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REACTIVITY OF POLYNUCLEAR AROMATIC HYDROCARBONS WITH O_2 AND NO IN THE PRESENCE OF LIGHT

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by

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ABSTRACT

The reactivity of 20 different aromatic hydrocarbons adsorbed on solid polystyrene fluffs with oxygen and nitric oxide in the presence of light has been studied. The reaction conditions simulated those encountered in polluted atmospheres. Among the compounds studied were anthracene, pyrene, naphthalene, chrysene, benz(a)anthracene and coronene. The photoexcited triplet and singlet states of the aromatic hydrocarbons react predominantly via the quenching of the fluorescence and phosphorescence by the paramagnetic O_2 and NO gases. The quenching of the triplets by oxygen occurs via the formation of an intermediate collision complex in which electrophilic exchange type interactions appear to be important. The probability of quenching per collisional encounter and the formation of singlet oxygen does not exceed 0.01 - 0.10 and depends on spin selection rules, the triplet energy, and the electron density (in the case of the monomethyl derivatives of benz(a)anthracene). In the case of NO quenching of the triplets this probability is much lower, in the range of 0.0005 - 0.005 and appears to be a charge-transfer process for molecules with a high triplet energy. The quenching of the singlet excited states by O_2 and NO is much more efficient than the quenching of the triplets and has a probability in the range of $\sim$ 0.30 - 1.0 and is not necessarily diffusion controlled. The most important contribution of the photoexcited aromatic hydrocarbons (per photon absorbed) to the photochemistry of atmospheres containing O_2 and NO appears to be the generation of singlet oxygen, since photochemical degradation of the compounds studied was negligible compared to quenching. The quenching probability of the triplets of the monomethyl derivatives of benz(a)anthracene by oxygen is compared to their carcinogenic and photodynamic activities. While the correlation with the carcinogenic activity is unclear, the relatively low photodynamic activity of the 7 and 12 monomethyl derivatives can be explained in terms of their low triplet lifetimes and lower probability of singlet oxygen formation per collisional quenching encounter.

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PUBLICATIONS RESULTING FROM THIS GRANT

1. R. Benson, "Interaction of Excited States of Polynuclear Aromatic Hydrocarbons with Oxygen and Nitric Oxide", Ph.D. Thesis, New York University, October 1973.
2. "Interaction of Triplets of Aromatic Hydrocarbons with Oxygen and Nitric Oxide", N.E. Geacintov, R. Benson and S. Pomeranz, Chem. Phys. Lett. 17, 280 (1972).
3. "The Quenching of Excited Triplets of Aromatic Hydrocarbons by Molecular Oxygen", R. Benson and N.E. Geacintov, J. Chem. Phys. 59, 4428 (1973).
4. "Deuterium Effect on the Quenching of Photoexcited Aromatic Hydrocarbon Triplets by Oxygen", R. Benson and N.E. Geacintov, J. Chem. Physics, 60, 3251 (1974).
5. In preparation (December 1973) "The Quenching of the Excited States of Benz(a)anthracene by Oxygen and Nitric Oxide", by N.E. Geacintov, R. Benson and J. Khosrofian, to be submitted to Chemical Physics Letters.

RESULTS PRESENTED AT MEETINGS OR CONFERENCES

1. International Conference on Luminescence, Leningrad, August 1972.
2. American Physical Society Meeting, New York, January 1973.

INTRODUCTION

This report summarizes the work performed under Grant Numbers AP ES 01 395-01, APO 1395-02, HEW - Public Health Service and later referred to as Grant 80193 from the Environmental Protection Agency. The period of support was about two years, from 06/01/71 to 05/31/72, and from 07/01/72 to 08/31/73. The findings are described in full in the Ph.D. thesis of Robert Benson who graduated in October 1973 and who was a graduate student supported by the EPA. The thesis is available from University Microfilms, Ann Arbor, Michigan.[1] In this report the main results of the research are summarized. The work is described in greater detail in the published papers.[2,3,4,5] Also, the results not yet written up as a paper are included in this report starting on page 8.

The summary gives an overall view of the results obtained in this study, while the published papers, preprints, draft of the forthcoming paper and R. Benson's thesis contain all the details.

OBJECTIVES

A detailed understanding of the physico-chemical properties and reactivities of polynuclear aromatic hydrocarbon carcinogens and allied non-carcinogens in simulated polluted atmospheres was sought. Of particular interest was the interaction of the aromatic hydrocarbons with components of polluted air such as oxygen, nitric oxide (NO), nitrogen dioxide (NO_2), and sulfur dioxide (SO_2) in the presence of light. The stability of these compounds and the eventual degradation products were to be assessed.

The long-range objective was to learn if there are any specific physical properties and chemical reactivities of polynuclear aromatic carcinogens which distinguish them from structurally similar non-carcinogens. The monomethyl derivatives of benz(a)anthracene provide an interesting system of carcinogenic molecules whose activity strongly depends on the position of the methyl group on the aromatic nucleus and their reactivity was studied from this point of view.

SCOPE OF THE RESEARCH PERFORMED

The originally proposed grant period of three years was reduced to two years in 1972. Consequently not all of the objectives were achieved. In particular the study of the reactivities of the polycyclic aromatic hydrocarbons with NO_2 and SO_2 were not performed.

The reactivity of the photoexcited states of 15 different aromatic hydrocarbons and five perdeuterated analogs with O_2 and NO were studied. This series included benz(a)anthracene and eight of its monomethyl derivatives. An effort was made to understand these reactivities from a theoretical point of view and to relate them to structural parameters of the aromatic hydrocarbons.

A technique was developed to study the reactivity of polycyclic aromatic hydrocarbons adsorbed on solid organic particles with various gases in the presence of light.

SIGNIFICANCE

Polycyclic aromatic carcinogens are present in urban polluted atmospheres and offer a potentially serious health hazard. This study has contributed to an understanding of the physico-chemical processes which occur when these polycyclic aromatic hydrocarbons adsorbed on organic particulates are irradiated in the presence of nitric oxide and oxygen. Neither of these components of polluted atmospheres leads to a significant quantum yield of degradation of the polycyclic aromatic hydrocarbons in the presence of light. However, the aromatic hydrocarbons act as efficient photocatalysts for the formation of the highly reactive singlet oxygen molecule (quantum efficiency per triplet photoexcited state formed $\lesssim$ 0.01 - 0.10) which is lethal to many living organisms.

SUMMARY OF RESULTS

1. The photoexcited triplet and singlet excited states of aromatic hydrocarbons are much more reactive than the ground state. A method was devised to study the reactivity of these states with gaseous oxygen and nitric oxide. It involves the preparation of fluff-like high surface/weight ratio organic particulates onto which the polycyclic aromatic hydrocarbons are adsorbed. The most suitable matrix was polystyrene and the best methods of sample preparation were determined.

2. The following aromatic hydrocarbons were studied (the structure is depicted on the following page): naphthalene, anthracene, chrysene, a,h-dibenzanthracene, pyrene, coronene, benz(a)anthracene and eight monomethyl derivatives of the latter (the 2,3,4,6,7,8,11 and 12 derivatives). Also perdeuterated anthracene, benz(a)anthracene, chrysene, pyrene and naphthalene were studied.

