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Reactions of the *tert*-Butylthiyl Radical with Organometallic Compounds and Alkenes[1]

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Abstract: Absolute rate constants for the reactions of the *tert*-butylthiyl radical with a variety of substrates were measured by using a combination of laser flash photolysis techniques and product studies. Reactions with organometallic substrates such as boranes, phosphines, and phosphites were extremely rapid with rate constants in the range 10^8–10^9 M^{-1} s^{-1}. By contrast, addition to a simple olefin, oct-1-ene, was ca. 100 times less rapid. However, 1,1-diphenyl- and 1,1-dicyclopropylethylene were remarkably efficient traps for *tert*-butylthiyl and scavenged the radical with rate constants of 9.9×10^8 and 2.4×10^8 M^{-1} s^{-1}, respectively.

Alkylthiyl radicals are a major class of reactive intermediates that are of importance in organic and biological systems, yet hardly any information exists on absolute rate constants for their reactions.[2] The only rate constants that have been determined for alkylthiyl radicals are those for their reactions with oxygen,[3,4] styrene, and terminal alkenes,[5,6] and, as we will show, some of these are erroneous. The paucity of absolute rate data reflects the difficulty of working with alkylthiyl radicals in time-resolved experiments since they are not readily detected optically or by electron paramagnetic resonance (EPR) spectroscopy.[7]

Relative rate constants for the reactions of alkylthiyl radicals are more abundant[2] but are limited in scope to reactions with simple olefins,[5,6] organoboron,[8] and organophosphorus substrates.[9] However, the synthetically important olefin addition reactions tend to be reversible,[6,8,9] which compounds the problems of kinetic analysis in these relatively simple cases.

In an attempt to overcome these difficulties, we have devised a flash photolysis technique for measuring the absolute rate constants of alkylthiyl radical reactions with alkenes and organometallic compounds. The approach overcomes the problems of reversible olefin addition and does not require that alkylthiyl radicals be detected directly.

Experimental Section

Materials. Di-*tert*-butyl disulfide was purified by distillation so as to remove impurities of tri- and tetrasulfides.[7] All other materials were purified by literature methods,[10] with the exception of organoboron compounds. These were used as received, since further manipulation tends to increase the impurities of oxidized materials.[11] 1,1-Dicyclopropylethylene was prepared by the method previously reported.[12]

Laser Flash Photolysis. The flash photolysis apparatus has been described in detail elsewhere.[13] Briefly, samples that had been purged with nitrogen were photolyzed with pulses from a nitrogen laser (337.1 nm; pulse width ca. 8 ns, up to 10 mJ/pulse). The reactive intermediates that were produced in the pulses were monitored using a detection system that consisted of a xenon monitoring lamp, monochromator, and photomultiplier tube. The output of the photomultiplier was fed to a transient digitizer, and the digitized signals were then stored and averaged in a computer, which was used to analyze the data.

EPR Experiments. Samples containing di-*tert*-butyl disulfide (1 M) and 1,1-diphenylethylene in isooctane as solvent were photolyzed directly in the cavity of a Varian E104 spectrometer. The photolysis source was a 1000-W mercury–xenon lamp, and the output of the lamp was filtered through an aqueous solution of cobalt and nickel sulfates, which removed most of the infrared and much of the visible radiation.

Results and Discussion

The reactions of arylthiyl radicals with a variety of vinyl monomers have been investigated in considerable detail by Ito and Matsuda.[14] Photolysis of diaryl disulfides proved to be a clean source of arylthiyl radicals that had UV–visible spectra, which could be monitored using flash photolysis techniques. These authors recognized that addition of the double bonds was reversible and, to simplify the reaction kinetics, they ran their reactions in the presence of oxygen. This had no effect on the arylthiyl radicals themselves but efficiently scavenged the carbon-centered radicals formed by their addition to olefins. Under conditions of efficient scavenging, the rate of disappearance of the arylthiyl radicals, as monitored by flash photolysis techniques, was equal to their rate of addition to the olefin in question (reactions 1 and 2).

$$\mathrm{ArSSAr} \xrightarrow{h\nu} 2\mathrm{ArS}^{\bullet} \tag{1}$$

$$\mathrm{ArS}^{\bullet} + \mathrm{CH_2{=}CHR} \rightarrow \mathrm{ArSCH_2\dot{C}HR} \xrightarrow{O_2} \text{peroxy radical} \tag{2}$$

It has been claimed[5] that alkylthiyl radicals, like their arylthiyl radical cogeners, absorb strongly in the UV–visible region and should therefore be ideal candidates for flash photolysis studies. However, these reports are almost certainly incorrect. The signals that were detected in these cases were most probably due to perthiyl radicals, RSS•,[7] that result from photolysis of tri- and tetrasulfides, which are common impurities in commercially available disulfides. Photolysis of carefully purified disulfide samples gives only extremely weak absorptions in this spectral region (vide infra), making it impossible to monitor the kinetic behavior of alkylthiyl radicals directly.

