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SUPPORTING INFORMATION

Title: Nucleophilic Reactivities of Ketene Acetals
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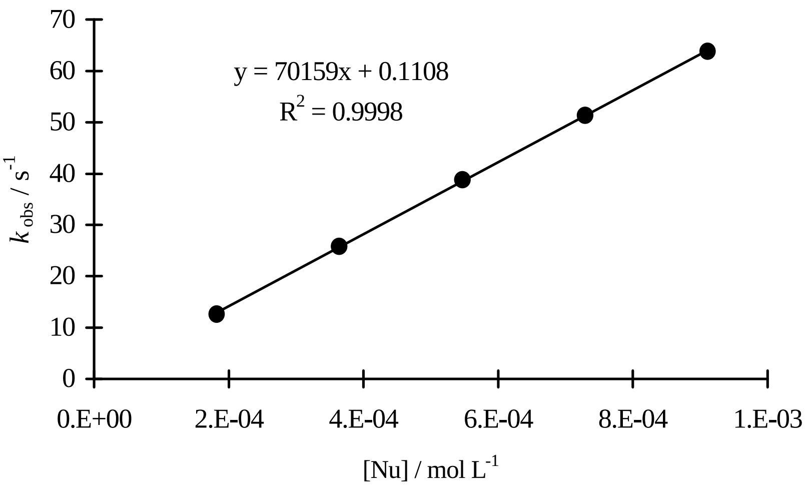
Contents

1. Kinetics of the reactions of 1,1-diethoxyethene (1a) with benzhydrylium ions

$(mfa)_2CH^+ BF_4^-$ (**2a**) (16.2 mg, 3.40×10^{-5} mol) was dissolved in 5.0 mL of CH_2Cl_2 ($c = 6.80 \times 10^{-3}$ M). 80.0 µL of this solution was diluted to 5.0 mL with CH_2Cl_2 ($c = 1.09 \times 10^{-4}$ M). 1,1-Diethoxyethene (**1a**) (97.1 mg, 0.836 mmol) was dissolved in 5.0 mL of CH_2Cl_2 (c = 0.167 M). 12.0 µL of this stock solution was diluted to 10.0 mL with CH_2Cl_2 ($c = 2.01 \times 10^{-4}$ M). In the stopped-flow instrument, the electrophile solution was mixed with the 10-fold volume of nucleophile solution to give the concentrations listed in the Tables. The course of the reactions was followed at 593 nm. A plot of k_{obs} versus concentration of [Nu] yielded a straight line, the slope of which corresponds to the second order rate constant (Run 1.1).

$(mfa)_2CH^+$ + 1,1-diethoxyethene (20 °C, CH_2Cl_2, stopped-flow, detection at 593 nm)

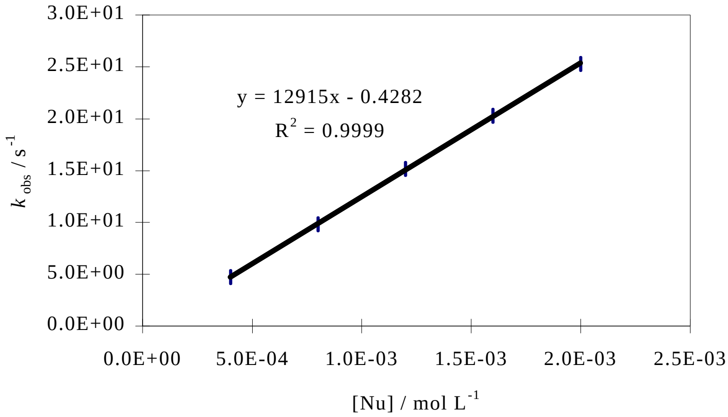
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
1.1	9.89×10^{-6}	1.82×10^{-4}	18.4	1.26×10^{1}
1.2	9.89×10^{-6}	3.64×10^{-4}	36.8	2.58×10^{1}
1.3	9.89×10^{-6}	5.47×10^{-4}	55.3	3.88×10^{1}
1.4	9.89×10^{-6}	7.29×10^{-4}	73.7	5.13×10^{1}
1.5	9.89×10^{-6}	9.11×10^{-4}	92.1	6.38×10^{1}



$k_2 = 7.02 \times 10^{4}\ M^{-1}\ s^{-1}$

$(dpa)_2CH^+$ + 1,1-diethoxyethene (20 °C, CH_2Cl_2, stopped-flow, detection at 672 nm)

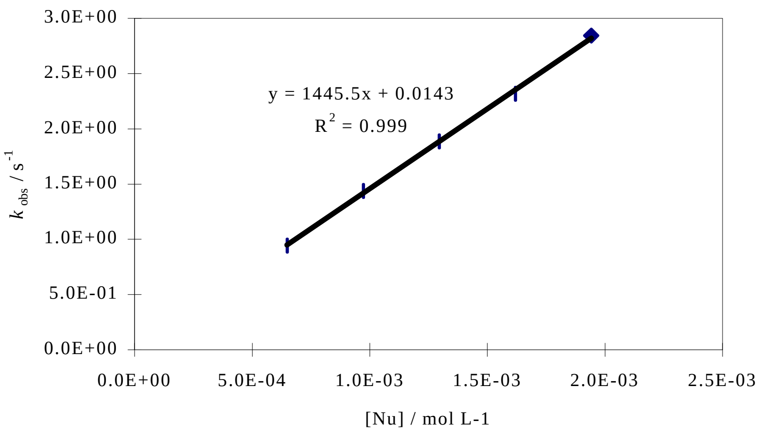
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
2.1	1.45×10^{-5}	4.00×10^{-4}	27.6	4.72
2.2	1.45×10^{-5}	7.99×10^{-4}	55.1	9.81
2.3	1.45×10^{-5}	1.20×10^{-3}	82.7	1.52×10^{1}
2.4	1.45×10^{-5}	1.60×10^{-3}	110	2.03×10^{1}
2.5	1.45×10^{-5}	2.00×10^{-3}	138	2.53×10^{1}



$k_2 = 1.29 \times 10^{4}$ M^{-1} s^{-1}

$(mpa)_2CH^+$ + 1,1-diethoxyethene (20 °C, CH_2Cl_2, stopped-flow, detection at 622 nm)

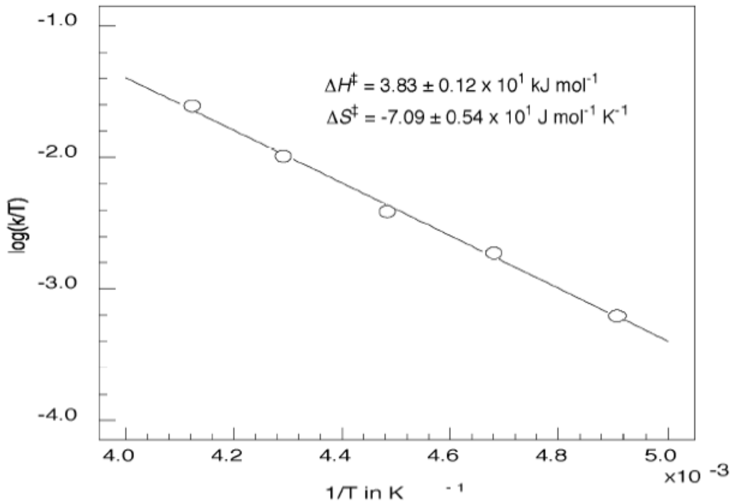
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
3.1	7.76×10^{-6}	6.47×10^{-4}	83.5	9.44×10^{-1}
3.2	7.76×10^{-6}	9.71×10^{-4}	125	1.44
3.3	7.76×10^{-6}	1.29×10^{-3}	167	1.89
3.4	7.76×10^{-6}	1.62×10^{-3}	209	2.32
3.5	7.76×10^{-6}	1.94×10^{-3}	250	2.84



