

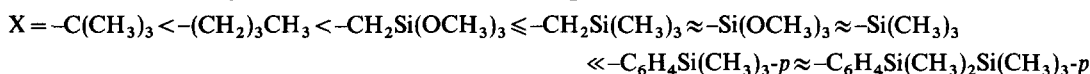
Flash photolysis study of initiation step in radical polymerization of Si-containing vinyl monomers: reactivities to arylthiyl radicals

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The initiation step in radical polymerization of Si-containing vinyl monomers with arylthiyl radicals (ArS^\cdot) has been studied by the flash photolysis method. Rate constants for reversible addition reactions of ArS^\cdot with various Si-containing vinyl monomers have been determined by the selective radical scavenging method. For each thiyl radical, the reactivities for $\text{CH}_2=\text{CHX}$ increased in the order:



The reactivity of the $\text{C}=\text{C}$ was increased by the substitution of the Si atom at vinyl and allyl positions. The polar and resonance factors of Si-containing monomers were evaluated from the kinetic data, which were compared with the Alfrey-Price $Q-e$ scheme obtained from the copolymerization data.

(Keywords: Si-containing vinyl monomer; arylthiyl radical; initiation step; flash photolysis)

INTRODUCTION

Si-containing polymers are known to be suitable for two-layer microlithography using an electron beam¹. Copolymers with Si-substituted styrenes are sensitive to deep u.v. light and are used as positive resists². It is important to understand the reactivity of Si-containing vinyl monomers in order to predict the polymerization process, copolymerization properties and structure of the polymers. For some Si-containing vinyl monomers, Alfrey-Price $Q-e$ values have been evaluated using copolymerization data³⁻⁵; the $Q-e$ values indicate that the silyl groups withdraw the electron on the double bond with slight conjugation.

Recently, fast kinetic methods such as laser flash photolysis and time-resolved e.s.r. spectroscopy have been applied to the elemental steps of radical polymerization⁶⁻⁸. In our previous papers, we reported that the initiation step in radical polymerization of various vinyl monomers with arylthiyl radicals (ArS^\cdot) can be monitored by the xenon flash photolysis method, from which the reactivities of vinyl monomers with ArS^\cdot were evaluated⁹⁻¹². In this report, we determine the rate constants of the initiation step of various Si-containing vinyl monomers with ArS^\cdot . In order to compare these kinetic data with the $Q-e$ values, copolymerization of *p*-pentamethyldisilylstyrene with methyl methacrylate was performed to evaluate the $Q-e$ value.

EXPERIMENTAL

Materials

Vinylsilanes and allylsilanes were purchased from Chisso Co.; they were used after purification by distillation. *p*-Trimethylsilylstyrene (Hokko Chemical Co.) was used after distillation. *p*-Pentamethyldisilylstyrene was prepared by the Grignard reaction of *p*-chlorostyrene with $(\text{CH}_3)_3\text{Si}(\text{CH}_3)_2\text{SiMgCl}$ in tetrahydrofuran, as described in the literature¹³. Commercially available *p*-t-butylstyrene (Scientific Polymer Product Inc.) was purified by distillation. 3,3-Dimethyl-1-butene (Tokyo Kasei Kogyo Co. Ltd) contained some reactive dienes; it was distilled after photolysis of diphenyl disulphide in the reagent. Methyl methacrylate for copolymerization experiments was used after removing inhibitor. Diaryl disulphides (ArSSAr) prepared from the corresponding arylthiols by the action of I_2 were purified by recrystallization from ethanol¹⁴. Cyclohexane and benzene were used as solvents after distillation.

Copolymerization procedure

Although the $Q-e$ values have been reported for some Si-containing vinyl monomers, some of them seem to be inconsistent in the literature³⁻⁵. The $Q-e$ value of *p*-pentamethyldisilylstyrene was determined in this study. Copolymerization of this monomer with methyl methacrylate was carried out at 60°C in degassed benzene solution in the presence of 2,2'-azobisisobutyronitrile as initiator (6 mM). The content of monomer moiety in the copolymer was calculated from ¹H n.m.r. data obtained with changing monomer feed.

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Flash photolysis experiments

The flash photolysis apparatus was of standard design equipped with two xenon flashlamps (Xenon Co. N851C; 8 μ s half-duration and 100J input energy)⁹⁻¹². The cyclohexane solution containing ArSSAr and vinyl monomer was degassed followed by the introduction of oxygen into the solution. The oxygen concentration in cyclohexane was calculated by Henry's law¹⁵.

