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SOURCE OF INEFFICIENCY IN PHOTOCHEMICAL TRIPLET CYCLO-  
ADDITION AND HYDROGEN ABSTRACTION REACTIONS

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ABSTRACT

The inefficiency of a photochemical reaction may result prior to the formation of intermediates in addition to arising from the partitioning of intermediates. We analyze, here, several well studied triplet photocycloaddition reactions in terms of "Salem Diagrams" and point out the factors which may be utilized in predicting the efficiency of a photocycloaddition. We also point out the existence of a correlation between the efficiency of a photocycloaddition and the experimental physical parameters which are related to the magnitude of spin-orbit coupling.

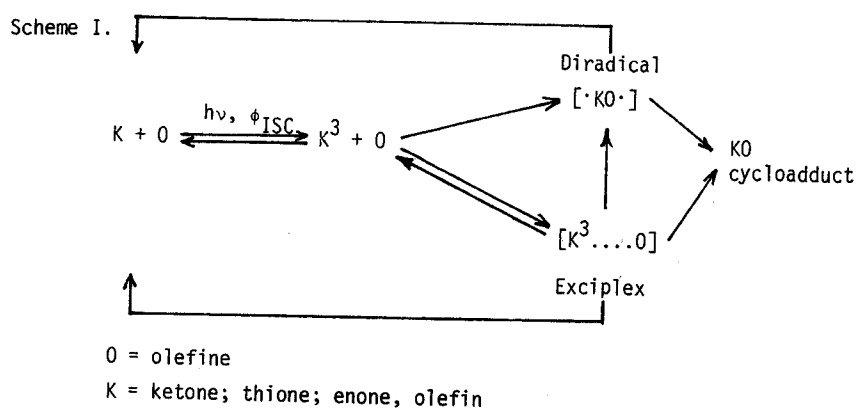
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The successful utilization of a photochemical reaction as a synthetic tool depends on the ability to predict the chemical yield and efficiency of a reaction in addition to the structure of products. The chemical yield (percent of reactant converted to products) of a reaction may depend on reversion of reactants as well as the partitioning of intermediates to various products. In contrast to thermal reactions, an inefficiency or a decrease in the product yield of a photochemical reaction may result prior to the formation of intermediates in addition to arising from the partitioning of intermediates. In this paper we analyze several well studied triplet photocycloaddition reactions in terms of "Salem Diagrams"<sup>1</sup> and point out the factors which may be utilized in predicting the efficiency of a photocycloaddition.

Knowledge of both the efficiency and reactivity of a photochemical process allows important conclusions to be made regarding "invisible chemical and physical processes" such as radiationless decay resulting in no apparent changes. The efficiency of a process may be measured in terms of quantum yield ( $\phi$ ) and reactivity in terms of the rate constant ( $k$ ) of a primary process. Ketones<sup>2</sup> and thiones<sup>3</sup> undergo addition to olefins to give oxetanes and thietanes via the triplet state. Similarly, olefins<sup>4</sup> and

enones<sup>5</sup> react with olefins to give cyclobutanes. In each of these cases the presence of a diradical intermediate during a triplet state reaction has been suggested. In some of these cases, it is proposed that an exciplex precedes the diradical. A general mechanism for the photocycloaddition is shown in Scheme I.

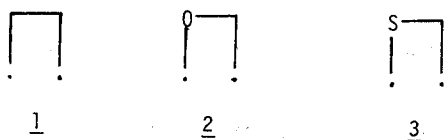


The quantum yield ( $\phi$ ) for product formation, which is a measure of the efficiency of triplet photocycloaddition, is given by equation (1) where  $\beta$  is the factor indicating the fraction of the intermediate(s) going on to give products, i.e., efficiency of the reaction.

$$\phi = \phi_{ISC} \beta \left\{ \frac{k_r[O]}{k_r[O] + k_d} \right\} \quad (1)$$

The efficiency of a photoreaction ( $\beta$ ) can readily be obtained from the plot of  $\phi^{-1}$  against  $[O]^{-1}$  as the inverse intercept. Some efficiency

constants obtained in this manner are shown in Table I. The rate constants ( $k$ ) for the addition of each of these triplets toward olefins are usually very large and commonly have been estimated<sup>2-5</sup> to be  $\sim 10^8$ . As can be seen from Table I, the efficiencies (as measured by  $\beta$ ) of cycloaddition for olefin, ketone and thione triplets are drastically different. The inefficiency observed in each of these cases has generally been attributed to the diradicals 1, 2 and 3 and/or exciplex intermediates. A priori, it is not clear why there should be such a large difference in their behavior towards competition between product formation and reversing to reactants.



