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Addition of Methanesulfonyl Radical to Alkenes and Alkenylsilanes

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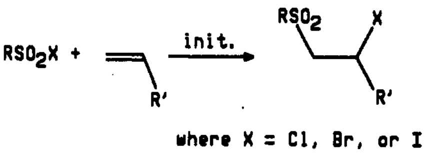
Relative reactivities of a series of olefins (alkenes, cycloalkenes, and alkenylsilanes) toward the electrophilic methanesulfonyl radical ($2^\bullet$) have been determined in acetonitrile at 0 °C. A kinetic treatment of the competitive photoinitiated addition of methanesulfonyl bromide (**1**) to olefins was developed and used to measure the relative reactivity and probe the reversibility of addition. The kinetic treatment was based on the irreversible addition of $2^\bullet$ to a reference olefin serving as a standard reaction. 1,1-Dicyclopropylethene (**14**, a "radical clock") was used as such a primary reference, and 1-hexene and 1-octene were employed as secondary references. **14** was 20 ± 4 times more reactive than 1-hexene, but the relative reactivities of several unactivated alkenes and alkenylsilanes vs 1-hexene were in a range from ca. 0.44 to 6.2. The absolute rate of addition of $2^\bullet$ to *n*-alkenes was estimated to be ca. one-tenth of the diffusion-limited rate. The study showed that, even within a family of closely related alkenes, steric and electronic effects have significant influence on olefin reactivity toward $2^\bullet$ as well as reversibility of the addition.

The kinetics and structure–reactivity relationships for the addition of sulfur-centered radicals to alkenes[1] are less known than similar reactions of carbon-centered radicals.[2] In particular, kinetic data for reactions involving alkylsulfonyl and arylsulfonyl radicals are lacking, although these radicals play a pivotal role in the halosulfonation of unsaturated hydrocarbons[1,3] (Scheme I) and in the technologically important free-radical copolymerization of olefins with SO_2.[4] For example, only recently, absolute rate constants became available for the addition of alkyl- and arylthiyl radicals to some alkenes.[5]

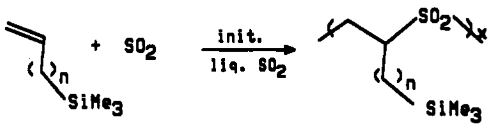
A common feature of addition reactions of sulfur-centered radicals to π-bonds is their reversibility. The unusually low ceiling temperatures, T_c, observed during copolymerization of alkenes with SO_2 are probably the best known manifestation of this phenomenon.[6] Early studies of such copolymerization systems showed that the structure of an alkene affects both the T_c[7] and alkene's reactivity toward the sulfonyl radicals. Thus, Hazell and Ivin[8] determined the relative reactivities of 10 olefins by copolymerizing them with cyclohexene in liquid SO_2. The reactivities varied from 0.79 for *trans*-2-butene/cyclohexene to 4.3 for the cyclopentene/cyclohexene pair. However, the copolymerization method is of limited use in structure–reactivity studies, since alkenes that are sterically crowded or substituted with electron-withdrawing groups do not copolymerize with SO_2.[4] Moreover, kinetic analysis of copolymerization near the T_c of one component is complicated.[8b,9]

Styrene derivatives form variable-composition copolymers with sulfur dioxide, but acrylate and methacrylate esters are essentially incapable of such copolymerization.[4] In order to determine relative reactivities of conjugated olefins toward several benzenesulfonyl radicals, Matsuda et al.[10] investigated competitive addition of benzenesulfonyl iodide to such olefins and found a linear relationship between log k_{rel} and the Alfrey-Price *e* or Hammett's σ_p values. While these results were in agreement with earlier reports on the strongly electrophilic and polar character of sulfonyl radicals,[3a] the thermal and photochemical instability of benzenesulfonyl iodides and their adducts with olefins makes unambiguous determination of the relative reactivities difficult. Notably, two unconjugated olefins, viz., 1-hexene and vinyl acetate, did not obey the above relationships.

Scheme I



Scheme II



We investigated free-radical copolymerization of several ω-alkenyltrimethylsilanes with SO_2 to obtain poly(ω-alk-

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enyltrimethylsilane sulfone)s, a new class of microlithographic materials (Scheme II).[11] In the course of these studies we found that the trimethylsilyl group in the position α or β to the double bond has a significant activating effect on its reactivity in the above reaction. For example, vinyltrimethylsilane (**11**) copolymerized readily with SO_2 below −10 °C,[11b] but its carbon analogue, 3,3-dimethyl-1-butene (**8**), failed to do so even at −78 °C. Allyltrimethylsilane (**12**), on the other hand, was >10 times more reactive during copolymerization with SO_2 than 1-alkenes.[12]

Recently, Jorgensen and Ibrahim[13] carried out ab initio calculations to elucidate the silicon stabilization effect in a series of small carbon-centered radicals and found this effect to be rather small (ca. 1–4 kcal/mol). Also, recent data by Wilt et al.[14] on the rates of hydrogen abstraction from tributyltin hydride by several simple organosilicon radicals have led to similar conclusions as does an earlier report by Jarvie and Rowley.[15] The latter investigators used a competitive addition technique to show that the relative reactivities of **12** and 3-butenyltrimethylsilane (**13**) toward trichloromethyl radical were only 1.96 and 1.31 times higher than the reactivity of **11**. In the same study, **12** was found to be 4 times *less* reactive than **11** toward the *n*-dodecylthiyl radical, but the kinetic analysis did not take into account the generally accepted reversibility of the addition of thiyl radicals to alkenes.

In the present study we sought to develop simple techniques to estimate the absolute rates and to determine the relative rates of addition of the methanesulfonyl radical ($CH_3SO_2^{\bullet}$, **2**$^{\bullet}$) to olefins. We were particularly interested in the effects of steric hindrance and substitution on the reactivity of nonconjugated π-bonds in acyclic and cyclic alkenes and alkenylsilanes. The reactivity data obtained for these model reactions were compared to those estimated by copolymerization of olefin pairs with sulfur dioxide.

Experimental Section

Analyses. GC analyses were carried out with use of a Varian 3400 gas chromatograph equipped with a 30-m Megabore column coated with a 5-μm methylsilicone stationary phase (DB-1, J&W Scientific) or, in some cases, a 15-m DB-5 column. To prevent the deposition of SiO_2 in the FID detector, a Ni-alloy, halogen-resistant thermal conductivity detector was used throughout this work. Helium at a flow rate of 10 or 20 mL/min. was used as a carrier gas. The injection port and detector temperatures were kept at 220 and 240 °C, respectively, and the column temperature was programmed from 40 to 180 °C. Retention times for the adducts were from 11 to 16 min. Except for a few cases mentioned in the text, no reaction between CH_3SO_2Br and the olefins occurred on the column.

Except for product **3P** and **14P** (the letter **P** after the olefin number denotes its regular addition product with **1**), whose ^1H and ^{13}C NMR spectra were obtained on a Brucker AM-500 spectrometer at 500 and 125.6 MHz, respectively, the remaining NMR spectra were obtained at 270 or 67.8 MHz on a JEOL JMR GX-270 in $CDCl_3$. Proton chemical shifts were referenced to internal $(CH_3)_4Si$, and those for ^{13}C, to the solvent peak ($CDCl_3$, δ 77.0). Low-resolution mass spectra were obtained on a Hewlett-Packard 5995 GC–MS instrument.

Materials. Alkenes and alkenylsilanes were purchased from Aldrich, Petrarch Systems, and Fluka or were synthesized by standard methods as described below. All olefins were purified by chromatography on neutral alumina (Aldrich) followed by flash distillation in the absence of air and stored in sealed vials under nitrogen at −15 °C. All reactants and solvents were handled with gas-tight syringes. Competitive addition experiments were carried out in anhydrous acetonitrile (Aldrich, SureSeal bottles), which was used as received. Methanesulfonyl bromide (**1**) was synthesized according to the literature procedure,[16] distilled several times, and stored under nitrogen at 4 °C. 4,4-Dimethyl-1-pentene (**9**) and 5,5-dimethyl-1-hexene (**10**) were synthesized by coupling *tert*-butylmagnesium chloride (Aldrich) with 3-bromo-1-propene and 4-bromo-1-butene, respectively, in THF in the presence of a catalytic amount of Cu^ICl.[17] 1,1-Dicyclopropylethene (**14**) was synthesized from dicyclopropyl ketone and triphenylmethylphosphonium bromide (Aldrich) by the standard Wittig procedure.[18] The purity of all reactants and solvents was checked by capillary gas chromatography. ^1H and ^{13}C NMR spectra of all olefins were in complete agreement with the assigned structures.

Isolation and Identification of Adducts. Pure samples of adducts of olefins with **1** necessary for structural identification and as GC calibration standards were obtained by preparing a solution of an olefin (20% v/v) and **1** (80 mol % vs the olefin) in 1.0 mL of $CDCl_3$ in a 5-mm-diameter glass NMR tube. After the ^1H and ^{13}C NMR spectra were recorded, the tube was immersed in an ice–water slush in a Petri dish and exposed for 3–5 min to UV radiation from a 500-W high-pressure Hg–Xe lamp (Optical Associates, Santa Clara, CA; $\lambda < 300$ nm, $I \simeq 22$ mW/cm^2). After their NMR spectra were recorded, the solutions were transferred into 15-mL glass vials and the volatiles were evaporated in a stream of dry nitrogen. The oily or crystalline residues were dissolved in $CDCl_3$ (0.75 mL) and spectra rerecorded. Some adducts to be used as GC calibration standards (i.e., from olefin **3**, **13**, and **16**) were recrystallized from cold acetone/pentane solutions to give fine white needles. Spectral data for all adducts are listed below, and their ^1H and ^{13}C NMR spectra are included in the supplementary material. Mass spectral data are reported only for the peaks with intensities larger than 5% of the base peak.

1-(Methylsulfonyl)-2-bromohexane (3P): ^1H NMR δ 0.93 (t, J = 7.3 Hz, 3 H), 1.31–1.56 (m, 4 H), 1.92 (dddd, J = 14.1, 10.2, 9.0, 4.7 Hz, 1 H), 2.03 (dddd, J = 14.1, 10.0, 5.2, 3.8 Hz, 1 H), 3.07 (s, 3 H), 3.48 (ddd, J = 15.1, 5.4, 1.0 Hz, 1 H), 3.68 (dd, J = 15.1, 7.4 Hz, 1 H), 4.43 (dddd, J = 9.0, 7.4, 5.4, 3.8 Hz, 1 H); $^{13}C\{^1H\}$ NMR δ 13.7, 21.7, 29.0, 38.3, 42.8, 45.5, 62.8; MS (*m/e*) 41, 43, 53, 55, 56, 63, 67, 79, 81, 83, 84, 121, 163, 165.

