THE MECHANISMS OF PHOTOREACTIONS IN SOLUTION. IX. ENERGY TRANSFER FROM THE TRIPLET STATES OF ALDEHYDES AND KETONES TO UNSATURATED COMPOUNDS[1]

By George S. Hammond, Nicholas J. Turro, and Peter A. Leermakers

Contribution No. 2783 from Gates and Crellin Laboratories, California Institute of Technology, Pasadena, California

Received January 2, 1962

cis ⇌ *trans* isomerization of the piperylenes, the 1,2-dichloroethylenes, and the 2-pentenes can be effected by irradiation in the presence of photosensitizers. Various carbonyl compounds have been used as sensitizers and the results form a coherent pattern if it is assumed that the key step in the photochemical reactions is transfer of triplet excitation. Presently available results indicate that transfer of energy probably occurs on every collision between a triplet and a second molecule if the transfer is exothermic. Endothermic transfers may occur but with reduced efficiency.
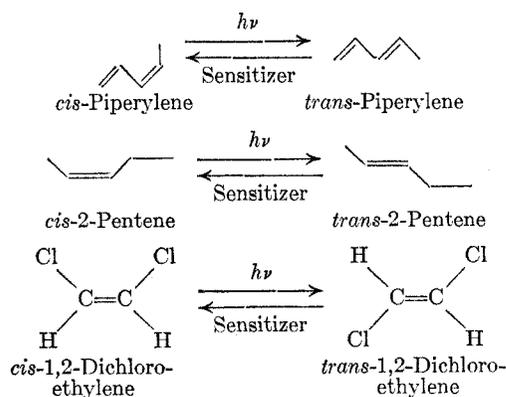
Recent work indicates that irradiation of several aromatic ketones and aldehydes in solution at ordinary temperatures produces triplet states of the carbonyl compounds in high quantum yield.[1-3] Among the interesting consequences of this fact is the possibility of making triplet states of other molecules by direct transfer of energy from carbonyl triplets to some second molecule.[3-7] Such an indirect path for the production of triplet states may be uniquely useful for two reasons. First, the quantum yield of triplets produced by direct irradiation may be low, or even vanishingly small, simply because the excited singlet states of many molecules decay directly to the ground singlet states without passing through triplet states. Such a case was observed in the study of the photolysis of ethyl pyruvate.[5] The quantum yield for decomposition sensitized by benzophenone was twice as large as the quantum yield in direct photolysis. The second advantage of the use of sensitizers in the production of triplets derives from the fact that the separation in energy between singlet and triplet states may vary widely from one system to another. Figure 1 illustrates the point using the comparison of benzophenone and a linear diene as an example. The $S_0 \rightarrow S_1$ transition of benzophenone has a maximum close to 3450 Å. and the phosphorescence spectrum has a maximum at 4100 Å.[8]; there is only a small separation between S_1 and T_1. On the other hand, the $S_0 \rightarrow S_1$ transition of conjugated, open-chain dienes has a maximum in the vicinity of 2300 Å. and T_1 lies in the vicinity of 4800 Å. The latter conclusion was reached by Evans[9] by study of the $S_0 \rightarrow T_1$ absorption of butadiene and isoprene in the presence of a high pressure of oxygen. The same conclusion

concerning the location of the triplet states of dienes can be adduced from the studies reported in this paper and communicated earlier in brief form.[6]

A consequence of the situation described in Fig. 1 is the possibility that the triplet state of a diene can be produced by irradiation with long wave length light which is not absorbed by the diene. As will be shown in this and subsequent papers, study of such phenomena can shed light on a variety of significant phenomena, *e.g.*, estimation of the energy levels of the triplet states of both donors and acceptors, clarification of the mechanisms of photochemical reactions, and increasing our understanding of the process of excitation-transfer. There will obviously be many cases in which photoreactions which would be difficult or impossible to carry out by direct irradiation can be run conveniently using light of relatively long wave lengths.

Results and Discussion

We have chosen *cis–trans* interconversion of the piperylenes (1,3-pentadienes), 2-pentenes, and 1,2-dichloroethylenes as convenient chemical processes for detection of energy transfer from triplet states of various sensitizers to unsaturated molecules. The most extensive work has been done with piperylenes.