RESULTS AND DISCUSSION

Copolymerization for $Q-e$ measurement

Figure 1 shows the ¹H n.m.r. spectrum of the copolymer of *p*-pentamethyldisilylstyrene (M_2) with methyl methacrylate (M_1). The compositions of monomer components in the copolymers were calculated from the ratio of the signals of the methyl hydrogen bonded with Si atoms (at 1.1 and 1.3 ppm) to those with ester (3.9–4.7 ppm). Figure 2 shows a plot of the contents of *p*-pentamethyldisilylstyrene moiety in the copolymer against the monomer feed. The monomer reactivities were determined by the Fineman-Ross method to be

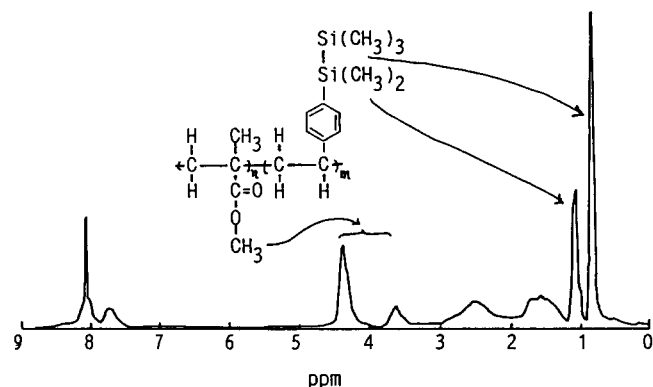


Figure 1 ¹H n.m.r. spectrum of *p*-pentamethyldisilylstyrene ($M_2 = 27.4$ mol%) - methyl methacrylate ($M_1 = 72.6$ mol%) copolymer

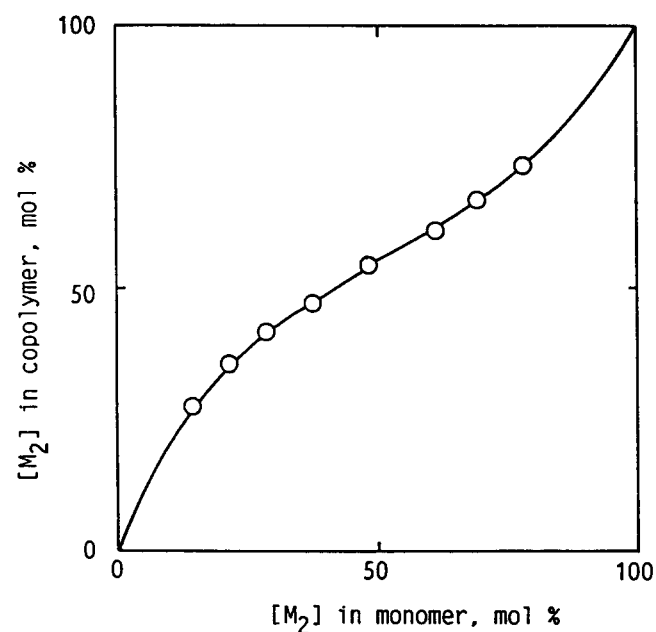


Figure 2 Monomer composition in copolymer of *p*-pentamethyldisilylstyrene and methyl methacrylate

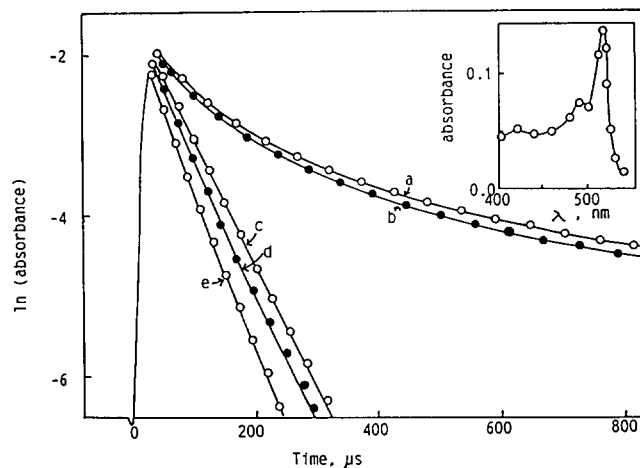


Figure 3 First-order plots for decay of *p*-BrC₆H₄S[·]; the transient spectrum is shown in the insert. (a) Without monomer and (b-e) [vinyltrimethylsilane]=0.4 M; (b) [O₂]=0, (c) [O₂]=1.4 mM, (d) [O₂]=2.0 mM and (e) [O₂]=11 mM

