

Thermodynamics and kinetic studies of insertion reaction between CCl and NH₃

Weijiang Si & Shuping Zhuo *

School of Chemical Engineering, Shandong University of Technology, Zibo 255091, China

Email: zhuosp@sdu.edu.cn

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Based on the quantum theoretical study of the insertion reaction of CCl with NH₃, the statistical thermodynamics and Eyring transition state theory with Wigner correction are used to compute the thermodynamic functions, the equilibrium constants, *A* factors and the rate constants in the temperature range 200-2000K. Results show that the reaction is thermodynamically dominant at low temperatures and kinetically favoured at higher temperatures.

CCl is one of the carbynes which have attracted the attention of the experimentalists and theoreticians¹⁻⁴. As an important class of reaction, the insertion of CCl into small molecules were studied with *ab initio* methods³. In order to further understand the thermodynamic and kinetic properties of CCl insertion reactions, we have investigated herein the thermodynamic and kinetic data of the CCl insertion reaction with NH₃ by general statistical thermodynamics and Eyring transition state theory with Wigner correction. This will provide us with insight into insertion reactions of CCl.

Computation methodology

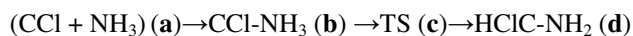
The calculations were carried out by general statistical thermodynamics (GST)⁵ and Eyring transition state theory (TST) with Wigner correction^{6,7} at 101.325 kPa and in the temperature range of 200-2000 K. The electronic energies and the harmonic frequencies of all species were calculated at (U)MP2(FC)/6-311+G(*d*, *p*) level by Gaussian 98 program⁸ and are listed in Table 1. The structures of the intermediate complex, transition state and product of the reaction in the present study are given in Fig. 1. All computations of the thermodynamic and kinetic quantities of this reaction were accomplished using an in-house developed program^{9,10}.

Results and discussion

Entropies and heat capacities

The theoretical study of CCl insertion reaction with NH₃ by standard *ab initio* molecular orbital

calculations at several theoretical levels³ shows that the reaction mechanism of CCl and NH₃ reaction is as follows:



Based on general statistical thermodynamics (GST), the thermodynamic data of the reactants, intermediate complex (CCl-NH₃), transition state (TS), and product (HCIC-NH₂) of this reaction are calculated and shown in Table 2.

From Table 2, it can be seen that the translational entropies, *S_t*, of CCl-NH₃, TS and HCIC-NH₂ are the same at the same temperature, and the translational entropies, *S_t*, of reactants CCl and NH₃ are relatively smaller at the same temperature, while the *S_t* value of CCl is larger than that of NH₃ at the same temperature. This is because the value of *S_t* of a system depends on the pressure, temperature and the molecular weight of the molecule, and is proportional to the molecular weight of the system. The rotational entropies, *S_r*, of CCl-NH₃, TS, HCIC-NH₂, CCl and NH₃ decrease gradually from CCl-NH₃ to NH₃ with the decrease of the rotational inertia of the above systems. The vibrational entropies, *S_v*, of HCIC-NH₂, TS, CCl-NH₃ show a small difference at the same temperature. Also, the molar heat capacities, *C_p*, of HCIC-NH₂, TS, CCl-NH₃ differ slightly at a certain temperature in the range 200-2000K, while *C_p* of CCl is smaller than that of NH₃ molecule at the same temperature.

Thermodynamic properties

The changes in the thermodynamic functions, $\Delta_r H_m^\theta$, $\Delta_r G_m^\theta$, $\Delta_r S_m^\theta$ and *K*(*T*) have been calculated for the overall reaction by Eqs 1 and 2 and are listed in Table 3.

