18, 65906-88-9; **19**, 116210-23-2; **19** (de-*N*-benzyl derivative), 116185-33-2; **20**, 116185-34-3; **21**, 116185-35-4; **22**, 116185-36-5; **23**, 116185-37-6; **24**, 116185-38-7; **27**, 101696-49-5; **28**, 101696-52-0; **29**, 101696-64-4; **30**, 101696-53-1; **31**, 101696-59-7; **32**, 101696-58-6; **33**, 101696-60-0; **34**, 101696-61-1; **36**, 116185-23-0; **37**, 116185-24-1.

Supplementary Material Available: Experimental procedures and spectral characterization for compounds in the 7′-8′ oxido route, ORTEP drawings and tables containing fractional coordinates, temperature factors, bond distances, bond angles, torsional angles, and anisotropic temperature factors for compounds **5** and **7** (18 pages). Ordering information is given on any current masthead page.

Kinetics of the Anion-Catalyzed Michael Reaction of Silyl Ketene Acetals. Initiation and Propagation Steps of Group Transfer Polymerization†

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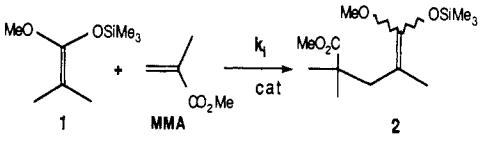
Abstract: The kinetics of the first three steps of "group transfer polymerization" (GTP) have been studied by stopped-flow FT-IR spectroscopy. The kinetic orders of the reaction of dimethylketene methyl trimethylsilyl acetal (**1**) with methyl methacrylate (MMA) have been determined for three anionic catalysts. The reactions catalyzed by bifluoride and benzoate salts were second and first order in catalyst, respectively, while a nonintegral rate was observed for a bibenzoate salt. The first-order rate dependence on fluoride donor **5** suggests that the second-order rate dependence on bifluoride results from the reaction of two HF_2^- ions and the initiator (**1**) to yield $H_2F_3^-$ and a 1:1 complex of fluoride ion and **1**. The activity of catalyst is primarily determined by the structure of the anion. The anions studied can be ranked in order of decreasing reactivity: $HF_2^- > C_6H_5CO_2^- > [(C_6H_5CO_2)_2H]^-$. The individual rates for the initiation (k_i) and the first (k_p^1) and second (k_p^2) propagation steps catalyzed by bibenzoate were determined with the following result: $k_i \approx k_p^1 \approx k_p^2$. It was found also that $k_i \approx k_p^1$ when the catalyst was benzoate. This study has demonstrated that $k_i \geq k_p$ for GTP, which is a kinetic requirement for producing polymer with low polydispersity.

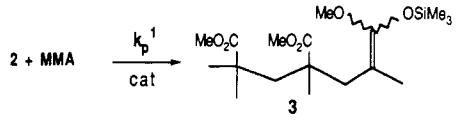
Previous communications from these laboratories have reported controlled polymerization of methacrylate monomers at ambient temperatures initiated by silyl ketene acetals in the presence of a suitable catalyst (group transfer polymerization, GTP).[1,2] The polymerization proceeds by repeated Michael additions of monomer to a growing chain end carrying the silyl ketene acetal functionality. The emphasis of most published work on GTP has been on utility and synthetic aspects of the process. Sogah and Farnham[3] provided compelling evidence for *intramolecular* silicon transfer based on exchange experiments. On the basis of ab initio calculations,[4] carbon–carbon bond formation appears to be the first event after formation of a pentavalent complex between the catalyst and the silyl ketene acetal. Wnek also reached a similar conclusion in a more recent study.[5] Bandermann has reported some kinetic results for GTP in acetonitrile solution,[6] but his work was complicated by side reactions. Müller and Mai[7,8] have also published the results of their kinetic investigations of GTP. The emphasis of Müller's work was on average propagation rates where the starting ratio of MMA to initiator was usually in excess of 100 and primarily involved catalysis by tris(dimethylamino)-sulfonium bifluoride, $TASHF_2$.

Reported here is a kinetic investigation of the anion-catalyzed reaction of dimethylketene methyl trimethylsilyl acetal (**1**) with methyl methacrylate (MMA). The rates for the initiation step and first two propagation steps of GTP have been measured individually using stopped-flow Fourier transform infrared spectroscopy (see Schemes I–III).[9] The discrete study of each of these three steps relied on independent synthesis of intermediates **2** and **3**.

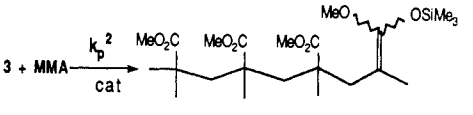
Scheme I



Scheme II



Scheme III



Experimental Section

Materials. Tetrahydrofuran (THF) and pentane were distilled from sodium and benzophenone. Acetonitrile (CH_3CN) was distilled from CaH_2. Solvents were stored and handled in a drybox. Commercially available methyl methacrylate was passed through a short column of

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(1) (a) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajan-Babu, T. V. *J. Macromol. Sci., Chem.* **1984**, *A21* (8 and 9), 943. (b) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. W. *Macromolecules* **1987**, *20*, 1473–1488, and references cited therein.

