

THE VACUUM AND VERY FAR UV PHOTOLYSIS OF 1-BUTYNE: THE EFFECTS OF ADDED MOLECULAR OXYGEN

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(Received February 20, 1985; in revised form April 24, 1985)

Summary

The photolysis of 1-butyne has been studied between 147.0 and 213.8 nm. The propene quantum yields measured either in the pure system or in the presence of small amounts of oxygen or nitric oxide lead to the conclusion that the propene formation results from reactions between oxygen atoms and 1-butyne. However, at pressures higher than 200 Torr, the decrease in the propene quantum yields indicates a high efficiency for the stabilizing process of the involved intermediates. Moreover, the increase in the ethylene quantum yield on the addition of small amounts of oxygen supports the idea that triplet excited species are active in the 1-butyne system, although proof is needed either to corroborate or to show up the weakness of this assumption.

1. Introduction

In a previous paper from this laboratory, we have shown that the addition of molecular oxygen to a photolytic mixture of 1,2-butadiene leads to the formation of propene [1]. The chemical mechanism involves the formation of oxygen atoms $O(^3P)$ and $O(^1D)$ through the direct photolysis of molecular oxygen [2, 3] especially at 147.0 nm at which wavelength the oxygen absorption coefficient is far from negligible [4]. In this report, we have observed similar behaviour in the 1-butyne-oxygen system, *i.e.* the addition of molecular oxygen gives rise to the formation of propene, although the quantum yields are much smaller. Moreover, a significant enhancement of the ethylene quantum yields is also measured, contrary to what is observed when nitric oxide is exchanged for oxygen [5]. In this report we shall try to explain such behaviour.

2. Experimental details

Most of the experimental details, including the analytical procedure and the 147.0 nm resonance lamp, have been described in the preceding paper

[1]. Details of the 163.3 and 174 nm resonance lamps and the actinometry have also been described elsewhere [6]. The same is true for the 184.9 and 213.8 nm lines [7]. At 213.8 nm, actinometry was carried out by comparison with the formation of ethylene and 1,3-butadiene in the photolysis of cyclohexene ($\Phi(\text{C}_2\text{H}_4) \approx \Phi(1,3\text{-butadiene}) \approx 0.30$ at a pressure of 30 Torr (4000 N m^{-2})) [8].

1-Butyne was an API product (stated impurity, $0.06 \pm 0.03 \text{ mol.}\%$). The analysis of the starting material shows the presence of propane ($62 \pm 4 \text{ ppm}$) and vinylacetylene ($5 \pm 1 \text{ ppm}$). Nitric oxide (commercial purity, 99.0%; from Matheson Gas Products, Canada) was used as received.

3. Results

As in the 1,2-butadiene system, the addition of molecular oxygen induces the formation of propene [1] (Fig. 1). At a constant 1-butyne pressure, the propene quantum yields start from zero (in the absence of oxygen), increase to a maximum value at an oxygen pressure of about 100 - 300 Torr and then slowly decrease at higher pressures. Similar behaviour is observed at 147.0 and 184.9 nm although the absolute quantum values are somewhat different; they are smaller at 184.9 nm.

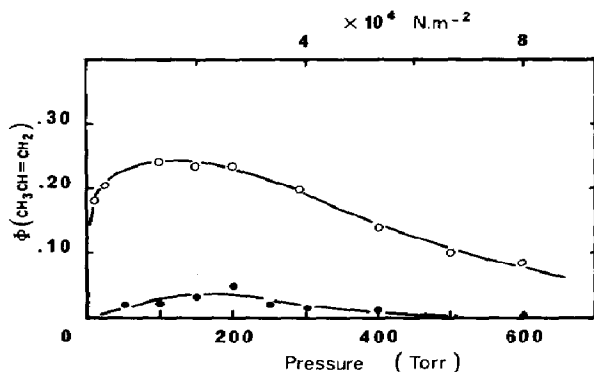


Fig. 1. The propene quantum yield measured in the 147.0 nm (○) and 184.9 nm (●) photolysis of the 1-butyne-oxygen mixtures vs. the oxygen pressure (1-butyne pressure, 1 Torr).

Table 1 shows the effects of the addition of a low percentage of either molecular oxygen or nitric oxide on the ethylene quantum yields. On the addition of oxygen, an enhancement of these values can be observed, and it is especially drastic at 147.0 nm. Moreover, the $\Phi_{\text{O}_2}(\text{C}_2\text{H}_4)$ values are higher than those measured in the pure 1-butyne system in agreement with the results of Hill and Doepker [5].

