Nitro and Nitroso Metathesis Reactions with Monomeric Zirconium Imido Complexes

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Supporting Information

I. Experimental

General Methods.

All manipulations were carried out under an inert atmosphere, using an N_2 glove box or standard Schlenk line techniques. Solvents were degassed using three freeze-pump-thaw cycles and dried over 3 Å activated molecular sieves (benzene-d_6, toluene-d_8), passed through an activated alumina column and sparged with nitrogen (benzene, hexane),[1] or distilled from purple Na/benzophenone ketyl (THF), prior to use. Bis-cyclopentadienyl(*t*-butylimido) zirconium complex (**1**),[2] was synthesized according to previously published procedures. Chlorotrimethylsilane was degassed using three freeze-pump-thaw cycles and vacuum transferred from CaH_2, and *p-N,N*-dimethylaminonitrosobenzene and nitrosobenzene were recrystallized from toluene prior to use.

All ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on 300 and 500 MHz spectrometers. ^{1}H NMR and $^{13}C\{^1H\}$ NMR chemical shifts (δ) are reported in parts per million (ppm) downfield of tetramethysilane and referenced to the residual protiated solvent peak. NMR yields were measured by integration of product resonances in single-scan ^{1}H NMR spectra, relative to integration of THF resonances.

Ambient Temperature ^{1}H NMR Monitoring of Formation of *tert*-butylazoxytoluene (2). A solution of imido complex **1** (15 mg, 0.041 mmol) in C_6D_6 (0.2 mL) was added to a solution of TMSCl (18 mg, 0.16 mmol) and *p*-nitrotoluene (5.6 mg, 0.041 mmol) in C_6D_6 (0.3 mL). The solution immediately turned dark brown. A spectrum obtained after 30 min showed *cis*-**2** : *trans*-**2** = 1.0 : 0.13; after 8 h, isomerization to *trans*-**2** was complete (45%). The yield of **4** was constant with time (80%). *trans*-**6** was identified as a minor byproduct of the reaction by GC-MS. Unreacted *tert*-butylazoxytoluene was present, though no imido **1** remained. An independently synthesized sample of *trans-tert*-butylazoxytoluene[3] exhibited identical GC-MS, ^{1}H NMR, and $^{13}C\{^1H\}$ spectra to that of *trans*-**2**. *cis*-**2**: ^{1}H NMR (300 MHz, C_6D_6) δ 6.78 (d, J = 8.1 Hz, 2H), 6.55 (d, J = 8.1 Hz, 2H), 1.85 (s, 3H), 0.99 (s, 9H). *trans*-**2**: ^{1}H NMR (300 MHz, C_6D_6) δ 8.18 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 9.0 Hz, 2H), 2.01 (s, 3H), 1.51 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 145.6, 130.0, 122.7, 59.1, 51.5, 26.3, 21.5. **4**: ^{1}H NMR (300 MHz, C_6D_6) δ 5.93 (s, 10H), -0.04 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 114.0, 1.81.

***t*-Butylazoxy-*t*-butane (6).** A solution of imido complex **1** (200 mg, 0.548 mmol) in C_6H_6 (1 mL) was added to a solution of TMSCl (230 mg, 2.1 mmol) and 2-methyl-2-nitropropane (53.8 mg, 0.522 mmol) in C_6H_6 (1 mL). The solution darkened slightly upon mixing. After 2 d, the crude reaction was purified by silica gel column chromatography (1:60 ether:pentane, faint UV absorbance used for visualization). Column fractions were kept cold (no water bath) during rotary evaporation of the solvent, due to the volatility of **6**. Removal of solvent afforded 20 mg (24%) of *trans*-**6** as a clear oil. Isolated yield was low because of the volatility of **6**. ^{1}H NMR (300 MHz, C_6D_6) δ 1.40 (s, 9H), 1.34 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 57.8, 33.6, 28.2, 24.1. Anal. Calcd for $C_8H_{18}N_2O$: C, 60.72; H, 11.47; N, 17.70. Found: C, 60.38; H, 11.83; N, 17.31.

Ambient Temperature ^{1}H NMR Monitoring of Formation of *t*-butylazoxy-*t*-butane (6). A solution of imido complex **1** (10 mg, 0.027 mmol) in C_6D_6 (0.2 mL) was added to a solution of TMSCl (12 mg, 0.11 mmol) and 2-methyl-2-nitropropane (3.3 mg, 0.032 mmol) in C_6D_6 (0.3 mL). No color change was observed. The reaction was monitored by ^{1}H NMR spectroscopy, and was complete after 24 h to form complex **4** and *trans*-**6** (95%). No *cis*-**6** was observed.

