THE EFFECTS OF AMINES ON THE FLUORESCENCE AND m-XYLENE YIELDS FROM o-XYLENE AT 253 nm AND 30 °C

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Summary

The photochemistry of gaseous o-xylene in the presence of pyridine, piperidine, methylamine and ammonia has been investigated at 253 nm. The quantum yields of fluorescence and of o-xylene → m-xylene isomerization were measured as a function of the pressure of the added amine gas. Quenching of the fluorescence of o-xylene by pyridine is very effective but smaller fluorescence quenching yields are obtained on using piperidine, methylamine or ammonia. The m-xylene yield at first increases and then decreases on increasing the pressure of pyridine. The present data indicate that the excited singlet state of o-xylene and the highly vibrationally excited ground electronic states may be involved in the formation of m-xylene. The effects of the amines on both the fluorescence and the m-xylene yields from o-xylene are observed to follow the order pyridine > piperidine > methylamine > ammonia. The quenching ability of the compound seems to be closely related to the degree of similarity between its structure and that of the o-xylene.

1. Introduction

The photochemistry of the aromatic molecules benzene, toluene and the xylenes has been studied extensively. The quantum yields of fluorescence and of the isomerization product m-xylene in the photolysis of o-xylene have been measured at the 253 nm absorption band [1, 2] and in the vacuum UV region (160 - 210 nm) [3, 4]. Fluorescence was not observed or was extremely small for xylene in the vapour phase at wavelengths below 210 nm [5]. In the photolysis of o-xylene, there are different views as to the mechanism of m-xylene formation. Wilzbach and coworkers [2] suggest that o-xylene → m-xylene isomerization proceeds through a benzvalene intermediate. Bryce-Smith and Longuet-Higgins [6] consider that the first excited singlet state should lead to benzvalene. Ward [3] suggests that the highly vibrationally excited ground electronic states may be involved in the o-xylene → m-xylene isomerization. Cundall and Voss [7] discount the exis-

tence of any form of triplet in the o-xylene $\rightarrow$ m-xylene isomerization reaction. The present work is concerned mainly with the quenching of the yields of fluorescence and of the o-xylene $\rightarrow$ m-xylene isomerization at 253 nm by pyridine, this compound being different from the quenchers most often used, such as olefins, xenon or oxygen.

Pyridine absorbs UV light in two regions [8]: 248 nm (π, π^* transition) and 265 nm (n, π^* transition). Neither fluorescence nor phosphorescence of pyridine vapour was measured in the region 240 - 300 nm [9]. The quantum yield of the triplet state of pyridine [9] is very small compared with those of benzene and the xylenes. No product has been found in the gas phase photolysis of pyridine at 248 and 265 nm [9]. Therefore pyridine is used as the quencher, because it is an aromatic molecule with excited singlet states whose energies are comparable with those of benzene and o-xylene. Rapid energy transfer from the excited singlet state of o-xylene to pyridine may be expected. Measurement of the quenching of the yields of fluorescence of o-xylene and of the o-xylene $\rightarrow$ m-xylene isomerization may give information on the isomerization reaction mechanism and the excited states involved in the formation of m-xylene.

The effects of piperidine, methylamine and ammonia on the quenching of o-xylene fluorescence and on the formation of m-xylene were also measured to see if the structure of the quencher molecule is of importance. The quenching of benzene fluorescence yields by these amines was also measured for comparison.

2. Experimental details

o-Xylene and benzene (Merck, gas chromatography grade) were used without further purification except for thorough degassing. Pyridine, piperidine, methylamine and ammonia (all Merck, reagent grade) were bulb-to-bulb distilled on a vacuum system.

A grease-free high vacuum system was used for all experiments. A T-shaped quartz cell 5 cm in length and 3 cm in diameter with a side window 2.5 cm in diameter was employed. The cell was encased in an aluminium block which reduced stray light and could be used as a furnace.

The light source was a Hanovia 100 W mercury lamp. The light was focused on the entrace slit of a Bausch and Lomb model 33-86-45 monochromator. The entrance and exit slits were both 2 mm in width. A parallel light beam of about 2 cm^2 cross-section was passed centrally through the axis of the cell for the photochemical experiments.

The transmitted light was monitored by an RCA 935 phototube and the fluorescence was measured by an IP 28 photomultiplier tube operated on 700 V.

