

PAKISTAN JOURNAL
OF
SCIENTIFIC AND INDUSTRIAL RESEARCH

Vol. 11, No. 2

April 1968

THE STUDY OF THE FIRST-ORDER DECAY OF TRIPLET NAPHTHALENE IN SOLUTION*

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(Received August 15, 1967)

The first-order decay of triplet naphthalene in solution is not consistent with the theory. Causes of discrepancies have been attributed to impurity quenching processes. The study of triplet decay rate constants of naphthalene in propylene glycol solution from 30° to -85° C has revealed two distinct behaviours of decay. Higher decay rates at room temperatures are accounted in terms of the concurrence of unimolecular decay and a bimolecular-diffusion-controlled reaction between the triplet molecule and an unknown efficient quenching impurity.

Introduction

Phosphorescence from most of the organic molecules at very low temperatures, in rigid glasses or in crystals is readily observed. Measurements of the phosphorescence luminescence provides a convenient means to study the properties of triplet molecules. In fluid solvents phosphorescence is usually too weak to be observed and the luminescence method is hardly suitable. However, the flash-photolysis method is very well adapted to this purpose. Owing to the different conditions of the experiment, it was not possible to link up the measurements done by the luminescence and flash-photolysis methods, but the technique of low temperature device¹ has extended the range of the flash-photolysis investigations down to liquid nitrogen temperature and the direct comparison between the two series of measurements is now possible. Present flash-technique permits the study of rate measurements from 120° to 190°C in suitable solvents.

Triplet lifetimes obtained from the phosphorescence decay at liquid nitrogen temperature are in most cases much longer than those measured from the decay of absorption spectrum, involving transitions to higher triplet levels. In the case of naphthalene for example, the phosphorescence lifetime is 2.6 sec.² but the lifetime in hexane solution is 9.1×10^{-3} sec.³ Detailed studies on the kinetics of the triplet state disappearance have shown that the intrinsic lifetime of the triplet state is deter-

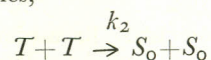
mined both by the radiative and radiationless decay to the ground state,

$$-\frac{dT}{dt} = k_0 [T] + k_1 [T] \quad (1)$$

Under fluid conditions both the processes are equally effective, but at liquid nitrogen temperature the contribution from the non-radiative process, k_1 , is less. This is why the lifetime of the triplet state in solution is so short.

Early findings of Porter and Windsor⁴ proposed viscosity dependence of triplet decay in solution. while the investigations of Jackson and Livingston⁵ pointed out that from 0.3 to 500 c.p. the rates appear to be independent of viscosity, but decrease with further increase in viscosity, reaching a lower limit at approximately 5×10^5 c.p. The results with viscous solvents exhibit that the energy of activation for triplet state decay is smaller than the energy for viscous flow, so the lower rates in viscous solvents could not be explained in terms of activation energy differences.

Higher rates in fluid solvents may be due to the bimolecular encounter between two triplet molecules,



The observed value of triplet annihilation constant k_2 indicates that triplet-triplet interaction is a diffusionally limited bimolecular process for a variety of solvents and over a 100° range of temperature. But under low light intensity condi-

*The experimental work was performed in the Physical Chemistry Laboratories of Chemistry Department, Sheffield University, U.K., during 1963-1964.

