

Flash Photolytic Generation of a Dithio Carbocation from 1,3-Dithiolane Derivatives and Its Reaction with Nucleophiles¹⁾

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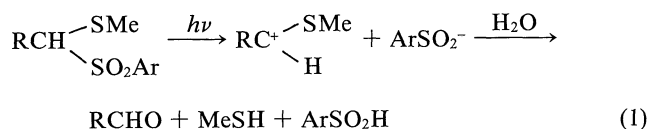
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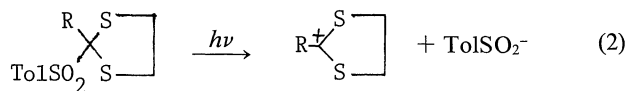
2-Phenyl-1,3-dithiolanylium ion is generated as a transient intermediate by flash photolysis of aqueous ethanol and acetonitrile solutions of 2-methoxy and other dithiolane derivatives with a xenon lamp. Decay of the absorption (342 nm) of the cation generated from the 2-methoxy derivative follows pseudo-first-order kinetics. Rate constants were measured for the reaction of the cation with various nucleophiles. Decay curves for the cations generated from 2-arylthio and 2-sulfonyl derivatives are steep and show second-order kinetic character owing to the recombination of the cation with the counter anions (thiolate and sulfinate).

Sulfur-stabilized carbocations are intermediates for acid-catalyzed reactions of ortho thioesters and thioacetals and their stability and reactivity have attracted considerable interest in relation to those of oxygen analogs.²⁾ Dithio carbocations are stable enough to be isolated as salts.^{3–7)} Chemistry of the isolated salts has been examined.^{2,8)}

Ogura⁹⁾ found that 1-(methylthio)alkyl aryl sulfones are easily hydrolyzed by photoirradiation of the aqueous solution. Thio carbocations are assumed as intermediates for this photosolvolysis.



This report suggested us that thio carbocations can be photochemically generated from appropriate precursors. This may provide us good means for examination of rapid reactions of the cations in ground state by using a flash-photolytic technique. We thus considered that, if a nucleofugal group of the precursor could be a main chromophore for the photolysis, the excited nucleofuge could be efficiently released to leave a ground-state carbocation. For such precursors for dithio carbocations, we have first chosen 2-(*p*-tolylsulfonyl)-1,3-dithiolanes, **1a** and **1b**.



1a, R=H

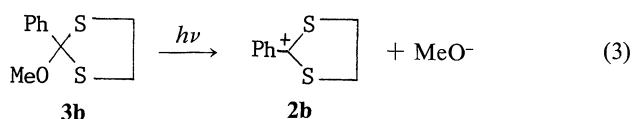
1b, R=Ph

Tol=*p*-CH₃C₆H₄

Irradiation of alcoholic solutions of the sulfone derivatives **1** with a low-pressure Hg lamp gave 2-alkoxy derivatives in high yields. Flash photolysis of aqueous solutions of **1** showed formation of the dithiolanylium ion **2**. However, because of high nucleophilicity of the accompanying sulfinate ion, kinetics of decay of the cation **2** was complicated. A 2-arylthio derivative also behaved similarly.

A 2-alkoxy derivative **3b** was later found to give the

carbocation **2b** on irradiation in spite of the non-light-absorbing nucleofugal group.^{1,10)}



Triarylcarbenium ions can be generated by photolysis of various precursors with a nucleofuge such as cyanide,^{11,12)} hydroxide,^{11,13–16)} acetate,^{17,18)} and phenoxide ion.^{17,18)} Nonabsorbing nucleofuges can be liberated by photolysis of suitable precursors. McClelland and co-workers^{14,17–19)} have extensively studied reactivities of these carbocations by flash photolysis. Reaction of 2-phenyl-1,3-dithiolan-2-ylum ion **2b** generated from **3b** with some nucleophiles is a main subject in the present paper but photolysis of other precursors **1** is also presented.

