Supporting Information

Clean and Efficient Transformation of CO₂ to Isocyanic Acid: The Important Role of Triatomic Cation ScNH⁺

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References

	EVD	Sc ⁺ -O	HN=CO	O=CO	Sc-N	N-H	Sc ⁺ -NH	σ^1
Mathad	EAP.	7.14	3.78	5.51	4.81	3.4	5.01	
Method		±0.05	±0.02	±0.004	±0.84	±0.16	±0.10	
References		[1]	[2]	[3]	[4]	[5]	[6]	
Hybrid Functionals	B1B95	6.95	3.94	5.60	4.03	3.18	5.27	0.36
	B1LYP	6.59	3.65	5.30	3.74	3.32	4.87	0.51
	B3LYP	6.85	3.82	5.51	4.13	3.50	5.08	0.31
	B3P86	7.17	4.11	5.83	4.54	4.05	5.40	0.38
	B3PW91	6.92	3.96	5.66	4.29	3.45	5.17	0.26
	M05	7.69	4.04	5.82	4.43	3.36	5.91	0.49
	M052X	6.89	3.77	5.37	3.35	3.30	5.16	0.61
	PBE1PBE	6.92	4.01	5.67	4.09	3.37	5.22	0.34
	X3LYP	6.80	3.83	5.51	4.04	3.49	5.05	0.35
	M06	7.54	4.08	5.83	4.32	3.28	5.85	0.47
	M062X	6.60	3.74	5.40	3.18	3.29	4.95	0.71
	BH&HLYP	5.62	3.36	4.90	2.61	3.20	4.07	1.20
	BMK	6.63	3.78	5.53	3.61	3.30	4.95	0.53
Pure Functionals	BPW91	7.59	4.18	5.98	5.15	3.47	5.70	0.44
	BLYP	7.49	3.98	5.77	4.96	3.46	5.62	0.33
	BP86	7.79	4.26	6.08	5.27	3.63	5.90	0.58
	BPBE	7.60	4.19	6.00	5.16	3.49	5.71	0.46
	M06L	7.68	4.15	5.88	4.98	3.28	5.22	0.33
	PBE	7.78	4.38	6.18	5.25	3.53	5.90	0.61
	TPSS	7.31	3.84	5.64	4.87	3.60	5.47	0.23

¹: $\sigma = \sqrt{\frac{\sum (x_i - x_{exp})^2}{n}}$, x_i is the DFT calculated bond dissociation energy and x_{exp}

is the experimental value.

Table S1. DFT-calculated and experimental bond dissociation energies. The values are

in unit of eV.

The methods for determinations of the collision rates of key intermediates with the cooling gas He ($k_{\text{collision}}$) and the conversion rates ($k_{\text{conversion}}$) of some steps as well as the rates for HNCO desorption from intermediates.

The details of collision rates of some key intermediates with the cooling gas He $(k_{\text{collision}})$. The effective pressure (*P*) of the cooling gas He is around 1.6 Pa in the LIT reactor. The number of collisions (*N*) experienced for some key intermediates, such as **I1** in **Figure 2**, with He atoms can be estimated by the following equation:⁷

$$k_{collision} = P_{\sqrt{\frac{8\pi}{m_{He}k_ET}}} (r_{He} + r)^2$$

in which m_{He} is the mass of He atom, r_{He} is the van der Waals radius of He atom (140pm), r is the radius of I1 (399 pm), k_{B} is the Boltzmann constant, and T is the temperature of the reactor (~ 298 K). The radius of I1 is calculated by $r = (d_{\text{O-H}} + r_{\text{O}} + r_{\text{H}})/2$, in which $d_{\text{O-H}}$ is the distance between terminal O_t atom and H_t atom (525 pm), r_{N} (152pm), r_{H} (120pm) and r_{H} are the van der Waals radii of N and H atoms, respectively. Therefore, the radius of I1 is r=399 pm, and the collision rate of I1 with He atoms is 4.5×10^5 s⁻¹. The values of $k_{\text{collision}}$ of I2 and I3 with He are 3.4×10^5 s⁻¹ and 4.6×10^5 s⁻¹, respectively. The results of collision rates are given in Table S2.

The Rice-Ramsperger-Kassel-Marcus theory (RRKM)⁸ was used to calculate the rate constant of traversing transition states from intermediates. For these calculations, the energy (*E*) of the reaction intermediate and the energy barrier (*E*[‡]) for each step were needed. The reaction intermediate possesses the vibrational energies (E_{vib}) of ScNH⁺ and CO₂, the center of mass kinetic energy (E_k), and the binding energy (E_b) which is the energy difference between the separated reactants (ScNH⁺ + CO₂) and the reaction complexes. The values of E_{vib} and E_b were taken from the DFT calculations and $E_k = \mu v^2/2$, in which μ is the reduced mass 25.4 and v is the velocity (≈ 623.09 m/s). The densities and the numbers of states required for RRKM calculations were obtained by the direct count method⁹⁻¹⁰ with the DFT calculated vibrational frequencies under the approximation of harmonic vibrations.

