

THE 147 nm PHOTOLYSIS OF EITHER OXYGEN OR NITROUS OXIDE IN THE PRESENCE OF 1,2-BUTADIENE: REACTIONS OF OXYGEN ATOMS

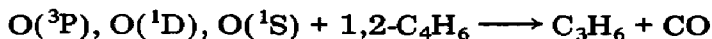
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Summary

The addition of molecular oxygen to the 147 nm photolysis of gaseous 1,2-butadiene leads to a large increase in the propene quantum yield. We have shown that this propene formation is linked to the production of oxygen atoms through the direct photolysis of molecular oxygen. Moreover, from the study of mixtures of nitrous oxide and 1,2-butadiene, it can be seen that O(³P), O(¹D) and O(¹S) atoms react with butadiene in similar reactions, and that O(¹D) and O(¹S) have reaction rates similar to their collision rate:



1. Introduction

Molecular oxygen is currently used as a radical scavenger in gaseous photolytic experiments [1, 2]. Sometimes, side effects are reported, but not always explained [3]. However, the chemistry of molecular oxygen is rather complex, especially because of the presence of various electronic states (see, for example, refs. 4 and 5). Thus, it is not surprising that the addition of a low percentage of molecular oxygen to photolytic mixtures makes them more complicated. These effects are potentially great at 147 nm since this wavelength is close to the top of the Schumann-Runge continuum: $k_{\text{O}_2}(147 \text{ nm}) = 400 \pm 50 \text{ atm}^{-1} \text{ cm}^{-1}$ [6].

In this report, we present the results obtained in the 147 nm photolysis of molecular oxygen in the presence of 1,2-butadiene. Moreover, in order to have a better view of the various O(³P), O(¹D) and O(¹S) atom reactions, nitrous oxide was also photolysed in the presence of the same diene.

2. Experimental details

Most of the experimental techniques have already been described. The resonance xenon lamp is equipped with an LiF window [7], and its emission spectrum was taken with a 0.5 m vacuum monochromator (235 GCA-McPherson instrument). The 8.40 eV (147 nm) line is the main line (much greater than 98%) between the cut-off of the window (about 105 nm) and the absorption threshold of any of the starting materials. Isobutylene actinometry was carried out; the quantities of propyne ($\Phi = 0.35$) and allene ($\Phi = 0.52$) were determined [8]. The number of photons entering the cell was of the order of $(5 - 10) \times 10^{15}$ quanta s^{-1} . The percentage of conversion (number of photons per number of 1,2-butadiene molecules) was always kept below 0.03%. In mixtures for which relatively high relative concentrations of diene were used, a decrease in the transmission through the window was observed. The transmission was restored by washing out the window with usual solvents.

1,2-Butadiene ($99.94 \pm 0.02\%$) was an API product. Its analysis shows only the presence of propane (40 ± 15 ppm). Isobutene (99.90%) was a Philips research grade product. It contained propane (44 ± 1 ppm) and isobutane (860 ± 30 ppm). Oxygen (research purity, 99.98%) and nitrous oxide (commercial purity, 99.0%) were used as received from Matheson Gas Products, Canada. All gases were used in a Pyrex vacuum line equipped with Teflon stopcocks, Wallace and Tiernan membrane manometers and a double-stage oil diffusion pump. The gas chromatographic procedure involved the use of either a squalane column [9] or a UCON LB550X20% column [10], at room temperature and at 50°C respectively. Both chromatographs are equipped with double flame-ionization detectors.

3. Results

3.1. Photolysis of 1,2-butadiene

The products observed in the photolysis of 1,2-butadiene, either pure or in the presence of 10% oxygen, are in agreement with the results reported by Doepker and Hill [3] (Table 1). Although there are some small discrepancies in the quantum values, the differences are probably not very significant. However, the vinylacetylene quantum yields must be taken into consideration. Reference 3 does not include absolute quantum values. For comparison, Doepker and Hill's results are rearranged by giving them the present vinylacetylene quantum yield value. The agreement between the two sets of experimental results is rather good except in the case of the acetylene yield. In a second series of experiments, Diaz and Doepker [11] give a somewhat different distribution of quantum values. Now, there is good agreement among the acetylene quantum yields, but poorer agreement among the vinylacetylene, 1,3-butadiene and propyne quantum values, although the absolute values are not poor. In fact, there is good agreement between our