3. The reactivity of the singlet and triplet photoexcited states of these aromatic hydrocarbons with gaseous oxygen and nitric oxide was studied by observing the quenching of the fluorescence and phosphorescence emissions of the singlet and triplet excited states respectively. The singlet lifetime is in the nanosecond range and was measured as a function of O_2 and NO pressure by the photon counting technique. The triplet lifetime was in the range of 10 msec to 15 sec and was measured by signal averaging techniques as a function of O_2 and NO gas pressure.

4. Both O_2 and NO give rise to radiationless transitions within the intermediate aromatic hydrocarbon - O_2 (or NO) collision complex which leads to a shortening of both the singlet and triplet lifetimes.

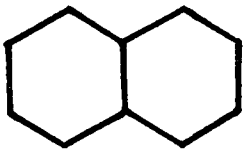
5. The probability of quenching by O_2 per collisional encounter is in the range of 0.01 - 0.10 for triplets and $\sim$ 0.3 - 0.7 for singlet excited states. For triplets the probability is decreased upon perdeuteration of the aromatic compounds. The results are consistent with a mechanism in which excited states of oxygen (singlet oxygen) are formed, which is in accord with the findings of other workers. Since the efficiency of formation by light of triplets exceeds 30%, these compounds appear to be efficient photocatalysts for the formation of singlet oxygen in polluted atmospheres.

Singlet oxygen does not appear to be formed upon quenching of the singlets.

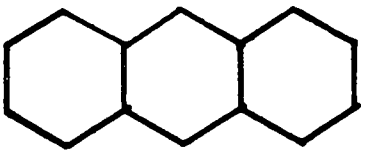
The quenching of the excited states by molecular oxygen was entirely reversible and the photochemical oxidation of the aromatic hydrocarbons is of minor importance in comparison to quenching of the singlet and triplet excited states.

6. The probability of quenching of triplets by O_2 and NO depends on spin selection rules, the triplet energy level (it decreases as the triplet energy increases), and to a lesser extent on methyl substituents and their location on the benz(a)anthracene nucleus. The quenching probability is due to an electrophilic interaction between O_2 and the aromatic molecule. If a methyl group is located at a site of high electron density, the O_2 quenching is less

Molecular Structures of Polynuclear Aromatic Hydrocarbons Studied



Naphthalene



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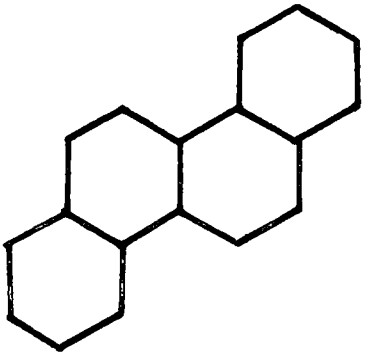

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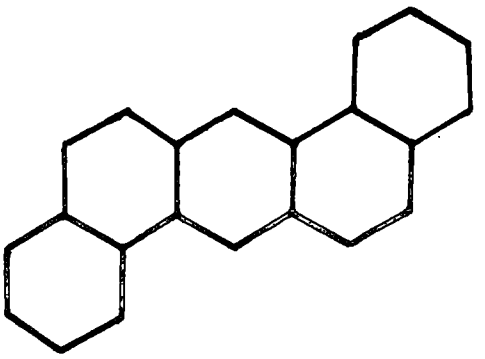
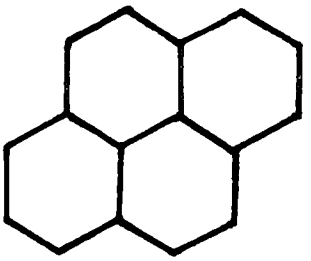
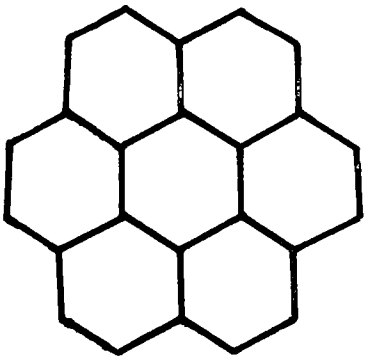


a,h-Dibenzanthracene

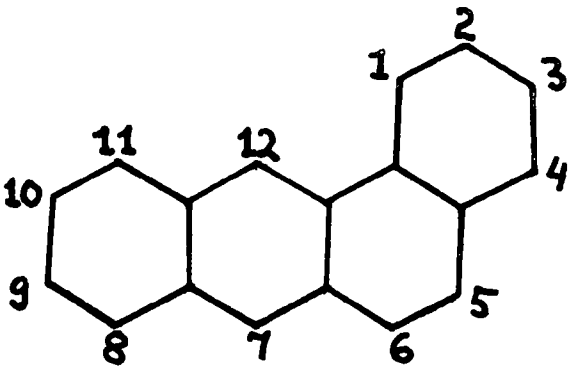


Pyrene



Coronene

Benz(a)anthracene



probable than when the methyl group is located at a site of low electron density. With NO quenching the site of the methyl group appears to be unimportant. This may be due to a charge-transfer quenching mechanism in the case of NO quenching, while in the case of O_2 quenching it appears to be mostly an exchange mechanism with only some charge-transfer character.

7. The probability of quenching of triplets by NO per collisional encounter is in the range of $\sim 0.0005 - 0.005$, thus much less efficient than in the case of O_2 quenching. The singlets on the other hand, with a probability of $\sim 0.8 - 1.0$ per encounter are somewhat more efficiently quenched by NO than by O_2. A charge-transfer mechanism is the most likely mechanism.

8. In the case of the quenching of triplets by NO, the fate of the excitation energy is much less clear than in the case of oxygen. In the case of oxygen part of the triplet energy is transferred to oxygen, resulting in the formation of the reactive singlet oxygen molecule. Nitric oxide does not possess any low-lying electronic excited states to which the energy could be transferred. Deuterium effect quenching experiments with NO indicate that only part of the excitation energy is dissipated by the C-H vibrational modes of the aromatic molecule. The rest is dissipated by the C-C modes, the matrix or the vibrations of the NO molecule.

9. Since NO is a minor component of polluted atmospheres, the photoexcited states decay primarily by reacting with oxygen via quenching, since the probability of quenching per encounter is fairly high, and oxygen is the dominant reactive molecule.

10. The reactivity of the benz(a)anthracene molecule and its monomethyl derivatives with oxygen was compared to their known biological activity. Some of these compounds are known to be carcinogenic. The most carcinogenic ones are the 6,7,8, and 12 derivatives. Within experimental error, these compounds also appear to display the lowest quenching constants, i.e. are least reactive with respect to quenching of triplets by oxygen. No special significance can be attached to this correlation, except that detoxifying reactions in vivo may render the more chemically reactive compounds harmless much more quickly than the chemically less reactive carcinogenic 6,7,8 and 12 derivatives. This would be a reasonable assumption if it could be shown that these detoxifying reactions are also electrophilic bimolecular reactions (as is oxygen quenching of the triplets).