To overcome this problem, we used 1,1-diphenylethylene as a probe molecule. This substrate reacts efficiently with alkylthiyl radicals, producing a substituted diphenylmethyl radical, **1**, that has a very strong absorption spectrum with λ_{max} at 329 nm (reactions 3 and 4). The reaction is demonstrably irreversible on the time scale of the flash photolysis experiments. It can therefore be used as a means of monitoring the lifetimes of alkylthiyl radicals in a variety of systems.

$$\mathrm{RSSR} \rightarrow 2\mathrm{RS}^{\bullet} \tag{3}$$

$$\mathrm{RS}^{\bullet} + \mathrm{Ph_2C{=}CH_2} \rightarrow \underset{\mathbf{1}}{\mathrm{Ph_2\dot{C}CH_2SR}} \tag{4}$$

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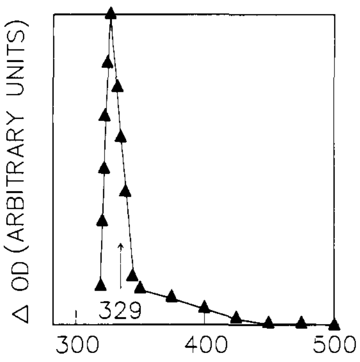

Figure 1. Transient optical absorption spectrum of radical **1** formed by photolysis of di-*tert*-butyl disulfide in the presence of 1,1-diphenylethylene.

Characterization, by EPR, of Alkylthiyl Radical Adducts to 1,1-Diphenylethylene. The laser flash photolysis technique is intrinsically a poor analytical method, and we therefore carried out independent experiments to verify that the probe system functioned in the way described by reactions 3 and 4. Simple EPR experiments provided the necessary proof.

Continuous photolysis at 25° of an isooctane solution containing di-*tert*-butyl disulfide (5% v/v) and 1,1-diphenylethylene (5% v/v) in the cavity of an EPR spectrometer gave a spectrum of **1** (R = *t*-Bu) with the following hyperfine splittings (G): $a^{H} = 3.04$ (*o*-Ph; 4 H); $a^{H} = 1.26$ (*m*-Ph; 4 H); $a^{H} = 3.32$ (*p*-Ph; 2 H); $a^{H^{\beta}} = 7.96$; $a^{H} = 0.22$ (*t*-Bu; 9 H). These values were in excellent agreement with data for related β-substituted 1,1-diphenylethyl radicals.[15] Similar experiments were carried out with dibutyl disulfide. An excellent spectrum of I (R = Bu) was obtained that was satisfactorily simulated using the parameters given above for the phenyl and β-hydrogens with $a^{H} = 0.50$ G ($-SCH_2$) and $a^{H} = 0.12$ G ($-SCH_2CH_2Et$). The EPR experiments provide compelling evidence that alkylthiyl radicals do indeed react with 1,1-diphenylethylene to give substituted diphenylmethyl radicals **1** and support the assignments based on optical absorption spectra (vide infra).

Flash Photolysis Experiments. Laser flash photolysis of isooctane solution containing di-*tert*-butyl disulfide (1 M) gave only extremely weak absorptions in the UV–visible region that were barely detectable. However, on addition of 1,1-diphenylethylene (0.025–0.05 M), a strong absorption spectrum was obtained with an absorption maximum at 329 nm, Figure 1. The spectrum is typical of those obtained for diphenylmethyl radicals[16] and was assigned to **1** on the basis of the shape of the optical absorption spectrum and the corroborating evidence obtained in the EPR experiments.

