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Environmental Effects on Phosphorescence. III. Oxygen Quenching of Naphthalene Triplets in Compressed Polymethylmethacrylate*

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Bimolecular, diffusion-controlled oxygen quenching shortens triplet lifetimes and reduces phosphorescence intensities of organic solutes embedded in polymethylmethacrylate at room temperature. Matrix compression reduces the quenching of naphthalene and naphthalene-d_8 triplets until at pressures of about 12 kbar the presence of oxygen is no longer felt and the pressure dependence of the lifetime in the 12–30-kbar range is indistinguishable from measurements on thoroughly deaerated samples. The activation volume for oxygen diffusion in this polymer is approximately +12 cm^3/mole, as measured from the phosphorescence lifetimes of naphthalene-d_8. The high-pressure results confirm that diffusional quenching is not responsible for the effects of pressure on phosphorescence lifetimes in deaerated polymer matrices.

INTRODUCTION

The oxygen molecule ($^3\Sigma_g^-$) is an efficient quencher of electronically excited molecules. Despite the wealth of experimental information, the nature of the quenching mechanism is still a partial mystery. This work addresses itself to oxygen quenching of aromatic hydrocarbon triplets in condensed media. Typical rates of $k_q \sim 10^9 M^{-1}\cdot\text{sec}^{-1}$ are found in fluids at room temperature.[1] The viscosity dependence of oxygen quenching rates has established a diffusion-controlled process.[2,3] Other experiments verified that oxygen does not form stable complexes with aromatic molecules[4] and that charge-transfer absorption spectra arise from collision contacts of solute and oxygen.[5,6] An increase in the oscillator strength (and hence radiative rate) of the T_1–S_0 absorption has been found at very high oxygen concentrations in solutions, with negligible effect on the energy levels.[7] In rigid media where diffusion can be essentially stopped, static quenching has been identified and related to an effective quenching radius.[8] Theoretical discussions of the oxygen quenching phenomena invoke radiationless intermolecular energy transfer to produce electronically excited oxygen,[9,10] or charge transfer[5,9,11] as well as electron-exchange[8,12] interactions as primarily responsible for enhancing the nonradiative triplet decay.

Polymer matrices are permeable to gases at room temperature, despite their macroscopic rigidity. Oxygen quenching of phosphorescence from aromatic solutes in plastics has been used to measure the diffusion coefficient of oxygen.[13,14] It is generally assumed that large aromatic molecules are essentially immobile in polymer matrices,[13] i.e., the polymer is rigid with respect to the solute and semifluid with respect to oxygen. Then the rate equation for triplet depopulation is

$$-d[T_1]/dt = (k^0 + k_q[\text{O}_2])[T_1], \qquad (1)$$

where $k^0 = k_p + k_p'$ gives the first-order triplet decay in the absence of quencher. The relative magnitudes of k_p and k_p' describe the importance of the radiative and

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nonradiative processes, respectively. The rate constant k_q is a measure of the probability that a triplet will be quenched by an encounter with oxygen during its lifetime. The intensity is decreased as well as the measured lifetime shortened by bimolecular diffusion-controlled quenching. The magnitude of k_q depends on temperature and the microscopic viscosity η of the medium ($k_q \sim T/\eta$). Equation (1) does not include those triplets which are immediately lost by static quenching. The latter process occurs on a shorter time scale and depends upon the time-averaged fraction of oxygen molecules within some critical radius R_0 of a given electronically excited solute molecule.

In the present work the phosphorescence intensities and lifetimes of perprotonated and perdeuterated naphthalene are examined in oxygen-containing polymethylmethacrylate (PMMA) as a function of pressure (0–32 kbar) at room temperature. It is found that at progressively higher pressures the quenching diminishes and eventually stops near $P \sim 12$ kbar. The triplet decay behavior above this pressure is independent of oxygen and solute concentrations and indistinguishable from previously reported results on thoroughly deaerated PMMA matrices.[15,16]