TABLE 1

Quantum yields measured in the photolysis of 1,2-butadiene at 147 nm

	Quantum yields ^a					
	This work ^b	From ref. 3 ^c	From ref. 11 ^b	This work ^d	From ref. 3 ^d	From ref. 11 ^e
Methane	0.05	0.04	0.04	0.01 ₄	0.03 ₅	0.03
Acetylene	0.15 ₅	0.10	0.13	0.17	0.14	0.17
Ethylene	0.05 ₄	0.04 ₅	0.03	0.06	0.06 ₂	0.04
Ethane	0.15 ₆	0.14 ₆	0.11	0.01	0.00 ₄	
Propene	0.01 ₃	0.00 ₉	0.01	0.05 ₅	0.04 ₈	0.01
Propyne	0.14	0.14 ₆	0.11	0.14	0.17	0.13
Allene	0.05	0.04 ₅	0.03	0.05	0.04 ₈	0.04
Vinylacetylene	0.34 ₄	0.34 ₄	0.22	0.35	0.35	0.31
C ₄ (?) ^f	0.09 ₃	0.04 ₅	0.05	0.09 ₅	0.07 ₈	0.10
1,3-Butadiene	0.08	0.06 ₆	0.14 ^g	0.07 ₃	0.07 ₅	0.06 ^g
2-Butene	0.11	0.07		0.00		

^a1,2-Butadiene pressure, 5.0 Torr (1 Torr = 133 N m⁻²).^bPure 1,2-butadiene.^cRelative values.^dRelative values; oxygen pressure, 0.5 Torr.^eRelative values; nitric oxide pressure, 0.5 Torr.^fThe retention time of this product is similar to that of 1-pentene on the squalane column [9], but it is a little less than twice that on the UCON column [10].^gIncludes 1-butyne.

oxygen experiments and Diaz and Doepker's nitric oxide experiments. We have no explanation for the discrepancies, although it is known that unsaturated products are sensitive to the percentage of conversion and the presence of unscavenged radicals. The quantum yields of these products decrease at high conversion. Finally it should be noted that the unidentified C₄ product has a retention time similar to that of 1-pentene on the squalane column [9], but is a little less than twice that on the UCON column [10]. From a consideration of the characteristics of both chromatographic columns, this product may be butatriene [9, 10]. The quantum yield of this product shows similar behaviour to that of vinylacetylene. Thus, it is probably formed through the loss of two hydrogen atoms [11].

3.2. Photolysis of mixtures of 1,2-butadiene and oxygen

For the photolysis of mixtures of 1,2-butadiene and oxygen, two main trends are evident from the results given in Table 2. First, the addition of oxygen to 1,2-butadiene leads to a large increase in the propene quantum yields; this quantum yield may be as high as 1.8. Conversely, the main product arising from the direct photolysis of 1,2-butadiene has a quantum yield decreasing from 0.35 to less than 0.02. The other C_nH_m quantum values also decrease in the same way.

TABLE 2

Quantum yields of propene and vinylacetylene measured in the 147 nm photolysis of 5 Torr of 1,2-butadiene with various pressures of oxygen

Oxygen pressure (Torr)	Quantum yields ^a		
	$\Phi(\text{C}_3\text{H}_6)$	$\Phi(\text{C}_4\text{H}_4)$	Φ^b
0.00	0.012 ₆	0.34 ₄	—
0.52	0.05 ₅	0.35	1.02 ₁
48	1.21	0.115 ₅	0.93 ₃
105	1.61	0.071 ₇	1.00 ₈
135	1.63 ₆	0.05 ₁	0.96 ₃
202	1.82	0.03 ₉	1.02 ₁
404	1.61	0.019 ₁	0.85 ₉
601	1.75 ₅	0.014 ₄	0.91 ₈
			$\Phi = 0.96_0$ ($\sigma = 0.06_1$)

^aThe quantum values are measured relative to the total absorbed photon beam.

^b $\Phi = 0.5 \{ \Phi_{\text{O}_2}(\text{C}_3\text{H}_6) - \Phi_{\text{C}_4\text{H}_6}(\text{C}_3\text{H}_6) \} + \Phi(\text{C}_4\text{H}_4)/0.35$ (see text).

