Enthalpies of Urea Adduct Formation of 3-, 5-, 7-, 9-Methylheptadecanes and 3-, 5-, 7-, 10-Methylnonadecanes

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Enthalpies of urea adduct formation of 3-, 5-, 7-, and 9-methylheptadecanes and those of 3-, 5-, 7-, and 10-methylnonadecanes were measured with a twin conduction microcalorimeter. The effects of presence and position of a side methyl group on the adductibilities of methylalkanes were observed.

1. Introduction

Enthalpies of adduct formation of methylalkanes cannot be measured accurately without difficulty owing to the low addutibilities of methylalkanes. For example, Terres *et al.*¹⁾ failed to measure enthalpies of adduct formation of methylalkanes with a Dewar type calorimeter. This showed that the low rate of temperature rise accompanying the very slow rate of methylalkane adduction made it difficult to determine accurately with an ordinary Dewar type calorimeter, since the adduct formation of methylalkane did not occur spontaneously as normal alkanes. Therefore, the choice of an appropriate calorimeter and means for accelerating the rate of adduct formation is essential for direct determination of enthalpies of adduct formation of methylalkanes. The choice of a reaction phase is also necessary to minimize the error associated with the measurement. Taking care of the factors mentioned above, the authors²⁾ already have succeeded in measuring the enthalpies of adduct formation of 2-methylalkanes which, among the methylalkanes, react most readily with urea and they have succeeded in deriving a formula which related the enthalpy of adduct formation with the carbon number (or chain length) of 2-methylalkanes.

In this study the enthalpies of adduct formation was measured for four methylheptadecanes and four methylnonadecanes except the 2-methyl isomers, all of which seemed to have smaller values of adductibilities than those of 2-methylalkanes. The effects of presence and position of a side methyl group on the enthalpy of adduct formation were discussed; moreover, the entropy changes in the adduct formation of methylalkanes were also dis-

cussed based on the values of enthalpy of adduct formation and equilibrium constants determined³⁾ in a previous study³⁾.

2. Experimental

2.1 Apparatus and Procedure

An Applied Electric Laboratory CM-204 S twin type calorimeter was used for measuring the enthalpy of urea adduct formation. Procedures were almost the same as those used in a previous study on urea adduct formation of 2-methylalkanes; however, a larger amount of methanol as an activator was necessary for smoother adduct formation. Since the increase in the methanol content increases the heat of solution appreciably when urea dissolves in the methanol, the following experimental procedure was included. An adduct of each methylalkane was prepared from 0.2 ml of methanol, 40 mg of urea, and 45 ml of the methylalkane in a reaction vessel prior to making the heat measurement. After the system had attained equilibrium at the reaction temperature, the ampule containing a weighed amount of powdered urea was broken into the reactor to form a urea adduct. This procedure allowed a smooth adduction reaction, which was carried out at 0, 5, and 10°C because low temperatures, however, above the melting point of methylalkanes, favored adduction.

2.2 Reagents

The eight methylalkanes were all synthesized by the Grignard method and identified by mass spectrometry. Purities of these methylalkanes were better than 99%, except 5-methylnonadecane (98%) as indicated by gas chromatography. Urea was recrystallized twice from its aqueous solution, dried, ground, sieved (under 250 mesh) and kept in a dessicator containing silica gel. Methanol was of G. R. grade.

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Table 1 Enthalpy of Urea Adduct Formation

Alkanes	Temp. (°C)	Urea (g)	Heats (cal)	Enthalpy of Adduct Formation $-\Delta H_u$ (kcal/mol-urea)	$m^4)$	Enthalpy of Adduct Formation, $-\Delta H_m$ (kcal/mol-methylalkane)
3-Methylheptadecane	0	0.2140	3.82	1.07		
"	0	0.2265	3.91	1.04	13.7	14.5
5-Methylheptadecane	0	0.3469	5.96	1.03		
"	0	0.3596	6.24	1.04	13.4	13.9
7-Methylheptadecane	0	0.2740	4.79	1.05		
"	0	0.2296	4.01	1.05	13.4	14.1
9-Methylheptadecane	0	0.1251	2.18	1.05	13.4*	14.1
3-Methylnonadecane	10	0.3285	7.02	1.28		
"	10	0.1812	3.80	1.26	14.9	18.9
5-Methylnonadecane	0	0.1429	2.96	1.24	14.8	18.4
7-Methylnonadecane	0	0.2653	5.40	1.22		
"	0	0.3076	6.30	1.22	14.6	18.0
10-Methylnonadecane	5	0.2428	5.04	1.25		
"	5	0.2367	4.75	1.20	14.6	18.0