Results and Discussion

Photolysis was carried out with a xenon lamp usually in 1:1 (v/v) ethanol–water and 1:1 (v/v) acetonitrile–water solutions. On flash irradiation of **3b**, the spectrum with a maximum absorption at 342 nm develops instantaneously and disappears slowly. The spectra of the transient intermediate were recorded with

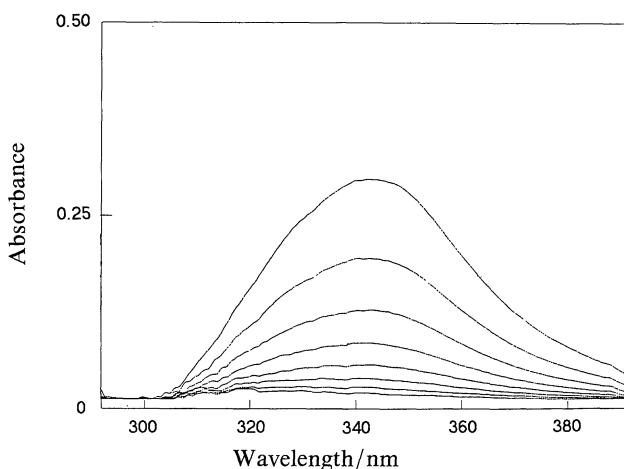


Fig. 1. Transient spectra observed on photolysis of **3b** in 1:1 (v/v) EtOH–H₂O at [HCl]=10^{–3} M. The time interval of the spectra was 120 ms.

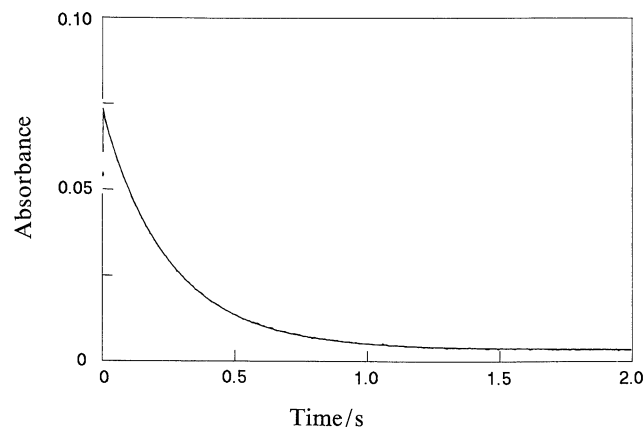


Fig. 2. A trace of the absorption at 342 nm on photolysis of **3b** in 1:1 (v/v) EtOH-H₂O at [HCl]=10⁻³ M. A theoretical pseudo-first-order curve is also drawn.

Table 1. Observed Rate Constants for Decay of **2b** in Aqueous Solutions^{a)}

[HCl]/M	$k_{\text{obsd}}/\text{s}^{-1}$	
	1:1 EtOH-H ₂ O	1:1 MeCN-H ₂ O
0	3.98	0.62
10 ⁻⁶	3.75	0.57
10 ⁻⁵	3.92	0.53
10 ⁻⁴	3.78	0.53
10 ⁻³	3.72	0.53
Average	3.83	0.56

a) Measured at 25°C and an ionic strength of 0.10 (KCl).

an MCPD detector in time intervals of order of milliseconds as shown in Fig. 1. The absorption maximum agrees with that observed for the cation **2b** in strong acid.⁴⁾ Time-dependent absorbance changes at 342 nm follow a pseudo-first-order decay curve as shown in Fig. 2. Bubbling of the solution with oxygen or argon did not affect the transient absorption spectrum or decay curve. The decay was not influenced by addition of acid but accelerated with added nucleophiles as will be presented below. From these observations the transient is identified as the free dithiolanylium ion **2b**. Further support for this intermediate was obtained by photosolvolysis that **3b** undergoes upon stationary irradiation with a low-pressure Hg lamp.¹⁰⁾

From a decay curve like that shown in Fig. 2, pseudo-first order rate constants k_{obsd} were obtained by the nonlinear least-squares curve fitting. In aqueous solutions, k_{obsd} is not affected with acid (Table 1). This decay of **2b** must be due to reaction with nucleophilic solvent. The k_{soln} in aqueous ethanol and acetonitrile solutions are 3.83 and 0.56 s⁻¹, respectively. Formation of a thioester was confirmed as a final product by stationary photolysis.¹⁰⁾

