ISOMERIZATION OF PIPERYLENE

THE DEPENDENCE ON THE CONCENTRATION OF SENSITIZER

Chemistry 80 Thesis

by

Ronald Counsell

Director of Research: Dr. G. S. Hammond

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I appreciate the opportunity to have associated with scientists of the caliber of Dr. Hammond's research group.

Abstract

The data support the idea that the physical transfer of energy from certain sensitizers to piperylene is a reversible process. That similar behavior was observed for 2-acetonaphthone and fluorenone suggests either that in these cases the quenching process is so exothermic that the controlling factor is the decay processes of piperylene triplets; or that as E_t of the sensitizer changes from 53 kcal. to 60 kcal. all four excited piperylene configurations are important. The observed behavior for benzil might be attributed to incomplete data, but perhaps the photostationary states of this compound should be studied more closely.

DEPENDENCE OF THE ISOMERIZATION OF PIPERYLENE ON SENSITIZER CONCENTRATION

Introduction

The physical transfer of energy between molecules in solution is known to be very complex. To better understand this phenomenon, the possibility of reversible energy transfer between a sensitizer and an acceptor was investigated.

Results and Discussion

This experiment on the isomerization of piperylene investigated the dependence of the composition of the photostationary state on the concentration of the sensitizer. The results obtained support the conclusion that the transfer of energy from a sensitizer to piperylene is reversible. The isomerization involved is the following:

cis-piperylene

trans-piperylene

Preliminary investigation did indicate a definite concentration effect, and the results obtained for benzil, 9-fluorenone, and 2-acetonaphthone were very similar. The results for benzil and 2-acetonaphthone were almost identical. All concentrations of benzophenone yielded photostationary states in which the piperylene was fifty-five per cent trans.

Table I is presented for future reference with regard to the behavior of benzil. Values previously reported by Turro[1] were obtained at sensitizer concentrations of 0.05 M. My values are inferred from plots of per cent trans vs. log [S], where [S] indicates sensitizer concentration. The information for benzil is based on one observation of each concentration, after eight hours of irradiation. This may very well constitute insufficient evidence.

Benzil introduced the problem of consumption of both piperylene and the sensitizer, so the final experiments were performed with fluorenone and 2-acetonaphthone. Both pure cis- and pure trans-piperylene were used as starting materials. Benzene solutions of the sensitizer and diene were frozen, evacuated, and sealed into pyrex test tubes. The tubes were irradiated for 10-15 hours by a 450-watt lamp in a water-cooled quartz well. The whole apparatus was in a water bath maintained at 20-25°C. The irradiated solutions were analyzed by vapor phase chromatography.

The fact that the information in Table II can be represented by the equation

(1) $$\% \text{ trans} = \text{Constant} + \log [S]$$

caused a good deal of confusion. However, the results may be interpreted with the help of a mechanism similar to that used to correlate experimentally observed variations of the quantum yield of a reaction with the concentration of sensitizer[2] and with the composition of the photostationary state[1].

If all the light is absorbed, the following kinetic scheme is proposed, where S indicates a sensitizer molecule, S^* indicates an excited sensitizer, t indicates trans-piperylene, and c indicates cis-piperylene.

(2) $S \xrightarrow{h\nu} S^*$ (rate = I)

(3) $S^* \xrightarrow{kd} S$

(4) $S^* + t \xrightarrow{k_1} t^* + S$

(5) $t^* \xrightarrow{k_{1a}} t$

(6) $t^* \xrightarrow{k_{1b}} c$

(7) $c + t \xrightarrow{k_{1c}} c^* + t$

(8) $S + t^* \xrightarrow{k_{1d}} S^* + t$

(9) $\underline{S}^* + \underline{c} \xrightarrow{k_2} \underline{c}^* + \underline{S}$

(10) $\underline{c}^* \xrightarrow{k_{2a}} \underline{c}$

(11) $\underline{c}^* \xrightarrow{k_{2b}} \underline{t}$

(12) $\underline{t} + \underline{c}^* \xrightarrow{k_{2c}} \underline{t}^* + \underline{c}$

13) $\underline{S} + \underline{c}^* \xrightarrow{k_{2d}} \underline{c} + \underline{S}^*$

At the photostationary state Rate ($t \rightarrow c$) = Rate ($c \rightarrow t$)

$$(14)\quad R_{t \rightarrow c} = \frac{k_{1b}\, k_1\, [\underline{S}^*][\underline{t}]_s}{k_{1b} + k_{1a} + k_{1d}[\underline{S}]}$$

$$(15)\quad R_{c \rightarrow t} = \frac{k_{2b}\, k_2\, [\underline{S}^*]\, [\underline{c}]_s}{k_{2b} + k_{2a} + k_{2d}[\underline{S}]}$$

and

$$(16)\quad \frac{[\underline{t}]_s}{[\underline{c}]_s} = \frac{k_2 s_{2b}}{k_1 k_{1b}} \times \frac{k_{1b} + k_{1a} + k_{1d}\,[\underline{S}]}{k_{2b} + k_{2a} + k_{2d}\,[\underline{S}]}$$

$\underline{S}^*$ may or may not be able to transfer energy back to the dienes.