S.S. Epstein and his co-workers have shown that there is a general correlation between the carcinogenic activity and photodynamic activity of close to 150 different compounds. An exception to this general rule are the 7 and 12 monomethyl derivatives of benz(a)anthracene, which are most carcinogenic, but photodynamically least active. Our studies indicate that the relatively low photodynamic activity of these two compounds is due to their lower probability per encounter of quenching (of triplets) by oxygen, and also to their faster triplet decay times. Short triplet decay times decrease the probability of a collision with O_2, and thus the probability of generation of singlet oxygen. The latter is the photodynamic lethal agent which causes the death of many living cells when they are irradiated in the presence of aromatic hydrocarbons and air.

REPORT ON WORK NOT PUBLISHED*

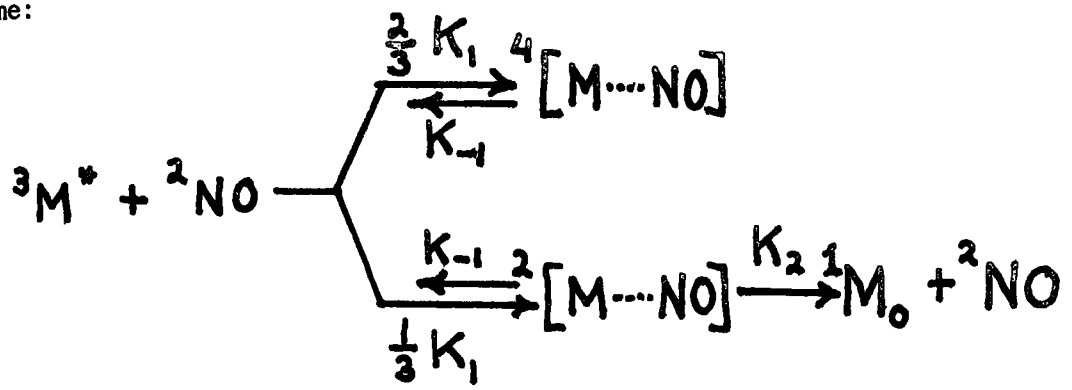
*Extracted (with minor editing) from the Ph.D. dissertation of R. Benson (New York University, 1973). A short paper entitled "The Quenching of the Excited States of Benz(a)anthracene by NO and O_2" based on this work is now in preparation (Dec. 1973).(5)

SECTION I

Quenching of Polynuclear Aromatic Hydrocarbons Triplet States by Nitric Oxide

Introduction

Nitric oxide is paramagnetic and is a doublet in its ground state. It is well known that NO quenches both singlet and triplet states of PAH* molecules (6). The lowest energy excited state of NO is at 37,900 cm^{-1}, which exceeds the lowest triplet energy levels and most of the lowest singlet levels of all the PAH molecules. This means that energy transfer to electronic states of NO is ruled out and that the pathway of quenching is therefore enhanced intersystem crossing. The quenching of a triplet PAH(^{3} M*) by NO can be represented by the following scheme:



(1)

The quenching constant can be written as:

$$\gamma = \frac{1}{3}K_1 \frac{K_2}{K_2 + K_{-1}} = \frac{1}{3}K_1 P \qquad (2)$$

where all the symbols have the same meaning as in O_2 quenching. The only difference in the expression for γ between O_2 and NO quenching is the spin statistical factor, which is 1/3 for NO quenching by the doublet enhanced intersystem crossing pathway, which is the only possible quenching pathway.

The Franck-Condon factors (F) involved in NO quenching of triplets, should be the same or somewhat smaller (if NO is vibrationally excited) than the Franck-Condon

*Polycyclic aromatic hydrocarbons

factor for unimolecular decay of the triplet. Thus, F should be much smaller for NO quenching than for O_2 quenching, because quenching by oxygen molecules involves partial energy transfer to the excited electronic states of oxygen which results in a smaller amount of excess energy (ΔE) to be dissipated by the aromatic molecule. Thus, if β_{el}^2, the electronic matrix element coupling initial and final states, is similar in magnitude in the quenching of triplets by both O_2 and NO, it is predicted that $K_2(NO) < K_2(O_2)$.

The experimental NO quenching constants should be simpler to interpret since there is only one quenching pathway, while there are three possible pathways in oxygen quenching. Calculations should also be simpler because the PAH-NO complex can be treated as a three electron problem, while the PAH-O_2 complex is a four electron problem.

We performed two separate studies on NO quenching: 1) we studied the effect of triplet energy and deuteration on $\gamma(NO)$ and 2) we studied the effect of methylation on the quenching of benz(a)anthracene.

The Dependence of $\gamma(NO)$ on the Triplet Energy

We measured the quenching constants, with NO, of the following PAH molecules: anthracene, benz(a)anthracene (BA), a,h-dibenzanthracene(a,h-DBA) and chrysene. The quenching constants, P values and K_2/K_{-1} values are listed in Table I. The P values are obtained from the following equation:

$$\frac{\gamma(NO)}{\gamma(O_2)} = \frac{\frac{1}{3}K_1 P(NO)}{\frac{1}{9}K_1 P(O_2)} = \frac{3P(NO)}{P(O_2)} \qquad (3)$$

Gijzeman et al (6) have measured $\gamma(NO)$ for a series of PAH molecules in various solvents using the photolysis technique. Their results, for hexane, are listed in Table 2.

It is obvious from our and Gijzeman et al's (6) results that NO quenching triplets is quite different from O_2 quenching. The plot of Gijzeman et al's value of γ (NO) versus E_T^* is shown in figure 1. We see that γ(NO) increases with E_T when E_T < 15,000 cm^{-1} and increases with decreasing E_T when E_T> 15,000 cm^{-1}. At low E_T, NO quenching is thus similar to O_2 quenching, but at high E_T, it is different.

Table 1: Quenching Constants γ, Probability of Quenching P and values of K_2/K_{-1} for Nitric Oxide Quenching of Aromatic Triplets in this Work.

Compound	γ X 10^3 $(\mu s)^{-1}$		P	K_2/K_{-1}
Anthracene	23	3	.017(.014-.020)	.018(.015-.021)
Benza(a)anthracene	9.5	.7	.0072(.0066-.0077)	.0072(.0067-.0078)
a,h-dibenzanthracene	2.0	.2	.0015(.0014-.0017)	.0015(.0014-.0017)
Chrysene	5.2	.4	.0040(.0037-.0043)	.0040(.0037-.0043)

Table II: Gijzeman et al's values for γ(NO) and P(NO) for Nitric Oxide Quenching of Aromatic Triplets in Hexane Solution

Compound	$E_T(cm^{-1})$	γ X $10^{-7}(lm^{-1}s^{-1})$	P
Triphenylene	23,300	72	.072
Phenanthrene	21,600	20	.020
Chrysene	20,000	10	.010
Coronene	19,100	4.6	.0046
a,h-dibenzanthracene	17,800	1.8	.0018
Benz(a)anthracene	16,500	1.3	.0013
Anthracene	14,700	0.84	.00084
3,4,8,9-dibenzpyrene	12,000	2.1	.0021
Tetracene	10,300	7.0	.007

*E_T... Energy of the triplet excited state.

