

DECOMPOSITION OF DIOXETANES: A UNIQUE PROBE INTO MECHANISM AND ENERGY TRANSFER PROCESSES†

CHRISTOPHER S. FOOTE and THOMAS R. DARLING

*Department of Chemistry, University of California,
Los Angeles, California 90024, USA*

ABSTRACT

3,4-Dimethyl-3,4-di-*n*-butyl-1,2-dioxetane breaks down thermally to give singlet excited 2-hexanone (5 per cent) and triplet 2-hexanone (3.5 per cent). This is in contrast to the very high yield of triplet acetone reported from tetramethyl dioxetane. The yields of excitation products are determined by measurement of the amounts of Norrish Type II photochemical products from 2-hexanone. The results are confirmed by quenching of the thermal process with 1,3-hexadiene. Photolysis of the dioxetane (> 369 nm) gives 4 per cent singlet 2-hexanone and 2.2 per cent triplet. The results are consistent with either a diradical intermediate or a concerted process of a very unusual type.

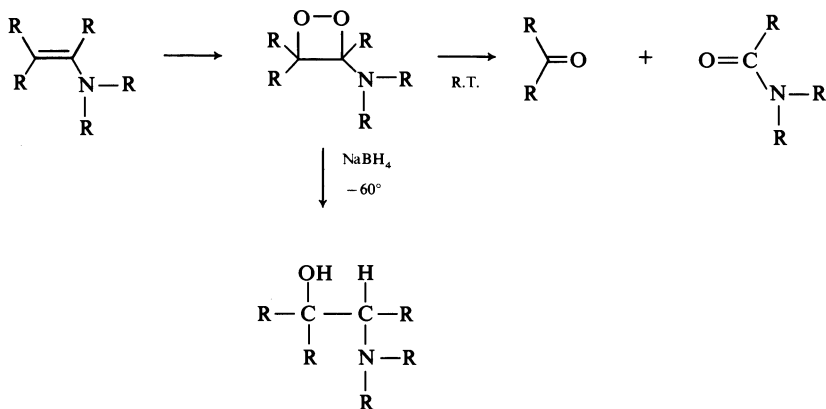
Photosensitized decomposition of this dioxetane produces an intriguing variation in the yields of photochemical product. The product ratio is characteristic of triplet and ground state product formation only; no excited singlet is produced. The highest yield of product is formed with biacetyl. Higher and lower energy sensitizers give less of the triplet product and more ground state product. The reasons for this seem to differ; the lower energy sensitizers produce very little excited state. The higher energy sensitizers quantitatively give triplet 2-hexanone as a product, but energy transfer from this excited product back to ground state sensitizer is very rapid. The rates of this process have been measured and exceed the diffusion-controlled rate, which suggests that the back transfer occurs within a solvent cage. The effect of solvent viscosity is consistent with this assumption. By this technique, rates of energy transfer exceeding 10^{12} s^{-1} have been determined. The dependence of this rate on energy separation shows that the intrinsic rate of energy transfer falls off as the gap between the donor and acceptor increases. The formation of sensitizer and acceptor within the solvent cage permits these exceedingly high rates to be measured directly. This system thus provides a unique probe for energy transfer mechanisms.

INTRODUCTION

Interest in 1,2-dioxetanes has grown rapidly in recent years. Our first entry into this area involved a study of the photosensitized oxidation of enamines^{1,2}. In this study, several enamines were found to undergo smooth 1,2-cycloaddition of singlet oxygen; at room temperature, products were isolated in which the CC double bond had been cleaved. That there was an

† Contribution No. 3355 from UCLA Department of Chemistry, supported by the National Science Foundation Grant No. GP-37165.

unstable intermediate in the reaction was demonstrated by photooxidation at low temperature followed by sodium borohydride reduction in the cold; from this process, β -hydroxyamines were isolated in excellent yield. We considered several structures for the intermediates, including dioxetanes; however, the n.m.r. spectra of the adducts were too complex for purely monomeric dioxetanes, and we concluded that polymeric species were present. Subsequent repetition of these experiments with careful control of concentration and temperature produced aminodioxetanes which, although they decomposed below room temperature, were subjected to low temperature cryoscopic molecular weight determination and found to be monomeric³. Their n.m.r. spectra were also consistent with formulation as monomeric dioxetanes.

