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THE PHOTOCHEMISTRY OF LIQUID 1,4-DIOXANE AT 184.9 nm AND 147.0 nm*

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Summary

Photodecomposition of 1,4-dioxane in a condensed phase at 184.9 nm proceeds with quantum yields as follows: $\phi(C_2H_4) = 0.55$, $\phi(H_2) = 0.26$ and $\phi(CO) = 0.03$. Quantum yields at 147.0 nm are $\phi(C_2H_4) = 0.52$, $\phi(H_2) = 0.28$ and $\phi(CO) = 0.03$. Quenching studies coupled with these quantum yield measurements in the liquid phase afford Stern–Volmer quenching constants in the range 17 - 36 M^{-1}. Nitrous oxide and benzene are used as quenchers of the excited state leading to H_2 and C_2H_4 photolysis products following irradiation at 184.9 and 147.0 nm. The quantum yield for the production of N_2 at 184.9 nm has been determined to be ≈ 0.70. At 147.0 nm $\phi(N_2) \approx 0.42$ in 1,4-dioxane–N_2O solutions. The transfer of energy proceeds less efficiently in the higher excited state than in the ground state at 184.9 nm for N_2 production. At 147.0 nm experiments in solution using I_2 as a radical scavenger show that 51% of the initially produced hydrogen atoms are scavenged by 2×10^{-2} M I_2. Fluorescence quenching experiments employing C_6H_6 and N_2O show Stern–Volmer quenching constants of 28 and 38 M^{-1}, respectively. The quenching results show that the excited state involved in fluorescence is the same as that involved in photodecomposition.

Introduction

In this paper previous work carried out in this laboratory [1] is extended to photolysis at 184.9 nm and 147.0 nm in the liquid phase. In this way it was hoped to determine the mechanism for the population of the emitting state and to determine from which state(s) dissociation into the main products of the photolysis occurred. In a few simple hydrocarbons values for the products of vacuum photolysis in gas and condensed phase as well as studies of the excited intermediate have been carried out [2]. The problem of the

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assignment of the excited state that transfers energy is not simple [3] and there is evidence for the existence of more than one state which can transfer energy. In the liquid phase a correlation has been sought between fluorescence quenching and energy transfer processes involving excited 1,4-dioxane. This study is mainly concerned with the primary photochemical processes involved in the decomposition of 1,4-dioxane.

Experimental

The 1,4-dioxane (Matheson Coleman and Bell spectroquality reagent) was purified by the method of Hentz and Sherman [3]. The purity of the sample was checked by gas chromatography and the H_2O content of the distilled 1,4-dioxane was found to be less than 10^{-3}%. Gas chromatography was conducted with a flame ionization detector (FID) using a 1/8 in × 8 ft stainless steel column packed with 80 - 100 mesh Poropak Q; the column was at 170 °C and the carrier gas was He. The purified dioxane was stored in a dry-box under nitrogen and dried with $LiAlH_4$ prior to use. Benzene (Fisher certified reagent) was distilled in a Nester–Faust spinning band column and no impurity was detectable by gas chromatography using a FID. Methylcyclohexane (Phillips research grade) was passed through a column of silica gel to remove olefinic impurities. Nitrous oxide (Air Products Co.) was passed through a tube containing sodium hydroxide to remove atmospheric water and carbon dioxide. On the vacuum line N_2O was trap-to-trap distilled three times, collecting the middle portion. Prior to use it was pumped for 30 min at − 196 °C. Using a mixture of dry ice and acetone the N_2O was then let into the vacuum system retaining the traces of water left.

The construction and operation of the Xe lamp followed with minor modifications the one described previously [4]. A Hanovia custom-built low pressure mercury discharge tube was used for 184.9 nm irradiation. Using an Eppley Thermopile the intensity ratio between the 184.9 and the 253.7 nm line of the Hg lamp was determined to be $\approx$ 0.26, which agrees well with previously reported values [5]. In the condensed phase 147 nm photolysis a combination of a Xe lamp and a reaction cell [6] was used. The decadic extinction coefficient of 1,4-dioxane [7] is 5050 M^{-1} cm^{-1} at 147 nm. All light was absorbed within a distance of 0.1 μm. To remove products from the window fast stirring was carried out during photolysis to avoid accumulation of the products. The transfer and measurement of 1,4-dioxane gas and the collection and measurement of gaseous products have been described before [3, 8]. Because of the low sensitivity of the FID to N_2O, the N_2O did not interfere with product analysis.

