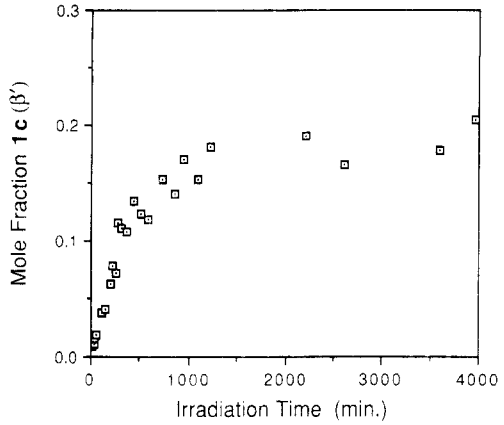


Figure 3. Experimental conversion (by NMR) to **1c** (β') vs irradiation time for xanthone sensitization of **1t**.

of these data for back reaction according to Lamola,[31] gave a Φ of 0.23.

In a separate experiment, 11.8 mg of **1t** and 50 mg of xanthone were dissolved in 1.5 cc of C_6D_6. One half of this solution was placed into an NMR tube containing 10.1 mg of thiophenol (sample A1) and the other half was placed into an empty NMR tube (sample A2). Both tubes were degassed, sealed, and irradiated together at 366 nm with periodic monitoring by NMR. Sample A1 was irradiated for 6.2 h and A2 for 15 h. The pss of A2 contained 17% **1c**, a lower value than found in the 313-nm irradiation. This discrepancy is probably due to light absorption by **1c**, which competes better with xanthone for light at 366 nm than at 313 nm. GC analysis of A2 showed **1t** and **1c** but no cyclopropane, ethylene, or pyrazoline **2**. Sample A1 showed no **1c** by NMR or GC but instead formed **13**, **21**, and diphenyl disulfide, as demonstrated by NMR and GC comparison with authentic samples (columns H, I, K).

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for financial support. G.A.B. gratefully acknowledges the ARCS Foundation for a fellowship. Flash photolysis experiments were carried out at the Center for Fast Kinetics Research at the University of Texas at Austin. The CFKR is supported jointly by the Biotechnology Research Technology Program of the Division of Research Resources of NIH (RR00886) and by The University of Texas at Austin.

Registry No. **1t**, 80201-75-8; **1c**, 80201-76-9; **2**, 80201-77-0; **9**, 109-98-8; **13**, 15601-98-6; **21**, 115962-98-6; **25**, 61377-11-5; **26**, 69517-15-3; **27**, 115963-00-3; pentane, 109-66-0; hydrogen, 1333-74-0; azoxycyclopropane, 33425-51-3; cyclopropylamine, 765-30-0; (cyclopropylazo)-*n*-propane, 115962-97-5; allylcyclopropane, 4663-23-4; *tert*-butylcyclopropane, 4741-87-1; *trans*-[2,3,3-$^2H_3$]-cyclopropanecarboxamide, 115962-99-7; acrolein, 107-02-8; 1,5-hexadiene, 592-42-7; (*tert*-butylazo)cyclopropane, 115963-01-4; *trans*-[2,3,3-$^2H_3$]phenylcyclopropane, 61377-10-4; bicyclopropyl, 5685-46-1; ethylene, 74-85-1; cyclopropane, 75-19-4.

Reactivities of Conjugated Dienes to Arylthiyl Radicals

Osamu Ito,* Saburo Tamura,† Kenkichi Murakami, and Minoru Matsuda

Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Katahira, Sendai 980, Japan, and Miyagi Vocational Training College, Tsukidate, Miyagi 987-22, Japan

Received March 30, 1988

The rate constants for the addition reactions of the arylthiyl radicals to various conjugated dienes have been determined by the flash photolysis method. For each arylthiyl radical, the absolute rate constant of 1,3-butadiene is close to that of styrene and is larger than that of 1-hexene by a factor of ca. 3500; the formation of the resonance stabilization of the allyl-type radical accelerates the reaction rate. The Hammett relation with varying substituents on the arylthiyl radicals was examined for each diene; the chloro and carboxylic substitutions on diene reduce the electron density of the conjugated double bond due to the inductive effect, vise versa for the methyl and methoxy substituents. The substitution at the terminal carbon of diene decreases the reactivity; the terminal position is predominantly attacked by the arylthiyl radical. The reactivity of 2,3-dimethoxy-1,3-butadiene is considerably lower than that of the 2,3-dimethyl derivative, suggesting an angular conformation for the former diene.