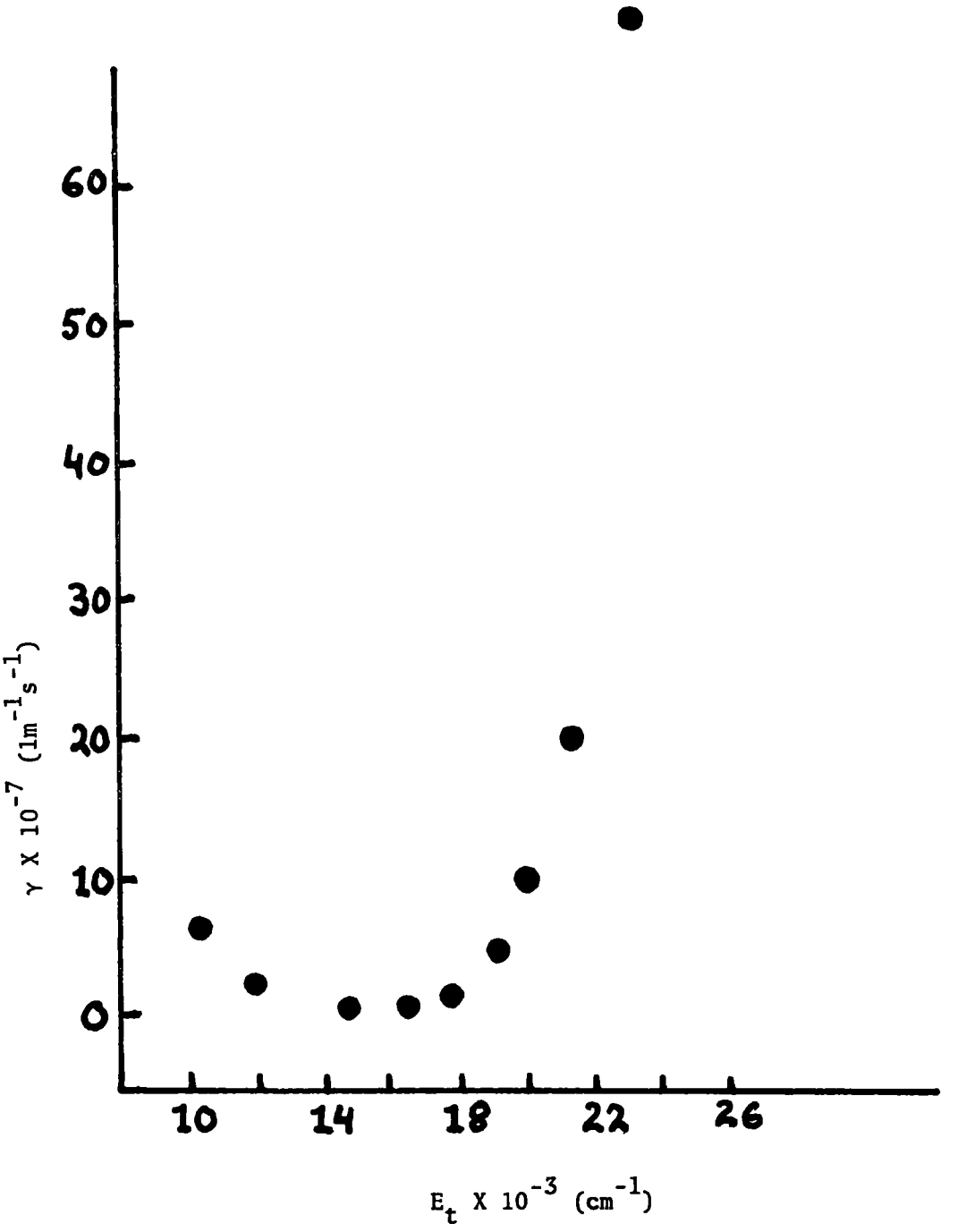


Figure 1 - Plot of Gijzeman et al's γ(NO) values versus Triplet Energy (in hexane solution).

The plot of γ obtained in the polystyrene matrix, versus E_T is shown in figure 2. It is evident by comparing figures 1 and 2 that there are differences between NO quenching in hexane and in polystyrene, in contrast to oxygen quenching (3).

The minimum value of γ in PS appears to be between 18,000-19,000 cm^{-1}, about 3,000 to 4,000 cm^{-1} greater than hexane.

Another difference between NO quenching in PS and in hexane are the values of P and K_2/K_{-1}, the values obtained in PS are larger by a factor of 2 - 20. This difference in part may be due to K_2, which obviously is not the same in the two media. The values of P(NO) in PS are obtained by assuming K_1 is the same for O_2 and NO in the PS; this assumption may be in error. However, it is clear that the values of P are small enough that $K_{-1} > K_2$, and thus γ itself is a measure of K_2/K_{-1}.

Gijzeman et al have interpreted their results in terms of an exchange mechanism at low E_T, which is similar to the quenching mechanism. As E_T increases, however, the charge transfer character of the intermediate complex increases and the CT mechanism appears to account for the triplet energy dependence of γ(NO) better than the exchange mechanism. β_{el}^2, the electronic matrix element coupling initial and final states, for a charge transfer mechanism is inversely proportional to the square of the difference in energy between the triplet (E_T) and the charge transfer state (E_{CT}):

$$\beta_{el}^2 = \beta_{CT}^2 \propto \frac{1}{(E_{CT} - E_T)^2} \qquad (4)$$

β_{CT}^2 will increase with a decreasing energy gap, $E_{CT} - E_T$. Gijzeman et al show that the gap $E_{CT} - E_T$ decreases as E_T increases, thus accounting for the increase in γ (NO) as E_T increases. At very low E_T, γ decreases with E_T, which is similar to oxygen quenching, indicating that Franck Condon factor dominates the quenching in this triplet energy domain.

