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配位化合物 CH₂LiX 的修正计算

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对于一系列配位化合物 CH₂LiX(X＝F，Cl)，根据统计热力学和含 Wigner 校正的 Eyring 过渡态理论(TST)，计算了热力学函数、平衡常数、速率常数、阿仑尼乌斯指前因子 A(100--1700K)。从这些结果来看，不同构型的稳定性是随实验温度变化的。两种构型可能在某一温度共存。这一结果是不同于仅通过电子结构能所作出的推断的。

关键词：　　　锂配合物　　　热力学函数　　　稳定性

有机锂

分类号：　　　O614.11　　　O642.1

REFINE CALCULATION OF THE COORDINATION COMPOUNDS-CH₂LiX

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For a serial carbenoid, CH₂LiX, thermodynamics and Eyring transition state theory (TST) with Wigner correction are used to compute their thermodynamic functions, equilibrium constants, rate constants and A factors, from 100K to 1700K. From these results, the stabilities of the isomers vary with temperature, two isomers may coexist at some temperature, which is contrary to the conclusion that made only based on electronic structure energy.

Keywords:　　　lithium coordination compound　　　thermodynamic function　　　stability

1 Introduction

A kind of organometallic intermediates with the general formula RR'CMX (M = metal, X = halogen) have been widely used in organic systheses[1,2]. In spite of the practical importance of carbenoids, little is experimentally known about their structure stabilities and even their existence. So a number of carbenoids and related systems have now been examined by calculations[3-5], the simplest model, CH₂LiX (X = F, Cl), a good starting point for understanding their nature, was thoroughly studied with many calculation methods[4,5]. But all the calculations only care about electronic structure energy, which is just one point to judge stability. So a refine calculation of the practical functions

about dynamics and thermodynamics is necessary, then we can understand the structure of CH₂LiX more scientifically.

Many methods about electronic structure energy had been done for the system, CH₂LiX. By comparing, structure 1 and structure 6 (Fig. 1) seem the most stable among their isomers if only through electronic structure energy, so Pople[4] and Qiu[5] made their conclusions like above. But as Davidson[6] and Ju[7] have pointed out, it is unsuitable to judge the reaction's direction only by electronic structure energy, the judging factor in thermodynamics is free energy (ΔG), which not only is related to electronic structure energy but also changes with temperature. And at low temperatures, the rate of structure conversion may be so little that we can't make a conclusion which structure will be expected to be observed. So refined calculations are necessary. The purpose of present work is to test the results of the quantum calculation at different experimental temperatures, it will be useful to understand the mechanism of CH₂LiX.
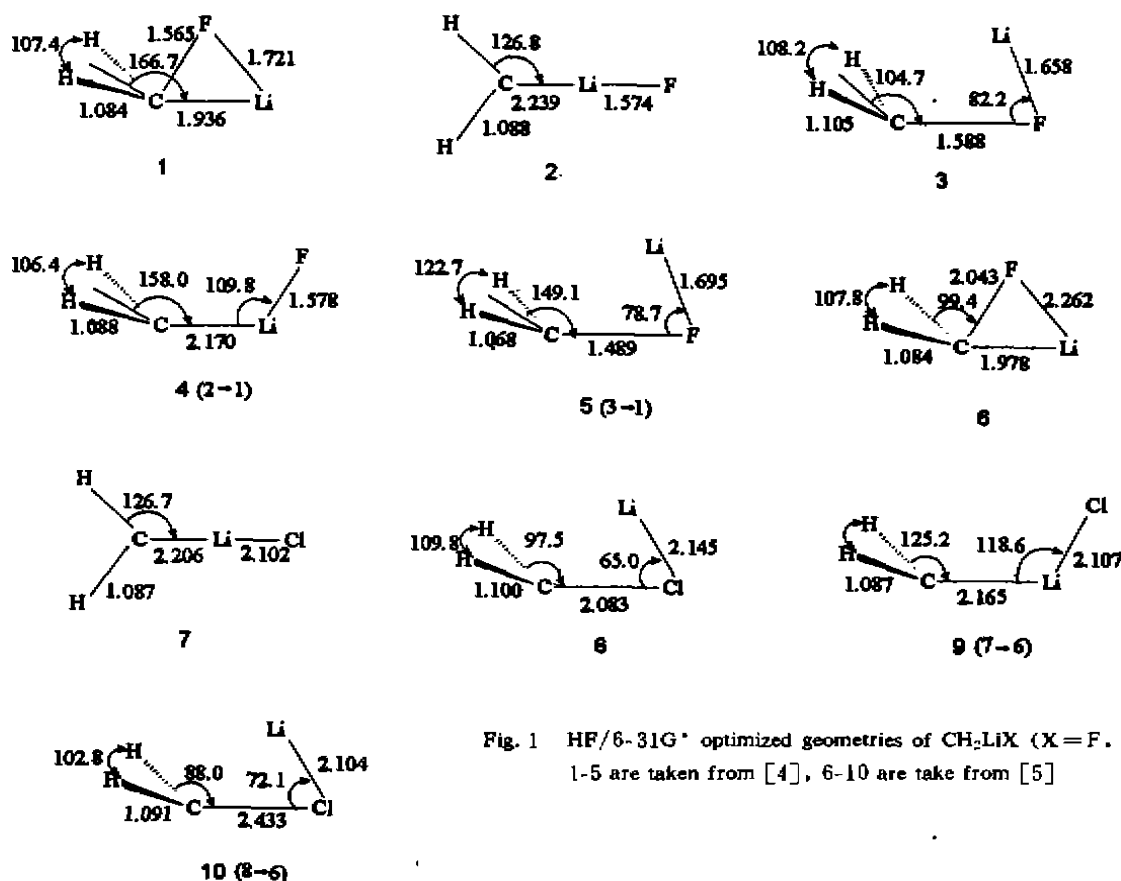