The assumptions that have been made are the following:

a) All light is absorbed. We see from the form of equation 21 that we will get the same answer regardless of the particular form of $I = I([\underline{S}])$.

b) There has been no consumption of piperylene. This is reasonable for large $[\underline{S}]$ where the photostationary state is reached quickly, and also for concentrations of sensitizer that are too dilute to be important in a chemical reaction.

c) $k_{1c} = k_{2c} = 0$

I have nothing to confirm this, but piperylene is expected to be a very inefficient sensitizer.

Table I

Composition of Photostationary States

Sensitizer	% t Counsell preliminary[a]	% t Counsell final	% t Turro[1]
Benzil	72	--	58
9-fluorenone	75	76	69
2-acetonaphthone	70	74	72
Benzophenone	56	--	57

[a]Starting with pure trans.

Table II

Dependence of Composition of Photostationary States on [S]

[S] (9-fluorenone)	% t from trans	% c from cis
1.0 M	82	83
10^{-1} M	79	78
10^{-2} M	66[c] 67[d]	66[c] 68[d]
10^{-3} M	69[c] 68[d]	62[c] (not at photostationary state)
10^{-4} M	64[c] 62[d]	
2-acetonaphthone		
1.0 M	78	84
10^{-1} M	76	75
10^{-2} M	75	71
10^{-3} M	67	69
10^{-4} M	70 (not at photostationary state)	

c irradiated for 10 hours.

d irradiated for 15 hours.