The decay of **1** was easily monitored using the flash photolysis apparatus and afforded a method of proving that the addition of $RS^{\bullet}$ was effectively irreversible on the time scale of the flash photolysis experiments. The overall reaction scheme is given in eq 3–6.

$$RS^{\bullet} + \mathbf{1} \rightarrow \text{products} \qquad (5)$$

$$2\,\mathbf{1} \rightarrow \text{products} \qquad (6)$$

Applying the steady-state condition to the concentration of $RS^{\bullet}$ leads to eq 7, which describes the rate of decay of I. Experimentally, it was found that the decay of **1** clearly followed second-order kinetics.

$$-d[\mathbf{1}]/dt = [\mathbf{1}]^2\{2k_6 + (2k_5k_{-4})/(k_4[Ph_2C{=}CH_2] + k_5[\mathbf{1}])\} \qquad (7)$$

The ratio of the observed second-order rate constant to the extinction coefficient of **1** was independent of the initial concentration of **1** when the latter was varied by the use of neutral density filters in the photolyzing laser beam. Moreover, it was also found that this ratio was independent of the concentration of diphenylethylene over the range 1×10^{-3}–1×10^{-2} M. These observations imply that $2k_6$ was the dominant term in eq 7 and hence that expression 8 was valid for these experiments.

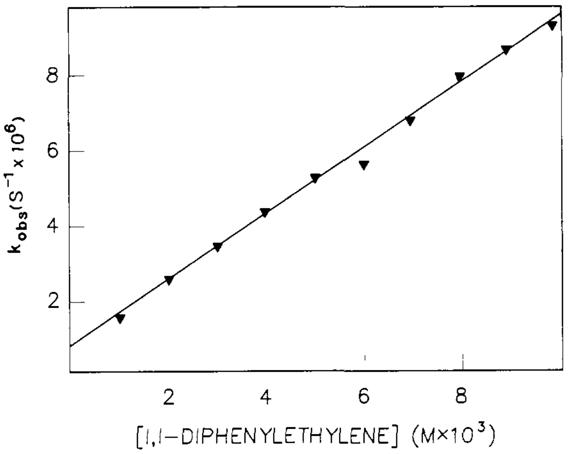

Figure 2. Plot of k_{obs} as measured by flash photolysis techniques versus the concentration of 1,1-diphenylethylene.

Table I. Rate Constants for the Reactions of the *tert*-Butylthiyl Radical with a Variety of Substrates at 298 K in Isooctane Solvent

substrates	$k_{sub} \times 10^{-8}$	substrates	$k_{sub} \times 10^{-8}$
$Ph_2C{=}CH_2$	9.9	$(MeO)_3P$	2.7
$(c\text{-}C_3H_5)_2C{=}CH_2$	2.4	$(EtO)_3P$	3.1
Et_3B	1.3	Bu_3P	9.0
$s\text{-}Bu_3B$	0.8		

$$2k_6 \gg (2k_5k_{-4})/(k_4[Ph_2C{=}CH_2] + k_5[\mathbf{1}]) \qquad (8)$$

Reactions 5 and 6 are radical–radical processes and will therefore have very similar rate constants; i.e., $k_5 \simeq 2k_6 \simeq 5 \times 10^9$ M^{-1} s^{-1}.[18] Moreover, under the flash photolysis conditions, the rate of formation of **1** was at least 1 order of magnitude greater than its loss, implying that $k_4[Ph_2C{=}CH_2] \gg k_5[\mathbf{1}]$. Applying these constraints to (8) leads to expression **9**, which indicates that loss of $RS^{\bullet}$ from **1** was not a complicating factor in the flash photolysis work.

$$k_4[Ph_2C{=}CH_2] \gg k_{-4} \qquad (9)$$

Having established that the addition of $RS^{\bullet}$ to 1,1-diphenylethylene was essentially irreversible on the laser flash photolysis time scale, it was a simple matter to measure the rate constant for the addition reaction, k_4, and rate constants for the reactions of $RS^{\bullet}$ with other substrates.

The growth of **1** was examined under the experimental conditions described above and followed pseudo-first-order kinetics with rate constants, k_{obs}, that were linearly dependent upon the olefin concentration, Figure 2. The rate constant of interest, k_4, was obtained[19] using eq 10, where k' represents the rate of decay of the thiyl radicals in the absence of olefin. The result obtained is reported in Table I.

$$k_{obs} = k' + k_4[Ph_2C{=}CH_2] \qquad (10)$$

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(19) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520. It is possible that this simple scheme may be complicated by the incursion of a secondary reaction in which an alkyl radical, produced in reactions 12 or 14, attacks the starting disulfide to form a thioether and to regenerate the *tert*-butylthiyl radical. However, combination of literature data on product and kinetic studies suggests that this process is too slow to affect the rate constants measured in this work. See: Barton, D. H. R.; Bridon, D.; Zard, S. Z. *Tetrahedron Lett.* **1984**, *25*, 5777. Newcomb, M.; Kaplan, J. *Tetrahedron Lett.* **1987**, *28*, 1615. We are grateful to a reviewer for suggesting this addendum to our paper.