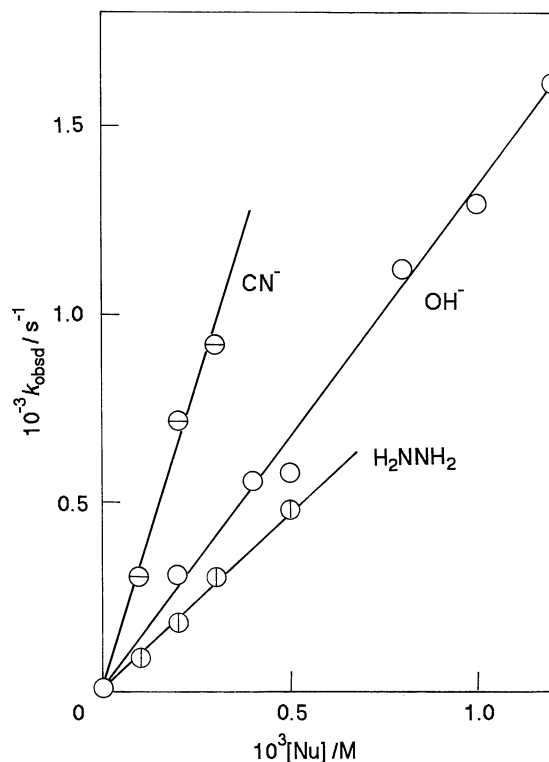
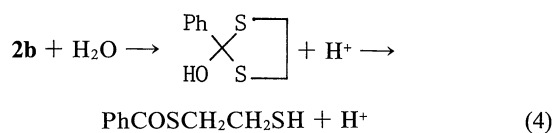


Fig. 3. Plots of k_{obsd} against concentrations of added nucleophiles for OH⁻ (○), CN⁻ (○), and hydrazine (○). Data for the latter two were taken in the presence of NaOH at [OH⁻]=10⁻⁴ M.

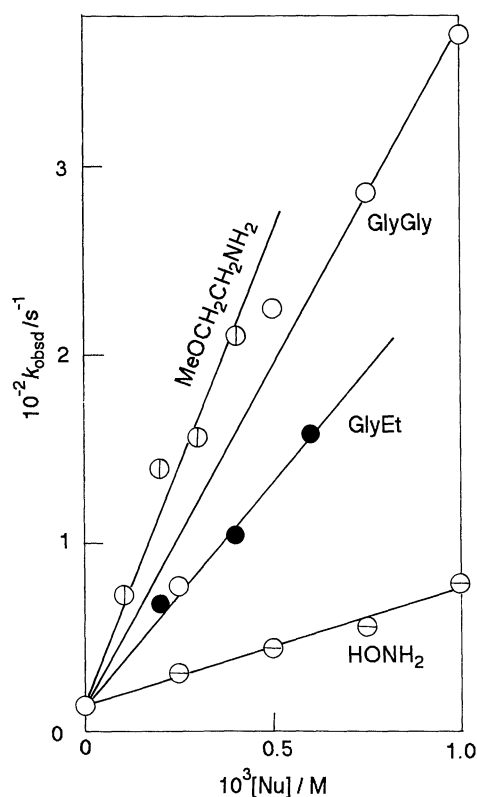


Fig. 4. Plots of k_{obsd} vs. concentrations of nucleophiles for 2-methoxyethylamine (○), glycylglycine (○), ethyl glycinate (●), and hydroxylamine (○). Rates were measured at [OH⁻]=10⁻⁴ M.

