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LASER FLASH PHOTOLYSIS STUDY OF THE REACTIVITY OF α-KETENYLBENZOCYCLOBUTENONE WITH WATER AND ALCOHOLS

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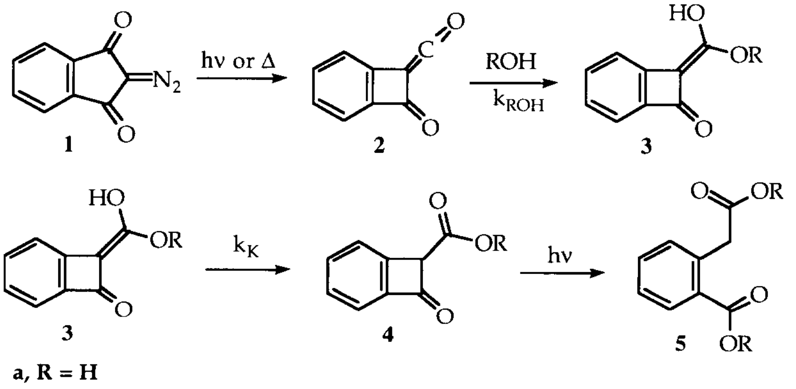
Abstract: Photolysis of 2-diazo-1,3-indandione leads to ketene formation via the Wolff rearrangement. Ketene **2** hydrates to produce enol **3a** that rearranges to **4a**. Homophthalic acid **5a** is formed by photodecomposition of **4a** upon prolonged irradiation.

Ketenes can be formed by photolysis of α-diazoketones via the Wolff rearrangement and the mechanism involved in this process has been widely studied.[1-3]

For cyclic α-diazoketones the Wolff rearrangement results in a ring contraction and is a useful method for the synthesis of benzocyclobutene derivatives from diazoindanones.[4-6] The gas phase pyrolysis (680 °C) of 2-diazo-1,3-indandione (**1**) followed by trapping in methanol gave satisfactory yields of the corresponding benzocyclobutenone-2-carboxylic acid methyl ester (**4b**).[4,5] However, the photolysis of **1** in methanol gave the diester of homophthalic acid (**5b**) along with lesser amounts of 1,3-indandione and 3-methoxyisocoumarin.[4] In this paper we propose that **4b** is formed during the photolysis of **1** in methanol solution, and further photolysis of **4b** resulted in its conversion to **5b** (Scheme 1). During photolysis of **1** in methanol (Rayonet reactor equipped with 300 nm lamps) we characterized **4b** and observed that the ratio **5b**/**4b** is dependent on the time of irradiation (ratio **5b**/**4b** = 2.31 and 10.87 for 5 and 60 min. of irradiation respectively). This implies that **5b** is formed by secondary photolysis of **4b** (Scheme 1). The photolysis of **1** in water gave the hydration products, **4a** and **5a**.



a, **R** = **H**
b, **R** = **CH_3**
c, **R** = **$C(CH_3)_3$**

Scheme 1

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Laser flash photolysis of **1** in water, methanol or isopropanol shows a transient species that has a strong absorption at 310 nm and a weaker band at 400 nm. Figure 1 shows the transient absorption spectrum measured after a 248 nm laser excitation of **1** in methanol. Both bands show the same kinetic behavior. Ketene **2** is formed instantaneously on the time scale of the laser pulse, leading to an initial absorption which is then followed by a slower increase over a period of ca. 100 ns. This rapid growth (top insert in Figure 1) is attributed to the formation of intermediate **3b**, and takes place with a lifetime of 290 ns. This lifetime is quite short compared with those for other ketenes; for example, the values in water are 27 ms, 210 μs and 1.5 μs for $CH_2=C=O$, $PhCH=C=O$ and $HOPhC=C=O$, respectively.[7-10] This absorbance finally decreases on a longer time scale due to the conversion of **3b** into the product **4b** (bottom insert in Figure 1). Previous investigators working with diazonaphthoquinones in water have also concluded that the changes are produced by two successive intermediates[2,3,11-13]

