Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material for

Theoretical study on the kinetics for hydrogen cyanide and hydrogen isocyanide reactions with methyl radical

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Table S1. Cartesian coordinates of important species of the M06-2X/6-311++G(2df,2p) optimized structure

HCN	C	0.00000000	0.00000000	-0.49468000
	H	0.00000000	0.00000000	-1.56121800
	N	0.00000000	0.00000000	0.64704200
HNC	H	0.00000000	0.00000000	1.42951600
	N	0.00000000	0.00000000	0.42906500
	C	0.00000000	0.00000000	-0.74287100
CH_3	C	0.00000000	0.00000300	0.00011500
	H	0.00000000	1.07982900	0.00011300
	H	0.93515600	-0.53991600	0.00011300
	H	-0.93515600	-0.53991600	0.00011300
IM1a	C	1.30030200	0.07248700	-0.00001600
	H	1.58798300	1.13306700	-0.00010200
	N	0.21887800	-0.47396100	0.00003500
	C	-1.10002200	0.14786000	-0.00000300
	H	-1.03407200	1.23845000	-0.00009300
	H	-1.64387700	-0.18801100	-0.88035300
	H	-1.64386000	-0.18786700	0.88041300
TS1a	C	-1.35449400	0.18208800	0.00000100
	H	-1.87783200	1.11822400	-0.00000500
	N	-0.44078900	-0.54813400	0.00000000
	C	1.38459300	0.15752100	0.00000000
	H	1.25838200	1.23142200	0.00016700
	H	1.76224000	-0.27531500	0.91428000
	H	1.76213900	-0.27504500	-0.91445100
IM2a	C	1.25059100	0.27273100	-0.00005700
	H	2.26343000	-0.13924900	-0.00005500
	N	0.22461100	-0.38543500	0.00002200
	C	-1.14273900	0.09891700	0.00002600
	H	-1.18283200	1.18839600	-0.00006400
	H	-1.65002100	-0.29056900	-0.88039200
	H	-1.64996400	-0.29042200	0.88054200
TS2a	C	1.26013600	0.13171100	0.00001100
	H	2.18688300	0.65305400	0.00007600
	N	0.20616000	-0.46337700	-0.00006300
	C	-1.13152600	0.15627400	0.00002400
	H	-1.06964200	1.24571500	-0.00009100
	H	-1.66611200	-0.19161100	-0.88151100
	H	-1.66590400	-0.19142800	0.88175800
TS3a	C	-1.36554500	0.34197400	0.00000100
	H	-1.22503300	-0.99812700	0.00000600
	N	-0.27514500	-0.30577500	-0.00000300
	C	1.15021300	0.08774000	0.00000100

	H	1.18174500	1.17820900	-0.00002200
	H	1.63064100	-0.30895100	0.88966700
	H	1.63065700	-0.30898900	-0.88964000
IM3a	C	1.36755100	-0.35544000	-0.00001300
	H	0.37269000	1.38016700	0.00001900
	N	0.30228800	0.36038000	0.00000400
	C	-1.07781800	-0.15291700	0.00000400
	H	-1.02373200	-1.23725600	-0.00001100
	H	-1.60168100	0.19227500	0.88943200
	H	-1.60168900	0.19229800	-0.88941100
TS8a	C	1.35088000	-0.26103500	0.00017400
	H	2.44803400	1.40636800	0.00027300
	N	0.19600600	-0.12355000	-0.00053500
	C	-1.20518600	0.09513200	0.00012600
	H	-1.40707000	1.16113900	-0.08262100
	H	-1.65594500	-0.42435300	-0.84212600
	H	-1.63122800	-0.28288600	0.92641800
CH_3NC	C	-1.47537200	-0.00000100	-0.00003000
	N	-0.31365300	0.00000000	-0.00001900
	C	1.10617900	-0.00000100	-0.00006300
	H	1.47083800	-0.01226600	-1.02424300
	H	1.46994400	0.89341100	0.50184300
	H	1.46994900	-0.88113600	0.52309200
IM1b	C	0.28299700	0.39482500	0.00003100
	H	0.41105200	1.48570500	0.00018500
	N	1.29847100	-0.31708100	-0.00018000
	C	-1.12771500	-0.14106700	0.00009400
	H	-1.65673800	0.21943800	-0.88144400
	H	-1.11875700	-1.22727300	-0.00008400
	H	-1.65655100	0.21915100	0.88186100
TS1b	C	0.62591100	0.48027200	0.00000300
	H	0.38982600	1.52740500	-0.00000300
	N	1.34639700	-0.43097200	0.00000000
	C	-1.44792000	-0.13727400	0.00000000
	H	-1.77631600	0.32014400	-0.92235200
	H	-1.32983900	-1.20902100	0.00008700
	H	-1.77639600	0.32028700	0.92225200
IM2b	C	0.19314700	-0.40150900	0.00000200
	H	2.11669600	-0.28695300	0.00000000
	N	1.24351500	0.23658400	-0.00000200
	C	-1.21245700	0.07973100	0.00000000
	H	-1.72908600	-0.30480200	0.87798500
	H	-1.24726800	1.17114500	-0.00000600
	H	-1.72908800	-0.30481200	-0.87797900