***tert*-Butylazobenzene (7a).** A solution of imido complex **1** (350 mg, 0.959 mmol) in C_6H_6 (2 mL) was added to a solution of TMSCl (390 mg, 3.7 mmol) and nitrosobenzene (97.7 mg, 0.913 mmol) in C_6D_6 (1 mL). The solution turned dark brown immediately. After 15 h, the crude product was purified by silica gel column chromatography (100% pentane) to give 124 mg (84%) *trans*-**7a** as a yellow oil. ^{1}H NMR (300 MHz, C_6D_6) δ 7.83 (d, J = 7.2 Hz, 2H), 7.08 (m, 3H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 130.3, 129.1, 122.6, 67.7, 27.1. Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.27. Found: C, 73.97; H, 8.60; N, 17.27.

Ambient Temperature ^{1}H NMR Monitoring of Formation of *t*-butylazobenzene (7a). A solution of imido complex **1** (15 mg, 0.041 mmol) in C_6D_6 (0.2 mL) was added to a solution of TMSCl (18 mg, 0.16 mmol) and nitrosobenzene (4.4 mg, 0.041 mmol) in C_6D_6 (0.3 mL) in an NMR tube. The solution turned yellow immediately upon mixing. A ^{1}H NMR spectrum acquired after 1.5 h showed a ratio *trans*-**7a** : *cis*-**7a** equal to 0.40 : 1.00, and **4** (> 95%). A ^{1}H NMR spectrum acquired after 20 h showed complete isomerization to *trans*-**7a** (> 95%). *cis*-**7a**: ^{1}H NMR (300 MHz, C_6D_6) δ 6.94 (t, J = 7.8 Hz, 2H), 6.80 (t, J = 7.5 Hz, 1H), 6.48 (d, J = 7.5 Hz, 2H), 1.09 (s, 9H).

Low Temperature ^{1}H NMR Monitoring of Formation of *t*-butylazobenzene 7a. In an inert atmosphere glove box, an NMR tube was charged with a pale tan solution of imido complex **1** (15 mg, 0.041 mmol) and TMSCl (18 mg, 0.16 mmol) in toluene-d_8 (0.3 mL), and fitted with a Cajon adaptor. A 0.25-mL gas-tight syringe was charged with a green solution of nitrosobenzene in toluene-d_8 (0.2 mL), and the tip was protected from air by insertion into a plastic stopper. Both solutions were removed from the box. On a Schlenk line, the solution of **1** and TMSCl was cooled to −78 °C, and the solution of nitrosobenzene was layered on top. The NMR tube was flame sealed under vacuum, and kept at −78 °C until the next step.

The NMR tube was removed from the −78 °C bath, quickly shaken, and dropped into a pre-cooled (−60 °C) spectrometer probe. At that time, a ^{1}H NMR spectrum showed 60% conversion to *cis*-**7a** and complex **4**. The probe was gradually warmed to −30 °C, at which point additional *cis*-**7a** (no *trans*-**7a**) and complex **4** began to grow in. No intermediate was observed.

Ambient Temperature ^{1}H NMR Monitoring of Formation *p*-*N*,*N*-dimethylaminophenylazo-*t*-butane (7b). In an inert atmosphere glove box, an NMR tube was charged with a pale tan solution of imido complex **1** (10 mg, 0.027 mmol) and TMSCl (12 mg, 0.11 mmol) in C_6D_6 (0.4 mL), and capped with a septum. A 0.5-mL gas-tight syringe was charged with a green solution of *p*-*N*,*N*-dimethylaminonitrosobenzene

(4.8 mg, 0.032 mmol) in C_6D_6 (0.4 mL), and the tip was protected from air by insertion into a plastic stopper. The NMR tube and the syringe were removed from the box.

