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Registry No. I-Cl, 824-47-5; III, 434-44-6; V, 1074-11-9; D₂, 7782-39-0; ³⁷Cl, 13981-73-2; C₆H₅CH=CH₂, 100-42-5; C₆H₅CH=CHCl, 622-25-3; C₆H₅CHClCHCl₂, 1674-29-9; C₆H₅CDO, 3592-47-0; benzaldehyde, 100-52-7; 2-phenyldithiane, 5425-44-5; 2-lithium-2-phenyldithiane, 53178-41-9.

Kinetic Study for Spin-Trapping Reactions of Thiyl Radicals with Nitroso Compounds

Osamu Ito* and Minoru Matsuda

Contribution from the Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Katahira, Sendai, 980 Japan. Received August 2, 1982

Abstract: The rate constants for the reactions of para-substituted benzenethiyl radicals with nitroso compounds have been determined by flash photolysis. For the benzenethiyl radical the rate constants ($M^{-1} s^{-1}$) decreased in the order pentamethylnitrosobenzene (3.2×10^8), nitrosobenzene (2.2×10^8), and 2-methyl-2-nitrosopropane (1.7×10^8). For each nitroso compound, the rate constants depend upon the para substituents of the benzenethiyl radicals. The Hammett plots vs. σ^+ yield a fairly good linear relationship; for pentamethylnitrosobenzene $\rho^+ = 0.68 \pm 0.02$ and for 2-methyl-2-nitrosopropane $\rho^+ = 0.80 \pm 0.02$. These ρ^+ values are interpreted both by the substituent effect on the thermodynamic stabilities of the thiyl radicals in the reactants and by the polar transition states. The solvent effects on the rate constants are quite small except for *p*-NH₂C₆H₄S· in which polar solvents reduce the rates.

The spin-trapping technique has been widely used to detect reactive free radicals.¹ It has been pointed out that this technique becomes more useful when absolute rate data for the trapping radicals are available.²⁻⁴ Rate constants for carbon-centered radicals³⁻¹⁰ and oxygen-centered radicals^{2,11,12} have been estimated by competition experiments, where the absolute rate constants were obtained on the basis of the reference reaction. This method is only applicable to the reactions generating stable spin adducts. The spin adducts of the thiyl radicals with nitroso compounds are unstable and only detectable during in situ generation of the radicals;¹³⁻¹⁵ therefore, it is necessary to follow directly the decay rates of the thiyl radicals in the presence of spin traps. We have shown in previous papers that the flash photolysis technique is very useful in determining the absolute rate constants for the reactions of the benzenethiyl radicals with vinyl monomers^{16,17}

Table I. a^N and $\tau_{1/2}$ Values of the Spin Adducts (R(*p*-XC₆H₄S)NO·) in Benzene at 24 °C^{a,b}

X	nitrosobenzene ^c		2-methyl-2-nitrosopropane	
	a^N , G	$\tau_{1/2}$, s	a^N , G	$\tau_{1/2}$, s
Br	11.53	2.6	17.03	1.4
Cl	11.56	2.8	17.13	1.1
H	11.54	0.98	16.75	0.75
<i>t</i> -C ₄ H ₉	11.60	0.90	17.23	0.49
CH ₃	11.66	0.87	17.28	0.41
OCH ₃	11.91	0.62	17.94	0.23
NH ₂	12.00	0.30	18.18	<0.10

^a The a^N values were estimated from 15.50 G of di-*tert*-butyl nitroxide as standard. ^b The a^N value for the pentamethylnitrosobenzene-*p*-ClC₆H₄S· adduct is 16.13 G, and its $\tau_{1/2}$ is 0.60 s. ^c The a^H (para) = a^H (ortho) = 2.50-2.60 G and a^H (meta) = 0.95-1.00 G.

and stable free radicals.¹⁸ In this study we applied this method to the spin-trapping reactions of the benzenethiyl radicals with nitroso compounds; the substituent effects of both the reactants and the solvent effect are examined on the basis of the absolute rate constants.