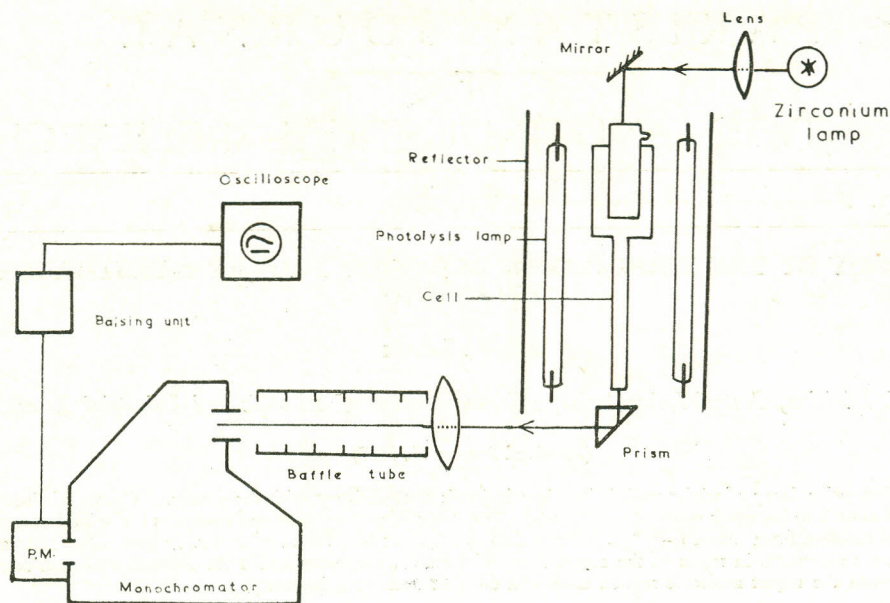


Fig. 1.—Diagram showing general arrangement of photoelectric flash photolysis apparatus.

tions, when triplet conversion is small and when the system is highly dilute, triplet-triplet annihilation process is relatively unimportant and the decay is found to be predominantly first-order in triplet concentration. Also it is of no use to consider triplet decay as a process which is rate-determined by energy transfer to the solvent, particularly since the rate attains its maximum value in the gas phase.⁶ Nor is there any apparent correlation of the structural features of the solvent, such as polarity, with the rate of triplet decay.

The observation that the dependence of decay rate is greatly reduced by using heavy atom substituents or very pure solvents,⁷ strongly supports the view that some quenching impurity in the system is responsible for strong dependence of the decay rates on solvent viscosity. In the present work, we have accepted this impurity quenching hypothesis and have tried to investigate thoroughly, the possibility of such quenching process, and also the viscosity range in which it predominantly effects the decay rate of the triplet state.

Experimental

(a) *Apparatus.*—A photoelectric flash-photolysis apparatus similar to the one described by Porter⁸ was used. Schematic diagram of the apparatus is shown in Fig. 1.

Light from a source was rendered parallel by a lens and made to reflect on the mirror placed at an angle of 45° to the direction of the light beam.

This made the beam bend at an angle of 90° . The beam then passed through the absorption cell placed in vertical housing fitted with flash lamps. The resulting beam was rendered horizontal by letting it through a triangular quartz prism and led through the system of baffles in the collimating tube, then into a monochromator. At the exit slit of the monochromator a photomultiplier was fitted, the output of which was fed via a biasing unit into the oscilloscope which could be triggered by the pulse firing the flash lamps. A Cossor 1418 camera was used to record the signals from

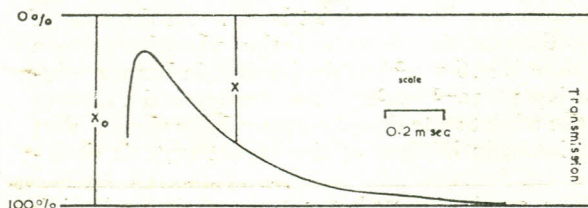
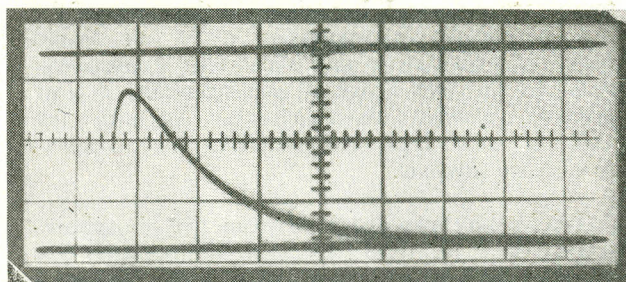


Fig. 2.—Oscillographic record showing the decay of triplet naphthalene in propylene glycol solution.