$k_2 = 1.45 \times 10^{3}$ M^{-1} s^{-1}

$(dma)_2CH^+$ + 1,1-diethoxyethene (CH_2Cl_2, J&M instrument, detection at 613 nm)

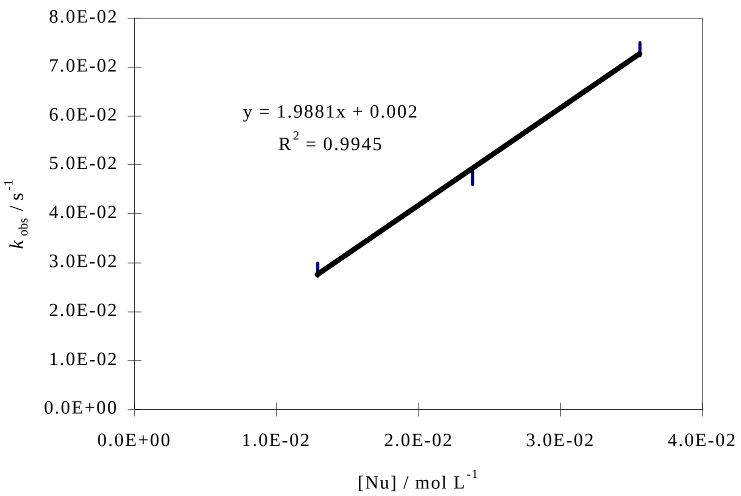
No.	T / °C	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
4.1	–69.4	6.46×10^{-5}	2.87×10^{-2}	444	1.27×10^{-1}
4.2	–59.5	9.05×10^{-5}	5.03×10^{-2}	556	4.01×10^{-1}
4.3	–50.1	4.69×10^{-5}	2.84×10^{-2}	606	8.66×10^{-1}
4.4	–40.1	5.98×10^{-5}	1.66×10^{-2}	278	2.38
4.5	–30.6	4.82×10^{-5}	5.08×10^{-3}	105	5.98



$k_2(20\ °C) = (1.79 \pm 0.31) \times 10^2\ M^{-1}\ s^{-1}$ (from the Eyring equation)

$(jul)_2CH^+$ + 1,1-diethoxyethene (20 °C, CH_2Cl_2, J&M instrument, detection at 642 nm)

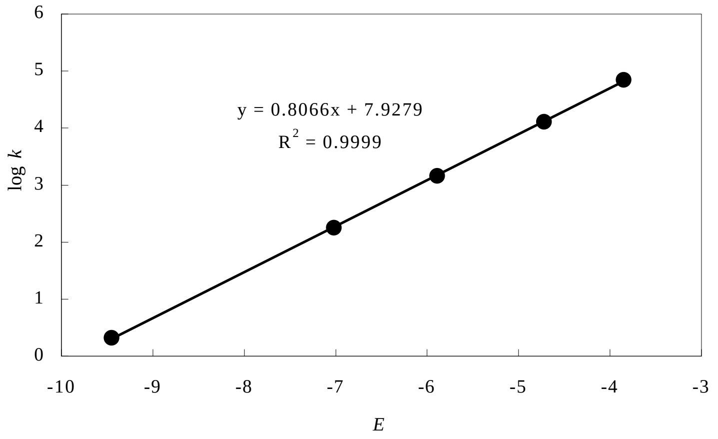
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
5.1	4.58×10^{-5}	1.29×10^{-2}	216	2.86×10^{-2}
5.2	5.97×10^{-5}	2.38×10^{-2}	520	4.73×10^{-2}
5.3	3.66×10^{-5}	3.56×10^{-2}	972	7.37×10^{-2}



$k_2 = 1.99\ M^{-1}\ s^{-1}$

Determination of the *N* and *s*-parameters of 1,1-diethoxyethene (**1a**)

Reference electrophiles	*E* parameters	k_2(20 °C) / M^{-1} s^{-1}
$(mfa)_2CH^+$	–3.85	7.02×10^4
$(dpa)_2CH^+$	–4.72	1.29×10^4
$(mpa)_2CH^+$	–5.89	1.45×10^3
$(dma)_2CH^+$	–7.02	1.79×10^2
$(jul)_2CH^+$	–9.45	1.99×10^0



N(**1a**) = 9.81

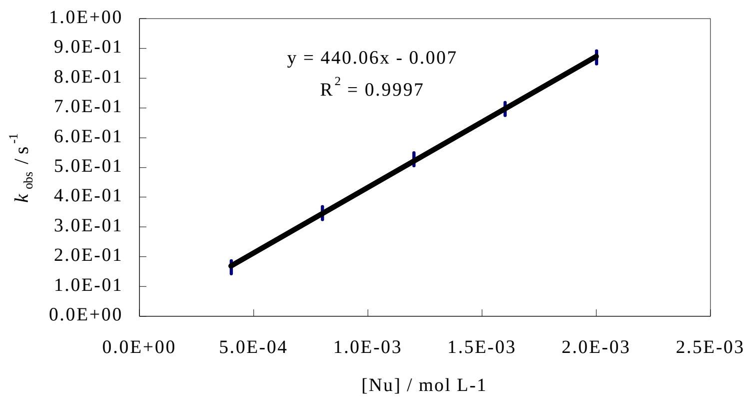
s(**1a**) = 0.81

2. Kinetics of the reactions of 1-butoxy-1-(trimethylsiloxy)ethene (1b) with benzhydrylium ions

$(dma)_2CH^+ BF_4^-$ (**2d**) (1.5 mg, 4.41×10^{-6} mol) was dissolved in 2.0 mL of CH_2Cl_2 (c = 2.20 × 10^{-3} M). 0.20 mL of this solution was diluted to 5.0 mL with CH_2Cl_2 (c = 8.80 × 10^{-5} M). 1-Butoxy-1-(trimethylsilyloxy)ethene (**1b**) (103.2 mg, 0.548 mmol) was dissolved in 5.0 mL of CH_2Cl_2 (c = 0.110 M). 40.0 μL of this stock solution was diluted to 10.0 mL with CH_2Cl_2 (c = 4.40 × 10^{-4} M). In the stopped-flow instrument, the electrophile solution was mixed with the 10-fold volume of nucleophile solution to give the concentrations listed in the Tables. The course of the reactions was followed at 613 nm. A plot of k_{obs} versus concentration of [Nu] yielded a straight line, the slope of which corresponds to the second order rate constant (Run 6.1).