* Presumed value

3. Results and Discussion

3.1 Enthalpies of Urea Adduct Formation of Methylheptadecanes and Methylnonadecanes

The urea adduct formation of methylalkanes can be expressed as follows:

where m : the molar ratio of urea and methylalkanes in adduct.

The results of enthalpy of urea adduct formation of methylheptadecanes and methylnonadecanes are shown in **Table 1**. The range of determined values for methylheptadecanes was from 1.04 to 1.07 kcal/mol-urea. Among the methylalkane isomers, no large difference in the heat of urea adduct formation per mol of urea was observed whenever there was a side methyl group attached. Enthalpies of urea adduct formation of methylheptadecanes are smaller than the enthalpy of urea adduct formation of 2-methylheptadecane (1.58 kcal/mol-urea)²⁾ by 0.5 kcal/mol-urea, and also smaller than the corresponding enthalpy of heptadecane (1.88 kcal/mol-urea)[†] by 0.8 kcal/mol-urea. Similarly, the enthalpies of urea adduct formation of methylnonadecanes are smaller than the enthalpy of urea adduct formation of 2-methylnonadecane (1.70 kcal/mol-urea) by 0.4~0.5 kcal/mol-urea, and also smaller than that of nonadecane (1.94 kcal/mol-urea)[†] by 0.7 kcal/mol-urea.

These results show the range of magnitude of influence of the position of the substituted methyl group on the enthalpy of adduct formation. As

[†] These values are calculated from ΔH (kcal/mol-alkane) and m shown by Terres et al.¹⁾

the composition (m : the molar ratio of urea to alkane) of each methylalkane adduct is known⁴⁾, the enthalpy of adduct formation per mol of alkane can be calculated from the heat of adduct formation per mol of urea determined in this study. Calculated values of enthalpy of adduct formation per mol of methylalkane are also given in **Table 1**. The values, 24.4 and 27.7 kcal/mol-alkane, respectively, for heptadecane and nonadecane are recalculated from the equation of Terres *et al.*¹⁾ The values of enthalpy of adduct formation per 1 mol of guest molecules are the largest for normal alkanes, intermediate for 2-methylalkanes; and the smallest for methylalkanes except 2-methylalkanes. Differences in the values among the individual isomers of methylalkanes except 2-methylalkanes are almost negligible. Differences in the enthalpies of adduct formation between 2-methylalkanes and other methylalkane isomers are equivalent to those of the enthalpies of adduct formation of the four methylenes in the range of $C_{18} \sim C_{20}$ studied, while the differences of those between normal alkanes and 2-methylalkanes having the same carbon numbers were equivalent for three methylenes²⁾.

3.2 Thermodynamic Functions for Adduct Formation of Methylalkanes

The ΔG° was determined for adduct formation of methylalkanes at 25°C from extrapolation of equilibrium constants at other temperatures (0~20°C). The ΔS° was also calculated from the value of ΔG° and heat of adduct formation (ΔH°) obtained in this study by assuming that ΔH° is constant in this temperature range (0~25°C). They are given in **Table 2**.

When methylalkane isomers are assumed to take the same enthalpy values in spite of their differences in the positions of side methyl groups, it is

Table 2 Thermodynamic Functions for Urea Adduct Formation at 25°C

Alkanes	ΔG° ($\frac{\text{kcal}}{\text{mol-alkane}}$)	ΔH° ($\frac{\text{kcal}}{\text{mol-alkane}}$)	ΔS° ($\frac{\text{cal}}{\text{mol-alkane}\cdot\text{K}}$)
Heptadecane	-4.1	-24	-67
2-Methylheptadecane	-2.9	-22	-64
3-Methylheptadecane	-2.3	-15	-43
5-Methylheptadecane	-1.5	-14	-42
7-Methylheptadecane	-1.4	-14	-42
9-Methylheptadecane	-1.7	-14	-41
Nonadecane	-4.8	-28	-78
2-Methylnonadecane	-3.1	-26	-77
3-Methylnonadecane	-2.6	-19	-55
5-Methylnonadecane	-2.1	-18	-53
7-Methylnonadecane	-2.1	-18	-53
10-Methylnonadecane	-2.1	-18	-53

