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SUPPORTING INFORMATION

Title: Nucleophilic Reactivities of Silyl Ketene Acetals and Silyl Enol Ethers Containing $(C_6F_5)_3SiO$ and $(C_6H_5)_3SiO$ Groups

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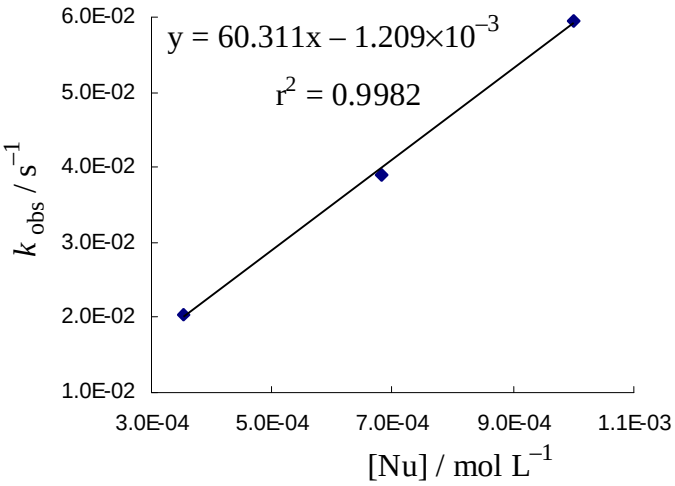
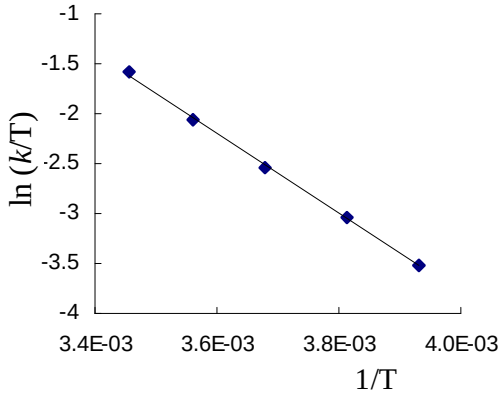
The last column lists $k_2 = k_{obs}/[Nu]$; a more precise value of k_2 is obtained as the slope of k_{obs} vs. [Nu] correlations. This value is used for further discussions.

Table 1. Kinetics of the reaction of tris(pentafluorophenyl)silyl ketene acetal **1a** with bis(*p*-*N*-morpholino)benzhydrylium ion (**4f**-BF_4). λ = 628 nm.

T, °C	[E], mol L^{-1}	[Nu], mol L^{-1}	k_{obs}, s^{-1}	[Nu] / [E]	Conversion, %	k_2, L mol^{-1} s^{-1}
20.0	1.741×10^{-5}	6.812×10^{-4}	3.893×10^{-2}	39.1	50	57.145
20.0	1.704×10^{-5}	1.000×10^{-3}	5.959×10^{-2}	58.7	50	59.584
20.0	1.796×10^{-5}	3.515×10^{-4}	2.046×10^{-2}	19.6	30	58.198
10.3	1.558×10^{-5}	6.263×10^{-4}	2.278×10^{-2}	40.2	50	36.368
0.2	1.353×10^{-5}	6.342×10^{-4}	1.354×10^{-2}	46.9	30	21.350
–10.2	1.613×10^{-5}	8.106×10^{-4}	1.028×10^{-2}	50.2	50	12.678
–19.0	1.796×10^{-5}	1.008×10^{-3}	7.660×10^{-3}	56.1	50	7.599