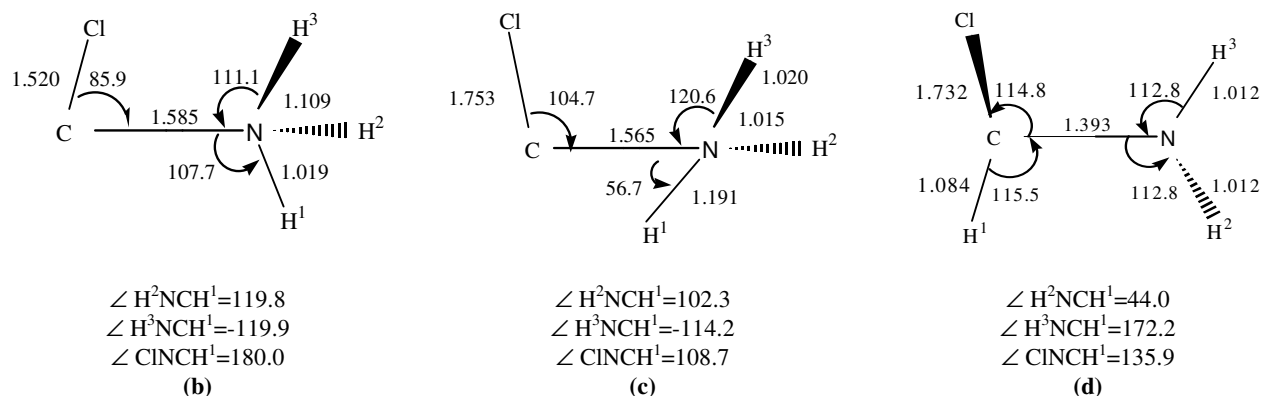
$$\Delta_r G_m^\theta = \Delta_r H_m^\theta - T \Delta_r S_m^\theta \quad \dots(1)$$

$$\text{and, } \Delta_r G_m^\theta = -RT \ln K(T) \quad \dots(2)$$

It is seen that in the temperature range 200-2000K, both the enthalpy changes ($\Delta_r H_m^\theta$) and the entropy changes ($\Delta_r S_m^\theta$) are negative, i. e., it is exothermic and of the entropy decrease type. Considering the changes

Table 1 — The electronic energies and harmonic vibrational frequencies of all species in CCl+NH₃ reaction at the (U)MP2(FC)/6-311+G(*d, p*) level

Molecules	Harmonic frequencies (cm ⁻¹)	Electronic energies (Hartree)
CCl(a)	913.9	-497.46987
NH ₃ (a)	1063.7, 1660.5, 1662.0, 3529.1, 3679.8, 3682.9	-56.41531
CCl-NH ₃ (b)	370.8, 492.8, 612.9, 673.5, 947.5, 1070.2, 1429.1, 1619.5, 1648.4, 2590.8, 3459.0, 3584.3	-553.90833
TS(c)	1799.51, 325.6, 390.4, 693.1, 754.6, 807.7, 1029.9, 1317.1, 1533.5, 2353.2	-553.87027
HCIC-NH ₂ (d)	309.5, 410.0, 690.7, 798.0, 833.7, 1144.9, 1269.6, 1403.1, 1645.4, 3232.6, 3573.3, 3689.5	-554.00020

Fig. 1 — The structures of the intermediate complex (**b**), transition state (**c**) and product (**d**) optimized at (U)MP2(FC)/6-311+G(*d, p*) level by Gaussian 98 program.

in thermodynamic functions, on the one hand, the reaction is favourable because of the negative ($\Delta_r H_m^\ominus$) enthalpy changes, while on the other hand, according to the negative entropy changes ($\Delta_r S_m^\ominus$), the reaction is unfavourable. However, according to Eq. 1, the Gibbs free energy changes ($\Delta_r G_m^\ominus$) are negative in the range 200-2000 K, i. e., it is a spontaneous reaction. The equilibrium constant $K(T)$ of this reaction falls quickly; the higher the temperature, the smaller is the equilibrium constant of the reaction. Therefore, from the view point of the conversion coefficient analysis, the CCl insertion reaction with NH₃ is thermodynamically dominant at lower temperatures.

