



JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

J. Am. Chem. Soc., 1998, 120(30), 7635-7636, DOI:[10.1021/ja9808346](https://doi.org/10.1021/ja9808346)

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1998 American Chemical Society

Revised 5-27-98

Supporting information for:

**Reversible 1,2-Migration of Hydrogen between Platinum
and Silicon via Intermediate Silylene Complexes**

Gregory P. Mitchell and T. Don Tilley*

Department of Chemistry

University of California at Berkeley

Berkeley, California 94720-1460

Experimental Section

All manipulations were performed under an inert atmosphere using standard Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Diethyl ether, pentane, benzene, benzene- d_6 , and toluene- d_8 were distilled from sodium/benzophenone and stored under nitrogen. Dichloromethane, dichloromethane- d_2 , and MeCN were distilled from CaH_2 and degassed with two freeze-pump-thaw cycles prior to use. The compounds $\text{Pt}(\text{PEt}_3)_3$ (Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1988**, 28, 119) and $(\text{Et}_2\text{O})\text{LiB}(\text{C}_6\text{F}_5)_4$ (Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, 2, 245), were prepared according to known procedures. Trimethylsilyl trifluoromethanesulfonate, Bu_4NBr , MeMgBr (1.4 M in Et_2O), Bu_3SnD , pyrazine, AIBN, SiCl_4 , HSiCl_3 , and HS^tBu were purchased from Aldrich and used as received. Triethylamine was purchased from Aldrich and distilled prior to use. Elemental analyses were performed by Desert Microanalytical Laboratories or the microanalytical laboratory at the University of California, Berkeley. All IR samples were prepared as Nujol mulls on CsI plates unless otherwise indicated and all absorptions are reported in cm^{-1} . All NMR spectra were recorded at room temperature in dichloromethane- d_2 , unless otherwise noted.

$\text{HSi}(\text{S}^t\text{Bu})_3$. This procedure was originally developed by Daniel Straus and is modified from a procedure described by Grumbine (Grumbine, S. K. Ph.D. Thesis, University of

California, San Diego, 1993). To 100 mL of Et₂O was added HSiCl₃ (4.0 mL, 39.6 mmol) and HS^tBu (15.6 mL, 139 mmol). Four 5 mL portions of NEt₃ (19.3 mL, 139 mmol) were added, generating heat and a white precipitate. The reaction mixture was stirred for 12 h before it was filtered through a medium porosity frit. The precipitate was then extracted with Et₂O (2 x 50 mL). Solvent was removed under reduced pressure from the combined extractions and previously collected filtrate, leaving a waxy solid. Sublimation of this solid (0.001 torr, 120 °C) gave pure product. Yield 67 % (7.9 g). Anal. Calcd for C₁₂H₂₈S₃Si: C, 48.59; H, 9.51. Found: C, 48.47; H, 9.71. Mp 83-87 °C. ¹H NMR (benzene-*d*₆, 300 MHz): δ 1.47 (s, 27 H, ^tBu), 6.29 (s, 1 H, SiH). ¹³C{¹H} NMR (benzene-*d*₆, 125 MHz): δ 34.6 (s, ^tBu), 47.7 (s, ^tBu). IR: 2960 s, 2959 s, 2144 m, 1456 s, 1394 w, 1365 s, 1216 w, 1160 w, 771 s, 571 s, 507 w.

***cis*-(PEt₃)₂Pt(H)Si(S^tBu)₃.** To a solution of Pt(PEt₃)₃ (0.315 g, 0.573 mmol) in pentane (5 mL) was added a pentane (10 mL) solution of HSi(S^tBu)₃ (0.170 g, 0.573 mmol). The reaction mixture was stirred for 30 min, during which time a white precipitate formed. The solvent was removed under reduced pressure and the residue was washed once with pentane (5 mL). The remaining white powder was then crystallized from diethyl ether at -78 °C. Yield 75% (0.313 g). Anal. Calcd for C₂₄H₅₈S₃P₂PtSi: C, 39.60; H, 8.03. Found: C, 39.82; H, 8.30. Mp 153-157 °C. ¹H NMR (benzene-*d*₆, 300 MHz): δ -4.05 (dd, ²J_{HP_{cis}} = 20.4 Hz, ²J_{HP_{trans}} = 170 Hz, ¹J_{HP_t} = 820 Hz, 1 H, PtH), 0.87 (m, 18 H, PEt₃), 1.50 (m, 6 H, PEt₃), 1.87 (s, 27 H, ^tBu), 2.11 (m, 6 H, PEt₃). ¹³C{¹H} NMR (benzene-*d*₆, 125 MHz): δ 8.71 (d, ²J_{CP} = 28 Hz, PEt₃), 19.04 (d, ¹J_{CP} = 22 Hz, PEt₃), 21.95 (d, ¹J_{CP} = 21 Hz, PEt₃), 35.81 (s, ^tBu), 47.47 (s, ^tBu). ³¹P{¹H} NMR (benzene-*d*₆, 121.5 MHz): δ 16.00 (d with ¹⁹⁵Pt satellites, ²J_{PP} = 16.65 Hz, ¹J_{PP_t} = 2270 Hz), 18.22 (d with ¹⁹⁵Pt satellites, ¹J_{PP_t} = 1735 Hz). ²⁹Si{¹H} NMR (59.6 MHz): δ 16.26 (dd with ¹⁹⁵Pt satellites, ²J_{SiP_{cis}} = 13.8 Hz, ²J_{SiP_{trans}} = 235 Hz, ¹J_{SiPt} = 1963 Hz). IR: 2100 s (PtH), 1250 m, 1210 m, 1150 s, 1040 s, 770 s, 720 s, 630 w, 560 w, 510 m.

***cis*-(PEt₃)₂Pt(H)Si(S^tBu)₂OTf (1).** Trimethylsilyl trifluoromethanesulfonate (0.130 g, 0.585 mmol) and **1** (0.280 g, 0.385 mmol) were weighed into separate flasks and each compound was dissolved in 7 mL of dichloromethane. The two solutions were combined and the mixture

was stirred for 8 h, after which time the volatile material was removed *in vacuo*. The white residue was then crystallized from a 1:1 dichloromethane/diethyl ether mixture at -78 °C. Yield 58% (0.169 g). Anal. Calcd for C₂₁H₄₉S₃O₃F₃P₂PtSi: C, 32.01; H, 6.27. Found: C, 32.14; H 6.47. Mp 100-102 °C. ¹H NMR (300 MHz): δ -4.77 (dd with ¹⁹⁵Pt satellites, ²J_{HP_{cis}} = 17.7 Hz, ²J_{HP_{trans}} = 144 Hz, ¹J_{HPt} = 770 Hz, 1 H, PtH), 1.05 (m, 18 H, PEt₃), 1.53 (s, 18 H, ^tBu), 1.96 (m, 12 H, PEt₃). ¹³C{¹H} NMR (75 MHz): δ 8.61 (s, PEt₃), 18.58 (d, ¹J_{CP} = 28 Hz, PEt₃), 21.55 (d, ¹J_{CP} = 27 Hz, PEt₃), 35.10 (s, ^tBu), 47.41 (s, ^tBu). ³¹P{¹H} NMR (121.5 MHz): δ 14.06 (d with ¹⁹⁵Pt satellites, ²J_{PP} = 19.00 Hz, ¹J_{PPt} = 2258 Hz), 19.60 (d with ¹⁹⁵Pt satellites, ¹J_{PPt} = 1963 Hz). ²⁹Si{¹H} NMR (59.6 MHz): δ 52.22 (dd with ¹⁹⁵Pt satellites, ²J_{SiP_{cis}} = 14.0 Hz, ²J_{SiP_{trans}} = 260 Hz, ¹J_{SiPt} = 1950 Hz). IR: 2925 s, 2064 m (PtH), 1238 m, 1155 m, 1031 s, 947 m, 758 w, 723 w, 634 m.

Observation of [cis-(PEt₃)₂HPt=Si(S^tBu)₂(Et₂O)][B(C₆F₅)₄] (2). (Et₂O)LiB(C₆F₅)₄ (10 mg, 0.013 mmol) and **2** (10 mg, 0.013 mmol) were added to an NMR tube. Dichloromethane-*d*₂ (ca. 0.5 mL) was condensed into the tube under vacuum at -196 °C. The solution was then warmed to -78 °C and was shaken until all the reactants had dissolved. The tube was then lowered into the NMR probe, which had previously been cooled to -80 °C. ¹H NMR (300 MHz, -80 °C): δ -5.35 (dd, ²J_{HP_{cis}} = 17.4 Hz, ²J_{HP_{trans}} = 139 Hz, ¹J_{HPt} = 750 Hz, 1 H, PtH), 0.95 (m, PEt₃), 1.09 (t, ³J_{HH} = 6.9 Hz, Et₂O), 1.46 (s, ^tBu), 1.89 (br m, PEt₃), 3.41 (br s, free Et₂O), 4.55 (br s, bound Et₂O). ³¹P{¹H} NMR (-50 °C, 121.5 MHz): δ 10.90 (d ¹⁹⁵Pt satellites, ²J_{PP} = 20.6 Hz, ¹J_{PPt} = 2231 Hz), 15.40 (¹J_{PPt} = 2044 Hz). ²⁹Si{¹H} NMR (-60 °C, 99.3 MHz): δ 86.30 (d with ¹⁹⁵Pt satellites, ²J_{SiP_{trans}} = 253 Hz (²J_{SiP_{cis}} not observed), ¹J_{SiPt} = 1986 Hz).