In order to better understand the factors responsible for the trend in inefficiencies for these reactions it is essential to know the potential energy surface which controls the motion of the molecule. A correlation diagram (Salem Diagram) for the cycloaddition of  $n, \pi^*$  state of carbonyl or thiocarbonyl compound to a double bond is shown in Figure 1. The diagram is constructed on the assumption that a diradical is the primary

TABLE I  
EFFICIENCIES OF TRIPLET CYCLOADDITION

SYSTEM	$\beta$	REF.	SYSTEM	$\beta$	REF.
Isoprene <sup>3</sup> - isoprene	1	4a	Adamantanethione <sup>3</sup> - ethylvinylether	$1.7 \times 10^{-3}$	3b
Cyclohexadiene <sup>3</sup> - cyclohexadiene	1	4b	Adamantanethione <sup>3</sup> - acrylonitrile	$1.2 \times 10^{-3}$	3b
Norbomadiene	1	4c	Adamantanethione <sup>3</sup> - adamantanethione	$1.4 \times 10^{-4}$	3b
Acetone <sup>3</sup> - cyclooctene	0.10	2c	Thiobenzophenone <sup>3</sup> - acrylonitrile	$2.0 \times 10^{-3}$	3c
Acetone <sup>3</sup> - 1-methoxy-1-butene	0.10	2c	Cyclohexenone <sup>3</sup> - cyclohexenone	0.74	5b,c
Acetone <sup>3</sup> - diethoxyethylene	$\sim 0.10$	2f	Cyclohexenone <sup>3</sup> - cyclohexene	1.0	5d
Benzophenone <sup>3</sup> - isobutylene	0.09	2g	Cyclopentenone <sup>3</sup> - cyclopentenone	0.36	5c
Benzophenone <sup>3</sup> - 2-butene	0.10	2g	Cyclopentenone <sup>3</sup> - cyclopentene	0.27	5e
Benzophenone <sup>3</sup> - furan (step 1)	0.03	2b	Cyclopentenone <sup>3</sup> - cyclohexene	0.48	5e
Benzophenone <sup>3</sup> - furan (step 2)	0.05	2b	Cyclopentenone <sup>3</sup> - <u>trans</u> -3-hexene	0.21	5e

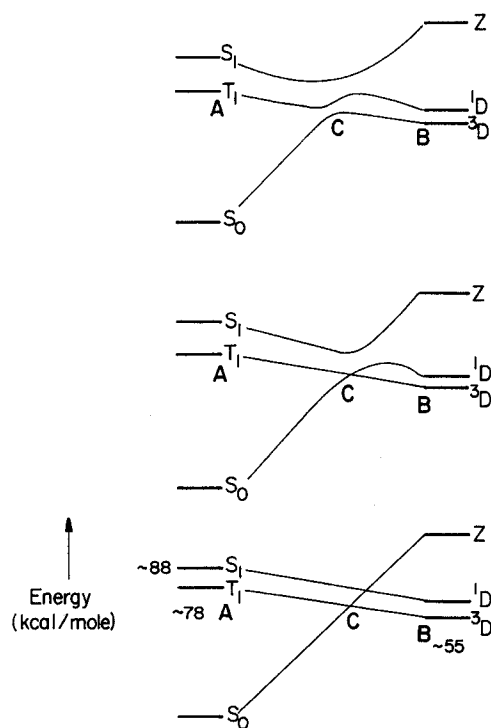
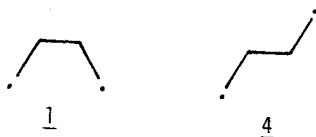


Figure 1: Salem Correlation Diagram for the  $n,\pi^*$  addition to double bond. Energy estimate is for the addition of acetone to ethylene and is based on group additivity and spectroscopic data.