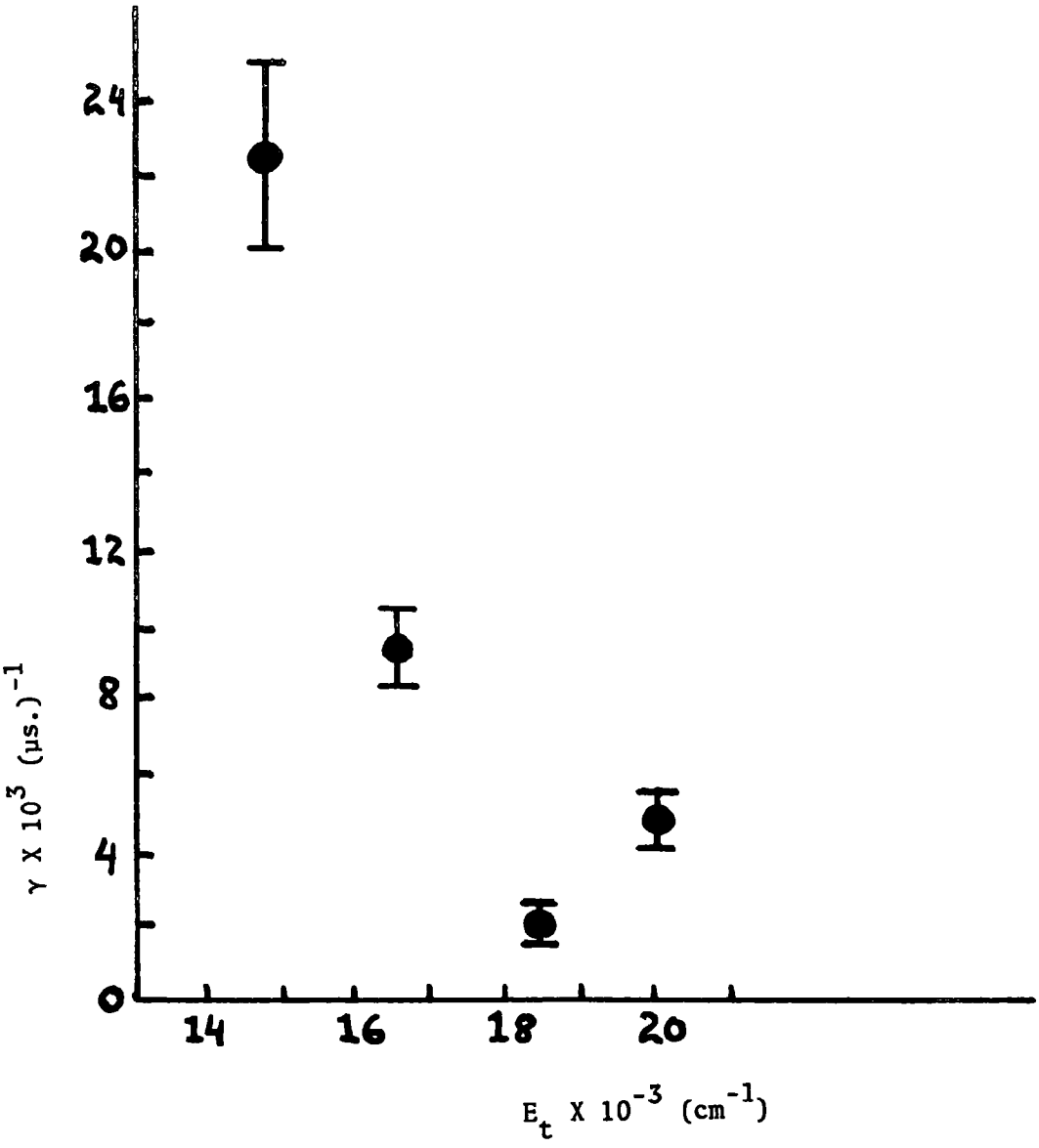


Figure 2 - Plot of our γ(NO) values versus Triplet Energy (in polystyrene matrix).

At high E_T, it is β^2_{CT} which dominates the variation in γ. The increase in β^2_{CT} appear to be large enough so that γ is increasing very rapidly despite the decreasing Franck-Condon factor with increasing E_T (see figure 1). This indicates the importance of the energy gap denominator in equation (4).

Gijzeman et al also studied solvent effects. They observed large decreases of one order of magnitude, for high E_T PAH compounds upon changing the solvent from hexane to acetonitrile. The decreases in γ with increasing polarity is smaller at lower E_T. In the very low E_T range (< 12,000), polarity has no effect on the γ. These solvent effects substantiate Gijzeman et al's interpretations of the variation of γ with E_T given above. The decrease in γ with increasing polarity has not been adequately explained, since in a charge transfer mediated quenching mechanism, one would expect γ to increase with increasing polarity of the solvent, because $E_{CT} - E_T$ should decrease.

The difference of 3,000 - 4,000 cm^{-1} in the two minima of the γ(NO) versus E_T curves (see fig. 1 and 2) between hexane and PS media can be explained by assuming that the average gap $E_{CT} - E_T$ is 3,000 - 4,000 cm^{-1} larger in PS. $E_{CT}-E_T$ can be approximately written as:

$$E_{CT} - E_T = I_P - E_A - E_T - C \qquad (5)$$

where: I_P is the ionization potential of the aromatic hydrocarbon

E_A is the electron affinity of NO (.9ev)[2]

C is the coulomb stabilization plus solvation energies of the complex.

The only difference between PS and hexane, in $E_{CT} - E_T$ will be found in the C term. Gijzeman et al, estimate that C = 4.1 ev, based on the analysis of their data. Based on a charge transfer mechanism Gijzeman et al write (in our notation):

$$\gamma = \frac{1}{3} K_1 \frac{K_2}{K_{-1}} = \frac{1}{3} \frac{K_1}{K_{-1}} \left(\frac{2\pi}{h} \rho \beta_{CT}^2 F \right) =$$

$$\frac{1}{3} \frac{K_1}{K_{-1}} \left(\frac{2\pi}{h} \rho \right) \left| \frac{\beta'_{CT}}{E_{CT} - E_T} \right|^2 10^{-\left(\frac{E_T - 4000}{\eta} \right) 10^{-4}} =$$

$$\frac{a}{(I_p - E_T - E_a - C)^2} \, 10^{-\left(\frac{E_T - 4000}{\eta} \right) 10^{-4}} \qquad (6)$$

where:

$$a = \frac{1}{3} K_1 / K_{-1} \left(\frac{2\pi}{h} \rho \right) (\beta'_{CT})^2$$

$$F = 10^{-\left(\frac{E_T - 4000}{\eta} \right) 10^{-4}}$$

All the factors in equation (6) are known except a and C. By plotting equation (6), the best fit is obtained when C = 4.1 ev. Subtracting .43 ev (3500 cm^{-1}, the difference in minima in fig. 1 and 2) from 4.1 ev, we estimate a value of 3.7 ev for C in our PS matrix.

The coulomb term for the iodine-benzene complex has been estimated to be 3 - 3.5 ev (3). Birk's (7) recently measured a value for C of 2.9 ev for the benzene -O_2 complex in the vapor phase. In the vapor phase where no solvation stabilization is present, C is smaller than in a non-gaseous state. Thus, we can say that our value of C for the polystyrene matrix is not unreasonable. Therefore, it is possible that the differences in the minima between the curves shown in figures 1 and 2 is due to the C term in equation (6).

From our own and Gijzeman et al's (6) results, the following can be said about NO quenching of triplets: At low triplet energies, the quenching appears to be similar to O_2 quenching in that $\gamma \alpha 1/E_T$; at high triplet energy NO quenching is dissimilar to O_2 quenching in that $\gamma \alpha E_T$. From these results it appears that the NO- PAH complex has charge transfer character which dominates the variation of the quenching constant, γ, when the triplet energy $E_T >$ 15,000 cm^{-1} in hexane, or $E_T >$ 18,500 cm^{-1} in PS, while at lower energies the Franck-Condon factors dominate the variation of γ with E_T.

Effect of Deuteration on γ (NO) in Polystyrene

We measured γ for deuterated BA.* The result is $\gamma = 4.8 \pm .4 \times 10^{-3}$ $(\mu s)^{-1}$ and $K_2/K_{-1} = 3.7 \times 10^{-3}$ (3.4×10^{-3} - 4.0×10^{-3}). Thus, there is a deuterium effect (see table III). It will be recalled that the analogous ratio for O_2 quenching is 1.2.