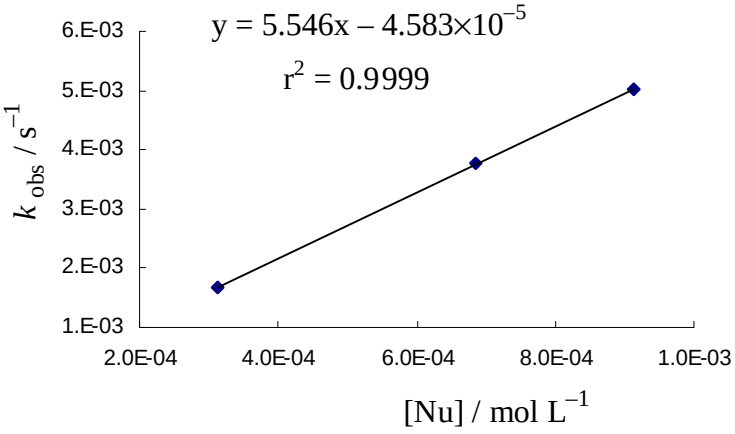
$\Delta H^{\neq} = 30.382 \pm 0.598$ kJ mol^{-1}

$\Delta S^{\neq} = -107.283 \pm 2.197$ J mol^{-1} K^{-1}

$k_2 = 60.311$ L mol^{-1} s^{-1}

Table 2. Kinetics of the reaction of tris(pentafluorophenyl)silyl ketene acetal **1a** with bis(*p*-*N*,*N*-dimethylamino)benzhydrylium ion (**4e**-BF_4). λ = 627 nm.

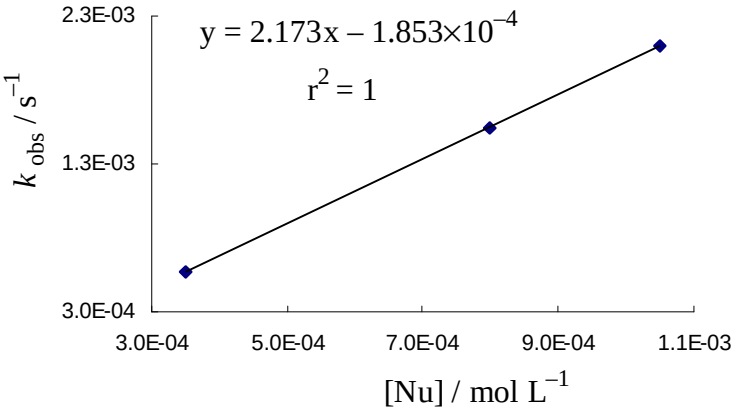
T, °C	[E], mol L^{-1}	[Nu], mol L^{-1}	k_{obs}, s^{-1}	[Nu] / [E]	conversion, %	k_2, L mol^{-1} s^{-1}
20.0	1.653×10^{-5}	3.113×10^{-4}	1.675×10^{-3}	18.8	50	5.382
20.0	1.521×10^{-5}	9.121×10^{-4}	5.004×10^{-3}	60.0	50	5.486
20.0	1.715×10^{-5}	6.857×10^{-4}	3.770×10^{-3}	40.0	80	5.498



$k_2 = 5.546$ L mol^{-1} s^{-1}

Table 3. Kinetics of the reaction of tris(pentafluorophenyl)silyl ketene acetal **1a** with bis(*p-N* -pyrrolidino)benzhydrylium ion (**4d**-BF_4). λ = 633 nm.

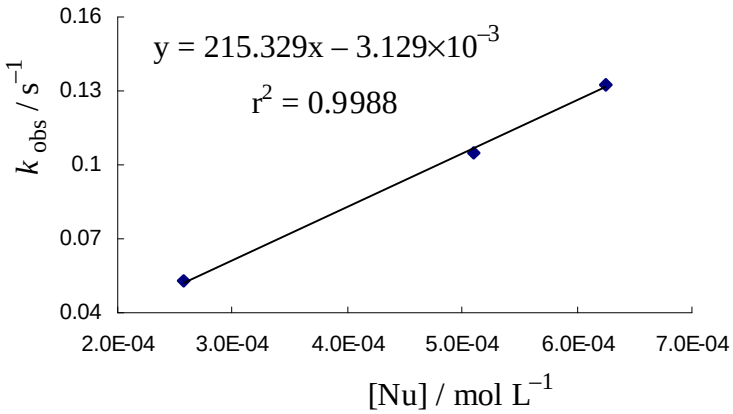
T, °C	[E], mol L^{-1}	[Nu], mol L^{-1}	k_{obs}, s^{-1}	[Nu] / [E]	Conversion, %	k_2, L mol^{-1} s^{-1}
20.0	1.725×10^{-5}	1.050×10^{-3}	2.097×10^{-3}	60.9	50	1.996
20.0	1.965×10^{-5}	7.978×10^{-4}	1.549×10^{-3}	40.6	50	1.942
20.0	1.724×10^{-5}	3.500×10^{-4}	5.748×10^{-4}	20.3	30	1.642