Observation of [(PEt₃)₂PtSiH(S^tBu)₂][B(C₆F₅)₄] (3). To an NMR tube were added **1** (10 mg, 0.013 mmol), (Et₂O)LiB(C₆F₅)₄ (10 mg, 0.013 mmol) and 0.5 mL of dichloromethane-*d*₂. After shaking, the formation of a cloudy white precipitate and a light yellow solution were noted. ¹H NMR (-30 °C): δ 1.10 (m, 18 H, PEt₃), 1.46 (s, 9H, ^tBu), 1.51 (s, 9H, ^tBu), 2.02 (br m, 12 H, PEt₃), 5.41 (d, ³J_{HP_{trans}} = 7.8 Hz, ²J_{HPt} = 110 Hz (³J_{HP_{cis}} not observed), SiH). ¹³C{¹H} NMR (125 MHz): δ 8.5 (br s, PEt₃), 8.8 (br s, PEt₃), 19.0 (br s, PEt₃), 21.8 (br s, PEt₃), 34.8 (br s,

^tBu), 35.3 (s, ^tBu), 136.0 (br s, B(C₆F₅)₄), 137.9 (br s, B(C₆F₅)₄), 139.8 (br s, B(C₆F₅)₄), 147.0 (br s, B(C₆F₅)₄), 149.1 (br s, B(C₆F₅)₄). ³¹P{¹H} NMR (-20 °C, 121.5 MHz, chloroform-*d*): δ 21.59 (²J_{PP} = 5.7 Hz, ¹J_{PPt} = 2335 Hz), 22.46 (¹J_{PPt} = 4086 Hz). ²⁹Si{¹H} NMR (-30 °C, 99.3 MHz): δ 23.59 (dd with ¹⁹⁵Pt satellites, ²J_{SiP} = 152, ²J_{SiP} = 252 Hz, ¹J_{SiPt} = 865 Hz).

***trans*-(PEt₃)₂MePtSiH(S^tBu)₂ (4).** To a cold (0 °C) Schlenk flask containing **1** (0.300 g, 0.381 mmol) and (Et₂O)LiB(C₆F₅)₄ (0.290 g, 0.381 mmol) was added 20 mL Et₂O. Compound **6** separated as a pale yellow oil over a period of 3 minutes. To this mixture was added MeMgBr (0.270 mL, 0.380 mmol) via syringe. The mixture was stirred for 15 min, during which time the oil became a fluffy precipitate. The volatiles were removed *in vacuo* and the residue was extracted with pentane (2 x 10 mL). Removal of the pentane from the combined extracts under reduced pressure gave **7** as an off white powder. Yield 40 % (0.109 g). Anal. Calcd for C₂₁H₅₂P₂S₂PtSi: C, 38.57; H, 8.02. Found: C, 38.31; H, 8.01. mp 163-165 °C (dec). ¹H NMR (400 MHz): δ 0.46 (t with ¹⁹⁵Pt satellites, ²J_{HPt} = 48.0 Hz, ³J_{HP} = 6.0 Hz, 3 H, PtMe), 0.96 (m, 18 H, PEt₃), 1.70 (s, 18 H, ^tBu), 2.00 (br s, 12 H, PEt₃), 5.93 (t with ¹⁹⁵Pt satellites, ²J_{HPt} = 50.8 Hz, ³J_{HP} = 17.2 Hz, 1 H, SiH). ¹³C{¹H} NMR (100 MHz): δ 5.6 (m, PEt₃), 10.4 (t with ¹⁹⁵Pt satellites, ¹J_{CPt} = 1094 Hz, ²J_{CP} = 19.1 Hz), 13.8 (m, PEt₃), 35.8 (s, ^tBu), 49.3 (s, ^tBu). ³¹P{¹H} NMR (161.98 MHz): δ 9.15 (s with ¹⁹⁵Pt satellites, ¹J_{PPt} = 2670 Hz). IR (KBr pellet): 2965 s, 2051 m (PtH), 1455 m, 1359 m, 1260 m, 1032 s, 799 m, 764 s, 720 m, 491 w.

***cis*-(PEt₃)₂BrPtSiH(S^tBu)₂ (5).** Compound **3** was generated in the same manner as for **4**. To this mixture was added via cannula Bu₄NBr (0.123 g, 0.380 mmol) dissolved in 10 mL of dichloromethane. The mixture was stirred for 2 h, after which time the volatiles were removed *in vacuo* and the residue was extracted with Et₂O (2 x 10 mL). Concentration to half volume under reduced pressure and cooling to -80 °C gave **5** as an off white powder. Yield 85 % (0.233 g). Anal. Calcd for C₂₀H₄₉P₂S₂BrPtSi: C, 33.42; H, 6.87. Found: C, 33.25; H, 6.50. mp 175-178 °C (dec). ¹H NMR (400 MHz): δ 1.03 (br s, 18 H, PEt₃), 1.60 (s, 18 H, ^tBu), 2.11 (br s, PEt₃), 2.35 (br s, PEt₃), 5.31 (vir t with ¹⁹⁵Pt satellites, ²J_{HPt} = 111 Hz, 1 H, SiH). ¹³C{¹H} NMR (100 MHz): δ 6.2 (m, PEt₃), 14.1 (m, PEt₃), 32.5 (s, ^tBu), 50.3 (s, ^tBu). ³¹P{¹H} NMR (161.98 MHz):

δ 11.84 (s with ^{195}Pt satellites, $^1J_{\text{PPt}} = 2510$ Hz), 13.04 (s with ^{195}Pt satellites, $^1J_{\text{PPt}} = 2834$ Hz). IR (KBr pellet): 2986 s, 2062 m (PtH), 1478 m, 1434 m, 1375 m, 1271 s, 1142 m, 1091 s, 934 m, 850 w, 721 w, 648 w.

Observation of *cis*-(PEt_3) $_2$ Pt(NCMe)SiH(S t Bu) $_2$][OTf] (6). To a solution of **1** (0.015 g, 0.019 mmol) in 0.5 mL dichloromethane- d_2 was added MeCN (300 μL , 5.54 mmol). ^1H NMR (400 MHz, 25 $^\circ\text{C}$): δ 1.09 (m, PEt_3), 1.46 (s, 18 H, ^tBu), 2.11 (br s, PEt_3), 4.90 (vir t with ^{195}Pt satellites, $^2J_{\text{HPt}} = 109$ Hz, 1 H, SiH) (coordinated MeCN signal was obscured by free MeCN). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, 25 $^\circ\text{C}$): δ 16.88 (br s with ^{195}Pt satellites, $^1J_{\text{PPt}} = 2589$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, -20 $^\circ\text{C}$): δ 16.57 (s with ^{195}Pt satellites, $^1J_{\text{PPt}} = 2538$ Hz), 16.87 (s with ^{195}Pt satellites, $^1J_{\text{PPt}} = 2595$ Hz). IR (MeCN solution): 2969 s, 2939 s, 2098 m (SiH), 1454 s, 1421 s, 1363 m, 1259 s, 1266 m, 1160 s, 1031 m, 860 w, 765 m, 725 m, 640 m, 754 w, 518 m, 414 w.