The normal irradiation time was 60 min. The photolysis products of o-xylene were identified by gas chromatography with a 3 m × 3 mm ss column packed with 10% thermon-1000 and 3% KOH on 80/100 mesh Chromosorb

W, and another ss column (6 ft × 1/8 in) packed with 5% sp-1200/1.75 Bentone 34 on 100/120 mesh Supelcoport was used. The product *m*-xylene was quantitatively analysed at 120 °C on a Shimadzu model GC-8A gas chromatograph with the 3 m × 3 mm ss column, which was equipped with a flame ionization detector and a Shimadzu model C-R1B data processor. Nitrogen was used as the carrier gas.

3. Results

The added foreign gases pyridine and piperidine absorb light at 253 nm and the fraction α of light absorbed by the *o*-xylene (or benzene) is calculated from the equation [10]

$$\alpha = \frac{a_1 p_1}{a_1 p_1 + a_2 p_2}$$

where a_1 and a_2 are the absorption coefficients of *o*-xylene and the added gas respectively and p_1 and p_2 are their corresponding pressures. The absorption coefficients of the pure compounds were obtained experimentally. Pyridine and piperidine do not emit light on 253 nm excitation. Methylamine and ammonia do not absorb light of wavelength 253 nm.

The quantum yields of fluorescence of *o*-xylene vapour were measured by using benzene ($\Phi_f = 0.19$ at 253 nm [11]) as the standard. The fluorescence yields of *o*-xylene as a function of the pressure of the foreign gas were determined and are shown in Table 1. The effects of the foreign gases on the fluorescence yield of benzene were also determined (see Table 1).

TABLE 1

Effects of amines on the fluorescence yields of *o*-xylene and benzene at 253 nm and 30 °C

Quencher (Torr)	Φ_f			
	Pyridine	*Piperidine*	*Methylamine*	*Ammonia*
4 Torr o-xylene				
0	0.342	0.342	0.342	0.342
2.8	0.098	0.228	0.332	0.228
5.6	0.045	0.138	0.313	0.222
8.4	0.031	0.112	0.280	0.220
11.2	0.023	0.072	0.260	0.215
10 Torr benzene				
0	0.18	0.18	0.18	0.18
2.8	0.041	0.127	0.18	0.155
5.6	0.019	0.122	0.17	0.154
8.4	0.013	0.109	0.16	0.153
11.2	0.009	0.071	0.15	0.150

Photolysis of *o*-xylene at 253 nm gave *m*-xylene as the major product and its quantum yield was also measured as a function of the added foreign

TABLE 2

Effect of amines on the isomerization yields of o-xylene to m-xylene at 253 nm and 30 °C for irradiation for 1 h

2 Torr o-xylene								
Pyridine (Torr)	0	0.2	0.5	1.4	2.8	5.6	8.4	11.2
m-xylene	0.02[a]	0.03	0.07	0.18	0.20	0.32	0.11	0.09
4 Torr o-xylene								
Pyridine (Torr)	0	5.6	11.2					
m-xylene	0.02[a]	0.17	0.09					
Piperidine (Torr)	0	5.6	11.2					
m-xylene	0.02[a]	0.10	0.10					
Methylamine (Torr)	0	5.6	11.2	22.4	44.8			
m-xylene	0.02[a]	0.03	0.05	0.03	0.02			

[a]The quantum yield of m-xylene was arbitrarily taken to be 0.02 without a foreign gas.

gases (see Table 2). The yield of m-xylene is very small on the addition of ammonia and was not measured quantitatively. Products other than m-xylene were not measured quantitatively. No products were observed in the photolysis of pure pyridine, piperidine or methylamine at 253 nm.

4. Discussion

o-xylene absorbs light at 253 nm to form the excited singlet state which may then emit fluorescence, cross over to the triplet state, isomerize to m-xylene through an intermediate such as benzvalene or may return to the ground electronic state. Pyridine is a planar aromatic molecule, and rapid energy transfer from excited singlet o-xylene (or benzene) to pyridine may occur. The data in Table 1 indicate that the quenching of fluorescence and thus of the excited singlet state of o-xylene (or benzene) is very effective, as expected.