(2) Webster, O. W. U.S. Patent 4417034, Nov 22, 1983; 4508880, April 2, 1985. Farnham, W. B.; Sogah, D. Y. U.S. Patent 4414372, Nov 8, 1983; 4524196, June 18, 1985; 4581428, April 8, 1986.

(3) Sogah, D. Y.; Farnham, W. B. *Organosilicon and Bioorganosilicon Chemistry: Structures, Bonding, Reactivity and Synthetic Application*; Sakurai, H., Ed.; Wiley: New York, 1985; Chapter 20.

(4) Dixon, D. A.; Sogah, D. Y.; Farnham, W. B., to be submitted for publication. Ab initio molecular orbital calculations using double-ζ basis sets augmented by polarization functions have been performed on model systems on the GTP potential energy surface. The results show a preference for a pentavalent anionic silicon intermediate and a hexavalent transition state for transfer of the silicon.

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neutral alumina in the drybox to remove inhibitors and acidic impurities. Dimethylketene methyl trimethylsilyl acetal (**1**) was prepared according to literature procedure[10] and was slowly distilled twice through a 24-in. spinning band column before use. The extinction coefficient for the C=C stretching band of **1** in the infrared spectrum was measured: $\nu_{C=C}$ = 1705 cm^{-1}; ϵ = 534. Tris(dimethylamino)sulfonium bifluoride ($TASHF_2$) was prepared according to a previously published procedure.[1b] The synthesis of tetrabutylammonium bibenzoate has been described elsewhere.[11] ^{19}F NMR spectra were recorded with a Nicolet NT200 spectrometer. ^1H NMR spectra were recorded with either a Nicolet NT300/WB or GE QE300 spectrometer. ^{29}Si and ^{13}C NMR spectra were recorded with a Nicolet NT300/WB spectrometer. GC/MS data were obtained with a Varian 3700 GC with a V. G. Micromass 16-F mass spectrometer or a Du Pont 21-491 mass spectrometer.

Methyl 2,2,4-Trimethyl-5-methoxy-5-(trimethylsiloxy)pent-4-enoate (2). A one-step procedure directly from MMA and **1** can be employed but gives material that cannot be considered entirely free of the catalyst used in the preparation.

Dimethyl 2,2,4-trimethylglutarate was prepared by quenching **2** (prepared by HgI_2-catalyzed MMA addition to **1**)[12] with methanol. The excess HgI_2 was best removed by precipitation as the insoluble Ph_3P complex in ethanol. Distillation then afforded a product that had analytical characteristics in accord with the literature.[13]

Dimethyl 2,2,4-trimethylglutarate (4.58 g, 0.023 mol), 28.5 g of chlorotrimethylsilane (33 mL, 0.248 mol), and 94 mL of THF were combined in a Schlenk flask in a drybox. A THF solution of lithium diisopropylamide (15.5 mL, 0.0294 mol; Lithium Corp., titrated with diphenylacetic acid just prior to use) was added slowly via syringe to the reaction mixture, which had been cooled to −78 °C. The solution was stirred for 3 h under argon and then allowed to warm slowly to 25 °C. Removal of volatiles and bulb-to-bulb distillation afforded the desired product as a slightly yellow oil.

Anal. Calcd for $C_{13}H_{25}O_4Si$: C, 57.11; H, 9.22; O, 23.41; Si, 10.27. Found: C, 56.95; H, 9.30; O, 23.21; Si, 9.63. IR (THF): $\nu_{C=C}$ = 1687 cm^{-1} (ϵ = 390). ^1H NMR (THF-d_8, TMS, 300 MHz): δ 0.170 (*E*), 0.155 (*Z*) (s, 9 H, $SiCH_3$); 1.094 (*Z*), 1.082 (*E*) (s, 6 H, *gem*-CH_3); 1.422 (*Z*), 1.376 (*E*) (s, 3 H, $=CCH_3$); 2.239 (*E*), 2.183 (*Z*) (s, 2 H, CH_2); 3.454 (*Z*), 3.38 (*E*) (s, 3 H, $C=COCH_3$); 3.537 (s, 3 H, $COOCH_3$). ^{13}C NMR (THF-d_8, TMS, 75 MHz): δ 0.17 (*E*), 0.28 (*Z*) ($SiCH_3$); 15.26 (*Z*), 16.37 (*E*) ($=CCH_3$); 25.9 (*E*), 25.89 (*Z*) (*gem*-CH_3); 42.69 (*Z*), 42.60 (*E*) (CH_2); 43.34 (*Z*), 43.24 (*E*) (CMe_2); 51.49 (*E*), 51.54 (*Z*) ($COOCH_3$); 55.98 (*E*), 57.55 (*Z*) ($=COCH_3$); 91.73 (*E*), 92.31 (*Z*) ($=CCH3$); 152.7 (*E*), 153.70 (*Z*) ($=COSi$); 178.3 (*E*), 178.28 (*Z*) ($C=O$).

The ^{29}Si (59.6 MHz, THF-d_8) spectrum displayed two signals at 18.992 (*Z*) and 20.732 (*E*) in a 97:3 ratio. The assignment of *Z* to the major stereoisomer of **2** was based on NOE experiments in the ^1H NMR spectrum. The critical effect was when the allylic methyl in the major isomer was irradiated and an enhancement was observed in the allylic methoxy.