IM3b	C	0.19003800	-0.42659400	0.00003300
	H	1.43725100	1.05089600	-0.00009100
	N	1.32394600	0.02892300	-0.00000800
	C	-1.19782900	0.10372900	-0.00000300
	H	-1.72972000	-0.25714700	0.87871400
	H	-1.19869100	1.19824700	-0.00007800
	H	-1.72971700	-0.25726800	-0.87867200
TS3b	C	0.17898900	-0.45326700	0.00000200
	H	2.12366000	0.57031400	-0.00000500
	N	1.25281200	0.09314900	-0.00000200
	C	-1.21330000	0.12644100	0.00000100
	H	-1.74531400	-0.23994000	0.87629500
	H	-1.19684800	1.21849400	-0.00000600
	H	-1.74531600	-0.23995000	-0.87628800
TS2b	C	0.23349200	-0.31549400	-0.00000200
	H	1.28570200	-0.97198500	0.00000500
	N	1.32493500	0.27714500	0.00000000
	C	-1.21217400	0.07188000	0.00000000
	H	-1.70164600	-0.33389400	0.88252400
	H	-1.28485300	1.16144800	-0.00000500
	H	-1.70165300	-0.33390500	-0.88251500
CH_3CN	C	-0.28225600	-0.00000600	0.00073400
	N	-1.42703600	0.00000300	-0.00031000
	C	1.17498100	0.00000000	-0.00006800
	H	1.54475800	-0.89241600	0.49964800
	H	1.54336500	0.01282600	-1.02331900
	H	1.54478000	0.87960500	0.52184600
TS4b	C	-0.17523900	-0.15938600	0.00001700
	H	-2.05201000	1.20752200	-0.00013000
	N	-1.33483600	-0.15037600	0.00003400
	C	1.26090600	0.06961700	-0.00002200
	H	1.70822400	-0.37924500	-0.88423600
	H	1.46551200	1.14146600	-0.00046300
	H	1.70812200	-0.37849300	0.88462500
TS5b	C	0.27405100	0.06166700	-0.00000100
	H	0.27068100	1.81455500	0.00005900
	N	1.40873300	-0.17321500	-0.00011300
	C	-1.18798300	-0.09515100	0.00007800
	H	-1.60949300	0.37736900	-0.88375100
	H	-1.42928000	-1.15613400	0.00023000
	H	-1.60944900	0.37761700	0.88379400