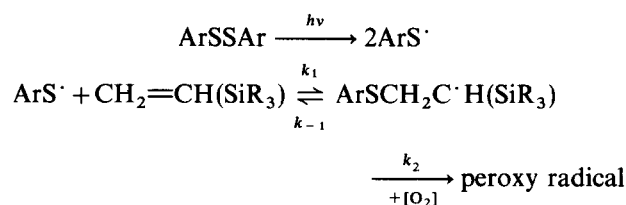
$1/r_1 = 0.32$ and $1/r_2 = 0.60$. Thus, $Q = 1.37$ and $e = -0.88$ were calculated from the reported $Q-e$ value for methyl methacrylate⁵. They are similar to those of *p*-*t*-butylstyrene ($Q = 1.37$ and $e = -0.90$). These Q values are slightly larger than those of *p*-trimethylsilylstyrene and unsubstituted styrene ($Q = 1.00$ and $e = -0.80$). These findings suggest that disilylstyrene is slightly more conjugative than monosilyl- and unsubstituted styrenes.

Flash photolysis measurements

By the flash photolysis of ArSSAr, transient absorption bands were observed in the visible region; an example is shown in the insert of Figure 3. They were attributed¹⁶⁻¹⁸ to ArS[·]. ArS[·] were not reactive with oxygen in the timescale of the xenon flash experiment. This finding is in good agreement with the reported low reactivity of CH₃S[·] towards oxygen in the gas phase¹⁹.

Figure 3 shows the decays of *p*-BrC₆H₄S[·] in the form of a first-order plot in the absence and presence of vinyl monomer and oxygen. When the solution was degassed, the decay of ArS[·] was not accelerated even by the addition of vinyl monomer, whereas the decay was accelerated by the addition of both vinyl monomer and oxygen to the solution. These observations indicate that the addition reaction of ArS[·] to vinyl monomers occurs in a reversible fashion and that the oxygen molecule selectively scavenges the carbon-centred radical, accelerating the decay of ArS[·]. These reactions are summarized in Scheme I, where vinylsilane (CH₂=CH(SiR₃)) is shown as a representative of other Si-containing vinyl monomers. The anti-Markovnikov addition mode of the thiyl radicals to Si-containing vinyl monomers has been reported²⁰⁻²². The role of the oxygen molecule as a

Scheme I



selective radical scavenger in the addition reaction of the thiyl radical with styrene was also confirmed by Gilbert *et al.*²³ using the e.s.r. method.

The decays of ArS[•] were influenced by concentrations of both vinyl monomer and oxygen. From Scheme 1, one can derive the equation⁹⁻¹²:

$$[\text{CH}_2=\text{CH}(\text{SiR}_3)]/k_{f0} = 1/k_1 + k_{-1}/k_1k_2[\text{O}_2] \quad (1)$$

where k_{f0} refers to the slope of the first-order plot in Figure 3. When the concentrations of vinyl monomer and oxygen were low, the decay kinetics consisted of mixed first and second order; for such a case, the k_{f0} value was evaluated by a method in the literature²⁴.

Figure 4 shows the plots of equation (1) for the reaction of vinyltrimethylsilane with different ArS[•]. The k_1 value can be determined from the intercept, and the equilibrium constant ($K = k_1/k_{-1}$) can be evaluated in the form Kk_2 from the slope. They are summarized in Tables 1 and 2 along with the values of the carbon analogues such as 3,3-dimethyl-1-butene and *p*-t-butylstyrene determined similarly in this study.

For each vinyl monomer, the k_1 values increase with the electron-withdrawing substituent of ArS[•]. For each ArS[•], the reactivities of Si-containing aliphatic vinyl monomers are higher than those of the carbon analogues. A similar tendency was observed for the addition reaction