Dimethyl 2,4,4-Trimethyl-2-[3-methoxy-2-methyl-3-(trimethylsiloxy)-prop-2-en-1-yl]glutarate (3). The synthesis of **3** was accomplished in three steps. The first step started from methyl methacrylate and followed a literature procedure[14] to afford methyl 2,2,4-trimethyl-4,6-dicarbomethoxyhept-6-en-1-oate of 95% purity. The second step involved hydrogenation of the carbon–carbon double bond. The alkene (5.235 g, 0.0175 mol) from step 1 was combined with 0.523 g of 5% $Pd/BaSO_4$ in 130 mL of ethanol. The mixture was stirred for 2 h at 25 °C under 1 atm of H_2. The catalyst was removed by filtration, and the crude product was distilled. The ^1H NMR spectrum was consistent with dimethyl 2,2,4,6-tetramethyl-4-carbomethoxy-1,7-heptadioate. ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 18.96, 19.94, 22.64, 29.14 (CCH_3); 35.24 (CH); 41.30, 44.63 (quat C); 45.50, 48.38 (CH_2); 51.47, 51.62, 51.59 (OCH_3); 176.76, 176.99, 178.43 (C=O). GC/MS (*m/e*) 271 ($P - OCH_3^+$), 243 ($P - CO_2CH_3^+$), 211, 201, 183.

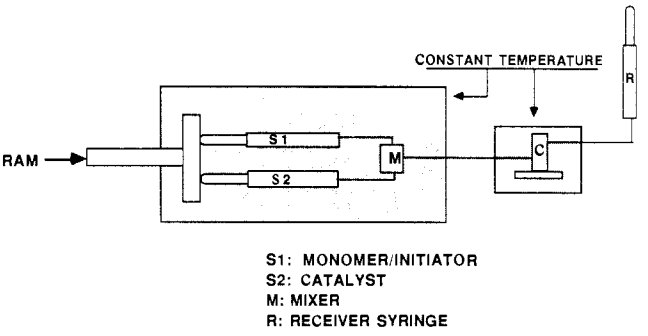

Figure 1. Stopped-flow FT-IR apparatus.

The hydrogenation product (3.662 g, 0.0121 mol) was combined with 15.1 g of chlorotrimethylsilane (17.6 mL, 0.138 mol) and 50 mL of anhydrous THF in a Schlenk flask in a drybox. The flask was connected to an argon line and cooled to −78 °C in a dry ice/acetone bath. While stirred rapidly, 7.7 mL (14.6 mmol) of 1.9 M lithium diisopropylamide in THF was added slowly via syringe. The solution was stirred for 3 h at −78 °C and then allowed to warm to 25 °C. The volatiles were removed in vacuo, and the product was isolated as a light yellow oil via bulb-to-bulb distillation.

Anal. Calcd for $C_{18}H_{33}O_6Si$: C, 57.88; H, 8.91; O, 25.70; Si, 7.52. Found: C, 58.22; H, 8.42; O, 25.46; Si, 8.01.

The proton spectrum displayed the following resonances. ^1H NMR (300 MHz, THF-d_8, TMS): δ 3.63, 3.61 (s, 6 H, CCO_2Me); 3.53 (*Z*), 3.46 (*E*) (s, 3 H, $=COMe$); 2.11–2.37 (m, 4 H, CH_2); 1.507 (*E*), 1.47 (*Z*) (s, 3 H, $=CCH_3$); 1.17 (*Z*), 1.147 (*E*) (s, 3 H, $C(CH_3)CO_2Me$); 1.07, 1.05 (s, 6 H, *gem-Me*); 0.259 (*E*), 0.241 (*Z*) (s, 9 H, $Si(CH_3)_3$). The ^{29}Si (59.6 MHz, THF-d_8) spectrum displayed two signals at 18.918 (*Z*) and 18.866 (*E*) in a 86:14 ratio. The assignment of stereochemistry was based on NOE experiments in the ^1H NMR spectrum.

Tris(piperidino)sulfonium Bifluoride ($TPSHF_2$). A mixture of 0.56 g of H_2O (31 mmol) and 165 mL of THF was added dropwise to 10.97 g (27 mmol) of tris(piperidino)sulfonium difluorotrimethylsiliconate[15] in 110 mL of THF under an inert atmosphere. The mixture was stirred for 1 h, and the volatiles were removed in vacuo. The residue was recrystallized in a drybox from THF/*n*-pentane to afford white crystalline tris(piperidino)sulfonium bifluoride ($TPSHF_2$), mp 99–99.5 °C. ^{19}F NMR (200 MHz, THF-d_8, $CFCl_3$): δ −151.17 (d, J_{HF} = 124 Hz).

Tris(piperidino)sulfonium Benzoate (TPSBz). To a stirred solution of 3.11 g of tris(piperidino)sulfonium difluorotrimethylsiliconate (7.85 mmol) in 80 mL of THF was added 1.41 g (2.24 mL, 7.2 mmol) of trimethylsilyl benzoate in 20 mL of THF. The reaction was conducted under an inert atmosphere. Upon addition of the trimethylsilyl benzoate, a precipitate immediately formed. The precipitate was recrystallized three times from *n*-pentane/THF to afford a white crystalline solid, mp 124–127 °C.