Rate constants, k_{sub} for the reactions of the *tert*-butylthiyl radical with other substrates, boranes, phosphines, and phosphites, were easily measured in similar experiments in which the concentration of 1,1-diphenylethylene was kept constant, and k_{obs} was monitored as a function of substrate concentration. The system is described by eq 11,[19] where k_0 is equal to $k' + k_4[\text{Ph}_2\text{C}{=}\text{CH}_2]$. The rate constants obtained for the various reactions are reported in Table I.

$$k_{\text{obs}} = k_0 + k_{\text{sub}}[\text{substrate}] \qquad (11)$$

Reaction Mechanisms. The substrates investigated do not react by a common mechanism with alkylthiyl radicals. As has already been demonstrated, the reaction with 1,1-diphenylethylene is a simple and irreversible radical addition (eq 4). However, the reactions with boranes and phosphines proceed via an S_H2 mechanism[8] in which the incoming thiyl radical displaces an alkyl group (eq 12). Thiyl radicals react with phosphites to form phosphoranyl radicals, II, that ultimately undergo fragmentation to give thiophosphates and alkyl radicals.[9,20-22] In these cases, the rate constant measured for the reaction by the flash photolysis approach describes the formation of the phosphoranyl radical intermediate (eq 13 and 14).

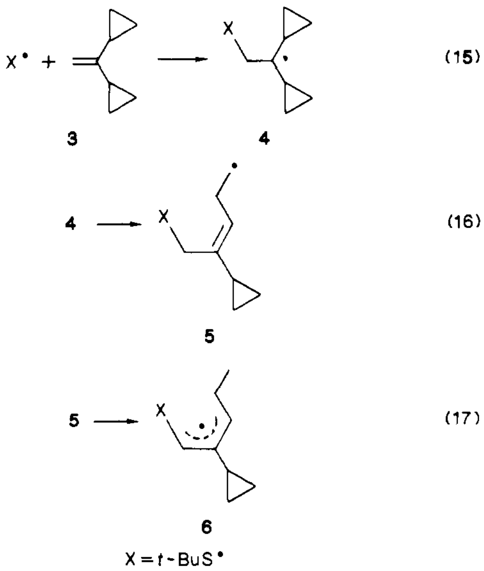
$$\text{RS}^\bullet + \text{R}'_3\text{M} \rightarrow \text{RSMR}'_2 + \text{R}'^\bullet \qquad (12)$$

$$\text{M} = \text{B or P}$$

$$\text{RS}^\bullet + (\text{R}'\text{O})_3\text{P} \rightarrow \text{RS}\dot{\text{P}}(\text{OR}')_3 \qquad (13)$$

$$\text{RS}\dot{\text{P}}(\text{OR}')_3 \rightarrow \text{R}^\bullet + \text{SP}(\text{OR}')_3 \qquad (14)$$

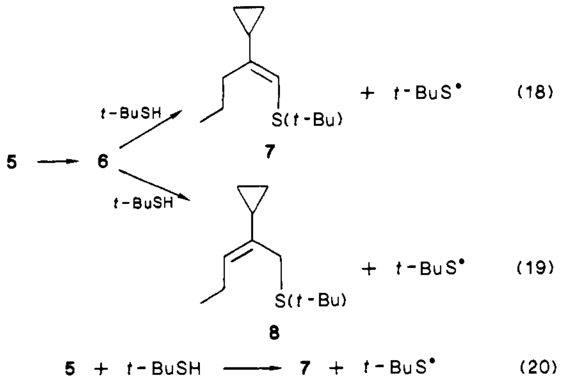
Thiyl radical addition to 1,1-dicyclopropylethylene (**3**) leads initially to a substituted dicyclopropylmethyl radical, **4**. Like its prototype, cyclopropylcarbinyl, it undergoes a rapid ring opening to give **5** that, at room temperature, is followed by a 1,5 intramolecular hydrogen shift to produce an allyl radical **6** (eq 15–17). The reactions are highly regiospecific and lead only to the isomers shown.[23]



Competition Experiments with Olefins. Although the rearrangements make the system fairly complex, the use of 1,1-dicyclopropylethylene has the advantage that the extremely rapid ring opening precludes the reversible loss of the *tert*-butylthiyl group. Accordingly, we used the olefin in the laser flash photolysis experiments expecting that its reactivity would typify those of simple olefins. However, this was not the case.

