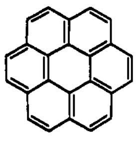
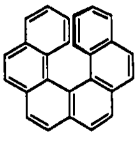
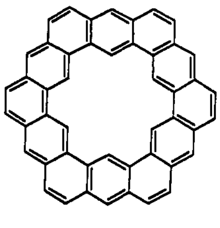


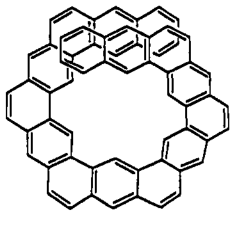
1



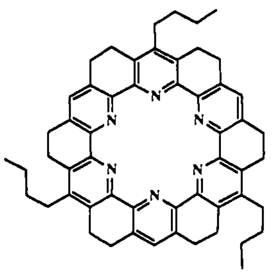
2



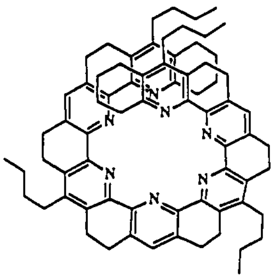
3



4



5



6

hydro-4(1*H*)-acridinone (**8**) by variations of previously reported methods[4b,d,e] (Figure 1). These intermediates were synthesized in several steps from cyclohexanone and valeraldehyde by published methods.[4b,d,e,6] Ketone **8** was converted to enone **9** by a new coupling procedure[7] using dimethylmethyleneammonium chloride.[8] Reaction of ketone **7** with enone **9** gave unsymmetrical heptacyclic terpyridyl **10**.[9] Ozonolytic cleavage of the benzylidene group in **10** gave heptacyclic ketone **11**,[9] the key intermediate for synthesis of expanded heterohelicenes. Homologation of **11** by reaction with ammonium acetate and **9** and chromatography of the crude product on basic alumina gave free ligand **12** (22%)[9] and a later fraction, which proved to be a sodium complex (**12**·Na$^+$).[10] Reaction of **11** with Bredereck's reagent[11] gave β-dimethylamino enone **13**, which was coupled with **11** by the method of Firestone.[12] Chromatography on basic alumina again gave two fractions, apparently containing free ligand **6** and **6**·Na$^+$.[13]

Geminal protons of **6** and **12** become diastereotopic when their enantiomeric helical conformations interconvert slowly. In free host **12** various methylene groups are observed as distinct two-proton multiplets in the 600-MHz ^{1}H NMR spectrum, indicating that helix inversion is rapid on the NMR time scale. The ^{1}H NMR spectrum of **12**·NaCF$_3$SO$_3$, prepared by treatment of **12** with sodium triflate in methanol, shows broadened CH$_2$ peaks due to slow helix inversion; the benzylidene peak remains sharp but is shifted upfield by 2.0 ppm. These results show not only that helix inversion is slow in **12**·Na$^+$ but also that complexation alters the helix conformation. Figure 2 shows that a large bathochromic shift of the longest wavelength UV absorption also occurs upon binding sodium.

We conclude that expanded helix **12** consists of rapidly interconverting enantiomers in solution; complexation of sodium increases the barrier to helix inversion. This potentially useful conformational change and the resulting optical response are more extreme than those observed in expanded systems comprising less than one full turn of a helix.[4a] Complexation and conformational properties of **6** are currently under investigation.[14]

Acknowledgment. We thank Richard Ludwig for recording 600-MHz ^{1}H NMR spectra and for assistance with preparing figures. This project was supported by the National Institutes of Health (GM 32937). The Bruker AMX-600 NMR instrument was obtained with grants from the NIH (RR05547A) and the NSF (CHE 8911350) and with support from the Center for Biotechnology and SUNY, Stony Brook.

---

(6) (a) Bell, T. W.; Cho, Y.-M.; Firestone, A.; Healy, K.; Liu, J.; Ludwig, R.; Rothenberger, S. D. *Org. Synth.* **1990**, *69*, 226–237. (b) Bell, T. W.; Rothenberger, S. D. *Tetrahedron Lett.* **1987**, *28*, 4817–4820. (c) Bell, T. W.; Firestone, A. *J. Org. Chem.* **1986**, *51*, 764–765.