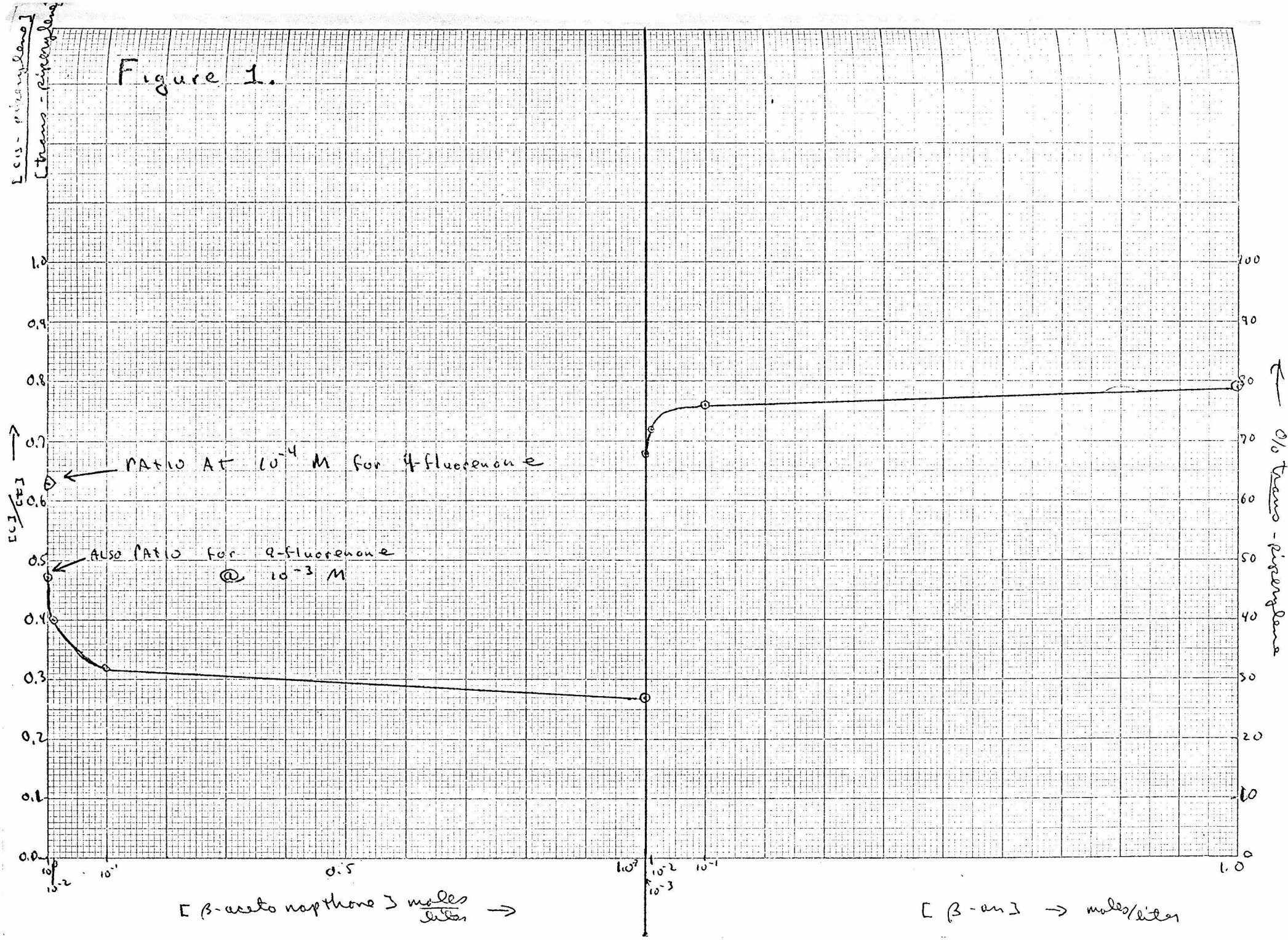
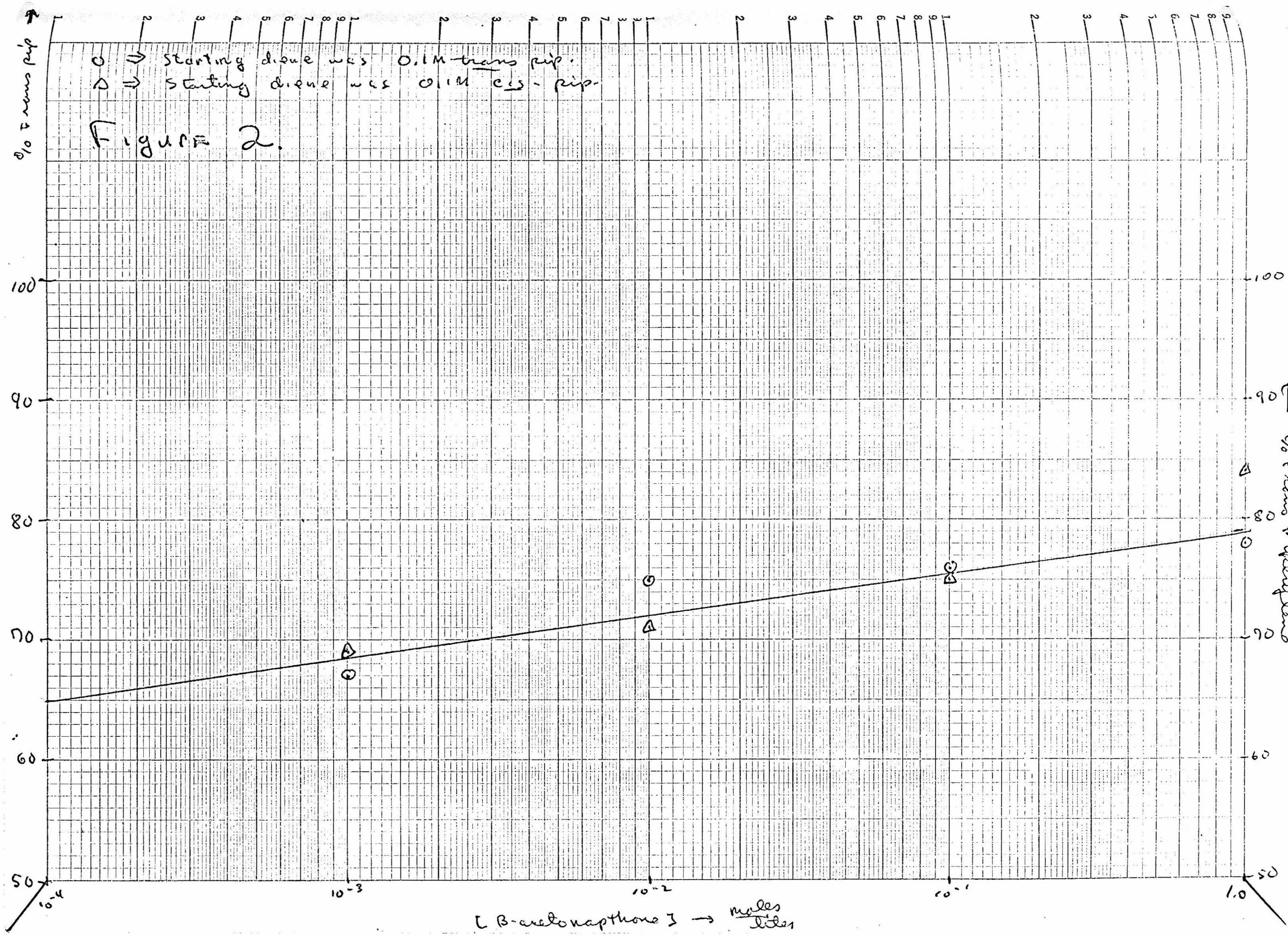