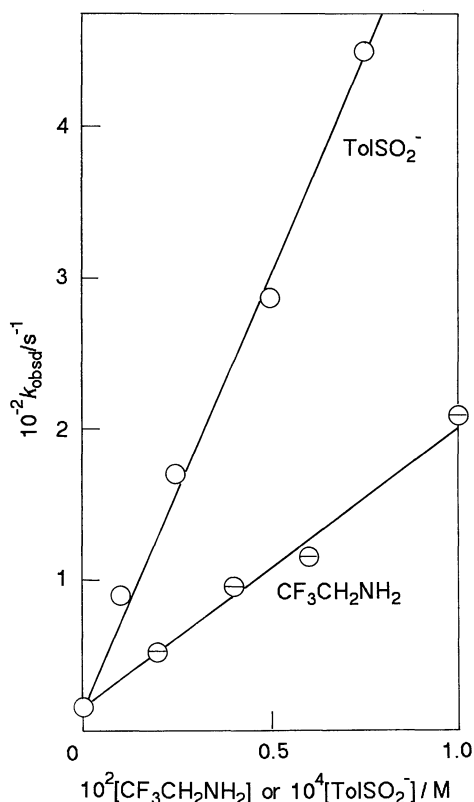
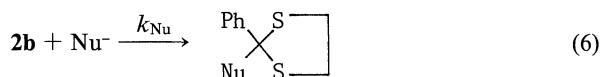


Fig. 5. Plots of k_{obsd} vs. concentrations of nucleophiles for *p*-toluenesulfinate (○) and 2,2,2-trifluoroethylamine (⊖). Rates were measured at $[\text{OH}^-] = 10^{-4}$ M.

Addition of sodium hydroxide greatly increases the decay rate as is seen in Fig. 3. The k_{obsd} increases linearly with $[\text{OH}^-]$. Contamination of carbon dioxide retards the reaction at $[\text{OH}^-] < 10^{-4}$ M ($M = \text{mol dm}^{-3}$). Other nucleophiles also accelerate the decay of the cation **2b**, following Eq. 5 (Figs. 3-5). The primary reaction involved is the addition of the nucleophile to **2b** (Eq. 6).

$$k_{\text{obsd}} = k_0 + k_{\text{Nu}}[\text{Nu}] \quad (5)$$



The nucleophilic reactions were mostly examined in the presence of hydroxide ion at $[\text{OH}^-] = 10^{-4}$ M to avoid formation of the conjugate acid of the nucleophile but contamination of CO_2 was not completely precluded. The rate constants obtained are summarized in Table 2.

Reaction of *p*-toluenesulfinate was also carried out in acidic aqueous acetonitrile solutions. The apparent second-order rate constants k_2 , where $k_{\text{obsd}} = k_0 + k_2[\text{TolSO}_2\text{H}]$, change sigmoidally with pH in the range 1–4 as shown in Fig. 6. This shows that only the sulfinate ion is a nucleophile but conjugate acid is unreactive. Since the fraction of the conjugate base is given by $K_a/(K_a + [\text{H}^+])$, the observed k_2 can be expressed

Table 2. Rate Constants for the Nucleophilic Reactions of **2b** in 1:1 (v/v) Aqueous Ethanol

Nucleophile	$\text{p}K_a^{\text{a)}$	$N_+^{\text{b)}$	$k_{\text{Nu}}/\text{M}^{-1} \text{s}^{-1}$
$\text{H}_2\text{O}/\text{EtOH}$	(−1.7)	0.73	$3.83^{\text{c)}$
OH^-	15.7	4.75	1.3×10^6
$(\text{CF}_3)_2\text{CHO}^-$	9.3		2.4×10^6
$\text{CF}_3\text{CH}_2\text{NH}_2$	5.7	3.45	1.8×10^4
$\text{EtOCOCH}_2\text{NH}_2$	7.75	4.40	2.4×10^5
$^- \text{OCOCH}_2\text{NHCOCH}_2\text{NH}_2$	8.13	4.69	3.6×10^5
$\text{MeOCH}_2\text{CH}_2\text{NH}_2$	9.20	5.07	4.6×10^5
HONH_2	5.97	5.05	6.4×10^4
H_2NNH_2	8.10	6.01	9.3×10^5
CN^-	9.40	4.12	3.2×10^6
TolSO_2^-	1.99		5.8×10^6
$p\text{-ClC}_6\text{H}_4\text{S}^-$	6.14 ^{d)}	9.10 ^{e)}	$4.5 \times 10^{8\text{f)}$

a) $\text{p}K_a$ of the conjugate acid. Taken from "Handbook of Biochemistry," ed by H. A. Sober, CRC Press, Cleveland, Ohio (1968). b) Nucleophilicity parameter.²²⁾ c) In s^{-1} . d) Taken from P. DeMaria, A. Fini, and F. M. Hall, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1969. e) A value for benzenethiolate. f) Evaluated in 1:1 (v/v) MeCN– H_2O .

