

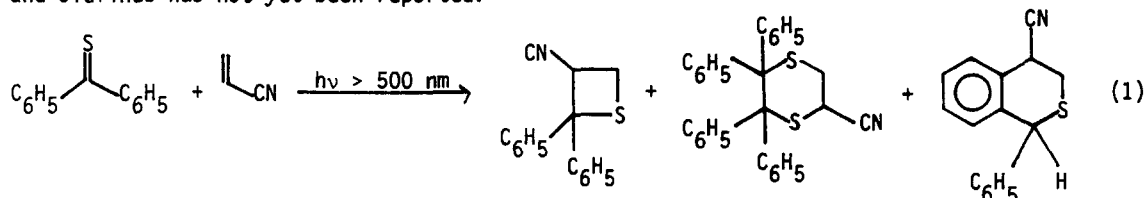
ON THE MECHANISM OF PHOTOCYCLOADDITION OF AROMATIC THIONES (n, π^* TRIPLET) TO MULTIPLE BONDS

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It has been established that thiones undergo cycloaddition to a variety of olefines, dienes, acetylenes and allenes to give thietanes, 1,4-dithianes and/or rearranged products (eq. 1) upon excitation to the first excited (n, π^*) state.¹ The general observation of regioselectivity, non-stereospecificity of addition, the geometric isomerization of olefines and the formation of rearranged products has led to the suggestion of a diradical intermediate in analogy with ketones during photocycloaddition to olefines.² Detailed mechanistic study on selected systems - thio-benzophenone^{3a} and adamantanethione^{3b} revealed several unique features of these reactions, including diffusion controlled self-quenching and the presence of highly reversible intermediate(s). The nature of the primary interaction between thione triplet (n, π^*) and olefines has not yet been reported.



We have measured the rate constants for the initial interaction of olefines with an electronically excited aromatic thione-xanthione, the results of which are presented in this communication. The method employed is the quenching of phosphorescence of xanthione⁴ ($1 \times 10^{-4} M$) at 25°C in nitrogen purged acetonitrile by various substrates. The rate constants for the primary step were evaluated from the slopes of Stern-Volmer plots ($k_q \tau$) knowing the lifetime (τ) of xanthione triplet under the same reaction conditions ($\sim 8 \pm 1.5 \times 10^{-7}$ sec). Results with mono-olefines, dienes, allenes, acetylenes and thiones are presented in the Table.⁵

The results of the study may be summarized as:

- (1) The rate constant for the interaction of xanthione triplet (n, π^*) with olefines depends upon the substituents on the olefine - the olefines substituted by electron donating groups being the best quenchers and the olefines substituted by electron withdrawing groups being poor

quenchers. (2) A linear correlation between $\log k_q$ and adiabatic ionization potential for enol ethers and dienes were observed but no linear correlation could be observed for all olefines and dienes together. (3) Allenes and acetylenes which are known⁶ to add to xanthione quench the triplet xanthione with a reasonably high rate constant ($\sim 10^8$). (4) Both adamantanethione and 3-thio-1,3-cyclobutanedione which have higher triplet energy (~ 53 kcal/mole) than xanthione (~ 42 kcal/mole) quench the triplet xanthione at close to diffusion controlled rates.

The primary interaction measured by quenching of triplet xanthione could be due to either classical energy transfer, direct bond formation leading to a biradical intermediate or formation of an excited state complex (exciplex). As the triplet energy of all substrates used here is well above that of xanthione the classical energy transfer would not be expected. The initial bond formation with multiple bonds would be expected to be directed by the radical-like character of sulphur in the n, π^* triplet of xanthione. In the absence of data for the radical derived from xanthione or any aromatic thiyl radical we compare our results with aliphatic thiyl radicals. The rate constants calculated⁷ for the attack of $\text{CH}_3\text{S}^\cdot$ upon cis-butene (2×10^7), ethylene (4.8×10^6) and butadiene (4.5×10^8) compare favorably with the ones we have measured for trans-2-pentene (2.6×10^7) and 1,3 pentadiene (1×10^9). In the case of carbonyl n, π^* triplets, the rate constants for addition of alkoxy radical and triplet ketone to multiple bonds differed by two orders of magnitude.⁸ This suggested a different behavior for the triplet ketone from the alkoxy radical. The close similarity observed in thiones is consistent with direct bond formation as the primary step. It is worth noting that thiyl radical has been shown to be electrophilic in nature and that a partial charge transfer character is generated in the transition state during the addition of thiyl radical to olefines as demonstrated by measuring the relative rates of addition of thiyl radical derived from dodecanethiol to various olefines.⁹