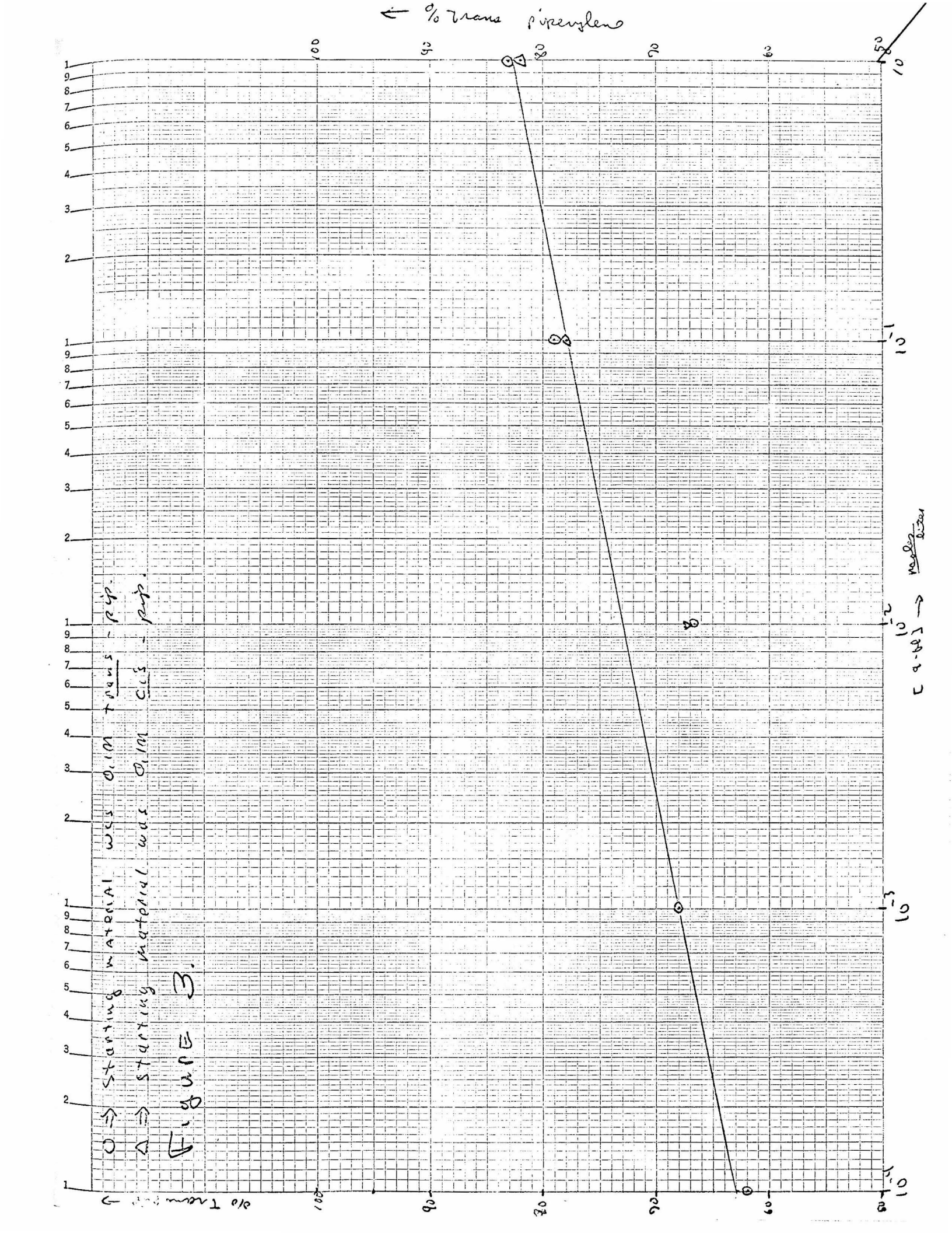


