THERMODYNAMIC PARAMETERS OF DEHYDROGENATION REACTIONS OF NORMAL PARAFFINS WITH A C_{10}–C_{15} HYDROCARBON COMPOSITION TO OLEFINS

N. A. Eliseev, O. D. Sterligov, and
G. V. Isagulyants

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In contrast to the n-alkanes and n-1-alkenes, there are no thermodynamic parameters for the isomeric n-alkenes with an internal double bond apart from a few exceptions [1]. The purpose of the present work was to consider the enthalpy and entropy differences for the dehydration of higher linear paraffins with a C_{10}–C_{15} composition to n-olefins and to compare these calculated differences in the differences given in the literature for other alkenes, particularly for the n-hexenes. The process studied may be schematically represented in the following form

$$\text{n-Alkane}\begin{cases}\longrightarrow \text{1-alkene} + H_2\\ \longrightarrow \text{cis-i-alkene} + H_2\\ \longrightarrow \text{trans-i-alkene} + H_2\end{cases}\qquad (1)$$

where i is the position of the double bond in the olefin molecule. For example, in the case of a C_{10} hydrocarbon composition, i = 2-5, and in the case of C_{15}, i = 2-7.

The thermodynamic properties of H_2, the n-alkanes, and the n-1-alkenes were taken from [1], and those of the isomeric monoolefins with a double bond in an internal position were calculated by the method of Benson and Buss [2-4]. As was shown in [4], the deviations of the calculated values from the reference values lie within the range of accuracy of the method.

All these data were used to calculate the enthalpy and entropy differences for the reactions in scheme (1) (Table 1). The thermodynamic parameters presented in Table 1 for the formation of the 1-alkenes were calculated from reference data.

From the data presented it is seen that the enthalpy and entropy differences for the formation of the 1-alkenes are scarcely dependent on the number of C atoms in the original alkane in agreement with the results in [5] on the hydrogenation of 1-alkenes to alkanes. In the case of the formation of the n-alkenes with an internal double bond, the thermodynamic parameters are dependent, although only slightly, on the length of the carbon chain in the hydrocarbon molecule: the enthalpy difference decreases, and the entropy difference increases. The data in Table 1 show that each reaction may be characterized by the arithmetic means of the respective thermodynamic parameters.

The reactions in scheme (1) are classified as so-called similar reactions of the same type, which were described in fairly great detail in [5], although only in the example case of the conversion of 1-alkenes into alkanes. There were no indications in that book as to how the thermodynamic parameters of reactions resulting in the formation of n-alkenes with an internal double bond vary. Some arguments on this subject can be obtained from an examination of the reactions in scheme (1) from the point of view of the additivity scheme described by Benson and Buss, according to which a hydrocarbon molecule may be represented as a system consisting of a set of definite groups. Alkanes consist of $C-(C)(H)_3$ and $C-(C)_2(H)_2$ groups, and in n-olefins there are, in addition, $C_\alpha-(H)_2$, $C_\alpha-(C)(H)$, $C-(C_\alpha)(C)(H)_2$, and $C-(C_\alpha)(H)_3$ groups, where C_α denotes the carbon atom with the double bond. If, for the sake of simplicity, these groups are designated, respectively, a, b, c, d, e, and f, then, for example, decane contains 2 a groups and 8 b groups, pentadecane contains 2 a groups and 13 b groups, 1-decene contains one a group, one c group, one d group, one e group, and 6 b groups, etc. If the group composition of all the hydrocarbons reacting, as well as the

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. N. E. Bauman Higher Technical School, Kaluzh Branch, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 745-748, April, 1987. Original article submitted July 9, 1985.

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TABLE 1. Enthalpy and Entropy Differences for the Formation of Monoolefins from Normal Paraffins with a C_{10}–C_{15} Hydrocarbon Composition