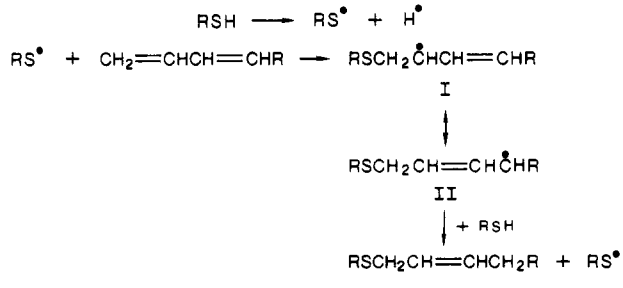
Introduction

Radical addition reactions of thiols to 1,3-conjugated dienes give predominantly 1,4-addition products, i.e., the thiyl radical attacks the terminal position and the carbon radical center at the 4-position of the allyl radical abstracts an hydrogen atom from thiol (Scheme I).[1,2]

In the co-presence of oxygen, 1-sulfide 2-ol compounds (i.e., $RSCH_2CH(OH)CH{=}CHR$) are produced, suggesting that the reaction of oxyggen occurs at the 2-position of the allyl radical (resonance structure I).[3] This finding also indicates that the arylthiyl radicals are not reactive to oxygen, since the sulfonyl or sulfinyl compounds are not found under an ordinal condition.

Although these studies based on the product analyses revealed the regioselectivity of the reactions, any systematic kinetic study for the reactivity of various dienes toward free radicals has not yet been reported. Some reaction rate

Scheme I



† Miyagi Vocational Training College.

(1) Oswald, A. A.; Griesbaum, K.; Thaler, W. A.; Hudson, B. E., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 3897.

0022-3263/88/1953-4758$01.50/0

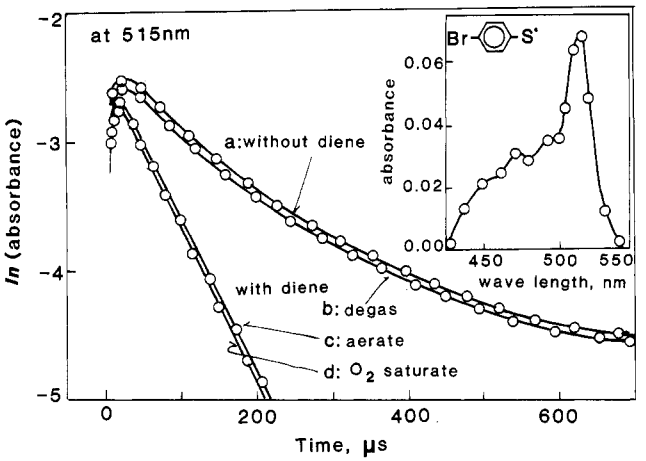


Figure 1. First-order curves for the decay of p-$BrC_6H_4S^{\bullet}$ (515 nm) in cyclohexane at 23 °C. Concentration of *trans*-piperylene = 1.5×10^{-4} M. Insert: Transient absorption spectrum of p-$BrC_6H_4S^{\bullet}$ at 30 μs after the flash photolysis of the corresponding disulfide (10^{-5} M).

Table I. Rate Constants (k_1) for Addition Reactions of p-$XC_6H_4S^{\bullet}$ with Various Dienes

	$k_1 \times 10^{-6}$ (M^{-1} s^{-1}) of $XC_6H_4S^{\bullet}$ at each λ_{max} (nm), X =					
diene[a]	MeO 517	Me 505	*t*-Bu 505	H 495	Cl 515	Br 515
BD	2.8	12	13	35	50	65
2-M-BD	4.5	16	18	47	120	130
2,3-DM-BD	11	41	42	90	210	240
2,3-DMeO-BD	0.8	9.6	10	18	40	55
2-Cl-BD	5.4	10	11	17	33	48
2,3-DCl-BD	6.8	14	14	19	37	47
t-1-M-BD	2.2	13	13	32	76	110
c-1-M-BD	2.6	13	16	60	75	140
1,4-DM-BD	1.6	10	12	22	45	42
1-M-4-CO_2M-BD	1.0	2.3	2.8	8	12	19
cy-HXD	7.5	36	41	90	240	270
1-MeO-cy-HXD	22	130	140	250	550	800
cy-HPD	1.2	6.8	6.3	22	28	36

[a] Abbreviation of dienes: BD; butadiene, 2M-BD; 2-methylbutadiene, 2,3DM-BD; 2,3-dimethylbutadiene, 2,3-DCl-BD; 2,3-dichlorobutadiene, cy-HXD; cyclohexadiene, cy-HPD; cycloheptadiene, and *c* and *t* refer to cis and trans respectively.

constants reported hitherto confirmed that conjugated dienes were more reactive than the nonconjugated monoenes.[4-6] In this study, we apply the flash photolysis method to obtain the rate constants for the addition reactions of the arylthiyl radicals to various conjugated dienes. The Hammett relation with changing the substituents of the arylthiyl radicals was also investigated to get information about the polar transition state of the reaction, which reflects the electron density of the dienes.