Figure 2 reports more systematic results obtained at 163.3 nm. Although there are no observable differences between the acetylene quantum yields measured in the presence of either oxygen or nitric oxide,

TABLE 1

Quantum yields of ethylene in the direct photolysis of 1-butyne^a

λ (nm)	Reference	$\Phi(\text{C}_2\text{H}_4)$	$\Phi_{\text{NO}}(\text{C}_2\text{H}_4)$	$\Phi_{\text{O}_2}(\text{C}_2\text{H}_4)$
123.6	[5]	0.09	0.09	0.12
147	[5]	0.14	0.12	0.20
147	— ^b	0.14	0.13	0.25
163.3	[6]	0.06 ₁	NM ^c	0.10 ₇
≈ 174	[6]	0.07	NM ^c	0.11
184.9	— ^b	0.02 ₆	0.02 ₃	0.06
213.8 ^d	— ^b	0.01 ₈	0.02 ₅	0.04 ₆

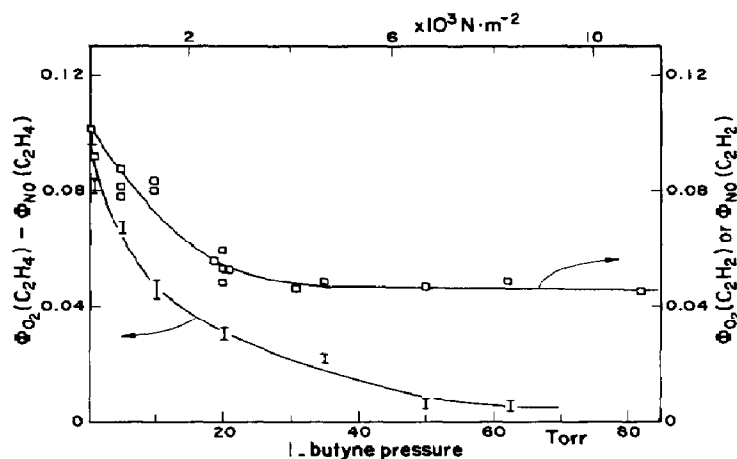
^aPressure of 1-butyne, 1 Torr (133 N m⁻²); additive, about 10%.^bThis work.^cNM, not measured.^dPressure of 1-butyne, 10 Torr.

Fig. 2. The photolysis of 1-butyne at 163.3 nm showing the effects of the addition of either molecular oxygen or nitric oxide on the ethylene and acetylene quantum yields at various pressures.

the differences between the $\Phi_{\text{O}_2}(\text{C}_2\text{H}_4)$ and $\Phi_{\text{NO}}(\text{C}_2\text{H}_4)$ values decrease with an increase in the pressure:

$$\Delta\Phi(\text{C}_2\text{H}_4) = \Phi_{\text{O}_2}(\text{C}_2\text{H}_4) - \Phi_{\text{NO}}(\text{C}_2\text{H}_4)$$

Finally, at 184.9 nm, the addition of a small percentage (0.1%) of oxygen to 1-butyne results in a sharp increase in the ethylene yield. Further addition of oxygen does not change this yield. Conversely, when nitric oxide is exchanged for oxygen, the ethylene quantum yield is not modified (Fig. 3).

4. Discussion

The vacuum and very far UV photolysis of 1-butyne is well known and need not be discussed [5, 6]. Let us only say that, at 147 nm, vinylacetylene

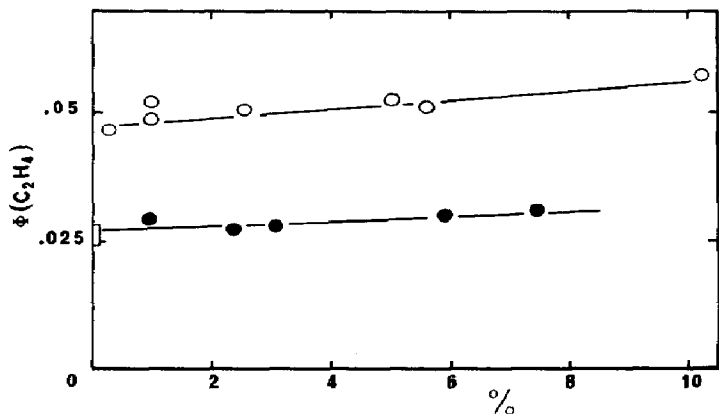


Fig. 3. The photolysis of 1-butyne at 184.9 nm showing the effects of the addition of a small percentage of either molecular oxygen (\circ) or nitric oxide (\bullet) (1-butyne pressure, 1 Torr).

is a major product formed in the fragmentation process of the photoexcited molecule. Conversely, allene, whose quantum value is strongly pressure dependent, is formed in secondary reactions involving hydrogen atoms [5, 6].