Pyridine quenches the fluorescence of o-xylene and should also decrease the yield of the product m-xylene if it is formed directly from the excited singlet state of the o-xylene. In this study of the photolysis of o-xylene vapour at 253 nm, the fluorescence yield is found to decrease rapidly with an increase in pyridine pressure, while the amount of the product m-xylene increases at low pyridine pressures and then decreases on increasing the pressure of pyridine, as shown in Table 2. The present data indicate that pyridine probably promotes the internal conversion of the excited singlet of o-xylene to highly vibrationally excited ground electronic states which may lead to the intermediate benzvalene and then isomerizes to the product m-xylene. At higher pressures of pyridine, collisional deactivation of the highly vibrationally excited ground electronic states of o-xylene by the pyridine would decrease the formation of intermediate benzvalene and thus the m-xylene yield. The reaction mechanism may be simply expressed as

$$X + h\nu \longrightarrow {}^1X^* \tag{1}$$

$${}^1X^* \longrightarrow X + h\nu_f \tag{2}$$

$$\longrightarrow {}^3X^* \tag{3}$$

$${}^1X^* + M \longrightarrow X^v + M' \tag{4}$$

$$X^v \longrightarrow I \tag{5}$$

$$I \longrightarrow m\text{-xylene} \tag{6}$$

$$X^v + M \longrightarrow X + M \tag{7}$$

$${}^3X^* \longrightarrow X \tag{8}$$

where X, ${}^1X^*$, ${}^3X^*$, X^v, I and M denote o-xylene, excited singlet, triplet state, highly vibrationally excited ground electronic states, the intermediate benzvalene and the collision partner molecule (such as pyridine) respectively. The absorption of light by pyridine and the resulting processes are not included in the above mechanism.

By the steady state approximation, the quantum yield of fluorescence o-xylene may be expressed by

$$\Phi_f = \frac{k_2}{k_2 + k_3 + k_q[M]} \tag{9}$$

or

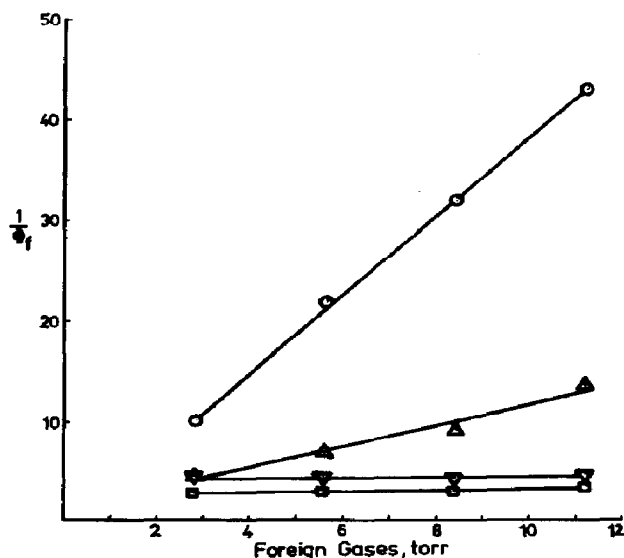$$\frac{1}{\Phi_f} = \frac{k_2 + k_3}{k_2 + (k_q/k_2)[M]} \tag{10}$$

Fig. 1. Quenching of fluorescence of o-xylene by foreign gases at 253 nm and 30 °C: ○, pyridine (slope, 3.73); △, piperidine (slope, 1.11); □, methylamine (slope, 0.12); ▽, ammonia (slope, 0.033).
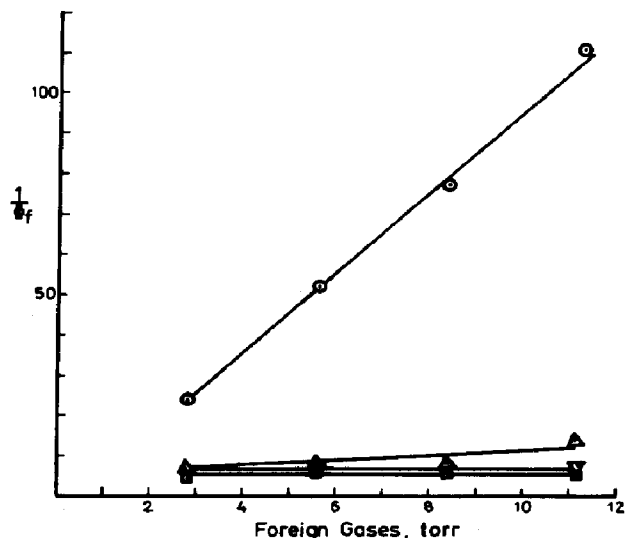
Fig. 2. Quenching of fluorescence of benzene by foreign gases at 253 nm and 30 °C: ○, pyridine (slope, 9.37); △, piperidine (slope, 0.48); □, methylamine (slope, 0.24); ▽, ammonia (slope, 0.021).

