

THE EXTINCTION COEFFICIENT FOR THE *p*-AMINOPHENYLTHIYL RADICAL AS DETERMINED BY REACTION WITH GALVINOXYL

ROGER R. LEMBKE, L. V. NATARAJAN and ROBERT R. KUNTZ

Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211 (U.S.A.)

(Received May 25, 1982; in revised form August 3, 1982)

Summary

The reaction of the *p*-aminophenylthiyl radical (RS) with galvinoxyl has been used to determine the extinction coefficient of RS in several solvents. Values of ϵ_{RS} range from $11\,000\text{ M}^{-1}\text{ cm}^{-1}$ in cyclohexane to $19\,000\text{ M}^{-1}\text{ cm}^{-1}$ in acetonitrile. The addition of RS to galvinoxyl and the second-order recombination of RS both proceed at nearly diffusion-controlled rates with rate constants of $(1.1 - 2) \times 10^9\text{ M}^{-1}\text{ s}^{-1}$. Rates of addition of RS to styrene have been determined to elucidate ground state radical solvation effects. In cyclohexane RS adds to styrene with a rate constant of $1.7 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$. Increasing the polarity of the solvent lowers this rate constant to a limiting value of $4.8 \times 10^3\text{ M}^{-1}\text{ s}^{-1}$ in acetone and more polar solvents.

1. Introduction

The reactions of substituted phenylthiyl radicals with vinyl monomers [1 - 3] and stable free radicals [4] have been investigated. The *p*-aminophenylthiyl radical (RS) is the most polar of these radicals studied [3, 5]. It reacts slowly with vinyl monomers [3] and its reactivity parameters are consistent with the electron-donating ability of the *p*-NH₂ substituent [2, 3].

During comparative kinetic investigations it was noted that the radical absorption of RS was much stronger than that of many other *p*-substituted phenylthiyl radicals at equivalent absorbances of the radical precursor disulfides and excitation intensities. Thyrión's data [6] support this observation. This result indicates either a higher extinction coefficient for RS or a higher relative quantum yield for RS production from the parent disulfide. Increasing solvent polarity causes a red shift in the RS absorption maximum λ_{max} [5], peak broadening and an increase in absorbance [5, 6] which suggest that the RS extinction coefficient ϵ_{RS} is involved in the higher observed absorbance.

This study was undertaken to determine ϵ_{RS} for RS in cyclohexane and more polar solvents. The stable free radical galvinoxyl (G) is a convenient probe for this purpose since it reacts readily with phenylthiyl radicals [4] and can be monitored spectrophotometrically. In addition to ϵ_{RS} the technique employed permits a determination of absolute rate constants for the reaction of RS with G and the second-order recombination of RS.

2. Experimental details

The RS radicals were generated by conventional flash photolysis of *p*-aminophenyl disulfide (RSSR). The flash systems employed have been described previously [7, 8]. Light from the excitation flash was filtered through 1 cm of a solution containing 10^{-3} M adenine, 1 M NiCl₂ and 1 M CoCl₂ which limited excitation to the 290 - 370 nm region.

The RSSR was purchased from Aldrich and recrystallized twice from heptane. G was purchased from Aldrich and used as received. All solvents were spectrophotometric grade and used as supplied.

The depletion of G in each experiment was determined by measuring the change in absorption, $[G]_0 - [G]_\infty$, of G in the kinetic apparatus at the RS monitoring wavelength or by taking aliquots of the solution before and after photolysis and measuring $\Delta[G]$ in a spectrophotometer at $\lambda_{\max}^G = 428$ nm. Both techniques gave identical results for $\Delta[G]$ when the corresponding extinction coefficients were used for converting absorbance to concentration. The method of measurement by aliquots was adopted for reasons of greater sensitivity.