k_2 = 2.173 L mol^{-1} s^{-1}

Table 4. Kinetics of the reaction of triphenylsilyl ketene acetal **1b** with bis(*N*-methyl-2,3-dihydro-1H-indol-5-yl)carbenium ion (**4c**-BF_4). λ = 640 nm.

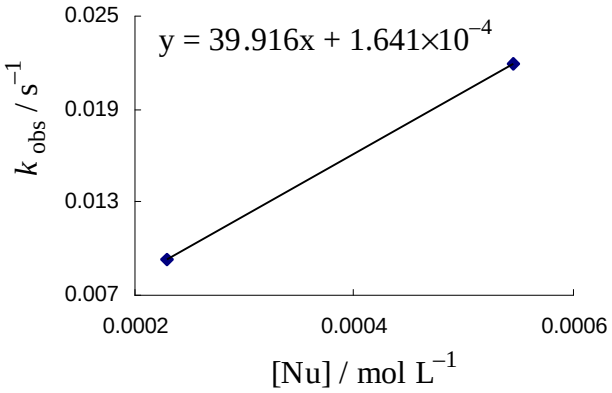
T, °C	[E], mol L^{-1}	[Nu], mol L^{-1}	k_{obs}, s^{-1}	[Nu] / [E]	conversion, %	k_2, L mol^{-1} s^{-1}
20.0	2.566×10^{-5}	5.099×10^{-4}	1.051×10^{-1}	19.9	50	206.088
20.0	9.332×10^{-6}	2.576×10^{-4}	5.284×10^{-2}	27.6	50	205.108
20.0	8.086×10^{-6}	6.250×10^{-4}	1.325×10^{-1}	77.3	50	212.062



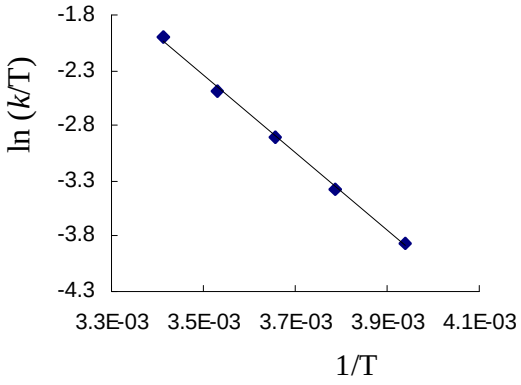
k_2 = 215.329 L mol^{-1} s^{-1}

Table 5. Kinetics of the reaction of triphenylsilyl ketene acetal **1b** with bis(julolidin-9-yl)carbenium ion (**4b**-BF_4). λ = 655 nm.

T, °C	[E], mol L^{-1}	[Nu], mol L^{-1}	k_{obs}, s^{-1}	[Nu] / [E]	?onversion, %	k_2, L mol^{-1} s^{-1}
20.0	1.106×10^{-5}	2.293×10^{-4}	9.318×10^{-3}	20.7	30	40.631
20.0	1.315×10^{-5}	5.454×10^{-4}	2.193×10^{-2}	41.5	80	40.217
10.0	1.727×10^{-5}	7.952×10^{-4}	1.865×10^{-2}	46.0	30	23.449
0.2	2.155×10^{-5}	9.921×10^{-4}	1.490×10^{-2}	46.0	80	15.024
–9.2	2.672×10^{-5}	1.385×10^{-3}	1.259×10^{-2}	51.8	50	9.085
–19.4	2.674×10^{-5}	1.386×10^{-3}	7.375×10^{-3}	51.8	80	5.320



