

KINETICS OF THE ADDITION OF *p*-AMINOPHENYLTHIYL RADICALS TO VINYL MONOMERS

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Summary

The kinetics of the addition of *p*-aminophenylthiyl radicals to vinyl monomers were studied in cyclohexane. Thiyl radicals, generated by flash photolysis of the *p*-aminophenyldisulfide, react with monomers in a reversible fashion. These addition rates show a good correlation with the electron density of the monomer double bond and with stability parameters of the resulting adduct.

1. Introduction

The photolysis of phenyldisulfides leads to the production of phenylthiyl radicals [1 - 3]. The absorption spectra of these radicals are substantially affected by substitution on the aromatic ring [4] and by solvent polarity [5]. The reactivity of several *p*-substituted phenylthiyl radicals with vinyl monomers has been determined [2, 4], as has the effect of *para* substitution of the radical on the addition rate to styrene and methylmethacrylate [4]. The *p*-chlorophenylthiyl radical adds to monomers with rate constants of $10^4 - 10^7 \text{ M}^{-1} \text{ s}^{-1}$ depending on the electron density in the double bond and the stability of the adduct radical [2].

Recently, the dipole moment of the *p*-aminophenylthiyl radical has been measured in both the ground state and the fluorescent state by determining the absorption and emission maxima of the radical as functions of solvent properties [5]. This radical shows a relatively high dipole moment in the ground state (4.3 debye) which may be explained by substantial delocalization of electrons in the radical. It is expected that the polar character and the resonance stabilization of this radical would have significant effects on its reactivity. Consequently, we investigated the kinetics of the addition of this radical to several vinyl monomers to elucidate these effects.

2. Experimental

The *p*-aminophenylthiyl radical (RS) was produced by flash photolysis of *p*-aminophenyldisulfide (RSSR) in cyclohexane at room temperature (20 ± 2 °C). The flash systems employed have been described previously [5, 6] and consist of a 300 J (10 μ s full width at half-maximum) flash from a xenon lamp. Observations were made either with a delayed spectroscopic flash and optical multichannel analyzer detection for absorption spectra, or with a continuous light source and photomultiplier detection for kinetic measurements. The radical absorption in cyclohexane ($\lambda_{\max} = 550$ nm) has already been characterized [5]. The absorption maximum and shape were not altered on the addition of monomers to the photolysis mixture.

The RSSR was purchased from Aldrich and was purified by recrystallization (twice) from *n*-heptane. Most experiments were conducted with an RSSR concentration of 7×10^{-6} M. Cyclohexane was Gold Label spectrophotometric grade from Aldrich and was used without purification. The monomers were the highest purity available from Aldrich or Matheson, Coleman and Bell and were used as received.

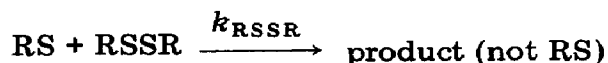
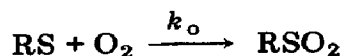
3. Results and discussion

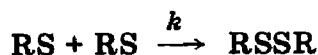
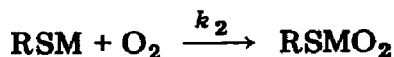
The only transient absorption found in the photolysis of RSSR may be attributed to the thiyl radical indicating that the primary photoprocess is cleavage of the S—S bond:



The decay of RS in deaerated cyclohexane follows second-order kinetics with $2k/\epsilon = (3.0 \pm 0.4) \times 10^5 \text{ cm s}^{-1}$. This decay profile is not changed significantly if the solution is oxygen saturated or if monomer is present in the deaerated solution. However, the presence of both monomer and oxygen enhances the decay of RS and the kinetics approach first order as the monomer concentration increases. These observations are consistent with those reported for the *p*-chlorophenylthiyl radical [2].