Figure 1.
[cis - piperylene] / [trans - piperylene]
RATIO AT 10^{-4} M for 4-fluorenone
ALSO RATIO for 9-fluorenone @ 10^{-3} M
[cis]/[trans]
% trans - piperylene
[β-aceto napthone] moles/liter
[β-an] → moles/liter
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
10
20
30
40
50
60
70
80
90
100
10^{-2}
10^{-1}
0.5
1.0
10^{-3}


○ ⇒ Starting diene was 0.1M trans pip.
△ ⇒ Starting diene was 0.1M cis - pip.
Figure 2.
% trans pip
100
90
80
70
60
50
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1.0
[B-acetonapthone] → moles/liter


← % trans piperylene
% Trans
Moles/liter →
○ ⇒ starting material was cis - pip.
△ ⇒ starting material was oil cis - pip.
Table 3.

d) I have excluded the equilibrium

(17) $$\underline{t}^* \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underline{c}^* .$$

If the triplets were in equilibrium, and if

$$R_{(t \rightarrow c)} = R_{(c \rightarrow t)}$$

as at the photostationary state, then changing the sensitizer concentration would not change the composition of the photostationary state. I have also ignored the possibility of

(19) $$\underline{S}^* + \underline{c} \longrightarrow \underline{t}^*$$

(20) $$\underline{S}^* + \underline{t} \longrightarrow \underline{c}^*$$

(21) $$\underline{S} + \underline{c}^* \longrightarrow \underline{t} + \underline{S}^*$$

(22) $$\underline{S} + \underline{t}^* \longrightarrow \underline{c} + \underline{S}^*$$

The exclusion of equations 19 and 20 is an immediate result of the Franck-Condon principle[3;(a)]. The occurrence of reactions 21 and 22, although improbable, would not change the form of equation 16.

From Figure 4 it can be seen that sensitizers with $T_1 \rightarrow S_o$[(b)] energies (i. e., E_t) of more than sixty kcal./mole produce the same photostationary state. It has been suggested that these sensitizers transfer energy to piperylene on every collision, whereas sensitizers with E_t less than sixty kcal. do not[1], that is, it is only for E_t greater than sixty kcal. that the transfer of energy is diffusion controlled. Below sixty kcal. the relative probability of sensitizing one isomer depends on the E_t of the sensitizer, and energy transfer to trans-piperylene becomes relatively inefficient as E_t decreases.

(a) Work in these laboratories indicates instances in which the lifetime of the excited state of one isomer is apparently so short that the Franck-Condon principle is disobeyed in the case of energy transfer.

(b) T_1 is the first triplet state and S_o is the ground singlet state.