Kinetic properties

There are two steps in this reaction: the first step, in which CCl reacts with NH₃ to obtain the intermediate complex (CCl-NH₃), is a non-barrier process which is the fast step of the reaction, and the second step, CCl-NH₃ (**b**) → TS (**c**) → HCIC-NH₂ (**d**), which is the rate determinant step of the overall reaction. The kinetic properties of A factor and rate constant of the reaction were calculated by Eyring transition state theory with Wigner correction. The pressure is

101.325 kPa and the selected temperature range is 200-2000K in steps of 200K. The rate constant expression can be written as,

$$k(T) = g(k_b/h) \exp(\Delta S_m^\ddagger/R - \Delta H_m^\ddagger/RT) \quad \dots(3)$$

$$g = 1 + \frac{1}{24} (h\nu^\ddagger/k_b T)^2 \quad \dots(4)$$

where g is the tunneling factor corrected by Wigner, k_b and h are Boltzmann's and Planck's constants respectively, R is the ideal gas constant, and ν^\ddagger is the imaginary frequency of the transition state, ΔH^\ddagger and ΔS^\ddagger are standard enthalpy and entropy of activation for the system respectively. The results are given in Table 3. As it can be seen in Table 3, the CCl insertion reaction with NH₃ takes place slowly below 200 K because of a small rate constant $k(T) < 6.6 \times 10^{-10} \text{ s}^{-1}$. With increase of temperature, the rate constant increases gradually, and the higher the temperature, the larger is the rate constant and the faster is the CCl reaction with NH₃. Therefore, from the viewpoint of rate constant analysis, the CCl

Table 2 — Thermodynamic data of all species in $(\text{CCl} + \text{NH}_3)(\mathbf{a}) \rightarrow \text{CCl-NH}_3(\mathbf{b}) \rightarrow \text{TS}(\mathbf{c}) \rightarrow \text{HCIC-NH}_2(\mathbf{d})$ reaction in the temperature range 200 -2000K

T (K)	S_t (J/mol·K)	S_r (J/mol·K)	S_v (J/mol·K)	S_{total} (J/mol·K)	$C_{p,m}$ (J/mol·K)	T (K)	S_t (J/mol·K)	S_r (J/mol·K)	S_v (J/mol·K)	S_{total} (J/mol·K)	$C_{p,m}$ (J/mol·K)
CCl (a)						CCl-NH₃ (b) — Contd					
200	154.35	52.45	0.09	206.89	29.60	1200	195.42	114.32	79.33	389.07	107.24
400	168.76	58.21	1.38	228.35	32.72	1400	198.62	116.24	91.11	405.97	111.96
600	177.18	61.58	3.28	242.04	34.76	1600	201.40	117.91	101.86	421.17	115.62
800	183.16	63.98	5.06	252.20	35.77	1800	203.84	119.38	111.74	434.96	118.48
1000	187.80	65.83	6.61	260.24	36.31	2000	206.03	120.69	120.84	447.56	120.73
1200	191.59	67.35	7.96	266.90	36.63	TS(c)					
1400	194.80	68.63	9.14	272.57	36.83	200	158.17	91.47	5.73	255.37	46.82
1600	197.57	69.74	10.18	277.49	36.96	400	172.58	100.12	21.87	294.57	67.56
1800	200.02	70.72	11.11	281.85	37.06	600	181.01	105.17	38.56	324.74	81.19
2000	202.21	71.59	11.95	285.75	37.12	800	186.99	108.76	53.68	349.43	90.33
NH₃ (a)						1000	191.63	111.54	67.17	370.34	97.05
200	135.81	42.87	0.04	178.72	33.50	1200	195.42	113.82	79.28	388.52	102.21
400	150.21	51.52	1.19	202.92	37.56	1400	198.62	115.74	90.22	404.58	106.23
600	158.64	56.58	4.08	219.30	43.64	1600	201.40	117.41	100.18	418.98	109.37
800	164.62	60.16	7.86	232.64	49.30	1800	203.84	118.88	109.29	432.01	111.84
1000	169.26	62.95	11.99	244.20	54.39	2000	206.03	120.19	117.68	443.90	113.80
1200	173.05	65.22	16.25	254.52	58.85	HCIC-NH₂ (d)					
1400	176.25	67.14	20.49	263.89	62.65	200	158.17	84.99	5.70	248.86	46.41
1600	179.03	68.81	24.63	272.47	65.81	400	172.58	93.63	21.57	287.78	67.70
1800	181.48	70.28	28.62	280.38	68.39	600	181.01	98.69	38.63	318.33	82.89
2000	183.67	71.59	32.43	287.69	70.51	800	186.99	102.28	54.38	343.65	93.06
CCl-NH₃ (b)						1000	191.63	105.06	68.57	365.26	100.56
200	158.17	91.97	4.42	254.56	45.47	1200	195.42	107.34	81.38	384.14	106.39
400	172.58	100.62	19.81	293.01	66.88	1400	198.62	109.26	93.01	400.89	110.99
600	181.01	105.68	36.52	323.21	82.16	1600	201.40	110.92	103.64	415.96	114.64
800	186.99	109.26	52.15	348.40	93.02	1800	203.84	112.39	113.40	429.63	117.54
1000	191.63	112.05	66.39	370.07	101.09	2000	206.03	113.70	122.40	442.13	119.86