A survey of the Table clearly reveals that the rate constants for quenching are dependent upon the substituents and are related to the ionization potential of the olefines. The slopes of linear plots of $\log k_q$ versus I.P. of quencher reflect the charge transfer contribution in the excited state complex such that when there is complete electron transfer the slope approaches $-17/\text{ev}$.¹⁰ The linear correlations that we have observed for enol ethers and dienes show slopes $\sim -0.5/\text{ev}$ indicating that there is only 3% electron transfer or charge transfer contribution in the primary complex between triplet xanthione and olefines. Therefore the stability of the complex, if any, is not derived from charge transfer character. Comparison of the rate constants for the

quenching of carbonyl (acetone and benzophenone)¹¹ and thione triplets by olefines (enol ethers) reveals the presence of 10-15% electron transfer or charge transfer contribution to the primary complex in the case of ketones in contrast to only 3% in the case of thiones. This difference in behavior becomes more understandable considering the electronic details of the mechanism. The triplet quenching process may be considered in terms of simple orbital pictures. Partial charge donation from the olefine π orbital to the 'n' orbital of the thione or ketone produces the initial complex. This depends upon the ionization potential of the olefine and the electron affinity of the carbonyl or thione triplet. The difference in charge contribution to the primary complex is consistent with the expected difference in the electron affinities of the orbitals involved, those being 2p in C=O and 3p in C=S, i.e., the half-filled thione 'n' orbital may be viewed as being less electrophilic than the carbonyl 'n' orbital.

In summary, we have reported the rate constants for the primary interaction of a model aromatic thione-xanthione with a variety of multiple bonds. Attention is drawn to the similarity in reactivity of thiyl radicals and thione triplets (n, π^*) towards olefines. Finally, we have shown that thiones are excellent quenchers of thione triplets.¹²

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TABLE

<u>Quenchers</u>	k_q ^a	<u>Quenchers</u>	k_q
<u>cis</u> -diethoxyethylene (7.38) ^b	1.9×10^9	tetramethylethylene (8.30) ^c	2.9×10^8
<u>trans</u> -diethoxyethylene (7.40)	2.8×10^9	2-methyl 2-butene (8.68)	2.8×10^8
1,1'-dimethyl 2-ethoxyethylene (7.7)	1.1×10^9	cyclopentene (9.01)	1.4×10^8
t-butylvinylether (8.19)	9.3×10^8	<u>trans</u> -2-pentene (9.06)	2.6×10^7
ethylvinylether (8.49)	4.4×10^8	methacrylonitrile (10.37)	1.8×10^7
2,5-dimethyl 2,4-hexadiene (7.46) ^b	3.1×10^9	<u>trans</u> -crotononitrile (10.23)	6.9×10^6
2-methyl 2,4-hexadiene (7.81)	2.5×10^9	acrylonitrile (10.92)	3.6×10^6
1,3-cyclooctadiene (8.68)	1.6×10^8	<u>trans</u> -dicyanoethylene (11.15)	5.5×10^5
1,3-cyclohexadiene (7.88)	2.3×10^9	diethylfumrate (10.5)	6.2×10^6
2,3 dimethyl 1,3-butadiene (8.54)	1.5×10^9	tetramethylallene	3.1×10^8
2-methyl 1,3-butadiene (8.60)	1.1×10^9	dimethylallene	1.0×10^8
1,3-pentadiene (8.44)	1.0×10^9	phenylacetylene	1.2×10^8
2-methyl 3,5-hexadiene	7.8×10^8	diphenylacetylene	7.1×10^7
2-chloro 1,3-butadiene	2.7×10^8	dimethylacetylenedicarboxylate	7.1×10^5
adamantanethione	7.8×10^9		
3-thio-1,3-cyclobutanedione	4.1×10^9		

^a from Stern-Volmer quenching of phosphorescence of xanthione in acetonitrile; error limits $\pm 15\%$;

^b adiabatic ionization potential;

^c vertical ionization potential.