$(dma)_2CH^+$ + 1-butoxy-1-(trimethylsiloxy)ethene (20 °C, CH_2Cl_2, stopped-flow, detection at 613 nm)

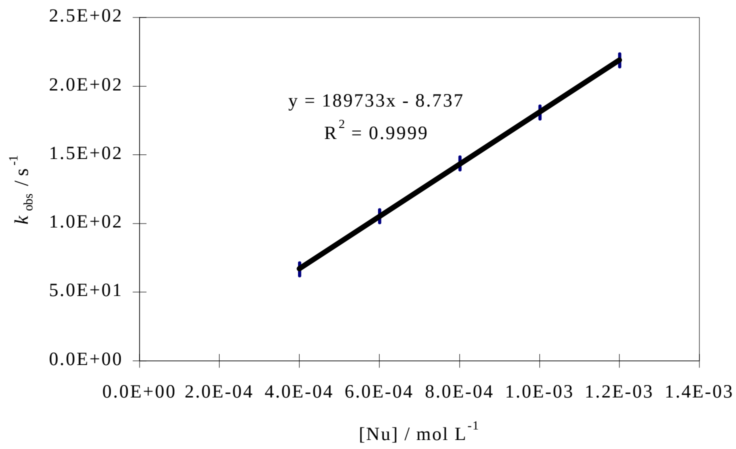
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
6.1	8.00×10^{-6}	4.00×10^{-4}	50.0	1.65×10^{-1}
6.2	8.00×10^{-6}	8.00×10^{-4}	100	3.47×10^{-1}
6.3	8.00×10^{-6}	1.20×10^{-3}	150	5.28×10^{-1}
6.4	8.00×10^{-6}	1.60×10^{-3}	200	6.97×10^{-1}
6.5	8.00×10^{-6}	2.00×10^{-3}	250	8.70×10^{-1}



$k_2 = 4.40 \times 10^2\ M^{-1}\ s^{-1}$

$(mfa)_2CH^+$ + 1-butoxy-1-(trimethylsiloxy)ethene (20 °C, CH_2Cl_2, stopped-flow, detection at 593 nm)

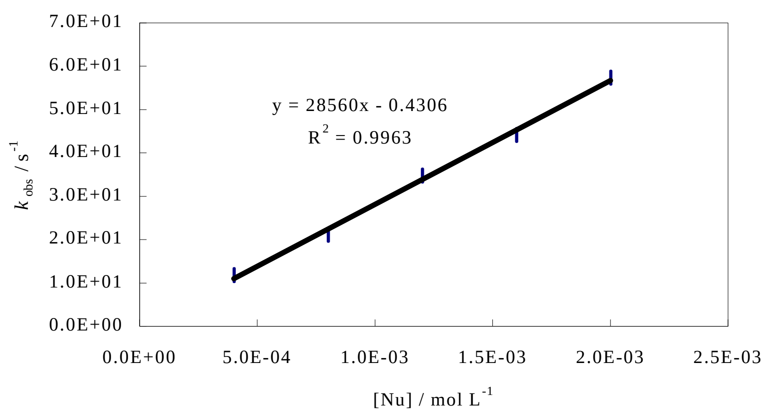
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
7.1	6.30×10^{-6}	4.00×10^{-4}	63.5	6.67×10^{1}
7.2	6.30×10^{-6}	6.00×10^{-4}	95.2	1.05×10^{2}
7.3	6.30×10^{-6}	8.00×10^{-4}	127	1.44×10^{2}
7.4	6.30×10^{-6}	1.00×10^{-3}	159	1.81×10^{2}
7.5	6.30×10^{-6}	1.20×10^{-3}	190	2.19×10^{2}



$k_2 = 1.90 \times 10^{5}\ M^{-1}\ s^{-1}$

$(dpa)_2CH^+$ + 1-butoxy-1-(trimethylsiloxy)ethene (20 °C, CH_2Cl_2, stopped-flow, detection at 672 nm)

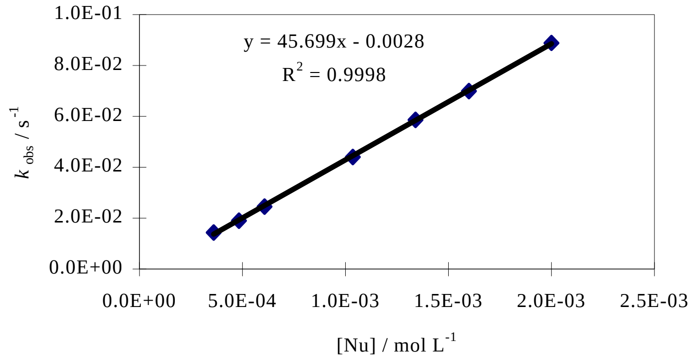
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
8.1	7.73×10^{-6}	4.00×10^{-4}	51.7	1.18×10^{1}
8.2	7.73×10^{-6}	8.00×10^{-4}	103	2.11×10^{1}
8.3	7.73×10^{-6}	1.20×10^{-3}	155	3.48×10^{1}
8.4	7.73×10^{-6}	1.60×10^{-3}	207	4.42×10^{1}
8.5	7.73×10^{-6}	2.00×10^{-3}	259	5.74×10^{1}



$k_2 = 2.86 \times 10^{4}\ M^{-1}\ s^{-1}$

$(thq)_2CH^+$ + 1-butoxy-1-(trimethylsiloxy)ethene (20 °C, CH_2Cl_2, J&M instrument for runs 9.1–9.5 and stopped-flow for runs 9.6–9.7, detection at 628 nm)

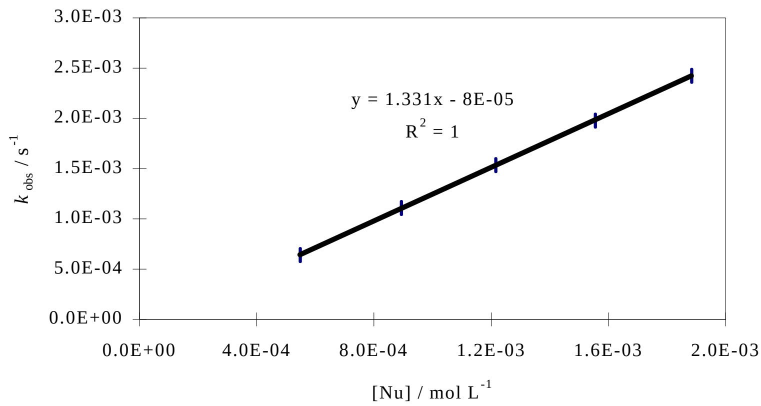
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
9.1	2.37×10^{-5}	3.61×10^{-4}	15.2	1.44×10^{-2}
9.2	2.38×10^{-5}	4.83×10^{-4}	20.3	1.92×10^{-2}
9.3	2.40×10^{-5}	6.07×10^{-4}	25.3	2.46×10^{-2}
9.4	2.22×10^{-5}	1.04×10^{-3}	46.7	4.40×10^{-2}
9.5	2.21×10^{-5}	1.34×10^{-3}	60.7	5.87×10^{-2}
9.6	2.55×10^{-5}	1.60×10^{-3}	62.7	6.97×10^{-2}
9.7	2.55×10^{-5}	2.00×10^{-3}	78.4	8.88×10^{-2}



$k_2 = 4.57 \times 10^1$ M^{-1} s^{-1}

$(lil)_2CH^+$ + 1-butoxy-1-(trimethylsiloxy)ethene in (20 °C, CH_2Cl_2, J&M instrument, detection at 639 nm)

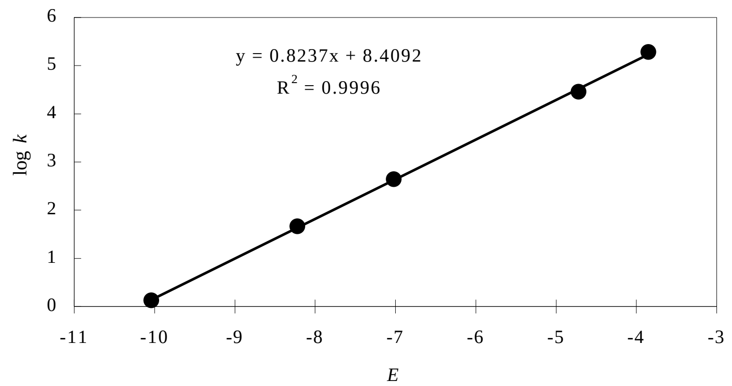
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
10.1	2.14×10^{-5}	5.47×10^{-4}	25.6	6.41×10^{-4}
10.2	2.15×10^{-5}	8.93×10^{-4}	41.5	1.11×10^{-3}
10.3	2.11×10^{-5}	1.22×10^{-3}	57.5	1.54×10^{-3}
10.4	2.12×10^{-5}	1.55×10^{-3}	73.5	1.98×10^{-3}
10.5	2.11×10^{-5}	1.88×10^{-3}	89.5	2.42×10^{-3}