(7) Bell, T. W.; Firestone, A.; Kwok, D.-I.; Ludwig, R., manuscript in preparation.

(8) Risch, N.; Esser, A. *Synthesis* **1988**, 337–339.

(9) Satisfactory ^{1}H NMR, ^{13}C NMR, IR, MS, UV-visible, and C, H, N microanalytical data were obtained.

(10) The ^{1}H NMR spectrum of this material was identical with that of **12**·NaCF$_3$SO$_3$. Continuous extraction of its solution in CHCl$_3$ with pure water gave free **12**.

(11) Bredereck, H.; Simchen, G.; Rebsdat, S.; Kantlehner, W.; Horn, P.; Wahl, R.; Hoffman, H.; Grieshaber, P. *Chem. Ber.* **1968**, *101*, 41–50.

(12) Firestone, A. Ph.D. Thesis, SUNY, Stony Brook, 1988.

(13) As observed for **12** and **12**·Na$^+$, the ^{1}H NMR spectrum of the first-eluted fraction was less broad than that of the later fraction. The principal high-mass peak in the FAB-MS spectra of both fractions was m/z 1052 (M + 23).

(14) During the course of this research we learned of efforts by G. Balavoine et al. (Université de Paris-Sud, Orsay) to prepare compounds of related structure.

Traveling Fronts of Methacrylic Acid Polymerization

John A. Pojman

Department of Chemistry and Biochemistry
University of Southern Mississippi
Hattiesburg, Mississippi 39406-5043

Received April 29, 1991

We report here the preliminary investigation of traveling fronts in methacrylic acid polymerization in unstirred solutions of the monomer and benzoyl peroxide, with and without a promoter.

An autocatalytic reaction in an unstirred vessel can support a constant-velocity wave front resulting from the coupling of diffusion to the chemical reaction. Numerous reactions in solution have been described in which a front of chemical reactivity propagates through the medium from the site of an initial concentration perturbation.[1-11] Traveling wave fronts in populations of short self-replicating RNA variants have been created in thin capillary tubes,[12] but fronts have not been studied in synthetic polymerization reactions. We have set out to do so in an attempt to observe ultimately the sorts of nonlinear propagation phenomena seen in solid-fuel, gasless combustion such as pulsating and spinning fronts.[13-15]

Coupling the exothermic addition polymerization of methacrylic

---

(1) Zaikin, A. N.; Zhabotinskii, A. M. *Nature* **1970**, *225*, 535–537.

(2) Winfree, A. T. *Science* **1973**, *181*, 937–939.

(3) Field, R. J.; Noyes, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 2001–2006.

(4) Reusser, E. J.; Field, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 1063–1071.

(5) Gribshaw, T. A.; Showalter, K.; Banville, D. L.; Epstein, I. R. *J. Phys. Chem.* **1981**, *85*, 2152–2155.

(6) Bazsa, G.; Epstein, I. R. *J. Phys. Chem.* **1985**, *89*, 3050–3053.

(7) Hanna, A.; Saul, A.; Showalter, K. *J. Am. Chem. Soc.* **1982**, *104*, 3838–3844.

(8) *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; Wiley: New York, 1985.

(9) Harrison, J.; Showalter, K. *J. Phys. Chem.* **1986**, *90*, 225–226.

(10) Szirovicza, L.; Nagypal, I. Boga, E. *J. Am. Chem. Soc.* **1989**, *111*, 2842–2845.

(11) Ross, J.; Müller, S. C.; Vidal, C. *Science* **1988**, *240*, 460–465.

(12) Bauer, G. J.; McCaskill, J. S.; Otten, H. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 7937–7941.

(13) Kaper, H. G.; Leaf, G. K.; Margolis, S. B.; Matkowsky, B. J. *Combust. Sci. Technol.* **1987**, *53*, 289–314.