The RRKM theory was used to calculate the rate to convert the most difficult step for the potential-energy surface (PES) of Reaction 1 in **Figure 2**. According to the DFT calculated energies, the rates of internal conversion ($k_{\text{conversion}}$) for processes of **I1** \rightarrow **TS1** and **I2** \rightarrow **TS2** are 8.2 × 10¹⁰ and 3.2 × 10¹¹ s⁻¹, respectively.

The variational transition state theory (VTST)⁸ was used to calculate the rate constants for HNCO desorption from intermediates **I2** and **I3** that carry vibrational energies of E_{vib} of ScNH⁺ and CO₂, E_k , E_b between ScNH⁺ and CO₂. The VTST calculations involve geometry optimizations of **I2** and **I3** by fixing the distance between HNCO and ScO⁺ moieties at various values. The density and number of states required for VTST calculations are obtained with direct count method⁹⁻¹⁰ by using the DFT-calculated vibrational frequencies under approximation of harmonic vibrations (see ref 16 for details). The rate constants (k_d) for HNCO desorption from **I2** and **I3** are estimated with the VTST calculations,¹¹ and the results are determined to be 8 × 10⁸ and 5 × 10⁸ s⁻¹, respectively, which are 3 orders of magnitude larger than $k_{collision}$ of **I2** and **I3** with He.



Figure S1. Variations of the relative intensities of the reactant and product cations in the reaction of ScNH⁺ and CO₂ with respect to the CO₂ pressures for 0.7 ms. The solid lines are fitted to the experimental data points by using the equations derived with the

approximation of the pseudo-first-order reaction mechanism.

	178 186		<u>299</u> <u>106</u>
¹ IS1 $C_{\infty v}$ 0.00	3 IS2 C_{s} 4.20	³ IS3 $C_{\infty v}$ 4.36	⁵ IS4 C _{∞v} 5.58
3 IS1 $C_{\infty v}$ 2.03	¹ IS2 C_{xy} 4.54	¹ IS3 $C_{\infty v}$ 4.54	3 IS4 $C_{\infty v}$ 5.85
⁵ IS1 C _{∞v} 4.22	5 IS2 C_{xy} 5.85	⁵ IS3 C _{∞v} 5.85	¹ IS4 $C_{\infty v}$ 6.38
⁷ IS1 C _s 8.67	⁷ IS2 $C_{\infty v}$ 8.57	⁷ IS3 $C_{\infty v}$ 8.57	⁷ IS4 $C_{\infty v}$ 8.84

Figure S2. DFT calculated 4 isomeric structures of **ScNH**⁺ cations and relative energies. The point group and electronic state are given under each structure. Some bond lengths are given in pm, respectively. The superscripts indicate the spin states.

Reactant		$\Delta E/\mathrm{eV}$	
		1) 1 ScO++ 1 H-N=C=O	-0.06
	ScO++HNCO	2) 1 ScO++ 1 H-O=C=N	1.30
		3) ¹ ScO ⁺ + ¹ H–C=N=O	2.66
		4) ${}^{1}ScO^{+}+{}^{3}N=C(H)=O$	3.31
		5) 1 ScO++ 3 H-N=O=C	3.73
		6) 1 ScO++ 1 H-O=N=C	3.75
¹ ScNH ⁺ + ¹ CO ₂		7) 1 ScO++ 1 H-C=O=N	6.05
		8) 1 ScO++ 4 N+ 2 H-C-O	6.34
	SCO +N+COH	9) 1 ScO ⁺ + 4 N+ 2 C-O-H	8.34
		10) 1 ScO++ 2 H+ 2 N-C-O	4.41
	ScO ⁺ +H+CON	11) 1 ScO ⁺ + 2 H+ 2 C–N–O	7.04
		12) 1 ScO++ 2 H+ 4 C-O-N	7.32
	ScO ⁺ +CO+NH	13) 1 ScO++ 1 CO+ 3 NH	3.76

Note that the energy given in **Figure 2** of the main text is ΔG_{298K} .

Table S2. The calculated thermodynamics of the reactions, involving all possible products. The zero-point vibrational corrected energies (ΔE_{0K} , not ΔG_{298K}) with respect to the separated reactants are given and in unit of eV. The superscripts indicate the spin

states.



Figure S3. NBO charge developments of key species along the reaction coordinates.



Figure S4. Schematic orbital diagrams based on a frontier orbital analysis for the processes $I1 \rightarrow TS1 \rightarrow I2$ shown in Figure 2 of the main text.



Figure S5: Time-of flight mass spectra for the reactions of mass-selected Sc^+ with He (a) and with NH₃ (**b**,**c**) for 1 ms. The effective reactant gas pressures are shown. Panel d is the variation of ion intensities with respect to the NH₃ pressures in the reactions of Sc^+ with NH₃. The solid lines are fitted to the experimental data points by using the equations derived with the approximation of the pseudo-first-order reaction mechanism.



Figure S6. The potential energy curve for the step of $I2 \rightarrow P$ obtained by using MCD method. The distances between the Sc and N atoms as well as the Sc and the C atoms in I2 were increased.

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