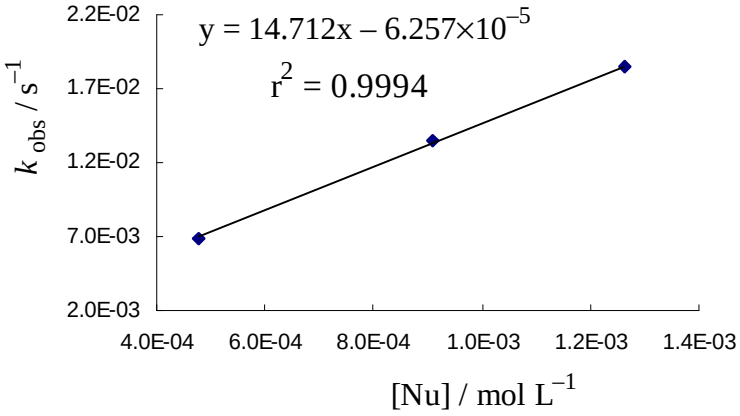
k_2 = 39.916 L mol^{-1} s^{-1}



$\Delta H^{\neq}$ = 29.142 ± 0.689 kJ mol^{-1}
$\Delta S^{\neq}$ = –115.003 ± 2.529 J mol^{-1} K^{-1}

Table 6. Kinetics of the reaction of triphenylsilyl ketene acetal **1b** with bis(lilolidin-8-yl)carbenium ion (**4a**-BF_4). λ = 660 nm.

T, °C	[E], mol L^{-1}	[Nu], mol L^{-1}	k_{obs}, s^{-1}	[Nu] / [E]	Conversion, %	k_2, L mol^{-1} s^{-1}
20.0	2.370×10^{-5}	4.766×10^{-4}	6.875×10^{-3}	20.1	30	14.425
20.0	2.256×10^{-5}	9.074×10^{-4}	1.345×10^{-2}	40.2	50	14.824
20.0	2.260×10^{-5}	1.263×10^{-3}	1.842×10^{-2}	55.9	80	14.591

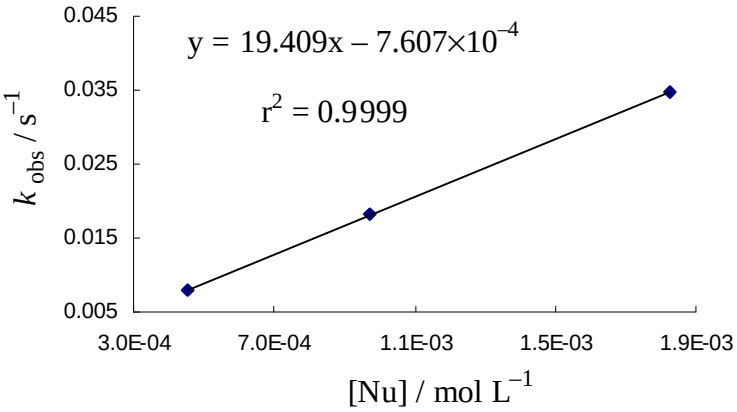


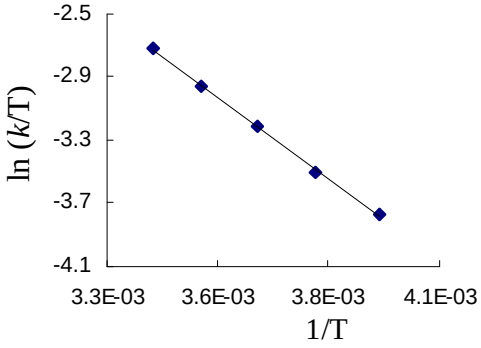
k_2 = 14.712 L mol^{-1} s^{-1}

Table 7. Kinetics of the reaction of 1-tris(pentafluorophenyl)silyloxycyclopentene **2a** with bis(4-methoxy)benzhydrylium ion (**4h**-BCl_4). λ = 528 nm.