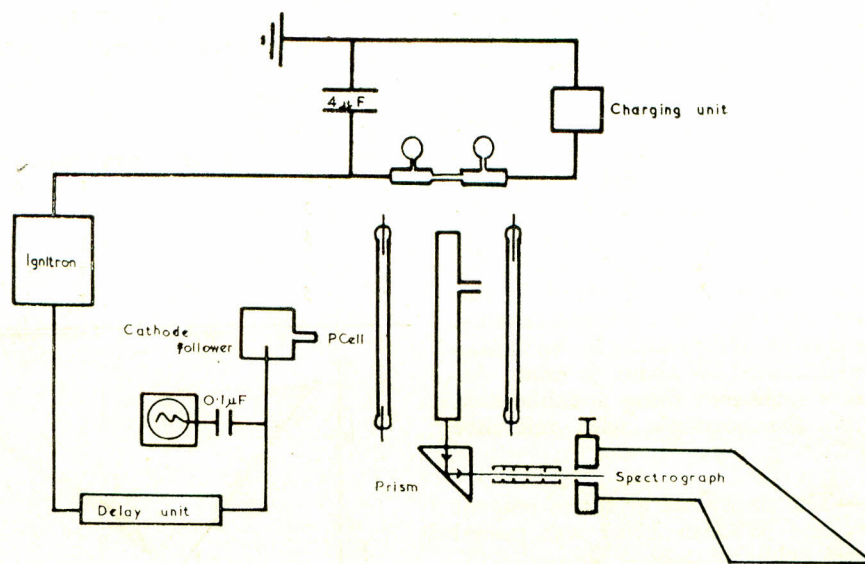


Fig. 3.—Diagram showing general arrangement of spectrographic flash photolysis apparatus.

the oscilloscope screen on a 35 mm Kodak high speed panchromatic film. The picture was then enlarged and traced on a graph paper for the measurements of rate constant. A typical trace along with the actual photograph is shown in Fig. 2.

The spectrographic flash-photolysis apparatus consisted of a Hilger medium-quartz spectrograph which was attached to an optical bench upon which the cell chamber and spectroscopic flash lamp were fixed. A baffle tube, with an internal diameter of 6 mm, was introduced between the cell chamber and the spectrographic slit to cut-off scattered light from the photolysis lamps. A Hilger seven-step neutral filter of rhodium on quartz used to calibrate the plate internally, was mounted in a specially constructed fitting in the front of the spectrograph. The general arrangement is shown by a schematic diagram in Fig. 3.

The absorption spectrum of the system was recorded before photolysis by firing the spectroscopic flash lamp. A series of exposures were then taken with different delays between photolysis-flash and spectroscopic-flash. Any scattered light and/or fluorescence emitted was recorded by firing the photolysis lamps only. Finally, by firing the spectroscopic lamp alone, the spectrum after the photolysis was recorded. The exposures taken on a plate, as shown in Fig. 4, illustrate these spectra.

Experiments at lower than room temperatures employed the low temperature device. This is shown in the diagram (Fig. 5). A special absorption cell was held vertically in a non-silvered

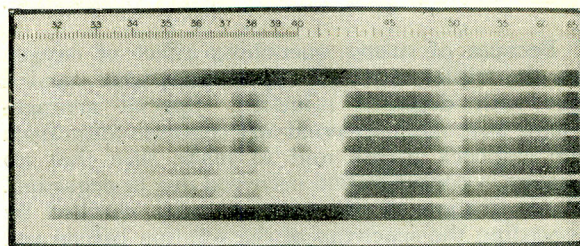


Fig. 4.—Photograph showing absorption spectrum of triplet naphthalene.