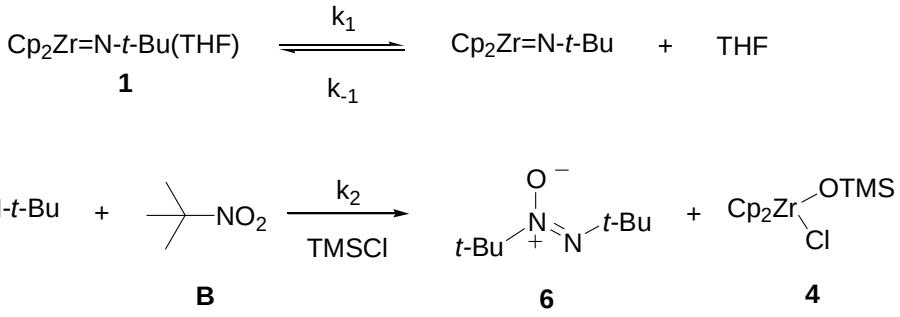
The solution of *p-N,N*-dimethylaminonitrosobenzene was injected into the NMR tube, which was shaken quickly to form a brown-green solution, and inserted into the NMR probe. A spectrum obtained after 4 min showed *cis*-**7b** : *trans*-**7b** = 86 : 14 and the presence of **4** (> 95%); after 8 min, *cis*-**7b** : *trans*-**7b** = 37 : 61; after 40 min, isomerization to *trans*-**7b** was complete (> 95%). *cis*-**7b**: ^{1}H NMR (300 MHz, C_6D_6) δ 6.58 (d, J = 9.0 Hz, 2H), 6.38 (d, J = 8.7 Hz, 2H), 2.44 (s, 6H), 1.23 (s, 9H). *trans*-**7b**: ^{1}H NMR (300 MHz, C_6D_6) δ 8.05 (d, J = 9.0 Hz, 2H), 6.48 (d, J = 9.0 Hz, 2H), 2.37 (s, 6H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 152.0, 143.7, 124.4, 111.8, 66.3, 39.8, 27.5. HRMS (EI) *m/z* calcd ($C_{12}H_{19}N_3$) 205.1579, found 205.1581 [M+].

Competition experiment between *p-N,N*-dimethylaminonitrosobenzene and nitrosobenzene. A solution of imido complex **1** (10 mg, 0.027 mmol) and TMSCl (12 mg, 0.11 mmol) in C_6D_6 (0.5 mL) was added dropwise to a rapidly stirred solution of nitrosobenzene (5.8 mg, 0.054 mmol) and *p-N,N*-dimethylaminonitrosobenzene (8.1 mg, 0.54 mmol) in C_6D_6 (0.5 mL). The solution turned dark green-brown immediately. A ^{1}H NMR spectrum obtained after 1.5 h showed **7b** : *cis*-**7a** + *trans*-**7a** = 69 : 31.

II. Kinetics Experiments.

Reaction of imido complex 1 with 2-methyl-2-nitropropane. Imido complex **1** (10.0 mg, 0.0274 mmol), 2-methyl-2-nitropropane (28.2 mg, 0.274 mmol), THF (22.2 μL, 0.274 mmol), chlorotrimethylsilane (12 mg, 0.11 mmol), and 1,4-dibromobenzene as an internal standard (12.9 mg, 0.0548 mmol) were dissolved in toluene-d_8, and transferred to a resealable J. Young NMR tube (total solution volume 0.595 mL). Product formation and starting material disappearance were monitored by ^{1}H NMR spectroscopy, and the probe temperature was calibrated with an ethylene glycol standard. The reaction exhibited clean pseudo first-order kinetics. We report rate constants k_{obs} which are independent of concentration of 2-methyl-2-nitropropane and THF, since these concentrations divide out when equal (see rate expression below). k_{obs} = 0.00043 s^{-1} (45.0 °C), k_{obs} = 0.00076 s^{-1} (56.0 °C), k_{obs} = 0.0016 s^{-1} (64.5 °C), k_{obs} = 0.0034 s^{-1} (74.5 °C). Experiments varying the concentration of THF, 2-methyl-2-nitropropane, or chlorotrimethylsilane revealed that the rate was zero order in [trapping agent] (chlorotrimethylsilane), inverse first order in [THF], and first order in [2-methyl-2-nitropropane], giving rise to the rate expression:

$$d[\mathbf{6}]/dt = d[\mathbf{4}]/dt = -d[\mathbf{1}]/dt = k_{obs}[\mathbf{1}] \qquad \text{where} \quad k_{obs} = k_1k_2[\mathbf{B}]/k_{-1}[THF]$$



Error in reproducibility was estimated to be ± ± 0.0001 s^{-1} at 64.5 °C based on standard deviation of data from a triplicate run. Errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from this estimation.