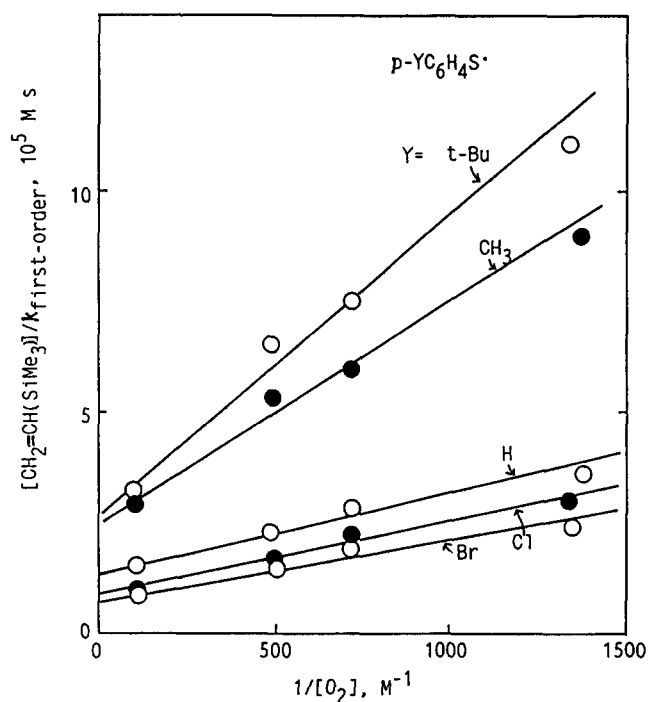


Figure 4 Plots of equation (1) for reaction of vinyltrimethylsilane with *p*-YC₆H₄S[•]

Table 1 Rate constants for addition reaction at 23°C in cyclohexane

Monomer	$k_1 \times 10^{-5} \text{ (M}^{-1} \text{ s}^{-1})$ for <i>p</i> -XC ₆ H ₄ S [•]					
	X = MeO	Me	t-Bu	H	Cl	Br
CH ₂ =CH(Si(CH ₃) ₃)	0.06	0.32	0.32	0.67	1.1	1.1
CH ₂ =CH(Si(OCH ₃) ₃)	0.04	0.23	0.26	0.77	0.85	1.2
CH ₂ =CH(C(CH ₃) ₃) ^a	—	<0.02	<0.02	0.04	0.08	0.08
CH ₂ =CHCH ₂ (Si(CH ₃) ₃)	0.04	0.20	0.25	0.59	0.80	1.1
CH ₂ =CHCH ₂ (Si(OCH ₃) ₃)	0.03	0.16	0.15	0.43	0.63	1.0
CH ₂ =CH(CH ₂) ₃ CH ₃ ^{a,b}	—	0.04	0.04	0.10	0.15	0.12
CH ₂ =CHC ₆ H ₄ Si(CH ₃) ₃ - <i>p</i>	40	160	150	510	1100	1200
CH ₂ =CHC ₆ H ₄ Si(CH ₃) ₂ Si(CH ₃) ₃ - <i>p</i>	28	210	170	430	1200	1200
CH ₂ =CHC ₆ H ₄ C(CH ₃) ₃ - <i>p</i>	28	250	190	500	1400	1500

^a In hexane

^b Cited from Ito *et al.*³²

Table 2 Equilibrium constants in the form of Kk_2

Monomer	$Kk_2 \times 10^{-7} \text{ (M}^{-1} \text{ s}^{-1})$ for <i>p</i> -XC ₆ H ₄ S [•]						
	X =	MeO	Me	t-Bu	H	Cl	Br
CH ₂ =CH(Si(CH ₃) ₃)	— ^a		1.5	1.5	5.0	6.3	6.7
CH ₂ =CH(Si(OCH ₃) ₃)	— ^a		1.4	1.3	3.3	5.2	4.8
CH ₂ =CH(C(CH ₃) ₃)	— ^a		— ^a	— ^a	0.12	0.19	0.22
CH ₂ =CHCH ₂ (Si(CH ₃) ₃)	— ^a		1.0	0.8	1.5	2.0	1.9
CH ₂ =CHCH ₂ (Si(OCH ₃) ₃)	— ^a		2.0	1.0	1.3	1.8	2.2
CH ₂ =CHC ₆ H ₄ Si(CH ₃) ₃ - <i>p</i>		450	6000	6100	— ^b	— ^b	— ^b
CH ₂ =CHC ₆ H ₄ Si(CH ₃) ₂ Si(CH ₃) ₃ - <i>p</i>		1700	12000	12000	— ^b	— ^b	— ^b
CH ₂ =CHC ₆ H ₄ C(CH ₃) ₃ - <i>p</i>		1200	8000	6600	— ^b	— ^b	— ^b

^a These Kk_2 values were not obtained because the decay curves were not considerably changed by the oxygen concentration; these Kk_2 values are smaller than $10^6 \text{ M}^{-1} \text{ s}^{-1}$