A mechanism which is adequate to describe the reactions of the RS radical includes the following steps:





The thiyl radical decay in this mechanism is described by the expression

$$-\frac{d[\text{RS}]}{dt} = k_o[\text{O}_2][\text{RS}] + k_{\text{RSSR}}[\text{RSSR}][\text{RS}] + k_1[\text{RS}][\text{M}] - k_{-1}[\text{RSM}] + 2k[\text{RS}]^2$$

When the oxygen concentration is high, the concentration of RSM may be approximated by a steady state assumption [2]. Making this substitution and setting the absorbance A equal to $\epsilon[\text{RS}]l$ leads to

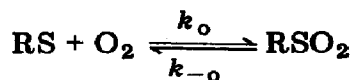
$$-\frac{d \ln A}{dt} = k_I + \frac{2k}{\epsilon l} A \quad (1)$$

where

$$k_I = k_o[\text{O}_2] + k_{\text{RSSR}}[\text{RSSR}] + \frac{k_1 k_2 [\text{O}_2][\text{M}]}{k_{-1} + k_2[\text{O}_2]}$$

In the absence of M, a plot of the left-hand side of eqn. (1) against A should give a slope equal to the second-order decay constant $2k/\epsilon l$ and an intercept equal to k_I . Second-order constants obtained in this manner agree with those determined by plots of $1/A$ against t .

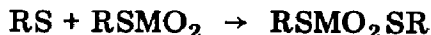
The intercepts of plots of eqn. (1) in the absence of monomer were small, but not negligible. The reaction of RS with oxygen appears to make only a minor contribution to this intercept since values of similar magnitude were found in degassed and oxygen-saturated solutions. Alkylthiyl radicals react with oxygen at diffusion-controlled rates [7] but arylthiyl radicals appear to have very low reactivity [2, 4]. It is more likely that RSO_2 is formed



but rapidly dissociates, favoring RS at equilibrium. Another contribution to the first-order disappearance in the absence of monomer is reaction with the parent disulfide.

Decreasing the initial RSSR concentration from 7×10^{-6} to 1.7×10^{-6} M resulted in a decrease in k_I from 1800 to approximately 300. The rate constant for this reaction may be assigned a value of about $10^8 \text{ M}^{-1} \text{ s}^{-1}$. This estimate is considered to be a lower limit since a relatively large fraction of the initial RSSR is destroyed in the excitation flash. Experimental error precluded the determination of k_o from the remaining portion of the intercept.

The addition of arylthiyl radicals to monomers is known to be reversible and again leads to no net decay of RS unless oxygen is present to trap RSM. Additional termination reactions which would be expected in the presence of monomer and oxygen seem to be unimportant since the second-order decays



do not show significant deviation from those observed in their absence. For each oxygen concentration the intercept for plots of eqn. (1) varied linearly with monomer concentration (Fig. 1) yielding a slope of

$$k_{\text{app}} = \frac{k_1 k_2 [\text{O}_2]}{k_{-1} + k_2 [\text{O}_2]}$$

Individual rate constants can be determined where an appreciable oxygen concentration effect exists. Since

$$\frac{1}{k_{\text{app}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2 [\text{O}_2]}$$

a plot of $1/k_{\text{app}}$ against $1/[\text{O}_2]$ permits the direct evaluation of k_1 and k_{-1}/k_2 (see Fig. 2). Rate constants obtained in this fashion appear in Table 1 and are compared with equivalent addition rates for the *p*-chlorophenylthiyl radical.

Oxygen concentration changes did not affect k_{app} for *n*-butyl vinyl ether and k_{app} was assumed to equal k_1 . Also, k_{app} changed by only 20% and