Results and Discussion

Transient Absorption Spectra. Figure 1 shows transient absorption spectra observed by the flash photodecomposition of bis(*p*-*tert*-butylphenyl) disulfide with the light between 350 and 450 nm. Since the spectrum immediately after flash (spectrum a) is similar to that generated from *p*-*tert*-butylbenzenethiol,

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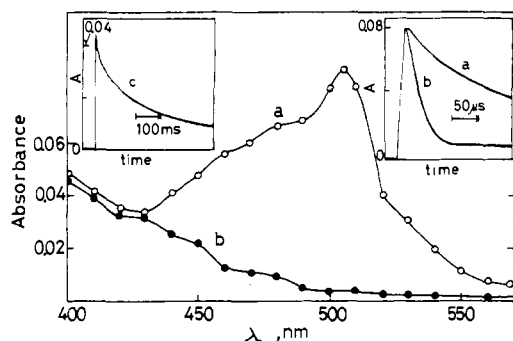


Figure 1. Transient absorption spectra produced by the flash photodecomposition of bis(*p-tert*-butylphenyl) disulfide (5×10^{-4} M) in benzene at 23 °C: (a) immediately after flash (ca. 30 μ s); (b) 500 μ s after flash. Insert: decay curves at 505 nm (a) without nitroso compound, (b) with 2-methyl-2-nitrosopropane (3.9×10^{-4} M); decay curve at 400 nm (c) with 2-methyl-2-nitrosopropane (3.9×10^{-4} M).

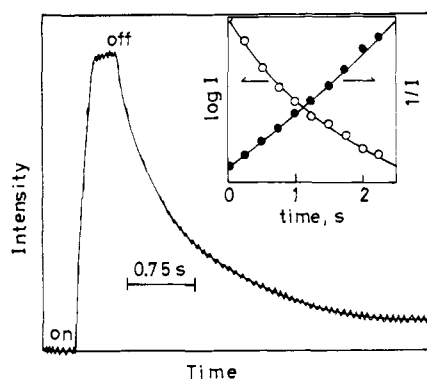


Figure 2. Time dependence of the ESR signal produced by the photolysis of bis(*p-tert*-butylphenyl) disulfide (10^{-3} M) in the presence of 2-methyl-2-nitrosopropane (10^{-3} M). Insert: decay kinetics of the relative intensity of the ESR signal after cutoff of the light.

spectrum a can be attributed to *p-t*-C₄H₉C₆H₄S \cdot . Similar absorption spectra were observed for other benzenethiyl radicals.^{17,19} Decay of the thiyl radical in the absence of spin trap (decay curve a in insert of Figure 1) obeys second-order kinetics, suggesting that the thiyl radical returns to the disulfide. The slope of the second-order plot (1/absorbance vs. time) yields $2k_r/\epsilon = 1.1 \times 10^6$ cm s⁻¹, where k_r and ϵ refer to the rate constant of recombination and molar extinction coefficient, respectively. Assuming the diffusion-controlled rate for recombination,¹⁸ we calculated the k_r value to be 10^{10} M⁻¹ s⁻¹ in benzene from the Debye equation;²⁰ the ϵ value and initial concentration of the thiyl radical generated by one flash exposure can be calculated to be 2×10^4 M⁻¹ cm⁻¹ and 10^{-6} M, respectively.²¹

The decay rate of the thiyl radical in the presence of 2-methyl-2-nitrosopropane (decay curve b in insert of Figure 1) is accelerated compared with that without the nitroso compound, and decay kinetics changes into first order. Decay curve b is composed of the fast and slow decay parts; the slow decay part yielded spectrum b in Figure 1. The decay profile at 400 nm shown in a long time scale (decay curve c) obeys second-order kinetics rather than first-order kinetics.