suggested that the adduct is more stable as ΔH° gets smaller. **Table 2** shows that ΔH° of adduction of each methylalkane becomes larger as the position of the side methyl group changes from the end carbon atom to the central one in a straight carbon chain. It would result from the change in the repulsive interaction between the side methyl group of methylalkane and the surrounding urea channel. Among the values of ΔS° of adduction of various alkanes which have equal straight carbon chain numbers, ΔS° s of normal alkanes take the largest negative values; ΔS° s of 2-methylalkane and other methylalkanes decrease in that order. Differences in the values of ΔS° s of adduction of branched methylalkanes other than 2-methylalkane are negligible.

As ΔS° mainly reflects the regularity of arrangement of the liquid-guest alkane in the host-urea

channel, it is suggested that arrangements of methylalkanes in the host-urea channel be fairly irregular in comparison with the regular arrangements of normal alkanes. It is also considered that methylalkanes other than 2-methylalkanes sterically fit into the host urea channel only with great difficulty, and they are forced to irregular arrangements in contrast to the ease with which 2-methylalkane fits into the host urea channel.

References

- 1) Terres, E., Sur, S. N., *Brennstoff Chem.*, **38**, 330 (1957).
- 2) Oshima, Y., Ohnuma, H., Akai, Y., Ohashi, H., *J. Japan Petrol. Inst.*, **19**, 665 (1976).
- 3) Oshima, Y., Ohnuma, H., *Nippon Kagaku Kaishi*, **1981**, 424.
- 4) Oshima, Y., Ohnuma, H., Akai, Y., Preprint of the 19th Meeting of Japan Petrol. Inst., p. 18 (1976).

要 旨

3-, 5-, 7-, 9-メチルヘプタデカンおよび 3-, 5-, 7-, 10-メチルノナデカンの尿素付加物生成熱

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メチルアルカンの尿素付加性が直鎖化合物に比べ低いことからその尿素付加物生成熱の測定は困難とされて来たが、本研究では双子型伝導微少熱量計の使用と反応相の適宜な選択、活性化剤メタノール添加量の増大などの工夫により、3-, 5-, 7-, 9-メチルヘプタデカン および 3-, 5-, 7-, 10-メチルノナデカン類の尿素付加物生成熱を測定した。メチルヘプタデカン類とメチルノナデカン類の尿素付加物生成熱はそれぞれ $1.0_4 \sim 1.0_7$ kcal/mol-urea, $1.2_1 \sim 1.2_8$ kcal/mol-urea の範囲にあった。これらの値は直鎖炭素数の等しい *n*-アルカンおよび 2-メチルアルカンよりもそれぞれ $0.7 \sim 0.8$ kcal/mol-urea, $0.4 \sim 0.5$ kcal/mol-urea だけ小さかった。上記付加物生成熱と付加物組成から計算されたアルカン 1 mol 当たりの付加物生成熱は、直鎖アルカンで最も大きく、次いで 2-メチルアルカンの順となり、そ

の他のメチルアルカンで最も小さいが、後者の各種異性体相互の差はほとんど認められなかった。付加物生成熱と尿素付加反応の平衡定数から求められた付加物生成にともなうエントロピー減少量は、同一主鎖炭素数のアルカンについて、直鎖アルカンで最も負に大きく、次いで 2-メチルアルカン、その他のメチルアルカンの順に小さくなるが、その他のメチルアルカンの相互間の相違は有意なものと認められなかった。これらの結果から直鎖アルカンが包接尿素管内で整然と配列しているのに比べ、メチルアルカンではその配列にすくなくぬれがあるものと推察された。ただしメチルアルカンの中では 2-メチルアルカンが包接尿素管への適合が容易であるのに対して、その他のメチルアルカンの適合は立体的にかなり困難であり、不規則配列を余儀なくされているものと考えられた。

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Keywords

Adduction enthalpy, Calorimetry, Methylheptadecane, Methylnonadecane, Urea adduct