

VISCOSITY DEPENDENCE OF DI-t-BUTYL PEROXIDE QUENCHING EFFICIENCY FOR TRIPLET NAPHTHALENE

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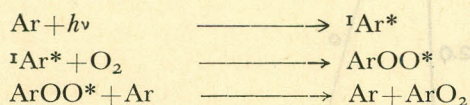
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Naphthalene triplet quenching by di-t-butyl peroxide at room temperature is not diffusion controlled. Bond dissociation energy of the peroxide is about 20 kcal less than triplet naphthalene, suggesting peroxide as efficient energy acceptor. The rate constant of triplet naphthalene quenching by di-t-butyl peroxide has been studied in propylene glycol as a function of viscosity. The ratio of $k_{\text{obs.}}/k_{\text{cal}}$, lies between 0.01-0.4, suggesting that quenching rates are slower than the diffusional rates. Contact charge-transfer mechanism for quenching of triplet naphthalene by peroxide is proposed which predicts that the rates of quenching will be slower than the encounter rates at all temperatures and viscosities.

Introduction

Absorption of radiation by an aromatic molecule may proceed in the following manner,



where ArOO^* represents an intermediate, and ArO_2 is a cyclic peroxide having an $-\text{O}-\text{O}-$ bridge across the rings. This suggests that even the purest sample of naphthalene may contain peroxide as an impurity formed during flashing. Since peroxides have a bond energy about 20 kcal/mole less than the energy of triplet naphthalene (55 kcal/mole), they might be expected to quench triplet naphthalene by energy transfer to repulsive triplet of the peroxide. And if the reaction between the triplet species and the peroxide is diffusion-controlled, the high rate constants observed for the decay of triplet naphthalene in solutions of moderate viscosities could be accounted for. But the measured value of k_Q for all the three peroxides studied, namely, hydrogen peroxide, t-butyl hydroperoxide and di-t-butyl peroxide are about 100 times lower than the diffusion-controlled rate constants,¹ showing that for peroxide the quenching rates at room temperatures are reaction-controlled and so could not account for the high rate constant value of naphthalene in solution.² Di-t-butyl peroxide is comparatively a stable peroxide and it was thought desirable to study its quenching effect over a wide range of viscosity.

Experimental

Apparatus.—A photoelectric flash photolysis apparatus described recently was used.³ This consisted of two quartz argon-filled flash lamps fired simultaneously by a 1 μF condenser charged

to 10 kV (50 J). The light from zirconum arc (Sylvania Electric Product Inc.) run from high capacity storage batteries, passed through the quartz cell, 22 cm long and an internal diameter of 1.5 cm, through a collimating tube, and into a Hilger model D 247 monochromator. At the exit slit was an RCA 931 A photomultiplier tube, the output of which was fed through a biasing unit into a Tcelectronix B545 oscilloscope triggered by the pulse which fired the flash lamps.

Temperature variation from -30 to -90°C was attained by controlling the rate of flow of dry nitrogen into the Dewar flask containing the absorption cell. All solutions were vigorously outgassed. Values for the viscosity of propylene glycol from -30 to -90°C were those reported by Stief.⁴

Material

Naphthalene was B.D.H. microanalytical grade. Di-t-butyl peroxide was obtained from T. Light and Co. The propylene glycol was A.R. grade Hopkins and Williams Ltd. Chemical; this showed 85% transmission at 2500 \AA in a 1-cm cell.

Di-t-butyl peroxide has a high vapour pressure and so the desired amount was degassed separately in a special ampule fitted with a break-seal device (Fig. 1) and mixed with the degassed naphthalene solution before flashing. Concentration of solutes before and after degassing was checked spectrophotometrically to ensure that no changes in concentration occurred during outgassing. The decay rates were measured by using a constant concentration of naphthalene (10^{-3}M). Rate measurements were made in increasing and decreasing manner of temperature variation and in random order. The mean of the two values thus obtained at one temperature was taken for calculation. This avoids any cumulative effect of successive exposure of the sample to flash irradiation and delay in temperature equilibration.

The temperature was controlled to $\pm 2^\circ\text{C}$. Rate constants determined from the slope of the first-order plots were reproducible to $\pm 10\%$.

Results

The observed pseudo first-order rate constants, k_{obs} , for the decay of triplet state in the presence of quencher is given by the equation,⁵

$$k_{\text{obs}} = k_1 + k_Q [Q] \quad (1)$$

where $[Q]$ is the concentration of the quencher in moles/l and k_1 is the rate constant in the absence of added quencher. The value of k_Q , the rate constant for quenching⁶ of naphthalene by di-*t*-butyl peroxide in propylene glycol, obtained was $7.8 \pm 0.3 \times 10^6 \text{ l mol}^{-1} \text{ sec}^{-1}$. The effect of viscosity on the quenching efficiency of di-*t*-butyl peroxide was measured by taking such a concentration of the peroxide (this was 10^{-2} M) that no triplet could be seen at room temperature. Under these conditions the triplet naphthalene formed was completely quenched by the peroxide. Viscosity variation was effected in propylene glycol by cooling. As the temperature was lowered the triplet naphthalene started showing up. The observed rate of the triplet decay decreased until a constant value was reached. After this, any change in viscosity by lowering the temperature did not effect the rate constant of triplet decay. The results are displayed in Fig. 2. Our plots showed the now familiar low and high viscosity regions.⁷ Values of k_{obs} at different temperatures in the presence of di-*t*-butyl peroxide are compared in Table 1 with k_1 . The results show that for di-*t*-butyl peroxide the temperature coefficient of the rate constants for quenching is similar to that of the decay of triplet naphthalene in the absence of any added quencher.