The ESR spectra observed during the photolysis of disulfides in the presence of nitroso compounds (RNO) are ascribed to the spin adducts with thiyl radicals ($R(p\text{-XC}_6\text{H}_4\text{S})\text{NO}\cdot$).¹³⁻¹⁵ The splitting constants of the nitrogen atom (a^N) are summarized in Table I; for each nitroso compound the substituent effect is ob-

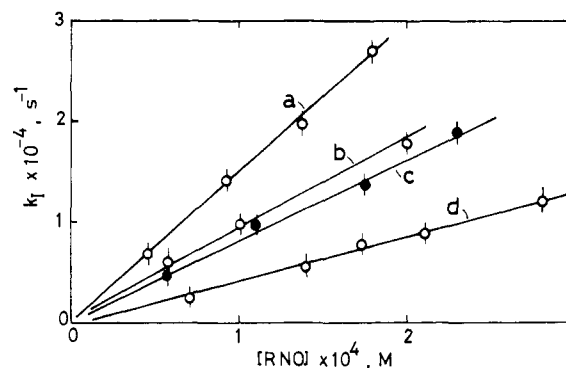
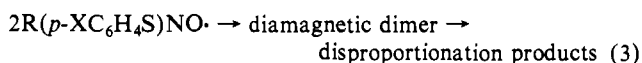
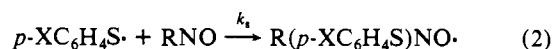
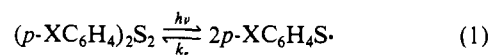


Figure 3. Pseudo-first-order plots: (a) *p*-CH₃C₆H₄S-nitrosobenzene; (b) *p*-CH₃OC₆H₄S-nitrosobenzene; (c) *p*-CH₃OC₆H₄S-pentamethyl-nitrosobenzene; (d) *p*-CH₃OC₆H₄S-2-methyl-2-nitrosopropane.

served with the change of the thiyl radicals. The time dependence of the signal intensity is shown in Figure 2. The decay curve after cutting off the light obeys second-order kinetics rather than first-order kinetics. The half-life, which may be a measure of the stabilities of the spin adducts, is approximately estimated from the initial part of the decay curves (Table I). Although these values are slightly greater than those estimated from the slow decay part of the flash photolysis profile, spectrum b in Figure 1 can be ascribed to the nitroxide. Faster decay rates in flash photolysis may be due to the concentration different from that of the ESR measurements or to the inadvertent photolysis of the spin adducts with the monitoring light of the flash photolysis experiments; from the latter reason, the half-lives estimated from the ESR measurements are listed in Table I.

The second-order decay of the spin adducts indicates that the decomposition mechanism of the spin adducts may include the dimerization process to the diamagnetic dimer before the fission of the bonds into the diamagnetic species, which may occur via disproportionation as Grillan and Ingold suggested (reaction 3 in Scheme I).²²

Scheme I



Estimation of Rate Constants. By the addition of nitroso compounds more than ca. 10^{-4} M, decay kinetics of the thiyl radicals change into first order (decay curves b in insert of Figure 1). Since the nitroso compound is in large excess compared with the thiyl radical generated by one flash exposure, the concentration of the nitroso compound may be kept constant during the reaction. When the concentration of the nitroso compound is low ($<10^{-4}$ M), decay kinetics is mixed order consisting of first order and second order. The second-order part is attributed to $k_1[p\text{-XC}_6\text{H}_4\text{S}\cdot]^2$, and the first-order part is attributed to $k_1[p\text{-XC}_6\text{H}_4\text{S}\cdot]$, where k_1 refers to $k_2[\text{RNO}]$. The k_1 values can be separated from the second-order part with a graphic method²³ and/or computer simulation method²⁴ by using the k_r/ϵ values estimated from the second-order plot in the absence of RNO. The decay rate of the thiyl radical can be expressed by eq 4. The processes for the

$$-d[p\text{-XC}_6\text{H}_4\text{S}\cdot]/dt = 2k_1[p\text{-XC}_6\text{H}_4\text{S}\cdot]^2 + k_2[p\text{-XC}_6\text{H}_4\text{S}\cdot][\text{RNO}] \quad (4)$$

reproduction of the thiyl radicals are not included in eq 4, since there may be large differences in the time scales between the consumption and reproduction of the thiyl radicals even if the thiyl

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(21) The diffusion rate constants calculated from the Debye equation are usually 2-4 times larger than the experimental values.²⁰ The initial concentration of the thiyl radical estimated in this study may contain such an uncertainty.