The actinometer used at 147 nm was cyclohexane for which $\phi(H_2)$ is 1.0 [9]. The intensity was approximately 2×10^{15} quanta per cell volume (3.5 ml) per minute. At 184.9 nm a 5 M aqueous solution of ethanol was used as an actinometer [10]. A value of 0.40 has been reported for the quantum yield of H_2 formation. Ethanol was purified by removing carbonyl compounds with dinitrophenylhydrazine and subsequent fractionation. The actinometer intensity was approximately 5.2 × 10^{16} quanta min^{-1} per 3.5 ml cell volume. During the fluorescence measurements the space between the Hg lamp window and the LiF and interference filters was constantly flushed with N_2 to remove O_2. In order to eliminate the 253.7 nm line a LiF filter (Harshaw Chemical Co., Cleveland, Ohio), which had been made selective by irradiation with gamma rays, was employed [11]. The interference filter (obtained from Dr. Willard, University of Wisconsin, Madison, Wisc.) was butted against the LiF disk to cut all radiation but the 184.9 nm.

The fluorescence cells were made airtight with high vacuum Teflon stopcocks fitted with dioxane-resistant 3-butyl-M rings. Employing front-face reflection the fluorescence emission was analyzed using a monochomator–photomultiplier IP-28 unit. The positions of emission spectra are uncertain to ± 1 nm.

Results

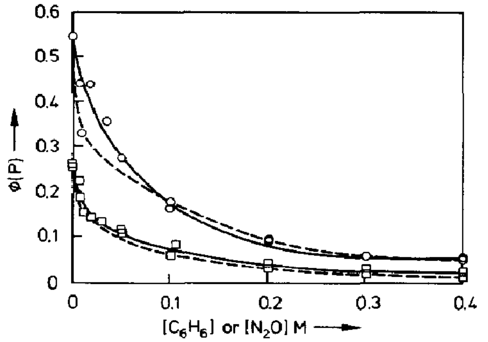
Quantum yields of photolysis are presented in Table 1.

TABLE 1

Quantum yields of formation of the primary products in the 184.9 nm and 147.0 nm photolysis of liquid 1,4-dioxane

	184.9 nm	147.0 nm
H_2	0.26 ± 0.03	0.28 ± 0.04
C_2H_4	0.55 ± 0.05	0.53 ± 0.06
CO	0.03 ± 0.01	0.04 ± 0.01

A number of quenchers have been used to gain insight into the lifetime of the excited state involved. Figure 1 shows the decrease of C_2H_4 and H_2 production as a function of C_6H_6 and N_2O concentration for 184.9 nm photolysis. In Fig. 2 the quenching results obtained using the same quenchers but following 147.0 nm photolysis are shown. The unquenchable yields can be seen to be of the same order of magnitude for both quenchers. Figure 3 shows the molecular nitrogen yields in liquid 1,4-dioxane with added N_2O following photolysis at 147.0 nm and 184.9 nm. The corresponding value of $\phi(N_2) = 0.69$ is found for 184.9 nm photolysis. A value of $\phi(N_2)$ for cyclohexane solutions 0.1 M in N_2O is 0.71 ± 0.05. With 147.0 nm photolysis the value for $\phi(N_2)$ attains a maximum of 0.38. In the upper state the value of $\phi(N_2) \approx 0.38$ indicates that 59% of the N_2O molecules in this upper state internally convert to the lowest excited state at 184.9 nm which is quenched by N_2O.