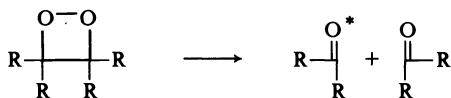


At the time the initial work was done¹, monomeric dioxetanes had not been isolated. Very shortly thereafter, however, Kopecky showed that dioxetanes could be made by the addition of positive halogen sources to olefins in the presence of concentrated hydrogen peroxide followed by treatment with base⁴. Richardson and his group also made important contributions in this area⁵. Then vinyl ethers were soon found to add singlet oxygen smoothly to give a variety of alkoxydioxetanes⁶. In addition, a few hydrocarbons have been found to give 1,2-cycloaddition with singlet oxygen to give dioxetanes⁷.

From the beginning, the cleavage of these dioxetanes has been of considerable interest. Numerous chemiluminescent processes are known which appear to involve dioxetanes as intermediates⁸. Several bioluminescent reactions are also believed to involve similar species^{8,9}. In addition, certain enzymatic cleavages seem to involve formal processes of the same type¹⁰. On orbital symmetry grounds, McCapra suggested that 1,2-dioxetanes should give electronically excited products on breakdown, since the reverse $2 + 2$ cycloaddition reaction is a forbidden process¹¹.

Virtually all of the dioxetanes which have been produced have been found to break down with chemiluminescence; since the products themselves

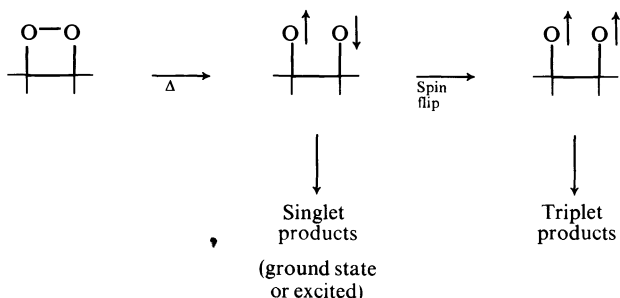
DECOMPOSITION OF DIOXETANES



are often not luminescent, a luminescent excitation acceptor is frequently added. Total luminescence yields have usually been very low, although Wilson and Schaap demonstrated an apparent excitation yield from 3,4-diethoxy-1,2-dioxetane near 100 per cent; however, the method used was indirect and subject to several assumptions¹². White was the first to trap the excitation energy produced by the breakdown of dioxetanes in the form of new chemical bonds, thus carrying out a form of photochemistry without light¹³. Excitation yields (uncorrected for possible quenching) of only a few per cent from various alkyl and aryl dioxetanes were reported.

Recently, Turro and his group have carried out extensive work in this area¹⁴. In 1972, Turro and Lechtken reported on the basis of several different types of evidence, that tetramethyldioxetane breaks down to give acetone, of which about 50 per cent is in the lowest triplet state, a trace in the lowest excited singlet state, and the remainder in the ground state¹⁵. They interpreted these results on the basis of a concerted process involving a coupling between a molecular motion during the cleavage and a spin flip, thus accounting for the fact that so much triplet was produced. A concerted process involving spin inversion is quite unusual, however.

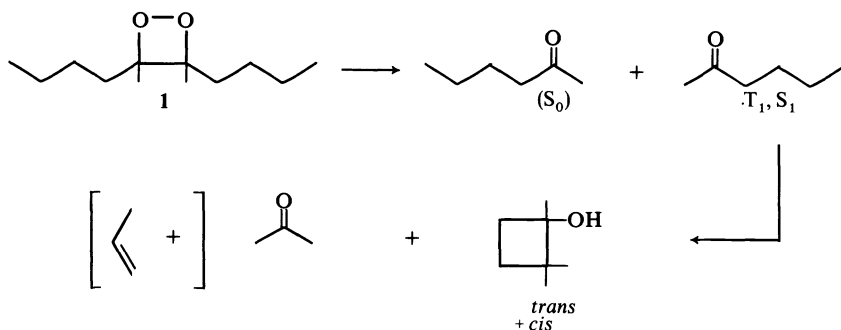
Richardson has interpreted his results and those of others as being consistent with initial cleavage of the O—O bond to give a 1,4-diradical, initially in a singlet state, which can undergo intersystem crossing, giving a triplet diradical; breakdown from these two diradical species gives products in the ground or first excited singlet, or in the triplet state, respectively¹⁶. Richardson has shown that this process is consistent with the expected thermochemical behaviour of the system. In particular, the activation energy for dioxetane decomposition is very close to the energy calculated to break the O—O bond, taking the ring strain into account.