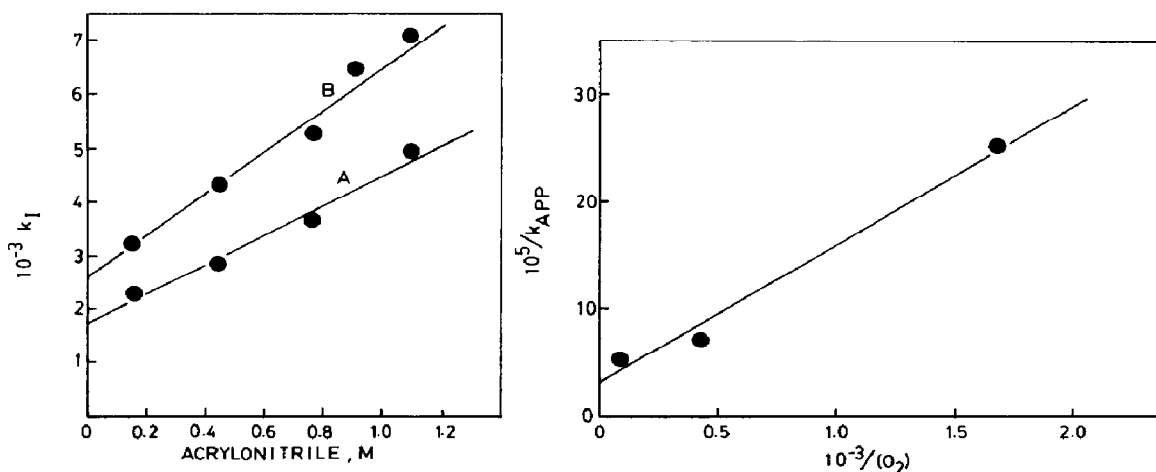


Fig. 1. The effect of acrylonitrile concentration on the first-order constant k_1 (eqn. (1)): A, oxygen saturated; B, air saturated; $[\text{RSSR}] = 7 \times 10^{-6}$ M in cyclohexane.

Fig. 2. The dependence of k_{app} on $[\text{O}_2]$ for the reaction of RS with methylmethacrylate in cyclohexane: $[\text{RSSR}] = 7 \times 10^{-6}$ M.

TABLE 1

Summary of rate constants for the addition of RS to monomers

Monomer	$k_1 \times 10^{-3}$ ($M^{-1} s^{-1}$)	k_1 (relative) ^a	$k_{-1}/k_2 \times 10^3$ (M)	$k_{-1} \times 10^{-6}$ (s^{-1})	K^b (M^{-1})
Styrene	167	1 (1)	1.89	1.89	0.088
Methyl- methacrylate	33	0.20 (0.1)	4.30	4.30	0.008
Methylacrylate ^c	5.2	0.031 (0.0078)	1.08	1.08	0.005
Acrylonitrile	5.9	0.035 (0.009)	5.14	5.14	0.0012
Methacrylo- nitrile ^c	23.8	0.142 (0.045)	0.42	0.42	0.057
<i>n</i> -Butyl vinyl ether ^d	1.4	0.0084 (0.0035) ^e	—	—	—
Acrylic acid ^f	5	0.03	Not determined		
Crotonic acid ^f	3	0.018	Not determined		

^aThe values in parentheses are for the *p*-chlorophenylthiyl radical [2].^b $K = k_1/k_{-1}$.^cA small oxygen effect limits the accuracy of k_{-1}/k_2 and values derived from this ratio.^dA negligible effect.^eThe value in parentheses is for isobutyl vinyl ether.^fThe rate is independent of the monomer concentration (see text).

25% for methylacrylate and methacrylonitrile respectively when the oxygen concentration was varied from 2.4×10^{-3} M (air saturated) to 1.15×10^{-2} M (oxygen saturated). Oxygen concentration effects are expected to be related to the dissociation rate of the adduct radical. The reaction of RSM with oxygen should be diffusion controlled with $k_2 = (2 - 7) \times 10^9 M^{-1} s^{-1}$. Assigning a constant value of $k_2 = 1 \times 10^9 M^{-1} s^{-1}$ permits relative estimates of k_{-1} in cases where an appreciable oxygen effect exists. This assignment has the additional advantage of permitting direct comparison with previous work [2, 4]. These data (Table 1) confirm that the lowest k_{-1} values occur in those cases showing the smallest oxygen effect which is consistent with a higher relative stability of the adduct radical. We expect, therefore, that the adduct to *n*-butyl vinyl ether is relatively stable and easily scavenged by oxygen even in air-saturated solutions, at a rate greater than the dissociation rate. The upper limit for k_{-1} in this case is estimated to be $2 \times 10^5 M^{-1} s^{-1}$.

The behavior of acrylic acid and crotonic acid is significantly different from that observed from other monomers in that k_1 is independent of monomer concentration from 0.05 to 1 M. This result suggests a chemical change of RS. The behavior is under investigation at present.