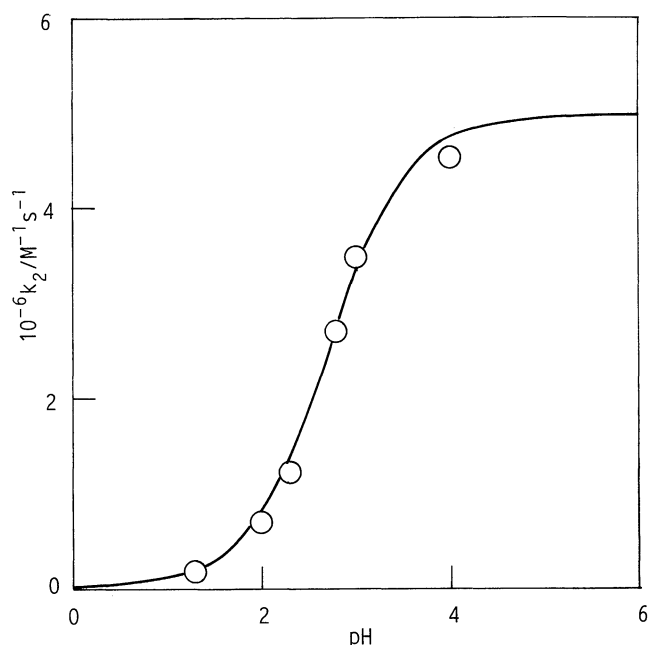


Fig. 6. Plots of apparent second-order rate constants against pH for the reaction of **2b** with *p*-toluenesulfinate in 1:1 (v/v) MeCN– H_2O . Acidity was controlled with HCl. The solid curve is a sigmoid with $\text{p}K_a = 2.7$, $k_{\text{min}} = 0$, and $k_{\text{max}} = 5 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$.

by Eq. 7 The theoretical curve in Fig. 6 is drawn with $\text{p}K_a = 2.7$ obtained spectrophotometrically for the sulfinic acid and limiting k_2 at lower and higher pH being 0 and $5.0 \times 10^6 \text{ M}^{-1} \text{s}^{-1} (k_{\text{Nu}})$. The k_{Nu} agrees reasonably well with that obtained in an alkaline aqueous ethanol solution.

$$k_2 = k_{\text{Nu}} K_a / (K_a + [\text{H}^+]) \quad (7)$$

Reaction of *p*-chlorobenzenethiol was examined in acidic aqueous acetonitrile solutions. The observed

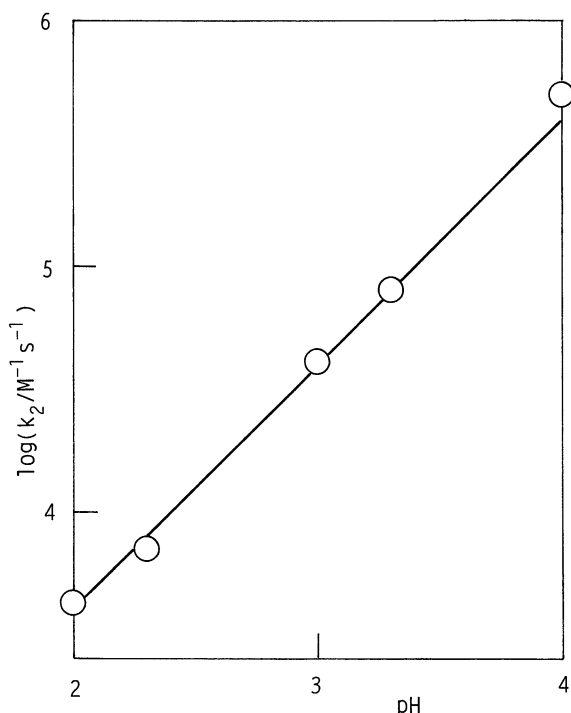


Fig. 7. Logarithmic plots of apparent second-order rate constants against pH for the reaction of **2b** with *p*-chlorobenzenethiol in 1:1 (v/v) MeCN-H₂O. Acidity was controlled with HCl.