Results and Discussion

The transient absorption spectrum observed by the flash photolysis of ($(p$-$BrC_6H_4)_2S_2$) is shown in the insert of Figure 1; since a similar absorption spectrum was observed by the flash photolysis of p-BrC_6H_4SH, the absorption band in the visible region was attributed to p-$BrC_6H_4S^{\bullet}$.[7]

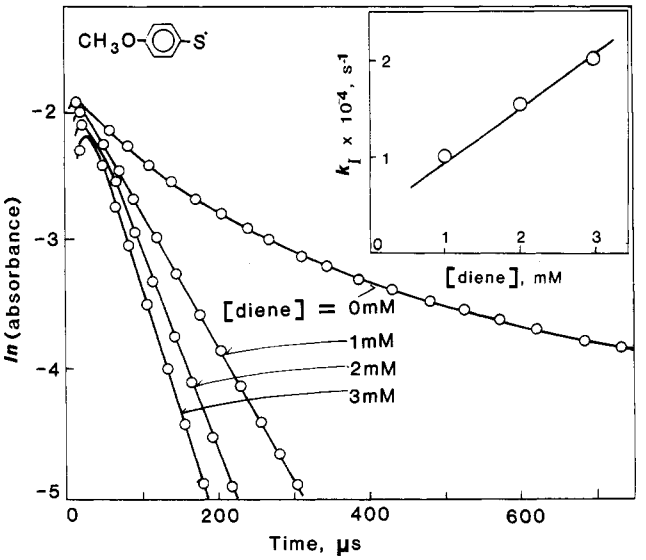


Figure 2. First-order decay curves of p-$MeOC_6H_4S^{\bullet}$ (517 nm) in the aerated cyclohexane solution in the presence of 1,3-cyclohexadiene. Insert: Pseudo-first order plot.

Scheme II

$$ArS^{\bullet} + RCH{=}CRCR{=}CHR \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArSCHR\dot{C}RCR{=}CHR \xrightarrow{k_2 + (O_2)} ArSCHR(OO^{\bullet})CR{=}CHR$$

The absorption maxima in the visible region for all arylthiyl radicals examined in this study are summarized in Table I.

The first-order plot for the decay of the thiyl radical is shown in Figure 1. Low reactivity of the arylthiyl radicals to oxygen was confirmed by similarity of the decay curve in an oxygen-containing solution to that without oxygen. The reversible addition reaction of the arylthiyl radicals with dienes was also revealed by the decay curves in Figure 1, i.e., on addition of diene, the decay rate in the degassed solution (curve b) was not accelerated compared with decay curve (a). Only when oxygen was added to a diene containing solution an increase in the decay rate of the thiyl radical was observed. The above findings indicate the following reaction scheme shown in Scheme II. Since both air- and oxygen-saturated solutions gave a similar decay rate (Figure 1), the backward reaction rate constants (k_{-1}) may be small in comparison with the rate constant for the reaction with oxygen ($k_2[O_2] > k_{-1}$ in Scheme II). Thus, the forward reaction rate constants (k_1) were obtained from the pseudo-first-order rate constant (k_I) which is the slope of the first-order plot observed in air-saturated solution.

Figure 2 shows the first-order decay curves in aerated solution with changing concentration of diene. The pseudo-first-order relation, $k_1 = k_I/[\text{diene}]$, was confirmed as shown in the insert of Figure 2. The rate constants for the addition reaction of six arylthiyl radicals to 13 conjugated dienes evaluated in this study are summarized in Table I. For each diene, the k_1 values increase with the

(2) Kellogg, R. M. In *Method in Free-Radical Chemistry*; Huyser, E. S. Ed.; Dekker: New York, 1969; Vol. 2, Chapter 1.
(3) Oswald, A. A.; Griesbaum, K.; Hudson, B. E., Jr. *J. Org. Chem.* **1963**, *28*, 2355.
(4) Thomas, J. K. *J. Phys. Chem.* **1967**, *71*, 1919.
(5) Lesclaux, R.; Roussel, P.; Veyret, B.; Pouchan, C. *J. Am. Chem. Soc.* **1986**, *108*, 3872.
(6) Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343.
(7) Ito, O.; Oomori, R.; Matsuda, M. *J. Am. Chem. Soc.* **1982**, *104*, 3934.