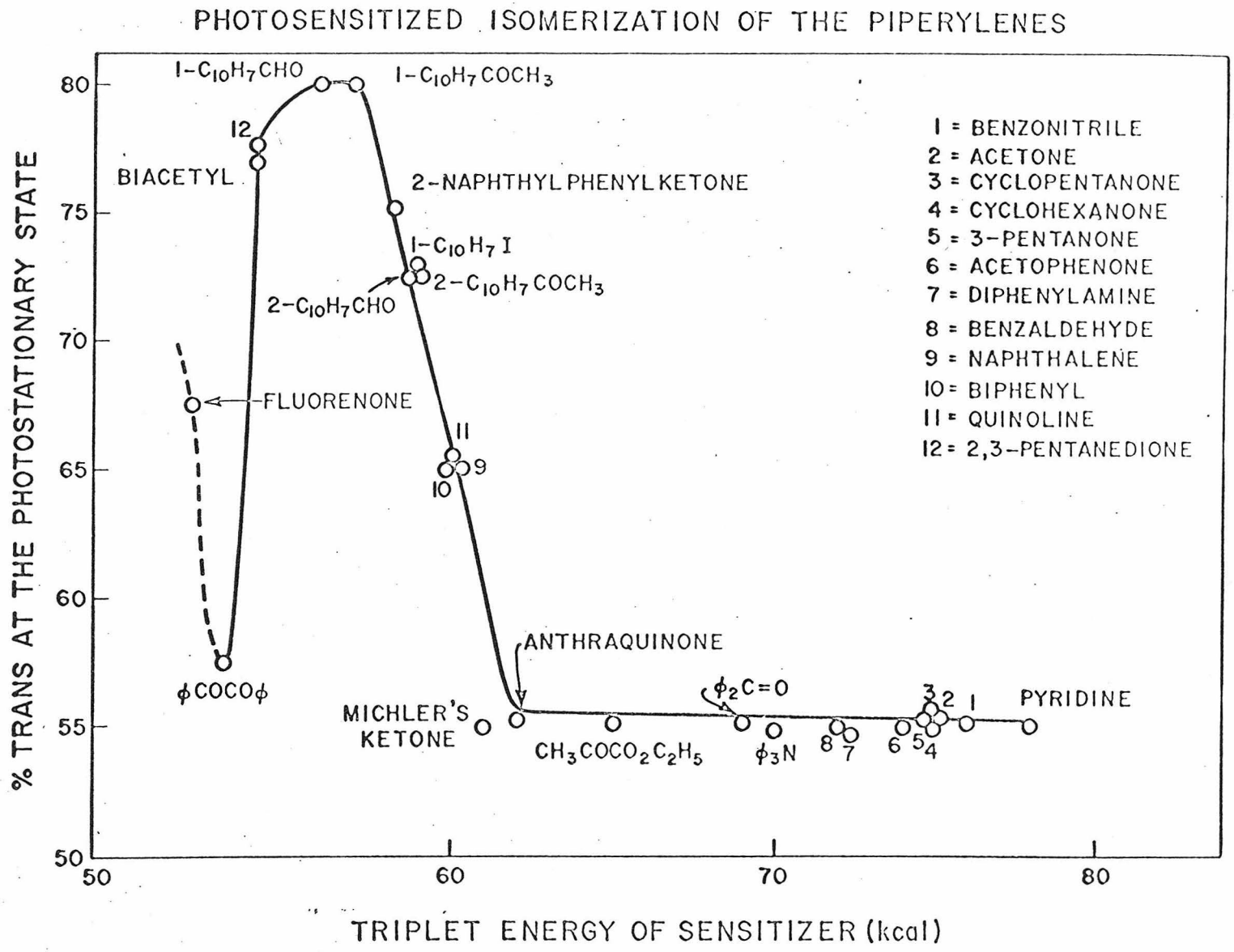


Figure 4 — From: Turro, N. J., thesis, Calif. Inst. of Tech., 1963

The conclusion that for E_t greater than sixty kcal. the photostationary state is dependent only on the decay processes of the triplets, can also be inferred from the kinetics. If the $T_1 \longrightarrow S_o$ transition of piperylene is insufficiently energetic, or if for any other reason $k_{1d} = k_{2d} = 0$ then the photostationary state is independent of the concentration of sensitizer. If the energy transfer is reversible, the photostationary state depends on quenching of piperylene triplets by the sensitizer. If quenching of trans-piperylene is more favorable, either because the triplet has a higher energy transition to the ground state, or because it has a longer lifetime than that of the cis-isomer, the photostationary state becomes richer in trans if the concentration of the sensitizer is increased. This can be seen by applying the extreme conditions $k_{1b} = 0$ and $k_{2b} = 0$ to equation 16. However, if E_t of the sensitizer decreases too much, excitation of piperylene is expected to become inefficient and no longer amenable to this analysis.

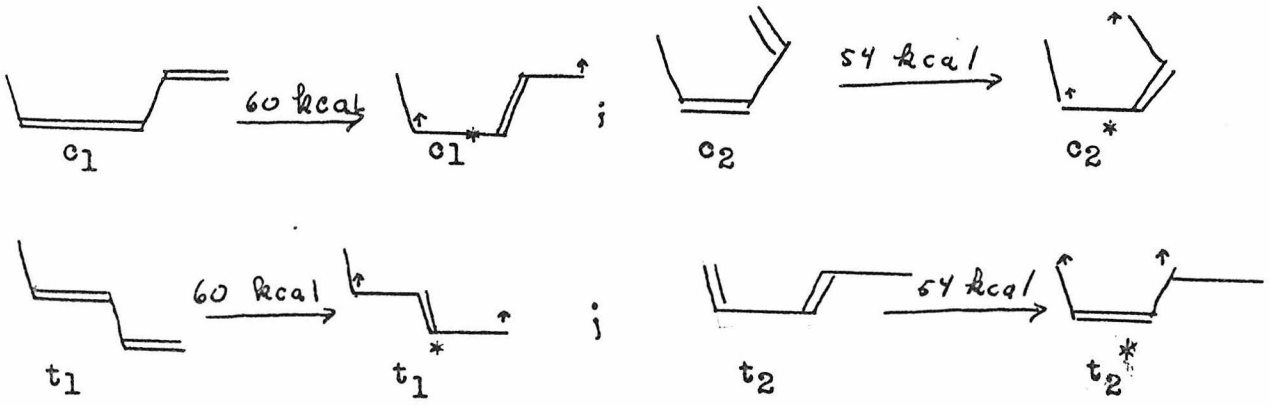
Experimental results indicate that the trans triplet is indeed being quenched more effectively, or that whatever is quenched decays to trans. At dilute concentrations, the photostationary state increases in trans richness very rapidly, but the trend levels off around 0.05 M S. This may be because the cis-isomer is not being quenched at low sensitizer concentrations, but is quenched at higher concentrations. At very high sensitizer concentrations the triplets would be quenched equally rapidly, and it is expected that the composition of the photostationary state will be constant because the photostationary state depends only on the energetics of excitation and on the decay processes of the triplets. It is probably only a confusing coincidence that the data follows equation 1.