T, °C	[E],[a] mol L^{-1}	[Nu], mol L^{-1}	k_{obs}, s^{-1}	[Nu] / [E]	Conversion, %	k_2, L mol^{-1} s^{-1}
20.0	3.936×10^{-5}	9.706×10^{-4}	1.827×10^{-2}	24.7	30	18.819
20.0	1.830×10^{-5}	4.512×10^{-4}	7.880×10^{-3}	24.7	30	17.464
20.0	2.221×10^{-5}	1.826×10^{-3}	3.460×10^{-2}	82.2	30	18.953
10.3	2.497×10^{-5}	7.408×10^{-4}	1.089×10^{-2}	29.7	80	14.696
–0.1	2.861×10^{-5}	8.070×10^{-4}	8.850×10^{-3}	28.2	50	10.966
–10.0	3.423×10^{-5}	1.124×10^{-3}	8.902×10^{-3}	32.8	50	7.922
–20.3	4.040×10^{-5}	1.386×10^{-3}	8.048×10^{-3}	34.3	30	5.807

[a] Gaseous BCl_3 was added to ionize **4h**-Cl





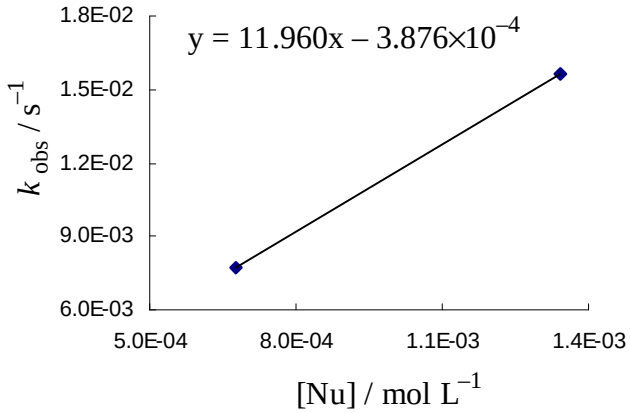
$\Delta H^{\neq}$ = 16.255 ± 0.286 kJ mol^{-1}

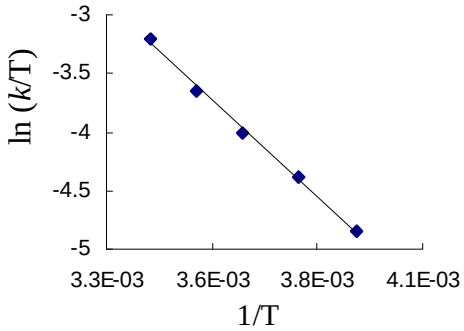
$\Delta S^{\neq}$ = –164.736 ± 1.052 J mol^{-1} K^{-1}

k_2 = 19.409 L mol^{-1} s^{-1}

Table 8. Kinetics of the reaction of 1-triphenylsilyloxycyclopentene **2b** with bis(*p*-*N*,*N*-diphenylamino)benzhydrylium ion (**4g**-BF_4). λ = 720 nm.

T, °C	[E], mol L^{-1}	[Nu], mol L^{-1}	k_{obs}, s^{-1}	[Nu] / [E]	Conversion, %	k_2, L mol^{-1} s^{-1}
20.0	1.634×10^{-5}	6.779×10^{-4}	7.720×10^{-3}	41.5	30	11.389
20.0	1.647×10^{-5}	1.342×10^{-3}	1.566×10^{-2}	81.5	50	11.671
10.3	3.464×10^{-5}	1.017×10^{-3}	7.542×10^{-3}	29.3	30	7.417
1.2	3.367×10^{-5}	1.021×10^{-3}	5.076×10^{-3}	30.3	30	4.970
–8.9	4.678×10^{-5}	2.021×10^{-3}	6.632×10^{-3}	43.2	30	3.281
–18.8	4.461×10^{-5}	2.699×10^{-3}	5.411×10^{-3}	60.5	30	2.005