^b These Kk_2 values are larger than $2 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$

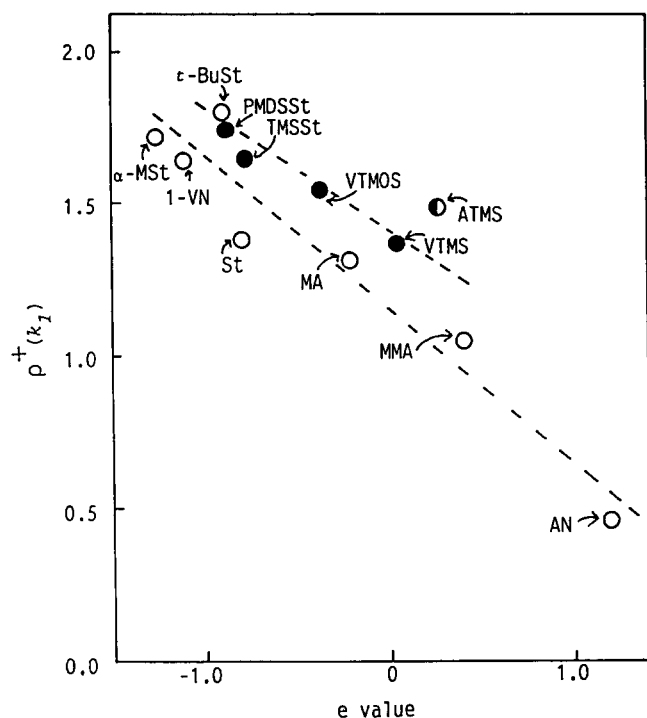
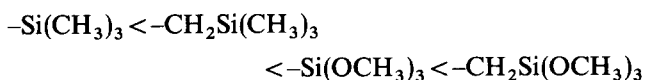


Figure 6 Plot of $\rho^+(k_1)$ vs. e value. Abbreviations of vinyl monomers: St, styrene⁹; t-BuSt, *p*-*t*-butylstyrene; PMDSSt, *p*-pentamethyldisilylstyrene; TMSSt, *p*-trimethylsilylstyrene; VTMS, vinyltrimethoxysilane; ATMS, allyltrimethylsilane; α -MSt, α -methylstyrene¹¹; 1-VN, 1-vinylnaphthalene¹²; MA, methyl acrylate¹⁰; MMA, methyl methacrylate⁹; and AN, acrylonitrile¹⁰

but these groups are far less electron-releasing than the standard phenyl group ($e = -0.8$). The Hammett-type substituent constants of these groups, however, are negative, indicating electron-releasing character, though they are weak: $-\text{Si}(\text{CH}_3)_3$, $\sigma_p = -0.07$ and $\sigma_m = -0.04$; and $-\text{CH}_2\text{Si}(\text{CH}_3)_3$, $\sigma_p = -0.22$ and $\sigma_m = -0.19$ ³⁰. The ρ^+ value of vinyltrimethylsilane is as large as that of styrene, which indicates a considerable electron-releasing character of the trimethylsilyl group. From the ρ^+ values, the electron-releasing ability increases in the order



The high electron-releasing ability of allylsilane would be caused by the hyperconjugative effect³¹. The $-\text{OCH}_3$ group attached to the Si atom indirectly increases the electron density of $\text{C}=\text{C}$.

A tendency that the reactivity increases with the stability of the carbon-centred radical can be confirmed in Tables 1 and 2. Compared with the absorption maxima (λ_{max}) in the u.v. region of these vinyl monomers (Table 3), the Kk_2 values increase with the shift of λ_{max} to longer wavelength.

CONCLUSIONS

The kinetic parameters for the addition reaction of arylthiyl radicals to Si-containing vinyl monomers were evaluated by applying the flash photolysis method to the photoinitiation step for the system involving Si-containing vinyl monomers and ArSSAr .

From the kinetic data for the reversible addition reaction process of ArS^\cdot with monomers, we can obtain the parameters such as ρ^+ and Kk_2 , which correspond to the e and Q values derived from the propagation rates of radical copolymerization, respectively. The silyl groups at the vinyl and allyl positions promote the reactivities of the double bonds, although the effect is weak for styrene derivatives.