Discussion

Work on the triplet naphthalene in solution has made it clear that solvent viscosity and temperature play a large part in determining the life time of triplet state. The influence of temperature on k_{obs} . (Fig. 2) may be the result of change of solvent viscosity with temperature. Combination of Smoluchawki⁸ and Stokes-Einstein equation,⁹ gives a simpler expression showing the relationship between k_Q and quenching rate constant, solvent viscosity.

$$k_Q = \frac{8 RT}{3000\eta} \quad (2)$$

Fairly accurate agreement between the experimental value of k_Q and those calculated from the Debye equation is found for diffusion-controlled

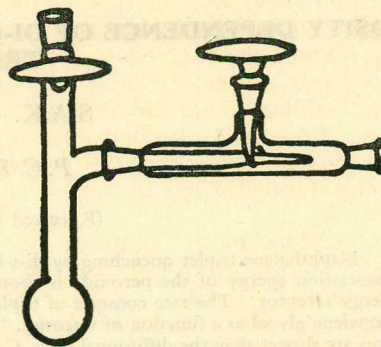


Fig. 1.—Ampule fitted with break-seal device.

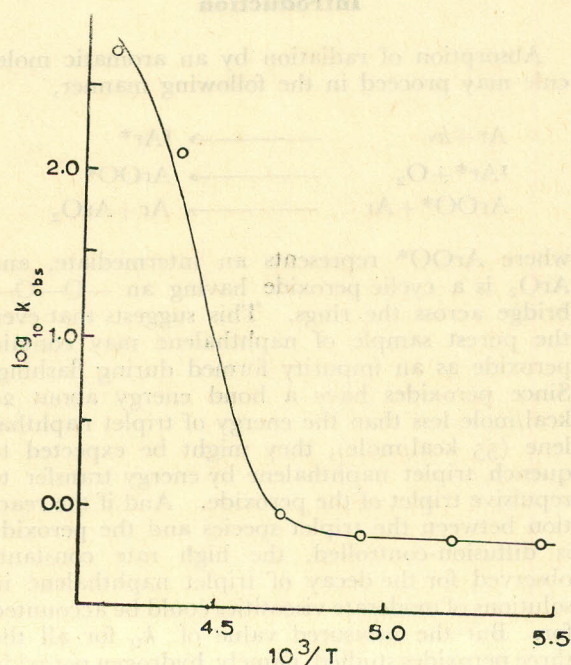


Fig. 2.—Plot of k_{obs} , pseudo first-order decay constant of triplet naphthalene against reciprocal of temperature in the presence of 10^{-2}M di-*t*-butyl peroxide.

TABLE I.

Temp $^\circ\text{C}$	k_1 sec^{-1}	k_{obs} sec^{-1}
- 30	13.18 ± 1.32	$7.41 \pm 0.7 \times 10^2$
- 40	4.37 ± 0.44	$2.5 \pm 0.3 \times 10^2$
- 50	1.45 ± 0.10	7.94 ± 0.7
- 60	0.69 ± 0.06	0.91 ± 0.09
- 70	0.58 ± 0.05	0.72 ± 0.07
- 80	0.55 ± 0.05	0.69 ± 0.07
- 90	0.52 ± 0.05	0.66 ± 0.06

processes provided the interacting molecules are spherically symmetrical with appreciably bigger molar volume than solvent molecule. These conditions put rather severe restrictions on the diffusional ability of the interacting molecules in solutions. Consequently the rate of reaction between the interacting species is greatly modified by the structural features of the solvent medium.

It is therefore more significant to investigate the relationship between $\log k_{\text{obs}}$ and $\log (\eta/T)$. This is shown in Fig. 3. The shape of this curve is almost identical to the Arrhenius plot of triplet naphthalene rate constant.³

Again considering the Debye equation,

$$k_Q = \frac{8RT}{3000\eta}$$

or

$$\ln k_Q = \ln \frac{8R}{3000} + \ln T - \ln \eta \quad (4)$$

here the variation in $\ln T$ values is small in the temperature range studied and could be neglected.

$$\therefore \ln k_Q = \text{constant} - \ln \eta \quad (5)$$

or

$$= \text{constant} - \frac{\Delta H}{2.303 RT} \quad (6)$$

where ΔH is the activation energy for viscous flow.