Table 3 — Thermodynamic and kinetic properties of the reaction, $\text{CCl} + \text{NH}_3 \rightarrow \text{HCIC-NH}_2$, in the temperature range 200-2000K

T (K)	$\Delta_r H_m^\ominus$ (kJ/mol)	$\Delta_r S_m^\ominus$ (J/mol·K)	$\Delta_r G_m^\ominus$ (kJ/mol)	$K(T)$	A	$k(T)$ (s ⁻¹)	E_a (kJ/mol)	g
200	-290.19	-136.74	-262.84	.44E69	.12E14	.66E-09	88.74	7.99
400	-291.97	-143.49	-234.57	.43E31	.27E14	.11E03	90.62	2.75
600	-291.69	-143.02	-205.88	.84E18	.41E14	.68E06	92.26	1.78
800	-290.40	-141.19	-177.45	.39E12	.51E14	.57E08	93.56	1.44
1000	-288.60	-139.19	-149.41	.64E08	.59E14	.86E09	94.54	1.28
1200	-286.52	-137.29	-121.77	.20E06	.64E14	.54E10	95.29	1.19
1400	-284.27	-135.56	-94.48	.33E04	.67E14	.20E11	95.88	1.14
1600	-281.93	-134.00	-67.53	.16E03	.69E14	.55E11	96.34	1.11
1800	-279.53	-132.59	-40.88	.15E02	.72E14	.12E12	96.71	1.09
2000	-277.10	-131.30	-14.49	.24E01	.73E14	.23E12	97.01	1.07

insertion reaction with NH_3 is kinetically favored at higher temperatures. In Table 3, the A factors of this reaction vary only slightly with the change of the temperature and hence, this reaction obeys the Arrhenius rate law with $\log A \approx 14$, in the temperature

range 200-2000 K. It is necessary to point out that the activation energy, E_a , obtained from the calculation with Wigner correction for this reaction increases with increasing temperature. It is obvious that these thermodynamic and kinetic properties of the reaction

cannot be predicted by only pure quantum chemical calculations. Therefore, it is of practical significance to discuss the changes of both equilibrium constant and rate constant with changes of temperature. Furthermore, combining these two factors, it is more suitable to choose the proper temperature for a certain reaction.

On the basis of discussion above, it can be concluded that in the temperature range 200-2000 K, for insertion reaction of CCl into NH₃, $\Delta_r H_m^\theta < 0$, $\Delta_r S_m^\theta < 0$ and $\Delta_r G_m^\theta < 0$, i. e., it is an exothermic, of negative entropy and spontaneous reaction. With increase of temperature, the equilibrium constants decrease while the rate constants increase in the range 200-2000 K. Thus, the CCl insertion reaction with NH₃ is thermodynamically dominant at low temperatures and kinetically favoured at higher temperatures. Therefore, it is important to consider both the rate constant and the conversion efficiency to choose the proper temperature for this kind of reaction.

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