$k_2 = 1.33$ M^{-1} s^{-1}

Determination of the *N* and *s*-parameters of 1-butoxy-1-(trimethylsiloxy)ethene (**1b**)

Reference electrophiles	*E* parameters	k_2(20 °C) / M^{-1} s^{-1}
$(mfa)_2CH^+$	–3.85	1.90×10^5
$(dpa)_2CH^+$	–4.72	2.86×10^4
$(dma)_2CH^+$	–7.02	4.40×10^2
$(thq)_2CH^+$	–8.22	4.57×10^1
$(lil)_2CH^+$	–10.04	1.33×10^0



N(**1b**) = 10.21

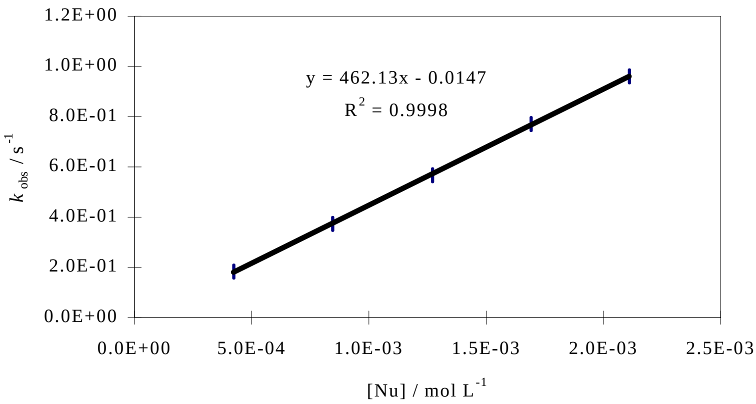
s(**1b**) = 0.82

3. Kinetics of the reactions of 1-butoxy-1-(*tert*-butyldimethylsiloxy)ethene (1c) with benzhydrylium ions

$(dma)_2CH^+$ BF_4^- (**2d**) (1.4 mg, 4.12 × 10^{-6} mol) was dissolved in 2.0 mL of CH_2Cl_2 (c = 2.06 × 10^{-3} M). 0.20 mL of this solution was diluted to 5.0 mL with CH_2Cl_2 (c = 8.23 × 10^{-5} M). 1-Butoxy-1-(*tert*-butyldimethylsilyloxy)ethene (**1c**) (133.4 mg, 0.579 mmol) was dissolved in 5.0 mL of CH_2Cl_2 (c = 0.116 M). 40.0 μL of this stock solution was diluted to 10.0 mL with CH_2Cl_2 (c = 4.64 × 10^{-4} M). In the stopped-flow instrument, the electrophile solution was mixed with the 10-fold volume of nucleophile solution to give the concentrations listed in the Tables. The course of the reactions was followed at 613 nm. A plot of k_{obs} versus concentration of [Nu] yielded a straight line, the slope of which corresponds to the second order rate constant (Run 11.1).

$(dma)_2CH^+$ + 1-butoxy-1-(*tert*-butyldimethylsiloxy)ethene (20 °C, CH_2Cl_2, stopped-flow, detection at 613 nm)

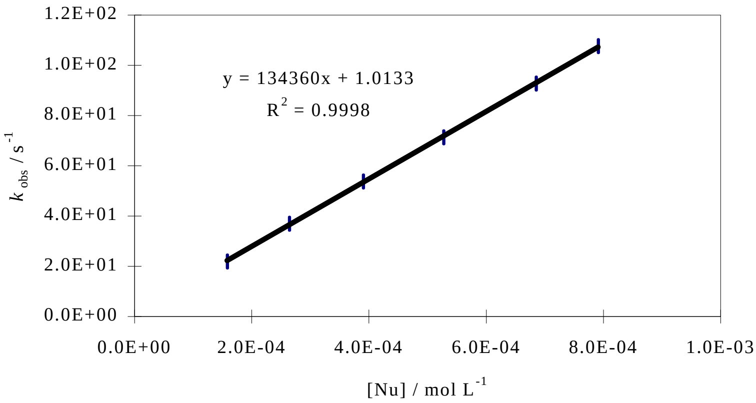
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
11.1	7.48 × 10^{-6}	4.22 × 10^{-4}	56.4	1.84 × 10^{-1}
11.2	7.48 × 10^{-6}	8.44 × 10^{-4}	113	3.73 × 10^{-1}
11.3	7.48 × 10^{-6}	1.27 × 10^{-3}	170	5.67 × 10^{-1}
11.4	7.48 × 10^{-6}	1.69 × 10^{-3}	226	7.70 × 10^{-1}
11.5	7.48 × 10^{-6}	2.11 × 10^{-3}	282	9.61 × 10^{-1}



k_2 = 4.62 × 10^2 M^{-1} s^{-1}

$(mfa)_2CH^+$ + 1-butoxy-1-(*tert*-butyldimethylsiloxy)ethene (20 °C, CH_2Cl_2, stopped-flow, detection at 593 nm)

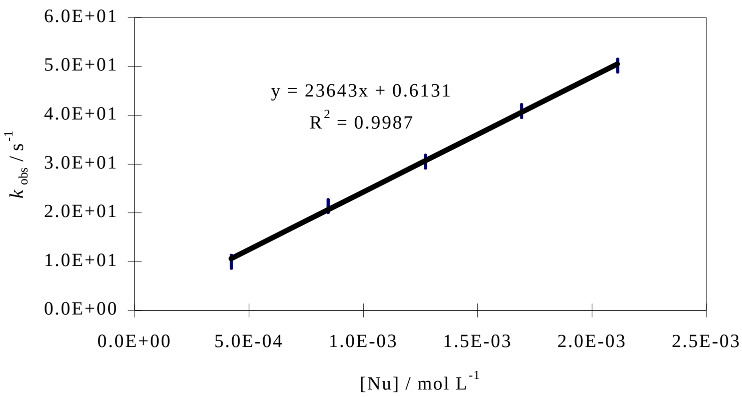
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
12.1	1.07×10^{-5}	1.58×10^{-4}	14.8	2.19×10^{1}
12.2	1.07×10^{-5}	2.64×10^{-4}	24.7	3.69×10^{1}
12.3	1.07×10^{-5}	3.90×10^{-4}	36.4	5.38×10^{1}
12.4	1.07×10^{-5}	5.27×10^{-4}	49.3	7.13×10^{1}
12.5	1.07×10^{-5}	6.85×10^{-4}	64.0	9.27×10^{1}
12.6	1.07×10^{-5}	7.91×10^{-4}	73.9	1.08×10^{2}



$k_2 = 1.34 \times 10^5$ M^{-1} s^{-1}

$(dpa)_2CH^+$ + 1-butoxy-1-(*tert*-butyldimethylsiloxy)ethene (20 °C, CH_2Cl_2, stopped-flow, detection at 672 nm)