Benzene solutions containing *cis*-piperylene and various aldehydes and ketones were irradiated using a medium-pressure mercury arc. Vapor chromatography was used to follow the production of *trans*-piperylene. In most instances the system reached a photostationary state after a few hours of irradiation. In one experiment pure

(1) (a) Presented at the International Symposium on Reversible Photochemical Processes, Durham, North Carolina, April, 1962; (b) Part VIII of the series is K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 1015 (1962).

(2) G. S. Hammond and W. M. Moore, *ibid.*, **81**, 6334 (1959); G. S. Hammond, W. M. Moore, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

(3) H. L. J. Bäckstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

(4) G. O. Schenck and R. Steinmetz, *Tetrahedron Letters*, No. **21**, 1 (1960).

(5) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2395 (1961).

(6) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *ibid.*, **83**, 2396 (1961).

(7) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, **83**, 2398 (1961).

(8) G. N. Lewis and M. Kasha, *ibid.*, **66**, 2100 (1944).

(9) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

trans-piperylene was used with benzophenone as a sensitizer. Conversion to the *cis* isomer was observed and at the termination of the experiment the *trans/cis* ratio was slightly higher than that observed in the experiments in which the *cis*-diene was used as a starting material. The result implies that the photostationary condition may not have been completely achieved in all experiments; however, the data reported in Table I all are derived from experiments in which conversions had become very slow; therefore, the tabulated values are at least close to those for the true photostationary states.

Two striking results emerge. First dibenzalacetone and 9-anthraldehyde, which have very low-lying triplet states, are completely inert as sensitizers; second, *different sensitizers give different photostationary mixtures.* Many hypotheses can be developed to account for these results and it seems inappropriate at this time to discuss all of the possibilities which come to mind. However, the trend suggests that a major controlling variable is the energy level of the lowest triplet state of the sensitizer. We have inferred from data reported elsewhere[10] that excitation transfer from benzophenone triplets to *cis*-piperylene is a diffusion-controlled process. It is reasonable to assume that the same is true of the transfer from benzophenone triplets to *trans*-piperylene. This implies that transfer is essentially a Franck–Condon process; *i.e.*, there is essentially no change in the nuclear position during the actual transfer. The planar triplet states of the dienes produced in this manner would, therefore, be formed in excited vibrational states and would decay by vibrational cascade to one or more unknown twisted forms.[11] Ultimately the triplets will return to their ground singlet states by thermal degradation. The latter process will produce the *cis* and *trans* isomers of piperylene in some ratio which cannot be predicted on any *a priori* basis. The data in Table I show that those compounds which have triplets lying 70 kcal. or more above their ground states produce photostationary mixtures in which the *trans/cis* ratio is about 1.25. The postulate which most easily accommodates this fact is the view that all of these sensitizers transfer energy to piperylene in diffusion-controlled reactions and that the factor 1.25 represents the natural[13] decay ratio. Presumptive evidence that the decay process is not influenced by the sensitizer was obtained in the case of benzophenone. Solutions containing 0.2 *M* piperylene and 0.05, 0.01,

(10) G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).

(11) The stable configuration of the lowest triplet state of linear dienes is unknown. However, the great stabilization (~20 kcal.) of the perpendicular form of ethylene[12] suggests that diene triplets probably will suffer distortion from planarity. Because twisting will sacrifice resonance energy, the actual configuration probably will be some compromise between planar and perpendicular configurations.

(12) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

(13) The term "natural" is used to indicate the *trans/cis* ratio produced by decay of piperylene triplets undisturbed by external influences. Even if our belief that the decay ratio is not influenced by the sensitizer is completely correct, the results still may not show the "natural" ratio. It is entirely possible that solvent effects on the decay process will be significant. Study of this problem is in progress.
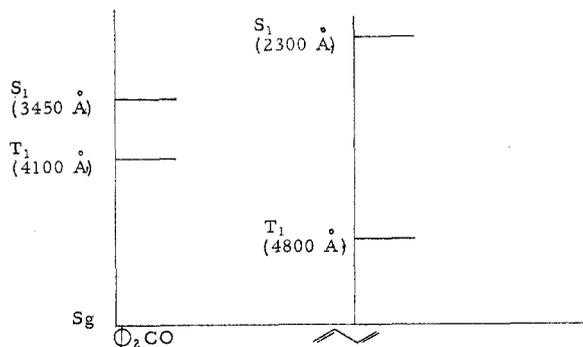