All experiments were performed at room temperature (24 ± 1 °C). Solutions used in determination of reactions of RS with G were deoxygenated by bubbling for 30 min with oxygen-free nitrogen just prior to photolysis. For determination of RS addition rates to styrene, aerated solutions were used to prevent dissociation of the adduct [3]. A few experiments were conducted using *p*-tolyl disulfide as the radical source. Techniques were the same except that λ_{\max} is 505 nm for the *p*-tolylthiyl radical.

3. Methodology and results

The RS extinction coefficient ϵ is defined in terms of the initial RS absorbance A_0^{RS} and concentration $[RS]_0$:

$$\epsilon_{RS} = \frac{A_0^{RS}}{[RS]_0 l} \quad (I)$$

Scattered light from the excitation flash precluded direct determination of A_0^{RS} and it was necessary to extrapolate the mixed order decay to initial time in order to determine this value. High concentrations of G are required to scavenge all RS radicals completely because of a rapid RS recombination

reaction [5]. Under these high concentration conditions $\Delta[G]/[G]_0$ was small and very sensitive to experimental errors. Consequently it was necessary to use lower concentrations of G where measurement of $\Delta[G]/[G]_0$ was more precise but scavenging of RS was not quantitative. A careful kinetic analysis is therefore required in order to determine the fraction of RS scavenged. Details of the data analysis for determination of A_0^{RS} and $[RS]_0$ appear below.

A_0^{RS} was determined as follows. In deoxygenated cyclohexane solutions the decay of RS can be described by [3]



In the absence of G the decay of RS is governed by

$$-\frac{d(RS)}{dt} = 2k_2[RS]^2 + k_3[RS][RSSR] + k_4[RS] \quad (II)$$

where $[RSSR] = [RSSR]_0 - [RS]/2$ if second-order recombination of RS is the dominant RS decay pathway as previously indicated [3]. Substitution of this relation into eqn. (II) and setting $[RS] = A^{RS}/\epsilon_{RS}l$ gives

$$-\frac{d(\ln A^{RS})}{dt} = k_I + k_{II}A^{RS} \quad (III)$$

where

$$k_I = k_3[RSSR]_0 + k_4$$

and

$$k_{II} = \frac{2k_2 - k_3/2}{\epsilon_{RS}l}$$

The constants k_I and k_{II} can be determined from a plot of $-d(\ln A^{RS})/dt$ versus A^{RS} [1 - 3] and typical data for cyclohexane appear in Fig. 1 and Table 1. The intercepts of these plots are very sensitive to the data fit. Consequently a more consistent set of values for k_I was determined by using an average value of $k_{II} = 1.68 \times 10^4 A^{-1} s^{-1}$ where A is the absorbance. These calculated values appear in Table 1, third column. A plot of the redetermined values of k_I versus $[RSSR]_0$ (Fig. 2) yields values of $k_3 = 1.5 \times 10^8 M^{-1} s^{-1}$ and $k_4 \approx 500 s^{-1}$.

The integrated form of eqn. (III) can be used to determine A_0^{RS} :

$$\ln\left(\frac{k_I + k_{II}A_t^{RS}}{A_t^{RS}}\right) = k_I t + \ln\left(\frac{k_I + k_{II}A_0^{RS}}{A_0^{RS}}\right) \quad (IV)$$

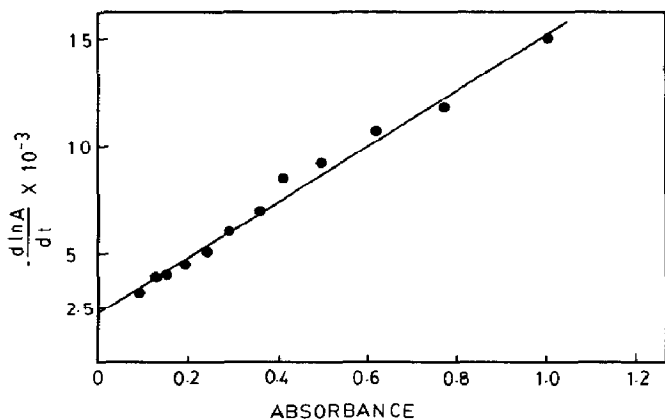


Fig. 1. Plot of eqn. (III) for the decay of RS in deoxygenated cyclohexane: $[RSSR]_0 = 6 \times 10^{-6}$ M.