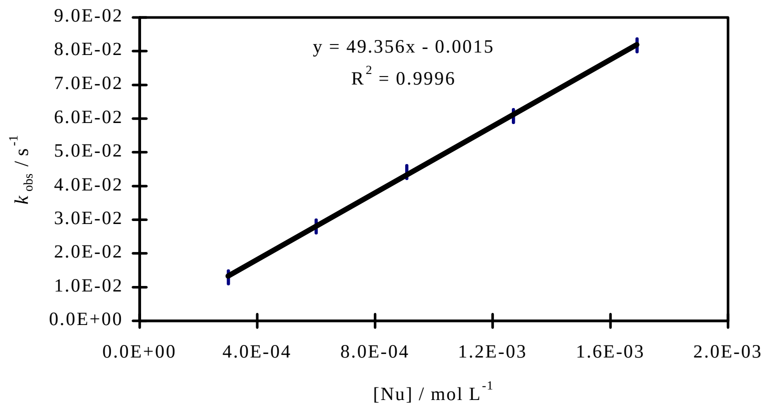
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
13.1	1.47×10^{-5}	4.22×10^{-4}	28.7	9.97
13.2	1.47×10^{-5}	8.44×10^{-4}	57.4	2.14×10^{1}
13.3	1.47×10^{-5}	1.27×10^{-3}	86.4	3.05×10^{1}
13.4	1.47×10^{-5}	1.69×10^{-3}	115	4.09×10^{1}
13.5	1.47×10^{-5}	2.11×10^{-3}	144	5.01×10^{1}



$k_2 = 2.36 \times 10^4$ M^{-1} s^{-1}

$(thq)_2CH^+$ + 1-butoxy-1-(*tert*-butyldimethylsiloxy)ethene (20 °C, CH_2Cl_2, J&M instrument for runs 14.1–14.3 and stopped-flow for runs 14.4–14.5, detection at 628 nm)

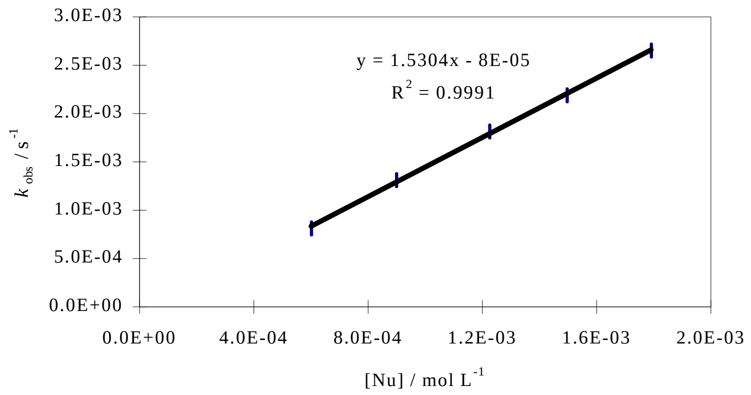
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
14.1	2.32×10^{-5}	3.01×10^{-4}	13.0	1.29×10^{-2}
14.2	2.31×10^{-5}	5.98×10^{-4}	25.9	2.80×10^{-2}
14.3	2.33×10^{-5}	9.07×10^{-4}	38.9	4.41×10^{-2}
14.4	1.67×10^{-5}	1.27×10^{-3}	76.0	6.08×10^{-2}
14.5	1.67×10^{-5}	1.69×10^{-3}	101	8.18×10^{-2}



$k_2 = 4.94 \times 10^1$ M^{-1} s^{-1}

$(lil)_2CH^+$ + 1-butoxy-1-(*tert*-butyldimethylsiloxy)ethene (20 °C, CH_2Cl_2, J&M instrument, detection at 639 nm)

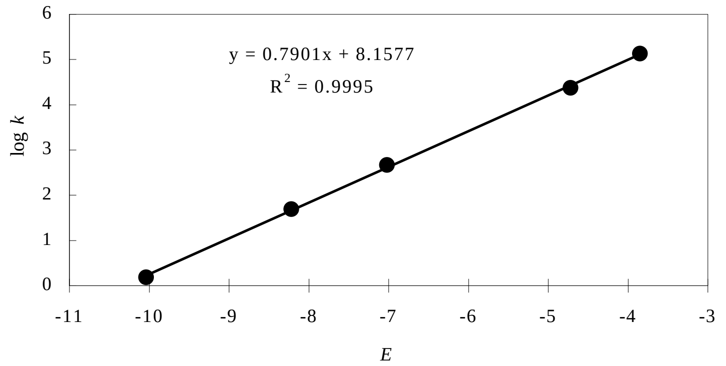
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
15.1	1.36×10^{-5}	6.00×10^{-4}	44.3	8.12×10^{-4}
15.2	1.35×10^{-5}	8.98×10^{-4}	66.4	1.31×10^{-3}
15.3	1.38×10^{-5}	1.23×10^{-3}	88.6	1.82×10^{-3}
15.4	1.35×10^{-5}	1.50×10^{-3}	111	2.19×10^{-3}
15.5	1.35×10^{-5}	1.79×10^{-3}	133	2.65×10^{-3}



$k_2 = 1.53$ M^{-1} s^{-1}

Determination of the *N* and *s*-parameters of 1-butoxy-1-(*tert*-butyldimethylsiloxy)ethene (**1c**)

Reference electrophiles	*E* parameters	k_2(20 °C) / M^{-1} s^{-1}
$(mfa)_2CH^+$	–3.85	1.34×10^5
$(dpa)_2CH^+$	–4.72	2.36×10^4
$(dma)_2CH^+$	–7.02	4.62×10^2
$(thq)_2CH^+$	–8.22	4.94×10^1
$(lil)_2CH^+$	–10.04	1.53×10^0



N(**1c**) = 10.32

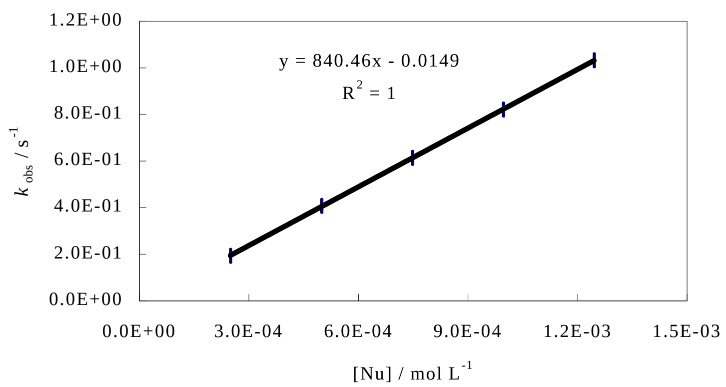
s(**1c**) = 0.79

4. Kinetics of the reactions of 1,1-bis(trimethylsiloxy)propene (1d) with benzhydrylium ions

$(dma)_2CH^+ BF_4^-$ (**2d**) (2.2 mg, 6.47×10^{-6} mol) was dissolved in 2.0 mL of CH_2Cl_2 ($c = 3.23 \times 10^{-3}$ M). 70.0 μL of this solution was diluted to 5.0 mL with CH_2Cl_2 ($c = 4.52 \times 10^{-5}$ M). 1,1-Bis(trimethylsilyloxy)propene (**1d**) (149.9 mg, 0.686 mmol) was dissolved in 5.0 mL of CH_2Cl_2 ($c = 0.137$ M). 20.0 μL of this stock solution was diluted to 10.0 mL with CH_2Cl_2 ($c = 2.74 \times 10^{-4}$ M). In the stopped-flow instrument, the electrophile solution was mixed with the 10-fold volume of nucleophile solution to give the concentrations listed in the Tables. The course of the reactions was followed at 613 nm. A plot of k_{obs} versus concentration of [Nu] yielded a straight line, the slope of which corresponds to the second order rate constant (Run 16.1).