Fig. 1　HF/6-31G* optimized geometries of CH₂LiX (X = F, Cl)
1-5 are taken from [4], 6-10 are take from [5]

2　Computational methods

The general statistical thermodynamics is used to calculate the thermodynamic functions and equilibrium constant, and Eyring transition state theory (TST) with Wigner correction is used to calculate

the A factors and rate constants. The geometric parameters and frequencies were taken from [4,5] and they were tested with Hartree-Fock (HF) theory at 6-31G^* basis set for all equilibrium structures and transition states. All computations of the thermodynamic and dynamic quantities were accomplished by self-compiled program.

3　Results and discussion

Table 1　Frequencies[a] with 6-31G[*]　　　　　　　　　　　　　cm^{-1}

1	2	3	4	5	6	7	8	9	10
3287	3306	3304	3306	3550	3325	3318	3170	3318	3140
3226	3230	2976	3229	3345	3267	3241	3092	3240	2978
1583	1559	1525	1559	1502	1568	1556	1565	1558	1510
1304	1023	1287	976	1167	1205	783	1228	801	1056
1214	741	1239	764	852	1051	683	1094	614	911
775	410	800	441	681	669	424	581	426	590
589	285	543	399	499	447	252	562	410	220
481	85	406	159	479	388	60	230	132	130
450	81	337	10 1i	109 1i	283	55	224	65i	32 1i

[a] 1-5 are taken from [4], 6-10 are calculated with Gaussian-92

Table 2　Thermodynamic and Dynamic Results for the Conversion I to J

I to J	T/K	ΔH/(kJ/mol)	ΔG/(kJ/mol)	ΔS/(J/mol·K)	$\ln \bar{K}$	k/s^{-1}	A
	100	−69.8	−11.5	−11.5	82.6	3.9E9[*]	4.2E12
	500	−75.5	−57.3	−36.4	13.8	8.3E11	2.9E12
2 to 1	900	−78.0	−41.8	−40.1	5.6	1.4E12	2.9E12
	1300	−79.2	−25.5	−41.3	2.4	1.8E12	2.8E12
	1700	−79.8	−8.9	−41.7	0.6	2.0E12	2.8E12
	100	−104.5	−104.4	−1.1	125.6	1.3	4.5E12
	500	−105.3	−103.0	−4.5	24.8	2.0E10	1.1E13
3 to 1	900	−105.6	−101.1	−5.0	13.5	3.2E11	1.3E13
	1300	−105.9	−99.0	−5.3	9.2	9.9E11	1.4E13
	1700	−106.1	−96.8	−5.5	6.9	1.8E12	1.4E13

· 3.9E9 = 3.9×10⁹

According to all the data listed in table 2, the difference of free energy (ΔG) is negative and the equilibrium constant is bigger than 1 at any given temperature, which means structure 1 is the most stable geometry of CH_2LiF. At low temperatures, the structure 1 is almost the only stable geometry, but when temperature rises, ΔG reduces sharply and at 1700K, existence of structure 2 can't be neglected, where the ratio of structure 1 to 2 is approximately 1.8 to 1. Structure 3 is minimal even at very high temperatures, because it has a big difference of electronic structure energy (ΔE) with structure 1. The other system, CH_2LiCl, as listed in table 4, has the same trend as CH_2LiF. Structure 6 is stable at low temperatures but when the temperature reaches a high level (above 1200K), ΔG becomes a positive number at equilibrium constant is smaller than 1, so the structure 7 will be more stable than structure 6. Also like structure 3, structure 8 can be neglected even at a high temperature.