second-order rate constants k_2 are dependent on acid concentration (Fig. 7). In this case, both the neutral thiol ArSH and thiolate ArS⁻ can be good nucleophiles, and the k_2 should obey Eq. 8.

$$k_2 = (k_{\text{ArS}^-}K_a + k_{\text{ArSH}}[\text{H}^+]) / (K_a + [\text{H}^+]) \quad (8)$$

In the pH region where $[\text{H}^+] \gg K_a$, Eq. 8 is reduced to Eq. 9 or 10.

$$k_2 = k_{\text{ArS}^-}K_a/[\text{H}^+] + k_{\text{ArSH}} \quad (9)$$

$$\log k_2 = -\log[\text{H}^+] + \log(k_{\text{ArS}^-}K_a + k_{\text{ArSH}}[\text{H}^+]) \quad (10)$$

The logarithmic plots of k_2 against pH ($-\log[\text{H}^+]$) fall on a straight line of a unit slope as is seen in Fig. 7. That is, $k_{\text{ArSH}}[\text{H}^+]$ is negligibly small at $[\text{H}^+] = 10^{-4}$ – 10^{-2} M as compared with $k_{\text{ArS}^-}K_a$ in Eq. 10. The reactive species of the thiol reaction is thiolate ion ArS⁻ even in the acidic media where most of the thiol is present in a conjugate acid form ArSH ($[\text{H}^+] \gg K_a$). The k_{ArS^-} for the thiolate ion was evaluated to be $4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ using $\text{p}K_a = 7.06$ for *p*-chlorobenzenethiol in 49:51 (v/v) ethanol–water solution.²⁰⁾

Flash photolysis of aqueous solutions of 2-(*p*-chlorophenylthio)-2-phenyl-1,3-dithiolane (**1c**) and the 2-sulfonyl derivative **1b** showed also formation of the cation **2b**. However, the decay curves of **2b** monitored at 342 nm in this photolysis are different from that

observed with **3b** and do not follow pseudo-first-order kinetics. The decay of **2b** generated from **1c** fitted the second-order kinetics while the decay observed with **1b** was usually a mixed first- and second-order reaction. These observations must be due to the recombination of **2b** with the accompanying counter anions in a free form. Both of the thiolate and sulfinate ions are very effective nucleophiles and recombination reaction can be a main reaction (in the thiolate case) or an appreciable one (in the sulfinate case) even at very low concentrations in the order of 10^{-6} M as generated by photolysis.

The unsubstituted dithiolanylium ion **2a** ($\lambda_{\text{max}} = 333 \text{ nm}$) can be generated from the sulfonyl precursor **1a**. The decay curve was also that of mixed first- and second-order reaction. Similar photolysis of 2-methoxy-1,3-dithiolane was also examined but no appreciable cation formation was observed, probably owing to the low efficiency of light absorption.

Photochemical bond cleavage can occur even if the chromophore of the molecule is not directly bonded to the atom involved in the bond breaking. The excess energy of the electronically excited molecule may be transferred to the vibrational states and cleavage of a weaker bond may lead to heterolysis in the present case. All the physical and chemical events in excited states take place in solution within a time scale of nanoseconds and the reactions we observed here are those of photochemical reaction intermediates in the ground state. The main chromophore of the present reaction must be the phenyl group. Although the C–S bondings have a weak absorption around 250 nm, they cannot be