Monoolefin	Paraffin						Arithmetic mean
	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	
	ΔH°_{298}, kJ						$\overline{\Delta H}^\circ_{298}$, kJ
1-Alkene	125.52	125.52	125.52	125.52	125.61	125.52	125.52
cis-2-Alkene	117.74	117.66	117.53	117.45	117.37	117,28	117,50±0.07
trans-2-Alkene	113.56	113.48	113.35	113.27	113.19	113,10	113.32±0.07
cis-i-Alkene	118.03	117.95	117.82	117.74	117,66	117.57	117.80±0.07
trans-i-Alkene	113.85	113.77	113,64	113.56	113,48	113.39	113,62±0.07
i	3, 4, 5	3, 4, 5	3 . . . 6	3 . . . 6	3 . . . 7	3 . . . 7	
	ΔS°_{298}, J						$\overline{\Delta S}^\circ_{298}$, J
1-Alkene	126.40	126,40	126,39	126.39	126.40	126.81	126,47±0.07
cis-2-Alkene	129.21	129.67	130.16	130.62	131,08	131.95	130.40±0.40
trans-2-Alkene	124.19	124.65	125.14	125.60	126.06	126.93	125.40±0.40
cis-i-Alkene	129.59	130.05	130,54	131.00	131.46	132,33	130.80±0.40
trans-i-Alkene	124,57	125.03	125,52	125.98	126.44	127.31	125.80±0.40
i	3, 4	3, 4. 5	3, 4, 5		3 . . . 6	3 . . . 7	
cis-i-Alkene (sym.)	123.83		124,78		125,70		124.80±0.50
trans-i-Alkene(sym.)	118.81		119,76		120.68		119,80±0.50
i (sym.)	5		6		7		

TABLE 2. Formulas for the Calculation of ΔF for the Formation of Monoolefins

No.	Reaction	ΔF
1	Alkane → 1-alkene+H_2	$c+d+e-a-2b+F_{H_2}$
2	Alkane →2-alkene+H_2	$f+2d+c-a-3b+F_{H_2}$
3	Alkane →i-alkene+H_2 *	$2e+2d-4b+F_{H_2}$

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*i = 3,4...

values of the group contributions, are known, the thermodynamic parameters of the reactions in scheme (1) can easily be calculated.

For example, for the reaction

$$\text{n-decane} \rightarrow \text{n-1-decene} + H_2$$

we have

$$\Delta F = F_{\text{1-decene}} + F_{H_2} - F_{\text{decane}} \tag{2}$$

where F denotes the thermodynamic parameters of the substance (the enthalpy or entropy) and ΔF denotes the thermodynamic parameter of the reaction (the enthalpy or entropy difference).

When the foregoing statements are taken into account, Eq. (2) may be expressed in terms of group contributions:

$$\Delta F = C_\alpha - (H)_2 + [C_\alpha - (C)\,(H)] + [C - (C_\alpha)\,(C)\,(H)_2] + \\ + 6\,[C - (C)_2(H)_2] + [C - (C)\,(H)_3] + F_{H_2} - 2\,[C - (C)\,(H)_3] - \\ - 8\,[C - (C)_2(H)_2]$$

Introducing the designations of the groups, we ultimately obtain

$$\Delta F = c + d + e - a - 2b + F_{H_2}$$

Similarly, for the reaction

$$\text{pentadecene} \rightarrow \text{1-pentadecene} + H_2$$

TABLE 3. Comparison of the Enthalpy Differences and Entropy Differences for the Dehydrogenation Reactions of C_{10}—C_{15} Hydrocarbons to Monoolefins with Data on Reactions Resulting in the Formation of Hexenes

Monoolefin	ΔH°_{298}, kJ			ΔS°_{298}, J		
	arithmetic mean ΔH^0_{298} (see Table 1)	calc. from group contributions (acc. to equats. in Table 2)	calculation from ref. data [1] (for C_6)	arithmetic mean ΔS^0_{298} (see Table 1)	calc. from group contributions (acc. to equats. in Table 2)	calculation from ref. data [1] (for C_6)
1-Alkene	125.52	126,51	125,52	126.50	128.58	126.80
cis-2-Alkene	117.50	118.10	118.11	130,40	128.11	128.70
trans-2-Alkene	113.32	113.92	113,30	125,40	123.09	122.80
cis-3-Alkene	117.80	118.39	119.58	130,80	128.49	
trans-3-Alkene	113.62	114.21	112.76	125.80	123.47	
cis-i-Alkene (sym.)				124,80	122.70	121,80
trans-i-Alkene (sym.)				119,80	117.70	117,00

Note. For hydrocarbons with C_6, C_8, C_{10}, C_{12}, and C_{14} compositions i (sym.) = 3-7, respectively.

we obtain

$$\Delta F = c + d + e + a + 11b + F_{H_2} - 2a - 13b = c + d + e - a - 2b + F_{H_2}$$