Anal. Calcd for $C_{22}H_{35}N_3O_2S$: C, 65.15; H, 8.70; O, 7.89; N, 10.36; S, 7.91. Found: C, 64.36; H, 8.93; O, 9.36; N, 9.70; S, 7.65. ^1H NMR (300 MHz, CD_3CN): δ 1.62 (s, 18 H, β,γ-H on piperidino ring), 3.17 (s, 12.3 H, α-H on piperidino ring), 7.22, 7.90 (m, 5 H, aromatic). The product did not display any ^{19}F resonances.

Tris(piperidino)sulfonium bibenzoate (TPSBB) was prepared in situ by mixing equimolar amounts of tris(piperidino)sulfonium benzoate and benzoic acid in THF. Attempts to recrystallize the bibenzoate salt with pentane/THF mixtures were unsuccessful.

Tris(piperidino)sulfonium fluorosiliconate–5 was prepared by adding 1,1-diphenyl-3,3-bis(trifluoromethyl)-3*H*-[2,1]benzoxasilole[16] (3.56 g, 8.4 mmol) to a solution of tris(piperidino)sulfonium difluorotrimethylsiliconate (3.16 g, 8.0 mmol) in 25 mL of THF. The solution was stirred for 1 h. Half of the solvent was removed in vacuo, and diethyl ether was added to complete precipitation of the product, which was filtered, washed with diethyl ether, and dried to provide 5.77 g (99% yield) of a white solid, mp 154–155 °C. Recrystallization from THF/diethyl ether

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(6) Bandermann, F.; Speikamp, H. D. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 335. Bandermann, F.; Sitz, H. D.; Speikamp, H. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*(1), 169. Bandermann, F.; Witkowski, R. *Makromol. Chem.* **1986**, *187*, 2691.
(7) Mai, P. M.; Müller, A. H. E. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 99.
(8) Mai, P. M.; Müller, A. H. E. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 247.
(9) The initiation step (Scheme I) produces **2** with living-end stereochemistry of *E*/*Z* = 70/30. The individual rates of MMA addition to (*E*)-**2** and (*Z*)-**2** were found to be identical within experimental error: Brittain, W. J., unpublished results.
(10) Ainsworth, C.; Chen, F.; Kuo, Y. N. *J. Organomet. Chem.* **1972**, *46*, 59.
(11) Dicker, I. B.; Cohen, G. M; Farnham, W. B.; Hertler, W. B.; Laganis, E. D.; Sogah, D. Y., submitted for publication in *Macromolecules*.
(12) Dicker, I. B. U.S. Patent 4732955, March 22, 1988.
(13) Lochmann, L.; Rodova, R.; Petranek, J.; Lim, D. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2295.
(14) Cacioli, P.; Hawthorne, D. G.; Laslett, R. L.; Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci., Chem.* **1986**, *A23*(7), 1839–52.
(15) Middleton, W. J. U.S. Patent 3940402, Feb 24, 1976.
(16) Prepared as previously described: Farnham, W. B.; Dixon, D. A.; Middleton, W. J.; Calabrese, J. C.; Harlow, R. L.; Whitney, J. F.; Jones, G. A.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1987**, *109*, 476.

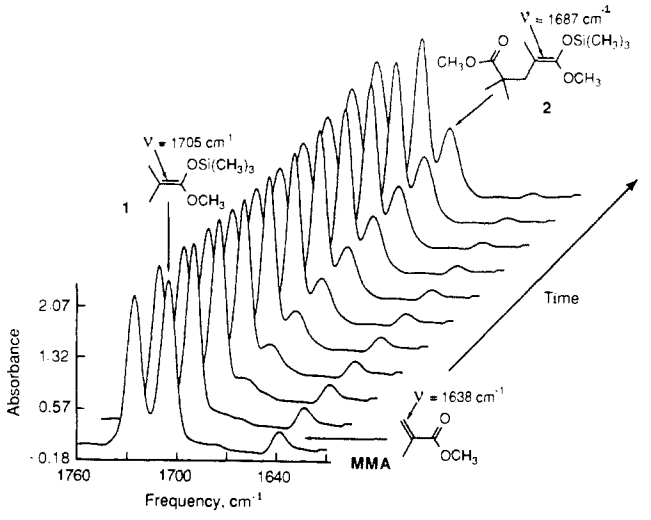


Figure 2. FT-IR spectrum vs time for GTP initiation (Scheme I) catalyzed by tetrabutylammonium bibenzoate.

(slow gradual addition of ether) gave 4.80 g; mp 157–158 °C.

Anal. Calcd for $C_{36}H_{44}F_7N_3OSSi$: C, 59.40; H, 6.09; N, 5.77; S, 4.40; F, 18.27. Found: C, 58.99; H, 6.10; N, 5.76; S, 4.49; F, 18.58. ^{19}F NMR (200 MHz, THF-d_8, $CFCl_3$): δ −73.84 (br s, 6 F), −110.79 (s, $^1J_{FSi}$ = 260 Hz, 1 F).

