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STUDIES OF TRIPLET NAPHTHALENE QUENCHING BY PEROXIDE

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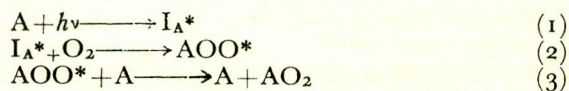
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The measured value of first-order decay constant of triplet naphthalene in solution as reported by different workers differs widely. Causes of variations have been attributed to varying amounts of impurity present in the solvent. This investigation was undertaken to determine whether the second-order quenching processes are due to the presence of peroxide. The values obtained for k_Q are lower than the diffusion-controlled rate constants, showing that for peroxide the quenching rates at room temperature are reaction-controlled and so could not account for the impurity quenching of naphthalene in solutions. Detailed measurements on t-butyl hydroperoxide revealed that naphthalene acts as a photosensitizer for the decomposition of peroxide.

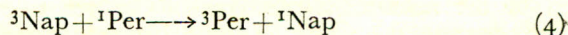
The temperature coefficient of the observed first-order decay constant for triplet naphthalene has different values in different temperature and viscosity regions.¹ The data suggest that some diffusion controlled pseudo-first-order bimolecular process is responsible for large k_T at room temperatures and moderate viscosities. Contribution from the trace amount of oxygen left in the degassed system is ruled out on the ground that the possible concentration of oxygen remaining in the system would not be sufficient to give the observed high rate constant values. Presence of second-order processes of any kind is also not possible because under the conditions triplet conversion is low.

The following processes are possible on the absorption of light by an aromatic molecule,



where AOO* represents an intermediate and AO₂ is a cyclic peroxide having an —O—O— bridge across the rings. This scheme suggests that commercially available material may contain the peroxide as an impurity and even if one tries to purify the compound the peroxide impurity may be introduced in the sample in the process of purification or on long storage if proper shielding from room light is not done.

It is now a well-known fact that the molecules which have triplet level of at least 1000⁻¹cm lower than the molecule under study can act as an efficient quencher. It is more likely that the peroxide has lower triplet level than triplet naphthalene and the triplet-triplet energy transfer process,



results in the enhancement of the decay rate of triplet naphthalene. Since the concentration of peroxide impurity is in trace amount no appreciable triplet-triplet absorption due to peroxide is expected to illustrate that its triplet state was produced when quenching took place.

To ascertain the possibility of naphthalene triplet quenching by a standing concentration of peroxide, we have deliberately added known amounts of peroxide to the naphthalene and have measured the resulting changes in the decay rates. Three peroxides, namely hydrogen peroxide, t-butyl hydroperoxide and di-t-butyl peroxide, were chosen for quenching studies.

Under low triplet conditions, the rate of triplet decay in the presence of an added quencher conform to the following equation²

$$-\frac{dT}{dt} = k_T[T] + [k_Q][Q][T] \quad (5)$$

where k_T is the first-order rate constant, k_Q is the second-order rate constant for quenching and [Q] the concentration of the quenching compound. The above equation can also be written as

$$-\frac{dT}{dt} = k_{obs}[T] \quad (6)$$

From equations 5 and 6 we get

$$k_{obs}[T] = k_T[T] + k_Q[Q][T] \quad (7)$$

$$\text{or } k_{obs} = k_T + k_Q[Q] \quad (8)$$

This is the equation of a straight line with an intercept k_T . Thus it is possible to measure k_Q without knowing the initial concentration of the reactants. A plot of k_{obs} against [Q] yields a linear plot of gradient k_Q .

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Experimental

Photoelectric monitoring of the triplet absorption was done by usual type of flash-photolysis apparatus. The general method has been described by Hoffman and Porter.³

Naphthalene was BDH microanalytical grade and was used without further purification. Di-*t*-butyl peroxide and *t*-butyl hydroperoxide supplied by Light Chemicals Ltd. were found to need no further purification. Hydrogen peroxide of BDH reagent grade was used. Propylene glycol of Hopkin and Williams G.P.R. grade chemical was passed through an activated silica gel column until it showed 95% transmission at 220 nm.

