lap the spectral range of the bands observed for the gaseous state. This observation, and the presence of a pronounced shoulder on the high-frequency side for ν_3 lead one to infer that CH_4 retains some rotational freedom inside the cavity, as has been observed for the molecule in the liquid state[2] and adsorbed on porous glass.[3]

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Service Infrarouge
Département de Recherches Physiques
Université Paris VI
75230 Paris Cedex 05, France

E. Cohen de Lara*
Y. Delaval

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Solvated Electrons from Excited (λ 185 nm) *p*-Dioxane[1]

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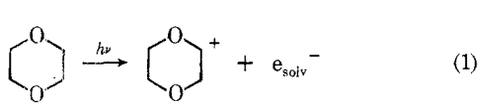
Sir: The photochemistry of *p*-dioxane has been studied in the gas and liquid phases. In the gas phase it decomposes (λ 147 nm) to give ethylene, hydrogen, carbon monoxide, and formaldehyde.[2] For the liquid phase (λ 185 nm) preliminary results indicate the formation of formaldehyde, ethylene, oxetane, acetaldehyde, 2-methyl-1,3-dioxolane, hydrogen, bis(dioxanyl), and some as yet unidentified products. CO, which is a major gas-phase photolysis product, is absent here.[3] Although light is absorbed within a small layer next to the cell window photolysis of the products is negligible at the dose rate employed in these experiments (8×10^{15} quanta sec^{-1} cm^{-2}). Here, we wish to report evidence to the effect that the formation of solvated electrons is the major process in the 185-nm photolysis of liquid *p*-dioxane and, even more pronounced, in its aqueous solution

N_2O-saturated *p*-dioxane yields N_2 with a quantum yield of $\Phi(N_2) = 0.58$. This value increases with increasing water content, and in an aqueous solution containing 20 vol % ($\hat{=}$ 2.35 *M*) *p*-dioxane $\Phi(N_2)$ approaches unity. Under these conditions neither water nor N_2O absorb to an appreciable extent since the molar extinction coefficients of water, N_2O, and *p*-dioxane at λ 185 nm are 0.026,[4] 80,[5] and *ca.* 3000[6] M^{-1} cm^{-1}, respectively. Quantum yields have been determined using $\Phi(H_2) = 0.4$[7] for the Farkas actinometer (5 *M* ethanol in water). The high yield of N_2 from N_2O-saturated solutions indicates that the photoexcited *p*-dioxane ejects an electron which reacts with N_2O according to eq 2.



$$e_{solv}^- + N_2O \longrightarrow N_2 + O^- \quad (2)$$

Further to test this is a competition study was made with protons as scavengers. H_2SO_4 was chosen because of the low molar extinction coefficient (24.3 M^{-1} cm^{-1}) of the HSO_4^- ion.[8] The presence of acid leads to processes 3 and 4.

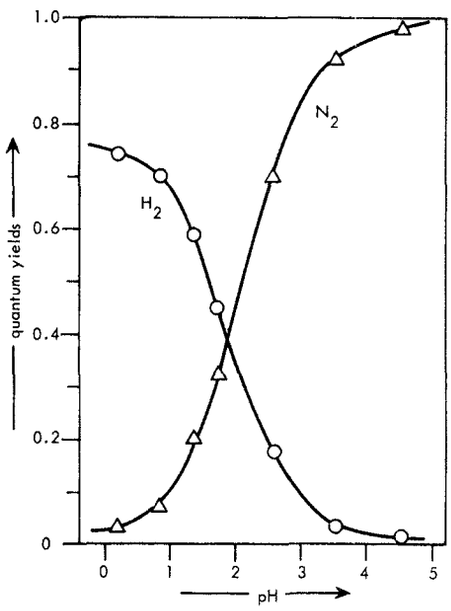
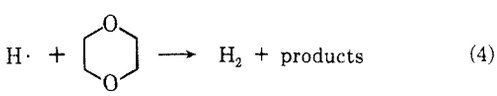


Figure 1. pH dependence of the quantum yields for H_2 (O) and N_2 (Δ) formation in N_2O-saturated solutions of *p*-dioxane in water (20 vol %).



$$e_{solv}^- + H^+ \longrightarrow H\cdot \quad (3)$$

$$H\cdot + \text{dioxane} \longrightarrow H_2 + \text{products} \quad (4)$$

Figure 1 shows the competition of $\Phi(N_2)$ *vs.* $\Phi(H_2)$ at a constant N_2O concentration (saturated $\approx 2.5 \times 10^{-2}$ M^{-1}) as a function of pH. The half-values of the two curves coincide within experimental error at pH 2 ± 0.15. Using published values[9] for the rate constants of reactions 2 and 3 (k_2 (in water) = 5.6×10^9 M^{-1} sec^{-1}, k_3 (in water) = 2.25×10^{10} M^{-1} sec^{-1}) the half-value is calculated at pH 1.85. It is noted that even though $\Phi(N_2)$ reaches unity in this competition study, $\Phi(H_2)$ does not. The reason for this may be the reaction of the H atom with the *p*-dioxanyl radical which would not lead to hydrogen formation. Reaction 4 is expected to increase with increasing temperature. Indeed in accordance with this expectation $\Phi(H_2)$ rises with increasing temperature and at 80° a value of 0.85 has been found. There is no similar effect that could decrease the N_2 yield. We therefore conclude that in aqueous solution an electron is ejected on 185-nm irradiation with a quantum yield of unity. The gas-phase ionization potential of *p*-dioxane is 9.5 eV.[10] The 185-nm quanta are equivalent to 6.7 eV. The energy gap of 2.8 eV will have to be filled by the solvation energy of the radical ions. The solvation free enthalpy of the electron in water is 1.8 eV.[11] In neat dioxane it is appreciably smaller.[12] The solvation free enthalpy of the radical cation is not known but larger positive ions such as Na^+ or Cs^+ ions have been reported to have solution free enthalpies of 4.25 and 2.95 eV, respectively,[13] in water.[14]

Whereas no emission from 185-nm excited dioxane is observed in the gas phase,[15] emission with λ_{max} 247 nm is observed in the liquid phase.[15,16] The quantum yield for this emission has been reported to be 0.029. On dilution with isooctane this emission is blue-shifted and strongly re-

duced. On dilution with water or methanol the emission is red-shifted and also strongly reduced. In a 1:1 (vol/vol) mixture of dioxane–water the emission has nearly vanished. Similar results have been observed by pulse radiolysis.[17] The emission found in the 185-nm photolysis of *p*-dioxane has been attributed to a fluorescence of an excimer species.[15] Baxendale, *et al.*,[17] have noted that N_2O suppresses strongly the fluorescence of anthracene in γ-irradiated *p*-dioxane. Since delayed charge neutralization had been excluded as the origin of the emission of neat *p*-dioxane under pulse radiolysis conditions the observed lifetime of about 2–3 nsec is believed to be due to fluorescent state formed by electron–radical cation recombination.[17] It has been observed[3] that the emission from the photoexcited *p*-dioxane can be suppressed by N_2O. Possibly the fluorescent state in the 185-nm photolysis also has a solvated electron–radical cation pair as its precursor.

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Institut für Strahlenchemie
Max-Planck-Institut für Kohlenforschung
D-4330 Mülheim a. d. Ruhr
West Germany

Clemens von Sonntag*
Heinz Bandmann

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