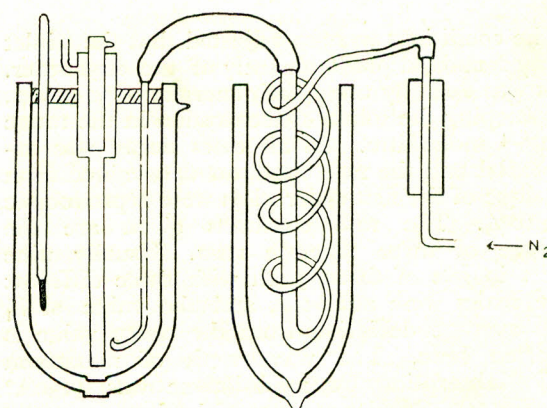


Fig. 5.—A schematic diagram showing the arrangement for low temperature apparatus.

fused silica Dewar flask, with double quartz windows in the base. The absorption cell had a 22 cm path-length and an internal diameter of 1.5 cm. The design of the cell ensured that no meniscus formed in the optical path when liquid

contracted on cooling. Temperature was controlled by passing nitrogen through a copper coil immersed in liquid nitrogen. The effluent gas entered the space between the Dewar flask and cell at several points along the length of the cell. It was possible to control the temperature to within $\pm 2^\circ\text{C}$. A slow stream of air was directed against the outside window of the Dewar to prevent condensation of atmospheric moisture. It was found that 20 min were required for the solution in the cell to attain the temperature measured in the Dewar flask, and consequently all measurements were taken only after the temperature in the Dewar flask had been maintained for about 30 min. All temperatures were measured using a calibrated copper/constantan thermocouple with reference junction at 0°C .

(b) *Material*.—The propylene glycol of reagent grade (Hopkins and William Ltd.) was passed through silica gel columns until it showed 95% transmission at 2500 \AA in a cell of 1 cm path-length. Naphthalene was B.D.H. microanalytical grade and was used without further purification.

Because of strong quenching effect of oxygen on the triplet state, all experiments were carried out with degassed solutions. Special arrangements were made to avoid any contamination from the stopcock grease and to make sure that no change in concentration occurred due to degassing. Concentration of the solutions were checked by recording the spectrum of the solution before and after degassing on an Ultracord spectrophotometer.

Results

The conditions were so adjusted that the triplet decay remained predominantly of the first-order. This was done by using flash energies of 50 joules, and keeping the solute concentration in the range of 10^{-4} moles/litre. In all cases decay was exponential and the rate constants determined from the slope of the first-order plots were reproducible to $\pm 10\%$. The rate constants given are the average of three separate runs. Usually nine traces in sets of three, each with three different time scales were analysed, and the value of k_1 with average deviation from the mean value is reported here. The wavelength of maximum triplet absorption for naphthalene was 4150 \AA (see Fig. 4). No dependence of the decay constant upon the initial concentration of naphthalene was observed. This is illustrated by the results in Table I.

The first-order rate constant for triplet decay of naphthalene in propylene glycol were also deter-

TABLE I.

Concentration of naphthalene (moles/litre)	First-order rate constant (sec^{-1})
1×10^{-2}	$1.3 \times 10^3 \pm 0.1$
1×10^{-3}	$1.4 \times 10^3 \pm 0.1$
1×10^{-4}	$1.2 \times 10^3 \pm 0.1$
5×10^{-5}	$1.3 \times 10^3 \pm 0.1$
1×10^{-5}	$1.2 \times 10^3 \pm 0.1$

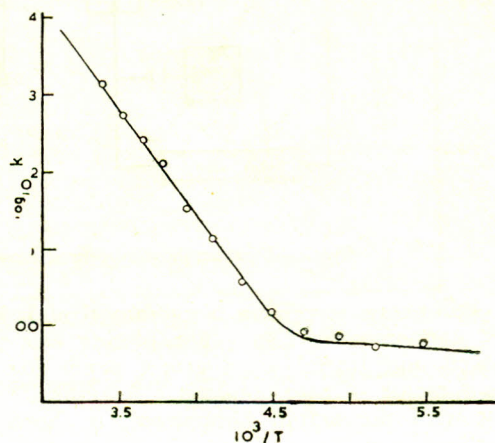


Fig. 6.—Plot of $\log k$ versus $1/T$ for triplet naphthalene in propylene glycol.