(14) Anselm-Tamburini, U.; Munir, Z. A. *J. Appl. Phys.* **1989**, *66*, 5039–5045.

(15) Matkowsky, B. J.; Sivashinsky, G. I. *SIAM J. Appl. Math.* **1978**, *35*, 465–478.

0002-7863/91/1513-6284$02.50/0

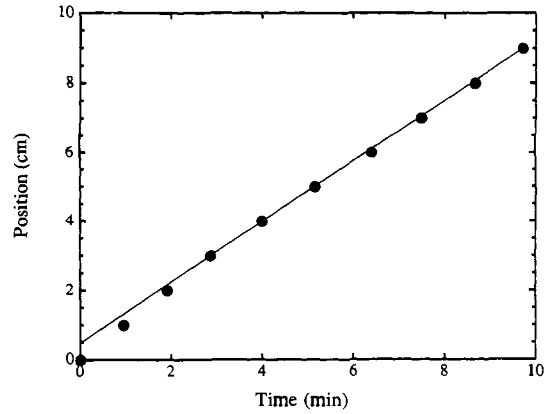


Figure 1. The position versus time of a traveling front of methacrylic acid polymerization. The position was determined visually by the presence of a sharp change from the monomer/initiator solution to solid polymer. Benzoyl peroxide concentration = 0.10 *m*.

acid to the thermal decomposition of the free-radical initiator benzoyl peroxide provides the necessary autocatalysis for traveling fronts.

Methacrylic acid (Aldrich) was obtained with MEHQ inhibitor. The inhibitor was removed by using a column provided by the supplier. However, the presence of the inhibitor was not found to affect the front velocities (given the large excess of initiator), and so the monomer was used without purification. Benzoyl peroxide (97%, Aldrich) and *N,N*-dimethylaniline (DMA) (Aldrich) was used as received.

The solution of monomer and peroxide was placed into a test tube that had been marked in 1-cm units. A 2-cm length of copper wire was heated in a modified soldering iron to over 100 °C and inserted into the solution. The solution quickly became green near the wire as the copper was oxidized by the benzoyl peroxide. Fronts were also initiated with a heated platinum wire; no difference in front velocities was observed. Some fronts were initiated by the addition of approximately $^1/_2$ mL of DMA to the top of the solution. The latter method provides the most controlled and effective initiation. The amount of time required for the front to propagate 1 cm was noted and the velocity calculated. The process was repeated along the length of the tube, and the results were averaged.

The temperature profile was measured by using a miniature thermocouple and an Orion digital thermometer attached to a strip chart recorder. The temperature versus time data was converted to a temperature versus position plot using the measured front velocity.

Constant-velocity fronts appear as slowly moving regions of solid polymer formation. The initial reaction can be quite vigorous, requiring the use of a hood with shield. Initiation with DMA is more controlled.

Figure 1 shows the front position versus time for one experiment. The initial burst of heat causes rapid propagation, but the front reaches a steady velocity after a few minutes. Visual observations of the fronts indicate a discontinuous change from unreacted monomer/initiator solution to white polymer mass. However, the temperature gradient is smooth, as indicated in the plot of temperature versus position in Figure 2. The temperature exceeds the boiling point of methacrylic acid (163 °C), so bubbles can form in the polymer mass. However, at low front velocities, the polymer is solid.

Because the autocatalyst is heat and the system is open to heat loss, the size of the tube affected the existence of a front. For an initiator concentration of 0.16 *m*, fronts would not propagate in tubes of inner diameter 1.1 cm or smaller. Adding the promoter DMA did allow the propagation of fronts in small tubes in which they would not propagate without it. As long as the front can produce a critical value of heat, the velocity is unaffected by the tube size, at least with these concentrations. However, fronts would not propagate in tubes immersed in water because of enhanced heat loss.