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Table II. Absorption Maxima (λ_{\max}) of p -XC₆H₄S· and the Rate Constants (k_s) for the Reactions between p -XC₆H₄S· and Nitroso Compounds in Benzene at 23 °C^a

X	λ_{\max} , nm	$k_s \times 10^{-8}, M^{-1} s^{-1}$		
		nitroso-benzene	pentamethyl-nitroso-benzene ^b	2-methyl-2-nitroso-propane
Br	515	4.0	4.8 (3.4)	2.2
Cl	515	3.6	4.2 (3.0)	2.5
H	495	2.2	3.2 (2.3)	1.7
<i>i</i> -C ₂ H ₅	505	1.4	2.5 (1.8)	0.94
CH ₃	505	1.5	2.2 (1.6)	1.0
OCH ₃	525	0.88	1.0 (0.74)	0.43
NH ₂	550	0.22		

^a Estimation errors are about 10%. ^b The Values after the correction of the dimer-monomer equilibrium, which are calculated by multiplication of the values before correction (in parentheses) by a factor of 1.4.

radicals are reproduced via reaction 3 or the backward process of reaction 2. The contribution of the reaction between the thiyl radical and nitroxide is assumed to be small; the rate constants for this type of reaction were estimated to be 10^8 – $10^9 M^{-1} s^{-1}$ in our previous paper,¹⁸ and the concentration of nitroxide generated via reaction 2 is lower than the initial concentration of the thiyl radical produced by one flash exposure (ca. $10^{-6} M$). Therefore, the first-order rate constant is calculated to be less than $10^3 s^{-1}$, while under our experimental conditions the first-order rate constants in the $10^4 s^{-1}$ range for the decay of the thiyl radicals were measured. Figure 3 shows the plots of the k_1 values vs. [RNO]; a fairly good pseudo-first-order relationship is found in each case. The slopes yield the rate constants k_s when the nitroso compound exists as a monomer. Nitrosobenzene and 2-methyl-2-nitrosopropane are known to be monomeric in dilute nonpolar solvent;^{25–27} the slopes of the pseudo-first-order plots can be made equal to the k_s values (Table II). Pentamethylnitrosobenzene is present as an equilibrium species between monomer and dimer; from the equilibrium constant ($3.6 \times 10^{-4} M$ at 26 °C),¹⁴ the monomer concentration is calculated to be ca. 70% when the total concentration is $10^{-4} M$. The dimer is inactive as a spin trap since the $n-\pi^*$ transition at 600–700 nm characteristic of the monomeric N=O bond disappears in the dimer, suggesting the single-bond character of the N–O bond.²⁵ Therefore, the true rate constants for pentamethylnitrosobenzene are estimated from multiplying the slopes of the pseudo-first-order plots by a factor of 1.4 (Table II).

For each thiyl radical the rate constants decrease in the order pentamethylnitrosobenzene > nitrosobenzene > 2-methyl-2-nitrosopropane. The reactivities seem to reflect the absorption maxima of the monomeric nitroso compounds (780, 760, and 670 nm in the above order) rather than the ESR parameters (a^N and $\tau_{1/2}$) of the spin adducts in the products; the transition state of the reaction is presumed to be reactant-like. The rate constant of CH₃O· with 2-methyl-2-nitrosopropane ($1.5 \times 10^8 M^{-1} s^{-1}$)¹² is of the same order of magnitude as those for the benzenethiyl radicals. The rate constants of the alkyl radicals with phenylnitroso compounds are in the range of 4×10^7 to $2 \times 10^8 M^{-1} s^{-1}$;^{7–9} they are compatible with the values for the thiyl radicals. For the reactions of the alkyl radicals with 2-methyl-2-nitrosopropane, the rate constants were estimated to be $(3-9) \times 10^6 M^{-1} s^{-1}$,^{7–9} which are 1 order of magnitude smaller than the values for the thiyl radicals. This difference can be attributed to the properties of the attacking radicals.