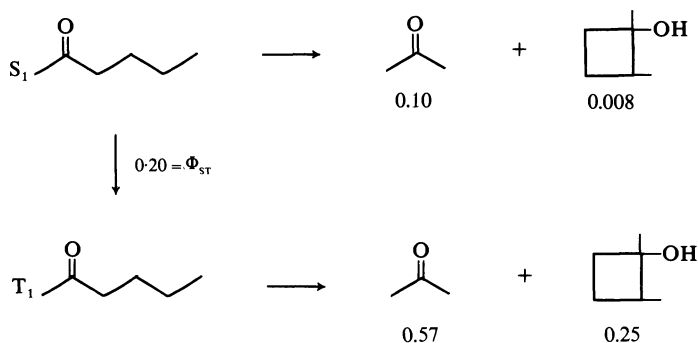
Richardson also found excitation yields of only a few per cent, using a chemical probe for excited states¹⁷. He interpreted this as consistent with a diradical intermediate.

We had been attempting for some time to design a system which contained

an intramolecular probe for excitation, and were finally able to prepare a suitable compound, 3,4-di-*n*-butyl-3,4-dimethyl-1,2-dioxetane(1)¹⁸. This compound would be expected to undergo thermal cleavage to give 2-hexanone in its ground or various excited states.



The excited state chemistry of 2-hexanone has been extensively studied, and involves a very rapid Norrish Type II process to give acetone and propylene along with 1,2-dimethylcyclobutanol. The efficiency of formation of various products depends on the excited state of the precursor, as shown in *Scheme 1*. Singlet 2-hexanone gives products inefficiently; most of the product involves cleavage and very little cyclobutanol is formed. Triplet 2-hexanone, on the other hand, gives products fairly efficiently, and substantial amounts of dimethylcyclobutanols are formed. Thus, simple product analysis could help to decide what excited state was involved.



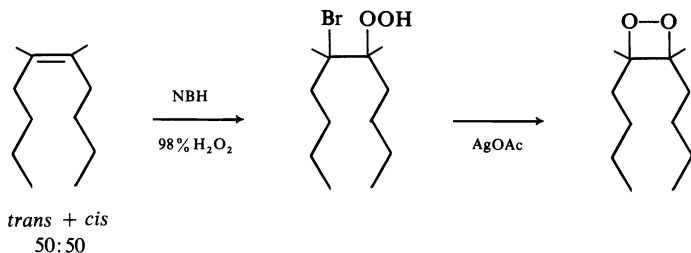
Scheme 1. Product yields from lowest excited singlet (S_1) and triplet (T_1) of 2-hexanone. Φ_{ST} denotes intersystem crossing yield. Balance of each state gives ground state starting material (all yields in decalin, 50°C).

RESULTS

A mixture of *cis* and *trans* olefins was readily prepared by pinacol reaction of 2-hexanone, and pyrolysis of the methyl orthoacetate of the resulting

DECOMPOSITION OF DIOXETANES

diol. This olefin mixture was converted (in poor yield) to the desired dioxetane by treatment with *N*-bromohydantoin and 98% H_2O_2 in ether followed by silver acetate (a modification of Kopecky's method⁴)[†].



Thermolysis of this dioxetane (0.01–0.05 M in decalin, 50°) produces a mixture of 2-hexanone, dimethylcyclobutanols[‡] (1.14%) and acetone (3.0%); propylene was not analysed. The ratio of acetone to dimethylcyclobutanols is intermediate between that expected from initial singlet formation (as in direct photolysis) and exclusive initial triplet formation. The results are summarized in *Table 1*. From the product ratio and the absolute amounts, it is calculated that α_1 (yield of singlet initially formed) is 5 per cent and α_3 (yield of triplet initially formed) is 3.5 per cent; 92 per cent of the product is ground state 2-hexanone.

Table 1. Product ratio from photolysis of 2-hexanone or thermolysis of 3,4-dimethyl-3,4-di-*n*-butyl-1,2-dioxetane (1) (decalin, 50°)

Source	Product ratio (acetone:dimethylcyclobutanols)
2-Hexanone	
Photolysis	3.69
Triplet component only	2.28
Dioxetane (1) thermolysis	2.65

These results were checked by a quenching experiment using 1,3-hexadiene as quencher (*Figure 1*). Since the dimethylcyclobutanol is formed largely from triplet 2-hexanone, it is readily quenched by hexadiene. Curvature in the quenching plot shows that there is a quenchable portion and a small amount of unquenchable reaction. The residual unquenchable portion of cyclobutanol formation can be removed arithmetically to give a Stern–Volmer plot for the triplet 2-hexanone (*Figure 1*); the Stern–Volmer quenching constant for the triplet part is 30 M^{-1} . For comparison, the photochemical quenching studies were repeated under conditions comparable to those which were necessary for the thermolysis. The Stern–Volmer constant of

[†] The dioxetane is a 50:50 mixture of *cis* and *trans* isomers, which react at identical rates; we have not yet been able to separate the isomers.