The data in Table I show that 1,1-dicyclopropylethylene is more reactive than trialkylboranes whereas Davies and Roberts[8] showed that a simple olefin, oct-1-ene was ca. 100 times *less* reactive than tributylborane in reactions with the *n*-butylthiyl radical. To resolve the apparent dichotomy, we carried out a series of competition experiments to establish the relative reactivities of dicyclopropylethylene and oct-1-ene with respect to *tert*-butylthiyl radicals.

The experiments were carried out by establishing a radical chain reaction between oct-1-ene, 1,1-dicyclopropylethylene, and *tert*-butyl mercaptan. The propagation steps for the reaction are described in eq 15 and 18–22. Although the route by which products **7** and **8** are formed is fairly complicated,[23] all that concerns us, in the present context, is that the sum of their yields reflects the extent of attack by *tert*-butylthiyl radicals at 1,1-dicyclopropylethylene.



While radical addition of *tert*-butylthiyl to 1,1-dicyclopropylethylene is effectively irreversible at 25 °C because of the rapid ring opening, the same is not true for addition to oct-1-ene and the possibility of reversible addition has to be considered in a description of the reaction kinetics (eq 21 and 22).

$$t\text{-BuS}^\bullet + \underset{\mathbf{9}}{\text{CH}_3(\text{CH}_2)_5\text{CH}{=}\text{CH}_2} \rightarrow \underset{\mathbf{10}}{\text{CH}_3(\text{CH}_2)_5\dot{\text{C}}\text{HCH}_2\text{S}(t\text{-Bu})} \qquad (21)$$

$$\mathbf{10} + t\text{-BuSH} \rightarrow \underset{\mathbf{11}}{\text{CH}_3(\text{CH}_2)_7\text{S}(t\text{-Bu})} \qquad (22)$$

Davies and Roberts[8] have analyzed the kinetics for such a situation, and we have followed their approach. Broadly speaking, finding a solution to the kinetic scheme depends upon the way in which product yields change as a function of oct-1-ene concentration. Obviously, high oct-1-ene concentrations will diminish the importance of the reversible loss of *tert*-butylthiyl. Although the scheme is conceptually simple, the kinetic description eq 23–27,

$$AB + (A - 1)C = k_{15}/k_{21} \qquad (23)$$

cannot be solved analytically and requires a numerical approach to solve for the two unknowns,[8] K and k_{15}/k_{21}, where $K = k_{-21}/k_{22}$ (eq 23–27) where and where the subscripts i and f denote the initial

$$A = D/(K + D) \qquad (24)$$

$$B = (2.303[\mathbf{9}]_i/[\mathbf{11}]_f)\log([\mathbf{3}]_i/[\mathbf{3}]_f) \qquad (25)$$

$$C = (2.303[\mathbf{9}]_i/[\mathbf{11}]_f)\log\left\{\frac{K + D + [\mathbf{3}]_f}{K + D + [\mathbf{3}]_i}\right\} \qquad (26)$$

$$D = [t\text{-BuSH}]_i - [\mathbf{3}]_i \qquad (27)$$

and final concentrations respectively.

To obtain the rate constants, we carried out six experiments under different conditions and treated K as a variable. The data are reported in Table II. For a given value of K we then calculated k_{15}/k_{21} for each of the experiments. The optimum value of K was taken to be that which brought all of the values of k_{15}/k_{21} into the best agreement as calculated by least-squares methods. Figure 3 shows a plot of the percentage deviation from the mean value of k_{15}/k_{21} as K was varied. The best fit, i.e., minimum deviation was obtained for $K = 0.034$ M and led to $k_{15}/k_{21} = 129 \pm 19$

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Table II. Product Yields and Relative Rate Constants for Competition Experiments Involving Oct-1-ene and 1,1-Dicyclopropylethylene

[*t*-BuSH]$_i$, M	[**3**]$_i$, M	[**3**]$_f$, M	[**9**]$_i$, M	[**11**] × 10^2, M	$(k_{15}/k_{21}) \times 10^{-2\,a}$
0.059	0.130	0.100	0.849	0.088	1.40
0.059	0.130	0.093	2.123	0.300	1.24
0.029	0.130	0.112	2.123	0.085	1.34
0.088	0.130	0.077	2.123	0.560	1.02
0.118	0.261	0.209	1.476	0.204	1.29