1-(Methylsulfonyl)-2-bromooctane (5P): ^1H NMR δ 0.88 (t, J = 7.0 Hz, 3 H), 1.20–1.60 (m, 8 H), 1.8–2.07 (m, 2 H), 3.07 (s, 3 H), 3.49 (dd, J = 5.4, 15.1 Hz, 1 H), 3.68 (dd, J = 15.1, 7.3 Hz, 1 H), 4.40 (m, 1 H); $^{13}C\{^1H\}$ NMR δ 13.9, 22.3, 26.8, 28.1, 31.4, 38.5, 42.7, 45.6, 62.7; MS (*m/e*) 41, 42, 43, 53, 55, 56, 57, 63, 67, 68, 69, 70, 79, 81, 111, 112, 191, 192, 193.

8-(Methylsulfonyl)-7-bromo-1-octene (6P): ^1H NMR δ 1.40–2.15 (m, 6 H), 3.06 (s, 3 H), 3.48 (dd, J = 5.8, 15.8 Hz, 1 H), 3.68 (dd, J = 7.3, 15.8 Hz, 1 H), 4.43 (m, 1 H), 4.97 (d, J = 9.5 Hz, 1 H), 5.01 (d, J = 17.1 Hz, 1 H), 5.79 (ddt, J = 17.1, 9.5, 6.5 Hz, 1 H); $^{13}C\{^1H\}$ NMR δ 26.4, 27.8, 33.3, 38.4, 42.8, 45.5, 62.9, 114.8, 138.2.

1,8-Bis(methylsulfonyl)-2,7-dibromooctane (6PD): ^1H NMR δ 1.45–1.75 (m, 2 H), 1.9–2.2 (m, 2 H), 3.07 (s, 3 H), 3.47 (dd, J = 5.9, 15.1 Hz, 1 H), 3.69 (dd, J = 7.0, 15.3 Hz, 1 H), 4.46 (m, 1 H); $^{13}C\{^1H\}$ NMR δ 25.8, 26.0, 37.9, 38.0, 42.8, 45.0, 62.5.

1-(Methylsulfonyl)-2-bromo-3,3-dimethylbutane (8P): ^1H NMR δ 1.11 (s, 9 H), 3.13 (s, 3 H), 3.52–3.68 (m, 2 H), 4.26 (dd, J = 7.8, 8.8 Hz, 1 H); $^{13}C\{^1H\}$ NMR δ 26.9, 36.2, 42.9, 58.0, 60.7; MS (*m/e*) 41, 55, 57, 67, 69, 81, 83, 136.

1-(Methylsulfonyl)-2-bromo-4,4-dimethylpentane (9P): ^1H NMR δ 1.02 (s, 9 H), 2.08 (d, J = 5.8 Hz, 2 H), 3.06 (s, 3 H), 3.49

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(dd, J = 5.4, 15.1 Hz, 1 H), 3.69 (dd, J = 7.3, 15.1 Hz, 1 H), 4.47 (ddt, J = 7.3, 5.4, 5.8 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR δ 29.6, 31.4, 40.6, 43.0, 52.3, 64.6; MS (m/e) 41, 43, 53, 55, 56, 57, 63, 65, 67, 69, 79, 81, 82, 97, 121, 161, 177.

1-(Methylsulfonyl)-2-bromo-5,5-dimethylhexane (10P): ^{1}H NMR δ 0.91 (s, 9 H), 1.31 (ddd, J = 3.2, 4.9, 14.1 Hz, 1 H), 1.49 (ddd, J = 13.2, 4.9, 14.1 Hz, 1 H), 1.80–2.08 (m, 2 H), 3.07 (s, 3 H), 3.49 (dd, J = 5.4, 15.4 Hz, 1 H), 3.68 (dd, J = 7.8, 15.4 Hz, 1 H), 4.41 (m, 1 H); $^{13}C\{^{1}H\}$ NMR δ 29.2, 29.9, 34.0, 40.8, 42.8, 46.3, 62.7; MS (m/e) 41, 43, 53, 55, 56, **57**, 67, 69, 79, 81, 95, 111, 135, 175, 215, 217.

1-(Methylsulfonyl)-2-bromo-2-(trimethylsilyl)ethane (11P): ^{1}H NMR δ 0.21 (s, 9 H), 3.12 (s, 3 H), 3.3–3.7 (m, 3 H); $^{13}C\{^{1}H\}$ NMR δ −3.5, 31.3, 43.3, 59.1; MS (m/e) 43, 45, 59, **73**, 74, 75, 85, 137, 138, 139, 152.

1-(Methylsulfonyl)-2-bromo-3-(trimethylsilyl)propane (12P): ^{1}H NMR δ 0.13 (s, 9 H), 1.53 (dd, J = 9.0, 15.1 Hz, 1 H), 2.53 (dd, J = 5.3, 15.1 Hz, 1 H), 3.06 (s, 3 H), 3.44 (dd, J = 5.3, 15.1 Hz, 1 H), 3.73 (dd, J = 7.8, 15.1 Hz, 1 H), 4.59 (m, 1 H); $^{13}C\{^{1}H\}$ NMR δ −1.1, 29.4, 42.9 (t), 65.6.

1-(Methylsulfonyl)-2-bromo-4-(trimethylsilyl)butane (13P): ^{1}H NMR δ 0.01 (s, 9 H), 1.70 (m, 2 H), 1.80–2.05 (m, 2 H), 3.12 (s, 3 H), 3.49 (dd, J = 5.3, 15.1 Hz, 1 H), 3.65 (dd, J = 7.8, 15.1 Hz, 1 H), 4.42 (m, 1 H); $^{13}C\{^{1}H\}$ NMR δ −2.0, 13.8, 33.6, 42.7, 48.8, 62.1; MS (m/e) 43, 45, 53, 54, 55, 59, **73**, 74, 75, 79, 137, 138, 139, 152, 153, 207, 271, 273.

(*E*)- and (*Z*)-1-(Methylsulfonyl)-2-cyclopropyl-5-bromo-2-pentenes (14P, ~1:1 mixture): ^{1}H NMR δ 0.51–0.57 (m, 2 H + 2 H), 0.7–0.8 (m, 2 H), 0.80–0.88 (m, 2 H), 1.6–1.7 (m, 1 H + 1 H), 2.70 (dt, J = 6.9, 6.8 Hz, 2 H), 2.91 (dt, J = 6.8, 6.4 Hz, 2 H), 2.95 (s, 2 H), 2.98 (s, 2 H), 3.42 (t, J = 6.9 Hz, 2 H), 3.49 (t, J = 6.4 Hz, 2 H), 3.60 (s, 3 H), 3.91 (s, 3 H), 5.56 (t, J = 7.3 Hz, 1 H), 5.72 (t, J = 7.3 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR δ 5.9, 6.5, 11.9, 17.4, 31.1, 31.4, 32.0, 39.4, 40.7, 57.4, 60.8, 128.3, 130.9, 134.5; GC–MS (m/e) (isomer I) 41, 51, 52, 53, 55, 63, 65, 67, 77, 78, 79, 80, 81, 91, 92, 93, 105, 106, **107**, 108, 186, 187, 188, 189, (isomer II) 41, 50, 51, 52, 53, 55, 63, 65, 66, 67, 77, 78, 79, 80, 81, 91, 92, 93, 105, 106, **107**, 108, 186, 187, 188, 189.

***trans*-1-(Methylsulfonyl)-2-bromocyclopentane (16P):** ^{1}H NMR δ 1.8–2.08 (m, 2 H), 2.20 (m, 3 H), 2.38 (m, 1 H), 3.00 (s, 3 H), 3.78 (ddd, J = 4.4, 6.3, 10.8 Hz, 1 H), 4.62 (dt, J = 6.3, 4.9 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR δ 23.9, 25.3, 38.4, 40.2, 46.6, 71.6

***trans*-1-(Methylsulfonyl)-2-bromocyclohexane (17P):** ^{1}H NMR δ 1.43 (m, 2 H), 1.78 (m, 2 H), 1.95 (m, 2 H), 2.42 (m, 2 H), 3.14 (s, 3 H), 3.32 (ddd, J = 8.3, 2.9, 7.6 Hz, 1 H), 4.49 (ddd, J = 8.3, 2.7, 8.7 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR δ 22.8, 23.9, 24.2, 36.1, 42.7, 47.6, 67.2.

***trans*-1-(Methylsulfonyl)-2-bromocycloheptane (18P):** ^{1}H NMR δ 1.35–1.62 (m, 2 H), 1.72–1.88 (m, 4 H), 2.0–2.4 (m, 4 H), 3.07 (s, 3 H), 3.61 (ddd, 5.4, 2.9, 10.5 Hz, 1 H), 4.90 (m, 1 H); $^{13}C\{^{1}H\}$ NMR δ 24.7, 24.8, 27.2, 29.3, 36.5, 40.9, 50.0, 73.3.

***trans*-3-(Methylsulfonyl)-4-bromo-1,1-dimethyl-1-silacyclopentane (19P):** ^{1}H NMR δ 0.27 (s, 3 H), 0.33 (s, 3 H), 1.22 (dd, J = 6.8, 15.6 Hz, 1 H), 1.39 (dd, J = 6.8, 15.6 Hz, 1 H), 1.44 (dd, J = 6.8, 15.6 Hz, 1 H), 1.84 (dd, J = 6.8, 15.6 Hz, 1 H), 3.11 (s, 3 H), 3.71 (q, J = 6.8 Hz, 1 H), 4.67 (q, J = 6.8 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR δ −2.1, −0.8, 11.9, 26.9, 41.6, 49.1, 71.2.

1-(Methylsulfonyl)-2-bromo-2-methylhexene (20P): ^{1}H NMR δ 0.94 (t, J = 7.3 Hz, 3 H), 1.38 (sext, J = 7.3 Hz, 2 H), 1.48–1.62 (m, 2 H), 2.07 (s, 3 H), 2.04–2.12 (m, 2 H), 3.02 (s, 3 H), 3.74 (s, 3 H); $^{13}C\{^{1}H\}$ NMR δ 13.8, 22.2, 28.1, 31.7, 43.7, 44.4, 64.4, 66.4.

1-(Methylsulfonyl)-2-bromo-2,3-dimethylbutane (22P): ^{1}H NMR δ 1.08 (d, J = 6.8, 3 H), 1.13 (d, J = 6.3 Hz, 3 H), 2.13 (sept, J = 6.3 Hz, 1 H), 2.09 (s, 3 H), 3.74 (d, J = 14.6 Hz, 1 H), 3.84 (d, J = 14.6 Hz, 1 H), 3.02 (s, 3 H); $^{13}C\{^{1}H\}$ NMR δ 18.9, 19.4, 30.1, 38.2, 43.8, 65.3, 71.5.