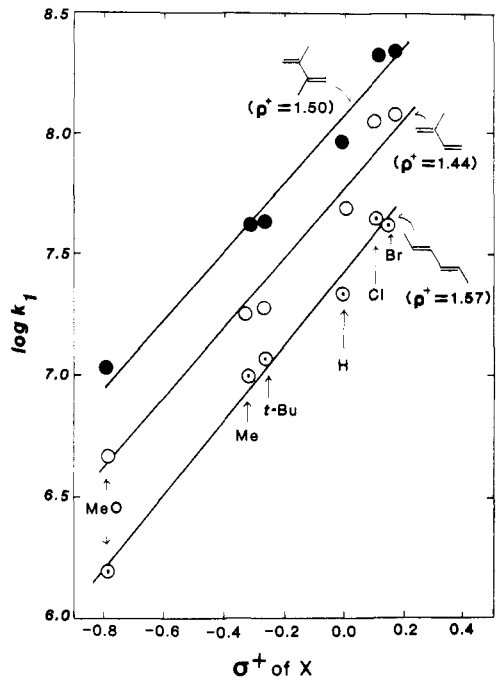


Figure 3. Hammett plot for log k_1 vs σ^+ of X in p-$XC_6H_4S^\bullet$.

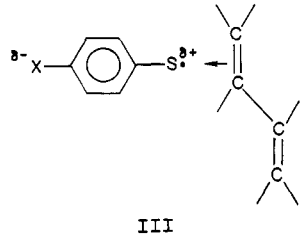
Table II. ρ^+ Values, Ionization Potentials, *e* and *Q* Values, and λ_{max} of Dienes

diene	ρ^+	I_P (eV)[a]	*e* value[b]	*Q* value[b]	λ_{max} (nm)[c]
BD	1.40	9.07	−1.05	2.39	217
2-M-BD	1.44	8.85	−1.22	3.33	220
2,3-DM-BD	1.50	8.71	−1.81	5.86	226
2,3-DMeO-BD	1.94	(8.0)			225
2-Cl-BD	0.98		−0.02	7.26	223
2,3-DCl-BD	0.77		0.48	2.86	
t-1-M-BD	1.70	8.59	−0.97	0.56	222
c-1-M-BD	1.68	8.63	−1.06	1.22	222
1,4-DM-BD	1.57	8.19			227
1-M-4-CO_2M-BD	1.20				258
cy-HXD	1.60	8.25			256
1-MeO-cy-HXD	1.64				268
cy-HPD	1.55	8.31			248

[a] References 14–16. [b] References 17–20. [c] References 21 and 22.

electron-withdrawing substituents on the arylthiyl radicals, vise versa for the electron-donating substituents. The Hammett plots for some dienes are shown in Figures 3 and 4 in which the linear correlations are found for the plot against σ^+ constants but not against σ constants; this indicates that the sulfur radical center is positively charged.[8]

The positive slopes indicate that the π-electron of diene transfers to the positively charged sulfur radical center in the transition state of the reaction.[9,10] The slope of the Hammett plot is a measure of the charge transfer (III) which reflects the electron density of the diene.[11–13] The



III

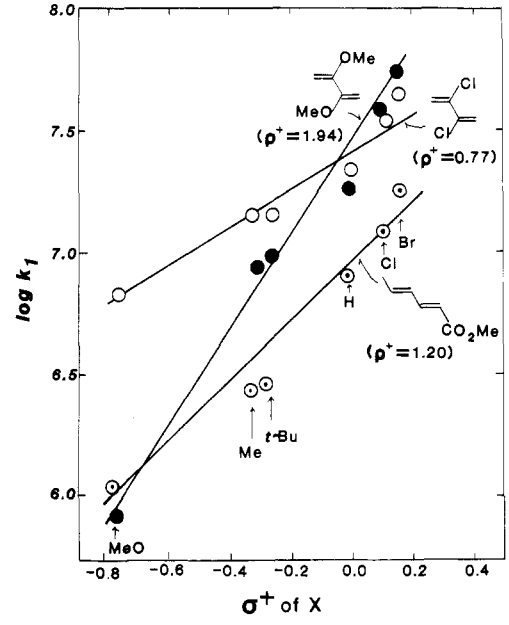


Figure 4. Hammett plot for log k_1 vs σ^+ of X in p-$XC_6H_4S^\bullet$.