$(dma)_2CH^+$ + 1,1-bis(trimethylsiloxy)propene (20 °C, CH_2Cl_2, stopped-flow, detection at 613 nm)

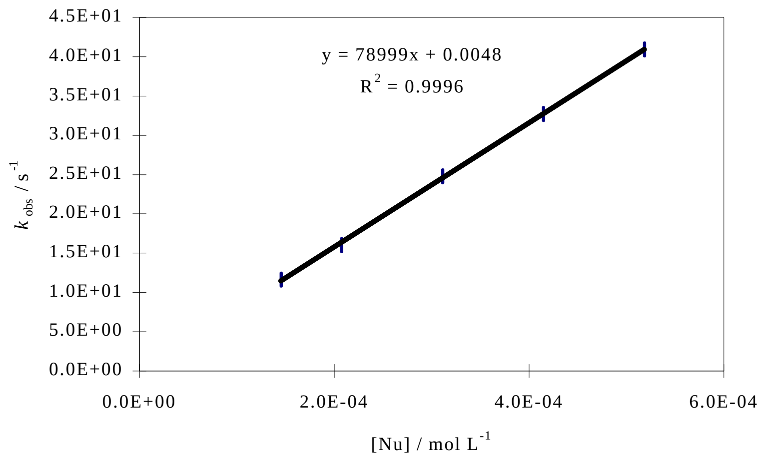
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
16.1	4.11×10^{-6}	2.49×10^{-4}	60.6	1.93×10^{-1}
16.2	4.11×10^{-6}	4.98×10^{-4}	121	4.07×10^{-1}
16.3	4.11×10^{-6}	7.47×10^{-4}	182	6.13×10^{-1}
16.4	4.11×10^{-6}	9.96×10^{-4}	242	8.20×10^{-1}
16.5	4.11×10^{-6}	1.25×10^{-3}	303	1.03



$k_2 = 8.40 \times 10^2$ M^{-1} s^{-1}

$(dpa)_2CH^+$ + 1,1-bis(trimethylsiloxy)propene (20 °C, CH_2Cl_2, stopped-flow, detection at 672 nm)

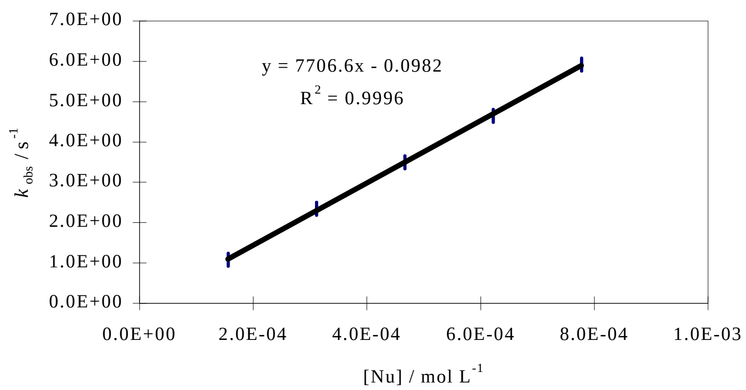
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
17.1	1.00×10^{-5}	1.45×10^{-4}	14.4	1.16×10^{1}
17.2	1.00×10^{-5}	2.07×10^{-4}	20.6	1.60×10^{1}
17.3	1.00×10^{-5}	3.11×10^{-4}	31.0	2.48×10^{1}
17.4	1.00×10^{-5}	4.15×10^{-4}	41.3	3.27×10^{1}
17.5	1.00×10^{-5}	5.18×10^{-4}	51.6	4.09×10^{1}



$k_2 = 7.90 \times 10^4$ M^{-1} s^{-1}

$(mpa)_2CH^+$ + 1,1-bis(trimethylsiloxy)propene (20 °C, CH_2Cl_2, stopped-flow, detection at 622 nm)

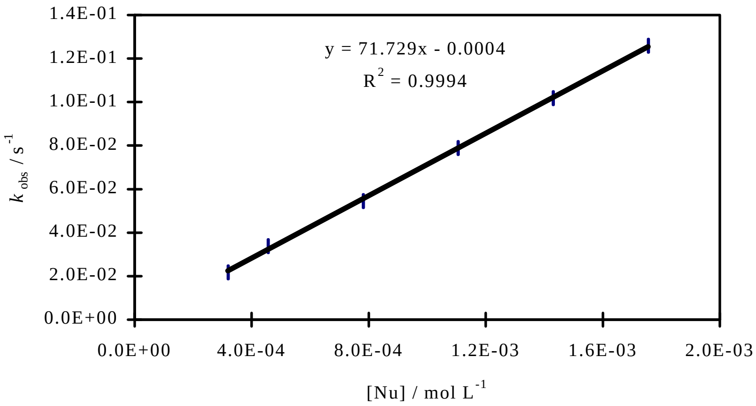
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
18.1	7.82×10^{-6}	1.55×10^{-4}	19.9	1.08
18.2	7.82×10^{-6}	3.11×10^{-4}	39.8	2.34
18.3	7.82×10^{-6}	4.66×10^{-4}	59.7	3.49
18.4	7.82×10^{-6}	6.22×10^{-4}	79.5	4.65
18.5	7.82×10^{-6}	7.77×10^{-4}	99.4	5.92



$k_2 = 7.71 \times 10^3$ M^{-1} s^{-1}

$(thq)_2CH^+$ + 1,1-bis(trimethylsiloxy)propene (20 °C, CH_2Cl_2, J&M instrument for run 19.1 and stopped-flow for runs 19.2–19.6, detection at 628 nm)

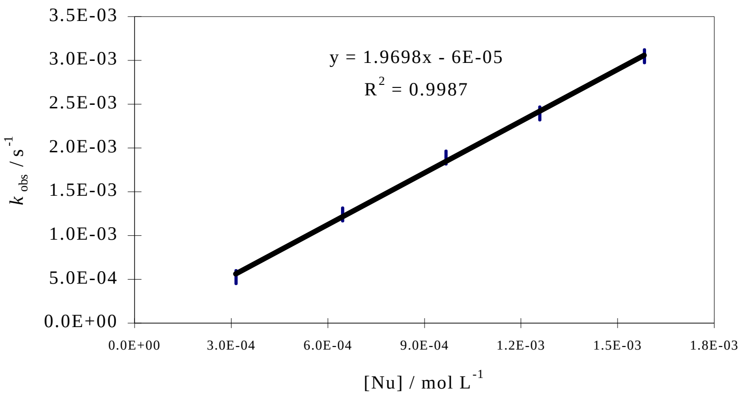
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
19.1	1.90×10^{-5}	3.18×10^{-4}	16.7	2.17×10^{-2}
19.2	9.33×10^{-6}	4.55×10^{-4}	48.8	3.38×10^{-2}
19.3	9.33×10^{-6}	7.80×10^{-4}	83.6	5.44×10^{-2}
19.4	9.33×10^{-6}	1.11×10^{-3}	118	7.89×10^{-2}
19.5	9.33×10^{-6}	1.43×10^{-3}	153	1.02×10^{-1}
19.6	9.33×10^{-6}	1.76×10^{-3}	188	1.26×10^{-1}



$k_2 = 7.17 \times 10^1$ M^{-1} s^{-1}

$(lil)_2CH^+$ + 1,1-bis(trimethylsiloxy)propene (20 °C, CH_2Cl_2, J & M instrument, detection at 639 nm)