1-(Methylsulfonyl)-2-bromo-1,1,2,2-tetramethylethane (23P): ^{1}H NMR δ 1.69 (s, 6 H), 2.14 (s, 6 H), 2.99 (s, 3 H); $^{13}C\{^{1}H\}$ NMR δ 22.4, 32.2, 40.0, 70.1, 72.5.

Competitive Addition Experiments. General Procedure. Stock solutions of alkenes in acetonitrile (approximately 0.1 M each, unless reported otherwise) containing cyclooctane (0.03 M) or chlorobenzene (0.03 M) as the internal GC standard were prepared under nitrogen in 30-mL vials sealed with Teflon-lined silicone rubber septa. One-milliliter aliquots of the stock solutions were withdrawn with a gas-tight syringe and injected through a rubber septum into a dry, nitrogen-filled, water-jacketed quartz cell (optical path 2 cm, volume 2.2 mL, Wilmad Glass) maintained at 0 °C (or other temperature) with a thermostating bath. After a brief temperature stabilization period, the required amount of methanesulfonyl bromide (8–120 μL) was injected with a gas-tight syringe and the solution was mixed by gentle shaking (*the syringes were immediately washed with acetone and dried to avoid corrosion of the stainless-steel needles*). The cell was irradiated for a period of 0.5–10 min with a water-cooled 100-W high-pressure mercury lamp (Hanovia 608A36) in all-quartz vessels, and after gentle stirring, the resulting solution was immediately analyzed by GC. Due to insufficient resolution on a DB-1 column, mixtures containing 1,1-dicyclopropylethene were analyzed with use of a 15-m-long DB-5 capillary column and chlorobenzene as the internal GC standard. The reproducibility of GC analyses was better than ±0.1 wt %, except for analyses of solutions containing 1 and 14 where the reproducibility was lower (usually ±0.3%, possibly due to a much higher reactivity of 14, its slow dark reaction with 1, or other factors). The observed relative reactivities, r_{obs}, for olefins 3–22 are plotted in Figures 1, 2, and 5–10, and the experimental details are given in the supplementary material.

The yields and product ratios were obtained from GC data after correction for the differences in the thermal conductivity detector response factors. The olefins were calibrated directly against the internal standard. In the case of products, absolute calibration was performed only for three representative adducts, viz., **3P** (alkenes), **13P** (alkenylsilanes), and **16P** (cycloalkenes). Since the detector response factors for these three products after correction for their respective molecular weights differed by less than ±7%, concentrations of the remaining products were calculated from their peak areas. The consumption of 1 was found to be proportional to the consumption of both olefins and the amount of products formed. Likewise, the amount of olefins consumed corresponded to the amount of products formed. Unless noted otherwise, the addition reaction was essentially quantitative, since only trace amounts of side products, totaling less than 1% of the olefins consumed, were detected by GC or NMR. In the absence of significant side reactions, the reactivity ratios, k_{obs}, were calculated from the initial and final concentrations of the two reacting olefins and/or their products. The values of r_{obs} data at high olefin concentrations were calculated only from product ratios.

Results and Discussion

Generation of $CH_3SO_2^{\bullet}$ Radicals. The choice of methanesulfonyl bromide as the source of sulfonyl radicals for the present study was based on literature reports on the reactivity and stability of sulfonyl halides and their addition products with alkenes.[3] For example, the addition of sulfonyl *chlorides* to unsaturated C–C bonds proceeds only at relatively high temperatures (80–140 °C) in the presence of a Cu salt catalyst.[3b] Sulfonyl *iodides*, on the other hand, are so reactive that they and their alkene adducts are often unstable at ambient temperatures and are decomposed by visible light.[3a,f,g,i]

Few examples of reactions of sulfonyl bromides with alkenes have been reported so far. Available data indicate, however, that the reactivity of sulfonyl bromides is intermediate between that of sulfonyl chlorides and iodides, since the bromides were reported to add cleanly to alkenes at 90–100 °C in the absence of light or catalyst.[3e,h] More recently, Block et al.[19] reported that $BrCH_2SO_2Br$ adds readily to alkenes at −20 °C upon exposure to UV light. We investigated a wide range of alkenes and found that a slow dark reaction of 1 with alkenes takes place at room temperature only if the alkene is unusually reactive, e.g., 14. The reaction is readily initiated, however, by irradiating acetonitrile solutions of olefins and 1 with UV light with $\lambda < 300$ nm, which is absorbed by the bromide. Methanesulfonyl bromide alone in CH_3CN was not

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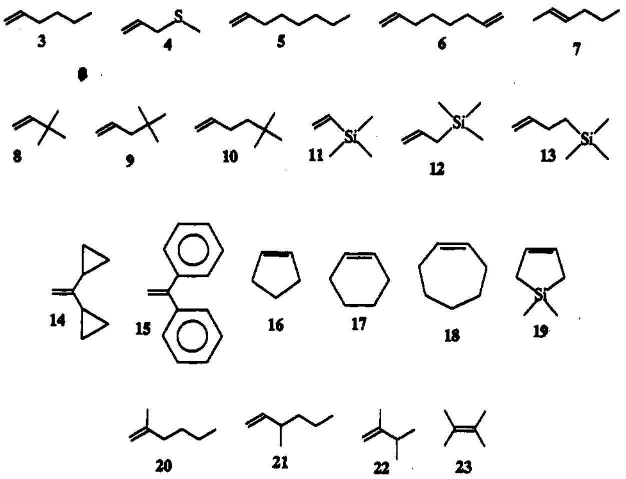
[19] Block, E.; Aslam, M. *J. Am. Chem. Soc.* **1983**, *105*, 6164.

Chart I



measurably decomposed when its 0.2 M solution was exposed to a very high incident dose of UV radiation (20 J/cm^2 at 260 ± 20 nm) at 0 °C. All adducts were stable in solutions under fluorescent lights at ambient temperature. Excluding a few cases discussed below, they were also stable at 220 °C (the temperature of the GC injector).

Reaction of 1 with Olefins. General Observations. The olefins selected for the present study were simple, nonconjugated alkenes and alkenylsilanes. Their structural formulas are shown in Chart I. The NMR analysis of freshly prepared adducts **3P**–**23P** indicated that, except for olefins **7** and **14**, all others gave a single 1:1 adduct with **1**. Substantial amounts of disubstituted adducts were obtained from α,ω-alkadiene **6**, especially at higher diolefin conversions. The diadduct obtained from **6** was sparingly soluble and had such a high boiling point that it invariably decomposed during attempted GC analyses on several columns under various conditions.

The NMR analysis of the freshly prepared allylsilane adducts **12P** and **19P** indicated that the expected 1:1 adducts are stable in solution, but they undergo complete β-elimination during GC analysis. **12P** could be isolated from the reaction mixture by concentrating it at room temperature in a stream of nitrogen provided no unreacted **1** was present. Otherwise, a β-elimination product, allyl methyl sulfone (Scheme V, **29**), was rapidly formed. The high lability of the β-bromoorganosilicon derivatives was not unexpected, since complete β-elimination was reported to occur during the attempted addition of methanesulfonyl chloride to allylsilane.[20] However, the formation of elimination products did not interfere with the quantitative analysis of unreacted olefins.

The reactions of 1,1-diphenylethene (**15**) and 2,3-dimethyl-1-butene (**23**) with **1** were very sluggish and the obtained reactivity ratios were irreproducible; thus, no reactivity data for these two alkenes are presented. In the case of the former, the strong UV absorption of the phenyl groups may prevent efficient initiation (eq 1) of the chain reaction. In the case of the latter, apparently the attack of radical **2**$^\bullet$ on the disubstituted sp^2 carbons is slow due to steric hindrance or the reaction is highly reversible due to a slow abstraction of bromine by the tertiary radical (see below).

The formation of oligomers or polymers was not observed.[21] Also, the amounts of 1,2-dibromides formed during addition of **1** to olefins **3**–**23** were insignificant ($\ll$1%). Excluding **7**, all acyclic olefins afforded adducts exhibiting only one regiochemistry; i.e., the methanesulfonyl group was attached to the terminal, less substituted carbon. This regiochemistry and the absence of significant amounts of 1,2-dibromides imply that **2**$^\bullet$ is the sole chain-carrying radical. These observations ensure that the relative reactivity of various olefins toward **2**$^\bullet$ can be determined unambiguously.

Kinetic Model. Kinetic treatment of the competitive reaction system investigated in the present work is complicated by the fact that the addition steps involving sulfonyl radicals may be reversible. Appropriate diagnostic tests had to be devised to determine the degree of reversibility of radical addition to a given olefin and to extract relative reactivities for a series of olefins.

In the absence of side reactions, such as hydrogen abstraction, isomerization, etc., and taking into account that the radical attack on the olefinic bond is initiated by **2**$^\bullet$, the photoinitiated competitive addition of **1** (MX) to two alkenes A and B is described by the reactions shown in Scheme III.

Scheme III

initiation:

$$\mathrm{MX} \xrightarrow[k_i]{h\nu} \mathrm{M}^\bullet + \mathrm{X}^\bullet \tag{1}$$

propagation:

$$\mathrm{M}^\bullet + \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{MA}^\bullet \tag{2}$$

$$\mathrm{M}^\bullet + \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{MB}^\bullet \tag{3}$$

$$\mathrm{MA}^\bullet + \mathrm{MX} \xrightarrow{k_3} \mathrm{MAX} + \mathrm{M}^\bullet \tag{4}$$

$$\mathrm{MB}^\bullet + \mathrm{MX} \xrightarrow{k_4} \mathrm{MBX} + \mathrm{M}^\bullet \tag{5}$$

termination:

$$2\mathrm{M}^\bullet \xrightarrow{k_t} \mathrm{M}_2, \text{ etc.} \tag{6}$$

Application of the steady-state approximation to [MA$^\bullet$] and [MB$^\bullet$] leads to the following general expression for the relative rate of disappearance of alkenes A and B:[22]

$$\frac{d[\mathrm{A}]}{d[\mathrm{B}]} = \frac{k_1}{k_2}\frac{[\mathrm{A}]}{[\mathrm{B}]}\frac{[\mathrm{MX}] + k_{-2}/k_4}{[\mathrm{MX}] + k_{-1}/k_3} \tag{7}$$

Assuming that [MX] is constant, integration of eq 7 leads to

$$r_{\mathrm{obs}} = \frac{\log([\mathrm{A}]_f/[\mathrm{A}]_i)}{\log([\mathrm{B}]_f/[\mathrm{B}]_i)} = k_{\mathrm{rel}}{}^{\mathrm{A/B}}\frac{[\mathrm{MX}] + k_{-2}/k_4}{[\mathrm{MX}] + k_{-1}/k_3} \tag{8}$$

where r_{obs} is the experimentally observed reactivity ratio of the two alkenes, $k_{\mathrm{rel}}{}^{\mathrm{A/B}} = k_1/k_2$, and the subscripts i and f denote initial and final concentrations of olefins A and B.