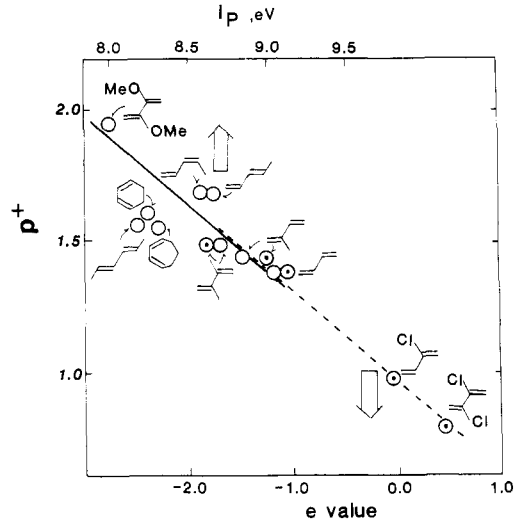


Figure 5. Correlation of ρ^+ vs I_p (○) or vs *e* value (⊙) of dienes.

ρ^+ values are summarized in Table II, in which some data showing the electronic properties of conjugated dienes such as the ionization potential,[14–16] Alfrey–Price's *Q*–*e* values,[17–20] and λ_{max}[21,22] are also listed.

In general, the reactivities of vinyl monomers are determined mainly by three factors; the resonance stabilization, polar contribution, and steric factor.[11–13] For dienes having similar polar contribution as shown in Figure 3, the height of the line corresponds to an extent of the resonance

(8) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1957**, *79*, 1913.
(9) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; Chapter 8.
(10) Ito, O. *J. Am. Chem. Soc.* **1983**, *105*, 850.
(11) Davis, W. H.; Pryor, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 6365.
(12) Viehe, H. G.; Janousek, Z.; Merenyi, R. *Substituent Effects in Radical Chemistry*; Nato ASI Ser. C, Vol. 189, 1986.
(13) Yoshizawa, H.; Ito, O.; Matsuda, M. *Brit. Poly. J.*, in press.
(14) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. *Helv. Chim. Acta* **1977**, *60*, 2213.
(15) Masclet, P.; Mouvier, G.; Bocquet, J. F. *J. Chim. Phys., Phys.-Chim. Biol.* **1981**, *78*, 99.
(16) Sustmann, R.; Schubert, R. *Tetrahedron Lett.* **1972**, 2739.
(17) Alfrey, T.; Price, C. C. *J. Polym. Sci.* **1947**, *2*, 101.
(18) Young, L. J. In *Polymer Handbook*; Branmdrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; p II-389.
(19) Petit, A.; Neel, J. *J. Polym., Sci., Polym. Chem. Ed.* **1986**, *24*, 883.
(20) Tdzhalilov, A. T.; Khashimova, S. M. *Uzb. Khim. Zh.* **1977**, 46.
(21) Phillips, J. P.; Feuer, H.; Thyagarajan, B. S. *Organic Electronic Spectra Data, VII*, Wiley: New York, 1970.
(22) Rao, C. N. R. *Ultra-violet and Visible Spectroscopy*; Butterworth: London, 1961.

Table III. Comparison of Rate Constants for Addition Reactions of Various Free Radicals to Dienes and Vinyl Monomers

	$k \times 10^{-6}$, M^{-1} s^{-1}							
	PhS·[a]	RS·[b]	CH_3S·[c]	CH_3·[d]	HCO·[e]	Bu_3Ge·[f]	t-BuO·[g]	OH·[h]
BD	35	69	700	1.3	0.33		(2.5)	40000
2-M-BD	47						(5.2)	61000
1-M-BD	32					40	(3.6)	
1,4-DM-BD	22							83000
CH_2=CHR	0.01	4.8	6	0.005	0.012	0.2	4.8	40000
CH_2=CHPh	20	1200		0.2		86	(1.8)	

[a] Flash photolysis method (this study and ref 7 and 24). [b] Rotating sector method (ref 28 and 29). [c] Laser induced fluorescence method (ref 30). [d] Pulse radiolysis method (ref 4). [e] Flash photolysis–laser resonance absorption method (ref 5). [f] Laser photolysis method (ref 6). [g] Relative rate method (ref 32). [h] Relative rate method (ref 33).

stabilization of the transition state in which the allyl-type radical is produced. Introduction of the methyl groups into the internal positions (2- and 3-positions) increases the resonance stabilization due to the hyperconjugation as the absorption maximum shifts to the longer wavelength (Table II). On the other hand, the steric hindrance lowers the line; the introduction of the methyl groups to the terminal carbons of the diene skeleton (i.e., 2,4-hexadiene) decreases the reactivity compared with the 2,3-dimethyl derivative. This also suggests that the attack of the arylthiyl radical to diene occurs predominantly at the terminal position.