Figure 4 can be interpreted on the basis of the energetics of sensitization. The hypothesis of irreversible energy transfer is consistent with the behavior

of sensitizers of E_t greater than sixty kcal., and reversible transfer is consistent with the observed dependence of the photostationary state on the concentration of certain sensitizers. An interesting conjecture is that as the concentration of moderately energetic sensitizers is decreased, the photostationary state will approach the composition observed for benzophenone, because the energy transfer again becomes irreversible. Piperylene triplets will decay via some path other than quenching by the sensitizer. However, if there is an appreciable energy difference between $\underline{t}^*$ and $\underline{c}^*$ then the particular composition depends also on the relative efficiencies of the two excitation processes.

Another observation to be explained is that the concentration dependence is the same, within experimental error, for both fluorenone and 2-acetonaphthone. (E_t for 2-acetonaphthone is 59 kcal.[4], E_t for fluorenone is 53 kcal.[5]) Related to this is the fact that four excited configurations of the dienes should be considered, although this discussion has only been concerned with two. Consideration of all these triplets in the kinetic scheme would still yield an expression for $[\underline{S}]$ linear in $[\underline{c}]$ and $[\underline{t}]$, although it might be more complicated. However, it might be interesting to mention them briefly.

$S_o \rightarrow T_1$ transitions are reported to occur at 59.6 kcal. for butadiene and 53.5 kcal. for 1.3-cyclohexadiene[6], and the values may be typical of the <u>trans</u> and <u>cis</u> configurations, respectively, of the excited states of dienes.[7]



In discussions I have heard, it is generally assumed that since the concentrations of $\underline{c}_1$ and $\underline{t}_1$ are probably much greater than the concentrations of $\underline{c}_2$ and $\underline{t}_2$, the former configurations are much more important. However, it may be that fluorenone can act as an effective sensitizer because excitation of the s-cis configurations become important.

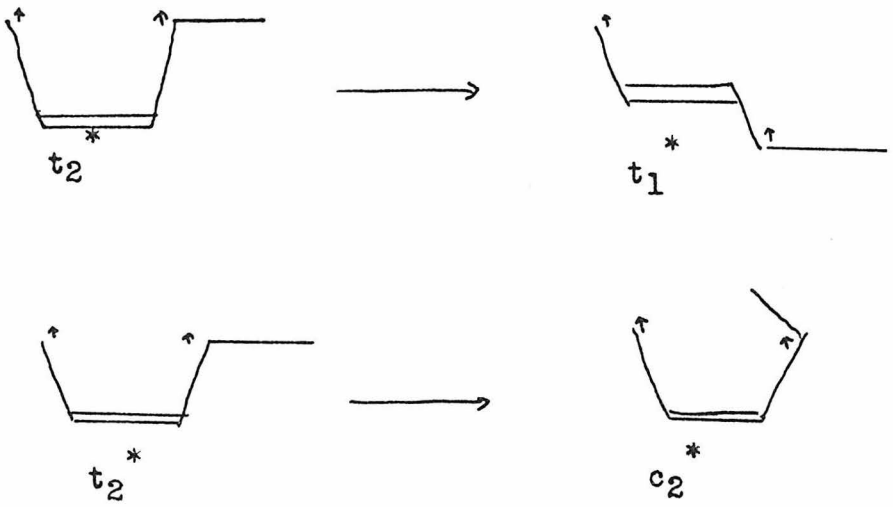
The similarity of behavior in the cases of fluorenone and 2-acetonaphthone argues for a quenching process so exothermic in these two cases that the photostationary state depends only on the decay process of the triplets. If the $S_o \longrightarrow T_1$ transition of the sensitizer were most important, one might be tempted to dismiss excitation of s-cis forms of the dienes. However, since there is nothing to indicate how quenching depends on the energetics of the system, the observed similarity does not constitute evidence for the predominance of the triplets of highest energy.

Another possibility is that the energy of the sensitizer is not as important for quenching as is the fact that the trans isomer may have a very long lifetime. A study of the photostationary states of 1-acetonaphthone and naphthalene or benzil might illuminate this point. When the data were plotted as, for example, % $\underline{t}$ vs. log [S], information might be derived from the relative slopes. If the lifetime of the triplet is the most important, the two graphs should be parallel. Unfortunately, if the difference in composition of the photostationary states is derived from the original excitation of piperylene, a difference in slope due to energy differences in quenching might be masked.