TABLE 1

Decay parameters of the *p*-aminophenylthiyl radical in deoxygenated cyclohexane

$[RSSR]_0 \times 10^6$ (M)	k_I (s^{-1})	$k_I^{calc a}$ (s^{-1})	$k_{II} \times 10^{-4} A^{-1}$ (s^{-1})
1	510	689	1.87
2	380	918	1.95
3	1499	812	1.39
4	1050	1019	1.86
6	2253	2100	1.29
8	1626	1750	1.73
		Average	1.68

^a Recalculated using $k_{II} = 1.68 \times 10^4 A^{-1} s^{-1}$.

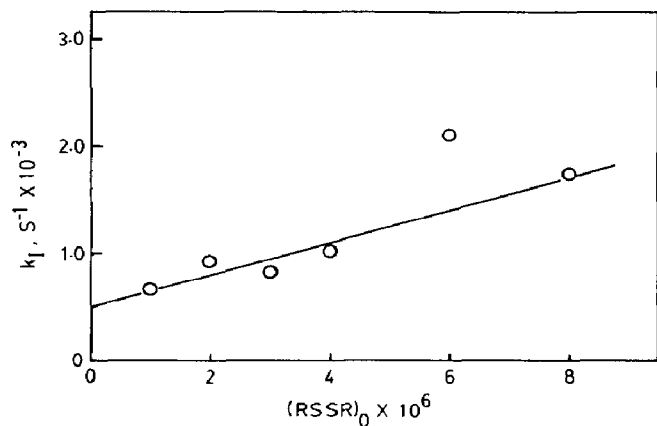


Fig. 2. Plot of k_I vs. $[RSSR]_0$ for the decay of RS in deoxygenated cyclohexane. The k_I values were recalculated based on $k_{II} = 1.68 \times 10^4 A^{-1} s^{-1}$. The value of k_I for $[RSSR]_0 = 6 \times 10^{-6}$ was excluded from the least-mean-squares fit.

The initial time ($t = 0$) was assigned to the time of mean excitation flash intensity as determined by numerical integration of scattered light from the excitation flash. A plot of the left-hand side of eqn. (IV) *versus* t gives a linear relationship for each RSSR concentration. When known values of k_1 , k_{11} and A_t^{RS} are used, A_0^{RS} can be determined from the intercept. Table 2 gives values of A_0^{RS} determined at several values of $[RSSR]_0$ along with k_1 from the slopes of this plot and the ratio of the calculated to the observed values of A^{RS} at 76 μ s. Values of A_0^{RS} were found to depend only on $[RSSR]_0$ and the flash intensity.

TABLE 2

A_0^{RS} as a function of $[RSSR]_0$

$[RSSR]_0 \times 10^6$ (M)	k_1^a (s^{-1})	A_0^{RS}	A_{exp}/A_{calc} (76 μ s)
1	649	0.242	0.95
2	799	0.540	0.98
3	948	0.815	0.97
4	1097	1.233	0.99
6	1396	1.768	0.99
8	1695	2.314	0.97

^a Values of k_1 determined from the fit to eqn. (IV).

$[RS]_0$ is determined as follows. G does not absorb appreciably in the 290 - 370 nm wavelength region used to dissociate RSSR. Separate experiments with G in deoxygenated cyclohexane indicated no depletion of G in the absence of RSSR. The extinction coefficient for G in cyclohexane was measured at $175\,000\text{ M}^{-1}\text{ cm}^{-1}$ and $\lambda_{max}^G = 428\text{ nm}$, which was used to monitor $\Delta[G]$, and at $740\text{ M}^{-1}\text{ cm}^{-1}$ and $\lambda_{max}^{RS} = 547\text{ nm}$.