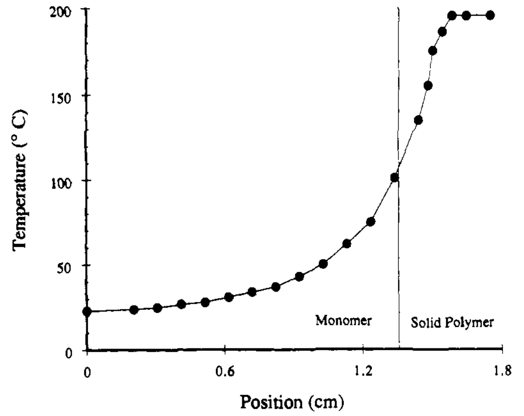


Figure 2. The temperature profile of a front was determined by placing a thermocouple in the center of a tube. The temperature as a function of time was measured and related to the position by using the front velocity. The vertical line indicates the position of the solution/solid polymer interface. Benzoyl peroxide concentration = 0.16 *m*.

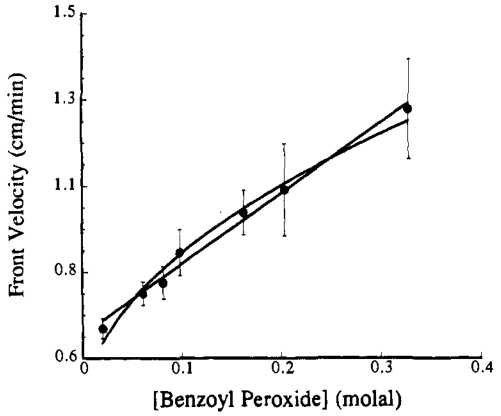


Figure 3. The front velocity as a function of the initiator concentration without promoter. The data were fit with a least-squares program to both a first-order (velocity = k_1[BPO] + constant) and a half-order dependence (velocity = $k_2[\mathrm{BPO}]^{1/2}$ + constant). Higher concentrations of benzoyl peroxide were not possible because of limited solubility.

Under isothermal conditions the rate of addition polymerizations which are initiated by the thermal cleavage of initiators is proportional to the square root of the initiator concentration when the steady-state approximation is valid.[16] The front velocity as a function of initiator concentration is shown in Figure 3. The data were fit to both a linear dependence and a square-root dependence. The precision of the data does not allow a distinction to be made. No higher concentrations of initiator were possible because of the limited solubility of benzoyl peroxide.

The polymer formed was not readily soluble in tetrahydrofuran (THF), so it was converted to the methyl ester with diazomethane. Gel permeation chromatography in THF reveals polymers with an extremely broad molecular weight distribution, with far more long polymer molecules than would be expected. The polydispersity index, the ratio of the weight average to the number average (M_w/M_n), equals 4, based on a calibration with polystyrene standards. The high viscosity of the polymer gel decreases the rate of bimolecular termination, which skews the distribution toward long polymers.[16-18]

The rate of benzoyl peroxide decomposition can be increased by the addition of the promoter *N,N*-dimethylaniline.[19] Figure 4 shows the effect of DMA on front velocity for a fixed concen-

---

(16) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, 1953.

(17) Trommsdorff, E.; Köhle, H. Lagally, P. *Makromol. Chem.* **1948**, *1*, 169–198.

(18) Norrish, R. G. W.; Smith, R. R. *Nature* **1942**, *150*, 336–337.

(19) Updegraff, I. H. In *Handbook of Composites*; Lubin, G., Ed.; Van Nostrand: 1982, pp 22–30.