A linear relationship between k_Q and viscosity is predicted from equation (5). But a significant departure from linearity is observed (Fig. 3). This is because of two reasons; firstly, two different quenching mechanisms are operative in the two sections of the curve and, secondly, ΔH , for propylene glycol varies⁴ from 9 kcal/mole in the range 22–49°C to 17 kcal/mole between –35 and –78°C.

On energy considerations di-*t*-butyl peroxide is expected to quench triplet naphthalene efficiently. But the observed value of k_Q is a factor of about hundred less than the encounter rate constant. The values of k_Q calculated from the Debye equation at different viscosities and those obtained experimentally are shown in Table 2.

The much poor agreement of k_Q (Debye) with k_Q (experimental) suggests that quenching rates are slower than the diffusional rates. The lower value of k_Q (experimental), apart from some improperly oriented collisions, may be due to a considerable rearrangement of the energy among

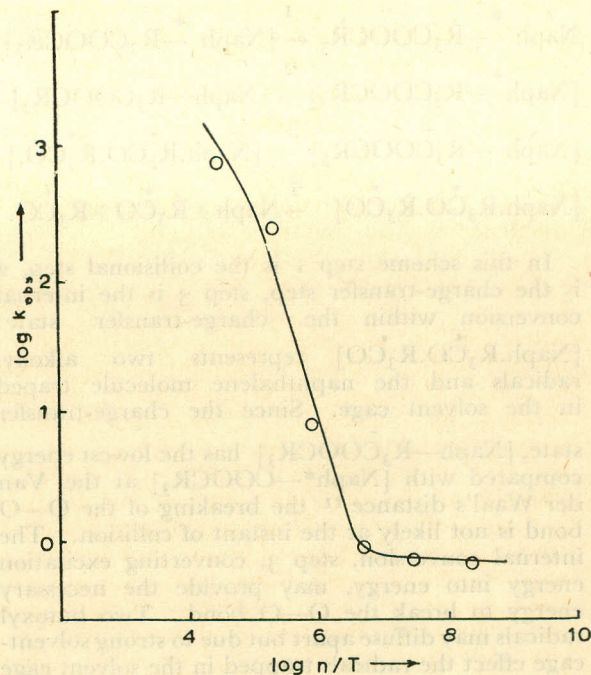


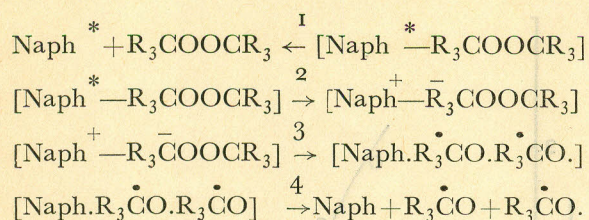
Fig. 3.—Variation of k_{obs} with η/T .

TABLE 2.

Viscosity c.p.	k_{cal} (Debye) l mole ⁻¹ sec ⁻¹	k_{exp} l mole ⁻¹ sec ⁻¹	$\frac{k_{\text{exp}}}{k_{\text{calc}}}$
1.00×10^4	5.40×10^5	7.28×10^4	0.13
4.47×10^4	1.16×10^5	2.47×10^4	0.20
1.78×10^5	2.78×10^4	6.49×10^2	0.02
1.00×10^6	4.73×10^3	22.0	0.01
5.62×10^6	8.02×10^2	14.0	0.02
4.47×10^7	95.88	14.0	0.15
1.26×10^8	35.71	14.0	0.4

the many degrees of freedom in the peroxide molecules, 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 seems to be some indication of increasing steric effect on the quenching probability as the size of —R group attached to the oxygen atom increases.¹

Although no chemical reaction between naphthalene and di-*t*-butyl peroxide could be inferred, yet the possibility of contact charge-transfer complex cannot be ruled out. Such a complex may not ordinarily respond to spectrophotometric investigations.¹⁰ The following mechanism may be considered.



In this scheme step 1 is the collisional step, 2 is the charge-transfer step, step 3 is the internal conversion within the charge-transfer state: $[\text{Naph} \cdot \text{R}_3\text{CO} \cdot \text{R}_3\text{CO} \cdot]$ represents two alkoxy radicals and the naphthalene molecule trapped in the solvent cage. Since the charge-transfer state, $[\text{Naph}^+ - \text{R}_3\text{COOCR}_3^-]$ has the lowest energy compared with $[\text{Naph}^* - \text{COOCR}_3]$ at the Van der Waal's distance,¹¹ the breaking of the O—O bond is not likely at the instant of collision. The internal conversion, step 3, converting excitation energy into energy, may provide the necessary energy to break the O—O bond. Two butoxy radicals may diffuse apart but due to strong solvent-cage effect the radicals trapped in the solvent cage recombine. That is why a significant decomposition at room temperatures was observed but at temperatures $< -30^\circ\text{C}$ no decomposition occurred. In naphthalene-peroxide system, the conditions for a charge-transfer are not very favourable, because the difference between the first ionization potential of naphthalene and di-*t*-butyl peroxide is small, the electron affinity of naphthalene is also not very encouraging. On this basis, it is pre-

dicted that step 2 is comparatively slower than step 1 and favour slower quenching rates than the encounter rates.

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