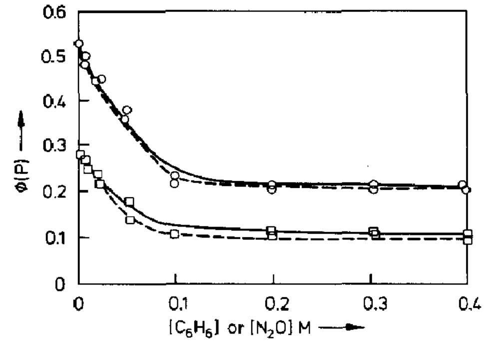
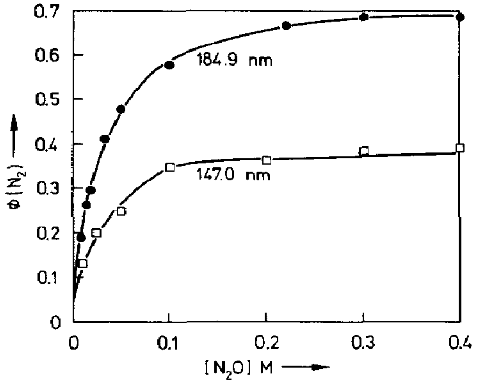


Fig. 1. Photolysis quantum yield of C_2H_4 and H_2 at 184.9 nm of liquid 1,4-dioxane using C_6H_6 and N_2O as quenchers at 25 °C: --o-- C_2H_4, --□-- H_2, both quenched by C_6H_6; —o— C_2H_4, —□— H_2, both quenched by N_2O.

Fig. 2. Photolysis quantum yield of C_2H_4 and H_2 at 147.0 nm of liquid 1,4-dioxane using N_2O and C_6H_6 as quenchers at 25 °C: --o-- C_2H_4, --□-- H_2, both quenched by C_6H_6; —o— C_2H_4, —□— H_2, both quenched by N_2O.



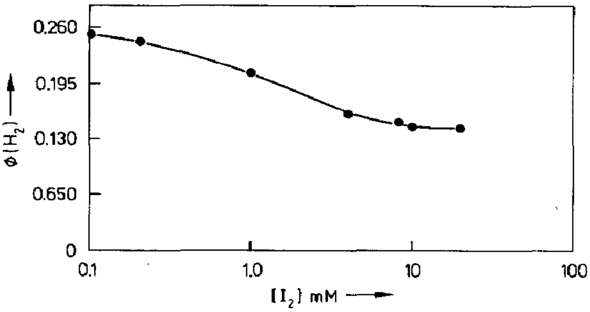


Fig. 3. Quantum yield of N_2 evolution at 147.0 nm and 184.9 nm in a solution of liquid 1,4-dioxane with added N_2O at 25 °C.

Fig. 4. Quantum yield of H_2 observed in 147.0 nm photolysis of liquid 1,4-dioxane when I_2 is added at 25 °C.

Iodine has also been added in the experiments to determine the degree of H atom involvement in the molecular hydrogen production after 1,4-dioxane photolysis. Concentrations of I_2 have been kept low so as to minimize excitation quenching by I_2. The concentration of I_2 is enough to scavenge the H atoms present [12].

The results of 147.0 nm photolysis when I_2 is added as a radical scavenger are shown in Fig. 4. The fact that $\phi(H_2)$ decreases with I_2 concentration indicates that both radical and molecular hydrogen are involved in the observed H_2 yield. In Fig. 5 fluorescence measurements monitored at the maximum of the reported emission [13] for 1,4-dioxane (245 nm) using N_2O, I_2 and C_6H_6 as quenchers are analyzed and the results obtained are presented in the form of Stern–Volmer plots.

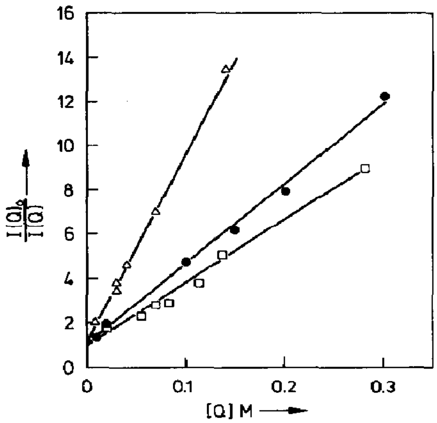


Fig. 5. Fluorescence quenching of liquid 1,4-dioxane observed at 245 nm using N_2O (●), C_6H_6 (□) and I_2 (△) as quenchers. The fluorescence of 1,4-dioxane has been induced at 184.9 nm.