The total absorbance at 547 nm following the excitation flash consisted of contributions from both RS and G. The concentration

$$A_{tot} = A^{RS} + A^G \quad (\text{V})$$

of G was limited experimentally by extinction of the monitoring beam through the 20 cm photolysis cell to less than $5 \times 10^{-5}\text{ M}$. Since $[RS]_0$ is $2[RSSR]_0$ or less, the ratio of $[G]_0/[RS]_0$ ranged from about 10 in the more favorable cases to less than 2. In most cases no more than 80% of RS could be scavenged by G and the fractional scavenging was determined kinetically.

The disappearance of RS in the presence of G is given by

$$-\frac{d[RS]}{dt} = k_1[RS][G] + 2k_2[RS]^2 + k_3[RS][RSSR] + k_4[RS] \quad (\text{VI})$$

Since photobleaching was unimportant in cyclohexane solutions, the change $\Delta[G]$ in G concentration measured the concentration of RS scavenged by

reaction (1). The change in concentration of G during the photolysis experiment was small and a correction to the absorbance measurement for changes in A^G was made by the approximate function

$$[G]_t = [G]_\infty + \frac{[RS]}{[RS]_0} \Delta[G] \quad (\text{VII})$$

The total solution absorbance is then

$$A_{\text{tot}} = A^{\text{RS}} + \epsilon_G l \left\{ [G]_\infty + \frac{\Delta[G] A^{\text{RS}}}{\epsilon_{\text{RS}} l [RS]_0} \right\} \quad (\text{VIII})$$

where $\epsilon_G = 740 \text{ M}^{-1} \text{ cm}^{-1}$ for G in cyclohexane. $[RSSR]$ can be expressed as

$$[RSSR] = [RSSR]_0 - \frac{\Delta[G]}{2} + \left(\frac{\Delta[G]}{[RS]_0} - 1 \right) \frac{[RS]}{2} \quad (\text{IX})$$

Substitution of eqns. (VIII) and (IX) into eqn. (VI) gives, on rearrangement,

$$-\frac{d\{\ln(A - A_\infty)\}}{dt} = \alpha(A - A_\infty) + \beta \quad (\text{X})$$

where

$$\alpha = \frac{(2k_2 - k_3/2)(A_0/\epsilon_{\text{RS}}l) + (k_1 + k_3/2) \Delta[G]}{A_0 + \epsilon_G l \Delta[G]}$$

$$\beta = k_3 \left([RSSR]_0 - \frac{\Delta[G]}{2} \right) + k_1 [G]_\infty + k_4$$

The rate constants for reaction of RS with G were determined by taking the intercepts β of the $-\frac{d\{\ln(A - A_\infty)\}}{dt}$ versus $A - A_\infty$ plots and plotting $\beta + k_3 \Delta[G]/2$ versus $[G]_\infty$ (Fig. 3). A value of $k_1 = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is determined using this technique when cyclohexane is the solvent.

The ϵ_{RS} can be determined from A_0 and $[RS]_0$. An estimate of $[RS]_0$ is obtained by using an approximate value of ϵ_{RS} to determine the fraction F of RS actually scavenged in each experiment:

$$F = \int_0^t \frac{k_1 [G]}{k_1 [G] + 2k_2 A_{\text{RS}}/\epsilon_{\text{RS}}l + k_3 [RSSR] + k_4} dt \quad (\text{XI})$$

where $[G]$ and A are determined from eqns. (VII) and (VIII) and eqn. (XI) is numerically integrated. The relation $\Delta[G]/F$ gives a second estimate of $[RS]_0$ and ϵ_{RS} and the procedure is repeated until consistent values are obtained. The results appear in Table 3 for various concentrations of $[RSSR]_0$ and $[G]$. The average value of ϵ_{RS} is $11000 \text{ M}^{-1} \text{ cm}^{-1}$ with a scatter of $\pm 10\%$.