For dienes with different ρ^+ values shown in Figure 4, the reactivities of dienes change with attaching radicals. It is revealed that the chloro and carboxylate substituents to butadiene decrease the electron densities of the dienes, whereas the methoxy (and methyl) substituents increase the electron densities. In Figure 5, the ρ^+ values are plotted against the ionization potentials or Alfrey–Price's e values of dienes; linear relations are seen for the both parameters. The larger the ρ^+ value, the higher the electron density of the diene. For various vinyl monomers, a similar linear relationship between the ρ^+ values and e values has been established in our previous studies.[23-25] The ρ^+ values of methyl sorbate (1.20) is similar to that of methyl acrylate (1.18).[7] By the Hückel MO method, the introduction of the substituents significantly influences the π-electron density at the terminal carbons of 1,3-butadiene of HOMO. Although the difference of the reactivities among dienes having different π-electron densities are generally determined by both the polar factor and the resonance factor, the comparison among the reactivities of dienes for the electron-donating arylthiyl radicals such as p-$MeOC_6H_4S$· may involve a less polar effect as presumed from the transition state (III); the reactivities are sensitive to the resonance factors. In the case of dienes without substituents at the terminal carbons, a tendency that k_1 values (for p-$MeOC_6H_4S$·) increase with the λ_{max} of dienes (Table II) was found except for the 2,3-dimethoxy derivative. Higher reactivities of the Cl-substituted dienes than that of unsubstituted diene toward p-$MeOC_6H_4S$· indicate the high resonance stabilization of the allyl radicals by the Cl substitution in spite of the electron-withdrawing power of the Cl atom. Since any decrease in the rate constants was not observed for 2,3-dichloro-1,3-butadiene compared with the 2-chloro derivative, the planar structure of two double bonds was suggested.[26]

Planarity of two double bonds in 2,3-dimethylbutadiene was also established by the spectroscopic method.[27] The reactivity of 2,3-dimethoxy-1,3-butadiene is lower than that of the 2,3-dimethyl derivative by a factor of ca. $^1/_{10}$ in spite of the high electron density of the former diene ($\rho^+ = 1.94$). This suggests an angular structure of two double bonds in the 2,3-dimethoxy-1,3-butadiene.

The reactivities of 1-methylbutadiene toward p-$MeOC_6H_4S$· are about half of 2-methylbutadiene, suggesting a little retardation effect due to the methyl group on one side of the terminal carbons. Any significant difference in the reactivities between *trans*- and *cis*-1-methylbutadiene was not recognized. Both isomers may contain the planar conformation during the reaction on going from dienes to the allyl radicals.

Methyl sorbate has similar reactivity to 1,4-dimethylbutadiene for p-$MeOC_6H_4S$·; with an increase of the electron-withdrawing power of the substituent on the arylthiyl radical, however, the difference in the reactivities was increased by the contribution of the polar factor.

A high reactivity of 1-methoxy-1,3-cyclohexadiene compared with cyclohexadiene was easily interpreted by the resonance factor as a shift of the absorption peak to the longer wavelength suggested. The reactivity of cyclohexadiene is considerably higher than that of 1,3-cycloheptadiene; this also agrees with the bathochromic shift. This bathochromic shift of cyclohexadiene was ascribed to the higher strain energy.[22] Indeed, the reactivity of 1,3-cycloheptadiene is similar to 2,4-hexadiene.

In the case of vinyl monomers, Alfrey–Price's Q value implies the resonance contribution to the addition reaction. As listed in Table II, the Q values for conjugated dienes are much larger than that of styrene (0.8). From the rate constants obtained by the flash photolysis method, such a large difference was not found between dienes and styrene ($k_1 = 2.0 \times 10^7$ M^{-1} s^{-1} for PhS·).[24] Some difference may be hidden in the polymerization or copolymerization behavior between the two monomers.