Discussion

Photophysical processes in the photolysis of 1,4-dioxane

The mechanism of deactivation proposed for an electronically excited molecule of 1,4-dioxane takes into account the formation of the monomer excited state D^* postulated in gas phase studies and aggregate formation (eqn. (7)) in liquid phase. Where D^* is the excited monomer produced either by absorption in the first (D^1) or third (D^3) absorption band, it is proposed that for 147.0 nm irradiation reactions (1) - (11) could take place. The state D^3 corresponds to a higher excited state of 1,4-dioxane associated with the third band. Steps (4) - (11) would take place at 184.9 nm.

$$D \xrightarrow{147.0\ \mathrm{nm}} D^3 \tag{1}$$

$$D^3 \rightarrow P \tag{2}$$

$$D^3 \rightarrow D^1 \tag{3}$$

$$D \xrightarrow{184.9\ \mathrm{nm}} D^1 \tag{4}$$

$$D^1 \rightarrow P \tag{5}$$

$$D^1 \rightarrow D \tag{6}$$

$$D^1 + Dn \rightarrow (Dn + 1)^1 \tag{7}$$

$$(Dn + 1)^1 \rightarrow Dn + D + h\nu \tag{8}$$

$$(Dn + 1)^1 \rightarrow P \tag{9}$$

$$(Dn + 1)^1 \rightarrow Dn + D \tag{10}$$

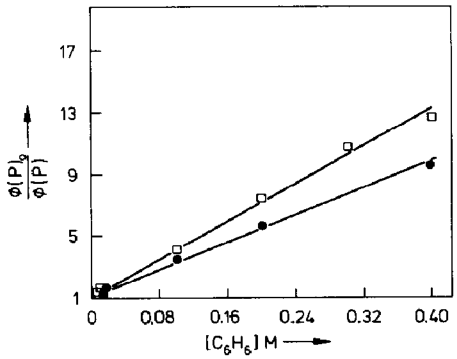
$$(Dn + 1)^1 + Q \rightarrow Q^1 + Dn + D \tag{11}$$

where D^3 is the third excited state, D^1 is the first excited state, P are products, Dn is the ground state of 1,4-dioxane and $(Dn + 1)^1$ is the singlet excimer.

Owing to the short lifetime of the excited state of the monomer of dioxane (2 ns) it is not expected that quenchers will receive excitation transfer from the monomer, and therefore it is proposed that excitation transfer involves steps (7) - (11) and the aggregate species. To explain the energy transfer from excited 1,4-dioxane to quenchers in the liquid phase, the nature of the aggregate involved would be the same as the one postulated by Hirayama *et al.* [13]. Equation (10) is suggested to show that there is no evidence for internal conversion of the aggregate at 184.9 nm. At a shorter wavelength (147.0 nm) it is possible that an excited monomer (D^3) is present as in steps (1) - (3) that partially equilibrates with 1,4-dioxane molecules and partially undergoes spontaneous dissociation giving photoproducts as in eqn. (2). Figures 1 and 2 show the quenching action of C_6H_6 and N_2O at 184.9 and 147.0 nm as a function of concentration of quencher. At 184.9 nm a plateau value of approximately 10% of the initial yield of H_2 and C_2H_4 is reached when either N_2O or C_6H_6 is applied up to 0.4 M concentration. At 147.0 nm a plateau value at about 40% of the initial observed quantum yields is reached using N_2O and C_6H_6 as quenchers up to 0.1 and 0.4 M concentration respectively. The 40% yield of products formed after photolysis at 147.0 nm is a result of decomposition from the upper excited state D^3 (eqn. (7)) which is too short lived to be quenched even at 0.4 M concentration of C_6H_6 and N_2O. Subtracting the residual yield component from the observed yields of H_2 and C_2H_4 production in Fig. 1 it is possible to obtain the reciprocal plot of the products observed *versus* concentration of quencher. For 184.9 nm the reciprocal plots of C_2H_4 and H_2 *versus* concentration of quencher used are presented in Figs. 6 and 7. The plots obtained in these figures follow Stern–Volmer kinetics and have the form