The change in the naphthalene triplet absorption upon flashing $10^{-3}M$ naphthalene in propylene glycol was studied at various concentrations of the peroxide used. No filter was used as suggested by the absorption spectrum of the peroxides. The concentration of the peroxide was varied in steps. As more peroxide was added, the decay rate of absorption due to triplet naphthalene was seen to decrease steadily. This took place in spite of the fact that no light from the photolysis flash lamps was absorbed by the peroxide. This was confirmed at each concentration by flashing of naphthalene solution at 415 nm when no absorption could be detected.

Results

t-Butyl Hydroperoxide.—The rate of decay of triplet naphthalene at various concentrations of *t*-butyl hydroperoxide (from 5×10^{-5} to $5 \times 10^{-4}M$) was measured by making linear first-order plots. The observed first-order rate constants were determined for various concentrations of hydroperoxide. The plots of k_{obs} versus the concentration of hydroperoxide is shown in Fig. 1. From the slope the quenching constant, $k_Q = 1.4 \pm 0.06 \times 10^7 \text{ l mol}^{-1} \text{ sec}^{-1}$ was obtained.

During preliminary observation it was noticed that the value of k_{obs} decreased with the number of flashes and so only the measurements of the first flash were used for calculating k_Q . To check

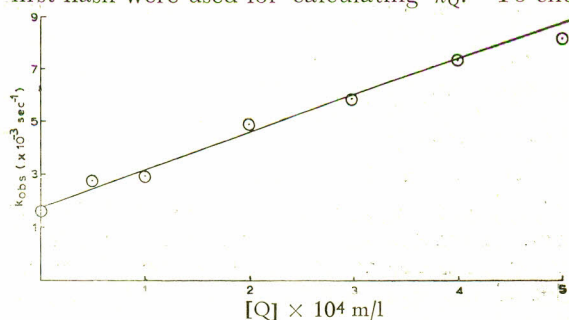


Fig. 1.—Plot used to obtain k_Q for the quenching of triplet naphthalene by *t*-butyl hydroperoxide.

that decomposition was not taking place on the vacuum line, sample solutions were degassed for about 4 hr. The concentration of hydroperoxide before and after outgassing was estimated iodometrically by reducing oxide with iodide in acid solutions and the liberated iodine titrated with standard thiosulphate solutions. No change in peroxide concentration before and after degassing was found. After flashing for about 25 times the cell was broken open and peroxide estimated. Again no change in peroxide concentration before and after flashing was found, but solution of peroxide containing naphthalene showed a decrease in hydroperoxide concentration. Estimates of hydroperoxide decomposition in the presence of naphthalene were made for each solution. Table I summarizes the results.

TABLE I

Peroxide concentration moles/l	$k_{obs} \times 10^{-3}$	Number of flashes (50 J)	Percent-age decomposition	Decomposition mole/flash
5×10^{-4}	8.2	6	4	3×10^{-6}
4×10^{-4}	7.3	6	5	3×10^{-6}
3×10^{-4}	5.9	8	9	3.3×10^{-6}
2×10^{-4}	4.9	18	33	3.6×10^{-6}
1×10^{-4}	3.0	25	75	3×10^{-6}
5×10^{-5}	2.8	5	90	9×10^{-6}

Di-t-butyl Peroxide.—Decomposition of peroxide in all mixtures was observed, therefore measurements at the first flash were taken for obtaining k_Q . The values of k_{obs} versus $[Q]$ is shown in Fig. 2. The value of k_Q obtained from the slope obtained was $7.8 \pm 0.3 \times 10^6 \text{ l mol}^{-1} \text{ sec}^{-1}$.