In Table III the rate constants for various radical addition reaction to dienes, nonconjugated monoenes, and styrene reported in the literature are summarized. For some alkylthiyl radicals, the rate constants for 1,3-butadiene measured with the rotating sector method[28,29] is 1 order smaller than that with the laser-induced fluorescence method.[30] The latter value seems to be rather reasonable, compared with the rate constants for arylthiyl radicals. The higher reactivities of the alkylthiyl radicals than those of the arylthiyl radicals were confirmed.

For $^{\bullet}CH_3$, HCO·, and $Bu_3Ge^{\bullet}$ the large ratios of the rate constants of conjugated dienes to nonconjugated monoenes were reported as shown in Table III. On the other hand, for oxygen-centered radicals such as ArCOO·,[31] t-BuO·,[32]

(23) Ito, O.; Matsuda, M. *J. Polym. Sci.*, in press.
(24) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 5732.
(25) Ito, O.; Matsuda, M. *J. Org. Chem.* **1982**, *47*, 2261.
(26) Hagen, K.; Hedberg, K.; Neisess, J.; Gundersen, G. *J. Am. Chem. Soc.* **1985**, *107*, 341.
(27) Danielson, D. D.; Hedberd, K. *J. Am. Chem. Soc.* **1979**, *101*, 3730.
(28) Sivertz, C. *J. Phys. Chem.* **1957**, *63*, 34.
(29) Graham, D. M.; Soltys, J. F. *Can. J. Chem.* **1969**, *47*, 2719.
(30) Jeffrey Balla, R.; Weiner, B. R.; Nelson, H. H. *J. Am. Chem. Soc.* **1987**, *109*, 4804.

and ȮH,[33] the selectivities are considerably small.

Experimental Section

Materials. Methyl-substituted dienes were commercially available. Chloro-substituted dienes were donated from Denki Kagaku Kogyo Co. Ltd. Diaryl disulfides which are the arylthiyl radical sources for the flash photolysis were prepared from the corresponding thiols.[34] Cyclohexane used as a solvent is of spectroscopic grade.

Apparatus and Procedure. The flash photolysis apparatus was a standard design with two xenon flash lamps (Xenon Corp. N-810C; half duration of 5 μs and input energy of 100 J).[35] Diaryl disulfide (< ca. 10^{-4} M in cyclohexane) was filled in a cylindrical quartz flash cell 10 mm in diameter and 100 mm long with optical flat windows at both ends. All rate constants were determined at room temperature (23 °C). For each flash, a fresh solution containing disulfide with diene in different concentration was prepared.

Acknowledgment. We are thankful to the Grant-in-Aid (No. 60540271/62540314) for Scientific Research from the Ministry of Education, Science and Culture. We also express our deep thanks to Mr. Y. Asada and Mr. Y. Miyata of Denki Kagaku Kogyo Co. Ltd. for their kind donation of chlorobutadienes.

(31) Chateanueuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1987**, *109*, 897.
(32) Encina, V.; Rivera, M.; Lissi, E. A. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1709.
(33) Ohta, T. *J. Phys. Chem.* **1983**, *87*, 1209.
(34) AmarField, A.; Grunwald, F. A. *J. Org. Chem.* **1951**, *16*, 946.
(35) Porter, G.; West, M. A. In *Technique of Chemistry*; Weissberger, A., Ed.; Wiley: New York, 1974; p 367.

Hydrolysis and Fe^{2+}-Induced Reduction of *N*-Aryl-*O*-pivaloylhydroxylamines: Aqueous Solution Chemistry of Model Carcinogens

Michael Novak* and Robert K. Lagerman

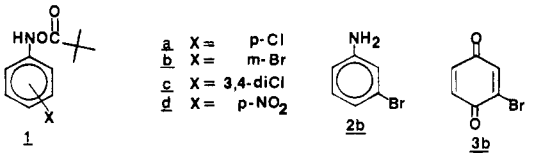
Department of Chemistry, Miami University, Oxford, Ohio 45056

Received March 14, 1988

The *N*-aryl-*O*-pivaloylhydroxylamines, **1a–d**, which serve as models for the carcinogenic metabolites of aromatic amines, decompose in aqueous media by heterolysis of the N–O bond. Substituent effects on rates of reaction and products of the decomposition of **1a–c** are entirely consistent with the intermediacy of a singlet nitrenium ion. The least reactive compound in the series *N*-(4-nitrophenyl)-*O*-pivaloylhydroxylamine (**1d**) yields 4-nitroaniline (**2d**) as its major decomposition product. This material may be formed through H• abstraction by a triplet ion, but a nitrene reaction appears to be more likely. In the presence of Fe^{2+} **1a–d** undergo rapid reduction to the corresponding anilines **2a–d**. This reaction requires complexation of the ester with Fe^{2+} and proceeds with heterolysis of the N–O bond since nearly quantitative yields of pivalic acid are isolated. The radical cations **25a–d** appear to be the most likely precursors to the reduction products.

