°	200°	300°
1-Butene=2-*cis*-Butene	− 1771	+ 1.8	− 1279	− 1234	− 1099	− 919	− 739
1-Butene=2-*trans*-Butene	− 2721	+ 2.4	− 2066	− 2006	− 1826	− 1586	− 1346
1-Butene=Isobutene	− 3588	+ 4.0	− 2496	− 2396	− 2096	− 1696	− 1296
2-*cis*-Butene=2-*trans*-Butene	− 950	+ 0.6	− 786	− 771	− 726	− 666	− 606
2-*cis*-Butene=Isobutene	− 1817	+ 2.2	− 1216	− 1161	− 996	− 776	− 556
2-*trans*-Butene=Isobutene	− 867	+ 1.6	− 430	− 390	− 270	− 110	+ 50
1-Pentene=2-Methyl-2-butene	− 5351	+ 5.8	− 3767	− 3622	− 3187	− 2607	− 2027
1-Pentene=3-Methyl-1-butene	− 1934	+ 4.0	− 842	− 742	− 442	− 42	+ 358
1-Pentene=2-Methyl-1-butene	− 3780	+ 4.0	− 2688	− 2588	− 2288	− 1888	− 1488
1-Pentene=2-*trans*-Pentene	− 2708	+ 2.4	− 2053	− 1993	− 1813	− 1573	− 1333
1-Pentene=2-*cis*-Pentene	− 1761	+ 1.8	− 1269	− 1224	− 1089	− 909	− 729
2-Methyl-2-butene=3-Methyl-1-butene	3417	− 1.8	+ 2925	+ 2880	+ 2745	+ 2565	+ 2385
2-Methyl-2-butene=2-Methyl-1-butene	1571	− 1.8	+ 1079	+ 1034	+ 899	+ 719	+ 539
2-Methyl-1-butene=3-Methyl-1-butene	1846	+ 0.0	+ 1846	+ 1846	+ 1846	+ 1846	+ 1846
2-cis-Pentene=2-*trans*-Pentene	− 947	+ 0.6	− 783	− 768	− 723	− 663	− 603
2-Methyl-2-butene=2-*trans*-Pentene	2643	− 3.4	+ 1714	+ 1629	+ 1374	+ 1034	+ 694
2-Methyl-2-butene=2-*cis*-Pentene	3590	− 4.0	+ 2498	+ 2398	+ 2098	+ 1698	+ 1298
3-Methyl-1-butene=2-*trans*-Pentene	− 774	− 1.6	− 1211	− 1251	− 1371	− 1531	− 1691
3-Methyl-1-butene=2-*cis*-Pentene	173	− 2.2	− 428	− 483	− 648	− 868	− 1088
2-Methyl-1-butene=2-*trans*-Pentene	1072	− 1.6	+ 635	+ 595	+ 475	+ 315	+ 155
2-Methyl-1-butene=2-*cis*-Pentene	2019	− 2.2	+ 1418	+ 1363	+ 1198	+ 978	+ 758
1-Hexene=2,3-Dimethyl-2-butene	− 6930	+ 8.2	− 4691	− 4486	− 3871	− 3051	− 2231
1-Hexene=3,3-Dimethyl-2-butene	− 4340	+11.1	− 1309	− 1031	− 199	+ 911	+ 2021
1-Hexene=4-Methyl-2-*trans*-pentene	− 4340	+ 6.4	− 2592	− 2432	− 1952	− 1312	− 672
1-Hexene=2,3-Dimethyl-1-butene	− 6530	+ 8.0	− 4345	− 4145	− 3545	− 2745	− 1945
1-Hexene=2-Ethyl-1-butene 2-Methyl-1-pentene	− 3440	+ 4.0	− 2348	− 2248	− 1948	− 1548	− 1148

Table 1.—(*Continued*)