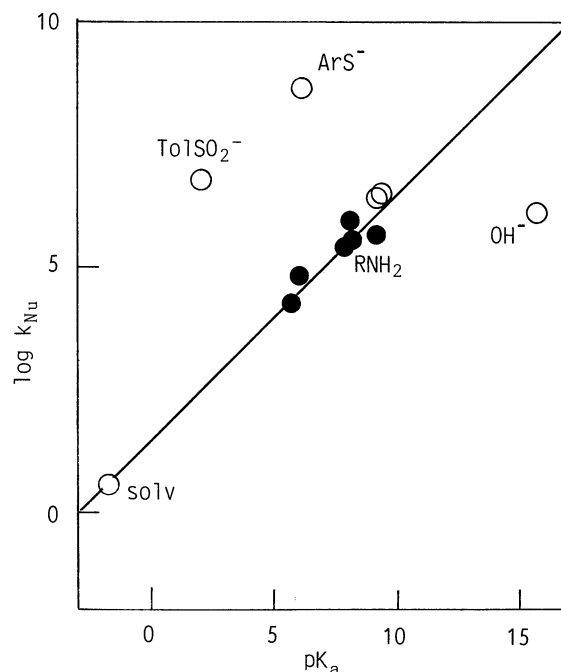


Fig. 8. Correlation of the rate constants with $\text{p}K_a$ for the nucleophilic reactions of **2b**. A point for k_{solv} is placed at $\text{p}K_a$ of H_3O^+ .

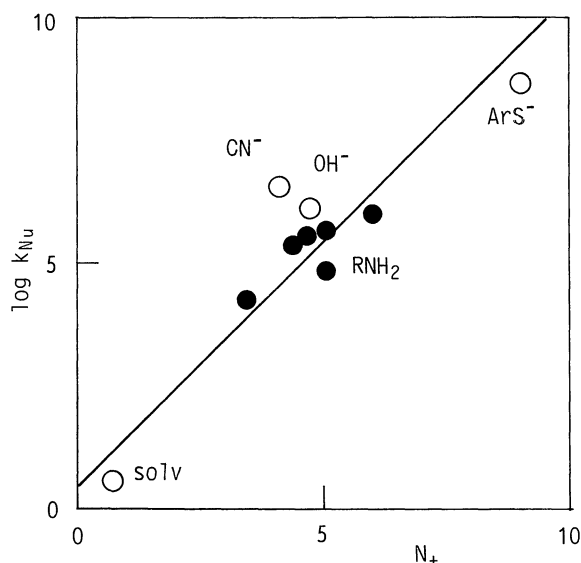


Fig. 9. Correlation of the rate constants with N_+ for the nucleophilic reactions of **2b**. The k_{solv} is plotted against N_+ of H_2O .

satisfactory light absorbers. The unsubstituted dithiolanylium ion **2a** cannot be generated by photolysis of the 2-methoxy derivative.

Rate constants for the nucleophilic reactions of **2b** are correlated with $\text{p}K_{\text{a}}$ of the conjugate acid of nucleophiles in aqueous solution (Fig. 8). Although the points for the thiolate and sulfinate ions deviate greatly upward, the points for amines closely fall on the line of a slope $\beta=0.5$. The “ α -effect” amines,²¹⁾ hydroxylamine or hydrazine, do not show appreciable deviations, indicating lack of enhanced reactivity. The thiolate and sulfinate deviations are additional examples of enhanced nucleophilicity of these sulfur nucleophiles.

The k_{Nu} are logarithmically plotted against Ritchie's N_+ nucleophilicity parameters²²⁾ in Fig. 9. Although considerable scatterings are evident, the points fall in the vicinity of a line of a unit slope. The slope of a similar correlation for a less stable triphenylmethylium ion ($\text{p}K_{\text{R}}=-6.63$) was found to be much smaller than unity.¹⁷⁾ The reactivity of the cation **2b** ($\text{p}K_{\text{R}}=2.5$)²⁾ seems to be in the range of category of the simple Ritchie relationship of a unit slope which was found for reactions of stable carbocations ($\text{p}K_{\text{R}}>1$) with nucleophiles.²²⁾

Experimental

Materials. Hydroxylamine hydrochloride, hydrazine hydrochloride, potassium cyanide, and potassium chloride were obtained from Wako Pure Chemical. Glycylglycine, ethyl glycinate, and 2,2,2-trifluoroethylamine hydrochloride were from Sigma Chemical. 2-Methoxyethylamine, 1,1,1,3,3,3-hexafluoro-2-propanol, and *p*-chlorobenzenethiol obtained from Aldrich were distilled. Sodium *p*-toluenesulfonate (Wako) was dried at 130 °C for 6 h. Ethanol and acetonitrile were distilled from activated magnesium and

calcium hydride, respectively.