Table III. The Deuterium Effect on Triplet Lifetimes, O_2 and NO Triplet Quenching Constants of Benz(a)anthracene

Process	ΔE
$(1/\tau(H)) / (1/\tau(D)) = 4.8$	E_T
$\gamma_H(O_2) / \gamma_D(O_2) = 1.2$	$E_T - E(^1O_2)$
$\gamma_H(NO)/\gamma_D(NO) = 2.0$	E_T

This result (i.e. $\gamma_H(NO)/\gamma_D(NO) > \gamma_H(O_2)/\gamma_D(O_2)$) can be explained in terms of the partial energy transfer from the excited aromatic triplet to O_2. This results in a lower ΔE (excess electronic energy) for O_2 quenching than in NO

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* We attempted to measure γ(NO) for other deuterated compounds also, but the results were erratic and are thus not reported.

quenching. This accounts for the larger deuterium effect in NO quenching.

The effect of deuteration on the triplet lifetime (in which $\Delta E = E_T$) of benz(a)anthracene is still larger and is about 4. (i.e. $(1/\tau(H))/1/\tau(D)=4$).

The deuterium effect on NO quenching is thus similar to O_2 quenching and unimolecular decay. This similarity indicates that in all three cases a substantial amount of energy remains on the aromatic molecule after quenching, (see table III).

According to our reasoning the Franck-Condon factor should be the same for unimolecular decay and NO quenching of the triplet state (ΔE values are approximately the same). Thus, the deuterium effect should be the same for both processes. However, we observe that the deuterium effect on the lifetime is larger than on $\gamma(NO)$. It is possible that nitric oxide is vibrationally excited during the quenching process. This would reduce ΔE (excess electronic energy) and consequently the F factor and deuterium effect would also be reduced. The exact amount of energy that is transfered to NO is not known but if we assume that three quanta of vibrational energy is transferred, then the deuterium effect is: $\gamma(H)/\gamma(D) = 3.35$*

Though the calculated deuterium effect is less than the deuterium effect on the triplet lifetime, it is still larger than the observed effect. We have no explanation for this anomalous small deuterium effect. The energy degradation mechanisms in the quenching process are thus not simply analogous to unimolecular decay. The F factors may not be the same in the two process, although in the case of oxygen quenching, this assumption appears to explain the deuterium effect in a reasonable manner.

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* $\Delta E = E_T - 3\ (1876\ cm^{-1})$ where $1876\ cm^{-1}$ is the fundamental frequency of NO.

Effect of Methyl Substituents on the Triplet State Quenching of Benz(a)anthracene by Nitric Oxide

A study of the effect of methyl groups substituents on O_2 quenching allowed us to characterize to some extent the actual physical interaction between the O_2 molecule and the triplet PAH.

We expect that a similar study with NO should also shed some light on the quenching mechanism.

In the following table the quenching rate constant, γ, for NO quenching of the triplet states of five compounds of the methyl BA family are listed.

Table IV. Quenching Constants for Nitric Oxide Quenching of the Methylated Benz(a)anthracene Triplets.

Compound	$\gamma(\mu S)^{-1} \times 10^3$
8 -Me-BA	4.8 ± .7
7 -Me-BA	5.6 ± .3
6 -Me-BA	5.0 ± .6
2 -Me-BA	5.1 ± .3
BA	8.3 ± .9

Discussion

The NO quenching constants of all of the BA derivatives studied are more than two orders of magnitude smaller than the quenching constants with oxygen. This difference can be explained by differences in K_1 or K_2. NO is physically about the same size as O_2, so that K_1 (NO) = K_1 (O_2). Thus the difference between γ(NO) and $\gamma(O_2)$ is probably due to differences in K_2. As mentioned before this difference is due to smaller Franck-Condon factors for NO quenching.

Also there may be differences in β_{e1}^2 between O_2 amd NO quenching.

Assuming that K_1 is the same for NO and O_2, P and K_2/K_{-1} values for NO quenching can be obtained from the O_2 quenching data by use of equation (3). In table V values of γ, P and K_2/K_{-1} are tabulated.

Table V. Quenching Constants (γ), Probability of Quenching (P) and Values of K_2/K_{-1} for Nitric Oxide Quenching of the Methylated Benz(a)anthracene Triplets

Compound	$\gamma(\mu s.)^{-1} \times 10^3$	$P \times 10^3$	$K_2/K_{-1} \times 10^3$
2 - MeBA	(5.1 ± .3)	4.2(4.5 - 4.0)	4.2(4.5 - 4.0)
6 - MeBA	(5.0 ± .6)	4.2(4.8 - 3.8)	4.2(4.8 - 3.8)
7 - MeBA	(5.6 ± .3)	4.6(4.9 - 4.4)	4.6(4.9 - 4.4)
8 - MeBA	(4.8 ± .7)	3.9(4.5 - 3.4)	4.0(4.6 - 3.4)
BA	(8.3 ± .9)	6.9(7.6 - 6.1)	7.0(7.7 - 6.2)

Besides being much smaller than $\gamma(O_2)$, $\gamma(NO)$ for the methylated BA compounds show a much different methyl group effect. There does not seem to be a steric effect, unlike O_2 quenching. This is supported by the fact that all of the methylated BA's have roughly the same value of γ, within experimental error. A methyl steric effect would result in values of $\gamma(NO)$ which would be dependent on the position of the methyl group, in analogy to the effects observed in oxygen quenching. Thus the methyl effect must be due to a bulk property of the BA molecule which changes upon methylation and which appears to be independent of the position of the Me group.

Ionization Potential

Since the quenching process with NO seems to involve a complex with considerable CT character, a bulk property of interest is the ionization potential. In table VI the ionization potentials of the different compounds studied are listed (2).

Table VI. Ionization Potential and Relative Energy Gap Between the Charge Transfer State and the Triplet State

Compound	Ip (ev)*	Ip - E_T (ev)
2 - MeBA	7.39	5.32
6 - MeBA	7.41	5.32
7 - MeBA	7.29	5.28
8 - MeBA	7.39	5.33
BA	7.50	5.42

* The Ip were estimated from CT absorption spectra

Equation 4 gives the expression for $\beta_{el}^2 \simeq \beta_{CT}^2$ for a charge transfer state, since

$\beta_{CT}^2 \alpha (E_{CT} - E_T)^{-2} = (\Delta E)^{-2}$, equation (5) is an expression for ΔE. If we make the reasonable assumption that only Ip changes significantly for the methyl benz(a) anthracene family, then we can represent ΔE by Ip - E_T. In table VI the values of Ip - E_T are tabulated.

According to the Ip - E_T values in table VI and invoking a charge transfer mechanism, BA should have the smallest quenching constant, and the methylated BA compounds should all have roughly the same value of γ which should be larger than γ(BA). This is not the case, and it is evident that this analysis does not explain the experimental observations.

If E_{CT} is located below E_T, then the experimental results make more sense. In this case ΔE would be smallest for BA, since it should have the highest energy charge transfer state. Again ΔE would be similar in size for the methylated BA compounds and larger than ΔE for BA. Thus γ for the methylated benz(a)anthracene

would be smaller than γ for BA according to equation (7).

This explanation of the observed results of NO quenching of triplet BA and its methyl derivatives assumes that E_{CT} is located below E_T. We can make an estimate E_{CT} according to eq. (9). The only unknown in this equation is C. Taking a value of C of 3.7ev as in the previous section, E_{CT} for BA is 2.94ev which is .86ev above the E_T level of 2.08ev. Because of this result it seems unlikely that E_{CT} would be below E_T. It is not impossible that C could have a value greater than 4.5ev; as shown in the previous section, Gijzeman et al (6) arrive at a value of C of 4.1 ev.