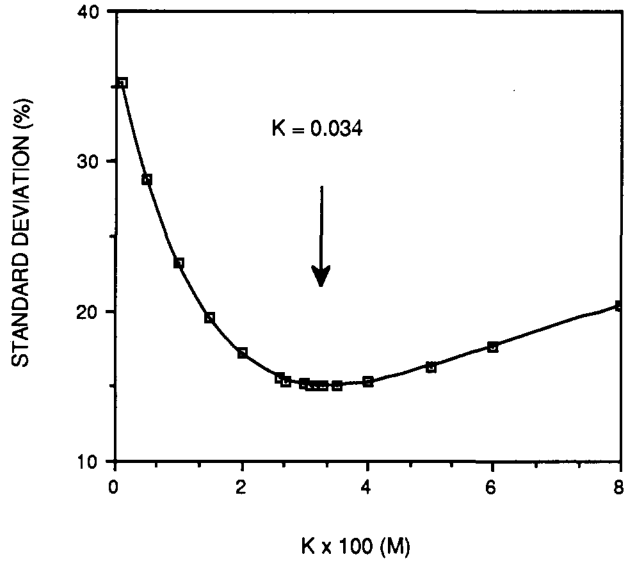

Figure 3. Plot of standard deviation of values of k_{15}/k_{21} from their mean as a function of selected values of K.

(Table II, Figure 3). Taking the rate constant for thiyl radical addition to 1,1-dicyclopropylethylene to be 2.4×10^8 M^{-1} s^{-1} (Table I) leads to the much lower value of $k_{21} = 1.9 \times 10^6$ M^{-1} s^{-1} for the thiyl radical addition to oct-1-ene.

The product studies confirm the conclusions from the laser flash photolysis results, i.e., 1,1-dicyclopropylethylene is indeed far more reactive than simple olefins as a substrate for radical addition. It is tempting to suggest that the effect is due to stabilization of radical **4** by interaction of the unpaired electron with the Walsh orbitals of the cyclopropyl groups.[24] However, recent calculations[25] imply that such interactions in cyclopropylcarbinyl are small and, by inference, would not be significant in this case. If the product radical is not highly stabilized, the obvious alternative is to postulate some special destabilization of the starting olefin, **3**. At this stage, we are unable to offer a definitive explanation for the high reactivity of 1,1-dicyclopropylethylene but note that the observation is supported by two experimental techniques.

Comparison with Literature Data. The results obtained in this work show that 1,1-dicyclopropylethylene is an atypical olefin in terms of radical addition. However, the results obtained for *tert*-butylthiyl addition to oct-1-ene are in reasonable accord with the rate constant for addition of butylthiyl radicals to pent-1-ene (7×10^6 at 25 °C) obtained by Sivertz and his colleagues,[6,26,27] bearing in mind that their value was criticized[8] as being too high since it led to an anomalously high value for the rate constant for self-reaction of the thiyl radical.[28]

Other comparisons with literature data are possible. For example, the value of $K = k_{-21}/k_{22} = 0.034$ M for the elimination/addition of *tert*-butylthiyl with oct-1-ene is similar to the value of $K = 0.05$ obtained[8] for the *n*-butylthiyl radical. In light of the procedure used to obtain K and the associated experimental errors, we feel that further interpretation of these values is unwarranted. However, the two independent experiments are, at the very least, mutually supportive.

Our results on the relative reactivities of a tri-*n*-alkylborane and oct-1-ene (Tables I and II) indicate that the borane is ca. 100 times more reactive toward thiyl radicals. Again, the result is in accord with a value of 110 obtained by Davies and Roberts.[8] The only area of conflict between our results and the literature data concerns the reactivities of phosphines and phosphites. We find them to be ca. 100 times more reactive than simple olefins using laser flash photolysis techniques while Walling and Pearson,[9] for example, find that triethyl phosphite is only ca. 6 times more reactive than cyclohexene as a scavenger for *n*-butylthiyl radicals. Although the effects of reversible addition to the olefin were not included in that study,[9] any contribution of this kind would tend to reduce this factor. At this stage, we are unable to identify the reasons for the difference.