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[20] This reaction has been reported for allylsilanes and sulfonyl chlorides reacting in the presence of a catalyst (Cu$^{\mathrm{I,II}}$Cl): Pillot, J.-P.; Dunogues, J.; Calas, R. *Synthesis* **1977**, 469.

[21] Unactivated alkenes do not homopolymerize by a free-radical mechanism under ambient temperature and pressure conditions. See, e.g.: Odian, G. *Principles of Polymerization*; McGraw-Hill: New York, 1970; pp 164 and 248.

[22] Hazell and Ivin[8a] obtained a similar expression for the copolymerization of two alkenes with SO$_2$. They assumed that the reaction proceeds by a separate addition of the three components ("mechanism 2" in the original paper).

Depending on the reversibility of addition of M$^\bullet$ (2$^\bullet$) to olefins A and B, three cases can be considered.

The simplest case, case 1, occurs when the addition of M$^\bullet$ to *both* olefins is effectively irreversible,[23] i.e., *when bromine abstraction by the adduct radical is significantly faster than the elimination of* 2$^\bullet$ ($k_{-1} \ll k_3$[MX] *and* $k_{-2} \ll k_4$[MX]). Under such conditions, r_{obs} is independent of [MX] and the relative reactivity can be calculated from the change in the concentration of either the substrates or the products by eq 9.[24]

$$r_{obs} = k_{rel}{}^{A/B} = \frac{\log(1 - [MAX]/[A]_i)}{\log(1 - [MBX]/[B]_i)} = \frac{\log([A]_f/[A]_i)}{\log([B]_f/[B]_i)} \quad (9)$$

Case 2 is applicable to situations in which *one* of the two addition reactions involving sulfonyl radicals is reversible; i.e., $k_{-1} \ll k_3$[MX] *or* $k_{-2} \ll k_4$[MX]. Equation 8 indicates that in such a case r_{obs} will depend on [MX]. However, if [MX] is approximately constant during the reaction (pseudo-first-order conditions), r_{obs} should be a linear function of [MX]$^{-1}$. The alkene reacting irreversibly with M$^\bullet$ is selected as the standard (alkene A in our example), and eq 8 can be rearranged to eq 10,[25] where $R = k_{-2}/k_4$

$$r_{obs} = k_{rel}{}^{A/B} + \frac{k_{rel}{}^{A/B}R}{[MX]} \quad (10)$$

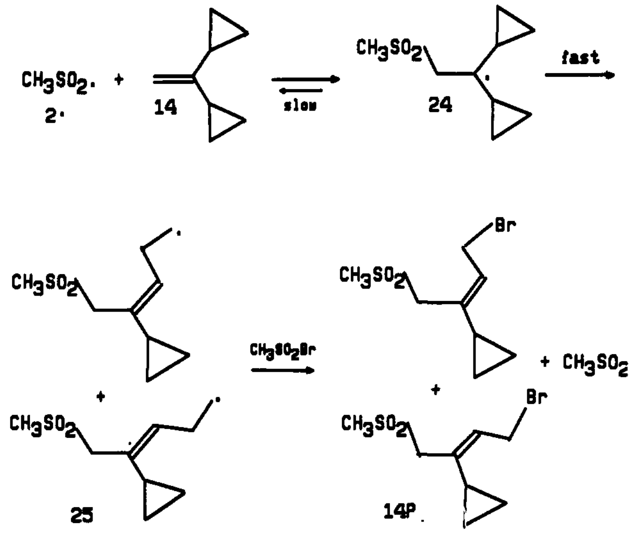
for alkene B and r_{obs} values are determined for various [MX]. The experimental values of r_{obs} in case 2 will always be greater than k_1/k_2, but they should approach the latter at high [MX]. Both the k_{rel} and R rate constant ratios[23] can be obtained from a linear plot of r_{obs} vs [MX]$^{-1}$.

Case 3 is applicable to olefin pairs in which *both* components react reversibly[23] with M$^\bullet$. Provided that [MX] is varied over a sufficiently wide range, significant curvature of both the r_{obs} vs [MX]$^{-1}$ and r_{obs} vs [MX] plots will be observed. Although in principle neither k_{rel} nor R can be uniquely determined for such olefin pairs, a special subcase is possible when the addition of 2$^\bullet$ to *both* olefins is *equally* reversible, i.e., when $k_{-1}/k_3 \simeq k_{-2}/k_4$. Under such conditions, r_{obs} will also be independent of [MX]. It should be noted, however, that in this case $r_{obs} = k_{rel}$ and the obtained relative reactivity, k_{rel}, is valid. Only independent kinetic tests could differentiate this subcase from case 1.

In summary, if [MX] is varied over a sufficiently wide range, three experimentally distinguishable outcomes may result. If r_{obs} is independent of [MX], then $k_{rel} = r_{obs}$ and the addition of 2$^\bullet$ to both olefins is either irreversible or equally reversible. If r_{obs} (or $1/r_{obs}$) is a linear function of [MX]$^{-1}$, the addition of 2$^\bullet$ to one olefin is irreversible and both r_{obs} and R may be determined. In the third case, the addition of 2$^\bullet$ to both olefins is reversible, but to a different extent. Both r_{obs} and $1/r_{obs}$ are nonlinear functions of [MX]$^{-1}$, and k_{rel} and R cannot be uniquely determined without additional tests.

Addition of 2$^\bullet$ to Standard Olefins. 1,1-Dicyclopropylethene (14) vs 1-Octene (5). The foregoing analysis underscores the importance of using a standard alkene to which radical 2$^\bullet$ adds irreversibly, since only under such conditions can both k_{rel} and R be unequivocally determined. Preferably, the irreversibility of addition of 2$^\bullet$ to the standard alkene should be ensured by a process other than bromine abstraction from 1. In this context, the data reported by Wagner et al.[26] may be a useful starting point for further discussion. They found that the rate of elimination of the *n*-butylsulfonyl radical from a 1,4-diradical formed via photoinduced intramolecular hydrogen abstraction within δ-(*n*-butylsulfonyl)valerophenone is ca. 7.8 × 10^5 s^{-1}. Thus, any process used to assure the irreversibility of the addition must have a rate faster than 1 × 10^7 s^{-1}. The well-known rapid rearrangement of the cyclopropylcarbinyl radical (24 → 25, Scheme IV, radical-clock reaction)[27] appeared to fulfill these requirements, since its statistically corrected rate at 25 °C was reported[28] as 1.3 × 10^8 s^{-1}, which should ensure that the addition of 2$^\bullet$ to 14 proceeds only in the forward direction.

Scheme IV



The addition of 1 to 14 resulted in the formation of an approximately equimolar mixture of two products having very similar GC retention times; thus, their separation has not been attempted. However, their ^{1}H NMR, ^{13}C NMR, and GC–MS spectra were consistent with the structure of the expected cis and trans adducts 14P (Scheme IV). No simple, unrearranged adduct was observed even at [1] = 1 M. It should be noted that the adduct of 2$^\bullet$ to 14 rearranges to two isomeric primary alkyl radicals that efficiently propagate the kinetic chain by abstracting bromine from 1 and regenerating 2$^\bullet$ (eqs 4 and 5; Scheme IV). Moreover, the rearrangement does not interfere with the determination of r_{obs}. On the basis of the above arguments, 14 was selected as a reference alkene for which we assumed that $k_{-1} = 0$.

Initial experiments involving competitive addition of 2$^\bullet$ to 14 in the presence of various olefins showed that the reactivity of 14 was more than 1 order of magnitude higher than that of other unconjugated alkenes. Elementary error analysis predicts that accurate determination of r_{obs} from eqs 8 or 10 in such a case is difficult. A secondary standard

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(23) It should be emphasized that in our study the reversibility, R, reflects only the relative rates of elimination of 2$^\bullet$ from the adduct radical and bromine abstraction from 1 by the same radical. Thus, observation of reversibility in the case of some olefins cannot be specifically attributed to the increased rate of elimination, k_{-X}.

(24) Russell, G. A. *Acc. Chem. Res.* **1989**, *22*, 1.

(25) Competitive addition of the thiyl radical to two reactants having vastly different reactivities (which justified the use of a different approximation) is discussed in: Davies, A. G.; Roberts, B. P. *J. Chem. Soc. B* 1971, 1830. More recent discussion is given in ref 5a.

(26) Wagner, P. J.; Sedon, J. H.; Lindstrom, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 2579.

(27) Reviews: (a) Wilt, J. W. In Reference 1a, Vol. I, Chapter 8, p 334. (b) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317. See also: (c) Campredon, M.; Kanabus-Kaminska, J. M.; Griller, D. *J. Org. Chem.* **1988**, *53*, 5393 and references cited therein.

(28) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024.

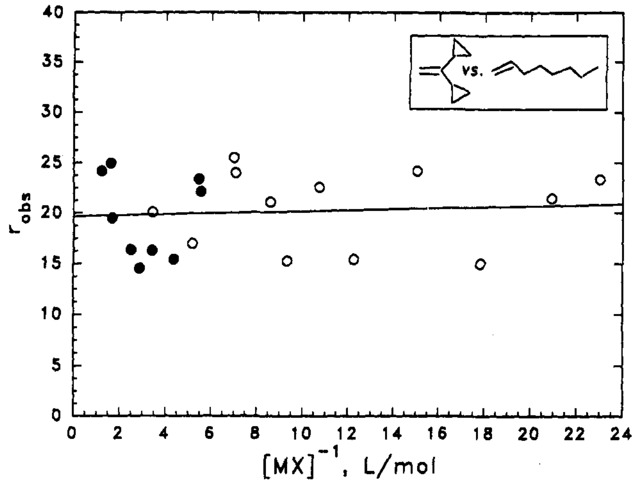


Figure 1. Observed relative reactivity, r_{obs}, of 1,1-dicyclopropylethene (**14**) vs 1-octene (**5**) toward the methanesulfonyl radical ($2^{\bullet}$) calculated from eq 8 as a function of the inverse average concentration of methanesulfonyl bromide, $[MX]^{-1}$, determined in acetonitrile at 0 °C. The initial concentrations of alkenes **14** and **5** were 0.02 (○) or 0.1 M (●). The regression line and the k_{rel} and R data listed in Table I were calculated from the combined data.

having lower reactivity toward $2^{\bullet}$ than **14** and, at the same time, reacting effectively irreversibly with $2^{\bullet}$, had to be identified (for the purpose of this study, the addition is considered effectively irreversible if $R \leq 0.01$). It should be sufficient to show for such a secondary standard that its relative reactivity toward $2^{\bullet}$ in competition with **14** is independent of $[MX]^{-1}$ over a sufficiently wide range of MX concentrations. Guided by the published structure–T_c relationships[7] and experimental considerations, 1-octene (**5**) was chosen as a candidate for such a standard.