$$\frac{\phi(P^0)}{\phi(P)} = 1 + k\tau$$

where τ is the lifetime of excited 1,4-dioxane and k is the quenching rate constant. The experimental values (Table 2) obtained in the 147.0 nm photolysis, when the unquenchable 40% component has been deducted (in the case of C_2H_4 or H_2), are equivalent to the results obtained in the 184.9 nm photolysis where the unquenchable component is only 9%. From Figs. 6 and 7 it is possible to obtain the values reported in Table 2. In this table can be seen the Stern–Volmer constants $k\tau$ obtained for the quenching of the C_2H_4 and H_2 products formed on photolysis at both 147.0 and 184.9 nm by the two quenchers employed. The quenching values are similar at 147.0 and 184.9 nm and this suggests that the same excited state is involved at both wavelengths. Therefore the quenching experiments involve eqns. (9) - (11) which represent aggregate formation since the monomer is too short lived to be quenchable. The unquenchable 40% product component following 147.0 nm photolysis indicates that an excited singlet above the first excited singlet is the precursor of products at these wavelengths. The



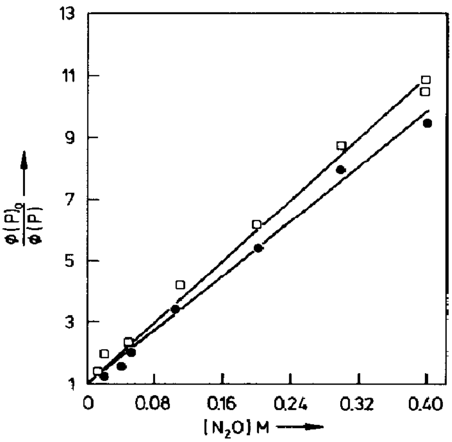


Fig. 6. Stern–Volmer plot of the products of photolysis *vs.* concentration of C_6H_6 observed in the 184.9 nm photolysis of liquid 1,4-dioxane: ● C_2H_4, □ H_2. $\phi(P)_0$ is the yield of products when no C_6H_6 is added; $\phi(P)$ is the yield of products in the presence of C_6H_6.

Fig. 7. Stern–Volmer plot of the products of photolysis *vs.* concentration of N_2O at 184.9 nm: ● C_2H_4, □ H_2. $\phi(P)_0$ is the yield of products when no N_2O is added; $\phi(P)$ is the yield of products in the presence of N_2O.

TABLE 2

	$k\tau(H_2)$	$k\tau(C_2H_4)$
184.9 nm		
C_6H_6	30.5 ± 0.4	22.0 ± 0.5
N_2O	24.4 ± 0.7	21.9 ± 0.9
147.0 nm		
C_6H_6	17.0 ± 0.3	20.7 ± 0.9
N_2O	17.4 ± 1.3	22.0 ± 0.3

unquenchable C_2H_4 or H_2 products formed after 184.9 nm photolysis are approximately 9%, and it is postulated that direct product formation (eqn. (5)) is responsible for this component and product formation at this wavelength. Since it has been mentioned that the unquenchable yield is about 9%, this reaction is relatively inefficient and the monomer excited state plays only a small role in the overall product formation observed on 184.9 nm photolysis. The fact that fluorescence produced by 184.9 nm excitation could be quenched indicates that an excited state aggregate is produced similar to the one described in eqn. (7) by $(Dn + 1)^1$ from which dissociation occurs. Step (8) has been reported by Lipsky (13) as fluorescence following excitation of 1,4-dioxane at 184.9 nm. The formation of N_2 is attributed to excited 1,4-dioxane species reacting with N_2O. If the evolution follows the process

$$D \xrightarrow{h\nu} D^* \qquad (12)$$

$$D^* \longrightarrow D \qquad (13)$$

$$D^* \longrightarrow P \qquad (14)$$

$$D^* + N_2O \longrightarrow N_2 + O + D \qquad k_3 \qquad (15)$$

D and D^* being the dioxane unexcited and excited molecule respectively, then a kinetic treatment for the evolution of N_2 can be represented by

$$\frac{1}{\phi(N_2)} = \frac{1}{\phi(N_2^0)} + \frac{1}{\phi(N_2^0)\,\tau k_3(N_2O)} \qquad (16)$$