A significant number of polycyclic aromatic amines and amides, including 2-aminofluorene and *N*-acetyl-2-aminofluorene, are known to be metabolized into potent carcinogens in laboratory animals.[1] These materials are metabolized, in part, via N-hydroxylation, and there is good evidence that sulfuric and carboxylic acid esters of the resulting *N*-arylhydroxylamines and *N*-aryl-*N*-hydroxyamides are among the more important carcinogenic metabolites of these compounds.[1] We have previously reported on the chemistry of sulfuric and carboxylic acid esters of *N*-hydroxyacetanilides, which are analogues of the metabolites of the polycyclic amides.[2] In aqueous solution these compounds undergo heterolysis of the N–O bond to yield *N*-acyl-*N*-arylnitrenium ion–sulfate ion or carboxylate ion pairs, which can undergo internal return or be attacked by nucleophiles and reducing agents.[2]

We are now investigating the chemistry of *N*-aryl-*O*-pivaloylhydroxylamines, **1**, which serve as models for the deacylated metabolites of the polycyclic amines. In a preliminary account of our work with **1b**, we interpreted the detection of significant amounts of 3-bromoaniline (**2b**) and 2-bromo-1,4-benzoquinone (**3b**) in terms of competition between heterolysis and homolysis of the N–O bond.[3]



However, our more recent work, reported in this paper, shows that both of these products arise because of reactions involving trace amounts of Fe^{2+} or Fe^{3+} in the aqueous

(1) Miller, J. A. *Cancer Res.* **1970**, *30*, 559–576. Kriek, E. *Biochim. Biophys. Acta* **1974**, *355*, 177–203. Miller, E. C. *Cancer Res.* **1978**, *38*, 1479–1496. Miller, E. C.; Miller, J. A. *Cancer* **1981**, *47*, 2327–2345. Garner, R. C.; Martin, C. N.; Clayson, D. B. In *Chemical Carcinogens*, 2nd ed.; Searle, C. E., Ed.; ACS Monograph 182; American Chemical Society: Washington, D.C., 1984; Vol. 1, pp 175–276. Beland, F. A.; Allaben, W. T.; Evans, F. E. *Cancer Res.* **1980**, *40*, 834–840. Beland, F. A.; Dooley, K. L.; Jackson, C. N. *Cancer Res.* **1982**, *42*, 1348–1354. Allaben, W. T.; Weis, C. C.; Fullerton, N. F.; Beland, F. A. *Carcinogenesis* **1983**, *4*, 1067–1070. Kadlubar, F. F.; Miller, J. A.; Miller, E. C. *Cancer Res.* **1976**, *36*, 2350–2359. Lai, C. C.; Miller, J. A.; Miller, E. C.; Liem, A. *Carcinogenesis* **1985**, *6*, 1037–1045. Delclos, K. B.; Miller, E. C.; Miller, J. A.; Liem, A. *Carcinogenesis* **1986**, *7*, 277–287. King, C. M.; Traub, N. R.; Lortz, Z. M.; Thissen, M. R. *Cancer Res.* **1979**, *39*, 3369–3372. Flammang, T. J.; Westra, J. G.; Kadlubar, F. F.; Beland, F. A. *Carcinogenesis* **1985**, *6*, 251–258. Flammang, T. J.; Kadlubar, F. F. *Carcinogenesis* **1986**, *7*, 919–926. Lai, C. C.; Miller, E. C.; Miller, J. A.; Liem, A. *Carcinogenesis* **1987**, *8*, 471–478.

(2) (a) Novak, M.; Pelecanou, M.; Roy, A. K.; Andronico, A. F.; Plourde, F. M.; Olefirowicz, T. M.; Curtin, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 5623–5631. (b) Novak, M.; Pelecanou, M.; Pollack, L. *J. Am. Chem. Soc.* **1986**, *108*, 112–120. (c) Novak, M.; Roy, A. K. *J. Org. Chem.* **1985**, *50*, 4884–4888.

(3) Novak, M.; Rovin, L. H.; Pelecanou, M.; Mulero, J. J.; Lagerman, R. K. *J. Org. Chem.* **1987**, *52*, 2002–2010.

0022-3263/88/1953-4762$01.50/0