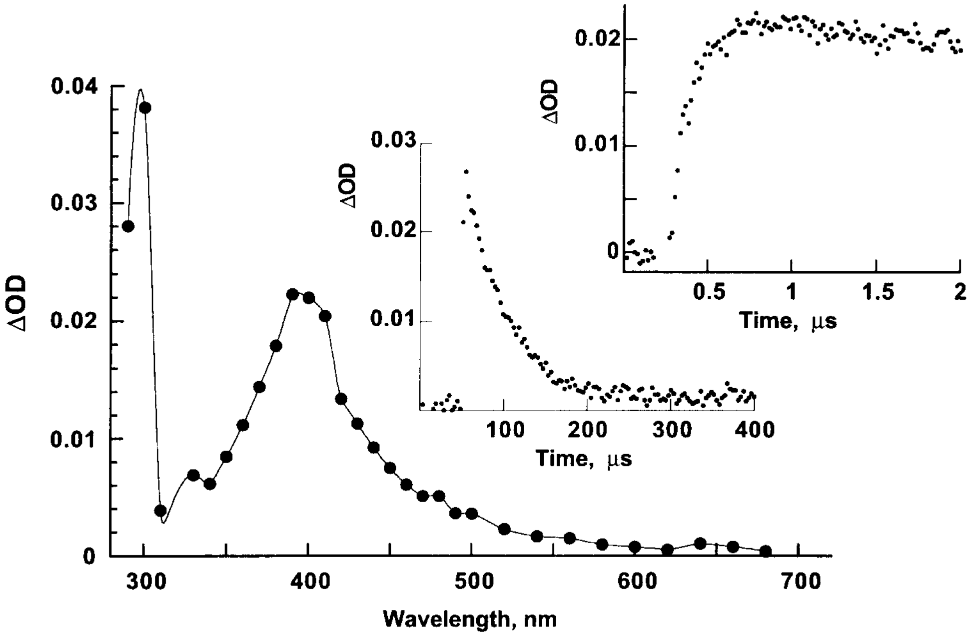

Figure 1. Transient absorption spectrum measured after (2.8 μs) 248 nm laser excitation of **1** in methanol. *Insert*: Growth and decay of the transient absorption at 390 nm.

The pseudo-first order rate constants for reaction of ketene **2** with water, deuterated water, methanol and isopropanol were obtained by monitoring the growth of the signal at 300 nm and are summarized in Table 1. The solvent isotopic effect (for water and D_2O) obtained for this reaction ($k_H/k_D = 1.3$) is in line with those expected for nucleophilic attack by a water molecule at the α carbon of the ketene.[3,8,14-18] The interaction of the HOMO of the nucleophile with the LUMO of the ketene occurs in the molecular plane.[19] It has been observed that substituents on the ketene may influence the kinetics by electronic and steric effects.[20] Our results reveal that electronic and steric effects in the nucleophile are also important. Methanol is observed to be more reactive than water as a nucleophile and methanol is five times more reactive than isopropanol with ketene **2**.

The rates of hydration of ketene **2** were also measured in aqueous buffer solution. As previously observed, k_{ROH} did not change with buffer concentration.[3,8,10,14,15,21]

Table 1. Pseudo first order rate constants (k_{ROH}) for the reaction of ketene **2** with hydroxylic solvents and for the reaction of the intermediate **3** (k_K).

solvent	k_{ROH}, s^{-1}	k_K, s^{-1} [a]
methanol	$(7.14\pm0.10) \times 10^6$	$(1.78\pm0.06) \times 10^4$
isopropanol	$(1.33\pm0.10) \times 10^6$	$(3.10\pm0.28) \times 10^3$
water	$(2.15\pm0.04) \times 10^6$	$(6.65\pm1.25) \times 10^3$
D_2O	$(1.67\pm0.05) \times 10^6$	—

[a] The rate of the reaction of the intermediate **3** was measured by monitoring the decay at 390 nm (methanol) or at 300 nm (isopropanol).

Pseudo-first order rate constant (k_K) for the reaction of the enol **3a** with water were determined in neutral buffer solution.[22] A series of solutions of different concentration of buffer were used. Figure 2 shows that the decay monitored at 310 nm is linearly dependent on the buffer concentration; and the intercept of this plot gave k_K.

It has been observed that the hydration of ketenes, to produce the enol, is the rate determining step, whereby the subsequent tautomerization of the enol intermediate to the carboxylic acid occurs too rapidly, thus preventing observation of the enol.[8,14-16] The enol can be stabilized by aromatic substituents[23,24] as in the case of intermediate **3**, thus retarding the tautomerization and facilitating the observation of the enol intermediate.[2,3,9,25]

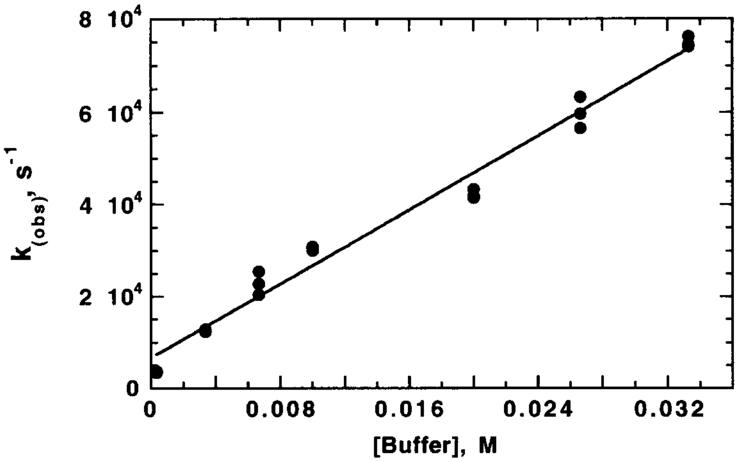

Figure 2. Relationship between buffer concentration and observed first order rate constant for the reaction of intermediate **3a**.

Thus, the diazo precursor **1** provides another example where the carboxylic acid enol can be readily detected as a result of the relative kinetics of its formation and decay ($k_{ROH} > k_K$) which allow for its concentration to build up during the laser experiment.

Experimental: Compound **1** was prepared from mesyl azide and 1,3-indanedione under basic conditions (m.p. 147°C, lit.[5] 149 °C) following the method described in the literature.[26,27] Laser photolysis experiments were carried out in a system similar to those reported elsewhere.[28,29]

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