where $\phi(N_2^0)$ is the limiting quantum yield for N_2 formation when all excited states are scavenged by N_2O and τ is the lifetime of excited 1,4-dioxane. In conformity with eqn. (12) a plot of $1/\phi(N_2)$ *versus* $1/N_2O$ is linear for 184.9 nm and 147.0 nm photolysis as shown in Fig. 8. In this figure the reciprocal of the intercept of the 184.9 nm plot gives a value of 0.70 ± 0.02 in agreement with the plateau value reported at this wavelength in Fig. 3. The value of $\phi(N_2^0)$ in cyclohexane is 0.71 showing that all of the excited state is susceptible to scavenging. At 147.0 nm the intercept gives a value of $\phi(N_2^0) = 0.42 \pm 0.02$. The ratio of $\phi(N_2^0)147.0/\phi(N_2^0)184.9$ is 0.60 and indicates that about 60% of the molecules excited at 147.0 nm internally convert to the lowest excited singlet. The value of $\phi(N_2^0) = 0.42$ is due to the fact that a portion of the excited states cannot be scavenged by N_2O (up to 60%). Since 40% of the product H_2 and C_2H_4 is not quenched by C_6H_6 and N_2O in 147.0 nm photolysis, the internal conversion from this state is 0.60. This observation is in agreement with the fact that $\phi(N_2)$ at 147.0 nm when N_2O is added to liquid 1,4-dioxane is 60% of the N_2 obtained when 185 nm light is used. From Fig. 8, $k\tau$ values of 18.6 ± 3.1 M^{-1} at 147.0 nm and 25.0 ± 1.0 M^{-1} at 184.9 nm are obtained. In the gas phase the dioxane monomer is present and it is suggested that the lowest vibrational level is at 192 nm (6.5 eV) as shown by the absorption spectra in the UV region [7]. In the liquid phase fluorescence of the excited aggregate [13] starts at 210 nm (5.90 eV). The lower energy in the exciplex (5.9 eV) is understood taking into consideration that the available excitation energy is spread over many molecules. Therefore a longer lived species is formed in step (7) of our mechanism with an electronic state lower than the monomer. A longer lifetime for such an aggregate would allow for an increase in the energy exchange probability of excited molecules with N_2O, and the increased energy transfer is reflected in the higher $\phi(N_2^0)$ at 184.9 nm (0.70) to the value observed at 147.0 nm (0.42).

Figure 5 shows the quenching of the fluorescence of 1,4-dioxane due to C_6H_6, N_2O and I_2. The Stern–Volmer relation for fluorescence quenching is $I(0)/I(Q) = 1 + k\tau(Q)$ where $I(0)$ and $I(Q)$ are the emission intensities in the absence and presence of concentration Q of quencher and τ is the lifetime of the emitting state in the absence of a quencher. Figure 9 shows the growth of C_6H_6 fluorescence in dioxane solution at 184.9 nm from which plot a

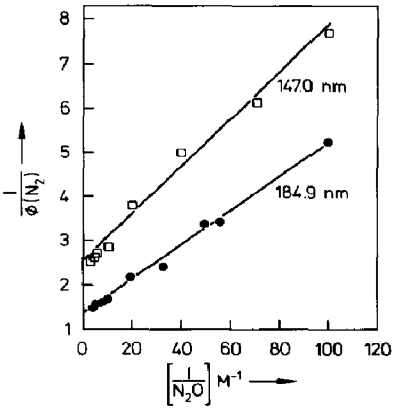


Fig. 8. Stern–Volmer plot of the quantum yield of N_2 produced *vs.* concentration of N_2O at 184.9 nm and 147.0 nm in 1,4-dioxane.

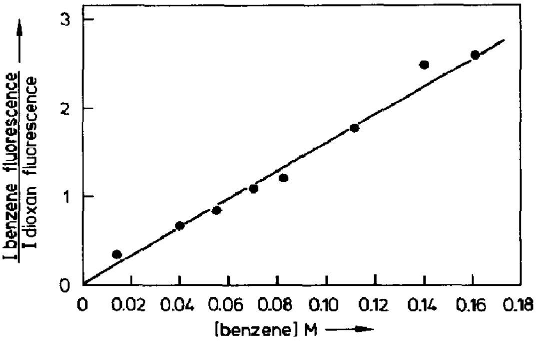


Fig. 9. Quenching of liquid 1,4-dioxane fluorescence by C_6H_6 photolyzed at 184.9 nm scavenger according to eqn. (20) and Table 4.