4.1. Propene formation

Propene was never reported to be a product in the 1-butyne photolysis. Its presence is clearly linked to the addition of molecular oxygen in the starting material. The reaction of the $O(^3P)$ atoms with 1-butyne as well as with 2-butyne [9 - 11] is well known [9, 10]. Thus, it is relatively safe to link the formation of propene to the direct photolysis of oxygen in a way similar to that proposed in the previous paper [1]. At constant 1-butyne pressure, the higher the oxygen pressure is, the greater is the absorption of light through this additive. In other words, the oxygen atom quantum yield increases with an increase in the partial pressure of oxygen. At 184.9 nm the smaller propene quantum yields are due to the small absorption coefficient of oxygen (Table 2).

However, at pressures around 100 - 300 Torr, the propene quantum yields pass through a maximum and then decrease at higher pressures, contrary to what was observed with the 1,2-butadiene system, in which the propene quantum values are stabilized around 1.8 [1]. This difference was indirectly observed by Havel [3] and Havel and Chan [9]. Their experimental procedure involved the formation of $O(^3P)$ atoms in the presence of either 1,2-butadiene or 1-butyne at pressures around 600 Torr. The relative quantities of propene observed are greater in the 1,2-butadiene system. Conversely, the formation of buten-2-one is more efficient in the butyne system. The mechanism proposed for the alkyne systems allows the occurrence of the stabilizing processes of [alkyne-O] excited intermediates [9]:



TABLE 2
Absorption coefficients of oxygen and 1-butyne

	Absorption coefficients ^a (atm ⁻¹ cm ⁻¹) for the following wavelengths				
	λ (nm)	147	163.8	184.9	213.8
Oxygen		400 [4]	75 [4]	0.9 [4]	—
1-Butyne		800 [13]	230 [13]	58 [12]	5.5 [12]

^aValues are not better than $\pm 10\%$.

$$\Delta H = 7.08 \text{ eV [14]}$$

$$\lambda = 147.0 \text{ nm, } \phi = 1.0$$



Unfortunately, nothing can be said about the fate of the O(¹D) atoms; they may or may not interfere with the propene formation. At 184.9 nm the direct photolysis of oxygen only produces O(³P) atoms [13]:



$$\Delta H = 5.115 \text{ eV}$$

$$\lambda = 184.9 \text{ nm, } \phi = 1.0$$

Figure 1 shows some differences in the propene quantum values measured at 147.0 and 184.9 nm. The maximum values of the propene quantum yields are 0.25 ± 0.03 and 0.04 ± 0.01 at 147.0 nm and 184.9 nm respectively. Moreover, at 600 Torr, the $\Phi(\text{C}_3\text{H}_6)$ values are decreased by 64% and about 90% at 147 nm and 184.9 nm respectively. In other words, the stabilizing process [4] seems to be more efficient at 184.9 nm than at 147 nm. This difference may be the result of the lower energy content of the $[\text{C}_4\text{H}_6\text{-O}]^\ddagger$ intermediates formed at 184.9 nm ($E(h\nu) = 6.67 \text{ eV}$) in comparison with that formed at 147.0 nm ($E(h\nu) = 8.40 \text{ eV}$). However, the available excess energy is higher at 184.9 nm: 1.55 eV in comparison with 1.32 eV at 147.0 nm. Another explanation would be to assume that O(¹D) atoms also react with 1-butyne and the resulting $[\text{C}_4\text{H}_6\text{-O}]^{\ddagger\ddagger}$ intermediates have shorter lifetimes and thus are more difficult to stabilize than those formed by O(³P) reactions:



4.2. Ethylene formation

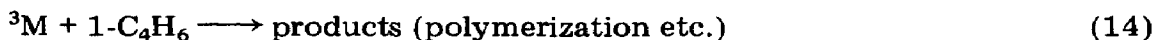
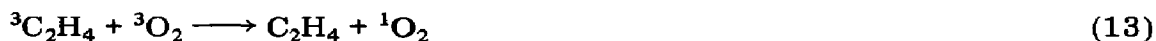
In the photolysis of unsaturated hydrocarbons the primary fragmentation of the photoexcited molecules involves the split of the C—C bond, and both saturated and unsaturated radicals are among the products. For example, the primary split of C—CH₃ bonds leads to the formation of methyl radicals. These can recombine and ethane is the product [15]. The addition of a small percentage of either molecular oxygen or nitric oxide inhibits ethane formation. In fact, both additives have well-known radical scavenging properties. Thus, it is generally anticipated that their addition will have the same effects, and in fact they are similar. The disproportionation of either vinyl or ethyl radicals with other radicals gives rise to ethylene formation. Thus, in the presence of nitric oxide, it may be assumed that the formation of ethylene is not the result of radical-radical reactions. Then, the differential effect $\Delta\Phi(\text{C}_2\text{H}_4)$ of oxygen and nitric oxide in the 1-butyne system must be questioned (Table 1). One major fragmentation process of the photoexcited 1-butyne molecule involves the break of the $\alpha(\text{C}-\text{C}_2\text{H}_5)$ bond [5, 6]: $\Phi(\text{C}_2\text{H}_5) \approx 0.10 \pm 0.05$ in the vacuum UV region. The reaction between these ethyl radicals and oxygen has been described previously [16, 17]. Two processes are considered:



The fraction of C_2H_5 converted to C_2H_4 increases from 0.1 to about unity with an increase in the temperature from 300 to 800 K (gas number density, about $(6 - 7) \times 10^{16}$ molecules cm^{-3}) [16] and it decreases to 0.07 at number densities higher than 2×10^{17} molecules cm^{-3} at room temperature [15]. Thus, with the present experimental conditions, it may be assumed that less than 7% of the C_2H_5 radicals is converted to ethylene. From the above-mentioned ethyl radical quantum yield, process (8) is far from sufficient to explain the measured $\Delta\Phi(\text{C}_2\text{H}_4)$ values. However, it may be assumed that the ethyl radicals are formed with an internal energy content sufficiently high that their "actual temperatures" are far from room temperature. Their behaviour is consequently modified. If it is so, with an oxygen-to-1-butyne ratio of 0.1, they lose their internal energy before colliding with oxygen molecules. Thus, process (8) can hardly explain the observed $\Delta\Phi(\text{C}_2\text{H}_4)$ values. Conversely, the reaction between radicals and nitric oxide leads to the formation of nitroso compounds [18], although some ethylene may also be formed through hydrogen atom transfer from ethyl radicals to nitric oxide [19].

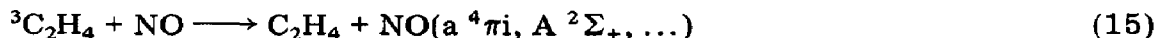
From a consideration of the nature of the fundamental triplet state of oxygen, and the relatively low level for its first singlet state, another mechanism may be proposed. Oxygen is known to be a good triplet quencher (see for example ref. 20). Of course the simplest reaction involves the quenching of the triplet ethylene molecule. However, the mechanism leading to this

$^3\text{C}_2\text{H}_4$ is not evident: it may be fragmentation of a singlet or a triplet excited 1-butyne molecule etc.:



It is very difficult to give support to one or other possibilities. It was proposed that triplet excited states are involved in the direct photolysis of acetylene; more precisely, it was suggested that metastable acetylene species are triplet vinylidene radicals, ${}^3(\text{H}_2\text{C}=\text{C})$ [21, 22]. Similar behaviour in the 1-butyne system cannot be ruled out. This assumption is hardly acceptable since nitric oxide is also known to be an efficient scavenger of triplet states [19] although the researchers have no indication that ${}^3\text{C}_2\text{H}_4$ may be scavenged by this additive.

If the ethylene triplet state is 3.2 eV above the ground state [23 - 26], the following process is exothermic by at least 1.5 eV [19]:



Conversely, the measured energy of the vertical $\tilde{\text{X}} \rightarrow \hat{\text{a}}$ transition (the first triplet state) of 1-butyne is 5.2 ± 0.1 eV and does not necessarily correspond to the 0-0 band of the transition. The onset of excitation of the $\tilde{\text{a}}$ state appears at 4.5 eV [27]. Thus, the quenching by nitric oxide of this state may be exothermic. The quenching of the second triplet state, the $\tilde{\text{b}}$ state, is likely to be exothermic.

Finally, a process involving oxygen atoms cannot be completely ruled out. However, it must be said that, at low oxygen concentration, the propene quantum yield increases with an increase in the oxygen pressure (Fig. 2). Conversely, the addition of a very low concentration of oxygen has a very strong effect on the ethylene quantum yield: this yield increases from 0.025 to 0.05. At a concentration higher than 0.3% of oxygen, the $\Phi_{\text{O}}(\text{C}_2\text{H}_4)$ value is rather constant. Thus, if oxygen atoms are involved, the mechanism must be somewhat different from that involved in the propene formation.

Acknowledgments

We would like to thank the Fonds de Formation de Chercheurs et d'Aide à la Recherche of the Province of Quebec for its generous support.

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