mined at 5°C intervals between $+25$ and -90°C . The results are shown in Fig. 6 as a plot of the observed first-order rate constant against the reciprocal of absolute temperature. These measurements were made in random order to avoid any cumulative effect of successive exposure of the sample to flash irradiation or delay in temperature equilibration. The results showed two characteristic regions: (i) a higher temperature, low viscosity region where rate constant decreases markedly with decrease in temperature, (ii) a low temperature, high viscosity region where rate constant is almost constant.

Discussion

Our results show that the first-order rate constant of naphthalene triplet decay does not depend on the initial concentration of naphthalene. The reaction between the triplet and normal molecule is, therefore, definitely excluded from our observations. The observed position of the triplet absorption bands is the same as has been reported by others. The initial concentration of the solute has been increased about thousand-fold, any impurity present in the solute should have changed

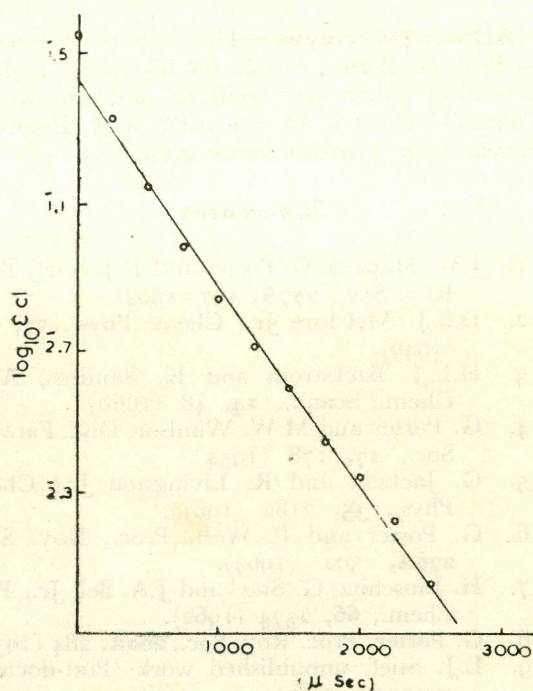


Fig. 7.—First-order plot obtained from a decay trace of triplet naphthalene in propylene glycol.

the decay rate appreciably. Consistency in the rate constant value rules out the possibility of any impurity in the solute. Our plots for triplet decay fit remarkably well in the first-order kinetics (see Fig. 7). Second-order processes of triplet-triplet annihilation do not seem to contribute to the observed rate of triplet decay under our conditions.

The sharp change in the temperature gradient of k_{obs} in the temperature range -55 to -65°C (see Fig. 6) might possibly be attributed to a sudden change in the activation energy of the viscous flow, presumably caused by a sudden change in the solvent structure. It is, therefore, more significant to investigate the relation between $\log \eta$ and $1/T$. Any discontinuity in the relation between viscosity and temperature would appear as a corresponding discontinuity in the relation between $\log k_{obs}$ and $1/T$. Viscosities of propylene glycol over the temperature range 30 to -90°C have been reported by Stief,⁹ and the linear relationship between $\log \eta$ and $1/T$ over the whole range of our kinetic measurements as reported by these authors leave no place of argument on these lines.

On the basis of our results we have discarded the contribution from second-order processes of any kind, but the possibility of a bimolecular reaction between the triplet molecule and some reactive species, either already present in the solvent or

formed in the system during the experiment, still exists. The concentration of this species as compared to the solute is so low that the resulting bimolecular reaction would be pseudo-first-order. Thus, in spite of this bimolecular quenching process the overall decay remains first-order in triplet concentration.