In order to obtain statistically significant data, numerous competition experiments were carried out for the **14**/**5** pair while the concentration of **1** was varied from 0.04 to 1 M (Figure 1). The large difference in reactivity between **5** and **14** ($k_{rel}^{14/5} = 20 \pm 4$) explains the considerable scatter of the $r_{obs}^{14/5}$ values, but the least-squares regression did not reveal a statistically significant dependence of k_{obs} on $[MX]^{-1}$. We thus conclude that the addition of $2^{\bullet}$ to 1-octene is irreversible under our reaction conditions.

The above results are consistent with those reported by Griller et al.[5a] who found that **14** is 129 ± 19 times more reactive than **5** toward the addition of *tert*-butylthiyl radical, making this olefin atypically reactive toward radical addition. If structure–reactivity relationships hold for these additions, this result also suggests that **14** is more reactive toward sulfonyl radicals than toward the thiyl ones. It appears, however, that the rate of addition of $2^{\bullet}$ to *n*-alkenes is near-diffusion-limited (see below); thus, the intrinsic relative reactivity for the **14**/**5** alkene pair toward $2^{\bullet}$ might in fact be higher.[29]

Similar relative reactivities and T_c values observed for several *n*-alkenes during their copolymerization with SO_2[7,8] suggested that their reactivities toward $2^{\bullet}$ should also be similar. This assumption was confirmed by carrying out direct competitive addition of **1** to 1-hexene and 1-octene at various [MX] (Table I; Figure 2), which led to a $k_{rel}^{3/5}$ value of 1.00 ± 0.01 (equal reactivity) and $R < 0.01$ (effective irreversibility). On the basis of these results, we concluded that the relative reactivities of various alkenes and alkenylsilanes can be determined at 0 °C by using either of these *n*-alkenes as secondary standards.

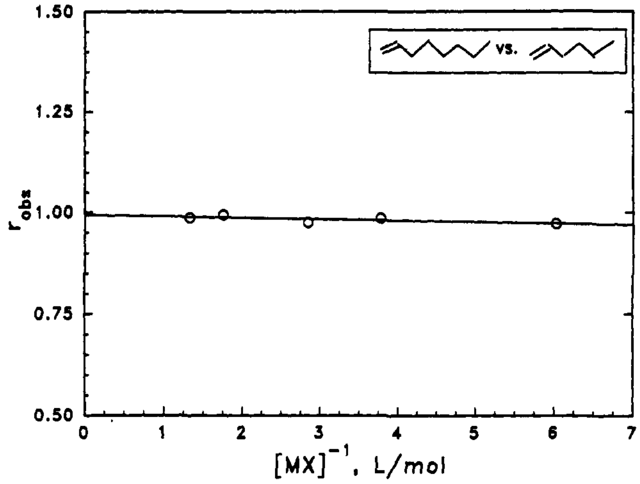
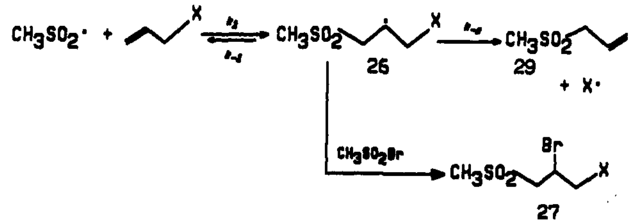


Figure 2. Relationship between r_{obs} for the competitive addition of $2^{\bullet}$ to 1-hexene (**3**) and 1-octene (**5**) vs $[MX]^{-1}$. The concentration of each alkene was 0.1 M. For other conditions, see Figure 1.

Scheme V



where X = Cl, Br, MeS, and MeSO.

Addition of $2^{\bullet}$ to Allylic Derivatives. In the study mentioned above, Wagner et al.[26] reported absolute elimination rate constants, k_{-X}, for several halogen and sulfur-centered radicals from the corresponding β-radical intermediates. For example, $BuSO^{\bullet}$ undergoes elimination from the corresponding β-radical 160 times faster than $BuSO_2^{\bullet}$. In agreement with these data, the addition of **1** to allyl methyl sulfoxide under experimental conditions employed in this work gave an elimination product **29**, but no adduct **27** ($X = CH_3SO$; Scheme V) was observed up to [**1**] = 1.6 M. Since the absolute rate of elimination of $BuSO^{\bullet}$ (whose properties are assumed to be similar to those of $MeSO^{\bullet}$) was estimated to be 1.3×10^8, the rate of bromine abstraction by the secondary radical **26** ($X = CH_3SO$) must be less than 1×10^7 M^{-1} s^{-1}.

The rapid elimination of $MeSO^{\bullet}$ from the adduct radical **26** ($X = CH_3SO$) ensures the irreversibility of the addition of $2^{\bullet}$ to the olefin. Thus, in principle, allyl methyl sulfoxide could also be used to verify irreversibility of the radical addition to other olefins, but its actual application for this purpose was complicated by significant photoinduced and thermal side reactions leading to several unidentified products. Nevertheless, in the competition reaction involving the addition of **1** to allyl methyl sulfoxide and **3**, the ratio of allyl methyl sulfone (**29**) to adduct **3P** was 0.18 ± 0.02 (from ^{1}H NMR)[30] and was constant for [**1**] from 0.2 to 1.6 M, thus confirming the irreversibility of addition of $2^{\bullet}$ to **3**.

Wagner's data[26] indicate that the elimination of $BuS^{\bullet}$ is only 2.9 times slower than that of $BuSO_2^{\bullet}$. Since the reactivities of the methyl and butyl derivatives should be

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[29] Maslak, P.; Sczepanski, J. J.; Minard, R. D.; Collins, L. A. *Tetrahedron Lett.* **1990**, *31*, 4261.

[30] Since the reactants reacted in the GC column, the product analysis was performed by the integration of ^{1}H NMR spectra.

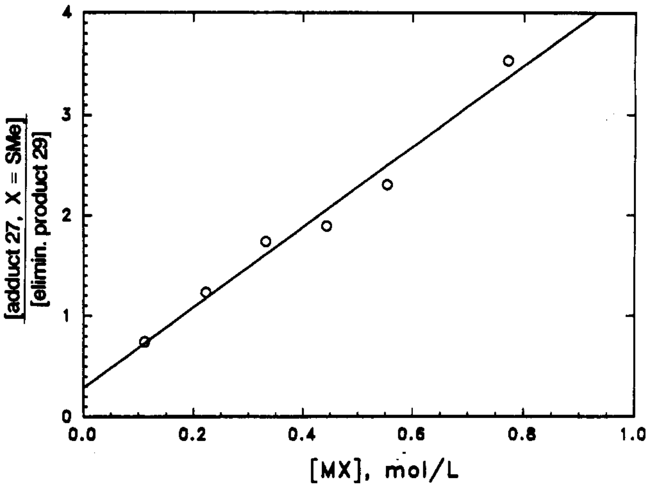

Figure 3. Ratio of 1-(methylsulfonyl)-3-(methylthiyl)-2-bromopropane (adduct 27, X = MeS) to allyl methyl sulfone (29, elimination product) as a function of [MX] during photoinitiated addition of 1 to allyl methyl sulfide (0.11 M) in acetonitrile at 0 °C.

similar, the elimination of MeS• from the adduct radical 26 (X = CH_3S) should be competitive with the bromine abstraction by 26 (Scheme V) as is the elimination of 2• in the case of some of the olefins studied. The results of experiments in which 1 was added to allyl methyl sulfide confirmed the above analysis. Thus, at low [1] (<0.1 M), allyl methyl sulfone was the major product[31] and only traces of adduct 27 (X = CH_3S) were detected. At higher [1] (>0.3 M), the adduct becomes the major product. Importantly, the competitive addition of 1 to allyl methyl sulfide and 1-hexene indicates that in both cases the addition of 2• is irreversible. Thus, the r_{obs} (calculated from the disappearance of the olefins and corrected for the formation of 29) is independent of [1] ($k_{rel}^{3/4} = 2.23 \pm 0.07$) within the range of [1] from 0.15 to 0.6 M.

These results suggest that, in contrast to data reported for butyl derivatives,[32] the elimination of MeS• from 26 is faster than the elimination of 2•. Under such circumstances and in agreement with the kinetics of Scheme V, the ratio of adduct 27 to 29 was a linear function of [1] (Figure 3). The slope of the line in Figure 3 corresponds to a ratio of the bimolecular rate of bromine abstraction from 1 by 26 (X = CH_3S) to the unimolecular rate constant for the elimination of CH_3S• from 26. This slope (4.0 M^{-1}) and the irreversibility of addition of 2• to 1-hexene imply that the rate of bromine abstraction from 1 by a secondary alkyl radical is similar in magnitude to the rates of elimination of MeS• or $MeSO_2$• from the adduct radical 26; i.e., it is on the order of 1×10^7 M^{-1} s^{-1}. Thus, under our experimental conditions, *the apparent irreversibility*[23] *of addition of* 2• *to simple alkenes is due to the rapid follow-up bromine abstraction.*

Allyl chloride reacted with 1 to give almost exclusively an adduct, 2-bromo-3-chloropropyl methyl sulfone (27, X = Cl). Even at concentrations of 1 as low as 0.015 M, less then 2% of the elimination product 29 was detected, indicating that the rate of chlorine elimination is slower than 2×10^5 s^{-1}. It thus appears that the elimination rate, k_{-Cl}, reported by Wagner et al.[26] is significantly overestimated.[33] Allyl bromide, on the other hand, gave mostly 1,2,3-tribromopropane as well as several other unidentified compounds. The former is readily formed by Br_2 addition to allyl bromide. Significant amounts of Br_2 were produced in this experiment, apparently by a rapid elimination of bromine from the adduct radical. The elimination of bromine from the corresponding β-radical is thus too rapid to allow for the formation of the regular adduct.