Hydrogen Peroxide.—Various concentrations of hydrogen peroxide were added to $10^{-3}M$ solution of naphthalene in propylene glycol and the observed rate of the triplet naphthalene decay was measured for each concentration from the first flash exposures. The quenching rate constant obtained from the plot (Fig. 3) was $1.7 \pm 0.03 \times 10^7 \text{ l mol}^{-1} \text{ sec}^{-1}$.

Discussion

The rate constant for quenching of triplet naphthalene by various peroxides obtained from the gradient of plots of k_{obs} against $[Q]$ and those calculated by the modified Debye equation⁴ are given in Table 2.

When solutions of *t*-butyl hydroperoxide in propylene glycol were flashed, no appreciable decomposition of the peroxide could be detected. This was checked by estimating the concentration of *t*-butyl hydroperoxide before and after photolysis by the iodide method.⁵ After adding naphthalene to these solutions a marked differenc

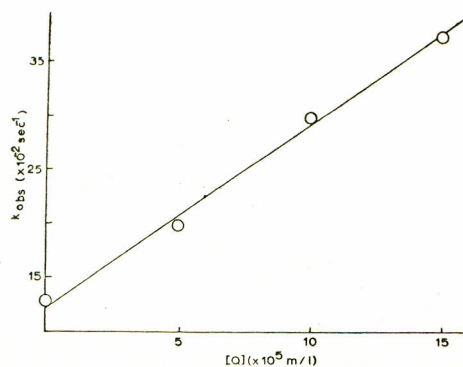


Fig. 2.—Plot of k_{obs} against the added concentration of di-*t*-butyl peroxide to 10^{-3} M solution of naphthalene in propylene glycol, used to calculate k_Q .

in the concentration of *t*-butyl peroxide before and after photolysis was observed. This is borne out by the results in Table 3. The amount of decomposition per flash was so high that after about five flashes, the value of k_{obs} measured for the solution containing 5×10^{-5} M of *t*-butyl hydroperoxide, was almost the same as for the rate constant in the absence of peroxide. A similar situation exists with di-*t*-butyl peroxide and hydrogen peroxide as well, but no quantitative determination was made.

This can happen if triplet naphthalene can transfer its energy to the unexcited peroxide molecule during an encounter. If the transferred energy is of the order of O—O bond fission energy, peroxide molecules will dissociate into radical

TABLE 2.—SECOND-ORDER RATE CONSTANTS FOR THE QUENCHING OF TRIPLET NAPHTHALENE BY PEROXIDE AT 20°C.

Solvent, propylene glycol; viscosity 40 c.p.

Quencher	k_Q (experimental) l mol ⁻¹ sec ⁻¹	k_Q (calc) l mol ⁻¹ sec ⁻¹
Hydrogen peroxide	1.7×10^7	2.4×10^8
<i>t</i> -Butyl hydroperoxide	1.4×10^7	2.4×10^8
Di- <i>t</i> -butyl peroxide	7.8×10^6	2.4×10^8

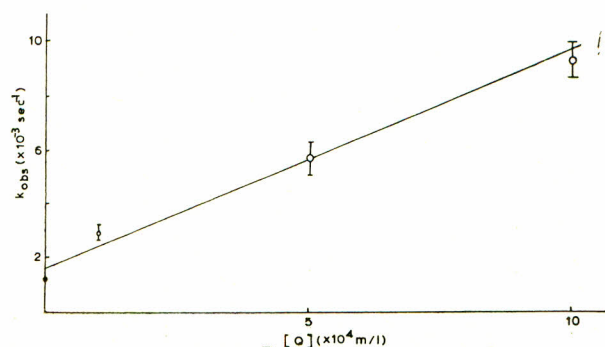


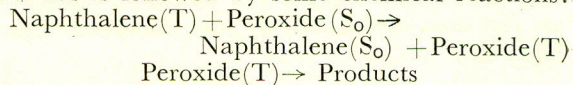
Fig. 3.—Plot of k_{obs} against $[Q]$ used to obtain k_Q for the quenching of triplet naphthalene by hydrogen peroxide.