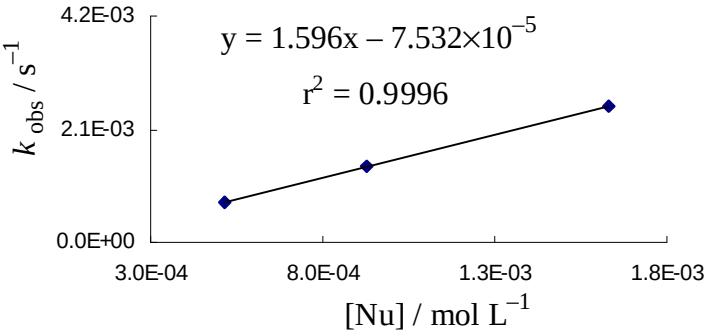
$\Delta H^{\neq}$ = 25.789 ± 0.869 kJ mol^{-1}

$\Delta S^{\neq}$ = –136.542 ± 3.183 J mol^{-1} K^{-1}

k_2 = 11.960 L mol^{-1} s^{-1}

Table 9. Kinetics of the reaction of 1-triphenylsilyloxycyclopentene **2b** with bis(*p*-*N*-morpholino)benzhydrylium ion (**4f**-BF_4). λ = 630 nm.

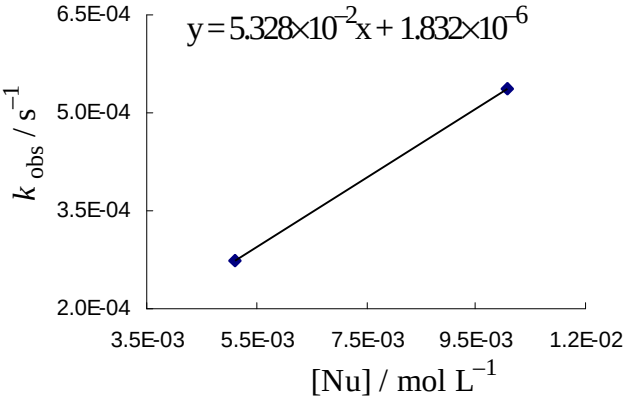
T, °C	[E], mol L^{-1}	[Nu], mol L^{-1}	k_{obs}, s^{-1}	[Nu] / [E]	conversion, %	k_2, L mol^{-1} s^{-1}
20.0	2.129×10^{-5}	9.283×10^{-4}	1.427×10^{-3}	43.6	50	1.537
20.0	2.243×10^{-5}	1.630×10^{-3}	2.519×10^{-3}	72.7	50	1.545
20.0	2.202×10^{-5}	5.123×10^{-4}	7.291×10^{-4}	23.3	30	1.423



k_2 = 1.596 L mol^{-1} s^{-1}

Table 10. Kinetics of the reaction of 1-triphenylsilyloxycyclopentene **2b** with bis(*p*-*N*,*N*-dimethylamino)benzhydrylium ion (**4e**-BF_4). λ = 645 nm.

T, °C	[E], mol L^{-1}	[Nu], mol L^{-1}	k_{obs}, s^{-1}	[Nu] / [E]	conversion, %	k_2, L mol^{-1} s^{-1}
20.0	1.180×10^{-4}	1.007×10^{-2}	5.382×10^{-4}	85.3	50	5.346×10^{-2}
20.0	1.201×10^{-4}	5.121×10^{-3}	2.747×10^{-4}	42.6	50	5.364×10^{-2}