RESULTS

Atmospheric Pressure

The PMMA samples are prepared as previously described.[15] After removal of gaseous residues at 120°C and 10^{-6} torr, the ~0.5-mm-thick plastic disks are exposed to a known pressure of oxygen at room temperature. The sample-loading and high-pressure apparatus, in which the atmospheric pressure runs are also made, have been described.[15] The oxygen pressures above the sample ranged from 10^{-3} to 10^2 torr in these experiments. Assuming that the 10^{-2}-torr oxygen atmosphere equilibrates with the plastic sample, a rate constant $k_q \sim 10^5 M^{-1} \cdot \text{sec}^{-1}$ is computed for naphthalene-d_8 from Eq. (1). This value is one order of magnitude lower than other estimates.[13,14] Differences in polymer molecular weight and experimental procedures can easily account for the difference. Since the solubility of oxygen in PMMA is unknown, quantitative studies as a function of quencher concentration could not be made. However, the maximum O_2 concentration which can be attained in these samples is probably reached somewhere below 10^{-1} torr oxygen pressure and is sufficient to quench all phosphorescence. Then an increase of the oxygen pressure by four orders of magnitude above 10^{-2} torr will increase the concentration in the plastic film by less than a factor of 10. The decay curves from samples exposed to oxygen pressures exceeding 10^{-3} torr are nonexponential at atmospheric pressure. The shortening in lifetime in the presence of oxygen[17] is accompanied by a large decrease in the steady-state phosphorescence intensity.

Activation Volume for Oxygen Diffusion

Matrix compression reduces and finally stops oxygen quenching at $P \sim 10$–14 kbar, as illustrated in Figs. 1 and 2. There is a wide scatter of "lifetimes" at low pressures, so that these points are not shown in Fig. 1. A gradual lengthening in lifetime is observed with increasing pressure. Evidently the initial effects of pressure are the shortening of diffusion path lengths, i.e., the number of voids or the free volume is being reduced under pressure.[18] The fact that the quenching rate constant has become insignificant relative to k^0 above ~12 kbar suggests that gross fluctuations in the microscopic matrix density have been removed and that increased compression for $P > 12$ kbar is predominantly due to a decrease in intermolecular separation.

Shaw[13] found a small activation energy for oxygen

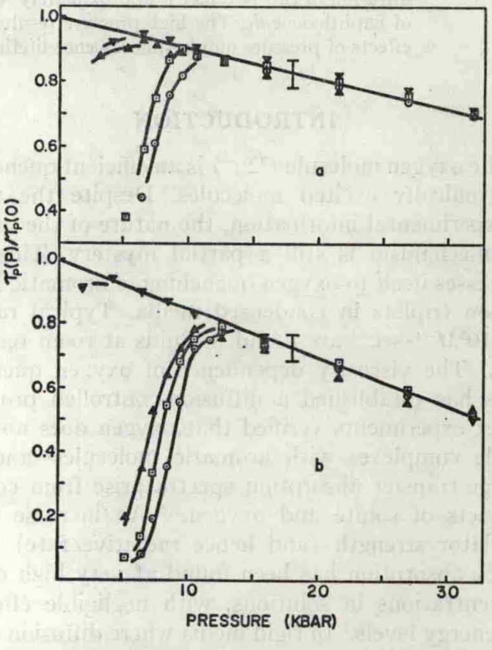

FIG. 1. The relative phosphorescence lifetimes $\tau_p(P)/\tau_p(0)$ of (a) naphthalene and (b) naphthalene-d_8 as a function of pressure on PMMA films containing O_2. The films were previously exposed to an oxygen atmosphere of 490 torr (⊙), 105 torr (⊡), 1 torr (△), and 5×10^{-3} torr (▽). The solubility of oxygen in the PMMA films is unknown. The intercept of unity at zero kbar pressure corresponds to 1.50 sec for naphthalene and 14.3 sec for naphthalene-d_8 and represents the triplet lifetime in the absence of oxygen.

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diffusion in PMMA, suggesting that oxygen and not solute molecules are diffusing through the "connected" voids. The pressure dependence of k_q may then be used to calculate an activation volume for oxygen diffusion. Since $\tau_p^{-1} \sim k_q \sim 1/\eta \sim D$, where the latter proportionality is due to the Stokes–Einstein relationship, we may write, for constant temperature,

$$d\ln\tau_p/dP = -d\ln D/dP = \Delta V^{\ddagger}/RT. \qquad (2)$$

Here D is the diffusion coefficient, $\Delta V^{\ddagger}$ the activation volume for diffusion, and τ_p^{-1} is the observed rate of triplet decay in the region where $k_q[O_2] > k^0$. It has been determined earlier[16] that the pressure dependence of k^0 in the absence of O_2 is small. The $\Delta V^{\ddagger}$ values are approximately +12 cm³/mole for naphthalene-d_8 and +4.2 cm³/mole for protonated naphthalene. The smaller value in the latter case arises in part because k^0 makes an appreciable contribution to the observed decay rate.