The addition rate of RS to monomers is enhanced by increasing the electron density in the double bond, as is evidenced by a linear correlation with "e" values for the monomers [8, 9] (Fig. 3). The addition rate also increases with adduct stability, as is evidenced by a reasonable correlation with *Q* values [9] for the conjugated monomers (Fig. 3). Also, the relative addition rates are consistent with those observed for the *p*-chlorophenylthiyl radicals [2].

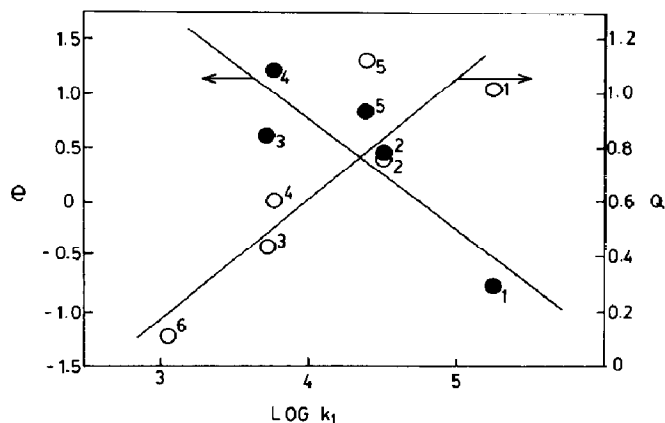


Fig. 3. A correlation of $\log k_1$ with electron density parameter "e" and adduct stability parameter Q values for monomers ($r^2 = 0.76$ for "e", $r^2 = 0.75$ for Q , where r^2 is the coefficient of determination): 1, styrene; 2, methylmethacrylate; 3, methylacrylate; 4, acrylonitrile; 5, methacrylonitrile; 6, *n*-butyl vinyl ether.

Stability of the radical adduct may also be described by the equilibrium constant $K = k_1/k_{-1}$ for adduct formation. Assuming $k_2 \approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$, these calculated values appear in Table 1 and generally indicate a positive ΔG° for the addition reaction.

Equilibrium constants for RS are lower than those observed for other phenylthiyl radicals [2, 4] (Table 2). This result is due to the combined effect of a lower addition rate of RS to monomers and a higher dissociation

TABLE 2

Comparison of rate constants for the reaction of *p*-substituted phenylthiyl radicals with styrene and methylmethacrylate^a

<i>p</i> -Substituent	$k_1 \times 10^{-6}$ ($\text{M}^{-1} \text{ s}^{-1}$)	k_1^c	$k_{-1} \times 10^{-5b}$ (s^{-1})	K^b (M^{-1})	Reference
Styrene					
—NH ₂	0.17		18.9	0.088	This work
—OCH ₃	2.6		7.7	3.4	4
—CH ₃	18		16	11	4
—H	20		11	19	4
—Cl	51		<1	>500	2,4
—NO ₂	400		—	—	4
Methylmethacrylate					
—NH ₂	0.033	0.20	43	0.008	This work
—OCH ₃	0.46	0.18	9.1	0.505	4
—CH ₃	2.7	0.15	5.8	4.66	4
—H	3.2	0.16	4.1	7.80	4
—Cl	5.4	0.11	4.9	11.02	2,4
—NO ₂	18	0.045	—	—	4

^aIn cyclohexane solvent at room temperature.

^bBased on $k_2 = 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

^cValues relative to addition to styrene.

rate of the adduct radical with k_1 showing a greater relative change than k_{-1} . Since the dissociation rates for all these radicals are of similar magnitude, the lower equilibrium constant is due primarily to the lower addition rate which is two orders of magnitude lower than that observed for the *p*-chlorophenylthiyl radical.

In general, the addition rates appear to be inversely proportional to the electron-donating ability of the *para* substituent (Table 2). In the case of RS, a considerable delocalization of electrons across the aromatic system and onto the sulfur does apparently contribute to the polarity and lowers the reactivity of the radical. Nevertheless, the radical still exhibits the electrophilic attack on double bonds which is characteristic of thiyl radicals.

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