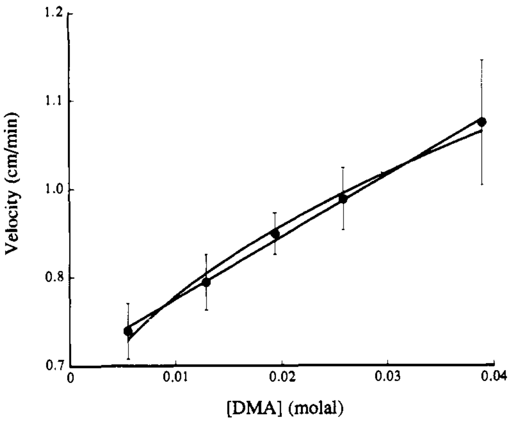


Figure 4. The front velocity as a function of the concentration of the promoter *N*,*N*-dimethylaniline (DMA) at a fixed initiator concentration, [benzoyl peroxide] = 0.041 *m*. The data were fit with a least-squares program to both a first-order (velocity = k_1[DMA] + constant) and a half-order dependence (velocity = k_2[DMA]$^{1/2}$ + constant). Higher concentrations of DMA were not possible because polymerization of the entire solution occurred at room temperature.

tration of initiator. It is not clear whether the front has first-order or half-order dependence on the promoter concentration. The advantage of a promoter is that it allows control over the front velocity without affecting the molecular weight distribution. However, if too much promoter is added, the entire solution polymerizes at room temperature.

Large density gradients are induced in the polymerizing solution by changes in chemical composition and temperature. Such gradients are known to cause free convection, which affects the traveling fronts.[20-22] Work will be forthcoming on convection and polymerization fronts.

---

(20) Pojman, J. A.; Epstein, I. R. *J. Phys. Chem.* **1990**, *94*, 4966-4972.

(21) Pojman, J. A.; Epstein, I. R.; McManus, T.; Showalter, K. *J. Phys. Chem.* **1991**, *95*, 1299-1306.

(22) Pojman, J. A.; Epstein, I. R.; Nagy, I. *J. Phys. Chem.* **1991**, *95*, 1306-1311.

Direct Observation of an Azetidinium Imide Intermediate in [$\pi^2 + \sigma^2$] Addition of 1,2,4-Triazoline-3,5-dione to Disilirane

Wataru Ando,* Masahiro Kako, and Takeshi Akasaka

Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305, Japan

Received December 31, 1990
Revised Manuscript Received June 8, 1991

The interaction between σ-electron donor and π-electron acceptor has attracted continuing interest.[1,2] Cyclopropanes react with tetracyanoethylene to produce [$\pi^2 + \sigma^2$] cycloaddition or ene reaction products, in which either diradicals or zwitterions have been postulated.[1c,d] However, no direct observation of the intermediate has been achieved. Our recent results that singlet oxygen inserts into the strained silicon–silicon σ bonds[3] in disilirane derivatives, via peroxonium ion intermediates,[4] prompted us to investigate the reaction of disiliranes with 4-substituted 1,2,4-triazoline-3,5-dione (TAD). Recently, the aziridinium imide and azomethinimine intermediates in TAD addition to C=C π bonds[5] and C=N π bonds[6] have been characterized by NMR spectroscopy. We report here the first spectroscopic observation of an intermediate in [$\pi^2 + \sigma^2$] addition of TAD to disilirane and assign its structure as an azetidinium imide.

Scheme I

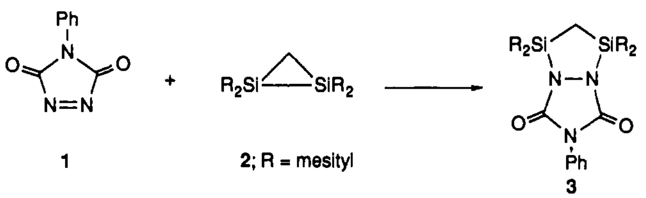
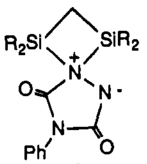


Table I. Coupling Constants ($J_{^{13}C-^{1}H}$ (Hz)) at the Methylene Carbons in **4** and Related Compounds

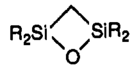
compd	^{13}C NMR (ppm)	$J_{^{13}C-^{1}H}$ (Hz)
2	4.05	137.65
5	21.40	128.60
4	5.81	127.18
6	17.50	124.50
3	8.24	119.67

When 4-phenyl-1,2,4-triazoline-3,5-dione (**1**) was added to a CHCl$_3$ solution of 1,1,2,2-tetramesityldisilirane (**2**)[4a] at room temperature in the dark, the red color of **1** rapidly disappeared. The crude reaction mixture was subjected to preparative HPLC, and recrystallization from hexane gave the corresponding adduct **3**[7] as a colorless crystal in 38% yield (69% yield by ^{1}H NMR). The spectra data are consistent with the 1,2,3,5-diazadisilolidine structure (Scheme I).