It should be mentioned that the arresting of oxygen quenching by pressure can be reversibly and repeatedly obtained provided the total illumination time is held to a minimum. Above 5 min or so of exposure to ultraviolet irradiation, oxygen removal by reaction with the polymer[19] is noticed. The intensities were also reproducible once the salt-sample interfaces[15] became fused on the first pressure cycle. Comparison of Figs. 1 and 2 reveals that at a given pressure of, say, 10 kbar, the ratios of steady-state intensities I_p are increased by a greater amount than the phosphorescent lifetimes τ_p are reduced. Deaerated samples also show[15] that percentage changes in I_p are greater than in τ_p. The explanation is related to the fact that in addition to τ_p other processes involving the singlet manifold, including $S_1 \rightsquigarrow T_1$ intersystem crossing, determine phosphorescence intensites. The diffusional nature of quenching is indicated by the larger intensity changes for the longer-lived triplet species. Of course, great uncertainties accompany the determination of the normalizing factor $I(0)$, since the intensities are so weak in the presence of O_2. This will not affect the shapes of the curves in Fig. 2, but the numerical values of the intensity ratios have only qualitative significance. Incidentally, the spectra from samples exposed to 10^{-3}–10^{-2} torr O_2 pressure yield identical red shifts to those observed for deaerated samples within experimental error.[15]

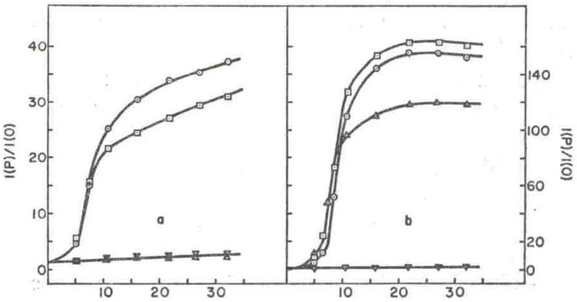

FIG. 2. The steady-state phosphorescence intensity ratios $I(P)/I(0)$ as a function of pressure P for (a) naphthalene and (b) naphthalene-d_8 in PMMA with different oxygen contents. The symbols identifying the relative oxygen content are the same as in Fig. 1. $I(0)$ is the intensity at 1 atm in the presence of the specified amount of oxygen.

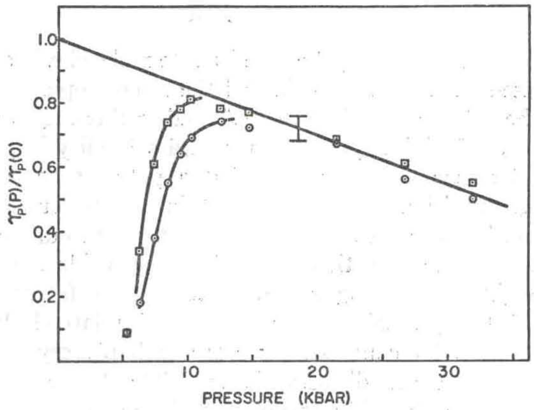

FIG. 3. The pressure dependence of the relative phosphorescence lifetimes of naphthalene-d_8 in PMMA films exposed previously to an atmosphere of 105 torr oxygen. The naphthalene-d_8 concentrations in the monomer solutions were $10^{-1}M$ (⊙) and $10^{-4}M$ (⊡).

Very High Pressures ($P \geq 12$ kbar)

The lifetimes become completely exponential and shorter again above 12 kbar, as illustrated in Fig. 1. The pressure dependence of τ_p is now linear and extrapolates to the 1-atm lifetime measured for deaerated samples. The "activation volumes,"[16] for triplet decay of naphthalene-h_8 and -d_8 when calculated from the 15–30-kbar plots of O_2-containing samples is the same as previously found in the absence of oxygen. Figure 3 demonstrates that the results are independent of solute ($10^{-4}M$–$10^{-1}M$) as well as oxygen concentration. Upon release of pressure, the quenching of oxygen is again observed. The intensities also change relatively little for naphthalene-d_8 in the 12–30-kbar range, as observed in the absence of oxygen. In the case of naphthalene, however, the intensities continue to rise above ~12 kbar, although less steeply than in the 5–12-kbar range. The difference in the intensity behavior of the two compounds is apparently real but not understood on the basis of presently available information. The feature that $\tau(P > 12\text{ kbar})$ is independent of $[O_2]$ in the matrix suggests that oxygen is not responsible for the observed effects in deaerated samples.[16]