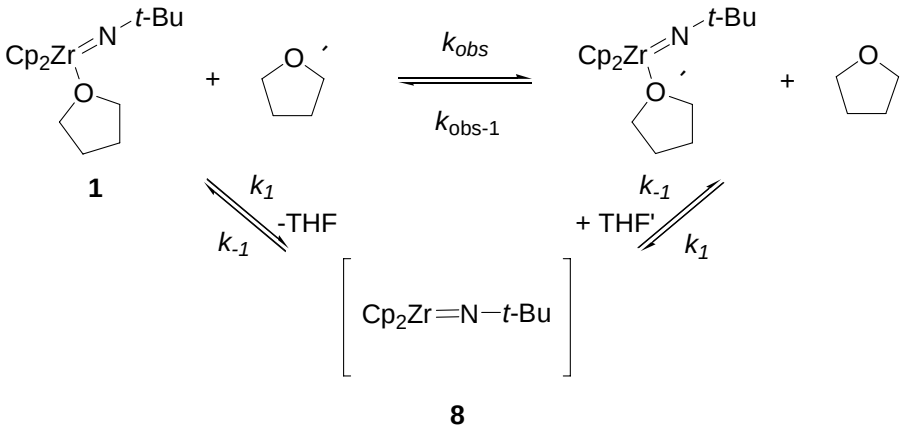
II. Kinetics Experiments continued.

Exchange between free and bound THF. Imido complex **1** (20.0 mg, 0.0548 mmol) and THF (4.4 μL, 0.0548 mmol) were dissolved in toluene-d_8, and transferred to a resealable J. Young NMR tube. A ^{1}H NMR spectrum obtained at ambient temperature showed distinct resonances for bound and free THF. The temperature was raised until each set of chemically equivalent THF resonances (separately) reached their respective coalescence point. Calibrating the probe temperature with an ethyleneglycol standard gave coalescence temperatures of 60.5 °C and 85.0 °C. Next, the sample was cooled to –10 °C and a spectrum at the ^{1}H NMR low-temperature limit was obtained.

The following equation allows for calculation of k_{obs} at coalescence:[4]

$$k_{obs} \approx \pi(\delta v)/2^{0.5}$$

were (δv) = the difference between the resonance frequencies (in Hz) of the bound and free THF at the low-temperature limit



Since **8** does not build up, k_{-1}[THF][**8**] >> k_1[**1**], and $k_{obs} \approx k_1$.

Sample Kinetics Data:

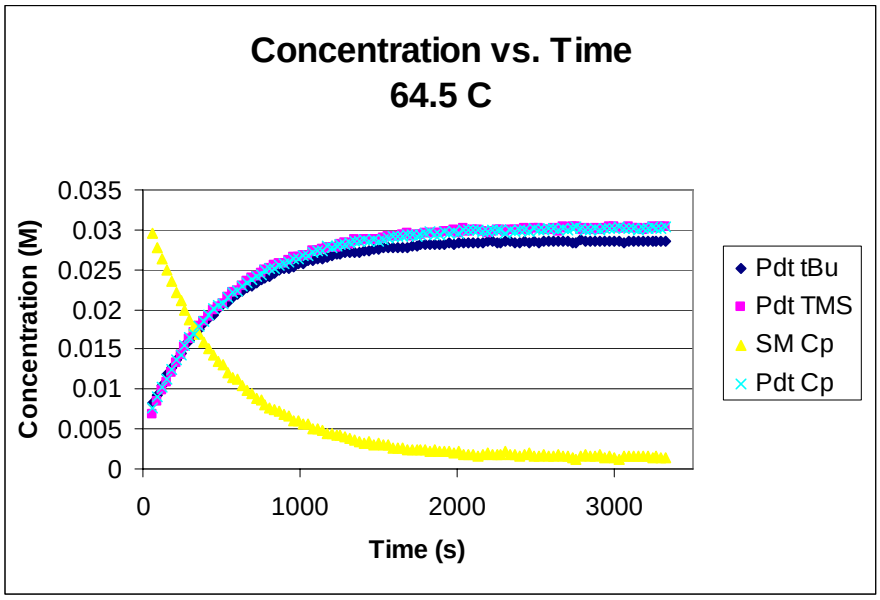


Figure S-1. [Product **4**], [Product **6**], and [Starting **1**] *v.* Time, at 64.5 ºC.