Under such conditions naphthalene will act as a photosensitizer for the decomposition of peroxide.

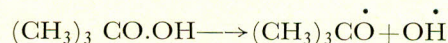
Mechanism of Triplet Naphthalene Quenching

The possibility of triplet energy transfer by the "trivial" process is highly unlikely under the conditions. The absorption bands of peroxide are far apart from the emission bands of naphthalene. The $S_0 \rightarrow S_1$ transitions in peroxide are farther removed towards the high energy side than $T_1 \rightarrow T_2$ transitions in naphthalene and is conclusive evidence that the singlet-triplet transfer, is forbidden on energy grounds.

The results that peroxide were used up as the mixture were flashed could be taken to indicate that quenching was by some chemical reaction. From the spectrophotometric and flash photographic investigation no indication about such a change could be made. However, it is possible that triplet-triplet energy transfer does take place and this is followed by some chemical reactions:



The thermal and photolytic decomposition of *t*-butyl hydroperoxide in various solvents has been studied.^{6,7} The primary reaction is a unimolecular fission of the O—O bond,



In case of di-*t*-butyl peroxide the products of

TABLE 3

10^{-3} M Naphthalene in propylene glycol + peroxide ($\times 10^4$ moles/l)	Peroxide estimated before photolysis ($\times 10^4$ moles/l)	Number of flashes (~ 50 J)	Peroxide estimated in the mixture after photolysis ($\times 10^4$ mole/l)	Concentration difference in the blank on flashing (moles/l)	Peroxide decomposed ($\times 10^5$ moles/l)
0.5	0.49 ± 0.02	5	0.05 ± 0.02	nil	4.4 ± 0.02
1.0	0.98 ± 0.02	25	0.21 ± 0.02	nil	7.7 ± 0.02
3.0	2.99 ± 0.01	8	2.70 ± 0.02	nil	2.9 ± 0.02
5.0	4.98 ± 0.01	4	4.79 ± 0.02	nil	1.9 ± 0.02

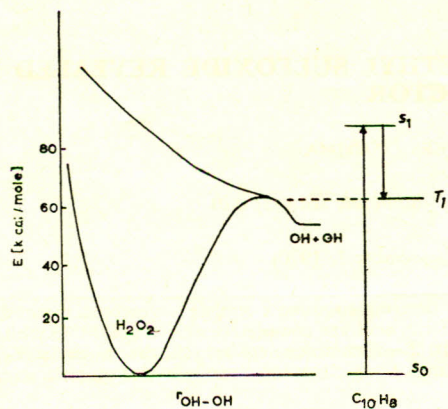


Fig. 4.—Potential energy diagram showing transfer of energy from triplet naphthalene to peroxide.

reaction are two alkoxy radicals. Similar is the case with H_2O_2 . Since only the breaking of a single bond between oxygen-oxygen atoms is involved, the situation is very similar to the decomposition of a diatomic molecule. If the energy transferred during an encounter is so much that the number of vibrational levels populated reaches the convergence limit, the repulsive triplet state will be reached by peroxide molecules. The energy of the triplet state of naphthalene is 61 kcal/mole. Transfer of this energy during an encounter will raise the ground state peroxide molecules to their repulsive triplet state and dissociation into respective fragments will proceed.

The maximum efficiency for such a process will be when the probability of transfer during an encounter approaches unity. The quenching rate constants obtained are about a factor of 10 less than calculated by the modified Debye equation,

$$k_d = \frac{8RT}{2000\eta}$$

This difference suggests that quenching rates are slower than the diffusional rate. The lower values of k_Q , apart from improperly oriented collisions, may be due to a considerable rearrangement of the energy among the many degrees of freedom in the peroxide molecule, with a resulting decrease in the formation of the activated complex. As a result of this, not every encounter between naphthalene molecules and peroxide molecules is fruitful in energy transfer. There also seems some indication of increasing steric effect on the quenching probability as the size of —R group attached to the oxygen atom increases.

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