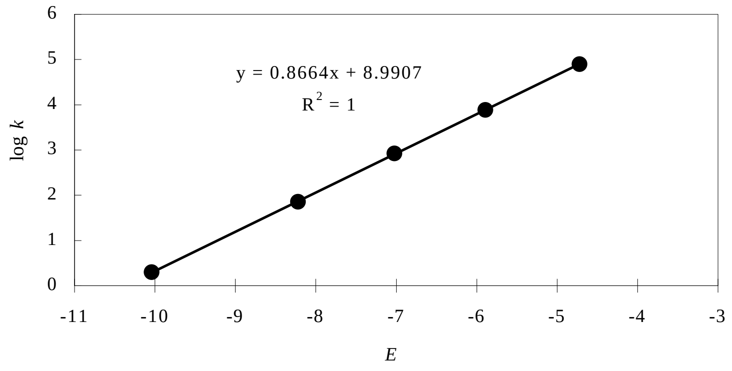
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
20.1	9.57×10^{-6}	3.14×10^{-4}	32.8	5.25×10^{-4}
20.2	9.85×10^{-6}	6.45×10^{-4}	65.5	1.24×10^{-3}
20.3	9.82×10^{-6}	9.66×10^{-4}	98.3	1.89×10^{-3}
20.4	9.59×10^{-6}	1.26×10^{-3}	131	2.40×10^{-3}
20.5	9.65×10^{-6}	1.58×10^{-3}	164	3.05×10^{-3}



$k_2 = 1.97$ M^{-1} s^{-1}

Determination of the *N* and *s*-parameters of 1,1-bis(trimethylsiloxy)propene (**1d**)

Reference electrophiles	*E* parameters	k_2(20 °C) / M^{-1} s^{-1}
$(dpa)_2CH^+$	–4.72	7.90×10^4
$(mpa)_2CH^+$	–5.89	7.71×10^3
$(dma)_2CH^+$	–7.02	8.40×10^2
$(thq)_2CH^+$	–8.22	7.17×10^1
$(lil)_2CH^+$	–10.04	1.97×10^0



N(**1d**) = 10.38

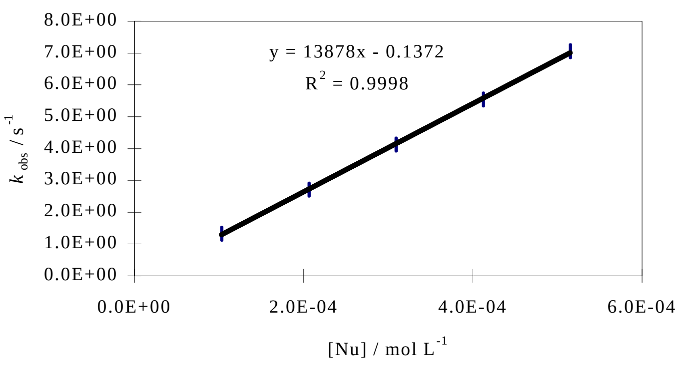
s(**1d**) = 0.87

5. Kinetics of the reactions of 3-methyl-2-(trimethylsiloxy)-4.5-dihydrofuran (1e) with benzhydrylium ions

$(dma)_2CH^+ BF_4^-$ (**2d**) (3.5 mg, 1.03×10^{-5} mol) was dissolved in 1.0 mL of CH_2Cl_2 (c = 1.03 × 10^{-2} M). 15.0 μL of this solution was diluted to 25.0 mL with CH_2Cl_2 ($c = 6.18 \times 10^{-6}$ M). 3-Methyl-2-(trimethysilyloxy)-4,5-dihydrofuran (**1e**) (88.5 mg, 0.514 mmol) was dissolved in 5.0 mL of CH_2Cl_2 (c = 0.103 M). 20.0 μL of this stock solution was diluted to 10.0 mL with CH_2Cl_2 ($c = 2.06 \times 10^{-4}$ M). In the stopped-flow instrument, the equal volumes of the electrophile and the nucleophile solutions were mixed to give the concentrations listed in the Tables. The course of the reactions was followed at 613 nm. A plot of k_{obs} versus concentration of [Nu] yielded a straight line, the slope of which corresponds to the second order rate constant (Run 21.1).

$(dma)_2CH^+$ + 3-methyl-2-(trimethysiloxy)-4,5-dihydrofuran (20 °C, CH_2Cl_2, stopped-flow, detection at 613 nm)

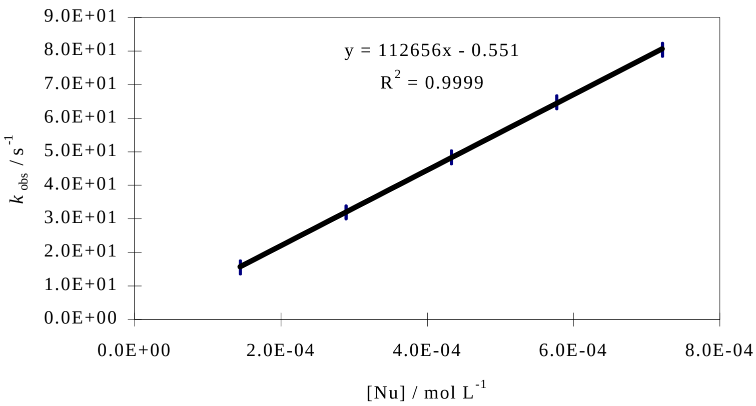
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
21.1	3.09×10^{-6}	1.03×10^{-4}	33.3	1.32
21.2	3.09×10^{-6}	2.06×10^{-4}	66.7	2.71
21.3	3.09×10^{-6}	3.09×10^{-4}	100	4.13
21.4	3.09×10^{-6}	4.12×10^{-4}	133	5.54
21.5	3.09×10^{-6}	5.15×10^{-4}	167	7.05



$k_2 = 1.39 \times 10^4$ M^{-1} s^{-1}

$(mpa)_2CH^+$ + 3-methyl-2-(trimethysiloxy)-4,5-dihydrofuran (20 °C, CH_2Cl_2, stopped-flow, detection at 622 nm)

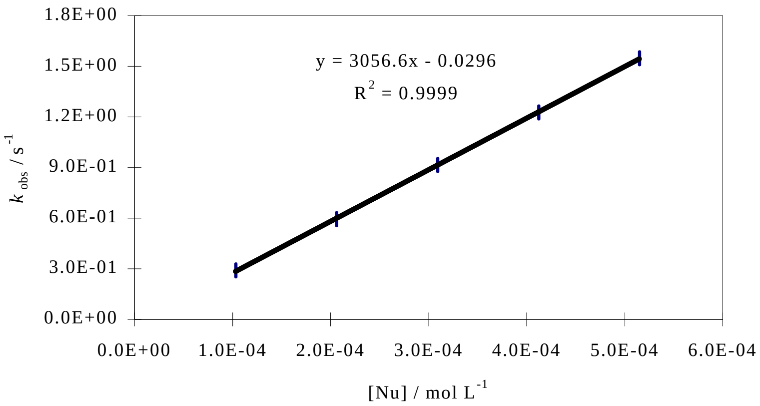
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
22.1	7.11×10^{-6}	1.44×10^{-4}	20.3	1.55×10^{1}
22.2	7.11×10^{-6}	2.88×10^{-4}	40.6	3.20×10^{1}
22.3	7.11×10^{-6}	4.33×10^{-4}	60.8	4.83×10^{1}
22.4	7.11×10^{-6}	5.77×10^{-4}	81.1	6.47×10^{1}
22.5	7.11×10^{-6}	7.21×10^{-4}	101	8.04×10^{1}



$k_2 = 1.13 \times 10^{5}$ M^{-1} s^{-1}

$(pyr)_2CH^+$ + 3-methyl-2-(trimethysiloxy)-4,5-dihydrofuran (20 °C, CH_2Cl_2, stopped-flow, detection at 620 nm)