Reactions	Free Energy Equations $\Delta F° = A+BT$		$\Delta F°$ cal./mol.				
	A	*B*	0°	25°	100°	200°	300°
1-Hexene=4-Methyl-2-*cis*-pentene	− 3340	+ 5.8	− 1756	− 1611	− 1176	− 596	− 16
1-Hexene=2-Methyl-2-pentene							
3-Methyl-2-*cis*-pentene	− 5040	+ 5.8	− 3456	− 3311	− 2876	− 2296	− 1716
3-Methyl-2-*trans*-pentene							
1-Hexene=3-Methyl-1-pentene							
4-Methyl-1-pentene	− 1740	+ 4.0	− 648	− 548	− 248	+ 152	+ 552
1-Hexene=3-*trans*-Hexene							
2-*trans*-Hexene	− 2540	+ 2.4	− 1885	− 1825	− 1645	− 1405	− 1165
1-Hexene=3-*cis*-Hexene							
2-*cis*-Hexene	− 1540	+ 1.8	− 1048	− 1003	− 868	− 688	− 508
2,3-Dimethyl-2-butene=3,3-Dimethyl-1-butene	2600	+ 2.9	+ 3392	+ 3465	+ 3682	+ 3972	+ 4262
2,3-Dimethyl-2-butene=4-Methyl-2-*trans*-pentene	2600	− 1.8	+ 2108	+ 2063	+ 1928	+ 1748	+ 1568
2,3-Dimethyl-2-butene=2,3-Dimethyl-1-butene	1400	− 0.2	+ 1345	+ 1340	+ 1325	+ 1305	+ 1285
2,3-Dimethyl-2-butene=2-Ethyl-1-butene							
2-Methyl-1-pentene	3500	− 4.2	+ 2353	+ 2248	+ 1933	+ 1513	+ 1093
2,3-Dimethyl-2-butene=4-Methyl-2-*cis*-pentene	3600	− 2.4	+ 2945	+ 2885	+ 2705	+ 2465	+ 2225
2,3-Dimethyl-2-butene=2-Methyl-2-pentene							
3-Methyl-2-*cis*-pentene	1900	− 2.4	+ 1245	+ 1185	+ 1005	+ 765	+ 525
3-Methyl-2-*trans*-pentene							
2,3-Dimethyl-2-butene=3-Methyl-1-pentene							
4-Methyl-1-pentene	5200	− 4.2	+ 4053	+ 3948	+ 3633	+ 3213	+ 2793
2,3-Dimethyl-2-butene=3-*trans*-Hexene							
2-*trans*-Hexene	4400	− 5.8	+ 2816	+ 2671	+ 2236	+ 1656	+ 1076
2,3-Dimethyl-2-butene=3-*cis*-Hexene							
2-*cis*-Hexene	5400	− 6.4	+ 3652	+ 3492	+ 3012	+ 2372	+ 1732
3,3-Dimethyl-1-butene=4-Methyl-2-*trans*-pentene	0.0	− 4.7	− 1284	− 1401	− 1754	− 2224	− 2694
3,3-Dimethyl-1-butene=2,3-Dimethyl-1-butene	− 1200	− 3.1	− 2047	− 2124	− 2357	− 2667	− 2977

Table 1.—(*Continued*)