***cis*-(PEt_3) $_2$ Pt(D)Si(S t Bu) $_3$.** This procedure is based on a previously reported preparation of HSiCl_3 (Pätzold, U.; Roewer, G.; Herzog, U. *J. Organomet. Chem.* **1996**, 508, 147). To a mixture of pyrazine (0.295 g, 3.7 mmol), Bu_3SnD (1.00 mL, 3.7 mmol), and AIBN (0.020 g, 0.12 mmol) in 15 mL benzene was added SiCl_4 (0.42 mL, 3.7 mmol) via syringe. After stirring for 8 h, HS^tBu (1.7 mL, 15 mmol) and NEt_3 (2.1 mL, 15 mmol) were added successively via syringe, generating a copious quantity of white precipitate. The mixture was stirred for an additional 8 h and then filtered. The precipitate was extracted with benzene (2 x 10 mL) and the extractions were then combined with the filtrate. Removal of the solvent under reduced pressure yielded a clear colorless oil, which was dissolved in pentane (10 mL) and then combined with a solution of $\text{Pt}(\text{PEt}_3)$ (1.00 g, 1.8 mmol) in 10 mL pentane. The reaction mixture was stirred for 30 min, during which time a white precipitate formed. Removal of the solvent under reduced pressure yielded a light yellow powder, which was washed once with pentane (5 mL). The remaining white powder was then crystallized from diethyl ether at -78 $^\circ\text{C}$. Yield 24% based on Bu_3SnD (0.642 g). ^1H NMR (benzene- d_6 , 300 MHz): δ 0.92 (m, 18 H, PEt_3), 1.51 (m, 6 H, PEt_3), 1.85 (s, 27 H, ^tBu), 2.10 (m, 6 H, PEt_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (dichloromethane- d_2 , 161.98 MHz): δ 14.44 (dt

with ^{195}Pt satellites, $^2J_{\text{PP}} = 17.00$ Hz, $^2J_{\text{PD}} = 23.00$ Hz, $^1J_{\text{PPt}} = 2219$ Hz), 18.22 (d with ^{195}Pt satellites, $^1J_{\text{PPt}} = 1749$ Hz). IR: 2968 s, 1508 s (PtD), 1250 m, 1210 m, 1150 s, 1040 s, 770 s, 720 s, 630 w, 560 w, 510 m.

***cis*-(PEt₃)₂DPTSi(S^tBu)₂OTf.** The procedure employed was identical to that for **1**, except for the use of *cis*-(PEt₃)₂Pt(D)Si(S^tBu)₃ instead of *cis*-(PEt₃)₂Pt(H)Si(S^tBu)₃. ^1H NMR (300 MHz): δ 1.08 (m, 18 H, PEt₃), 1.53 (s, 18 H, ^tBu), 1.88 (m, 6 H, PEt₃), 2.00 (m, 6 H, PEt₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz): δ 14.37 (q with ^{195}Pt satellites, $^2J_{\text{PP}} = 19.4$ Hz, $^2J_{\text{PD}} = 19.4$ Hz, $^1J_{\text{PPt}} = 2260$ Hz), 19.85 (d with ^{195}Pt satellites, $^1J_{\text{PPt}} = 1959$ Hz). IR: 2925 s, 1483 m (PtD), 1238 m, 1155 m, 1031 s, 947 m, 758 w, 723 w, 634 m.

Rate Dependence on [CH₃CN]. In a glove box, a standard solution of CH₃CN (151.8 mg, 3.698 mmol) in dichloromethane-*d*₂ was prepared using a 1.00 mL volumetric flask. A standard solution of **1** (0.0201 g, 0.0255 mmol) in dichloromethane-*d*₂ was similarly prepared and placed in a greaseless Schlenk flask. A total of five NMR tubes were prepared with the following quantities of CH₃CN solution: 15 μL , 75 μL , 150 μL , 225 μL , and 295 μL . The appropriate quantity of dichloromethane-*d*₂ was added to each tube to bring the total volume to 500 μL . Outside of the glove box, the NMR tubes were cooled to -78 °C and 200 μL standard solution of **1** was added to each via syringe through a septum. Each sample was kept at -78 °C until insertion into the pre-cooled (10 °C) NMR probe and each reaction was monitored by ^1H NMR spectroscopy for 3 hours. The NMR spectroscopic data were acquired with one scan and without sample spinning. Relative quantities of starting material and product were determined by integration of the ^tBu region of the ^1H NMR spectrum. Initial (< 10 % completion) rate constants obtained in the order of lowest [CH₃CN] to highest were: $1.7 \times 10^{-4} \text{ s}^{-1}$, $1.4 \times 10^{-4} \text{ s}^{-1}$, $1.3 \times 10^{-4} \text{ s}^{-1}$, $1.4 \times 10^{-4} \text{ s}^{-1}$, $1.5 \times 10^{-4} \text{ s}^{-1}$. Approach to equilibrium plots are given below (Figures 1-5).

Kinetic Isotope Effect Determination. Two portions of **1**, each consisting of 5.0 mg (0.0063 mmol), were weighed into NMR tubes and each were dissolved in 700 μL dichloromethane-*d*₂. Two solutions of **1-d** were similarly prepared. The NMR tubes were cooled to -78 °C and CH₃CN (6 μL , 0.11 mmol) was added to each via syringe through a septum. The

reactions were monitored as before at 10 °C. Average k_{init} values: **1**, $1.3 \times 10^{-4} \text{ s}^{-1}$; **1-d**, $1.0 \times 10^{-4} \text{ s}^{-1}$. Initial rate plots are given below (Figures 6-9).

Rate Dependence on [OTf] at Constant Ionic Strength. NMR samples in 700 μL dichloromethane- d_2 were prepared as follows. Sample 1: $[\text{Bu}_4\text{N}][\text{OTf}]$ (generated from Bu_4NBr and AgOTf in dichloromethane) (0.012 g, 0.031 mmol), **1** (0.005 g, 0.006 mmol). Sample 2: $[\text{Bu}_4\text{N}][\text{OTf}]$ (0.007 g, 0.018 mmol), $[\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ (generated from Bu_4NBr and $(\text{Et}_2\text{O})\text{LiB}(\text{C}_6\text{F}_5)_4$ in dichloromethane) (0.012 g, 0.013 mmol), **1** (0.005 g, 0.006 mmol). Sample 3: $[\text{Bu}_4\text{N}][\text{OTf}]$ (0.002 g, 0.006 mmol), $[\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.023 g, 0.025 mmol), **1** (0.005 g, 0.006 mmol). The NMR tubes were cooled to -78 °C and CH_3CN (6 μL , 0.11 mmol) was added to each via syringe through a septum. The reactions were monitored as before at 10 °C. k_{init} values: Sample 1, $2.1 \times 10^{-4} \text{ s}^{-1}$; Sample 2, $1.9 \times 10^{-4} \text{ s}^{-1}$; Sample 3, $2.2 \times 10^{-4} \text{ s}^{-1}$. Approach to equilibrium plots are given below (Figures 10-12).

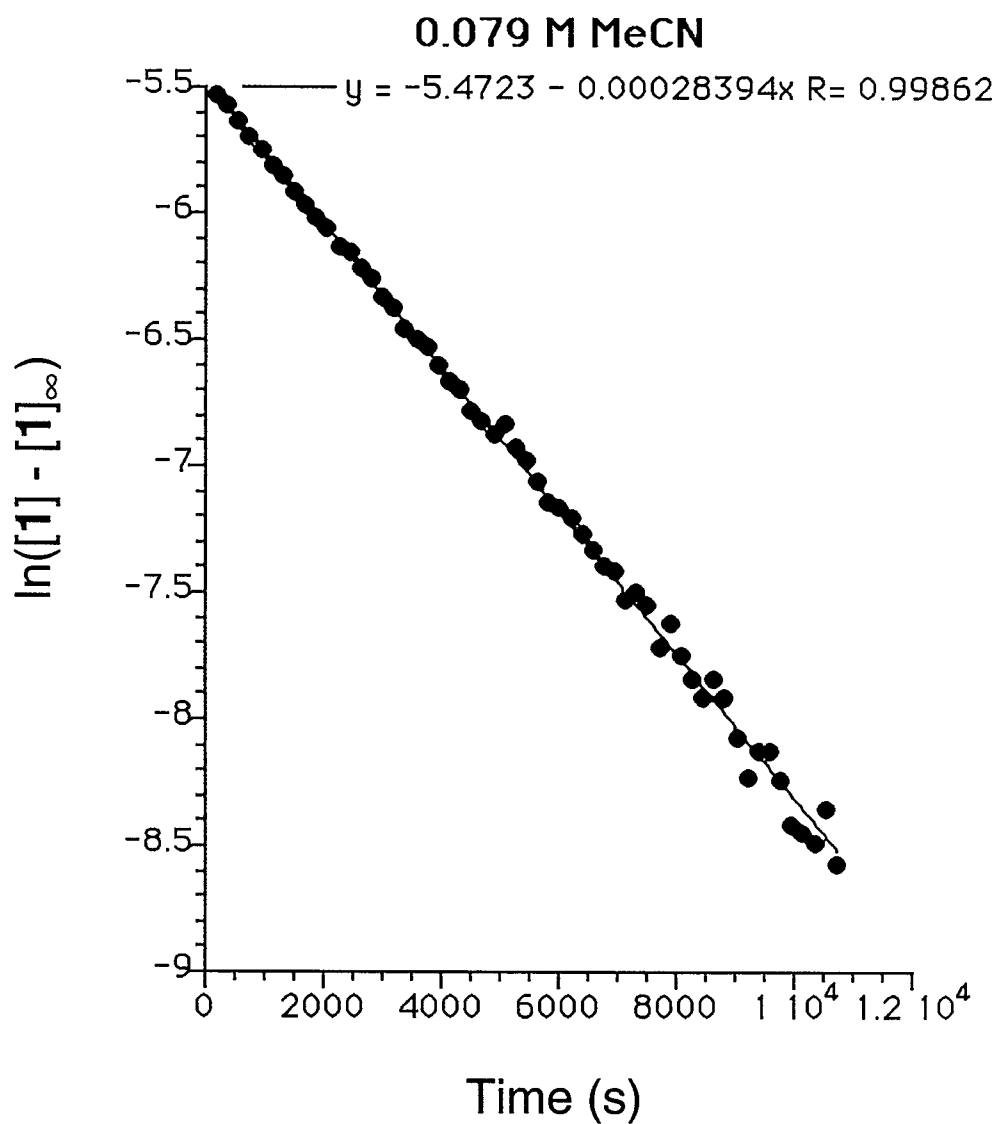


Figure 1. Plot of $\ln([1] - [1]_{\infty})$ vs. time in the reaction of **1** with MeCN (0.079 M).