Several other solvents were investigated in a similar manner to determine the effects of solvent polarity on the reactivity and extinction coefficients of RS. In addition, the rate of RS reaction with styrene was de-

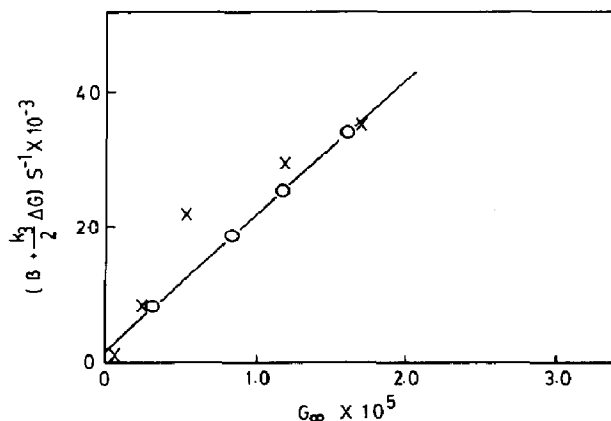


Fig. 3. Plot of $\beta + k_3 \Delta[G]/2$ vs. $[G]_\infty$ for the reaction of RS with G in cyclohexane: $[RSSR]_0 = 8 \times 10^{-6}$ M; O, *p*-aminophenyl disulfide; X, *p*-tolyl disulfide.

TABLE 3

Extinction coefficients for the *p*-aminophenylthiyl radical in cyclohexane

$[RSSR]_0 \times 10^6$ (M)	$[G]_0 \times 10^5$ (M)	f_{sc}^a	ϵ ($M^{-1} \text{ cm}^{-1}$)
4	0.494	0.376	10000
4	1.14	0.588	8800
4	1.95	0.718	11360
4	4.79	0.853	13600
2	0.449	0.555	11800
2	1.04	0.747	10300
2	1.86	0.842	9500
		Average	10800 ± 1300

^aFraction of RS scavenged by G.

terminated as previously described [3] since this relatively slow reaction might substantiate the solvation changes associated with a change in ϵ_{RS} . A summary of these data appears in Table 4.

4. Discussion

Several sources of error are inherent in the procedure used to determine ϵ_{RS} which involves the combination of several quantities which are not all independent. Based on experimental scatter, values of k_3 and k_4 would appear to have approximate uncertainties of $\pm 50\%$. These values, however, make only minor modifications in the determination of ϵ_{RS} . The most significant errors appear to arise from uncertainties in A_0 (and/or k_{II}) and $\Delta[G]$. A large number of determinations gave k_{II} consistently within the

TABLE 4

Summary of the reactivity and extinction coefficient of the *p*-aminophenylthiyl radical in various solvents

<i>Solvent</i>	<i>D</i> ^a	λ_{\max} (nm)	ϵ_{RS} (M ⁻¹ cm ⁻¹)	$k_1 \times 10^{-9}$ (M ⁻¹ s ⁻¹)	$k_2 \times 10^{-4}$ (M ⁻¹ s ⁻¹)	$k_{STY} \times 10^{-4}$ (M ⁻¹ s ⁻¹)
Cyclohexane	2.02	547	11000	2.0	1.9	17
Isopropyl ether	3.5	572	(13000) ^b	(0.017) ^c	1.9	1.4
Ethyl acetate	6	575	(11000) ^{b, d}	1.3	1.6	0.83
Acetone	20.2	585	(8000) ^b	— ^e	1.9	0.48
Methanol	32.6	594	15000	1.2	1.1	0.44
Acetonitrile	36.2	585	19000	1.5	1.7	0.49

^a Dielectric constant.

^b Calculated from $\epsilon = \epsilon^{\text{cyclohexane}}(1.68 \times 10^4/k_{II})$ in which k_2 is assumed to be identical in all cases.