Stopped-Flow FT-IR Apparatus. The rates were measured with a rapid-mixing apparatus interfaced to a rapid-scan FT-IR spectrometer (Figure 1). The rapid-mix equipment (System 1000 Chemical Quench Apparatus, Update Instruments, Inc., Madison, WI) was modified for use with organic solvents. The syringes and mixer were redesigned so that no O-rings were in contact with solutions. The Update Instruments system uses a microprocessor-controlled positive displacement dc motor, which has an optical encoder board to ensure constant velocity. This is in contrast to most rapid-mix systems, which use constant force, variable-velocity motors. The mixer geometry is a T-arrangement with narrow inlet tubes (0.0008-in. diameter) feeding into a mixing chamber (0.0225-in. diameter), which has four wire grids (75 mesh nickel) to induce turbulence. The mixer has a 2-μL dead volume, and under typical operating conditions, the minimum time of mixing is 6 ms.[17] Two solutions, one containing the catalyst and the other a mixture of monomer and initiator, were loaded into stainless-steel syringes in a drybox. Under typical conditions, the mechanical ram would displace the contents of both syringes into a T-mixer at linear stream velocities of 700 cm/s (N_{re} > 7000). The mixed solution was directed into a flow-through optical cell mounted in the sample chamber of the FT-IR spectrometer.

The rapid-mix apparatus was interfaced to a Nicolet 20SXB FT-IR spectrometer. Typically, a full spectrum was taken every 0.091 25 s. After 2000 rapid scans, the sample was then monitored at less frequent intervals (30 s) until a 40-min total reaction time elapsed. The reaction progress was followed by changes in the C=O and C=C region of the spectrum (1760–1600 cm^{-1}) where the solvent, THF, does not absorb. Figure 2 displays a stacked plot of this region versus time. A major advantage of this experimental technique is the ability to simultaneously monitor both products and reactants. The primary diagnostic for kinetics was the area of the monomer C=C stretch at 1637 cm^{-1} (ϵ = 86). On the basis of the first-order integral for the decrease in the area of this peak, time conversion plots gave lines from which apparent rates could be calculated.

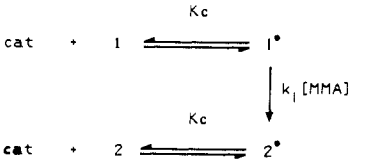
Reaction conditions for the kinetics always employed a 2-fold excess of the starting silyl ketene acetal (**1**–**3**) relative to MMA. GC analysis of optical-cell contents following kinetic runs consistently indicated that >85% of one product was obtained, which corresponded to addition of 1 equiv of MMA to the starting silyl ketene acetal.

The kinetic experiments were done under isothermal conditions. The solutions were preequilibrated by immersion of the syringes in a constant temperature bath. The mixer was also immersed in the bath and the whole system allowed to come to constant temperature for roughly 30 min prior to execution of a kinetic run. In addition, the optical cells mounted in the spectrometer were equipped with jackets for fluid circulation. Two kinds of optical cells were used for experiments: (1) a microcircle ATR cell (Spectra-Tech) or a modified transmission cell (Harrick Scientific). Thermocouples were used to monitor temperature in the cell and syringe bath. Typical temperature variation was less than 0.5 °C over the course of an experiment.

All rates are based on multiple determinations where the values reported represent the weighted mean. The standard error reported is at the 95% confidence interval.

(17) Vidrine, W., Nicolet Analytical Research Laboratory, Madison, WI, private communication.

Scheme IV



Kinetic Model

According to the current view of GTP, the anionic catalyst coordinates with the silicon of the silyl ketene acetal and generates a pentavalent siliconate.[3] In its complexed form, the silyl ketene acetal undergoes a Michael reaction with the methyl methacrylate. The equilibrium constant, K_c, for the formation of the pentacoordinate silicon will vary depending on the nature of the anion. K_c may also vary depending on the chemical event (i.e. initiation or propagation) and also on the stereochemistry of the silyl ketene acetal functionality.[9] A kinetic model for initiation is shown in Scheme IV; the asterisk indicates a catalyst complex. The rate of reaction is given by

$$R = -\mathrm{d[MMA]}/\mathrm{d}t = k_i[\mathrm{MMA}][\mathbf{1}^*] \quad (1)$$

Substituting for [**1***] leads to

$$R = k_i K_c[\mathbf{1}][\mathrm{cat}][\mathrm{MMA}] \quad (2)$$

The integrated form of eq 2 is

$$\ln([\mathrm{MMA}]_0/[\mathrm{MMA}]) = k_i K_c[\mathbf{1}][\mathrm{cat}]t \quad (3)$$

It is assumed that [**1**] $\approx$ [**1**]$_0$. This assumption is reasonable because [**1**]$_0$ = 2[MMA]$_0$ and also because the rates were based on initial slopes of the time–conversion plots. It is recognized that there will be error associated with the use of the initial slopes method for determining the rates. However, it was found that error of precision for repeat rate determinations exceeded the accuracy error associated with the initial slope method. Also, the kinetics is the same when [**1**]$_0$ = 5[MMA]$_0$, which further supports the assumption [**1**] $\approx$ [**1**]$_0$ over the period of the reaction on which the rate is based. With this assumption and the assumption that [cat] remains relatively constant, eq 3 can be simplified to eq 4.