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DISCUSSION

Oxygen quenching of excited solute molecules in compressed PMMA has elucidated the microscopic nature of the polymer matrix. Meares[20] made a thorough study of gas diffusivity, permeability, and solubility in polyvinylacetate. He concluded that a polymer below its glass transition temperature contains a sufficient number of holes to accommodate an equilibrium number of gas molecules. Further, these holes or voids may be thought of as being linked to form tunnels through which the gas molecules can move with relatively little resistance. By contrast, there are probably crystalline regions in which diffusion is negligible. However, the solutes are probably trapped in the amorphous, disordered regions so that the solute sites can easily be reached by gaseous quencher. The gradual lengthening of phosphorescence lifetime with pressure clearly illustrates the shortening of tunnels by compression. Surland[18] observed that void fractions of less than 0.05% have pronounced effects on the compressibility of the matrix at low (0–3 kbar) pressures. The distribution and relative importance of quasiliquid regions determine the 1-atm lifetimes which may typically fluctuate by 10% in different sample preparations. The extent of disorder may also change after a sample has been compressed at very high pressures and produce changes in the 1-atm values. Since the triplet decay is susceptible to these voids, caution must be exercised in using plastics in optical spectroscopy. On the other hand, long-lived triplets represent convenient probes of the microscopic environment.

It is unfortunate that the phosphorescence behavior could not be followed quantitatively as a function of oxygen concentration. Nevertheless, the experiments clearly demonstrate the consequences of diffusional quenching and the effect of pressure on it. The present results provide some information about activation volumes for oxygen diffusion in PMMA. The different values $\Delta V^\ddagger$ for the two solutes may be ascribed to the contributions from k^0 in the case of naphthalene and to the non-uniformity of the medium, i.e., there are differences in the sizes and lengths of the "connected" voids. The latter factor would be important when the quenchable solutes have different lifetimes. The magnitude of $\Delta V^\ddagger$ measures the reduction in microscopic fluidity of the matrix or the increased viscosity η. As for liquids,[21,22] these experiments show an exponential dependence of η on P, i.e., linear $\ln\tau_p$-vs-P plots in the region where diffusional quenching is observable. Of course, the exact functional dependence of η or D on pressure cannot be deduced from these experiments. The numerical values of $\Delta V^\ddagger$ for oxygen diffusion in PMMA are reasonable since this process has a low activation energy $\Delta E^\ddagger$ of ~ 250 cal/mole, according to Shaw.[13] For comparison, the self-diffusion in liquid pentane is characterized by $\Delta V^\ddagger = 11.4$ cm^3/mole and $\Delta E^\ddagger = 990$ cal/mole.[21] Activation volumes for oxygen quenching in liquids have not been measured.

These experiments do not provide information about the physical mechanism of diffusional quenching. One principal reason for doing these experiments, however, was to determine the origin of the pressure shifts in lifetimes reported previously for deaerated samples.[15,16] The present results above 12 kbar reveal that the reduction in lifetime at higher pressures is not due to any dynamic quenching process resulting from the diffusion of oxygen or any other quencher or from rotational diffusion of the solute. All these processes have larger $\Delta V^\ddagger$ values of opposite sign to those measured for phosphorescence lifetimes above 12 kbar. Since the slope of $\ln\tau_p$ vs P above $P = 12$ kbar is independent of oxygen content, static quenching is also not responsible for the pressure-enhanced electronic relaxation from the triplet state. Static quenching should have no effect on lifetimes,[8,13] but it may be responsible for the subtle differences in the pressure dependencies of the intensities of the two naphthalenes (Fig. 2) and the fact that the percentage changes in I are much larger than in τ_p. If static quenching occurs within some critical distance ($R_0 \sim 10.5$ Å),[8] then the quencher concentration within R_0^3 increases with increasing pressures.

It is plausible that the enhanced electronic relaxation at high pressures is due to a volume (or density) effect. The solvent shell around a solute is filled below 12 kbar, and above this pressure an isotropic decrease in the intermolecular separation commences. This solvent shell defines the volume or polarizability of the solute molecule. Hodgkins and Woodyard[23] reported a correlation between triplet lifetime and ground-state polarizability. More significant would be a correlation with the *difference* in polarizability of triplet and ground singlet states. This difference would be proportional to the "activation volumes" reported previously for various solutes in PMMA.[16] Further experiments are underway to explore this volume effect in electronic relaxation.

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