Fig. 1.—Correlation of the excited states of benzophenone and linear, conjugated dienes.

and 0.001 *M* benzophenone were irradiated for long periods of time. Although the rate of isomerization decreased as the concentration of sensitizer was decreased, the same photostationary state was ultimately reached in each of the experiments. This result implies that the fate of the piperylene triplets is not influenced by formation of complexes with the sensitizer.[14]

The failure of dibenzalacetone and 9-anthraldehyde to function as sensitizers almost certainly indicates that the triplets derived from them have insufficient energy to promote either of the isomeric piperylenes to triplet states. This clearly marks the $S_0 \rightarrow T_1$ transition of the piperylenes as requiring more than 53 kcal.; *i.e.*, the transition lies at wave lengths shorter than 5400 Å. This conclusion is in good agreement with the observations of Evans,[9] who assigned the O → O band of the $S_g \rightarrow T_1$ transition of butadiene at 4800 Å.

What, then, is responsible for the interesting variations in the photostationary states established in the presence of sensitizers which have triplets lying between 53 and 70 kcal. above their ground states? Scrutiny of the data reveals that there is a monotonic relationship between decreasing energy of the triplets and increasing *trans/cis* ratio at the steady state. A simple hypothesis can be advanced to account for this relationship. *If the excess energy of the ground vibrational T_1 state of the sensitizer is less than the energy of the O → O component of the $S_0 \rightarrow T_1$ transition of the receiver, excitation-transfer will be an endothermic process and will, presumably, begin to become measureably inefficient.* There is no reason to expect the efficiencies of the transfer processes involving the *cis*- and *trans*-dienes to decrease at the same rates. The data indicate that transfer to the *trans* isomer becomes inefficient more rapidly than does transfer to the *cis* isomer. If the energetics of the transfer process were the only controlling factor, we would conclude that the $S_0 \rightarrow T_1$ transition of *trans*-piperylene lies at slightly shorter wave length than the same transition of the *cis* isomer; furthermore, the singlet–triplet transitions of both isomers lie between 4600 and 5400 Å.

If the inferences are correct, the method provides

(14) The extreme opposite point cannot be rigorously excluded; *i.e.*, if complexes of very great stability were formed between the carbonyl compound and piperylene triplets, all of the triplets might be complexed even though the concentration of the former is very low. Semi-intuitive reasoning makes such a condition seem unlikely, especially so since a large number of sensitizers give *trans/cis* ratios close to 1.25.

an easy means for estimation of energy levels of the triplet states of compounds for which phosphorescence data are unavailable. Cases in point are acetone, phenanthrenequinone, and fluorenone. The data in Table I indicate tentative assignment of the energies of the triplet states of these compounds as >70, ~65, and ~62 kcal., respectively.

TABLE I

ISOMERIZATION OF cis-PIPERYLENE[a]

Sensitizer	E_T of sensitizer, kcal.[b]	trans/cis ratio at stationary state
Acetophenone	74	1.23
Benzaldehyde	72	1.23
Acetone	?	1.23
Butanone	?	1.23
3-Pentanone	?	1.23
Cyclohexanone	?	1.23
Cyclopentanone	?	1.23
Benzophenone	70	1.30
Anthraquinone	?	1.30
Ethyl pyruvate	~68	1.35
Phenanthrenequinone[c]	?	1.65
Fluorenone	?	1.95
Benzil[d]	62	2.15
2-Acetonaphthone	59	2.55
2.3-Pentanedione	53	3.10
Biacetyl	56	10–13
1-Naphthaldehyde	57	10–13
Dibenzalacetone[d]	53	No reaction
9-Anthraldehyde	~40	No reaction
Salicylaldehyde	~70	No reaction
p-Hydroxybenzaldehyde	?	1.2
o-Methoxybenzaldehyde[d]	?	1.2
2,4-Dihydroxybenzophenone	?	No reaction
2-Hydroxybenzophenone-4-methoxy	?	No reaction

[a] Benzene solutions, 0.1 M in sensitizer and olefin. [b] Ref. 8 except that those marked ~ are estimated by us. [c] Ratio of peak heights in chromatograms of incompletely separated mixtures. [d] Olefin slowly consumed during reaction.