^c Represents rate constants for the complex between G and the solvent (see text).

^d Photobleaching precluded accurate measure of $\Delta[G]$ (see text).

^e Dark reaction prevents measurement (see text).

range illustrated in Table 1 for cyclohexane. Thus error limits of $\pm 20\%$ can be assigned to k_{II} in all solvents. In cyclohexane, no photobleaching or dark reactions complicate the measurement of $[G]$ and $\Delta[G]$ can be reproduced to $\pm 10\%$. The values of ϵ_{RS} for different $[RSSR]_0$ and a wide range of G concentrations fall well within the higher of these uncertainty values ($\pm 20\%$). In acetonitrile and methanol a small amount of photobleaching was found to occur (about 10% and about 30% of $\Delta[G]$ respectively), depending on $[G]_0$, and corrections were made to the measured value. Nevertheless, the values of ϵ_{RS} and k_2 in these solvents should still be considered to have uncertainties of about $\pm 20\%$. In ethyl acetate photobleaching was a major fraction of $\Delta[G]$ and the experimental values have a much greater uncertainty ($\pm 50\%$).

Within the experimental errors, the rate constants for RS combination appear to be the same and are approximately diffusion controlled with values ranging from 1.1×10^9 to 1.9×10^9 M⁻¹ s⁻¹ in solvents with a dielectric constant range of 2.02 (cyclohexane) to 37 (acetonitrile). The value $k_{II} = 2k_2/\epsilon_{RS}$ was accurately determined in all solvents. If it is assumed that k_2 is constant in all reported solvents and equal to the most accurately determined value (*i.e.* 1.9×10^9 M⁻¹ s⁻¹ in cyclohexane), then it is possible to calculate the ϵ_{RS} in solvents where the experimental observations are uncertain (ethyl acetate) or impossible to obtain (acetone and isopropyl ether). These values are listed in Table 4 (footnote b).

The extinction coefficients ϵ_{RS} increase with solvent dielectric constant from 11 000 M⁻¹ cm⁻¹ for cyclohexane to 19 000 M⁻¹ cm⁻¹ for acetonitrile. The calculated value of ϵ_{RS} for ethyl acetate is 3000 M⁻¹ cm⁻¹ units higher than the experimental estimate and, considering the increasing trend of ϵ_{RS} with solvent dielectric constant, the calculated value is probably the more acceptable one. In isopropyl ether G formed a stable complex with either the

ether or possibly an impurity. This complex had the same spectral characteristics as uncomplexed G but with a much lower value of ϵ_G ($33\,000\text{ M}^{-1}\text{ cm}^{-1}$ at $\lambda_{\text{max}}^G = 428\text{ nm}$). This complex was stable to photobleaching and reacted very slowly with RS, thus precluding an experimental determination of ϵ_{RS} . In acetone a dark reaction occurs between G and RSSR producing a new broad absorption band centered at 570 nm. This band interferes with determination of RS decay kinetics and no experimental determination of ϵ_{RS} was attempted. The extinction coefficients reported here for RS are somewhat higher than those reported for the *p*-chlorophenylthiyl radical ($5000 - 9000\text{ M}^{-1}\text{ cm}^{-1}$ [4]) and an order of magnitude higher than those for alkylthiyl radicals [9]. The *p*-aminophenylthiyl radical has a more polar character than its *p*-Cl analog because of the greater electron-donating ability of the *p*-NH₂ group. The increase in extinction coefficient with solvent polarity and the shifts to longer $\lambda_{\text{max}}^{\text{RS}}$ both suggest a charge stabilization of the highly polar excited state of the radical [5]. The broadening of the absorption spectrum with solvent polarity and relatively high extinction coefficient are consistent with an intramolecular charge transfer character of the transition.