A carbon dioxide-free solution of sodium hydroxide was prepared by dissolving metallic sodium in dry ethanol and dilution with freshly boiled water and titrated with a standard hydrochloric acid.

2-Methoxy-2-phenyl-1,3-dithiolane (**3b**) was prepared from the dithiolanylium perchlorate as described previously.^{4,10)}

2-(*p*-Tolylsulfonyl)-1,3-dithiolane (1a). To a solution of 1,3-dithiolan-2-ylthio perchlorate, prepared from 1,2-bis(1,3-dithiolan-2-ylthio)ethane (5.6 mmol),⁴⁾ in acetonitrile (30 cm³) was added dry sodium *p*-toluenesulfonate (11.4 mmol) and stirred for 3 h at room temperature. After removal of most of the solvent in vacuo, the residues were dissolved in chloroform, washed with aqueous potassium carbonate, and dried over MgSO_4 . Removal of the chloroform gave crude solids. Recrystallizations from benzene afforded **1a** in 17% yield. Mp 142–143 °C. Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}_3$: C, 46.12; H, 4.65; S, 36.94%. Found: C, 46.04; H, 4.56; S, 36.48%. ¹H NMR (CDCl_3) $\delta=2.45$ (s, 3H), 3.40 (s, 4H), 5.35 (s, 1H), 7.23–8.0 (m, 4H). UV (heptane): $\lambda_{\text{max}}=226$ nm (ϵ 12000).

2-Phenyl-2-(*p*-tolylsulfonyl)-1,3-dithiolane (1b). Reaction of 2-phenyl-1,3-dithiolan-2-ylthio perchlorate obtained from benzoyl chloride and 1,2-ethanedithiol⁴⁾ with sodium *p*-toluenesulfonate in the same way as **1a** gave crystalline **1b** in 35% yield (based on benzoyl chloride). Mp 131–132 °C (benzene-ethanol). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{S}_3$: C, 57.11; H, 4.79; S, 28.59%. Found: C, 56.94; H, 4.73; S, 28.12%. ¹H NMR (CDCl_3) $\delta=2.36$ (s, 3H), 3.28–3.75 (m, 4H), 6.29–7.50 (m, 9H). UV (heptane): λ_{sh} 250 nm (ϵ 10000).

2-(*p*-Chlorophenylthio)-2-phenyl-1,3-dithiolane (1c). To a solution of the dithiolanylium perchlorate, prepared from 25 mmol of benzoyl chloride and 1,2-ethanedithiol,⁴⁾ in acetonitrile (30 cm³) was added an acetonitrile solution of *p*-chlorobenzenethiol (25 mmol) and excess triethylamine under stirring. After standing for 4 h at room temperature, the solvent was mostly removed by vacuum evaporation. The residues were dissolved in ether, washed with sodium bicarbonate, and dried over MgSO_4 . The remaining solids after removal of the ether were recrystallized from benzene-hexane to give white plates in an overall yield of ca. 30%. Mp 106–107 °C. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{ClS}_3$: C, 55.45; H, 4.03; S, 29.60%. Found: C, 55.27; H, 4.03; S, 29.03%. ¹H NMR (CDCl_3) $\delta=3.53$ (m, 4H), 7.1–7.5 (m, 9H).

Flash Photolysis. A flash-photolytic apparatus Union RA-412 equipped with a xenon flash lamp (half-height width, ca. 10 s) was used for photolysis. A tungsten lamp was employed with a Pyrex filter for a source of detection light (stationary). Data were fed to and processed with a Union RA-401 processor linked through a photomultiplier or an MCPD (multichannel photodiode array) detector. Rate constants are obtained by nonlinear least-squares curve fittings (the damping Gauss-Newton method) of the decay curves.

Reactions were carried out in 1:1 (v/v) ethanol–water or 1:1 (v/v) acetonitrile–water usually at an ionic strength of 0.10 maintained with KCl and at 25 °C kept constant with circulating water. The initial substrate concentration was usually 5×10^{-4} M and a stock solution in ethanol or acetonitrile was prepared by weighing. Solutions of nucleophiles were also prepared by weighing. A necessary amount of the substrate stock solution was added with a microsyringe to the reaction solution in a cuvette immediately before photolysis.

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