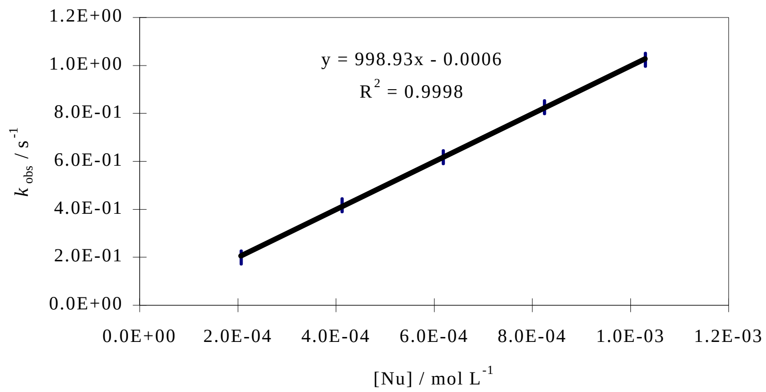
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
23.1	4.43×10^{-6}	1.03×10^{-4}	23.2	2.90×10^{-1}
23.2	4.43×10^{-6}	2.06×10^{-4}	46.5	5.95×10^{-1}
23.3	4.43×10^{-6}	3.09×10^{-4}	69.7	9.15×10^{-1}
23.4	4.43×10^{-6}	4.12×10^{-4}	92.9	1.23
23.5	4.43×10^{-6}	5.15×10^{-4}	116	1.55



$k_2 = 3.06 \times 10^{3}$ M^{-1} s^{-1}

$(thq)_2CH^+$ + 3-methyl-2-(trimethysiloxy)-4,5-dihydrofuran (20 °C, CH_2Cl_2, stopped-flow, detection at 628 nm)

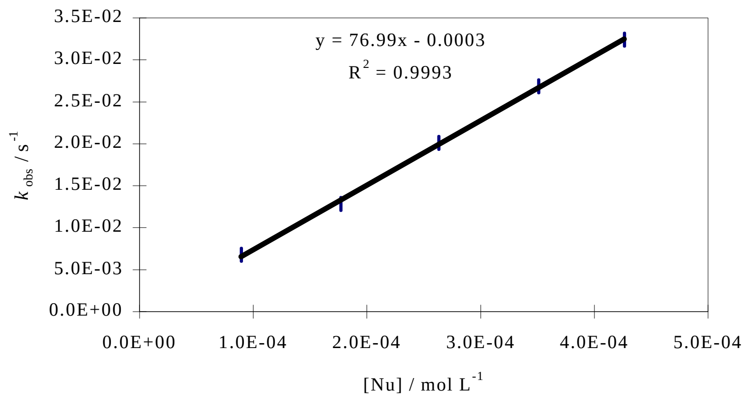
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
24.1	9.38×10^{-6}	2.06×10^{-4}	22.0	2.00×10^{-1}
24.2	9.38×10^{-6}	4.12×10^{-4}	43.9	4.16×10^{-1}
24.3	9.38×10^{-6}	6.18×10^{-4}	65.9	6.18×10^{-1}
24.4	9.38×10^{-6}	8.24×10^{-4}	87.9	8.26×10^{-1}
24.5	9.38×10^{-6}	1.03×10^{-3}	110	1.02



$k_2 = 9.99 \times 10^2$ M^{-1} s^{-1}

$(jul)_2CH^+$ + 3-methyl-2-(trimethysiloxy)-4,5-dihydrofuran (20 °C, CH_2Cl_2, J&M instrument, detection at 642 nm)

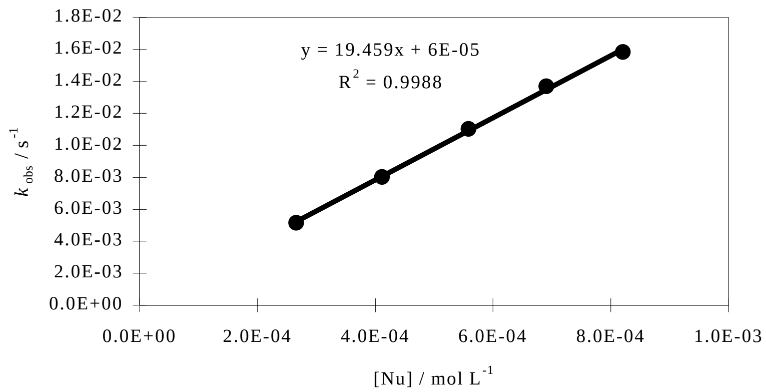
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
25.1	4.55×10^{-6}	8.93×10^{-5}	19.6	6.76×10^{-3}
25.2	4.51×10^{-6}	1.77×10^{-4}	39.2	1.29×10^{-2}
25.3	4.48×10^{-6}	2.63×10^{-4}	58.8	2.01×10^{-2}
25.4	4.47×10^{-6}	3.51×10^{-4}	78.4	2.69×10^{-2}
25.5	4.35×10^{-6}	4.26×10^{-4}	98.0	3.24×10^{-2}



$k_2 = 7.70 \times 10^1$ M^{-1} s^{-1}

$(lil)_2CH^+$ + 3-methyl-2-(trimethysiloxy)-4,5-dihydrofuran (20 °C, CH_2Cl_2, J&M instrument, detection at 639 nm)

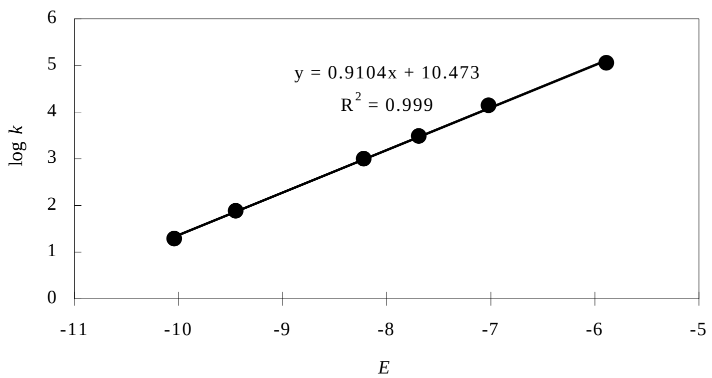
No.	[El] / M	[Nuc] / M	[Nu] / [El]	k_{obs} / s^{-1}
26.1	6.70×10^{-6}	2.66×10^{-4}	39.7	5.16×10^{-3}
26.2	6.92×10^{-6}	4.12×10^{-4}	59.5	8.03×10^{-3}
26.3	7.04×10^{-6}	5.58×10^{-4}	79.3	1.10×10^{-2}
26.4	6.97×10^{-6}	6.91×10^{-4}	99.1	1.37×10^{-2}
26.5	6.90×10^{-6}	8.21×10^{-4}	119	1.58×10^{-2}



$k_2 = 1.95 \times 10^1\ M^{-1}\ s^{-1}$

Determination of the *N* and *s*-parameters of 3-methyl-2-(trimethysiloxy)-4,5-dihydrofuran (**1e**)

Reference electrophiles	*E* parameters	k_2(20 °C) / $M^{-1}\ s^{-1}$
$(mpa)_2CH^+$	–5.89	1.13×10^5
$(dma)_2CH^+$	–7.02	1.39×10^4
$(pyr)_2CH^+$	–7.69	3.06×10^3
$(thq)_2CH^+$	–8.22	9.99×10^2
$(jul)_2CH^+$	–9.45	7.70×10^1
$(lil)_2CH^+$	–10.04	1.95×10^1



N (**1e**) = 11.50

s (**1e**) = 0.91