Table S2. Lennard-Jones Parameters used in ME/RRKM Calculations

species	ε/K	σ/A
He	10.2	2.55
intermediates	1382.4	4.05

Table S3. Results of T1 value

Species	State	T1 diagnostics	Species	State	T1 diagnostics
HCN	1	0.013	CH_4	1	0.007
HNC	1	0.016	TS4b	2	0.028
CH_3	2	0.008	TS5b	2	0.032
TS1a	2	0.037	TS6b	2	0.038
TS2a	2	0.028	TS7b	2	0.020
TS3a	2	0.020	TS8b	2	0.031
TS4a	2	0.030	TS1c	2	0.055
TS5a	2	0.025	TS2c	2	0.052
TS6a	2	0.025	IM1b	2	0.032
TS7a	2	0.033	IM2b	2	0.025
TS8a	2	0.016	IM3b	2	0.026
TS1b	2	0.037	IM4b	2	0.031
TS2b	2	0.019	IM1a	2	0.031
TS3b	2	0.017	IM2a	2	0.029
TS4b	2	0.028	IM3a	2	0.017
TS5b	2	0.032	IM4a	2	0.019

In order to determine the barrier of the H-abstraction reaction, we compared reaction ($CN+CH_4 \rightarrow HCN+CH_3$) that share the same transition state and have been extensively studied. CN radical is difficult to describe by typical spin-free methods that produce a large amount of spin contamination in this system and the geometry and energy probably unreliable. In Glowacki's[45] work, the restricted open-shell treatment yields more reliable energies and geometries, and the accurate single-point energies were obtained by UCCSD(T)-ROHF calculations. Density functional theory (DFT) combined with 6-31G(d) basis sets was used to reproduce fairly closely the more accurate CCSD(T) PES profile of $CN+C_3H_8$. It was determined that the best performance was achieved using a restricted open-shell treatment of BB1K with a modified 56% exact Hartree-Fock exchange. We used the M06-2X functional (54% Hartree-Fock) combined with 6-31G(d) to calculate the structure and frequency. Accurate single-point energies were obtained by ROCCSD(T) combined with the aug-cc-pvtz basis set. To verify the transition state and energy barrier calculated by this method, the rate constant for the H-abstraction channel to form $HCN+CH_3=CN+CH_4$ has been calculated in both the forward and reverse directions and compared with the available data.

Table S4. Relative energies (ΔE (0K)), relative enthalpies (ΔH (298 K)), relative Gibbs free energies (ΔG (298 K)) by ROHF method

Species	ROCCSD(T)/aug-cc-pVDZ//M06-2X/6-31G(d)		
	ΔE(0K)(kcal/mol)	*ΔH*(298K)(kcal/mol)	*ΔH*(298K) Expt.
CH_3+HCN	0	0	-
TS1c	21.98	21.11	-
CH_3+HNC	13.89	14.03	14.89
TS2c	32.29	31.41	-
CN+CH_4	21.10	20.72	20.79

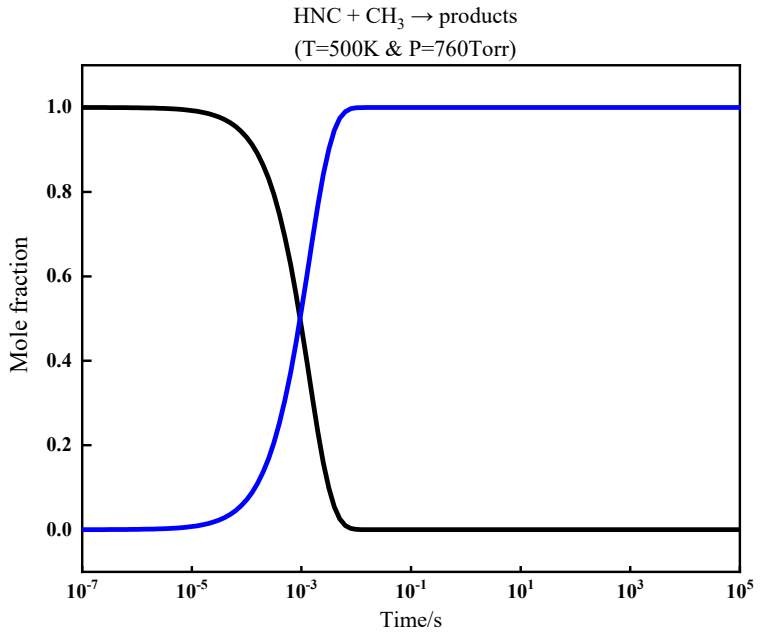

Figure S1. Time-resolved species profiles for the HNC + CH_3 → products, simulated at 500 K and 760 Torr