Stern–Volmer constant for the quenching of the excited dioxane of 29 M^{-1} can be obtained. The quenching of H_2 production by C_6H_6 has been shown in Table 2 to exhibit Stern–Volmer constants of 30.5 and 17 M^{-1} at 184.9 and 147.0 nm respectively. The fact that these values observed in photodecomposition are similar to the values observed in fluorescence using C_6H_6 as quencher indicates that in both processes the same dioxane singlet is involved or that if two different states are present they must be singlets with the same lifetime. Using the Svenshnikoff equation for fluorescence quenching [14] the radii of different aggregates are reported in Table 3.

Considering the oxygen case first, C_2H_4 production decreases by about 21% in an oxygen-saturated solution (4.2×10^{-3} M O_2)* and corresponds to a value of $k\tau = 145 \pm 14$ M^{-1}. Using the value of the lifetime for the excited state of 1,4-dioxane reported by Lipsky [13], Halpern and Ware [15] calculated an effective encounter radius for the reaction of at least 13 Å. It was concluded that the excited state being quenched was an aggregate. An estimate for the diffusion coefficient of N_2O and C_6H_6 shows a ratio of 1.37 [16] using the inverse radius relation. This conclusion is in agreement with the results of others [13, 15, 17, 18] that excited singlet 1,4-dioxane has a lifetime of 2 ns. This study also shows that the same quantum yields of main product formation in the photolysis of 1,4-dioxane at 147.0 nm and 184.9 nm are observed. The fact that dissipation of excitation energy at 147.0 nm occurs before decomposition may provide an explanation for the quantum yield values observed at this wavelength when compared with the results obtained at 184.9 nm.

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*This value of solubility was determined at 25 °C by degassing a saturated solution of O_2 in a vacuum line.

TABLE 3

Dioxane molecules in fluorescence aggregate quenching studies

Quencher	kT (M^{-1})	Diffusion coefficient	Aggregate radius (A)	Dioxane molecular/ exciplex
O_2	145	4.0×10^{-5}	14.4	4.2
C_6H_6	28	1.4×10^{-5}	21.2	6.0
N_2O	38	1.7×10^{-5}	11.1	3.1
I_2	71	1.5×10^{-5}	21.5	6.2

Chemical decomposition mechanism for 1,4-dioxane

Iodine has been used as a radical scavenger. Experimental results are shown in Fig. 4 for concentrations of I_2 between 0.1 and 20 mM at 147.0 nm irradiation. At 10 mM (I_2) a plateau is reached. The competition taking place when I_2 is added is presumed to be as follows:

$$H + RH \rightarrow R + H_2 \qquad k_1 \tag{17}$$

$$H + I_2 \rightarrow HI + H \qquad k_2 \tag{18}$$

The rate constant for H atom abstraction of 1,4-dioxane is $5 \times 10^6\ M^{-1}\ s^{-1}$ [19] and the value for H atom abstraction of I_2 is $4 \times 10^{10}\ M^{-1}\ s^{-1}$ [12]. Using these rates, 88% of the H_2 observed is quenched if the product has only a radical precursor. Since only 45% is quenched, then 51.5% of the H_2 yield has a radical precursor. From this consideration and the experimental points shown in Fig. 4 it is possible to apply the relation

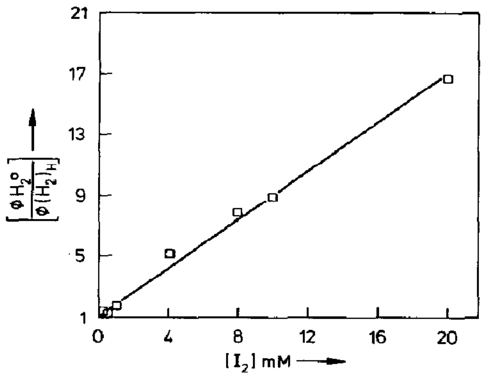

Fig. 10. Quantum yield of hydrogen production in the presence of added I_2 as an H atom at 25 °C.