Reactions	Free Energy Equations $\Delta F^\circ = A+BT$ [illegible]		ΔF° cal./mol.				
	A	*B*	0°	25°	100°	200°	300°
3,3-Dimethyl-1-butene=2-Ethyl-1-butene 2-Methyl-1-pentene	900	− 6.1	− 766	− 918	− 1376	− 1986	− 2596
3,3-Dimethyl-1-butene=4-Methyl-2-*cis*-pentene	1000	− 5.3	− 447	− 580	− 977	− 1507	− 2037
3,3-Dimethyl-1-butene=2-Methyl-2-pentene 3-Methyl-2-*cis*-pentene 3-Methyl-2-*trans*-pentene	− 700	− 5.3	− 2147	− 2280	− 2677	− 3207	− 3737
3,3-Dimethyl-1-butene=3-Methyl-1-pentene 4-Methyl-1-pentene	2600	− 6.1	+ 934	+ 782	+ 324	− 286	− 896
3,3-Dimethyl-1-butene=3-*trans*-Hexene 2-*trans*-Hexene	1800	− 8.7	− 576	− 793	− 1446	− 2316	− 3186
3,3-Dimethyl-1-butene=3-*cis*-Hexene 2-*cis*-Hexene	2800	− 9.3	+ 260	+ 28	− 670	− 1600	− 2530
4-Methyl-2-*trans*-pentene=2,3-Dimethyl-1-butene	− 1200	+ 1.6	− 763	− 723	− 603	− 443	− 283
4-Methyl-2-*trans*-pentene=2-Ethyl-1-butene 2-Methyl-1-pentene	900	+ 2.6	+ 1610	+ 1675	+ 1870	+ 2130	+ 2390
4-Methyl-2-*trans*-pentene=4-Methyl-2-*cis*-pentene	1000	− 0.6	+ 836	+ 821	+ 776	+ 716	+ 656
4-Methyl-2-*trans*-pentene=2-Methyl-2-pentene 3-Methyl-2-*cis*-pentene 3-Methyl-2-*trans*-pentene	− 700	− 0.6	− 864	− 879	− 924	− 984	− 1044
4-Methyl-2-*trans*-pentene=3-Methyl-1-pentene 4-Methyl-1-pentene	2600	− 2.6	+ 1890	+ 1825	+ 1630	+ 1370	+ 1110
4-Methyl-2-*trans*-pentene=3-*trans*-Hexene 2-*trans*-Hexene	1800	− 4.0	+ 708	+ 608	+ 308	− 92	− 492
4-Methyl-2-*trans*-pentene=3-*cis*-Hexene 2-*cis*-Hexene	2800	− 4.6	+ 1544	+ 1429	+ 1084	+ 624	+ 164
2,3-Dimethyl-1-butene=2-Ethyl-1-butene 2-Methyl-1-pentene	2100	− 4.0	+ 1008	+ 908	+ 608	+ 208	− 192

Table 1.—(*Continued*)

Reactions	Free Energy Equations $\Delta F^\circ = A+BT$		ΔF° cal./mol.				
	A	*B*	0°	25°	100°	200°	300°
2,3-Dimethyl-1-butene=4-Methyl-2-*cis*-pentene	2200	− 2.2	+ 1599	+ 1544	+ 1379	+ 1159	+ 939
2,3-Dimethyl-1-butene=2-Methyl-2-pentene							
3-Methyl-2-*cis*-pentene	560	− 2.2	− 101	− 156	− 321	− 541	− 761
3-Methyl-2-*trans*-pentene							
2,3-Dimethyl-1-butene=3-Methyl-1-pentene							
4-Methyl-1-pentene	3800	− 4.0	+ 2708	+ 2608	+ 2308	+ 1908	+ 1508
2,3-Dimethyl-1-butene=3-*trans*-Hexene							
2-*trans*-Hexene	3000	− 5.6	+ 1471	+ 1331	+ 911	+ 351	− 209
2,3-Dimethyl-1-butene=3-*cis*-Hexene							
2-*cis*-Hexene	4000	− 6.2	+ 2307	+ 2152	+ 1687	+ 1067	+ 447
2-Ethyl-1-butene							
2-Methyl-1-pentene=4-Methyl-2-*cis*-pentene	100	+ 1.8	+ 592	+ 637	+ 772	+ 952	+ 1132
2-Ethyl-1-butene 2-Methyl-2-pentene							
2-Methyl-1-pentene=3-Methyl-2-*cis*-pentene	− 1600	+ 1.8	− 1108	− 1063	− 928	− 748	− 568
3-Methyl-2-*trans*-pentene							
2-Ethyl-1-butene							
2-Methyl-1-pentene=3-Methyl-1-pentene	1700	+ 0.0	+ 1700	+ 1700	+ 1700	+ 1700	+ 1700
4-Methyl-1-pentene							
2-Ethyl-1-butene =3-*trans*-Hexene							
2-Methyl-1-pentene 2-*trans*-Hexene	900	− 1.6	+ 463	+ 423	+ 303	+ 143	− 17
2-Ethyl-1-butene =3-*cis*-Hexene							
2-Methyl-1-pentene 2-*cis*-Hexene	1900	− 2.2	+ 1299	+ 1244	+ 1079	+ 859	+ 639
4-Methyl-2-*cis*-pentene=2-Methyl-2-pentene							
3-Methyl-2-*cis*-pentene	− 1700	+ 0.0	− 1700	− 1700	− 1700	− 1700	− 1700
3-Methyl-2-*trans*-pentene							
4-Methyl-2-*cis*-pentene=3-Methyl-1-pentene							
4-Methyl-1-pentene	1600	− 2.0	+ 1054	+ 1004	+ 854	+ 654	+ 454