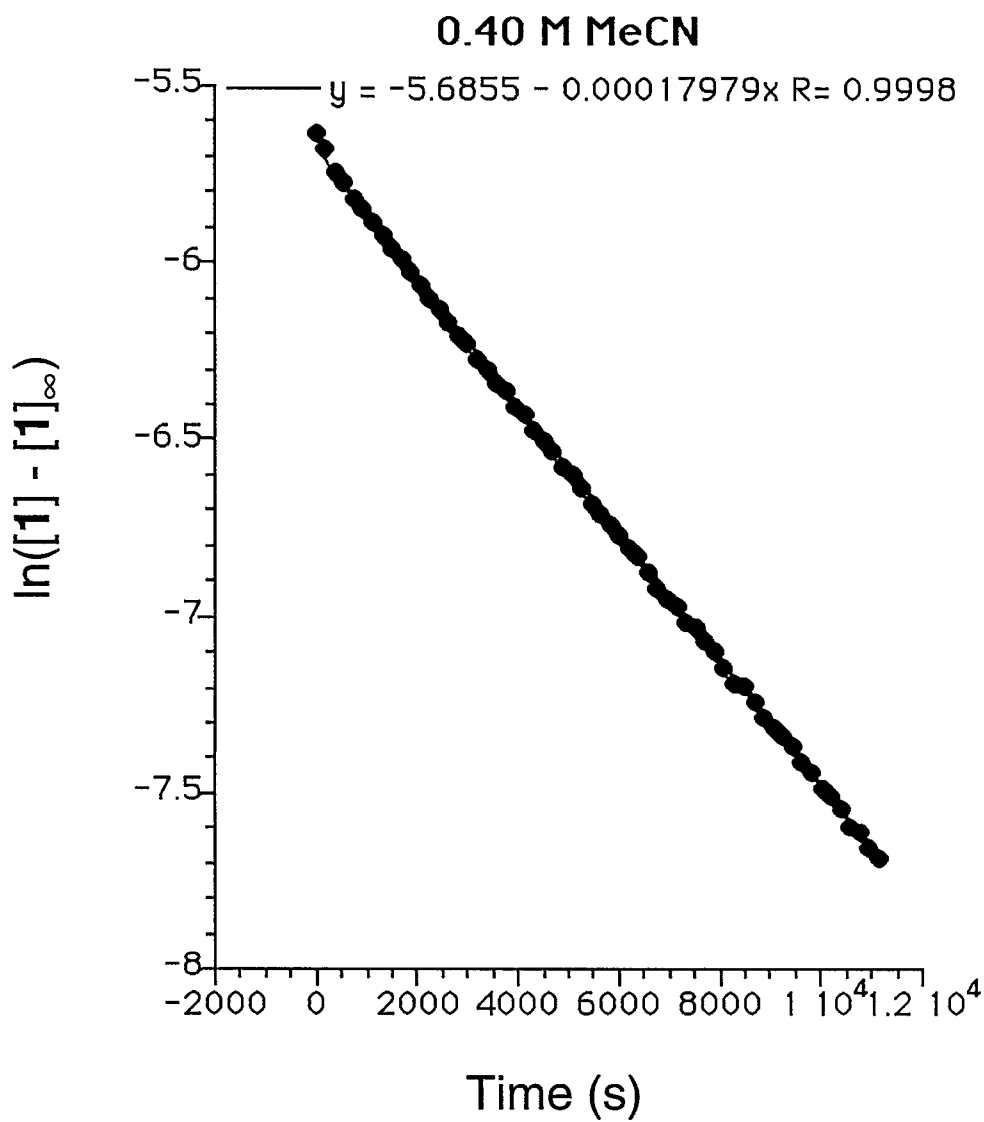


Figure 2. Plot of $\ln([1] - [1]_{\infty})$ vs. time in the reaction of **1** with MeCN (0.40 M).

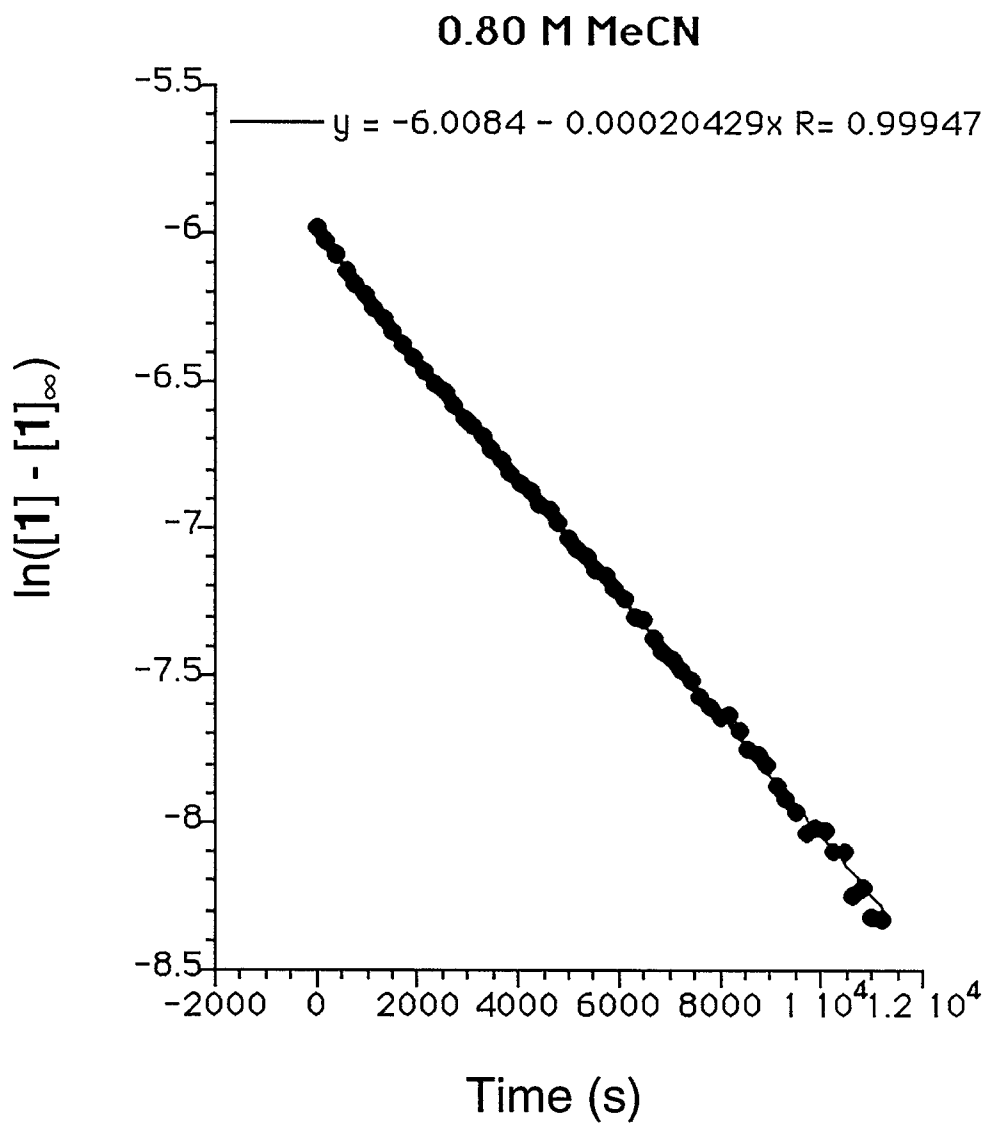


Figure 3. Plot of $\ln([1] - [1]_{\infty})$ vs. time in the reaction of **1** with MeCN (0.80 M).