The reactivities of the benzenethiyl radicals toward the C=C bond with the phenyl group are higher than those with the alkyl group; the former rate constants are 10^7 – $10^8 M^{-1} s^{-1}$, and the latter ones are ca. $10^4 M^{-1} s^{-1}$.^{16,17,28} The influence of the substituents

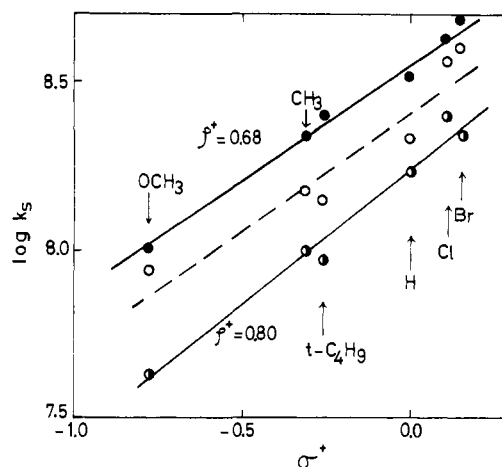


Figure 4. The Hammett plots of $\log k_s$ vs. σ^+ : (O) nitrosobenzene; (●) pentamethylnitrosobenzene; (◐) 2-methyl-2-nitrosopropane.

Table III. Solvent Effects on the Rate Constants (k_s) at 23 °C^a

solvent	$k_s \times 10^{-8}, M^{-1} s^{-1}$		
	p -CH ₃ C ₆ H ₄ S· nitroso-benzene	2-methyl-2-nitroso-propane	p -NH ₂ C ₆ H ₄ S· nitroso-benzene
cyclohexane	2.0	1.3	0.42
benzene	1.5	1.0	0.22
acetonitrile	1.7	1.1	0.08
methanol	1.8	1.2	0.04

^a The estimation errors are about 10%.

on the reactivities of N=O is smaller than that of C=C; the substituent influences indirectly on the stabilization of an unpaired electron on the oxygen atom of the spin adduct with nitroso compound (R(PhS)N–O·), while the substituent can conjugate directly with the radical center produced by the anti-Markovnikov addition of the thiyl radicals toward CH₂=CHR (PhSCH₂–C·HR).

Substituent Effect of Benzenethiyl Radicals. For each nitroso compound, the rate constants in Table II vary with the substituents in the benzenethiyl radicals. The Hammett plots vs. σ^+ (Figure 4) yielded linear lines rather than the plots vs. σ . This suggests that the resonance factors contribute to the reactivities in addition to the polar factor and that the resonance contribution is well included in the substituent constant σ^+ . The slopes of Figure 4 yield $\rho^+ = 0.80 \pm 0.02$ for 2-methyl-2-nitrosopropane and $\rho^+ = 0.68 \pm 0.02$ for pentamethylnitrosobenzene. For nitrosobenzene, although there are some deviations from linearity, $\rho^+ = \text{ca. } 0.7$ can be estimated. In general, the Hammett relationship reflects the substituent effects on the thermodynamic stabilities of the reactants and products and the polar nature of the transition state:

$$\rho^+(\text{reactivity}) = \alpha\rho^+(\text{stability of reactant}) + \beta\rho^+(\text{stability of product}) + \gamma\rho^+(\text{polar transition state}) \quad (5)$$