$$\ln([\mathrm{MMA}]_0/[\mathrm{MMA}]) = k_{app}t \quad (4)$$

$$k_{app} = k_i K_c[\mathbf{1}]_0[\mathrm{cat}] \quad (5)$$

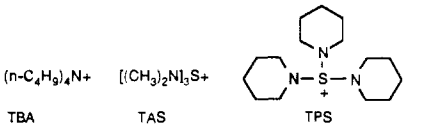
An analogous kinetic model is valid for the chemical events in Schemes II and III, which leads to the following equations for the first (eq 6) and second (eq 7) propagation steps.

$$k_{app} = k_p^1 K_c[\mathbf{2}]_0[\mathrm{cat}] \quad (6)$$

$$k_{app} = k_p^2 K_c[\mathbf{3}]_0[\mathrm{cat}] \quad (7)$$

Results and Discussion

The most common catalysts for GTP are nucleophilic anions such as carboxylates and bifluoride, typically as tetrabutylammonium (TBA) or tris(dimethylamino)sulfonium (TAS) salts.



The advantage of sulfonium salts such as TAS is that it is easier to prepare them as anhydrous. The tetrabutylammonium ion, however, confers better solubility in THF, thus eliminating a common requirement of TAS salts for a polar cosolvent like acetonitrile. Substitution of tris(piperidino)sulfonium (TPS) for TAS improves THF solubility substantially.[15] As part of the kinetic investigation of GTP, TPS salts of bifluoride, benzoate,

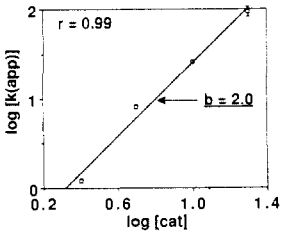


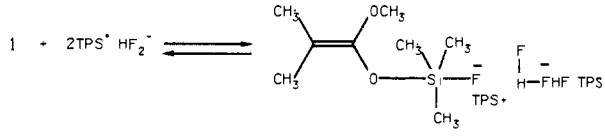
Figure 3. Rate-order plot for GTP initiation catalyzed by tris(piperidino)sulfonium bifluoride.

Table I. $TPSHF_2$ Rate Dependence for GTP Initiation[a]

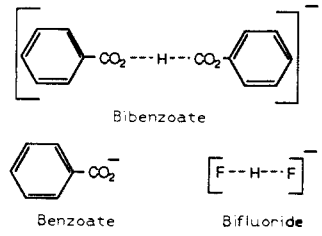
$[TPSHF_2]$, M × 10^5	k_{app} ± SE, s^{-1} × 10^3	$[TPSHF_2]$, M × 10^5	k_{app} ± SE, s^{-1} × 10^3
2.5	1.21 ± 0.04	10.0	25.5 ± 0.5
5.0	8.1 ± 0.4	20.0	93 ± 12

[a] $[1]_0$ = 0.25 M, $[MMA]_0$ = 0.125 M, THF, 27 °C.

Scheme V



and bibenzoate were synthesized. All three TPS catalysts, which were synthesized from a common precursor, $TPS^+F_2Si(CH_3)_3^-$, showed good THF solubility.



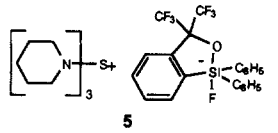
I. Catalyst Rate Order. The kinetic order of catalyst has been studied for a series of anionic catalysts. A bilogarithmic plot of apparent rate constant versus catalyst concentration based on eq 8 will give a line whose slope equals n (rate order of catalyst).

$$\log (k_{app}) = \log (k_i K_c [1]_0) + n(\log [cat]) \quad (8)$$

Bifluoride. Apparent rate constants, k_{app}, at different concentrations of tris(piperidino)sulfonium bifluoride ($TPSHF_2$) are given in Table I for the addition of MMA to**1** (Scheme I). Figure 3 shows that rate of MMA consumption has a *second-order rate dependence on* $TPSHF_2$ concentration (i.e. n = 2).

Corroboration of n = 2 for $TPSHF_2$ was obtained from a similar study of $TASHF_2$ in 9:1 THF/CH_3CN over a concentration range of 0.001–0.000 25 M. A bilogarithmic plot of the data gave a line whose slope was 2.1. Two possible interpretations for a second-order HF_2 dependence are a transition state for monomer addition that involves (1) a 2:1 HF_2/**1** hexavalent silicon complex or (2) a 1:1 fluoride/**1** complex (Scheme V). In the second hypothesis, F^- donation to silicon could occur concurrently with hydrogen bond formation between HF and a second HF_2^- molecule.[18]

It is experimentally difficult to distinguish between the two hypotheses. However, it has been possible to establish that catalyst **5** (which is a source of F^-) catalyzes initiation with a first-order



5

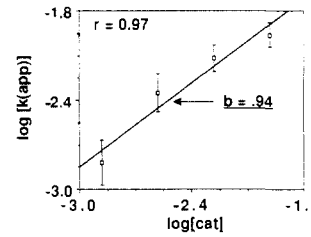


Figure 4. Rate-order plot for GTP initiation catalyzed by **5**.