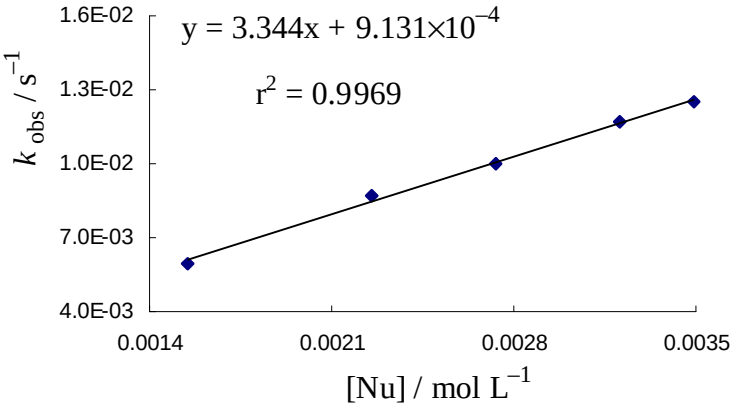


$k_2 = 5.328 \times 10^{-2}$ L mol^{-1} s^{-1}

Table 11. Kinetics of the reaction of 2-tris(pentafluorophenyl)silyloxypropene **3a** with bis(4-methoxy)benzhydrylium ion (**4h**-BCl_4). λ = 528 nm.

T, °C	[E],[a] mol L^{-1}	[Nu], mol L^{-1}	k_{obs}, s^{-1}	[Nu] / [E]	Conversion, %	k_2, L mol^{-1} s^{-1}
20.0	3.542×10^{-5}	1.542×10^{-3}	5.956×10^{-3}	43.6	50	3.861
20.0	3.773×10^{-5}	2.254×10^{-3}	8.665×10^{-3}	59.7	50	3.845
20.0	3.433×10^{-5}	2.734×10^{-3}	9.969×10^{-3}	79.6	50	3.647
20.0	4.436×10^{-5}	3.496×10^{-3}	1.250×10^{-2}	78.8	30	3.577
20.0	4.073×10^{-5}	3.209×10^{-3}	1.173×10^{-2}	78.8	30	3.656

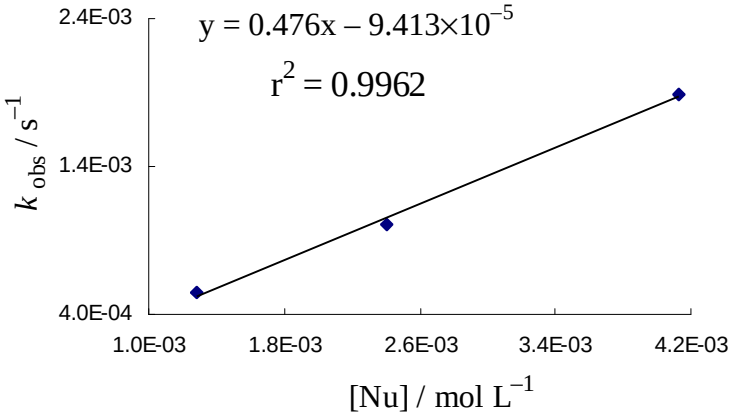
[a] Gaseous BCl_3 was added to ionize **4h**-Cl



k_2 = 3.344 L mol^{-1} s^{-1}

Table 12. Kinetics of the reaction of bis(*p*-*N*,*N*-diphenylamino)benzhydrylium (**1g**-BF_4) ion with 2,3-dihydrofuran **2d** at 20.0 °C. λ = 710 nm.

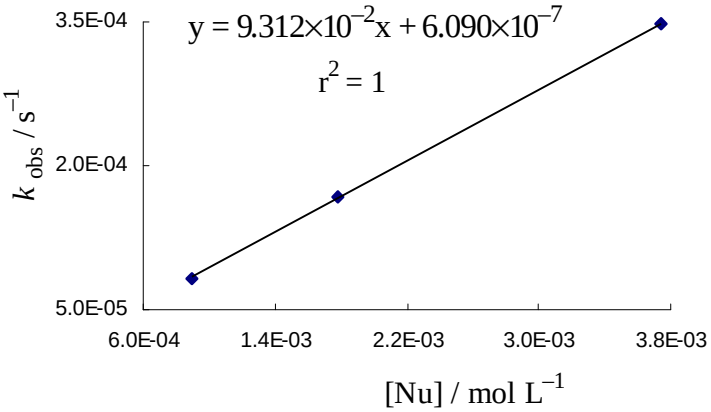
[E], mol L^{-1}	[Nu], mol L^{-1}	[Nu] / [E]	[CF_3CH_2OH], mol L^{-1}	[2,6-Lutidine], mol L^{-1}	k_{obs}, s^{-1}	Conv., %	k_2, L mol^{-1} s^{-1}
3.413×10^{-5}	2.408×10^{-3}	70.5	7.207×10^{-4}	3.853×10^{-5}	1.005×10^{-3}	80	0.417
3.643×10^{-5}	1.285×10^{-3}	35.3	7.694×10^{-4}	4.113×10^{-5}	5.472×10^{-4}	50	0.426
4.254×10^{-5}	4.126×10^{-3}	97.0	1.267×10^{-3}	5.147×10^{-5}	1.891×10^{-3}	50	0.458