[‡] The *trans*:*cis* ratio is 1.41; ratio in photochemical reaction of 2-hexanone under same conditions: 1.43. The ratio does not appear to differ for singlet and triplet reactions.

2-hexanone photolysis is 32 M^{-1} , and agrees favourably with the value from thermolysis. The quenching studies yield a value of α_1 of 7 per cent and α_3 of 3 per cent, in reasonable agreement with the values from the product distribution studies.

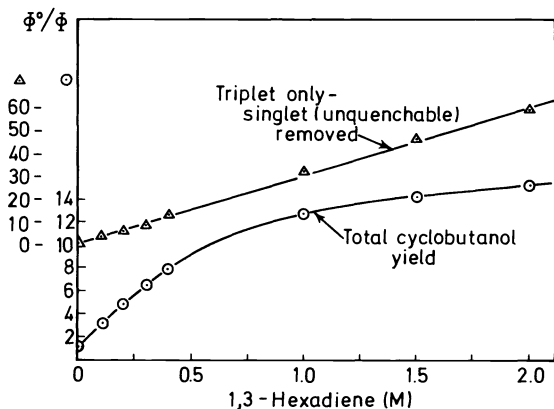
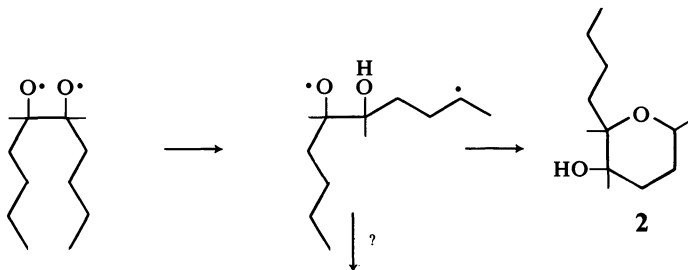


Figure 1. Quenching of dimethylcyclobutanols from thermolysis of **1** by 1,3-hexadiene. (○) Total quenching plot; (△) Stern-Volmer plot of triplet portion only (unquenchable singlet portion removed).

Thus both independent studies lead to the conclusion that comparable amounts of singlet and triplet are produced, with slightly more singlet than triplet. That the product-forming intermediates actually are singlet and triplet 2-hexanone and not, for example, diradicals, is shown by the following:

- (1) The identity of the Stern-Volmer constant for the thermal and photochemical reactions is good evidence that triplet 2-hexanone is an intermediate in the thermolysis.
- (2) The unquenchable portion of the thermolysis gives a product ratio comparable to that of singlet 2-hexanone.
- (3) The dimethylcyclobutanols are formed in the same ratio as in the photolysis of 2-hexanone.
- (4) If a diradical were intermediate, one might have expected that some of compound **2** would be formed if γ -H abstraction in this intermediate mimics Norrish II cleavage, but no evidence for this product was found



Norrish II cleavage

DECOMPOSITION OF DIOXETANES

These results differ strikingly from the earlier results with tetramethyldioxetane¹⁵. It is not obvious how a change from two methyl groups to two butyl groups can change the excited state distributions so strikingly, and further investigation in this area is obviously called for. It does seem difficult, however, to rationalize the present results by means of a concerted mechanism, although the results do not rule one out definitively. A diradical mechanism seems much more easily accommodated.

Dioxetane **1** was also subjected to direct photolysis (wavelength > 360 nm). The same products were formed with a rather similar distribution to that of the thermolysis; the calculated excitation yields are $\alpha_1 = 4$ per cent, $\alpha_3 = 2.2$ per cent. This result should again be contrasted with the results of Turro *et al.* for tetramethyldioxetane, where at 366 nm the results were 10 per cent and 43 per cent respectively¹⁵. In the present case, the energy surface reached by direct photolysis seems to resemble that produced by thermolysis very closely and gives, if anything, slightly less excited product. Again, a diradical mechanism does not seem unreasonable.

Striking results were obtained on sensitized irradiation. In all cases, the products consisted exclusively of 2-hexanone and of acetone and dimethylcyclobutanols in a ratio identical to that produced from triplet 2-hexanone. The total yield of products derived from excited 2-hexanone depends strongly on sensitizer and on solvent; *Figure 2* shows the results in decalin and in

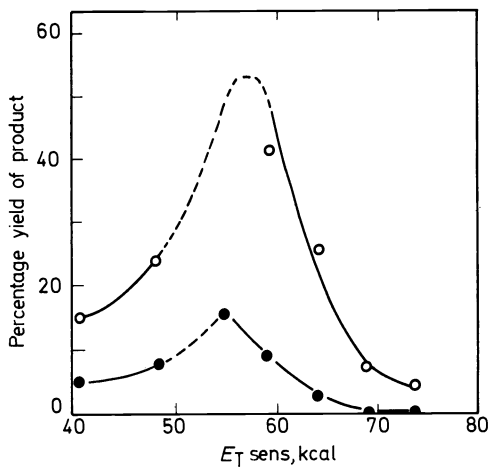


Figure 2. Yield of products from sensitized decomposition of **1** by various sensitizers in pentane (○) and decalin (●) at room temperature.