The inverse effect on γ of increasing the polarity of the solvent could also be explained by assuming that E_{CT} is smaller than E_T. Increasing the polarity of the solvent would decrease E_{CT} because of increased stabilization due to solvation. This would result in ΔE increasing as the polarity increases.

In summary, the experimental results can be explained by assuming that E_{CT} lies below E_T, but it is difficult to justify placing the E_{CT} level below E_T since the coulomb energy term C does not appear to be sufficiently large. This hypothesis can be verified or dismissed only after an independent determination of E_{CT} becomes available.

Promoting Modes - Another possible explanation of the methyl substituent effect is that a promoting mode causes the transition from the neutral complex to the charge transfer complex $(M....NO) \rightarrow (M^+....NO^-)$. This hypothesis assumes that E_{CT} is higher than E_T. Thus the presence of the methyl groups on the BA ring system would result in a decreased probability of thermal population of the promoting mode. This is because the more modes there are in the molecule, the less the probability that any particular mode is excited. The promoting mode hypothesis can also explain the deuterium effect. This is because the C-D modes being "softer" (lower $\hbar w$) would have more energy in them than C-H modes. This results

in the promoting mode having lower probability of being excited.

It is hard to see how a promoting mode mechanism could explain the variation of γ with E_T as shown in figure 2, or the solvent effect observed by Gijzeman et al. Because of these deficiences the promoting mode mechanism is not considered a likely one.

Other Mechanisms - Another possible explanation of the methyl substituent effect, which could also explain the solvent effect, is to be found in the energy independent part of β_{CT}^2. β_{CT}^2 can be expressed as:

$$\beta_{CT}^2 = \frac{\beta_{CT}'^2}{(E_{CT} - E_T)^2} \qquad (7)$$

It can be shown that $\beta_{CT}'^2$ is proportional to $4S^2/R^2$, where S is the overlap integral between appropriate wave functions of the quencher and PAH in the CT complex, R is the distance between the charge centers. $\beta_{CT}'^2$ should decrease with increasing R.

The methyl groups, because of the inductive effect, should cause the PAH cation in the CT complex to be less positive than in the unsubstituted PAH cation. Thus the electrostatic attraction is reduced resulting in an increased R value, and thus to a decreased $\beta_{CT}'^2$ value.

The solvent effect (a decrease in γ(NO) with increase in polarity of the solvent), could be explained in the same way. Increasing the polarity of the solvent would result in greater solvation and a slight increase in the distance between charge centers in the complex, which would result in decreased values of $\beta_{CT}'^2$. As shown before, increasing the polarity would also decrease E_{CT} and should thus increase $\beta_{CT}'^2$. It is hard to say which of these two effects, which are due to an increased solvent polarity, are more important than the other.

The analysis of our results of the methyl substituent effect on NO quenching of triplet BA is not satisfactory. The best explanation of the methyl effect,

$E_{CT} < E_T$, does not seem reasonable. The other explanations are speculative. More experiments must be done to elucidate the quenching process. The most important would be to try to locate the charge-transfer state energy level. The promoting mode mechanism could be checked by temperature experiments.

SECTION II

Quenching of Singlet Excited States of PAH's by Oxygen and Nitric Oxide

In an effort to characterize the polystyrene matrix we have measured the quenching constants by O_2 and NO, of the following singlet excited aromatic molecules: benz(a)anthracene (BA), 2-Me-benz(a)anthracene (2 MeBA), 7-MeBA, 12-MeBA, 4 - MeBA, naphthalene (O_2 only), and pyrene. The quenching constants K_q, are listed in Table VII.

Table VII. Lifetimes in vacuum, oxygen (1 atm.), and nitric oxide (1 atm.), and quenching constants $K_q(O_2)$, $K_q(NO)$ of some aromatics

Compound	τ(VAC)	$\tau(O_2)$	τ(NO)	$k_q(O_2)$	k_q(NO)
	(ns)	(ns)	(ns)	$(\mu s)^{-1}$	$(\mu s)^{-1}$
BA	43.6 ± .1	41.7 ± .1	40.5 ± .1	1.5(1.2-1.6)	2.4(2.1-2.6)
2 - MeBA	38.0 ± .1	36.9 ± .1	34.6 ± .04	1.1(0.8-1.2)	3.4(2.8-3.7)
7 - MeBA	47.2 ± .04	45.8 ± .1	43.6 ± .1	0.8(0.5-0.9)	2.2(2.0-2.4)
12-MeBA	33.1 ± .1	32.4 ± .1	30.6 ± .1	0.9(0.7-1.2)	3.3(3.0-3.6)
4 - MeBA	38.2 ± .1	36.9 ± .1	33.9 ± .1	1.2(1.1-1.5)	4.4(4.2-4.6)
Naphthalene	95 ± 2			2.3 ± .1	-
Pyrene	306 ± 4			0.8 ± .1	1.0 ± .1

From the data in Table VII it is obvious that singlet quenching is not diffusion controlled since the quenching constants are not identical to each other. Thus the porous polystyrene matrix experiments appear to be more similar to vapor phase (8) than to liquid phase (9) experiments with regards to quenching. Thus it can be concluded that P (the probability of quenching per encounter) for singlet quenching is less than unity. The value of P for singlet quenching by O_2 can be estimated from the following expression:

$$P(S) = 1/9(\gamma(S)/\gamma(T))P(T) \qquad (8)$$

The analogous expression for P(S) for NO quenching of singlets is:

$$P(S) = 1/3(\gamma(S)/\gamma(T))P(T) \qquad (9)$$

Using equation (8) and (9) we obtain for benz(a)anthracene -

$$\begin{aligned} P(S) &= .7P(T) \text{ for } O_2 \\ P(S) &= 88.6P(T) \text{ for NO} \end{aligned} \qquad (10)$$

Thus the probability of quenching of singlets by oxygen is less than for triplets, while the opposite is true for nitric oxide.

Intuitively one would expect in general that P(S) > P(T) because the Franck-Condon factors for singlet quenching should be much larger than for triplet quenching, (i.e., $E_{S_1} - E_{T_1}$, (or E_{T_2}) < $E_{T_1} - E_{S_0}$) if one assumes, as Potashnik et al have indicated (10) that triplet states are produced in quenching. Thus, the larger nitric oxide quenching constants of singlets as compared to triplets is understandable in terms of Franck-Condon factors. The smaller O_2 quenching constants of singlets as compared to triplets on the other hand, is not understandable in terms of Franck-Condon factors.

It has been shown that the likely quenching pathway for singlets is enhanced intersystem crossing (10). If the T_2 state is lower in energy than the S_1 state, it is likely that the T_2 state, rather than the T_1 state, will be the final state of the quenching process. This is because the energy gap ($E_{S_1} - E_{T_2}$) will be smaller and consequently the Franck-Condon factor will be larger than if T_1 is the final state. In Table VIII the quenching constants of three of the aromatic compounds studied is compared with the energy gap $E_{S_1} - E_{T_i}$ where T_i is the triplet state closest to S_1 in energy but still being below the S_1 state.