Table II. Initiation Rate Dependence on Concentration of Catalyst **5**[a]

[**5**], M × 10^3	k_{app} ± SE, s^{-1}	[**5**], M × 10^3	k_{app} ± SE, s^{-1}
1.31	0.0015 ± 0.0005	5.25	0.008 ± 0.002
2.63	0.005 ± 0.001	10.5	0.011 ± 0.002

[a] $[1]_0$ = 0.25 M, $[MMA]_0$ = 0.125 M, THF, 25 °C.

Table III. TBA Bibenzoate (TBABB) Rate Dependence for GTP Initiation[a]

[TBABB], M × 10^3	k_{app} ± SE, s^{-1}	[TBABB], M × 10^3	k_{app} ± SE, s^{-1}
1.25	0.057 ± 0.001	12.5	0.108 ± 0.004
5.3	0.064 ± 0.001		

[a] $[1]_0$ = 0.25 M, $[MMA]_0$ = 0.125 M, THF, 27 °C.

dependence. The data and corresponding plot are given in Table II and Figure 4. The results with **5** substantiate that a fluoride ion donor can catalyze the reaction and n = 1. This fact does not completely rule out either theory for explaining second-order bifluoride catalysis but is more consistent with the second hypothesis involving the equilibrium in Scheme V.

Müller and Mai[7] reported a first-order dependence for $TASHF_2$ under their conditions: $[MMA]_0$ = 0.18 M, $[1]_0$ = 0.001 M. However, their kinetic runs were complicated by induction periods and other deviations from linearity in their first-order plots of monomer conversion. We did not observe induction periods in our work. It is difficult to make a meaningful comparison of our results with those of Müller because of the different conditions and experimental approaches used. However, the experiments reported here were devised so that intermediates could be observed. Furthermore, by using stopped-flow FT-IR spectroscopy, changes in the reaction progress could be monitored at 50-ms intervals. Therefore, our rate order with respect to bifluoride concentration is for addition of monomer and not another reaction.

Benzoate. The rate order of an oxyanion catalyst, tris(piperidino)sulfonium benzoate (TPSBz), has also been determined. The reaction steps depicted in Schemes I and II were individually studied at three different concentrations of TPSBz (0.000 13, 0.0005, and 0.008 M). The concentrations of reactants were identical with those in the bifluoride work ($[MMA]_0$ = 0.125 M and $[1]_0$= 0.25 M for the study of initiation and $[2]_0$ = 0.25 M for the first propagation step). Data analysis like that used for bifluoride indicated that rate dependence for initiation and the first propagation step was *first order in TPSBz*.

Bibenzoate. The rate order determination of tetrabutylammonium bibenzoate (TBABB) afforded unusual results. The apparent rate constants for three concentrations of catalyst are given in Table III. When this data is plotted in a bilogarithmic fashion, a slope of 0.3 is obtained. One possible explanation is that catalysis by bibenzoate anion actually occurs through a complex of the silicon and a benzoate anion. The benzoate anion would come from the dissociation of the bibenzoate into benzoic acid and the monoanion.[11,19] Paucity of information on the magnitude of such equilibria in bioxyanions makes it difficult to quantitatively predict the rate order with respect to bibenzoate catalysis. At present, we are further investigating the nature of

(18) Higher aggregates of HF_2^- have been discussed in the literature, see: Gennick, I.; Harmon, K. M.; Potvin, M. M. *Inorg. Chem.* **1977**, *16*, 2033. Also, see: Fujiwara, F. Y.; Martin, J. S. *J. Am. Chem. Soc.* **1974**, *96*, 7625.

(19) We found that 33% of TBABB is dissociated into benzoic acid and TBA benzoate in methanol. It was not possible to determine the extent of dissociation in THF.

Table IV. Third-Order Rates[a] for GTP Initiation Catalyzed by Bibenzoate Anion[b]

catalyst cation (concn, M)	$k_iK_c \pm$ SE, $L^2/mol^2 \cdot s$
tris(piperidino)sulfonium (0.0018)	142
tetrabutylammonium (0.001 25)	168

[a] $k_iK_c = k_{app}/[cat][1]_0$. [b] $[MMA]_0 = 0.125$ M, $[1]_0 = 0.25$ M, THF, 25 °C.

Table V. Rates for GTP Initiation Catalyzed by Tris(piperidino)sulfonium Salts[a,b]

catalyst anion	$k_iK_c \pm$ SE
bifluoride	$(9 \pm 1) \times 10^6$ $L^3/mol^3 \cdot s$
benzoate	$(1.8 \pm 0.2) \times 10^3$ $L^2/mol^2 \cdot s$
bibenzoate	34 ± 1 $L^2/mol^2 \cdot s$

[a] $k_iK_c = k_{app}/[cat]^n[1]_0$. [b] $[MMA]_0 = 0.125$ M, $[1]_0 = 0.25$ M, THF, 25 °C.

bibenzoate catalysis and hope to more fully explain the chemistry in a future paper.

$$TBA^+[(C_6H_5CO_2)_2H]^- \rightleftarrows TBA^+C_6H_5CO_2^- + C_6H_5CO_2H$$

II. Influence of Catalyst Structure on Rate. This work has provided information about the relative importance of the anion and cation structures in a GTP catalyst. To explore the role of the cation, the rates of two salts having a common anion (TPS bibenzoate and TBA bibenzoate) are given in Table IV. The data indicate that the counterion in GTP catalysts is not a significant contributor to overall reactivity, at least when it is a noncoordinating organic cation.