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REFERENCES

- 1 Gozdz, A. S., Dijkamp, D., Schubert, R., Wu, X. D., Klausner, C. and Bowden, M. J. 'Polymers for High Technology: Electronics and Photonics', *ACS Symp. Ser.* 1987, **346**, 334
- 2 Ito, S., Ono, H., Kim, S. J. and Matsuda, M., Preprints IUPAC MACRO 88, Kyoto, 1988, p. 542
- 3 Scott, C. E. and Price, C. C. *J. Am. Chem. Soc.* 1959, **81**, 2670
- 4 Sakurai, H., Tominaga, K. and Kumada, M. *Bull. Chem. Soc. Jpn.* 1966, **39**, 1279
- 5 Young, J. L. 'Polymer Handbook', (Eds. J. Brandrup and E. H. Immergut), Wiley, New York, 1975, p. II-387
- 6 Irie, M., Masuhara, H., Hayashi, K. and Mataga, N. *J. Phys. Chem.* 1974, **78**, 341
- 7 Schnabel, W. *J. Radiat. Curing* 1986, **13**, 27
- 8 Kamachi, M., Kuwata, K., Sumiyoshi, T. and Schnabel, W. *J. Chem. Soc. Perkin Trans. 2* 1988, 961
- 9 Ito, O. and Matsuda, M. *J. Am. Chem. Soc.* 1979, **101**, 5732
- 10 Ito, O. and Matsuda, M. *J. Am. Chem. Soc.* 1981, **103**, 5781
- 11 Ito, O. and Matsuda, M. *J. Org. Chem.* 1982, **47**, 2261
- 12 Yoshizawa, H., Ito, O. and Matsuda, M. *Br. Polym. J.* 1988, **20**, 441
- 13 Saigo, K., Proc. 53rd Annual Meeting of the Japan Chemical Society, 1986, p. II-1B05
- 14 Tarbell, D. S. and Fukushima, D. K. *Org. Synth.* 1947, **27**, 81
- 15 Murov, S. I. 'Handbook of Photochemistry', Marcel Dekker, New York, 1973, p. 89
- 16 Thyron, F. C. *J. Phys. Chem.* 1973, **77**, 1478
- 17 Burkey, T. J. and Griller, J. *J. Am. Chem. Soc.* 1985, **107**, 246
- 18 Franz, J. A., Bushaw, B. A. and Alnajjar, M. S. *J. Am. Chem. Soc.* 1989, **111**, 268
- 19 Tyndall, G. S. and Ravishankara, A. R. *J. Phys. Chem.* 1989, **93**, 2426
- 20 Jarvie, A. W. P. and Rowley, R. J. *J. Chem. Soc. (B)* 1971, 2439
- 21 Kutuyev, G. A., Nigametzyanov, R. T., Cherkasov, R. A. and Pudovik, A. N. *Zh. Obshch. Khim.* 1978, **48**, 753
- 22 Voronkov, M. G. and Sorokin, M. S. *Zh. Obshch. Khim.* 1984, **54**, 2020
- 23 Gilbert, B. C., Kelsall, P. A., Sexton, M. D. G., McConnachie, G. D. G. and Symon, M. C. R. *J. Chem. Soc. Perkin Trans. 2* 1984, 629
- 24 Closs, G. L. and Rabinow, B. E. *J. Am. Chem. Soc.* 1976, **98**, 8190
- 25 Münger, K. and Fischer, H. *Int. J. Chem. Kinet.* 1985, **17**, 809
- 26 Sakurai, H., Hosomi, A. and Kumada, M. *J. Org. Chem.* 1969, **34**, 1764
- 27 Weidner, U. and Schweig, A. *J. Organometal. Chem.* 1972, **39**, 261
- 28 Howard, J. A. 'Free Radicals', (Ed. J. K. Kochi), Wiley, New York, 1973, Vol. II, p. 1
- 29 Brown, H. C. and Okamoto, Y. *J. Am. Chem. Soc.* 1957, **79**, 1957
- 30 Hammett, L. P. 'Physical Organic Chemistry', McGraw-Hill Kogakusha, Tokyo, 1970, p. 356
- 31 Yuriev, V. P., Panasenko, A. A., Khvostenko, V. I., Khaliov, L. M., Yasman, Y. B., Timoshenko, M. M., Chizhov, Y. V., Zykov, B. G., Furlei, I. I. and Rafikov, S. R. *J. Organometal. Chem.* 1979, **166**, 169
- 32 Ito, O., Omori, R. and Matsuda, M. *J. Am. Chem. Soc.* 1982, **104**, 3934