TABLE 3

Quantum yields of propene and vinylacetylene measured in the 147 nm photolysis of 150 Torr of nitrous oxide with various pressures of 1,2-butadiene

1,2-Butadiene pressure (Torr)	Quantum yields ^a			
	$\Phi(\text{C}_3\text{H}_6)$	$\Phi(\text{C}_4\text{H}_4)$	$1 - \Phi(\text{C}_4\text{H}_4)/0.35^b$	Φ^c
2	0.46 ₂	0.07 ₀	0.80	0.66 ₂
5	0.46 ₂	0.11 ₀	0.68 ₆	0.77 ₆
10	0.28	0.17 ₃	0.50 ₆	0.77 ₄
15	0.29 ₈	0.24 ₆	0.29 ₇	1.00
30	0.14 ₆	0.28 ₂	0.19 ₄	0.95 ₂

^aThe quantum values are measured relative to the total absorbed photon beam.

^bThis value is the fraction of light absorbed by N_2O .

^c $\Phi = \Phi(\text{C}_3\text{H}_6) + \Phi(\text{C}_4\text{H}_4)/0.35$.

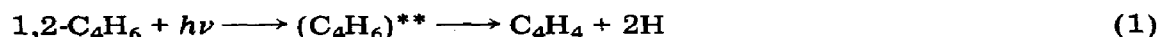
3.3. Photolysis of mixtures of nitrous oxide and 1,2-butadiene

Although in the photolysis of mixtures of nitrous oxide and 1,2-butadiene, 1,2-butadiene is the working parameter, the results are, at least partially, similar to those reported for the previous mixtures. For example, the $\Phi(\text{C}_n\text{H}_m)$ values increase with an increase in the 1,2-butadiene relative concentration (Table 3). Moreover, the $\Phi(\text{C}_3\text{H}_6)$ values again increase with an increase in the relative concentration of oxygen. However, these $\Phi(\text{C}_3\text{H}_6)$ values are now less than 0.5.

4. Discussion

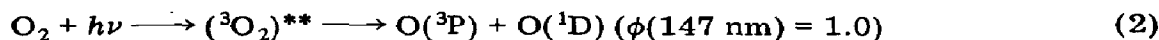
4.1. Fragmentation of photoexcited 1,2-butadiene

The fragmentation of the photoexcited 1,2-butadiene molecules is relatively well known [3, 11]. Thus, it is not necessary to come back to this point, except to recall that the main fragmentation process involves the formation of vinylacetylene. This product is formed concurrently with two hydrogen atoms. Since no dramatic pressure effect was observed, it was not possible to determine whether this process implies the elimination of two hydrogen atoms either in two successive steps or only in one process. Thus, the following reaction is sufficient to exemplify the vinylacetylene formation:



4.2. Photolysis of mixtures of 1,2-butadiene and oxygen

In the photolysis of mixtures of 1,2-butadiene and oxygen, the results clearly show a decrease in the vinylacetylene quantum yields with an increase in the oxygen concentration (Table 2). Since the vinylacetylene is known to be formed in the fragmentation processes of the photoexcited 1,2-butadiene molecule, the $\Phi(\text{C}_4\text{H}_4)$ values may be used to calculate the fraction of light absorbed through 1,2-butadiene. In other words, this assumption implies that there is no interference between the photoexcited 1,2-butadiene and oxygen molecules. However, the increase in the propene quantum yield follows the augmentation of the partial pressure of oxygen. At this wavelength, the photolysis of molecular oxygen is well known [12]. The absorption of a 147 nm photon gives rise to the formation of two oxygen atoms with a quantum yield of unity. The fundamental $\text{O}(^3\text{P})$ atom is not known to react quickly with molecular oxygen. Conversely, it does react in a rather clean way with 1,2-butadiene, leading to propene formation [13]:

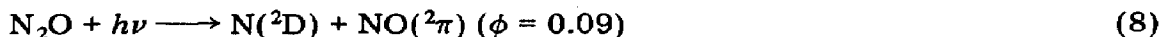
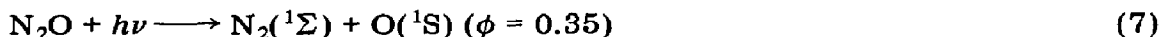
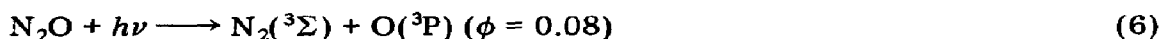
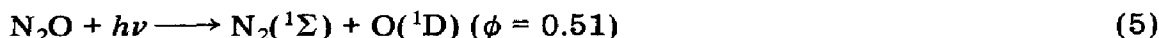