Thermochemistry. The enthalpy change associated with the equilibrium $k_{-21}/k_{21} = K$ can be crudely estimated by half assuming A factors for the elimination of *t*-BuS$^\bullet$ from **10** and the addition of *t*-BuS$^\bullet$ to oct-1-ene. Taking $A_{-21} = 10^{13.4}$ s^{-1} and $A_{21} = 10^9$ M^{-1} s^{-1} [29] together with $K = 0.034$ M leads to $\Delta H_{-21} = 8.1$ kcal mol^{-1} at 300 K. This means that elimination of *t*-BuS$^\bullet$ from **10** is significantly endothermic and that its importance in these experiments is due to a favorable A factor.

The problems of reversible addition to 1,1-diphenylethylene are less pronounced (vide supra) because the two phenyl groups stabilize the *t*-BuS$^\bullet$ adduct to that olefin. Comparing BDE($\mathrm{Me_2CH{-}H}$) with BDE($\mathrm{Ph_2CH{-}H}$)[30] suggests that this effect is of the order of −11 kcal mol^{-1}, so that elimination of *t*-BuS$^\bullet$ from **1** would be ca. 19 kcal mol^{-1} endothermic.

The value of ΔH_{-21} of 8.1 kcal mol^{-1} for the elimination of *t*-BuS$^\bullet$ from *t*-$\mathrm{BuSCH_2\dot{C}H(CH_2)_6Me}$ bears an interesting comparison with the enthalpy required to eliminate MeS$^\bullet$ from $\mathrm{MeSCH_2\overline{CHCHCH_2}}$ (18.7 ± 3.3 kcal mol^{-1}).[31] This second radical has the benefit of allylic stabilization that can be roughly estimated from BDE($\mathrm{Me_2CHH}$) and BDE($\mathrm{MeCH{=}CHCH{-}H}$) to be 12.5 ± 2 kcal mol^{-1}.[30] Given the magnitude of the experimental errors, this factor accounts rather well for the differences in the thiyl radical elimination processes.

Addition of PhS$^\bullet$ to olefins[14] appears to be far more readily reversible than the corresponding reactions involving *t*-BuS$^\bullet$. Again, thermochemistry accounts for this difference since the bonds formed between sulfur and carbon are 10 kcal mol^{-1} weaker for PhS$^\bullet$ than for *t*-BuS$^\bullet$.[17]

Summary

tert-Butylthiyl radicals were found to react rapidly with organoboron and phosphorus compounds with absolute rate constants

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(28) This criticism may not be strictly valid in the light of new data on radical self-reaction in solvents of low viscosity,[18] which indicates that rate constants for these processes are substantially higher than the value of 2×10^9 M^{-1} s^{-1} that was assumed to be correct.[8] Indeed, the apparently "anomalous" value of 6×10^{11} M^{-1} s^{-1} for the self-reaction of butylthiyl radical[6,26,27] could be correct if there is rapid triplet–singlet intersystem crossing for such radical pairs so that the "spin statistical factor" is unity. This kind of relaxation may be very effective for alkylthiyl radicals since their EPR lines, in solution, are very broad, indicating that they have highly anisotropic g tensors.[28b] Under these conditions a Δ_g intersystem crossing mechanism for geminate radical pairs in a solvent cages might be extremely efficient. (b) See: Burkey, T. J.; Hawari, J. A.; Lossing, F. P.; Lusztyk, J.; Sutcliffe, R.; Griller, D. *J. Org. Chem.* **1985**, *50*, 4966 and references cited therein.

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in the range 10^8–10^9 M^{-1} s^{-1}. Rate constants for the reactions with olefins showed large variations with 1,1-dicyclopropyl- and 1,1-diphenylethylene being ca. 2 and 3 orders of magnitude, respectively, more reactive than oct-1-ene.

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Registry No. *t*-BuS, 16812-19-4; $Ph_2C{=}CH_2$, 530-48-3; $(c\text{-}C_3H_5)_2C{=}CH_2$, 822-93-5; Et_3B, 97-94-9; *s*-Bu_3B, 1113-78-6; $(MeO)_3P$, 121-45-9; $(EtO)_3P$, 122-52-1; Bu_3P, 998-40-3; oct-1-ene, 111-66-0.