product and that the addition occurs via a co-planar orientation. The sterically favored coplanar addition of  $\pi,\pi^*$  olefin may produce either a "cis" diradical (1) or a "trans" diradical (4) as the primary product.<sup>6</sup> The "Salem Diagram" for each of them is similar in form and is shown in Figure 2. No thermochemical or electronic (symmetry) imposed barrier is



expected for addition from the lowest triplets of olefins, enones, thiones and ketones.<sup>7</sup>

A striking feature of the correlation diagrams is a crossing between triplet surfaces ( $T_1 - {}^3D$ ) and singlet surfaces ( $S_0 - {}^1D$  or  $S_0 - Z_1$ )

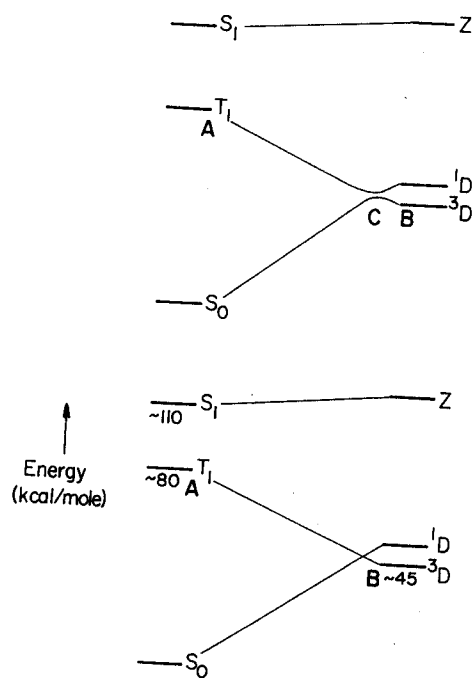


Figure 2: Salem Correlation Diagram for  $\pi, \pi^*$  addition to double bond.  
Energy estimate is for the dimerization of ethylene.

at point C. In the absence of spin-orbit coupling the triplet cycloaddition may be considered as the smooth movement of the supercomplex  $[K^3 + O]$  from point A to B (diradical) through C. This motion of the complex on the upper surface towards the triplet diradical will always compete with electronic decay (radiative and non-radiative) to the ground state surface. If an electronic jump occurs between A and C no net chemical change occurs and an inefficiency is introduced. Therefore, the inefficiency of cycloadditions involving  $n, \pi^*$  states does not necessarily result from the intermediate but may occur on the way to the intermediate.

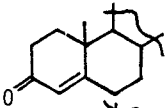
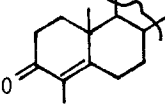
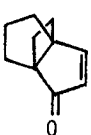
The probability of jump from one adiabatic surface to the other will depend, among other factors, upon the energy gap between the two surfaces.<sup>8</sup> The two important excited surfaces involved in our discussion are singlet and triplet, respectively. The probability of a jump from  $T_1$  to  $S_0$  will also be determined by the surface crossing and by the spin-orbit coupling between the two states when the super-complex possesses geometries near that corresponding to the Zero Order crossing (point C in Figure). In the absence of effective spin-orbit coupling the jump from the triplet to the ground surface will not effectively compete with the chemical change occurring by the forward movement of the complex. From the above



model it is clear that the jump between the triplet surface and ground state surface or the efficiency of cycloaddition is dependent on (a) spin-orbit coupling; (b) the presence of a surface crossing and (c) the rate of motion along the surface. The Salem diagram suggests a common topology for all  $n, \pi^*$  additions to ethylenes, i.e., a  $T_1 - {}^3D$  surface crossing. There is no reason of which we are aware to suppose that the rate of motion of the representative point is significantly different for the systems being compared. It seems plausible, therefore, that spin-orbit coupling might serve as the dominating parameter determining reaction efficiency. We attempt here to correlate the observable physical parameters representing spin-orbit coupling to the inefficiency of a reaction. Rate constants for intersystem crossing ( $k_{ISC}$ ), the lifetime of the triplet ( $\tau_{T_1}$ ) and  $\epsilon$  for  $S_0 \rightarrow T_1$  absorption reflect a measure of spin-orbit coupling between the reactive ( $T_1$ ) and ground ( $S_0$ ) states. The available data<sup>9</sup> for functional groups of interest is shown in Table II.