pentane. The maximum product yield obtained is 41 per cent in pentane with 2-acetonaphthone as sensitizer. The results go along with a remarkable variation in the quantum yield for disappearance of dioxetane, which is near unity for 9,10-dibromoanthracene but reaches nearly 100 for xanthone

in decalin. These results are shown in *Table 2*. It is apparent that a quantum chain process of some sort is occurring.

Table 2. Sensitized decomposition of 1 in decalin (50:50 mixture of isomers) and pentane

Sensitizer	E_T (k cal ^a /mol)	Decalin		Pentane		
		Φ_{-D}^b	α_{et}	Φ_{-D}^b	α_{et}	α_3^c
9,10-Dibromoanthracene	40	1.1	~0.6	1.0	— ^d	0.17
Benzanthrone	47	1.6	0.81	1.2	0.38	0.45
Biacetyl	55	4.3	0.82	— ^e	— ^e	0.95
2-Acetonaphthone	59	6.5	0.89	1.8	0.47	0.95
Thioxanthone	66	5.2	0.96	1.9	0.66	0.88
Benzophenone	69	23	≥0.99	7.9	0.91	0.96
Xanthone	74	97	>0.99	27	0.97	0.99

^a Ref. 23.

^b Extrapolated to infinite dioxetane concentration.

^c Average value from decalin and pentane (numbers differ by less than five per cent).

^d Insufficient chain reaction to accurately determine α_{et} .

^e Extra-cage quenching due to low viscosity of pentane and high concentration of sensitizer required.

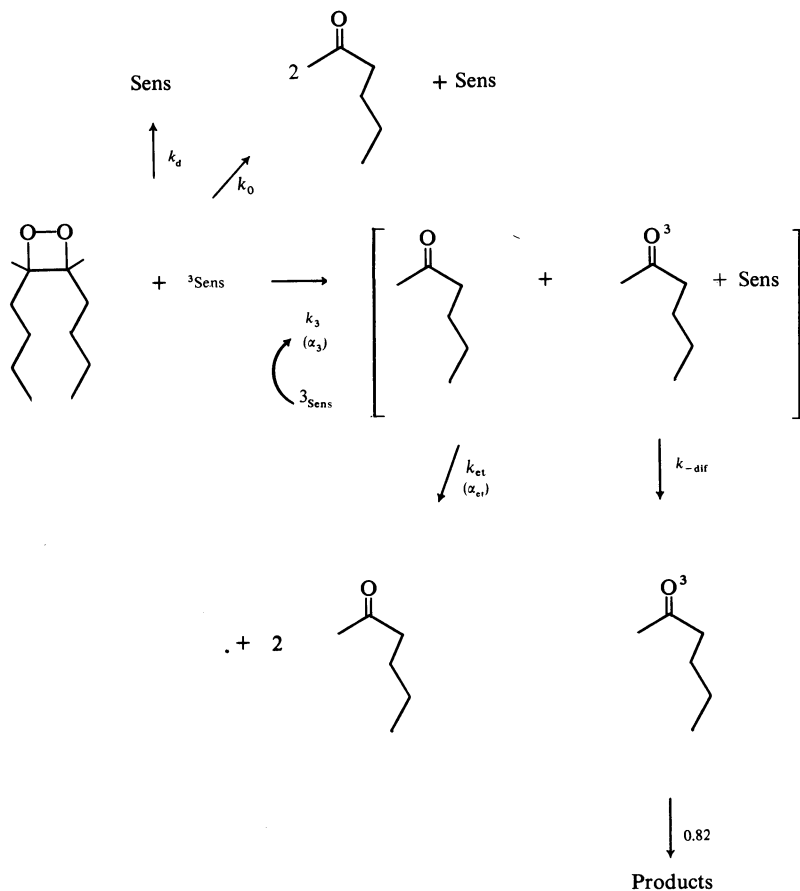
A quantum chain process was observed by Lechtken, Yekta and Turro with tetramethyldioxetane; the triplet acetone produced sensitized the breakdown of further dioxetane, giving more excited acetone, etc.^{14, 19}. This process cannot be occurring here, because the triplet of 2-hexanone is too short-lived ($\tau \sim 10^{-8}$ sec) to be trapped by 10^{-2} M dioxetane.