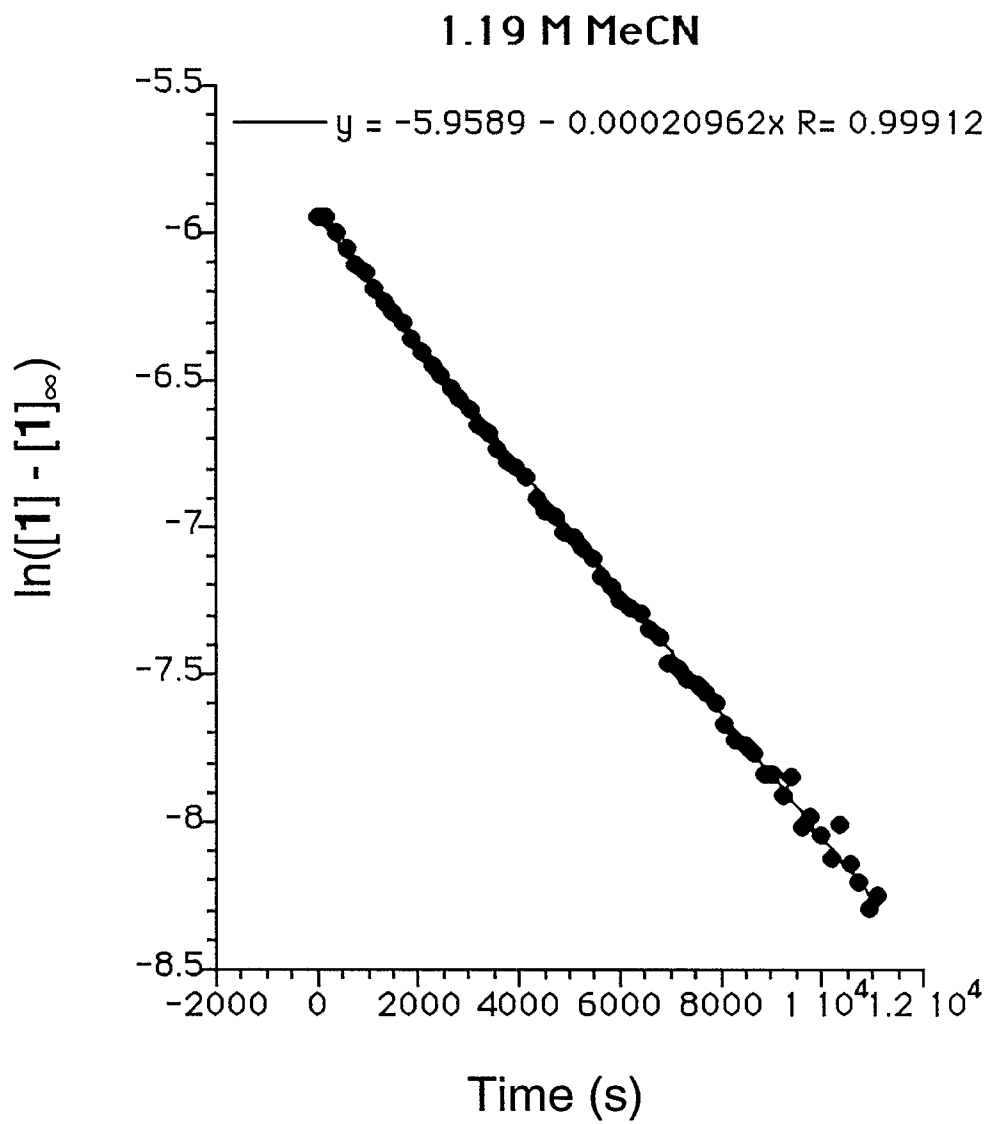


Figure 4. Plot of $\ln([1] - [1]_{\infty})$ vs. time in the reaction of **1** with MeCN (1.19 M).

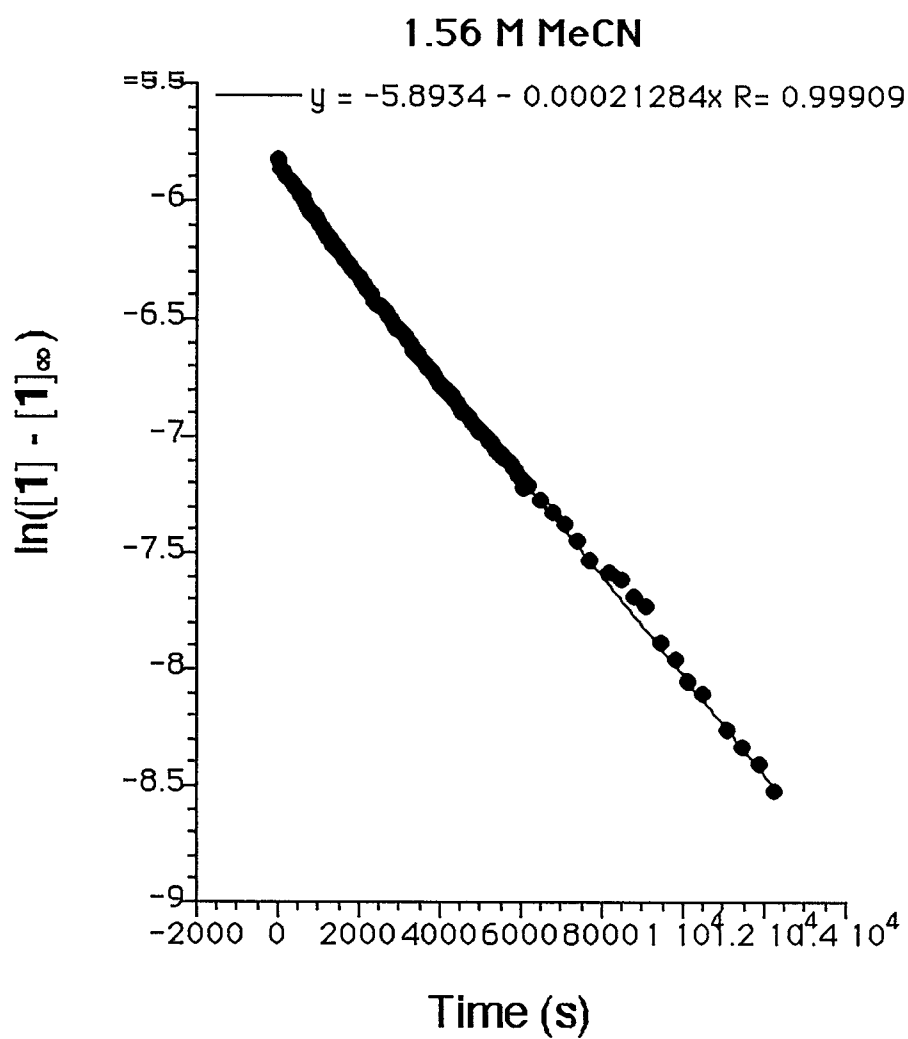


Figure 5. Plot of $\ln([1] - [1]_{\infty})$ vs. time in the reaction of **1** with MeCN (1.56 M).