Table 3　Entropies of Different Structures　　J/mol · K

I		100K	500K	900K	1300K	1700K
1	St	131.0	165.5	177.7	185.3	190.9
	Sv	0.18	23.6	48.7	68.9	85.4
	Sr	74.9	94.9	102.3	106.9	110.2
	S	207.1	284.1	328.7	361.1	386.6
2	St	132.0	165.5	177.7	185.3	190.9
	Sv	15.5	63.9	92.7	114.0	132.0
	Sr	71.0	91.1	98.4	103.0	106.0
	S	218.6	320.5	368.9	402.4	428.3
3	St	132.0	165.5	177.7	185.3	190.9
	Sv	0.58	27.4	53.1	73.5	90.2
	Sr	75.6	95.7	103.0	107.6	110.9
	S	208.2	288.6	333.8	366.4	392.0
4	St	132.0	165.5	177.7	185.3	190.9
	Sv	3.4	35.3	59.1	77.3	92.0
	Sr	80.7	100.8	108.1	112.7	116.0
	S	216.1	301.5	344.9	375.3	399.0
5	St	132.0	165.5	177.7	185.3	190.9
	Sv	0.1	20.8	43.0	60.5	75.0
	Sr	74.5	94.6	101.9	106.5	109.8
	S	206.7	280.8	322.6	352.4	375.7

St: translational　Sv: vibrational　Sr: rotational

Table 4　Thermodynamic and Dynamic Results for the Conversion I to J

I to J	T/K	ΔH/(kJ/mol)	ΔG/(kJ/mol)	ΔS/(kJ/mol)	lnK	k/s⁻¹	A
7 to 6	100	−36.5	−35.2	−13.8	42.3	4.5E10	2.7E12
	500	−41.0	−24.2	−33.6	5.8	9.4E11	1.9E12
	900	−43.0	−10.0	−36.6	1.3	1.3E12	1.9E12
	1300	−44.0	4.8	−37.5	−0.44	1.4E12	1.9E12
	1700	−44.5	19.9	−37.9	−1.4	1.5E12	1.8E12
8 to 6	100	−125.9	−125.7	−2.4	151.2	1.4E10	1.0E13
	500	−126.5	−123.7	−5.6	29.8	5.4E12	4.0E13
	900	−126.6	−121.4	−5.8	16.2	1.4E13	4.9E13
	1300	−126.9	−119.1	−6.0	11.0	2.0E13	5.2E13
	1700	−127.1	−116.7	−6.1	8.3	2.6E13	5.4E13

The most stable geometry varies with temperature. The electronic structure energy (E), the production of quantum calculation, is not related to temperature. But in chemistry, a real scientific judging factor of the direction of a reaction is free energy (G), which concerns not only electronic structure energy, but also entropy (S) and temperature (T). So when temperature rises, the ΔE may be no longer the only dominant factor. As listed in table 3, the translational entropy (St) is with the same results among three structures at a given temperature, while the rotational entropy (Sr) and the vibrational entropy (Sv) are different. Because St is a function of formula weight (M), pressure (P) and temperature (T), three isomers have the same formula weight, thus St has the same results.

Sr is decided by rotational inertia (I), different geometries have different I, so three structures have different Sr. Sv is decided by frequencies, as listed in table 1, the frequencies of three structures are different. So different structures will have different entropies. Because ΔS isn't equal to zero, though little, the product of ΔS and T will reach the same level as ΔE at a enough high temperature, then ΔE will not be the only dominant factor. The two systems, CH_2LiF and CH_2LiCl, conform to this rule. The ΔE of reaction 7 to 6 is small enough, so its direction can convert at a high temperature.

Seen from dynamics, a quick equilibrium for structure conversiton is necessary. Reactions 2 to 1, 7 to 6 and 8 to 6 have large reaction rate constants (Table 2), which can be considered the equilibrium reaches in a moment. But the rate constant of reaction 3 to 1 is so small at low temperature (100K) that though the ΔG is very large for 3 to 1, structure 1 may be not the dominated structure. In Table 2 and Table 4, the A factors of the reactions change little with temperature, so the above reactions follow the Arrhenius rate law.

4　Conclusion

To simple carbenoids, $CH_2LiX(X=F, Cl)$, the structure with the lowest electronic structure energy (E) isn't always the most stable structure, if ΔE is less than 50 kJ · mol^{-1}, another structure may be more stable in an experimental temperature. The reaction rate constant of 3 to 1 is very small when the temperature is less than 100K, so the two structures, 1 and 3 may coexist. All of these results are different with the previous conclusions[4,5].

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