The physical quenching of $\text{O}(^1\text{D})$ to $\text{O}(^3\text{P})$ proceeds with a rate constant of $0.75 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [14]. Thus, it appears that one 147 nm photon, absorbed by oxygen, may eventually lead to the formation of two $\text{O}(^3\text{P})$ atoms, and the propene formation is easily linked to the absorption of light through molecular oxygen. In fact, the sum $\Phi(\text{C}_3\text{H}_6)/2 + \Phi(\text{C}_4\text{H}_4)/0.35$ must be unity since each term is a measurement of light absorbed either by oxygen or by 1,2-butadiene (Table 2). In this expression, $\Phi(\text{C}_3\text{H}_6)$ is the actual propene quantum yield corrected for the small amount of propene formed in the pure 1,2-butadiene system. The values are reported in Table 2, fourth column, and confirm the expected mechanism.

Finally, it is not known whether the reaction of O(¹D) atoms involves their physical quenching by 1,2-butadiene or whether they react in a process similar to O(³P) atoms. It is pertinent at this point to recall that O(¹D) atoms react through C—H insertion with neopentane at a rate similar to the collision rate [14, 15].

4.3. The photolysis of mixtures of nitrous oxide and 1,2-butadiene

In order to find out the kind of reaction involved in the previous mixtures, the 147 nm photolysis of mixtures of nitrous oxide and 1,2-butadiene was studied (Table 3). The 147 nm photolysis of nitrous oxide is relatively well known and, of course, more complex than that of oxygen [16, 17]. The main processes of the fragmentation mechanism may be written as follows:



Moreover, O(¹D) atoms react with nitrous oxide with a high rate constant, giving rise to the formation of either N₂ + O₂ or 2NO [14, 18]. The same is also probably true for the O(¹S) atoms [14]. As far as the nitrogen atoms (²D) or the triplet nitrogen molecules (³Σ) are concerned, little is known about their behaviour. However, it was admitted that the N₂(³Σ) reacts with N₂O, giving rise to the additional formation of O(³P) atoms [16]:



$$k[\text{O}(^1\text{D}) + \text{N}_2\text{O}] = (2.2 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [14, 19]$$

$$k[\text{O}(^1\text{S}) + \text{N}_2\text{O}] = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [20]$$



Thus, the total oxygen atom quantum yield is probably close to unity. In the presence of a low percentage of 1,2-butadiene, part of the incident light is absorbed by N₂O, and O(³P) atoms lead to the occurrence of process (3). Table 3 shows that, in the presence of 1,2-butadiene at a pressure of 2 Torr, almost 80% of the incident photon beam is absorbed by N₂O. With a propene quantum yield of 0.46, at least 60% of the N₂O photochemistry leads to the formation of propene. Thus, the propene quantum yield is much higher than the expected O(³P) quantum yield ($[\phi\{\text{process (6)}\} + \phi\{\text{process (10)}\}] \times 0.80 = 0.136$), and other processes must be efficient as far as propene formation is concerned. Although O(¹D) and O(¹S) atoms react with N₂O with high rate constants [19, 20], they also probably react with higher rate constants with 1,2-butadiene.

In the presence of 1,2-butadiene at pressures of 15 - 30 Torr 80% - 100% of the photoexcited N_2O molecules lead to the formation of propene (Table 3) and the total quantum yield $\Phi(C_3H_6) + \Phi(C_4H_4)/0.35$ is unity. Since propene is not a major product of the 1,2-butadiene photolysis ($\Phi_{C_4H_6}(C_3H_6) \leq 0.01_3$), it may be concluded, on the assumption that the photolysis of the mixture of nitrous oxide and 1,2-butadiene behaves as two independent systems (*i.e.* the photolysis of nitrous oxide plus that of 1,2-butadiene without the mutual interference of the photoexcited molecules), that each photon absorbed by nitrous oxide leads to the formation of propene. (It is likely that process (8) does not eventually lead to propene, although nothing can be said about the behaviour of $N(^2D)$ and $NO(^2\pi)$. Conversely, process (6) may lead to two propene molecules through processes (3) and (10). Thus, process (6) counterbalances the inefficiency of process (8).) Since the reactions of $O(^1D)$ and $O(^1S)$ atoms with nitrous oxide lead to the disappearance of the propene promoters, it is reasonably safe to say that all $O(^1S)$ and $O(^1D)$ atoms react with 1,2-butadiene with rate constants probably close to the collision rate constant, and propene is a product of such reactions.

Acknowledgments

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