Hence it follows that the thermodynamic parameters for all the reactions of scheme (1) leading to the formation of a 1-alkene will have the same values regardless of the number of C atoms in the hydrocarbon in agreement, as was pointed out, with the data presented in [5]. Similar relationships were obtained for the formation of 2-alkenes and 3-alkenes (Table 2). From the relations presented it follows that the parameters of similar regions are calculated with the use of the same formula and evidently have the same values. Thus, the conclusion that the thermodynamic parameters of reactions are not dependent on the number of C atoms in the molecule of the hydrogen, which applied to the formation of 1-alkenes, may be extended to the formation of isomeric alkenes with a double bond in an internal position. However, when the thermodynamic parameters of reactions are calculated with the use of the proposed formulas, corrections for the symmetry and cis—trans isomerism must be introduced in the necessary cases. As an example of the use of the proposed relations, we shall calculate the entropy difference for the synthesis of a cis-2-alkene and a trans-2-alkene.

According to Table 2, we may write

$$\Delta S = f + 2d + e - a - 3b + S^0_{H_2}.$$

Substituting in the group contributions (a, b, d, e, and f) from [2, 3] and the entropy of H_2 from [1], we obtain ΔS = 119.84 J. A correction for the symmetry of the molecules, which is equal to $-R \log \sigma_t$, where R is the universal gas constant, and σ_t is the total symmetry number, must be added to the calculated values of ΔS. In the case of an alkene, $\sigma_t = 2 \cdot 3^2$, and in the case of a 2-alkene, $\sigma_t = 3^2$.

When these corrections are taken into account, we have

$$\Delta S = 119.84 - 18.27 + 24.03 = 125.60 \text{ J}.$$

Introducing a correction for the cis—trans isomerism [3], we obtain the final results:

$$\text{for a cis-2-alkene, } \Delta S^0_{298} = 125.60 + 2.51 = 128.11 \text{ J}.$$

$$\text{for a trans-2-alkene, } \Delta S^0_{298} = 125.60 - 2.51 = 123.09 \text{ J}.$$

The values obtained coincide within the range of accuracy of the calculation with the entropy differences for the formation of cis- and trans-2-hexene from n-hexane calculated on the basis of reference data [1]: for cis-2-hexene, 128.70 J; for trans-2-hexene, 122.80 J.

Since the entropy of a hydrocarbon is lower the more symmetric the molecule is [2, 3], the entropies of molecules with symmetric and asymmetric positioning of the double bond are different. This, of course, has an effect on the entropy differences for reactions. In the case under consideration, 5-decene, 6-dodecene, and 7-tetradecene are symmetric molecules; therefore, the reactions resulting in the formation of these isomers are characterized by smaller entropy differences than in the case of other reactions (see Table 1).

The thermodynamic parameters of the formation of different monoolefins calculated from the group contributions (on the basis of the equations in Table 2) differ slightly from the arithmetic means taken from Table 1 (Table 3). The divergence for the entropy differences reaches 2.3 J, but even in that case, it is <2%.

A comparison with the enthalpy and entropy differences for the formation of isomeric hexenes from n-hexane calculated from the reference data shows that the thermodynamic parameters of the reactions vary monotonically as the number of C atoms in the hydrocarbon is increased; however, these changes are insignificant within the scope of the C_{10}—C_{15} hydrocarbons with a normal structure and are possibly due to a systematic error in the calculation. For these reasons, these values may be assumed to be constant. Their mean values are close to the data corresponding to the n-hexenes. Thus, the thermodynamic parameters of the reactions resulting in the formation of higher n-olefins with an internal double bond from the corresponding n-paraffins are determined by the position of the double bond in the alkene molecule.

CONCLUSIONS

1. The enthalpy and entropy differences for the formation of 1-alkenes, as well as n-olefins with a double bond in an internal position in the cis and trans forms, as a result of the dehydrogenation of C_{10}—C_{15} n-paraffins under standard conditions have been calculated.

2. Relations for the calculation of the thermodynamic parameters of the reactions (the enthalpy and entropy differences) from group contributions have been derived. Satisfactory agreement between the results obtained on the basis of the calculated and reference data has been demonstrated.

3. The enthalpy and entropy differences for the formation of n-olefins are practically not dependent on the length of the hydrocarbon chain and are determined by the position of the double bond in the molecule of the n-olefin.

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