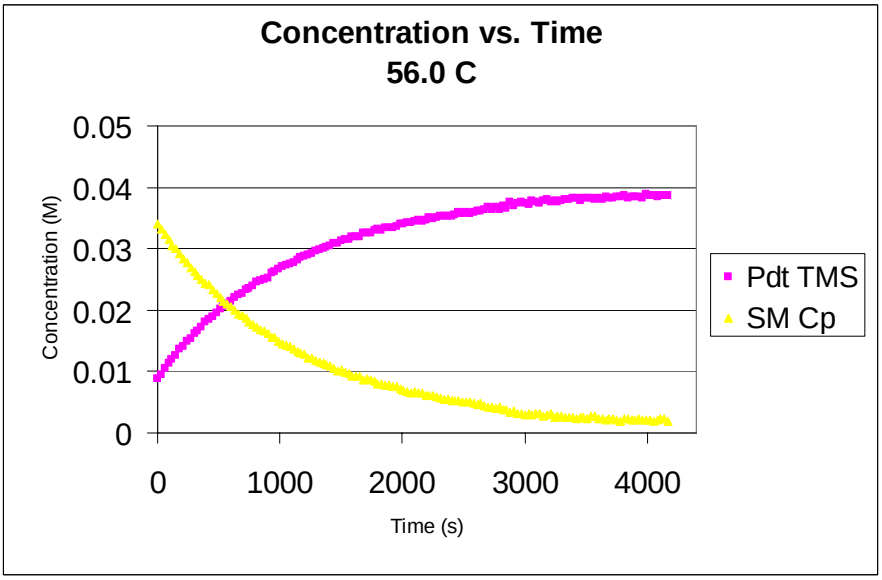


Figure S-2. [Product **4**] and [Starting **1**] *v.* Time, at 56.0 ºC.

Sample Kinetics Data Continued:

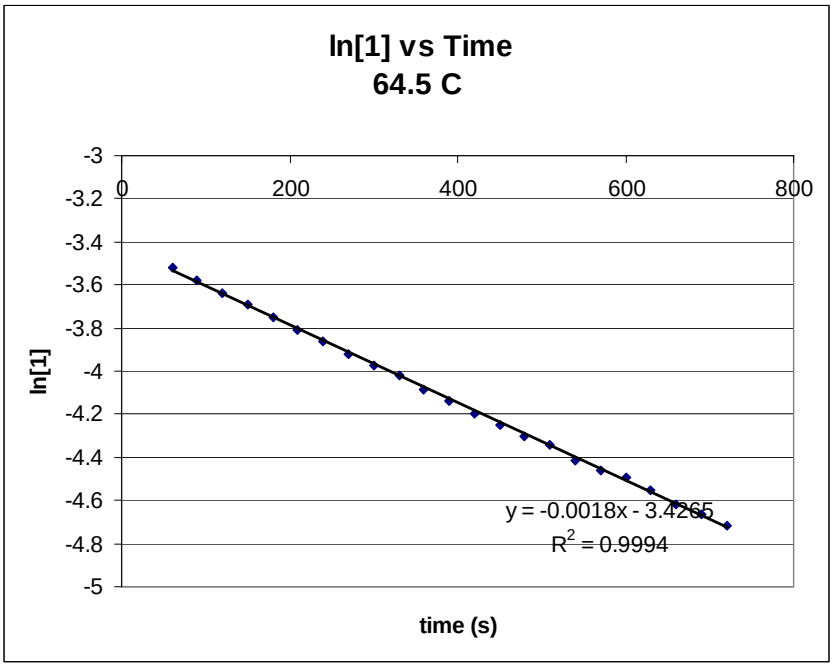


Figure S-3. ln[**1**] *v.* Time, at 64.5 ºC.

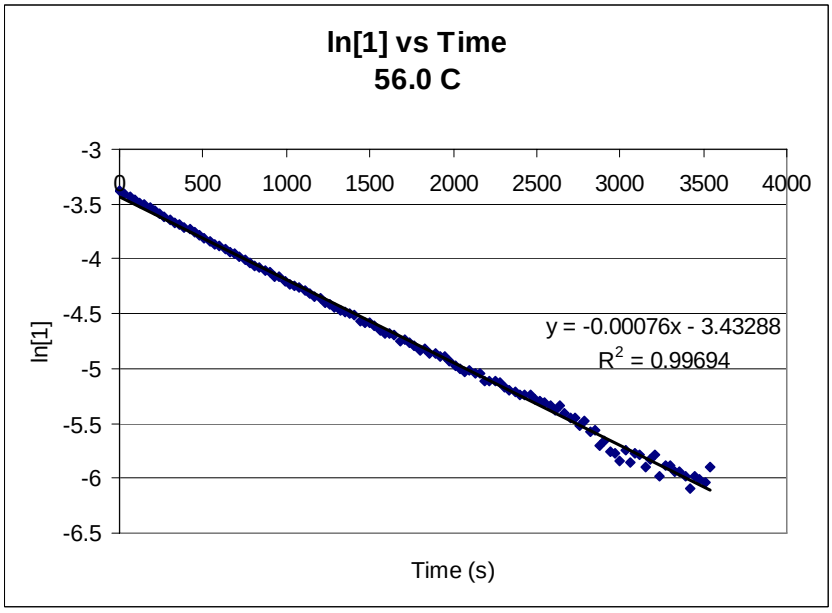


Figure S-4. ln[**1**] *v.* Time, at 56.0 ºC.