One process which explains these results is shown in *Scheme 2*. Triplet sensitizer can decay (k_d) or sensitize formation of two molecules of ground state 2-hexanone (k_0) or the formation of one ground state and one triplet 2-hexanone (k_3). The triplet 2-hexanone is of higher energy than the initial sensitizer, and can transfer energy back to the sensitizer (k_{et}), regenerating triplet sensitizer, which can sensitize the decomposition of a further dioxetane. The efficiency with which triplet sensitizer forms triplet 2-hexanone is α_3 , and the efficiency with which the back transfer occurs is defined as α_{et} .

Because of the short lifetime of triplet 2-hexanone, capture by dioxetane or sensitizer at the concentrations used is negligible. Thus, it appears likely that the back transfer to the sensitizer occurs within a solvent cage from a fragment of the original reaction partner. This strongly suggests that triplet 2-hexanone is formed directly in the energy transfer process, or at least by way of no intermediate with lifetime longer than 10^{-10} second, since otherwise the sensitizer would have diffused away. We then consider the scheme shown in which energy transfer (k_{et}) competes with diffusion of the species from the cage (k_{-dif}). In this scheme, $\alpha_{et} = k_{et}/(k_{et} + k_{-dif})$.

The following equations can then be derived for the observables, P (yield of chemoelectronic products, acetone and dimethylcyclobutanol) and Φ_{-D} (quantum yield for loss of dioxetane), where D is dioxetane and α_0 is the fraction of encounters between triplet sensitizer and dioxetane which yield only ground state 2-hexanone. The factor 82 comes into the

DECOMPOSITION OF DIOXETANES



Scheme 2. Quantum chain process for photosensitized decomposition of 1. α_3 denotes efficiency of formation of triplet 2-hexanone; α_{et} is efficiency of back transfer

product equation because 82 per cent of triplet 2-hexanone gives Norrish II products; the rest gives ground state 2-hexanone.

$$P(\%) = 82\alpha_3(1 - \alpha_{et})$$

$$\Phi_{-D} = \Phi_{3\text{sens}} \left[\frac{k_d}{k_0 + k_3} [\text{D}]^{-1} + \alpha_0 + \alpha_3(1 - \alpha_{et}) \right]^{-1}$$

At limiting high dioxetane concentrations, the first term of the second equation is negligible[†], and the two equations can be solved for α_3 and α_{et} .

[†] In practice, in order to use lower dioxetane concentrations, the second equation is integrated and an approximation technique used for its solution.

The values so determined are listed in *Table 2*. It will be noted that α_3 (the yield of triplet 2-hexanone) is almost unity for triplet sensitizers over 50 kcal in triplet energy. It is substantially lower with benzanthrone (47 kcal) and 9,10-dibromoanthracene (40 kcal); however, in no case is any appreciable excited singlet 2-hexanone formed (i.e. $\alpha_0 + \alpha_3 = 1.0$). The fraction α_{et} also increases in the same range, but approaches unity with thioxanthone (66 kcal) in decalin, and with benzophenone (69 kcal) in pentane. The complicated product yield curve of *Figure 2* is thus seen to be a combination of two factors: (1) an increasing efficiency of triplet formation over the range 40 to 55 kcal, and (2) an increasing efficiency of back transfer to sensitizer (which does not lead to chemelectronic products) above 65 kcal.

DISCUSSION

According to diffusion theory, in an ordinary energy transfer process in which donor and acceptor must diffuse together, the observed rate of energy transfer (k_{et}^{obs}) is equal to $k_{dif}[k_{et}/(k_{et} + k_{-dif})]$ where k_{dif} is the encounter diffusion rate, k_{et} is the 'inherent' energy transfer rate, and k_{-dif} is the rate at which the pair diffuse apart from the cage²⁰. An approximate expression is

$$k_{-dif} = 6D/\sigma^2$$

where σ is the combined encounter radius of the two molecules involved in the energy transfer (assumed here to be $\approx 5 \text{ \AA}$) and D is the sum of the individual diffusion constants for the two species²¹. From this equation, the value of k_{-dif} for 2-hexanone in pentane is $18 \times 10^{10} \text{ s}^{-1}$, and that in decalin is $1.8 \times 10^{10} \text{ s}^{-1}$. Using these values and the values of α_{et} in *Table 2*, values for k_{et} can be calculated; the values are listed in *Table 3*.