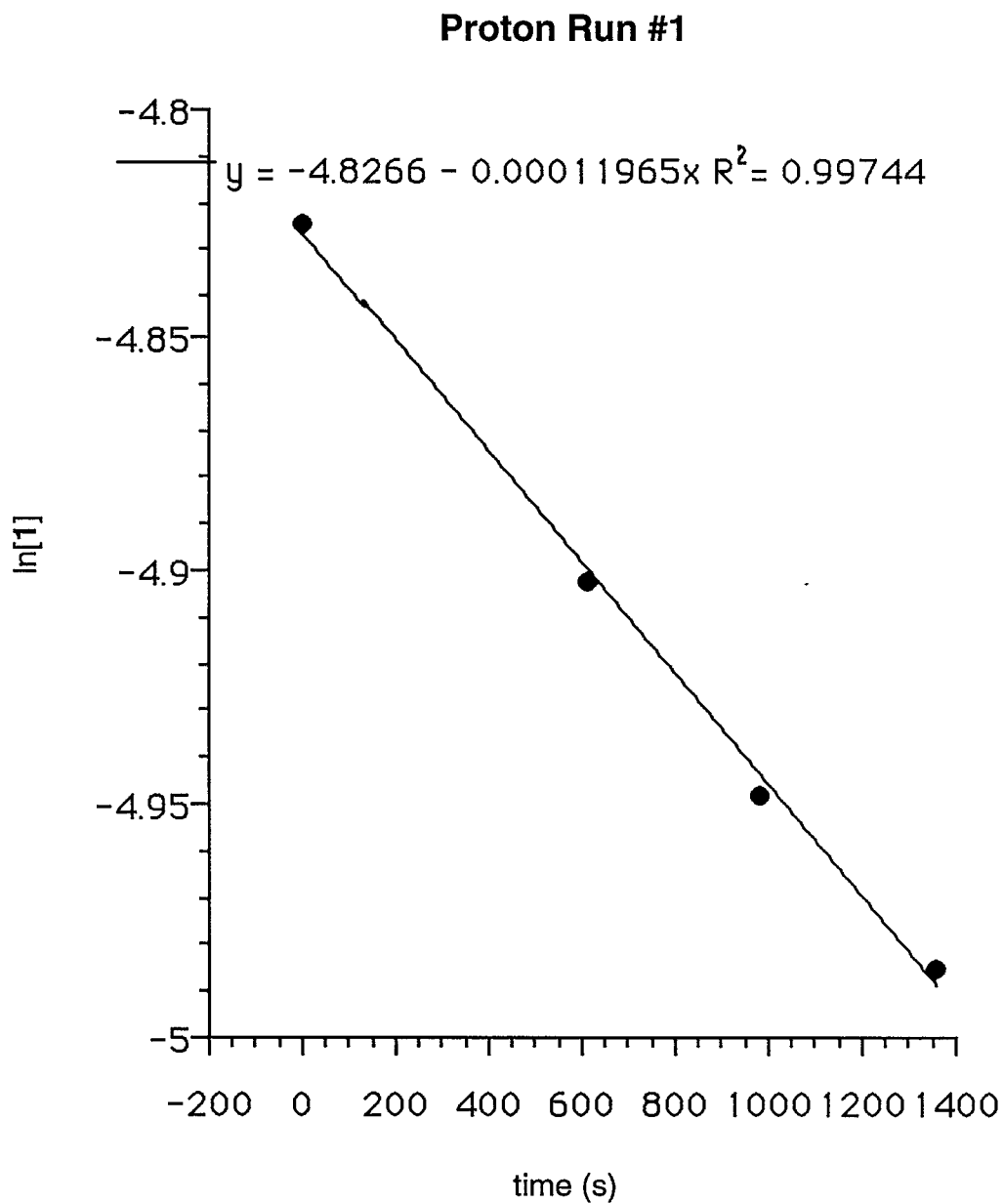


Figure 6. Plot of ln[1] vs. time in the reaction of **1** with MeCN (< 10% completion).

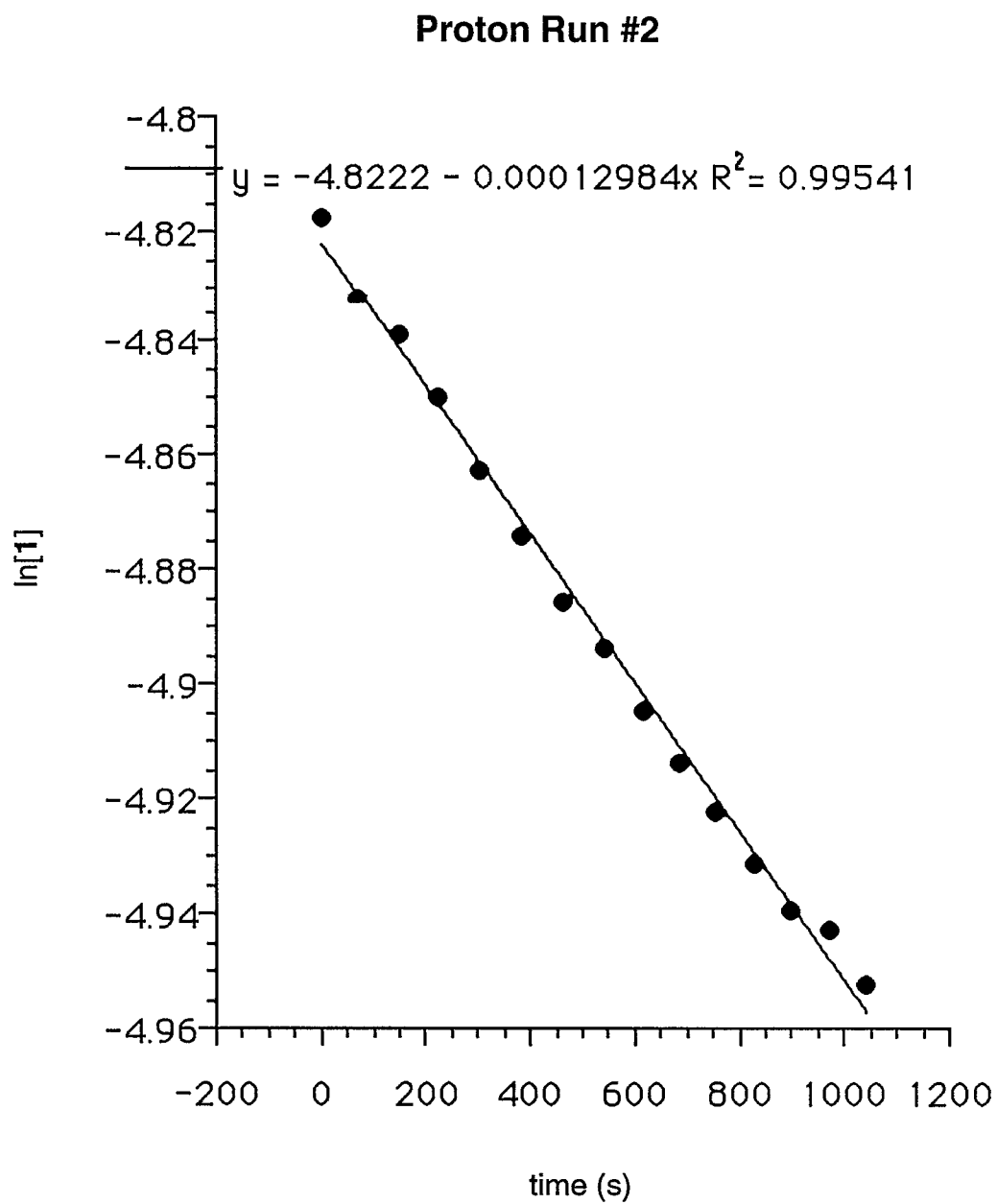


Figure 7. Plot of $\ln[1]$ vs. time in the reaction of **1** with MeCN (< 10% completion).