Kinetically Stable Complexes of Alkali Cations with Rigidified Calix[4]arenes: Synthesis, X-ray Structures, and Complexation of Calixcrowns and Calixspherands

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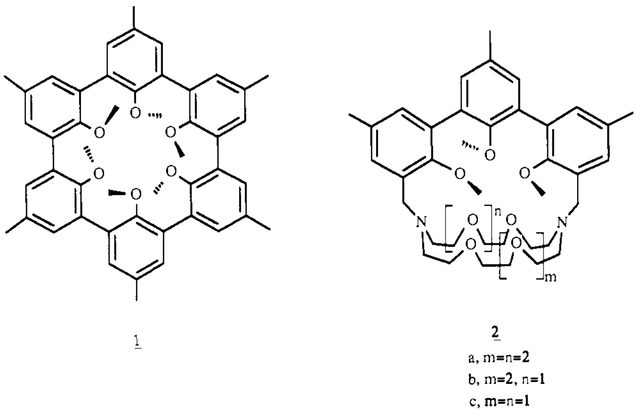
Abstract: Selective 1,3-dialkylation of the phenolic groups of *p-tert*-butylcalix[4]arene (**3**) with methyl or benzyl tosylate yields **7a** (75%) and **8** (95%), respectively. Subsequent bridging of the two remaining phenolic groups in **7a** or **8**, by reaction with polyethylene glycol ditosylates, gives *p-tert*-butylcalix[4]arene crown ethers (**4b**, **4c**, and **4e**). Reaction of **7a** with 3,3″-bis(bromomethyl)-2,2′,2″-trimethoxy-5,5′,5″-trimethyl-1,1′:3′,1″-terphenyl (**10**) in the presence of NaH or KH produces the corresponding NaBr and KBr complexes of the calixspherand **6**. Decomplexation of the **6**·NaBr and **6**·KBr complexes in H_2O/CH_3OH (4:1) requires long reaction times and high temperatures, indicating a high *kinetic* stability. The X-ray structure of **6**·NaPic confirmed the flattened partial cone conformation of the calixarene moiety in this complex. The free energies of complexation ($\Delta G°$) of the calixcrown ether alkali picrate (MPic) complexes vary from −6 to −12 kcal·mol^{-1} ($CDCl_3$). The calixspherand **6** forms kinetically "stable" complexes with Na^+ ($k_d^{298} = 6.0 \times 10^{-9}$ s^{-1}), K^+ ($k_d^{298} = 1.0 \times 10^{-8}$ s^{-1}), and Rb^+ ($k_d^{298} = 6.9 \times 10^{-5}$ s^{-1}). The rates of complexation vary between 1.3×10^4 and 2.5×10^5 M^{-1}·s^{-1}. The calculated free energies of complexation of **6** with MPic salts in $CDCl_3$ at 298 K are −16.8 (**6**·Na^+), −18.1 (**6**·K^+), and −13.0 (**6**·Rb^+) kcal·mol^{-1}, respectively. The high thermodynamic and kinetic stabilities of these complexes are explained in terms of a high degree of preorganization of the calixspherand and the highly hydrophobic collar around the molecular cavity. This prevents solvent molecules to assist in the decomplexation process.

The thermodynamic and kinetic stabilities of the alkali cation complexes of macrocyclic polyethers incorporating meta-coupled anisyl (or anisyl and cyclic urea) units have been studied in detail by Cram et al.[1] Increased substitution of ethyleneoxy moieties in crown ethers by meta-coupled anisyl units enhances the thermodynamic stability of the corresponding alkali cation complexes. The result of the work of Cram and co-workers on the effect of anisyl oxygen atoms as ligating sites can be summarized in the following statement about preorganization: "the more highly hosts and guests are organized for binding and for low solvation prior to their complexation, the more stable will be their complexes".[1] The spherands (e.g., **1** (Chart I)) are the ultimate demonstration of the preorganization principle, and spherand **1** is the best host for the small alkali cations Li^+ and Na^+. Spherand **1** rejects the larger alkali cations K^+, Rb^+, and Cs^+.

The preorganization principle not only affects the *thermodynamic* stability but also has a pronounced effect on the *kinetic* stability of the alkali complexes of the spherands. The anisyl groups in the spherands provide the preorganized ligating donor sites, and they shield the cavity from solvent molecules. As a result, the rates of complexation by the spherands are decreased and the rates of decomplexation are even more decreased, when compared with flexible crown ethers. Slow decomplexation on the human time scale of alkali cation complexes is limited to the anisyl spherands like **1**, but these spherands only complex Li^+ and Na^+ ions.

Chart I[a]



[a] The bars at the phenyl rings and at the oxygen atoms indicate methyl groups.

Our interest in macrocyclic host molecules with preorganized cavities is related to the possible application of radioactive Rb^+ isotopes in organ imaging. Therefore, we have focused our work on the synthesis of spherand-type host molecules that have a larger

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