Table 3. Energy transfer rates from 2-hexanone to various sensitizers

Sensitizer	$k_{et} (\text{s}^{-1} \times 10^{-10})^a$		E_{excess} (kcal/mol)
	Decalin	Pentane	
9,10-Dibromoanthracene	2.6	— ^b	27
Benzanthrone	7.2	11	34
Biacetyl	7.7	— ^c	42
2-Acetonaphthone	14	16	46
Thioxanthone	41	35	53
Benzophenone	(large) ^d	180	56
Xanthone	(large) ^d	580	61

^a Rate of energy transfer within caged pair.

^b Insufficient chain reaction to determine.

^c High sensitizer concentration required gives extra-cage quenching here.

^d Too large to evaluate; at least as large as pentane values.

The calculated rates in the two solvents are in excellent agreement. It is apparent that all the rates exceed the rate for diffusion out of the cage (as they must if energy transfer is to compete with diffusion). If this process did not compete effectively, each collision of sensitizer ($E_T > 50 \text{ kcal}$) with dioxetane would give an 82 per cent yield of products. The rates range up to the extraordinarily high values of $6 \times 10^{12} \text{ s}^{-1}$. It is clear that, if these rates are for

the same process observed for ordinary solution energy transfer, the rates would be severely limited by diffusion with all sensitizers. However, it is not certain that this is a valid comparison, as will be discussed later.

The effect of increasing solvent viscosity from pentane ($\eta = 0.23$ cP) to decalin ($\eta = 2.4$ cP, 50:50 mixture of *cis* and *trans* isomers) is to make cage quenching much more substantial, and both increase the chain length and decrease the amount of photochemical products formed. Another indication that this energy transfer is a cage process is that oxygen does not affect the chain length or alter the yield of products.

The unique feature of these experiments is that donor and acceptor are produced already within the solvent cage; we can thus obtain an independent measure of the term α_{et} . Wagner and Kochevar studied quenching of triplet valerophenone by 2,5-dimethyl-1,2,4-hexadiene²¹ and other quenchers. Their experimental values of α_{et} were 0.31 in pentane and 0.93 in cyclooctane ($\eta = 2.16$ cP); the values of α_{et} calculated for these two solvents (based on an assumed inherent k_{et} of 9×10^{10}) were 0.33 and 0.83, respectively. These values may be compared to those observed in our system with benzanthrone (which has a comparable k_{et} , $9 \times 10^{10} \text{ s}^{-1}$), where the values are 0.38 in pentane and 0.81 in decalin, in fair agreement.

The variation of α_{et} (and therefore k_{et}) with the triplet energy of the sensitizer is particularly intriguing. The largest rates are achieved with the sensitizers with the highest energy triplets, i.e. in those compounds in which the difference in energy between 2-hexanone triplet (≈ 78 kcal) and the accepting sensitizer triplet is the smallest. Two possible explanations for this behaviour have occurred to us. One is that a 'Franck-Condon matching' phenomenon limits the maximum inherent energy transfer rate. This phenomenon is well known in the case of singlet energy transfer; a well-worked-out example has recently been reported by Steel and Engel²². However, in the case of triplet excitation transfer, it is not possible to obtain Franck-Condon factors directly, because the triplet-triplet absorption spectrum is not known; in addition, many of the sensitizers probably have more than one triplet state below the triplet of 2-hexanone. A second possible explanation is that the 2-hexanone-sensitizer caged pair, when formed initially, has substantial excess energy. This energy is given by

$$E_{\text{excess}} \text{ (kcal/mol)} = 65 + E_{\text{t}}^{\text{sens}} - 78$$

The heat of reaction for conversion of the dioxetane to two ketone molecules is 65 kcal/mol²³ and the triplet energy of 2-hexanone is 78 kcal/mol[†]. Table 3 lists the excess energies. It is by no means obvious whether these excess energies should be related in a meaningful way to the energy transfer rates; among other problems is that with xanthone (excess energy 61 kcal/mol), the energy transfer rate is estimated to be $580 \times 10^{10} \text{ s}^{-1}$; this is on the order of a few molecular vibrations, and excess energy would probably not have time to be dissipated. With the smaller excess energies, for example with benzanthrone (excess energy 34 kcal/mol), the rate constant is 'only'

† Assumed to be the same as acetone²³.

$9 \times 10^{10} \text{ s}^{-1}$, which allows sufficient time for loss of excess vibrational energy to the surroundings.

Whatever the final explanation of these phenomena turns out to be, it is obvious that this system has led to intriguing behaviour that will continue to occupy us for some time before it is completely understood.