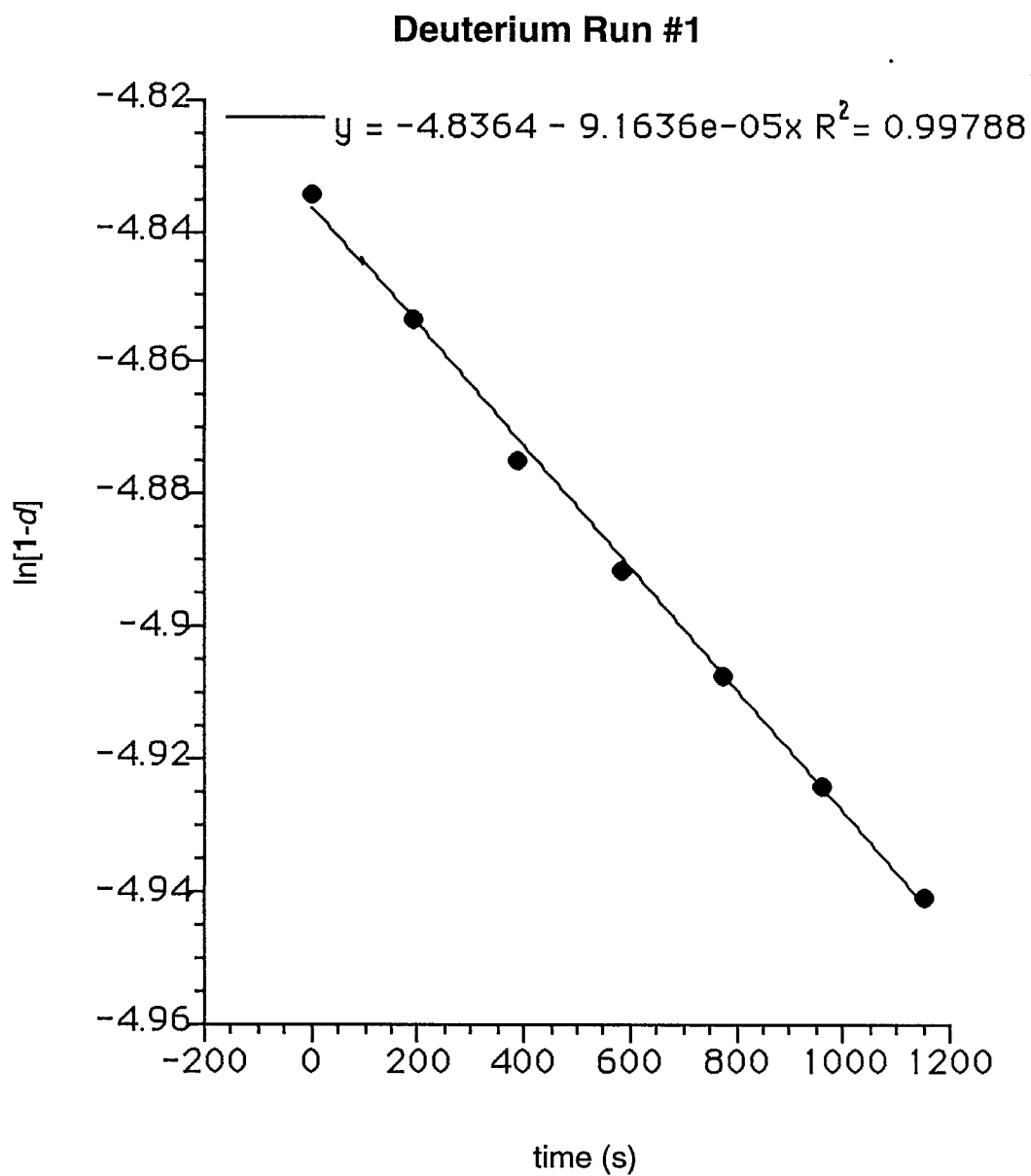


Figure 8. Plot of $\ln[1-d]$ vs. time in the reaction of **1-d** with MeCN (< 10% completion).

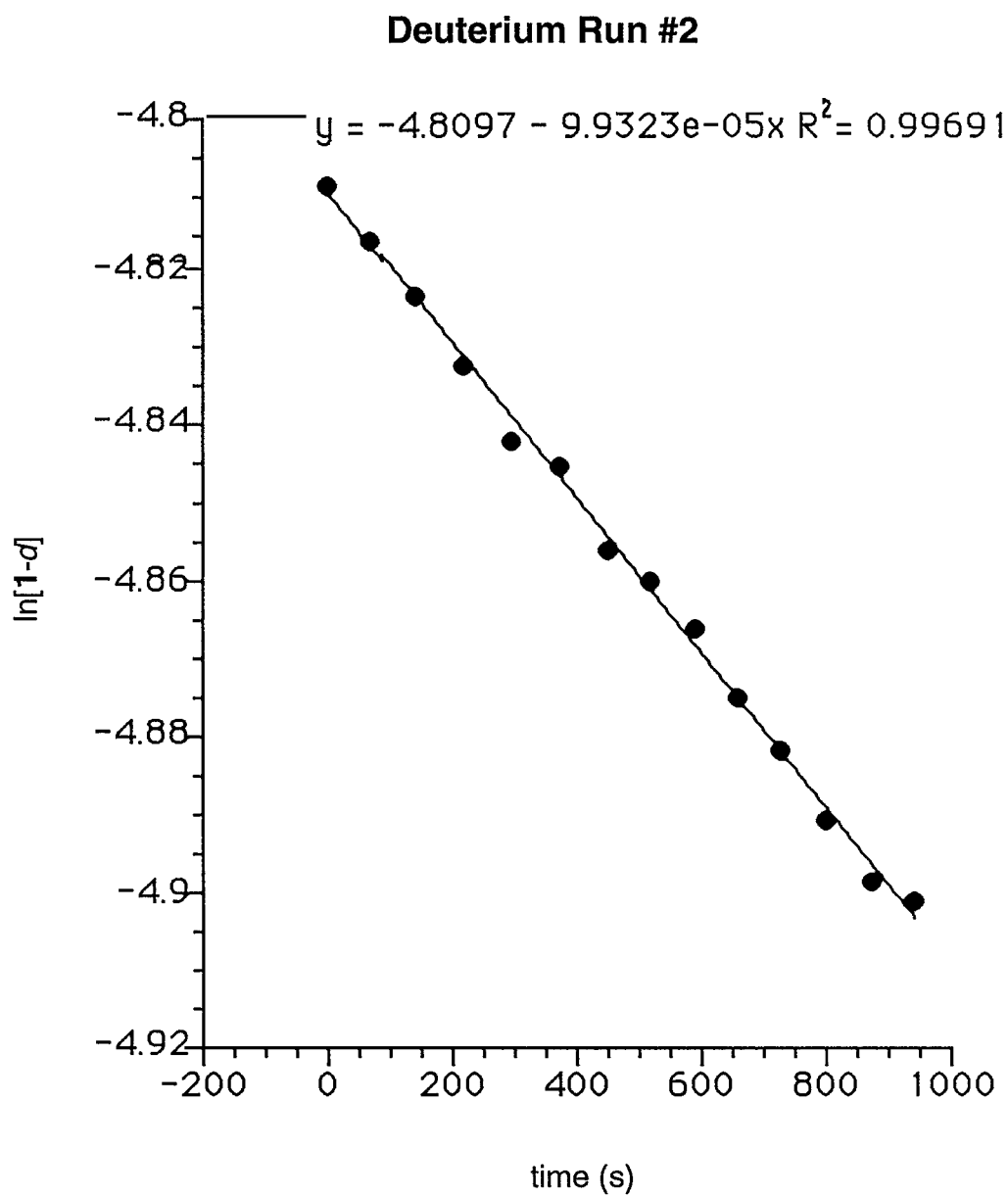


Figure 9. Plot of $\ln[1-d]$ vs. time in the reaction of **1-d** with MeCN (< 10% completion).

POOR QUALITY ORIGINAL

17

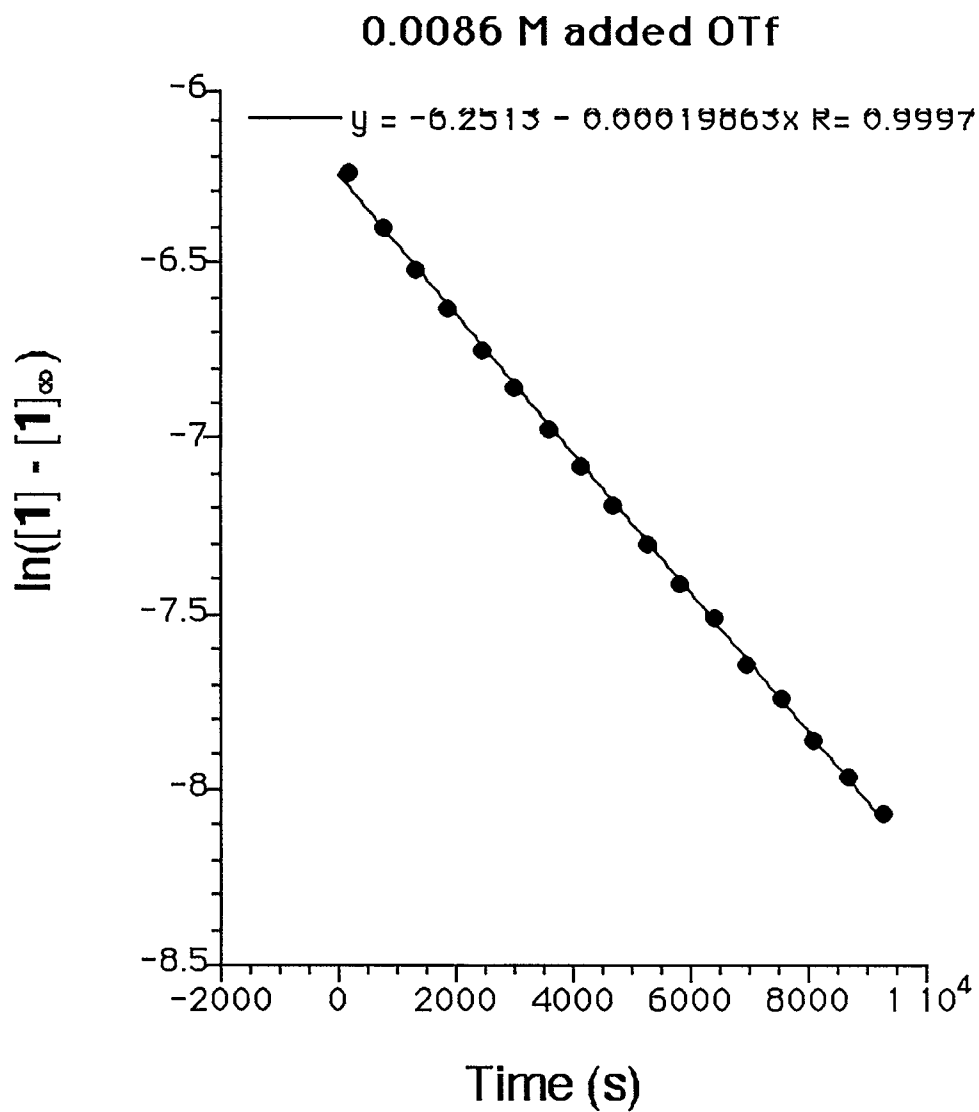


Figure 10. Plot of $\ln([1] - [1]_{\infty})$ vs. time in the reaction of **1** with MeCN in the presence of 0.0086 M $[\text{Bu}_4\text{N}][\text{OTf}]$.