The last five entries in Table I show the results of a preliminary study of compounds containing o-hydroxybenzoyl groups. Such compounds, notably o-hydroxybenzophenone and its derivatives, are widely used as photostabilizers; i.e., when incorporated in materials such as films and fibers they often afford prolonged protection against photochemical degradation. Three compounds: salicylaldehyde, 2-hydroxybenzophenone, and 2,4-dihydroxybenzophenone containing the characteristic structure were studied and found to be completely inactive as sensitizers for the isomerization of the piperylenes. In contrast, both p-hydroxybenzaldehyde and o-methoxybenzaldehyde were very effective sensitizers. From these facts we infer that the excited states of compounds containing the o-hydroxybenzoyl group either (1) are not degraded by way of triplet states, or (2) give triplet states incapable of transferring energy to the dienes.
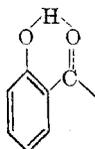
The phenomenon seems to be associated with the presence of internal hydrogen bonds.

The presence of such a structure may favor the $S_1 \rightarrow S_0$ degradation relative to intersystem crossing ($S_1 \rightarrow T_1$). The effect might be due to disturbance of usual relationships between $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excited states or it might be due to the existence of special, chemical implementation of the $S_1 \rightarrow S_0$ process.[15]

Alternatively, the triplet states of the hydrogen bonded molecules might be very short lived or might have very low energies.[17]
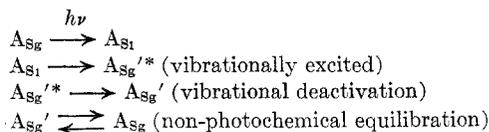
Endothermic Transfer Reactions.—Evans[9] located the O–O band of the $S_0 \rightarrow T_1$ absorption spectrum of ethylene at 3480 Å. (80 kcal. mole^{-1}). Consequently we anticipated that transfer of excitation from the triplet states of most carbonyl compounds to unconjugated alkenes would be rather inefficient. Such has proven to be the case. Irradiation of benzene solutions containing cis- or trans-2-pentene and sensitizers such as acetone, benzophenone, or acetophenone effects very slow isomerization. Prolonged irradiation produces in each case mixtures which appear to be fairly close to photostationary states since similar compositions are obtained starting with either isomer. Benzil and fluorenone cause very slow isomerization of cis-pentene. 2-Acetonaphthone

TABLE II

PHOTOSENSITIZED ISOMERIZATION OF 2-PENTENES

Sensitizer	Starting material	trans/cis Ratio after various times of irradiation[a] 2 days	5 days	8 days
Acetone[b]	cis-2-Pentene	0.8	~1.9	1.7
Acetone[b]	trans-2-Pentene	2.2	1.91	1.9
Benzophenone	cis-2-Pentene	3.6	6.1	..
Benzophenone	trans-2-Pentene	7.8	7.7	6.6
Acetophenone	cis-2-Pentene	..	3.2	3.6
Acetophenone	trans-2-Pentene	7.1	5.2	4.6 (10 days—3.9)
Benzil	cis-2-Pentene	0.16	0.3	0.8
Fluorenone	cis-2-Pentene	..	0.15	0.18

[a] Reaction run in parallel to effect approximate equivalence of illumination. [b] Reaction run in neat acetone.

(15) For example, tautomers of the parent structure may be produced. Conversion of an excited singlet of a molecule, A, to a vibrationally excited, ground singlet of an isomer, A', may provide a fast route for non-irradiative decay of excited states.

$A_{S_g} \xrightarrow{h\nu} A_{S_1}$

$A_{S_1} \longrightarrow A_{S_g}'*$ (vibrationally excited)

$A_{S_g}'* \longrightarrow A_{S_g}'$ (vibrational deactivation)

$A_{S_g}' \rightleftarrows A_{S_g}$ (non-photochemical equilibration)

In order for such a mechanism to have any significance in the case at hand, it would be necessary to assume that the tautomer, A', is the non-hydrogen bonded, trans-enol.[16]
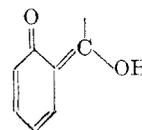
(16) See N. C. Yang, J. Am. Chem. Soc., 83, 2213 (1961), for evidence that a formally similar reaction occurs with o-methylacetophenone.

(17) The compounds in question have relatively low lying $\pi-\pi^*$ singlet states since the compounds have intense maxima ($E \sim 20,000$) near 3500 Å. Consequently the lowest triplets of these molecules may have the $\pi-\pi^*$ configuration and lie at low energy levels. See reference 18 for a discussion of a similar problem.