It has been mentioned earlier that in the absence of all quenching processes, the lifetime of triplet species in solution is mainly determined by radiative and radiationless intersystem crossing to the ground state. All terms in the rate equation,

$$-\frac{dT}{dt} = k_0[T] + k_1[T] + k_2[T]^2 + k_3[T][G] + \sum_Q k_Q[Q][T] \quad (2)$$

except the first two should be zero or very small. The temperature coefficient of k_1 and k_0 are not very large as indicated by the lower section of the curve in Fig. 6. Observed decay rate constant at -85°C and these extrapolated to 25°C (Fig. 6) are,

k_{obs} at 25°C (extrapolated)	k_{obs} at -85°C (observed)
1.2 sec^{-1}	0.5 sec^{-1}

Observed value of k_{obs} at room temperature is $1.3 \times 10^3 \text{ sec}^{-1}$. Such a large difference in the extrapolated and observed values of the first-order rate constant support the view that the decay at room temperature and in solution is dominated by the impurity quenching bimolecular process. The non-linearity of the Arrhenius plot indicates that the impurity quenching process depends on the rate of diffusion of the reacting species in the solvent, and the quenching occurs at every encounter. Since the diffusional process can operate effectively in lower viscosity region, the domain of impurity quenching process should be confined within this region. This is, in fact what we have observed. The sharp change in temperature coefficient of k_{obs} at about -55°C shows that the decay above this temperature is mainly due to pseudo-first-order quenching process. Although truly unimolecular processes still contribute, but because of very fast pseudo-first-order quenching process which is diffusionally limited, the overall decay shows viscosity dependence. The impurity quenching process in the high viscosity region gets very weak because of the restricted movements of the molecules. Therefore, the behaviour of triplet decay in this region is truly unimolecular which shows very little dependence on the viscosity of the solvent.

The approximate concentration of the quenching species responsible for higher rates can be estimated as follows. Since the quenching process is diffusion controlled, the Debye equation,¹⁰

$$k_d = 8RT/2000\eta \quad (3)$$

can be used to calculate the quenching constant from the knowledge of solvent viscosity and temperature only. Then using the relation,

$$k_{\text{obs}} = k_0 + k_I + k[Q] \quad (4)$$

where k_I and k_0 are negligible under the condition; $[Q]$, the concentration of the quenching species is estimated. The results of our calculations are,

Solvent	Viscosity	k_{obs}	k_d	Impurity (Calculated)
Propylene glycol	40. c.p	$1.3 \times 10^3 \text{sec}^{-1}$	$2.4 \times 10^8 \text{l/mol/sec}$	$5.9 \times 10^{-7} \text{mol/lit}$

It is not surprising that such a small concentration of the unknown impurity remains unidentified in the solvent which was subjected to intensive purification.

Acknowledgement.—The author is grateful to Prof. G. Porter, F.R.S. for his advice and for providing laboratory facilities, and also to the Pakistan Council of Scientific and Industrial Research for a maintenance grant.

References

1. J.W. Hilpern, G. Porter and L.J. Stief, Proc. Roy. Soc., **277A**, 437 (1964).
2. D.S.J. McClure Jr., Chem. Phys., **17**, 905 (1949).
3. H.L.J. Backstrom and K. Sandros, Acta. Chem. Scand., **14**, 48 (1960).
4. G. Porter and M.W. Windsor, Disc. Faraday Soc., **17**, 178 (1954).
5. G. Jackson and R. Livingston Jr., Chem. Phys., **35**, 2182 (1961).
6. G. Porter and P. West, Proc., Roy. Soc., **279A**, 302 (1964).
7. H. Linschitz, G. Steel and J.A. Bell Jr., Phy. Chem., **66**, 2574 (1962).
8. G. Porter, Proc. Roy. Soc., **200A**, 284 (1950).
9. L.J. Stief, unpublished work (Post-doctoral research), 1963.
10. A.D. Osborne and G. Porter, Proc. Roy. Soc., **284A**, 9 (1965).