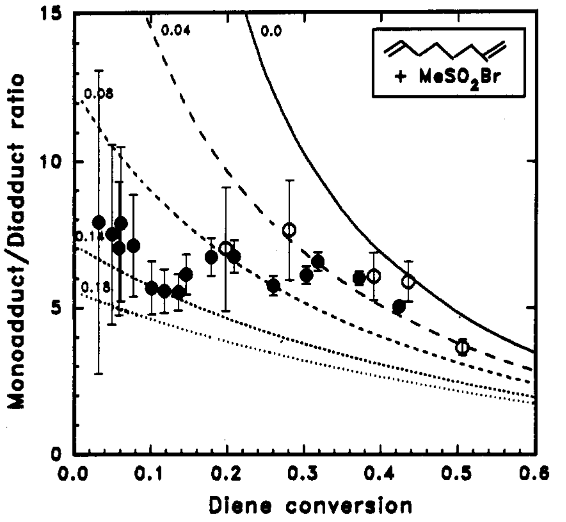

Figure 4. Monoadduct to diadduct ratios obtained for addition of 1 to 6 as a function of the degree of conversion of 6. The indicated error bars correspond to standard deviations calculated by the error propagation method and are based on the experimentally estimated 0.1 wt % errors in the analysis of [6] and [MX]. The initial concentration of 1,7-octadiene was 0.1 (●) or 0.02 M (○). The curves represent eq 11 for *z* values of 0, 0.04, 0.08, 0.14, and 0.18.

Addition of 2• to 1,7-Octadiene. Estimate of the Absolute Rate of Addition. To evaluate the relative reactivity data appropriately (see below), it would be desirable to have an estimate of the absolute rate of addition of 2• to alkenes. Specifically, if the addition reaction were near-diffusion limited, the observed relative reactivity might be influenced by the diffusive processes.[29,34] In the absence of absolute rate constants, we decided to use a simple kinetic test capable of detecting near-diffusion-limited reactions. This test,[35] originally developed to probe the dynamics of alkyl chains in radical-chain reactions, is especially well-suited for the task. As applied to our situation, the test involves the addition of 1 to 1,7-octadiene (6). The addition of 2• to the diene in the first propagation step (Scheme III) generates an adduct radical that abstracts bromine from 1. This reaction regenerates 2• in the direct vicinity (in the solvent cage) of the other double bond in the molecule. If the addition reaction is near-diffusion limited, 2• can add to the "remote" double bond in competition with the separation of the reacting partners. In such a case, the diadduct is formed "directly" from the diene, without the intervention of the free-floating monoadduct. Thus, the monoadduct to diadduct ratio can serve as a sensitive measure of the in-cage reaction.

This kinetic scheme can be solved analytically for the chain reactions in question. It can be shown (eq 11; Figure

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[31] Under the reaction conditions employed, the methylthiyl radical eliminated from 26 (X = CH_3S) adds to allyl methyl sulfide giving—after bromine abstraction from 1—2-bromo-1,3-bis(methylthio)propane (28) in the amount equivalent to that of 29. Most likely, there is also some dimethyl disulfide formed via recombination, but it regenerates the thiyl radicals on irradiation with deep UV.

[32] It is possible, however, that the solvent effect contributed to the change in relative reactivity; Wagner's data were obtained in benzene.

[33] The rate reported by Wagner et al.[26] may reflect the rate of internally assisted elimination.

[34] In the extreme, if the addition were diffusion limited, the apparent reactivity would reflect only relative diffusional mobility of the olefins and not their intrinsic reactivities.

[35] Maslak, P.; Narayanasami, R.; Skell, P. S. In preparation. Compare also: Maslak, P. *J. Am. Chem. Soc.* **1989**, *111*, 8201.

Table I. Relative Reactivity, $k_{rel}^{A/B}$, and Reversibility, R, for the Addition of Radical 2• to Olefins and Alkenylsilanes at 0 °C

olefin A	olefin B	$[A]_i$, mol/L	$[B]_i$, mol/L	[1] range, mol/L	$k_{rel}^{A/B}$	R
14	5	0.02–0.1	0.03–0.1	0.05–0.85	20 ± 4	0.00 ± 0.01
3	4	0.05	0.05	0.15–0.6	2.23 ± 0.07	0.00 ± 0.01
3	5	0.1	0.1	0.2–0.8	0.99 ± 0.01	0.00 ± 0.01
3	7	0.1	0.1	0.2–0.8	1.40 ± 0.03	0.08 ± 0.01
3	8	0.1	0.1	0.2–1.0	1.68 ± 0.02	0.07 ± 0.01
3	9	0.1	0.1	0.2–0.8	1.21 ± 0.04	0.06 ± 0.01
3	10	0.1	0.1	0.2–0.8	1.04 ± 0.01	0.01 ± 0.01
3	11	0.1	0.1	0.2–0.8	0.97 ± 0.03	0.00 ± 0.01
3	12	0.1	0.1	0.2–0.8	0.40 ± 0.01	0.00 ± 0.01
3	13	0.1	0.1	0.2–0.8	0.98 ± 0.03	0.00 ± 0.01
3	16	0.1	0.1	0.2–0.8	0.44 ± 0.01[a]	0.00 ± 0.01
3	17	0.1	0.1	0.2–0.8	0.87 ± 0.01[a]	0.02 ± 0.01
3	18	0.1	0.1	0.2–0.8	0.59 ± 0.02[a]	0.09 ± 0.01
3	19	0.1	0.1	0.2–0.8	0.69 ± 0.02[a]	0.00 ± 0.01
3	20	0.1	0.1	0.2–1.0	0.16 ± 0.01	0.01 ± 0.01
3	21	0.1	0.1	0.2–0.9	1.46 ± 0.01	0.01 ± 0.01
3	22	0.1	0.1	0.2–0.8	0.31 ± 0.01	0.01 ± 0.01

[a] Statistically uncorrected relative reactivities.

4; see also Appendix A, supplementary material) that the monoadduct (M) to diadduct (D) ratio is only a function

$$\frac{M}{D} = \frac{2x - 2 + 2(1 - x)^{(1+2z)/(2+2z)}}{2 - x - 2(1 - x)^{(1+2z)/(2+2z)}} \tag{11}$$

of the degree of conversion of the diene, x, and the cage parameter, $z = k_a/k_{esc}$, where k_a is the in-cage rate constant of addition and k_{esc} is the rate constant for the diffusional separation of reactants. If these two rate constants are of comparable magnitude, the overall rate of addition of 2• to the olefin is given by $k_{obs} = k_d z/(z + 1)$ where k_d is the diffusion-limited rate constant and k_{obs} is equivalent to k_1 or k_2 of Scheme III.

Although the presence of the diadduct was confirmed by spectroscopic methods, this compound could not be quantified by GC due to its thermal decomposition. The monoadduct to diadduct ratios were therefore obtained by following the disappearance of the diene ($\Delta_1 = [6]_i - [6]_f$) and 1 ($\Delta_2 = [1]_i - [1]_f$). Since the addition of 1 to 1,7-octadiene was exceptionally clean, the amounts of monoadduct and diadduct formed could be calculated from the stoichiometry of the reaction. Thus, at any time during the reaction, $[D] = \Delta_2 - \Delta_1$ and $[M] = 2\Delta_1 - \Delta_2$. To verify the mass balance, the amount of monoadduct determined directly, was compared with that calculated based on the reaction stoichiometry. In all cases the agreement was excellent (Table VI, supplementary material). The results are plotted in Figure 4. Although the data in Figure 4 show some scatter, all the points indicate that the amount of diadduct formed is larger than expected for a slower than diffusion reaction (see the top curve for $z = 0$). This result suggests a near-diffusion-limited addition reaction with $k_{obs} \simeq 0.1k_d$. On the basis of the viscosity of acetonitrile at 0 °C (0.442 cP), the absolute rate of addition 2• to n-alkenes (see below) may be estimated as ca. 1×10^9 M^{-1} s^{-1}.

Competitive Addition of 2• to Monosubstituted Alkenes and Alkenylsilanes. In order to identify structural factors affecting the reactivity of olefins and alkenylsilanes, relative reactivities toward 2• have been determined for several simple monosubstituted alkenes 8–13 (see Chart I). In this series of olefins, both steric and electronic factors vary in a systematic way; i.e., the electropositive and/or sterically bulky substituent is at the positions α, β, or γ to the monosubstituted π-bond. δ-Substituted analogues were not included in this series, since the effect of such a remote substituent on the rate of free-radical reactions should be negligible.

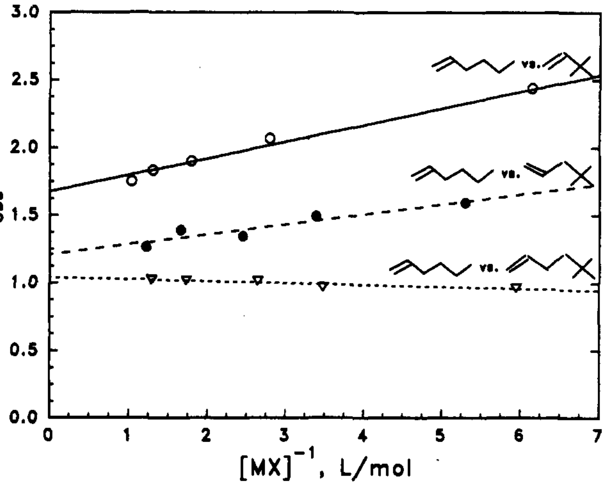

Figure 5. Relationship between r_{obs} and $[MX]^{-1}$ for 1-hexene vs *tert*-butyl-substituted 1-alkenes: 3,3-dimethyl-1-butene (8, ○), 4,4-dimethyl-1-pentene (9, ●), and 5,5-dimethyl-1-hexene (10, ▽). The concentration of each alkene was 0.1 M. For other details, see Figure 1.

Competitive addition of 1 to olefins 8–13 in the presence of 3 as a reference alkene at various initial concentrations of 1 afforded a series of r_{obs} values that, when plotted against $[1]^{-1}$, gave $k_{rel}^{A/B}$ and R values (eq 10) as discussed previously for the 14/5 and 3/5 alkene pairs (unless noted otherwise, A represents 1-hexene).

The three *tert*-butyl-substituted alkenes 8–10 reacted readily with 1, although they differed markedly during their attempted free-radical copolymerization with SO_2. Thus, while 8 did not copolymerize with SO_2,[12] 9 was reported to form a copolymer up to T_c = 14 °C.[7] The copolymerization of 10 with SO_2 has not yet been reported, but we found that it proceeds without difficulty. We have previously reported that all three ω-alkenyltrimethylsilane analogues of these branched alkenes, i.e., ω-alkenylsilanes 11–13, readily copolymerize with SO_3 under free-radical initiation conditions.[11]

Plots of r_{obs} vs $[1]^{-1}$ for the 3/8, 3/9, and 3/10 systems are shown in Figure 5, and those for 3/11, 3/12, and 3/13, in Figure 6. The k_{rel} and R data calculated from eq 10 are summarized in Table I. Plots of r_{obs} vs $[MX]^{-1}$ for the first two alkene pairs have a significant slope that, according to our analysis (vide supra), indicates that the addition of 2• to 8 and 9 is significantly reversible, most likely for steric reasons (R = 0.07 and 0.06 for 8 and 9, respectively).