Table VIII. Singlet Quenching Constants $K_q(O_2)$, $K_q(NO)$ and $E_{S_1} - E_{T_i}$

Compound	$K_q(O_2)$	$K_q(NO)$	$E_{S_1} - E_{T_i}$	T_i
Pyrene	0.75	0.99	10,000	T_1
BA	1.6	2.51	9,500	T_1
Naphthalene	2.2	-	1,500	T_2

There is a rough correlation between both $K_q(O_2)$ and $K_q(NO)$ and $E_{S_1} - E_{T_i}$ but not enough compounds were studied to check the validity of the correlation. (Although we have an oxygen quenching constant for DBA, no data on the T_2 level could be found.) If the correlation is true it would indicate that variation in the Franck-Condon factor dominates variation in the quenching constants of singlets as well as of triplets. However, since this dominance did not hold true for NO quenching of triplets in those cases where charge transfer interaction in the intermediate complex was shown to be important, it is not obvious that Franck-Condon factors will dominate in singlet quenching by either O_2 or NO in such cases. With a charge transfer mechanism there are two important energy gaps to consider. These are either $E_{S_1} - E_{T_i}$ which determines the Franck-Condon factor, and $E_{CT} - E_{S_1}$ which determine the magnitude of β^2_{CT} (see equation (4)). $E_{CT} - E_{S_1}$ can be estimated from the equality $Ip - E_{S_1} - E_A - C$, where E_A is .5ev for O_2 and .9ev for NO, and we take 3ev as the value for C for both the O_2 and NO complex. In table IX values of $K_q(O_2)$, $K_Q(NO)$ and $(1/E_{CT}-E_{S_1})^2$ are listed.

Table IX. Quenching Constants $K_q(NO)$, $K_q(O_2)$ and values of $(E_{CT} - E_{S_1})^{-2}$ for the aromatic compounds studied

Compound	$K_q(O_2)$ (μs.)$^{-1}$	$(E_{CT}-E_{S_1})^{-2}$	$K_q(NO)$	$(E_{CT} - E_{S_1})^{-2}$
	oxygen		nitric oxide	
Benz(a)anthracene	1.6	1.6	2.51	6.57
Pyrene	0.78	1.98	0.99	9.18
Naphthalene	2.2	0.77	-	-

There seems to be no correlation between $K_q(O_2)$ or $K_q(NO)$ with $(E_{CT} - E_{S_1})^{-2}$ as one would expect. It is obvious that our models for singlet quenching are too simple or missing some crucial factor or concept since we cannot obtain any correlation between $K_q(NO)$ or $K_q(O_2)$ and E_{S_1} or Ip of the PAH. Such correlations were found with triplet quenching. The reason for this difficulty may be that the Franck-Condon factors are large in singlet quenching, so that subtle changes in ρ (density of final states factor) or β_{e1}^2 may dominate variations in the singlet quenching constants.

The Effect of Methyl Substituents on the Quenching of Singlet States of Benz(a)-anthracene by Oxygen and Nitric Oxide

Oxygen

The methyl group substituent effect appears to be the same for singlet quenching as for the triplet quenching by O_2. Therefore, the methyl effect on singlet quenching appears to be steric in nature. Thus the quenching constant is a function of the position of the methyl group. The 7 and 12 methyl derivatives of BA again have the lowest quenching constants indicating that oxygen acts as an electrophilic agent. Thus most of the conclusions made from the methyl effect on triplet state quenching by O_2 can also be made for singlet state quenching by O_2. In summary these conclusions are 1) singlet quenching is not similar to a 1,4-cycloaddition reaction, 2) or to free radical attack, 3) the effect of the methyl groups is mainly steric, thus O_2 must attack the singlet excited molecule around the perimeter of the molecular skeleton, and 4) oxygen acts as an electrophilic agent.

Nitric Oxide

The methyl effect on singlet quenching by NO does not appear to be similar to the methyl effect on triplet quenching by NO. The methyl effect on NO quenching of triplet states was not steric in nature but electronic. The methyl group reduces the ionization potential of the BA molecule; this decrease is independent

of the methyl groups position. With singlet quenching by NO the quenching constants in Table VII do not appear to be steric in the same sense as with O_2 quenching. If this were true then $K_q(NO)$ for BA and 7 - Me - BA should be very different, yet the observed $K_q(NO)$'s are similar in magnitude. A similarity of $K_q(NO)$ magnitudes for BA and 7-Me-BA and a 30% range in $K_q(NO)$ for the other methyl derivatives studies indicates that the ionization potential is not important in determining the magnitude of $K_q(NO)$. Thus a CT mechanism does not appear likely from our results. We come to the conclusion that the data for singlet state quenching by NO of the methyl derivatives of BA does not allow us to make any conclusion about the methyl effect.

Summary of Results and Conclusions of Singlet State Quenching of Aromatic Molecules by Oxygen and Nitric Oxide

The most important result of the singlet state quenching studies is that the quenching is not diffusion controlled. This result indicates that the porous polystyrene matrix is more akin to the vapor state than the liquid state, where singlet quenching is invariably diffusion controlled. A very tentative conclusion about singlet state quenching is that the quenching constant is inversely proportional to the energy gap between the S_1 state and the next lowest triplet state (T_1 or T_2). The methyl effect on singlet quenching by O_2 appears to be similar to the methyl effect on triplet quenching. On the basis of the experimental results, no definite conclusions are possible about the methyl effect on NO quenching of singlet states.

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16. ABSTRACT The reactivity of 20 different aromatic hydrocarbons adsorbed on solid polystyrene fluffs with oxygen and nitric oxide in the presence of light has been studied. The reaction conditions simulated those encountered in polluted atmospheres. Among the compounds studied were anthracene, pyrene, naphthalene, chrysene, benz(a)anthracene and coronene. The photoexcited triplet and singlet states of the aromatic hydrocarbons react predominantly via the quenching of the fluorescence and phosphorescence by the paramagnetic O_2 and NO gases. The quenching of the reiplets by oxygen occurs via the formation of an intermediate collision complex in which electrophilic exchange type interactions appear to be important. The probability of quenching per collisional encounter and the formation of singlet oxygen does not exceed 0.01-1.10 and depends on spin selection rules, the triplet energy, and the electron density (in the case of the monomethyl derivatives of benz(a)anthracene). In the case of NO quenching of the triplets this probability is much lower, in the range of 0.0005-0.005 and appears to be a singlet excited states by O_2 and NO is nuch more efficient than the quenching of the triplets and has a probability in the range of ~ 0.30-1.0 and is not necessarily diffusion controlled. The most important contribution of the photoexcited aromatic hydrocarbons (per photon absorbed) to the photochemistry of atmospheres containing O_2 and NO appears to be the generation of singlet oxygen, since photochemical degradation of the compounds studied was negligible compared to guenching. The quenching probability of the triplets of the monomethyl derivatives of benz(a)anthracene by oxygen is compared to their carcinogenic and photodynamic activities. While the correlation with the carcinogenic activity is unclear, the relatively low photodynamic activity of the 7 and 12 monomethyl derivatives can be explained in terms of their low triplet lifetimes and lower probability of singlet oxygen formation per collisional quenching encounter.

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