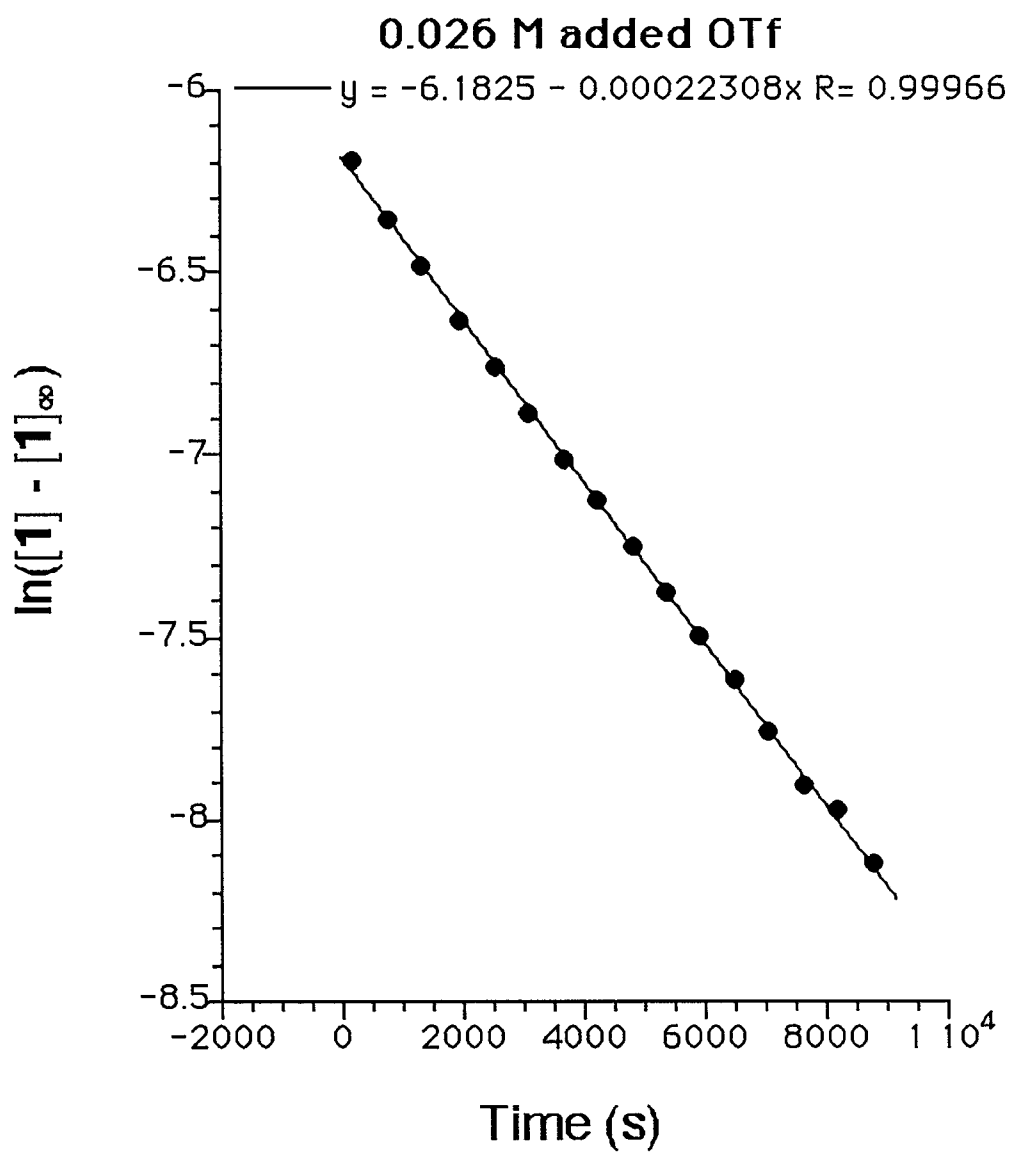


Figure 11. Plot of $\ln([1] - [1]_{\infty})$ vs. time in the reaction of **1** with MeCN in the presence of 0.026 M $[\text{Bu}_4\text{N}][\text{OTf}]$.

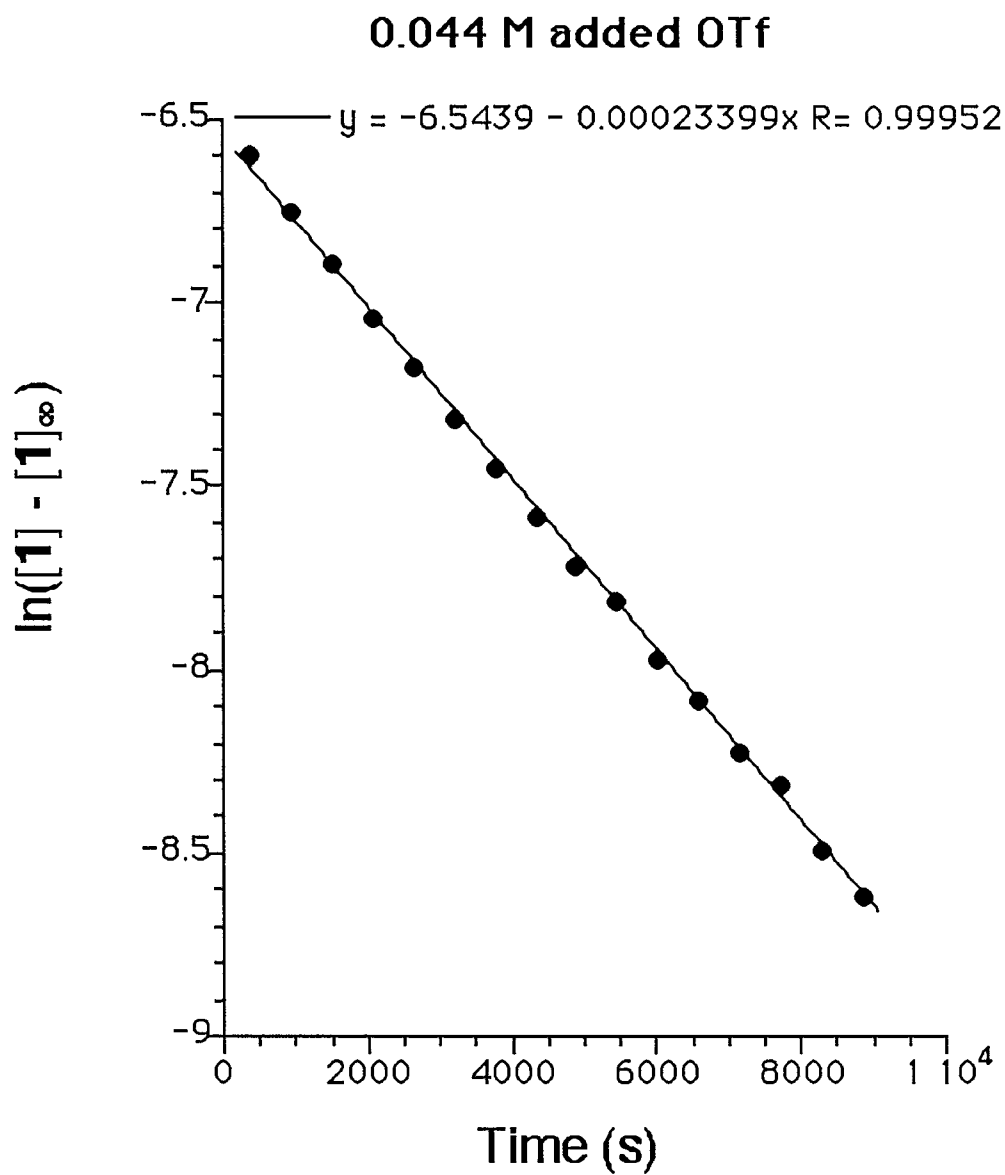


Figure 10. Plot of $\ln([1] - [1]_{\infty})$ vs. time in the reaction of **1** with MeCN in the presence of 0.044 M $[\text{Bu}_4\text{N}][\text{OTf}]$.