The reactivity of the RS radical with styrene decreases with solvent polarity from $k_{\text{STY}} = 1.7 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$ in cyclohexane to a limiting value of about $4.8 \times 10^3\text{ M}^{-1}\text{ s}^{-1}$ in acetone ($D = 20$) and more polar solvents. These rate constants reflect the stabilization of the ground state radical by solvation. Ito and Matsuda [10] concluded that the decrease in the rate of addition of RS to styrene with increasing solvent polarity resulted from the decreased ability of RS to lose solvation molecules in formation of the transition state. In the present work this stabilization appears to change very little above $D \approx 20$. Therefore the increase of ϵ_{RS} in methanol and acetonitrile can be attributed primarily to solvation of the more polar excited state of RS.

The rate of addition k_1 of RS to G can be determined much more precisely than k_2 . When $[G]_0$ is much greater than $[\text{RS}]_0$, changes in the concentration of G due to reactions with RS or photobleaching are minor. Under these conditions the latter part of the RS decay is essentially first order. The values of k_1 vary from 1.2×10^9 to $2 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ and are nearly identical with the experimental values of k_2 in each solvent studied. It can be concluded that RS reacts with G at nearly a diffusion-controlled rate. Nakamura *et al.* [4] reported values of k_1 ranging from $6.2 \times 10^8\text{ M}^{-1}\text{ s}^{-1}$ for *p*-chlorophenylthiyl radicals to $3.5 \times 10^8\text{ M}^{-1}\text{ s}^{-1}$ for *p*-methoxyphenylthiyl radicals and found a correlation between k_1 and the Hammett substituent constant σ^+ . To be consistent with this trend, k_1 for RS would be nearly an order of magnitude lower than the observed value. A few experiments were carried out with *p*-tolyl disulfide to try to resolve this discrepancy. These data also appear in Fig. 3 and, although the data scatter is large owing to low absorbance of the *p*-tolylthiyl radical, this species appears to have a rate constant identical with that for RS in cyclohexane. We are unable to account for differences in these determinations. However, consistency of the value of k_1 in the present experiments over a range of G concentrations (Fig. 3) and solvents supports the validity of the current measurement.

Values of k_4 of about 500 s^{-1} were found in cyclohexane, isopropyl ether and ethyl acetate, but $k_4 \approx 0$ in other solvents studied. If this first-order decay involves hydrogen atom abstraction from the solvent with k_4' (solvent) $\approx 500 \text{ s}^{-1}$, then k_4' would be about $50 \text{ M}^{-1} \text{ s}^{-1}$ which is similar to that found for the reaction of *p*-chlorophenylthiyl radicals with cumene [1].

Acknowledgment

The authors gratefully acknowledge support of this research by Public Health Service Grant AG00200.

References

- 1 O. Ito and M. Matsuda, *J. Am. Chem. Soc.*, **101** (1979) 1815.
- 2 O. Ito and M. Matsuda, *J. Am. Chem. Soc.*, **101** (1979) 5732.
- 3 L. V. Natarajan, R. R. Lembke and R. R. Kuntz, *J. Photochem.*, **15** (1981) 13.
- 4 M. Nakamura, O. Ito and M. Matsuda, *J. Am. Chem. Soc.*, **102** (1980) 698.
- 5 G. H. Morine and R. R. Kuntz, *Chem. Phys. Lett.*, **67** (1979) 552.
- 6 F. C. Thyron, *J. Phys. Chem.*, **77** (1973) 1478.
- 7 R. F. Evans, W. A. Volkert, R. R. Kuntz and C. A. Ghiron, *Photochem. Photobiol.*, **24** (1976) 3.
- 8 G. H. Morine and R. R. Kuntz, *Photochem. Photobiol.*, **33** (1981) 1.
- 9 M. Z. Hoffman and E. Hayon, *J. Phys. Chem.*, **77** (1973) 990.
- 10 O. Ito and M. Matsuda, *J. Am. Chem. Soc.*, **104** (1982) 568.