Table S5. The calculated rate constants ($cm^3molecule^{-1}s^{-1}$)

Temperatur		HCN+CH_3		HNC+CH_3	RA5	RA11	RB7	RB9
e	10000 Torr	760 Torr	1 Torr	760 Torr	760 Torr	760 Torr	760 Torr	760 Torr
300	4.97E-20	3.88E-20	4.68E-21	2.08E-18	3.83E-20	4.22E-22	1.01E-18	1.09E-18
400	2.41E-18	1.60E-18	1.71E-19	7.64E-17	1.53E-18	8.87E-20	3.65E-17	4.00E-17
500	2.61E-17	1.23E-17	2.55E-18	7.32E-16	1.02E-17	2.12E-18	3.45E-16	3.88E-16
600	1.08E-16	4.48E-17	1.86E-17	3.53E-15	2.73E-17	1.75E-17	1.64E-15	1.89E-15
800	5.31E-16	3.18E-16	2.71E-16	2.83E-14	4.91E-17	2.66E-16	1.27E-14	1.56E-14
1000	1.86E-15	1.61E-15	1.58E-15	1.07E-13	4.01E-17	1.52E-15	4.64E-14	6.11E-14
1300	1.00E-14	9.86E-15	9.84E-15	4.02E-13	2.22E-17	8.87E-15	1.61E-13	2.38E-13
1600	3.72E-14	3.71E-14	3.71E-14	9.72E-13	1.34E-17	3.01E-14	3.61E-13	5.98E-13
2000	1.42E-13	1.41E-13	1.21E-13	2.22E-12	8.18E-18	9.75E-14	7.39E-13	1.42E-12

Table S6. The extended Arrhenius parameters for the rate constants (760 Torr)

Rate constants	A	n	E (J mol^{-1})
k_{tot} (HCN+CH_3)	1.68×10^{-27}	4.41	23605
k_{tot} (HNC+CH_3)	4.49×10^{-16}	1.39	34278

Note that the fit is not perfect in the low-temperature region

Table S7. Comparison of calculation and experiment of molecular structure

HCN	Experimental data[a]	Calculation (M06-2X/6-311++G(2df,2p))
C-H (Å)	1.06	1.06
C-N (Å)	1.15	1.14
H-C-N (degrees)	180.0	180.0
HNC	Experimental data[b]	Calculation (M06-2X/6-311++G(2df,2p))
N-H (Å)	0.98	0.99
C-N (Å)	1.17	1.16
H-C-N (degrees)	180.0	180.0
CH_3CN	Experimental data[a]	Calculation (M06-2X/6-311++G(2df,2p))
C-C (Å)	1.45	1.45
C-N (Å)	1.15	1.14
C-H (Å)	1.10	1.08
H-C-H (degrees)	109.5	109.1
H-C-C (degrees)	109.4	109.8
CH_3NC	Experimental data[c]	Calculation (M06-2X/6-311++G(2df,2p))
C-H (Å)	1.09	1.08
C-N (Å)	1.16	1.16
C-N (Å)	1.42	1.41
H-C-H (degrees)	109.4	109.3
H-C-N (degrees)	109.6	109.5

a. G. Herzberg, Electronic spectra and electronic structure of polyatomic molecules, van Nostrand, 1966.

b. L. Gurvich, I. Veyts, C. Alcock, Thermodynamic properties of individual substances, Hemisphere Pub, Co., New York. 1989.

c. Kuchitsu. Landolt-Bornstein: Group II: Atomic and Molecular Physics Volume 15: Structure Data of Free Polyatomic Molecules. Springer-Verlag, Berlin, 1987.