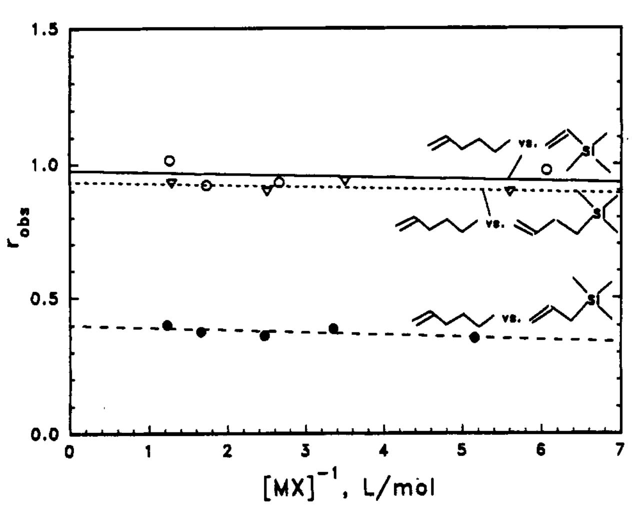

Figure 6. Plots of r_{obs} vs $[MX]^{-1}$ for 1-hexene vs vinyltrimethylsilane (11, ○), allyltrimethylsilane (12, ●), and 3-butenyltrimethylsilane (13, ▽). The concentration of each alkene was 0.1 M. For other details, see Figure 1.

The r_{obs} for the least sterically hindered alkene 10 was independent of [MX], indicating that the addition of 2• to 10 is essentially irreversible. The relative reactivity of 1-hexene vs each of the three monosubstituted alkenes (k_{rel}) decreased with the distance of the bulky *tert*-butyl group from the double bond and was found to be 1.68, 1.21, and 1.04 for the 3/8, 3/9, and 3/10 alkene pairs, respectively. In other words, the reactivity of these alkenes is only slightly influenced by steric effects (see below).

ω-Alkenyltrimethylsilanes 11–13 were more reactive than their carbon analogues 8–10 toward radical 2•. Thus, k_{rel} = 1 for 3/11 and 3/13 olefin pairs, but 12 was 2.5 times more reactive than the reference alkene, 1-hexene (Figure 6; Table I). These results indicate that the substitution of the quaternary carbon atom by silicon in alkenes 8–10 results in a 1.7-fold increase in the reactivity of 11 (α-Si), a 3-fold increase for 12 (β-Si), and no significant change for 13 (γ-Si).

The slope of the r_{obs} vs $[1]^{-1}$ plots for the three 3/ω-alkenyltrimethylsilane pairs was equal to zero, indicating irreversible addition of 2• to these compounds. The obtained reactivities are consistent with the reactivity trends observed during preliminary copolymerization experiments with SO_2.[12] Thus, the silicon substituents accelerate the addition, most likely due to electronic effects or by a partial relief of steric congestion (in comparison to the *tert*-butyl derivatives).

While the increased reactivity of organosilicon derivatives toward 2• parallels the reactivity trends during copolymerization with SO_2, the reactivity range reported here is narrower. The difference may be due to the fact that, during the alternating copolymerization of olefins with SO_2, the steric and electronic environment in the vicinity of the growing chain terminus may markedly affect individual addition steps.

Addition of 2• to Cycloalkenes. The results of competitive addition of 1 to four cycloalkenes 16–19 with 3 serving as the reference olefin are plotted in Figure 7. The statistically uncorrected relative reactivities, k_{rel}, and reversibility data, R, listed in Table I reveal that the addition of 2• to cycloalkenes is markedly dependent on the ring size of the reacting cycloalkene. For example, 16 is the most reactive among the cycloalkenes studies ($k_{rel}^{3/16}$ = 0.44), and the addition of the sulfonyl radical to this olefin is irreversible[23] at 0 °C ($R \simeq 0$, Table I). Cyclohexene (17) is less reactive than cyclopentene ($k_{rel}^{3/17}$ = 0.88), and elimination of 2• from the adduct radical becomes significant at 0 °C (R = 0.02). Interestingly, while the elimination reaction is even more significant for cycloheptene (18; R = 0.08), this olefin is more reactive than cyclohexene ($k_{rel}^{3/18}$ = 0.57).

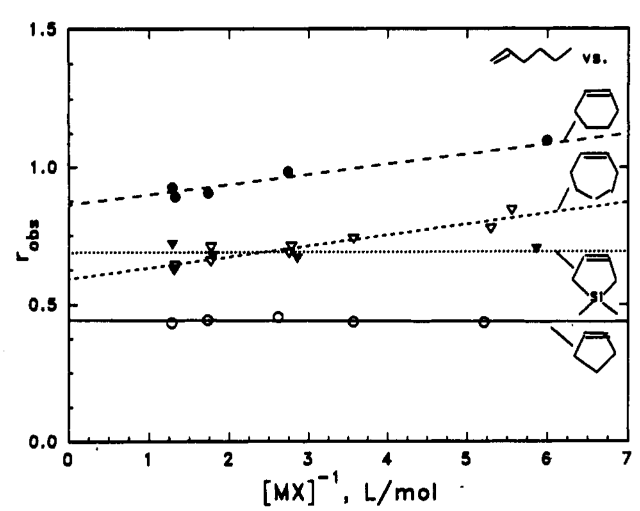

Figure 7. Plots of r_{obs} vs $[MX]^{-1}$ for 1-hexene and four cycloalkenes: cyclopentene (16, ○), cyclohexene (17, ●), cycloheptene (18, ▽), and 1,1-dimethyl-1-silacyclo-3-pentene (19, ▼). The concentration of each alkene was 0.1 M. For other details, see Figure 1.

The relative reactivities of cycloalkenes 16–18 obtained by us are in a qualitative agreement with the copolymerization ratios published by Hazell and Ivin.[8] These authors showed that cycloalkenes 16–18 are more reactive[36] than 1-alkenes (copolymerization ratios recalculated for these cycloalkenes using 3 as a standard are 0.33, 1.41, and 0.45). Excluding ethylene, cyclopentene exhibits also the highest T_c (+103 °C), while the corresponding T_c values for 17 and 18 are 24 and 11 °C, respectively.[7]

The reactivity of 19 ($k_{rel}^{3/19}$ = 0.69) was intermediate between that of 16 and 17; the addition of 2• to this cyclic allylsilane was irreversible. Also, 19 copolymerized with SO_2 significantly slower than did 16.[12] The NMR data and molecular models of 19P imply that there is significant interaction between two Si-bonded methyl groups and the bromine and methanesulfonyl substituents (see NMR data for 19P in the Experimental Section). Thus, steric hindrance is a probable cause of the low rate of addition of 2• to 19 as compared to that for 16.

The addition of 2• to cycloalkenes proceeds at the cis-configured sp^2 carbon centers; thus, its rate should be affected by the relative change in the steric strain upon rehybridization of the carbon skeleton. The addition of 2• to an internal linear olefin might be an appropriate reference point free of any ring-strain component, to which previously discussed results for cycloalkenes might be compared. The relative reactivity for the 3/7 pair toward 2• was, therefore, also determined (Figure 8, the top short dashed line). The reactivity of 7 was lower than that of cycloalkenes ($k_{rel}^{3/7}$ = 1.39), and the addition was markedly reversible (R = 0.08). Interestingly, *trans*-2-butene was reported to be only half as reactive as *cis*-2-butene during copolymerization with SO_2,[8] which suggests that the cis isomer of 7 formed by the isomerization of the starting trans isomer would be used up faster than the latter. As a result, the kinetic analysis of this reaction system becomes rather complicated. It is also noteworthy that the reported T_c for the copolymerization of 2-heptene with SO_2 was very low (−39 °C).[7]

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[36] After a statistical correction, only cyclopentene is significantly more reactive than hexene.

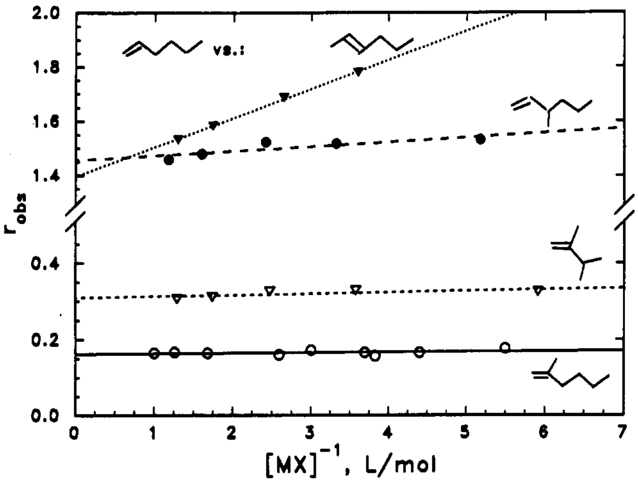

Figure 8. Relationship between r_{obs} and $[MX]^{-1}$ for alkene pairs **3**/**20** (○), **3**/**21** (●), **3**/**22** (▽), and **3**/**7** (▼). The concentration of each alkene was 0.1 M. For other details, see Figure 1.

Addition of 2$^\bullet$ to Other Branched 1-Alkenes. The effect of branching on the reactivity and reversibility of the addition of **2**$^\bullet$ to alkenes was further investigated for compounds **20**–**23**. Such studies seemed particularly interesting in view of earlier findings[4,7] showing that 1,1-dialkyl-substituted ethenes exhibit very low T_c's during copolymerization with SO_2. Such olefins copolymerize with SO_2 only if one of the substituents is no larger than methyl and when the main chain is branched no closer to the double bond than at position 4.

Because of the strong deactivating effect of branching on T_c, the copolymerization method could not be used to determine the reactivity of many branched alkenes. However, compounds shown in Chart I reacted with **2** without difficulty with only two exceptions, viz., **15** and **23**. Interestingly, **15** was reported to be very reactive toward the *tert*-butylthiyl radical.[5] Although strong UV absorption at $\lambda < 300$ nm by the phenyl groups in **15** might interfere with the efficient photodissociation of **1**, the cause of its low reactivity remains unclear.