(18) G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc., 84, 207 (1962).

is no sensitizer. The data are summarized in Table II.

Somewhat similar results were obtained with the isomeric 1,2-dichloroethylenes. A number of the higher energy sensitizers produced mixtures which apparently were photostationary. The results are given in Table III. There are, however, interesting contrasts between the experiments obtained with the pentenes on the one hand and with the dichloroethylenes on the other. Experiments run in parallel in which the two compounds were irradiated in acetone solution indicated that the rate of sensitized isomerization of cis-2-pentene was somewhat, but not a great deal, more rapid than the rate of isomerization of trans-1,2-dichloroethylene. In contrast the dichloroethylenes isomerized much more rapidly than the pentenes in the presence of low energy sensitizers such as fluorenone and benzil. These results show that factors other than energy balance must be important in determining the efficiencies of some of the energy transfers. Further study of the problem is in progress.

<div align="center">

TABLE III

Photosensitized Isomerization of trans-1,2-Dichloroethylene

</div>

Sensitizer[a]	cis/trans in photostationary mixtures
CH$_3$COCH$_3$	~2.1
CH$_3$COC$_6$H$_5$	3.1
C$_6$H$_5$COC$_6$H$_5$	4.5
C$_6$H$_5$COCOC$_6$H$_5$	4.0–4.1
β-C$_{10}$H$_7$COCH$_3$	No reaction
Fluorenone	2.5[b]

[a] Benzene solutions, except for acetone which was used without solvent. [b] Reaction ceased because of build up of quenchers in the solution.

Lewis and Kasha[3] reported that trans-1,2-dichloroethylene phosphoresces with a O–O band at 3970 Å. (72 kcal.). This position seems anomalously low and conceivably could be due to the presence of impurities; the suspicion is increased by the report that the corresponding dibromo- and diiodoethylenes have almost the same phosphorescence as the dichloro compound. If the assignment is correct, transfer of energy from the triplets of acetone and acetophenone to dichloroethylene would be exothermic and might be expected to be diffusion-controlled. The fact that isomerizations sensitized by the two ketones arrive at different photostationary states is inconsistent with this view. The rates of isomerization of dichloroethylenes are clearly less than the rates of isomerization of piperylenes under similar conditions. This result, in itself, does not compel the conclusion that energy transfer is inefficient since the latter conclusion may be adduced from the recent report of Cundall and Milne,[19] who observed that dichloroethylenes induce isomerization of the 2-butenes in the vapor phase with concomitant quenching of the isomerization of the former. It is very likely that there is a significant barrier to rotation in the triplets of the dichloroethylenes. This is consistent with the view that the lowest triplet of dichloroethylene has considerable $n \rightarrow \pi$ character; i.e., :Cl–CH = CHCl:. Such a configuration should stabilize the planar configuration relative to the perpendicular form.

Experimental

Analysis.—All mixtures were analyzed by vapor chromatography. In every case it was possible to prepare a column which would separate the pairs of cis–trans isomers. Columns used to accomplish such separations were: piperylene, 12 ft. of dimethylsulfalone (20%) (separation not complete); 2-pentenes, 12 ft. silver nitrate in ethylene glycol or 12 ft. β,β'-oxydipropionitrile (25%); 1,2-dichloroethylenes, 12 ft. Apiezon J or 12 ft. β,β'-oxydipropionitrile (25%).

All experiments reported in this paper were carried out using a Hanovia quartz immersion reactor. In the experiments with piperylene a filter having a cutoff at 2800 Å. was used. Other experiments were carried out with unfiltered light. In experiments designed to establish photostationary states solutions were placed in quartz or Pyrex cells designed for use in the Beckman DU spectrophotometer. The cells were strapped to the inner jacket of the reactor. This technique allows several experiments involving prolonged irradiation to be carried out simultaneously; however, the procedure also makes comparison of rate data inaccurate because the conditions of illumination are not exactly reproducible.

All reactions were run in benzene solution unless otherwise indicated. The concentration of both sensitizer and olefin was approximately 0.1 M in most experiments.

(19) R. B. Cundall and D. G. Milne, J. Am. Chem. Soc., 83, 3902 (1961).

(20) D. Craig, ibid., 65, 1006 (1943).