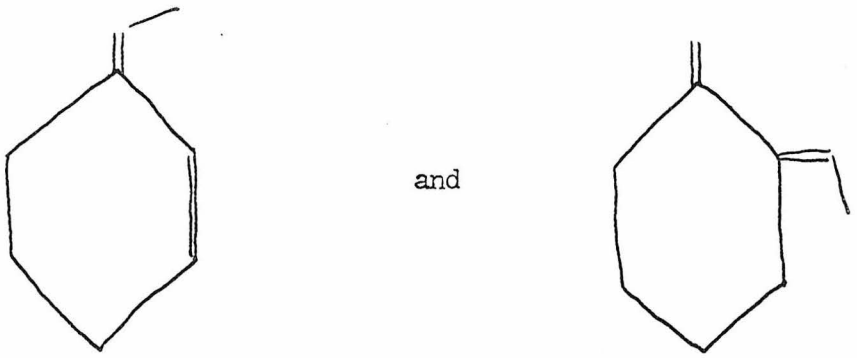
It is interesting to note that Figure 4 shows a decrease in trans-richness of the photostationary state as E_t decreases past 55 kcal. This might be explained by assuming that energy transfer becomes irreversible, or that for some reason the cis isomer is quenched more effectively, although I am not

prepared to defend these statements. Since the pronounced minimum at 54 kcal. is based only on benzil, perhaps the photostationary state of this compound should be investigated more thoroughly. If the photostationary state for 0.05 m benzil were approximately 70% trans, the above suggestions might be more interesting.

The discussion is complicated by ignorance of the energy barriers involved in changes of the following sort:



These could play an important role in the isomerization of piperylene, and work now in progress by Liu of these laboratories should be very interesting. Useful compounds for such a study are the following:



Experimental

Materials

Benzene--Mallinckrodt reagent, thiophene free, purified by vapor phase chromatography, followed by washing with H_2SO_4 and distillation. The benzene was stored over sodium wire in a brown bottle.

Benzophenone--Matheson, Coleman, and Bell reagent, recrystallized from hot hexane. m. p. 47-48°.

2-acetonaphthone--Eastman Kodak white label, recrystallized from hot ligroin. m. p. 53°.

9-fluorenone--Matheson, Coleman, and Bell reagent, recrystallized from hot ligroin. m. p. 83-84°.

Benzil--Matheson, Coleman, and Bell reagent, distilled at atmospheric pressure. b. p. 89-90°.

trans-piperylene--Matheson, Coleman, and Bell technical grade, b. p. 38-42°. The trans isomer was separated by preparative vapor phase chromatography on the Megachrome. The column was $AgNO_3/CH_2OHCH_2OH$, 6 ft. x 3/8 inches.

cis-piperylene--Matheson, Coleman, and Bell technical grade. The mixture was added slowly to an excess of maleic anhydride. This eliminated most of the trans, and the mixture was further purified on the Megachrome, on a 6 ft. x 5/8 in. Apiezon J column.

Procedure: Solutions 1.0 M in sensitizer were prepared with carefully weighed samples of sensitizer. More dilute solutions were prepared by diluting stock solutions of 0.5 M sensitizer in benzene, adding enough piperylene to make the solution 0.1 M in diene. The solution was added to a constricted pyrex test tube, frozen and degassed once, and then sealed into the evacuated tube. The samples were strapped to the outside of a water-cooled quartz well, and the apparatus was immersed in a 20-25° water bath. The sample was irradiated by a Hanovia medium-pressure 450-watt lamp for 10-15 hours.

The irradiated samples were analyzed by vapor phase chromatography. The columns used were 4.8 ft. x 1/8 inch, packed with 2.5 ml of β, β' - oxydipropionitrile at the inlet side and 2.3 ml of saturated $AgNO_3$ on ethylene glycol at the outlet. These columns enabled one sample to be analyzed every hour or so, so a manifold was constructed to allow nitrogen to be blown through two such columns while a third was being used.

The chromatograph used was a Loenco model 15B with thermocouple detector.

In most cases the criterion for the photostationary state was that samples starting from pure cis and from pure trans had reached the same composition. However, there was not enough cis-piperylene for the 10^{-4} M samples, so the criterion here was that two successive trans samples had reached the same composition.

Footnotes

[1]N. J. Turro, Ph. D. thesis, Calif. Inst. of Tech., 1963.

[2]W. R. Moore, G. S. Hammond, and R. P. Foss, J. Am. Chem. Soc., 83, 2789 (1961)

[3]G. M. Barrow, Introduction to Molecular Spectroscopy, McGraw-Hill, New York, 1962, p. 233.

[4]G. N. Lewis and M. Kasha, J. Am. Chem. Soc., 66, 2100 (1944).

[5]Mr. Jack Saltiel, private communication.

[6]D. F. Evans, J. Chem. Soc., 1735 (1960).

[7]G. S. Hammond and R. S. Liu, J. Am. Chem. Soc., 85, 477 (1963).