Table 1.—(*Concluded*)

Reactions	Free Energy Equations $\Delta F^\circ = A+BT$		ΔF° cal./mol.				
	A	*B*	0°	25°	100°	200°	300°
4-Methyl-2-*cis*-pentene=3-*trans*-Hexene 2-*trans*-Hexene	800	− 3.4	− 129	− 214	− 469	− 809	− 1149
4-Methyl-2-*cis*-pentene=3-*cis*-Hexene 2-*cis*-Hexene	1800	− 4.0	+ 708	+ 608	+ 308	− 92	− 492
2-Methyl-2-pentene 3-Methyl-2-*cis*-pentene 3-Methyl-2-*trans*-pentene=3-Methyl-1-pentene 4-Methyl-1-pentene	3300	− 1.8	+ 2808	+ 2763	+ 2628	+ 2448	+ 2268
2-Methyl-2-pentene 3-Methyl-2-*cis*-pentene 3-Methyl-2-*trans*-pentene=3-*trans*-Hexene 2-*trans*-Hexene	2500	− 3.4	+ 1571	+ 1486	+ 1231	+ 891	+ 551
2-Methyl-2-pentene 3-Methyl-2-*cis*-pentene 3-Methyl-2-*trans*-pentene=3-*cis*-hexene 2-*cis*-hexene	3500	− 4.0	+ 2408	+ 2308	+ 2008	+ 1608	+ 1208
3-Methyl-1-pentene 4-Methyl-1-pentene=3-*trans*-Hexene 2-*trans*-Hexene	− 800	− 1.6	− 1237	− 1277	− 1397	− 1557	− 1717
3-Methyl-1-pentene=3-*cis*-Hexene 4-Methyl-1-pentene=2-*cis*-Hexene	200	− 2.2	− 401	− 456	− 621	− 841	− 1061
3-*trans*-Hexene=3-*cis*-hexene 2-*trans*-Hexene=2-*cis*-Hexene	1000	− 0.6	+ 836	+ 821	+ 776	+ 716	+ 656
1-Octene=2,4,4-Trimethyl-1-pentene	− 8260	+15.1	− 4136	− 3759	− 2626	− 1116	+ 394
1-Octene=2,4,4-Trimethyl-2-pentene	− 9860	+16.9	− 5245	− 4822	− 3555	− 1865	− 175
2,4,4-Trimethyl-1-pentene=2,4,4-Trimethyl-2-pentene	− 1600	+ 1.8	− 1108	− 1063	− 928	− 748	− 568

Summary.

(1) For the discussion of the general trend of isomerization reactions of unsaturated hydrocarbons, the free energy equations as a function of temperature, convenient for practical calculations, are derived, based on some of the more recent data available.

(2) With the aid of these simple free energy equations, ΔF's at 0°, 25°, 100°, 200° and 300°C. are computed and tabulated.

(3) Some correlations in connection with these thermodynamical calculations for isomerization reactions are presented.

(4) In general, isomerization reactions of hydrocarbons with a few exceptions are favoured thermodynamically at a lower temperature, as found in the case of saturated hydrocarbons.

(5) As we have already stated in the case of saturated hydrocarbons, isomerization reactions from those of simpler structure to the more complicated and branched are favoured thermodynamically, more or less, at a lower temperature.

(6) As in the case of saturated hydrocarbons, the conclusion given by Rossini that isomeric form is more stable than the normal form is also found to be reasonable, as far as our calculation indicates.

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