Not surprisingly, it is the anion structure that dominates the reactivity of the catalyst. The rate dependence on anion structure was determined by comparison of the initiation rates (Scheme I) for three tris(piperidino)sulfonium salts. Table V contains the rates obtained by plotting k_{app} versus $[cat]^n$. The slope of this line was divided by $[1]_0$ to give the values in Table V. One cannot quantitatively compare the reactivity of the three anions because the value of K_c is probably different for each catalyst. Despite the lack of information regarding the magnitude of K_c, the catalysts can be ranked in a qualitative fashion:

$$HF_2^- \gg C_6H_5CO_2^- > [(C_6H_5CO_2)_2H]^- \quad \text{(decreasing } k_iK_c\text{)}$$

III. Relative Rates of Initiation vs Propagation. The kinetic requirement for a polymer's molecular weight distribution that is described by a Poisson distribution is $k_i \geq k_p$. The fact that GTP does give a narrow MW distribution would argue strongly for this kinetic requirement. To confirm this rate relationship between propagation and initiation, the rate values for the first several steps of GTP were determined with different catalysts. By the "single-event" approach, where discrete chemical events are studied, individual rates can be determined with high reliability.

Table VI. Third-Order Rates for TBABB Catalysis of GTP[a]

chemical event	rate $\pm$ SE, $L^2/mol^2 \cdot s$
initiation	$k_iK_c = 34 \pm 1$
first propagation step	$k_p^1K_c = 48 \pm 1$
second propagation step	$k_p^2K_c = 28 \pm 2$

[a] $[TBABB] = 0.0125$ M, $[MMA]_0 = 0.125$ M, THF; $[1]_0$, $[2]_0$, and $[3]_0 = 0.25$ M.

When tetrabutylammonium bibenzoate (TBABB) is used, rates of MMA addition have been determined for the first three steps of GTP (Schemes I–III). The third-order rates for TBABB catalysis are listed in Table VI. As part of the rate-order study of tris(piperidino)sulfonium benzoate (TPSBz), the discrete third-order rates for the first two steps (Schemes I and II) were determined (taken from the slope of a k_{app} vs [cat] plot and divided by the starting silyl ketene acetal concentration):

$$k_iK_c = 1800 \pm 150 \text{ L}^2/\text{mol}^2 \cdot \text{s}$$

$$k_p^1K_c = 1600 \pm 400 \text{ L}^2/\text{mol}^2 \cdot \text{s}$$

We conclude that, for TBABB catalysis, $k_i \approx k_p^1 \approx k_p^2$. Likewise, for TPSBz catalysis, it was found that $k_i \approx k_p^1$. Therefore, both catalysts satisfy the relationship that $k_i/k_p \geq 1$.

Conclusions

Methodology for kinetic study of the Michael reactions of silyl ketene acetals has been developed. The reaction rates and the kinetic rate order of catalyst depend on the structure of the catalyst anion. The anions studied can be ranked in order of decreasing reactivity: $HF_2^- > C_6H_5CO_2^- > [(C_6H_5CO_2)_2H]^-$. The reactivity of the catalyst is independent of the counterion. The rate order of HF_2^- for GTP initiation is 2. On the basis of the first-order dependence of catalyst **5**, which is a source of F^-, the preferred interpretation is that shown in Scheme V. Catalysis by TPSBz occurs with a first-order dependence on catalyst concentration.

The discrete rates for the first several steps of GTP catalyzed by TBA bibenzoate and TPS benzoate have been determined. For processes catalyzed by either, the individual rates were approximately equal.

Acknowledgment. I thank Dotsevi Y. Sogah and William B. Farnham for invaluable discussions. I am also grateful to William B. Farnham for the preparation of compound **5** and to David H. Davies for his technical assistance.

Registry No. 1, 31469-15-5; **2**, 109796-34-1; **3**, 116232-82-7; **5**, 116299-99-1; MMA, 80-62-6; $TPSHF_2$, 113122-15-9; TPSBz, 116232-84-9; TPSBB, 116263-40-2; dimethyl 2,2,4-trimethylglutarate, 17072-61-6; chlorotrimethylsilane, 75-77-4; methyl 2,2,4-trimethyl-4,6-dicarbomethoxyhept-6-en-1-oate, 116232-83-8; dimethyl 2,2,4,6-tetramethyl-4-carbomethoxy-1,7-heptadioate, 54060-77-4; tris(piperidino)sulfonium difluorotrimethylsiliconate, 116346-76-0; trimethylsilyl benzoate, 2078-12-8; 1,1-diphenyl-3,3-bis(trifluoromethyl)-(3*H*)-[2,1]benzoxasilole, 91454-72-7.