REFERENCES

- ¹ C. S. Foote and J. W.-P. Lin, *Tetrahedron Letters*, 3267 (1968).
- ² C. S. Foote, J. W.-P. Lin and S.-Y. Wong, *Preprints of the Division of Petroleum Chemistry, American Chemical Society*, 14, A93 (1969).
- ³ A. A. Dzakpasu, Master's Thesis, UCLA (1971);
C. S. Foote, A. A. Dzakpasu and J. W.-P. Lin, *Tetrahedron Letters*, in press.
- ⁴ K. R. Kopecky, J. H. Van de Sande and C. Mumford, *Canad. J. Chem.* 46, 25 (1968);
K. R. Kopecky and C. Mumford, *Canad. J. Chem.* 47, 709 (1969).
- ⁵ W. H. Richardson and V. E. Hodge, *Tetrahedron Letters*, 2271 (1970);
W. H. Richardson and V. E. Hodge, *J. Amer. Chem. Soc.* 93, 3996 (1971).
- ⁶ P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.* 92, 3223 (1970);
S. Mazur and C. S. Foote, *J. Amer. Chem. Soc.* 92, 3225 (1970);
G. Rio and D. Bricout, *Bull. Soc. Chim. France*, 3555 (1971);
P. D. Bartlett, G. D. Mendenhall and A. P. Schaap, *Ann. NY Acad. Sci.* 171, 79 (1970).
A. P. Schaap, *Tetrahedron Letters*, 1757 (1971).
- ⁷ J. H. Wieringa, J. Strating, H. Wynberg and W. Adam, *Tetrahedron Letters*, 169 (1972);
A. P. Schaap and J. R. Faler, *J. Amer. Chem. Soc.* 95, 3381 (1973);
N. M. Hasty and D. R. Kearns, *J. Amer. Chem. Soc.* 95, 3380 (1973);
J. Rigaudy, P. Capdevielle and M. Maumy, *Tetrahedron Letters*, 4497 (1972);
P. le Roux and J.-J. Basselier, *CR Acad. Sci., Paris*, 271, 461 (1970).
- ⁸ F. McCapra, *Quart. Rev. Chem. Soc.* 20, 485 (1966);
F. McCapra, *Progr. Org. Chem.* 8, 321 (1971).
T. Wilson and J. W. Hastings, *Photophysiology* 5, 49 (1970).
- ⁹ F. McCapra, Y. C. Chang and V. P. Francois, *Chem. Commun.* 22 (1968);
T. A. Hopkins, H. H. Seliger, E. H. White and M. W. Cass, *J. Amer. Chem. Soc.* 89, 7148 (1967).
- ¹⁰ O. Hayaishi and M. Nozaki, *Science*, 164, 389 (1969);
J. Rigaudy, C. Deletang, D. Sparfel and N. K. Cuong, *CR Acad. Sci., Paris*, 267, 1714 (1968);
J. Rigaudy, *Pure Appl. Chem.* 16, 169 (1968);
J. E. Baldwin, H. H. Basson and H. Krauss Jr, *Chem. Commun.* 984 (1968).
- ¹¹ F. McCapra, *Chem. Commun.* 155 (1968).
- ¹² T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.* 93, 4126 (1971).
- ¹³ E. H. White, J. Wiecko and C. C. Wei, *J. Amer. Chem. Soc.* 92, 2167 (1970);
E. H. White, J. Wiecko and D. F. Roswell, *J. Amer. Chem. Soc.* 91, 5194 (1969).
- ¹⁴ N. J. Turro, P. Lechtken, N. E. Shore, G. Schuster, H.-C. Steinmetzer and A. Yekta, *Accounts Chem. Res.* 7, 97 (1974).
- ¹⁵ N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.* 94, 2887 (1972); 95, 264 (1973).
- ¹⁶ H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.* 92, 6553 (1970);
W. H. Richardson, M. B. Yelvington and H. E. O'Neal, *J. Amer. Chem. Soc.* 94, 1619 (1972).
- ¹⁷ W. H. Richardson, F. C. Montgomery and M. B. Yelvington, *J. Amer. Chem. Soc.* 94, 9277 (1972).
- ¹⁸ T. R. Darling and C. S. Foote, *J. Amer. Chem. Soc.* 96, 1625 (1974).
- ¹⁹ P. Lechtken, A. Yekta, and N. J. Turro, *J. Amer. Chem. Soc.* 95, 3027 (1973);
N. J. Turro, N. E. Shore, H.-C. Steinmetzer and A. Yekta, *J. Amer. Chem. Soc.* 96, 1936 (1974).
- ²⁰ A. M. North, *Quart. Rev. Chem. Soc.* 20, 421 (1966).
- ²¹ P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.* 90, 2232 (1968).
- ²² P. S. Engel, L. D. Fogel and C. Steel, *J. Amer. Chem. Soc.* 96, 327 (1974).
- ²³ N. J. Turro, *Molecular Photochemistry*, pp 132, 182. Benjamin: New York (1967).