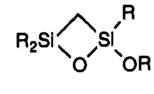
The analogy between the reactivity of $^1O_2$ and that of TAD suggests the intermediacy of an azetidinium imide **4**. Addition of **1** to **2** was monitored by low-temperature ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy in deuteriochloroform. After standing at room temperature for 60 s, a mixture of disilirane **2** and 1.2 equiv of **1** in a Pyrex NMR tube was rapidly cooled down to −78 °C, and the spectra were recorded at −55 °C. A series of new resonances in the ^{13}C NMR spectrum appeared at δ 157.29 (s), 150.70 (s),



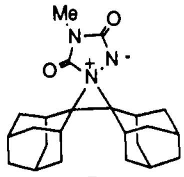
4



5



6



7

---

(1) (a) Gassman, P. G. *Acc. Chem. Res.* **1971**, *4*, 128. (b) Tsuji, T.; Nishida, S. *Acc. Chem. Res.* **1984**, *17*, 56. (c) Gassman, P. G.; Mansfield, K. T.; Murphy, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 1131. (d) Hoffman, H. H. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (e) Martin, T.; Kampureier, L. A. *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 236. (f) Adam, W.; Beinhauer, A.; De Lucchi, O.; Rosenthal, R. J. *Tetrahedron Lett.* **1983**, *24*, 5727.

(2) (a) Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695. (b) Roth, W. R.; Karner, F.-G. *Chem. Ber.* **1983**, *116*, 2717. (c) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 1131.

(3) Charge-transfer interactions of silicon–silicon σ bonds with tetracyanoethylene have been studied: (a) Traven, Y. F.; West, R. *J. Am. Chem. Soc.* **1973**, *95*, 6824. (b) Sakurai, H.; Kira, M.; Uchida, T. *J. Am. Chem. Soc.* **1973**, *95*, 6826. (c) Sakurai, H.; Kamiyama, T. *J. Am. Chem. Soc.* **1974**, *96*, 6192.

(4) (a) Ando, W.; Kako, M.; Akasaka, T.; Nagase, S.; Kawai, T.; Nagai, Y.; Sato, T. *Tetrahedron Lett.* **1989**, *30*, 6705. (b) Ando, W.; Kako, M.; Akasaka, T.; Kabe, Y. *Tetrahedron Lett.* **1990**, *31*, 4177.

(5) (a) Nelsen, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 5548. (b) Squillacote, M.; Mooney, M.; De Felippis, J. *J. Am. Chem. Soc.* **1990**, *112*, 5364.

(6) (a) Akasaka, T.; Sonobe, H.; Sato, R.; Ando, W. *Tetrahedron Lett.* **1984**, *25*, 4757. (b) Sato, R.; Sonobe, H.; Akasaka, T.; Ando, W. *Tetrahedron* **1986**, *42*, 5273.

(7) **3**: mp 293–295 °C; IR (CCl$_4$) 1746, 1690 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.29–7.44 (m, 5 H), 6.78 (s, 8 H), 2.31 (12 H, s), 2.12 (s, 24 H), 1.70 (s, 2 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 153.65 (s), 143.22 (s), 140.22 (s), 130.92 (s), 129.50 (d), 129.09 (d), 128.30 (s), 128.25 (d), 125.98 (d), 23.67 (q), 21.26 (q), 8.26 (t); ^{29}Si NMR (78 MHz, CDCl$_3$) δ −12.87; exact mass calcd for $C_{45}H_{51}N_3O_2Si_2$ 721.3515, found 721.3518.

0002-7863/91/1513-6286$02.50/0