k_2 = 0.476 L mol^{-1} s^{-1}

Table 13. Kinetics of the reaction of 2,3-dihydrofuran **1d** with bis(*p*-*N*-morpholino)benzhydrylium ion (**4f**-BF_4) at 20.0 °C. λ = 632 nm.

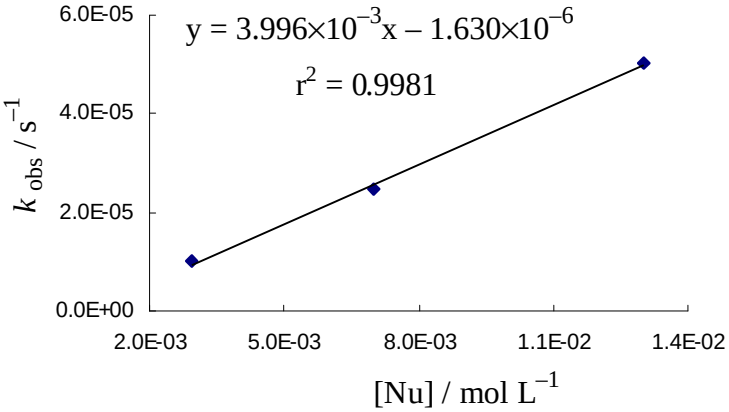
[E], mol L^{-1}	[Nu], mol L^{-1}	[Nu] / [E]	[CF_3CH_2OH], mol L^{-1}	[2,6-Lutidine], mol L^{-1}	k_{obs}, s^{-1}	Conv., %	k_2, L mol^{-1} s^{-1}
4.580×10^{-5}	3.735×10^{-3}	81.6	1.145×10^{-3}	4.049×10^{-4}	3.482×10^{-4}	30	9.321×10^{-2}
4.506×10^{-5}	1.778×10^{-3}	39.5	1.126×10^{-3}	3.983×10^{-4}	1.671×10^{-4}	30	9.400×10^{-2}
4.528×10^{-5}	8.935×10^{-4}	19.7	1.132×10^{-3}	4.004×10^{-4}	8.316×10^{-5}	30	9.308×10^{-2}



$k_2 = 9.312 \times 10^{-2}$ L mol^{-1} s^{-1}

Table 14. Kinetics of the reaction of 2,3-dihydrofuran **1d** with bis(*p*-*N*,*N*-dimethylamino)benzhydrylium ion (**4e**-BF_4) at 20.0 °C. λ = 648 nm.

[E], mol L^{-1}	[Nu], mol L^{-1}	[Nu] / [E]	[CF_3CH_2OH], mol L^{-1}	[2,6-Lutidine], mol L^{-1}	k_{obs}, s^{-1}	Conv., %	k_2, L mol^{-1} s^{-1}
1.399×10^{-4}	7.006×10^{-3}	50.1	3.895×10^{-3}	1.078×10^{-3}	2.470×10^{-5}	50	3.526×10^{-3}
1.364×10^{-4}	1.300×10^{-2}	95.4	3.672×10^{-3}	1.030×10^{-3}	5.009×10^{-5}	50	3.852×10^{-3}
1.418×10^{-4}	2.940×10^{-3}	20.7	3.819×10^{-3}	1.071×10^{-3}	1.007×10^{-5}	30	3.426×10^{-3}



$k_2 = 3.996 \times 10^{-3}$ L mol^{-1} s^{-1}