Although the a^N and $\tau_{1/2}$ for each nitroso compound change with the substituents of the benzenethiyl moiety (Table I), we can presume that the thermodynamic stabilities of the adducts do not affect the reactivities because of the indirect influence of the substituents to the radical center and/or because of the reactant-like transition state ($\beta\rho^+(\text{stabilities of product}) \approx 0$). The stabilities of the para-substituted benzenethiyl radicals have been found to correlate with σ^+ ; $\rho^+(\text{stability of reactant}) = 1.40$.²⁹ If we adopt $\alpha = 0.25$ from Semenov's empirical value for the exothermic radical reactions,³⁰ about half of the observed ρ^+ value

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for the reactivity comes from the first term in eq 5. Then, the remaining ca. half of ρ^+ for the reactivity can be attributed to the positive $\gamma\rho^+$ (polar transition state); positive γ suggests the resonance structures such as $[p\text{-XC}_6\text{H}_4\text{S}^-\text{,RNO}^+]$.³¹ This polar transition state is similar to that proposed for the benzyloxy radical trapping with substituted phenyl *N*-tert-butyl nitrones by Janzen, Evans, and Nishi,³² while the opposite tendency was reported for the *tert*-butoxy radical² and the primary alkyl radical.⁴

Solvent Effect. For the alkyl radical Ingold et al. found the polar solvent effect on the spin-trapping rates.³³ In Table III, the rate constants for *p*-CH₃C₆H₄S[•] and *p*-NH₂C₆H₄S[•] in various solvents are shown in Table III. Other substituents such as Cl and CH₃O groups show a similar effect to the CH₃ group. Although we can find some tendencies that polar solvents accelerate the rates for *p*-CH₃C₆H₄S[•] compared with that in benzene and that the rate in cyclohexane is the fastest, differences are too small to distinguish from the experimental errors. On the other hand, the rates for *p*-NH₂C₆H₄S[•] are greatly reduced in benzene and in polar solvents compared with that in cyclohexane. Neither the solvation of nitroso compounds nor that of the spin adducts can be attributed to such large solvent effects. The specific solvation of *p*-NH₂C₆H₄S[•] was found in the solvent shifts of the absorption maxima^{34,35} and in the addition rates with styrene.³⁵ Therefore, the decreases of the rates in the polar solvents and in benzene are interpreted as follows: the polar solvents that stabilize *p*-NH₂C₆H₄S[•] in the reactants desolvate in the transition state, which results in an increase in the activation energy of the reaction.

Experimental Section

Commercially available 2-methyl-2-nitrosopropane (Aldrich) was used without further purification. Nitrosobenzene was used after recrystallization in the dark. Pentamethylnitrosobenzene was prepared by the

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method of Smith and Taylor.³⁶ Disulfides were purified by recrystallization. Solvents were of spectrophotometric grade. Samplings and measurements were made in the dark to prevent inadvertent photolysis.³⁷

The ESR spectra of the spin adducts were measured with a Varian E4 EPR spectrometer during the photolysis of disulfides (ca. 10⁻³ M) with the light between 350 and 450 nm (500-W high-pressure Hg lamp) in the presence of nitroso compounds (ca. 10⁻³ M). Decay of the ESR signals was followed by a fast recorder or by a transient memory. The xenon flash photolysis apparatus was of standard design; input energy was 150 J and the half-duration of xenon flash lamps was ca. 10 μs. By the use of light filters, disulfides were flash decomposed with light between 350 and 450 nm and the photolysis of the nitroso compounds was avoided.³⁷ In the case of 2-methyl-2-nitrosopropane, formation of di-*tert*-butyl nitroxide, which is produced by the inadvertent photolysis of the nitroso compound, was observed in small amounts (less than 5% compared to the spin adduct with the thiyl radical). In order to reduce the photodecomposition of 2-methyl-2-nitrosopropane by the monitoring light at ca. 500 nm, band-pass filters of 10 nm were used.