A comparison of Tables I and II reveals the existence of a correlation between the efficiency ( $\beta$ ) of photocycloaddition and  $\epsilon$  for  $S_0 \rightarrow T_1$  absorption. A similar correlation between  $\epsilon$  and  $k_{ISC}$  and  $\tau_{T_1}$  is also readily seen. Olefins which have poor  $k_{ISC}$  and  $\epsilon$  ( $S_0 \rightarrow T_1$ ) are the most

TABLE II.

	$S_1 \xrightarrow{\epsilon} T_1$	$k_{ISC}$	$\tau_{T_1}$ (77°K)	Ref.
Ethylene	$10^{-4}$	--	--	(9a)
Acetone	$10^{-1}$	$5 \times 10^8$	$0.33 \times 10^{-3}$ sec	(9b)
Benzophenone	$10^{-1}$	$10^{11}$	$5.0 \times 10^{-3}$ sec	(9c)
Thiobenzophenone	8.9	$>10^{11}$	$4.4 \times 10^{-5}$ sec	(9d)
Xanthione	8.0	$>10^{11}$	$4.8 \times 10^{-5}$ sec	(9e)
Adamantanethione	5.0	$>10^{11}$	$1.2 \times 10^{-4}$ sec	(9d)
	--	--	$27 \times 10^{-3}$ sec	(11)
	--	--	$58 \times 10^{-3}$ sec	(11)
	--	--	$<10^{-3}$ sec	(10)

efficient ( $\beta \approx 1$ ) in undergoing cycloaddition. Thiones, which have high  $k_{ISC}$  and  $\epsilon$  ( $S_0 \rightarrow T_1$ ) and short triplet lifetime, are the least efficient during cycloaddition [ $\beta \approx 10^{-3}$ ]. Ketones which are intermediate to ethylenes and thiones in terms of efficiency during cycloaddition

( $\beta \approx 10^{-3}$ ) also have intermediate values for  $\epsilon$ ,  $k_{ISC}$  and  $\tau_{T_1}$ . Thus, it appears that the efficiency of intersystem crossing that occurs near  $\underline{C}$  can partly be judged from the spectroscopic properties of the chromophore undergoing photoreaction. The above conclusion is further strengthened by the behavior of enones. Cyclopentenones whose lowest triplet is dominated by  $n, \pi^*$  character<sup>10</sup> are less efficient ( $\beta \sim 0.3$ ) than cyclohexenones ( $\beta \sim 0.8$ ) whose triplets have more  $\pi, \pi^*$  character,<sup>11</sup> both during dimerization and cycloaddition to olefin. The larger spin-orbit coupling ( $n, \pi^* > \pi, \pi^*$ ) correlates with lower cycloaddition efficiency (note the triplet lifetime of cyclohexenones is longer than that of cyclopentenones - Table II).

The above model can also be utilized for the internal hydrogen abstraction (Type II) process. It is known that both ketones<sup>12</sup> and thiones<sup>13</sup> undergo intramolecular hydrogen abstraction from the triplet states to produce the diradical 5 and 6 respectively. The Salem diagram for hydrogen abstraction from  $n, \pi^*$  states is topologically homeomorphic with that for cycloaddition by  $n, \pi^*$  state to ethylene. The efficiency of product formation from these diradicals differs drastically between ketones and thiones.<sup>12,13</sup> The efficiency of product formation in non-



polar solvents for ketone and thione triplet has been estimated to be  $10^{-1}$  and  $<10^{-4}$  respectively. In the latter case, the rate constant for internal hydrogen abstraction is not known. If it is similar to ketones ( $\sim 10^8$ ), the large inefficiency observed in the case of thiones is consistent with large spin-orbit coupling observed for thiones, so that the inefficiency may occur on the way to 6 rather than from 6.

In conclusion, we have pointed out the existence of a correlation between the efficiency of photocycloaddition and the experimental physical parameters which are related to the magnitude of spin-orbit coupling. It is of interest to note that the efficiency of photoreactions should no longer be judged simply from the behavior of the same diradical derived from different sources as an inefficiency may result prior to the formation of the diradical intermediate.<sup>14</sup> Finally, it must be noted that solvent may also play an important role in determining the efficiency of a reaction as the existence of crossing between surfaces is determined by the energies of  $T_1$ ,  $S_1$ ,  $^1D$  and  $Z$  which are sensitive to solvent polarity.

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