The plots of $1/\Phi_f$ *versus* the added foreign gas pressure [M] give straight lines as shown in Figs. 1 and 2. From the slopes of the straight lines one can calculate the quenching rate constant k_q if k_2 is known. The values of k_2 used were 6.54×10^6 s^{-1} for *o*-xylene and 2.3×10^6 s^{-1} for benzene [12]. The values of k_q are listed in Table 3.

TABLE 3

Rate constant of fluorescence quenching of *o*-xylene and benzene at 253 nm and 30 °C

Quencher	$k_q \times 10^{-9}$ $(M^{-1} s^{-1})$	
	o-Xylene (4 Torr)	*Benzene (10 Torr)*
Pyridine	460.5	406.8
Piperidine	137.1	20.8
Methylamine	14.1	10.4
Ammonia	4.1	0.9

For the quantum yield Φ_m of *m*-xylene we have

$$\Phi_m = \frac{k_5 k_q [M]}{(k_5 + k_7[M])(k_2 + k_3 + k_q[M])} \tag{11}$$

and

$$\Phi_m \approx \frac{k_q[M]}{k_2 + k_3} \tag{12}$$

if $k_q[M] \ll k_2 + k_3$ and $k_7[M] \ll k_5$ in eqn. (11) at low pyridine pressures.

The data in Table 2 generally agree with the predictions of eqns. (11) and (12), and the above mechanism seems to be valid for the o-xylene–pyridine system.

Pyridine has the greatest effects on both the fluorescence and the m-xylene yields from o-xylene, while piperidine, methylamine and ammonia have little or no influence. Piperidine, although cyclic, is not a planar aromatic molecule, and its effects on the fluorescence and the m-xylene yields are smaller than that of pyridine, as one may expect. Methylamine and ammonia have little or no effect because they are very different in structure from o-xylene or benzene. The rates of quenching of the excited singlet o-xylene by these amine molecules are closely related to the structure of the quencher molecule.

Acknowledgment

References

1 W. A. Noyes, Jr., and D. A. Harter, J. Am. Chem. Soc., 91 (1969) 2875.
 W. A. Noyes, Jr., and D. A. Harter, J. Phys. Chem., 75 (1971) 2741.
2 K. E. Wilzbach and L. Kaplan, J. Am. Chem. Soc., 86 (1964) 2307; 87 (1965) 404.
 L. Kaplan, K. E. Wilzbach, W. G. Brown and S. S. Yang, J. Am. Chem. Soc., 87 (1965) 675.
3 H. R. Ward, J. Am. Chem. Soc., 89 (1967) 2367.
4 H. R. Ward and C. I. Barta, J. Am. Chem. Soc., 90 (1968) 5347.
5 C. L. Braun, S. Kato and S. Lipsky, J. Chem. Phys., 39 (1963) 1645.
 T. A. Gregory, F. Hirayama and S. Lipsky, J. Chem. Phys., 58 (1973) 4679.
6 D. Bryce-Smith and H. C. Longuet-Higgins, Chem. Commun., (1966) 593.
7 R. B. Cundall and J. R. Voss, Chem. Commun., (1968) 902.
8 S. K. Lower and M. A. El-Sayed, J. Chem. Rev., 66 (1966) 199.
9 J. Lemaire, J. Phys. Chem., 71 (1967) 612.
10 S. Y. Ho, R. A. Gorse and W. A. Noyes, Jr., J. Phys. Chem., 77 (1973) 2609.
11 W. A. Noyes, Jr., W. A. Mulac and D. A. Harter, J. Chem. Phys., 44 (1966) 2100.
 M. G. Rockely, Chem. Phys. Lett., 50 (1977) 427.
12 Photochem., 4 (1973) 246 - 247.
 W. A. Noyes, Jr., and D. A. Harter, J. Am. Chem. Soc., 91 (1969) 7585.