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Registry No. Ph(*p*-BrC₆H₄S)NO, 84751-91-7; Ph(*p*-ClC₆H₄S)NO, 84751-92-8; Ph(PhS)NO, 62991-74-6; Ph(*p*-*t*-C₄H₉C₆H₄S)NO, 84751-93-9; Ph(*p*-CH₃C₆H₄S)NO, 72054-13-8; Ph(*p*-OCH₃C₆H₄S)NO, 84751-94-0; Ph(*p*-NH₂C₆H₄S)NO, 84751-95-1; *t*-C₄H₉(*p*-BrC₆H₄S)NO, 84751-96-2; *t*-C₄H₉(*p*-ClC₆H₄S)NO, 71899-51-9; *t*-C₄H₉(PhS)NO, 59504-24-4; *t*-C₄H₉(*p*-*t*-C₄H₉C₆H₄S)NO, 84751-97-3; *t*-C₄H₉(*p*-CH₃C₆H₄S)NO, 66729-86-0; *t*-C₄H₉(*p*-OCH₃C₆H₄S)NO, 74928-94-2; *t*-C₄H₉(*p*-NH₂C₆H₄S)NO, 84751-98-4; (*p*-BrC₆H₄)₂S₂, 5335-84-2; (*p*-ClC₆H₄)₂S₂, 1142-19-4; Ph₂S₂, 882-33-7; (*p*-*t*-C₄H₉C₆H₄)₂S₂, 7605-48-3; (*p*-CH₃C₆H₄)₂S₂, 103-19-5; (*p*-OCH₃C₆H₄)₂S₂, 5335-87-5; (*p*-NH₂C₆H₄)₂S₂, 722-27-0; *p*-BrC₆H₄S, 31053-90-4; *p*-ClC₆H₄S, 31053-91-5; PhS, 4985-62-0; *p*-*t*-C₄H₉C₆H₄S, 81372-23-8; *p*-CH₃C₆H₄S, 31053-92-6; *p*-OCH₃C₆H₄S, 31053-93-7; *p*-NH₂C₆H₄S, 31053-95-9; 2-methyl-2-nitrosopropane, 917-95-3; nitrosobenzene, 586-96-9; pentamethylnitrosobenzene, 65594-36-7.

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Mechanistic Investigation of the Copper-Catalyzed Reactions of Diphenyliodonium Salts

Thomas P. Lockhart

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Abstract: The reaction of diphenyliodonium hexafluoroarsenate (PIFA) with copper(II) benzoate in alcohol solvent gives iodobenzene and alkyl phenyl ether, the arylation product, in high yield along with small amounts of phenyl benzoate and benzene. With diphenyliodonium bromide (PIBr), a substantial yield of bromobenzene is obtained along with iodobenzene and the ether. In nonnucleophilic solvent, CH₂Cl₂, PIFA yields appreciable amounts of iodobenzene, benzene, biphenyl, and phenyl benzoate. In CH₂Cl₂, PIBr gives a high yield of bromobenzene and iodobenzene and low yields of benzene and biphenyl. Cu^I is shown to be the catalytically active oxidation state of copper, based in part on the chemistry observed with independently prepared copper(I) benzoate. Phenyl radical intermediates are ruled out in the reactions of PIFA and PIBr in methanol and CH₂Cl₂, and their chemistry is contrasted with that observed with a benzenediazonium salt. A mechanism involving a phenylcopper(III) intermediate is proposed which concisely accounts for the reaction products observed with PIFA and PIBr in both nucleophilic and nonnucleophilic solvents.

Diaryliodonium salts have been the subject of considerable research interest since the turn of the century. In particular, they have been investigated for their ability to arylate a wide variety of nucleophilic substrates.¹ More recently, their utility in initiating

cationic polymerization has been reported.² Evidence for the occurrence of both nucleophilic aromatic substitution (S_NAr) and electron-transfer pathways in the reaction of diaryliodonium salts

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