Sample Kinetics Data Continued:

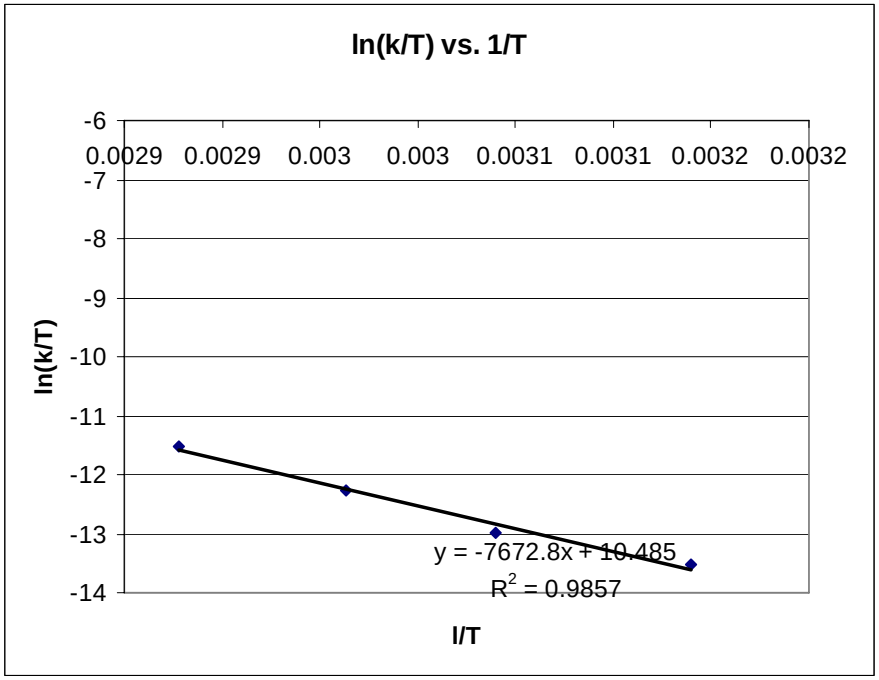


Figure S-5. ln(k/T) *v.* 1/(Temperature (K)).

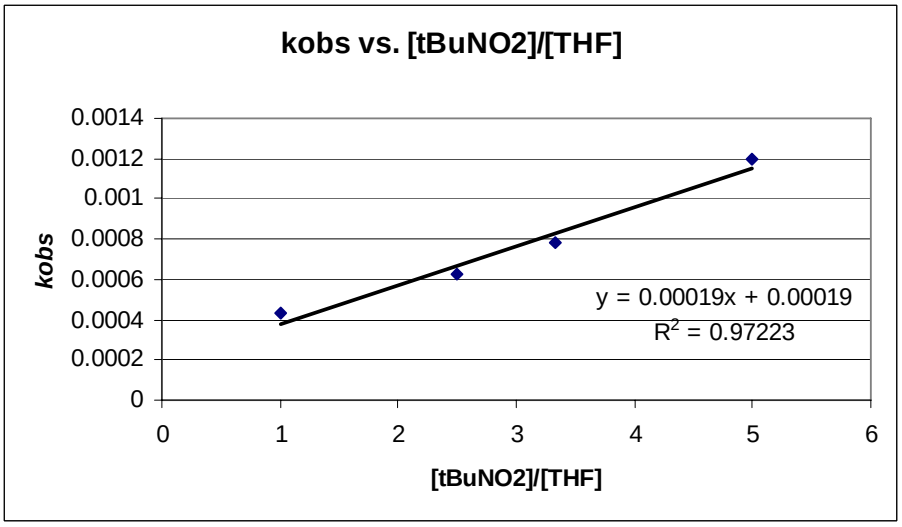


Figure S-6. k_{obs} *v.* [$tBuNO_2$]/[THF], showing inverse first order dependence of k_{obs} on [THF].

References:

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