TABLE 4

Iodine scavenging of H in 147.0 nm photolysis

I_2 (mM)	$\phi(H_2)_{obs}$	$\phi(H_2)_H$	$\dfrac{\phi(H_2)^0}{\phi(H_2)_{Hobs}}$	$\dfrac{\phi(H_2)^0}{\phi(H_2)_{Hcalc}}$
0.10	0.250	0.116	1.15	1.08
0.20	0.242	0.108	1.24	1.16
1.00	0.210	0.076	1.76	1.80
4.00	0.160	0.026	5.15	4.20
8.00	0.151	0.017	7.90	7.40
10.00	0.149	0.015	8.95	9.00
20.00	0.142	0.008	16.70	17.00

$$\phi(H_2)_H = \phi(H_2)_{obs} - 0.515\ (H_2)^0 \tag{19}$$

where $\phi(H_2)_H$ is the quantum yield for the H scavenged by I_2 and $\phi(H_2)^0$ is the quantum yield for the hydrogen produced via molecular elimination. The ratios are reported in Table 4. Iodine scavenging of H in 147.0 nm photolysis (according to Table 4) is shown in Fig. 10. The equation

$$\frac{\phi(H_2)^0}{\phi(H_2)_H} = 1 + \frac{k_2\,[I_2]}{k_1\,[RH]} \tag{20}$$

represents the proposed mechanism. An attempt to describe the modes of decomposition of 1,4-dioxane is consistent with the reported scheme of photolysis at 147 nm. In liquid phase the following primary quantum yields are estimated:

$$C_4H_8O_2 \rightarrow C_2H_4 + CO + H_2 + CH_2O \qquad \phi_{21} = 0.03 \tag{21}$$

$$C_4H_8O_2 \rightarrow C_2H_4 + 2CH_2O \qquad \phi_{22} = 0.52 \tag{22}$$

$$C_4H_8O_2 \rightarrow H + X \qquad \phi_{23} = 0.14 \tag{23}$$

$$C_4H_8O_2 \rightarrow H_2 + X \qquad \phi_{24} = 0.11 \tag{24}$$

This estimation is based on Table 1, in which $\phi(CO) = 0.03$ is represented here by eqn. (21). Since the total yield of C_2H_4 is 0.55 then the decomposition step in ϕ_{22} assigns for the remaining C_2H_4 a quantum yield of 0.52. The total $\phi(H_2)$ is 0.26. From this total 0.03 has been assigned in eqn. (21) and for the remaining H_2 (as shown by eqn. (19)) 51.5% has a radical precursor. This leads to an assignment of $\phi_{23} = 0.14$ for the production of H atoms and $\phi_{24} = 0.11$ for the molecular elimination of H_2. The sum

$$\phi_{21} + \phi_{22} + \phi_{23} + \phi_{24} = 0.80$$

This indicates that we have accounted for the main reaction pathways and that the proposed mass balance is a fair appraisal of the main steps in the reaction. The symbol X denotes undetected product which probably is an oxygenated product [1]. Since in the photolysis of 1,4-dioxane the C_2H_4 and H_2 yields are reduced similarly by addition of quenchers, this suggests a common excited state precursor. Such a mechanism would be complex and it seems that not merely the unimolecular decomposition of 1,4-dioxane would yield the observed products. Radicals are involved in the production of CO,.H_2 and C_2H_4 as well as other products. By iodine experiments it has been shown that H_2 originates from two different sources in almost equal portions as shown in Fig. 4. Ethylene is, of course, expected to act as a scavenger for hydrogen atoms to give ethyl radicals

$$H + C_2H_4 \rightarrow C_2H_5 \qquad (25)$$

The fact that a straight line for production of C_2H_4 is observed suggests that the mechanism for C_2H_4 production proceeds via molecular elimination. The H atoms produced add to the C_2H_4 present and the yields of C_2H_4 (which at the temperature of the experiments also have secondary reactions of free radicals) involve disproportionation and recombination processes leading to the re-formation of C_2H_4 molecules reported in the observed results.

Process (21) proceeds with an exothermicity of 26 kcal [22]. Direct elimination of aldehydes by photolysis of ethers has been recently proposed (21). If decomposition of 1,4-dioxane occurs through C—O bond scission then the HCHO (20) is formed with energy of 34 kcal mol^{-1} in a unimolecular decomposition process.

In an energy balance processes (23) and (24) proceed with comparable endothermicities of 94 and 83 kcal mol^{-1}. Iodine experiments have shown that quantum yields of H and H_2 are about the same. On the basis of similar energetics the probability of elimination of H atoms *versus* H_2 molecules are about equal as observed in this case.

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