The two 1,1-dialkylethenes investigated by us, viz., 2-methyl-1-hexene (**20**) and 2,3-dimethyl-1-butene (**22**), were considerably more reactive than **3** toward **2**$^\bullet$ ($k_{rel} = 0.16$ and 0.31, respectively; Table I, Figure 8). The apparently irreversible addition of **2**$^\bullet$ to these alkenes was particularly interesting in light of the very low T_c exhibited by 2-methyl-1-pentene (−34 °C) during copolymerization with SO_2.[7] We also found that a methyl group in position 3 of 1-alkene (3-methyl-1-hexene, **21**) causes only a small decrease in its reactivity ($k_{rel}^{3/21} = 1.45$), but the reversibility of addition became noticeable ($R = 0.02$).

Variable-Temperature Experiments. Previous studies of copolymerization of alkenes with SO_2 suggest that the activation energies, ΔE_a, for the addition of sulfonyl radicals to alkenes are small (several kilocalories per mole) and only weakly dependent on the olefin structure.[37,38] One could thus expect a weak temperature effect on k_{rel} as was indeed observed during copolymerization studies.[8] The effect of temperature on reversibility, R, particularly in the vicinity of T_c for a given alkene, could be more pronounced.

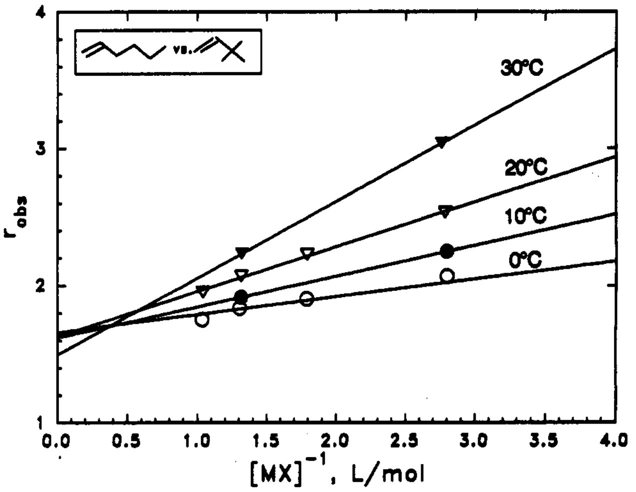

Figure 9. Effect of temperature on r_{obs} for the addition of **1** to the 1-hexene/3,3-dimethyl-2-butene (**3**/**8**) pair. The reaction was carried out at 0 (○), 10 (●), 20 (▽), and 30 °c (▼). The concentration of each alkene was 0.1 M. For other details, see Figure 1.

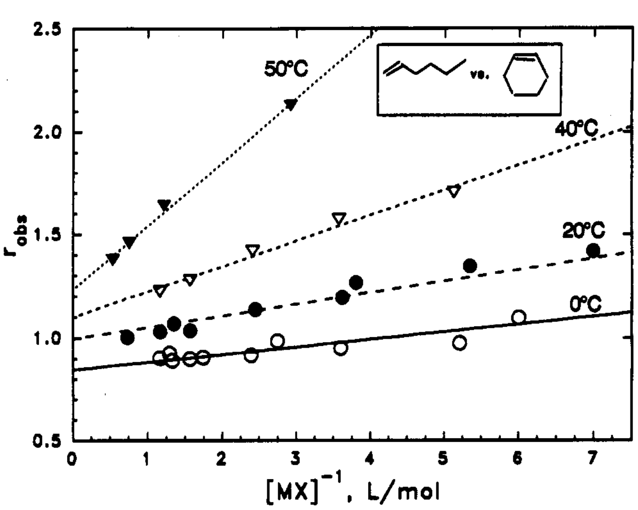

Figure 10. Effect of temperature on r_{obs} for the addition of **1** to a mixture of 1-hexene and cyclohexene (**3**/**17**). The reactions were carried out at 0 (○), 20 (●), 40 (▽), and 50 °C (▼). The concentration of each alkene was 0.1 M except for the last experiment (at 50 °C) for which it was ca. 0.5 M. For other details, see Figure 1.

Table II. Effect of Temperature on the Relative Reactivity, k_{rel}, and Reversibility, R, for the Addition of 2$^\bullet$ to 1-Hexene (3, A)/3,3-Dimethyl-1-butene (8, B) and 1-Hexene (3, A)/Cyclohexene (17, B) Mixtures[a]

1-hexene/3,3-dimethyl-1-butene			1-hexene/cyclohexene		
temp, °C	$k_{rel}^{A/B}$	R	temp, °C	$k_{rel}^{A/B}$	R
0	1.68	0.07	0	0.87	0.02
10	1.62	0.14	20	0.93	0.08
20	1.63	0.20	40	1.06	0.14
30	1.56	0.30	50	1.23[b]	0.25[b]

[a] Initial concentration of each alkene was ca. 0.1 M. The range of [**1**] from 0.2 to 1.0 M in MeCN (see also supplementary material). [b] Initial concentration of each alkene was ≃0.5 M.

We have investigated the effect of temperature on k_{rel} and R for two alkene pairs, viz., **3**/**8** and **3**/**17**, for which $R > 0$ was found at 0 °C. The upper temperature limit of such studies is necessarily limited by the onset of a reversible addition of **2**$^\bullet$ to the standard alkene **3**, for under such conditions eq 10 is no longer valid. However, *n*-alkenes exhibit conveniently high T_c's (60–64 °C),[7] suggesting that the reversible addition of **2**$^\bullet$ to such compounds may become significant in the vicinity of 45–50 °C. As discussed above, it would be manifested by a nonlinear dependence of r_{obs} on both [**1**] and $[\mathbf{1}]^{-1}$. The effect of

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[37] Gozdz, A. S. *Macromolecules* **1990**, *23*, 907.

[38] Thoi, H. H.; Iino, M.; Matsuda, M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20*, 564.

temperature on relative reactivities and reversibilities observed for the two alkene pairs **3**/**8** and **3**/**17** is shown in Figures 9 and 10. The calculated k_{rel} and R data are listed in Table II. The temperature effect on k_{rel} for the **3**/**8** pair was small as might be expected for so similar reaction sites (monosubstituted π-bonds). This effect was noticeable, however, in the case of the **3**/**17** pair, most likely due to the dissimilarity of the two reacting unsaturated sites. The apparent reversibility R markedly increases at higher temperatures for both alkene pairs studied.

Concluding Remarks

The photoinitiated competitive addition of **1** to a mixture of two alkenes is a reliable, convenient, general, and sensitive method of investigation of structure–reactivity relationships for free-radical addition reactions to π-bonds. The method is amenable to standardized and accurate experimental procedures. The problem of reversibility of addition of **2**$^\bullet$ to olefins is minimized by the use of **1**, which serves as an excellent bromine atom donor in the second propagation step. The rapid bromine transfer makes the addition irreversible for simple *n*-alkenes. It is competitive with the elimination of **2**$^\bullet$ in some other cases, allowing for the determination of the "reversibility index", R. It should be emphasized that R reflects only the ratio of the two rates. The apparent reversibility observed for some substituted olefins is most likely due to a change in both the elimination rates (k_{-1} or k_{-2}) and bromine abstraction rates (k_3 or k_4), in comparison to that for *n*-alkenes. For example, the bromine abstraction by a tertiary radical is expected to be slower than that by the secondary one, but the elimination of **2**$^\bullet$ should follow the same trend. When absolute rates of bromine abstraction by carbon-centered radicals become available, more accurate estimates of the "absolute" reversibility of addition will be possible.

By using a strongly electrophilic radical **2**$^\bullet$ and by a judicious choice of alkenes in which only one molecular parameter (atom type, spacer or ring size) is varied in a systematic manner, we were able to evaluate the relative importance of these factors on the reactivity of the double bond. Semiempirical molecular orbital (MO) calculations carried out by several methods[37] indicate that the addition reactions of sulfonyl radicals to olefins have early (i.e., reactant-like) transition states. This conclusion is confirmed by the estimated rate of addition of **2**$^\bullet$ to *n*-alkenes, which is near-diffusion limited. Reactions with early transition states can be treated conveniently by the perturbation approach. Perturbational MO theories of chemical reactivity predict[39] that, in the case of a strongly electrophilic radical such as **2**$^\bullet$, the dominant interaction will be between the singly occupied MO (SOMO) of the radical and the highest occupied MO (HOMO) of the olefin. One might thus expect that the relative rates of addition should correlate well with the ionization potentials of the olefins. Indeed, such a trend is observed. Dialkyl-substituted or silicon-substituted olefins whose ionization potentials are lower by ca. 0.4 eV than those of simple *n*-alkenes[40] are more reactive. It is apparent, however, that steric considerations also play an important role in the addition. For example, 1-hexene (**3**) and 3,3-dimethyl-1-butene (**8**) have essentially identical ionization potentials (9.44 and 9.45 eV), but the latter is significantly less reactive. On the other hand, the silicon analogue of **8**, viz. **11**, is slightly more reactive than **3**, probably for electronic reasons (lower ionization potential), although the effect of the C–Si bond lengthening (by ca. 0.03 nm compared to the length of the C–C bond)[41] leading to a partial relief of the transition state strain cannot be excluded. The largest silicon substitution effect is observed for the β-Si-substituted alkene **12**. This effect is mostly of the electronic nature. The σ-orbital of the C–Si bond is in conjugation with the double bond, thus lowering its ionization potential significantly (by 0.75 eV in comparison to its carbon analogue **9**). Similar effects account for the known silicon-stabilization effects observed for carbocations and radicals.[13] The most reactive olefin **14** has the lowest ionization potential of all the olefins studied. It is very likely that it reacts with **2**$^\bullet$ at a diffusion-limited rate.

Good agreement of the obtained relative reactivities with the copolymerization ratios of these alkenes with SO_2[8] supports our conclusion that the two methods of measuring the reactivity are sensitive to the same structural factors. However, the reactivity scale based on the copolymerization data appears to be wider than that obtained by the present method. We believe this to be caused by the more stringent steric requirements of the growing macroradical than those necessary for the reaction of two small molecules. Relative reactivities reported here are a useful prediction of the reactivity ratios during copolymerization of olefins with SO_2.

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Supplementary Material Available: Tables III–XIV giving experimental details of competitive addition reactions for Figures 1–10, derivation of eq 11 (Appendix A), and ^1H and ^{13}C NMR spectra of adducts **3P**–**23** (54 pages). Ordering information is given on any current masthead page.

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[39] (a) Fukui, K.; Yonezawa, T.; Nagata, Ch. *J. Chem. Phys.* **1957**, *27*, 1247. (b) Fukui, K. *Theory of Orientation and Stereoselection*; Springer: Berlin, 1975. (c) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: Chichester, 1989.

[40] Experimental values of ionization potentials were taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Supplement 1), 1. IP's were calculated by the MNDO-PM3 semiempirical MO method with the MOPAC 5.0 program: QCPE 455. *QCPE Bull.* **1989**, *9*, 10.

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