

ON THE CHOICE OF RADICAL SCAVENGERS IN THE PHOTOLYSIS OF *CIS*-2-BUTENE AND 1-PENTENE AT 147 nm

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(Received June 21, 1976; in revised form September 16, 1976)

Summary

We have studied the effect of small quantities of O₂, NO, NO₂, SO₂, HI, and H₂S added as radical scavengers in the 8.4 eV (147 nm) photolysis of *cis*-2-butene and of 1-pentene-*d*₁₀. Efficiency of methyl radical scavenging is in the decreasing order HI > NO₂ > NO > O₂ > H₂S > SO₂. NO₂, SO₂ and H₂S initiate the *cis-trans* isomerization of 2-butene. HI produces a deposit of iodine on the window; SO₂ and H₂S produce a sulphur deposit decreasing in each case the transmission of the window. HI and *cis*-2-butene are in competition to scavenge hydrogen atoms: $k(\text{H} + \text{HI})/k(\text{H} + \text{cis-2-butene}) = 21.2 \pm 1.1$. HI scavenges allyl radicals formed in the pentene photolysis; H₂S does not. Finally we have observed fragmentation reactions of the photoexcited *cis*-butene and 1-pentene molecules which were not previously observed:



Introduction

In earlier studies on the photolysis of various alkenes in the vacuum u.v. region we have used O₂ and H₂S as radical scavengers. Although O₂, interacting with the radicals formed during the photolysis, gives rise to oxygenated compounds that could not be analyzed H₂S permits a qualitative as well as a quantitative measurement of the principal radicals formed:



We have noted earlier that in employing these radical scavengers it gives rise to certain complications [1]. In order to understand their role, particularly to appreciate their advantages and drawbacks we have carried out a systematic study of *cis*-2-butene and 1-pentene-*d*₁₀ at 147 nm (8.4 eV) and the observed effects on addition of O₂, NO, NO₂, SO₂, H₂S and HI in low proportions (0 - 15%).

Experimental

The gaseous reactants used are of Matheson of Canada Research Grade (purity 99%) except 1-pentene- d_{10} which is of Merck Sharp and Dohme of Canada (purity > 99%). The reaction mixtures were prepared on a mercury-free vacuum line made of Pyrex glass equipped with Teflon stopcocks. Pressure measurements were made using metallic membrane manometers (Wallace and Tiernan). The samples of HI were prepared using an oil manometer (Octoil; $d = 0.98$). The pressure of the olefin was kept at 2.0 Torr (266 N/m^2) in all the irradiations. The irradiations were carried out in 1100 cm^3 cell into which the Xe resonance lamp was fitted. The emission of the lamp (with a LiF window of 1 mm thickness) consisted of a principal line at 147 nm (8.4 eV) of 98% and 129.6 nm (9.57 eV) of 2%. The lamp was powered by 125 W microwave generator (Raytheon PGM-10X1). The output of the lamp was about 1.5×10^{14} photons/s except in the case of a series of experiments in the presence of H_2S , where the output was about 1.8×10^{13} photons/s.

The chromatographic analyses were made at room temperature on a squalane column (25%) using a dual flame ionization detector. In the case of 1-pentene- d_{10} , ethylene and propylene products were separated by preparative gas chromatography on an alumina column heated between 30 and 150°C using a thermal conductivity detector. The samples were then introduced into the mass spectrometer CEC-21 104 for isotopic analysis.

Results

The quantum yields of the products are reported in the Tables and Figures. In tabulating the results it was assumed that the quantum yield of allene is not altered by the presence of additives [1a]. This supposition is corroborated by the fact that the quantity of allene remain unaltered on addition of additives, except in the case where the transmission of the window was diminished (see discussion). In the presence of SO_2 , H_2S and HI a deposit of S and I_2 was observed on the window which slowly diminished the transmission. Besides allene, quantum yields of other components such as acetylene, propylene, and propyne practically remained constant. In the case of 1,3-butadiene, it was observed that its yield slightly diminished with the increase in the additive concentration (Table 1). However, it can be seen that the variation is often within the limits of experimental errors. In the case of 1-pentene [1b] the yields are reported relative to allene: Φ (allene) = 0.128. The yields of acetylene were also observed to be constant: Φ (acetylene) = 0.065 ± 0.005 over the HI concentration range 0 - 5%.

The mass spectrometric analysis of propylene and ethylene produced in the photolysis of a mixture of 1-pentene- d_{10} : HI (2.0 : 0.1) are as follows:

$$\text{D}_2\text{HC-CD} = \text{CD}_2/\text{C}_3\text{D}_6 = 85(\pm 3)/15$$

TABLE 1

Photolysis of *cis*-2-butene at 147 nm (8.4 eV) in the presence of additives: quantum yields^a

Additives (%)	O ₂ 0.5 → 10.0	NO 0.5 → 3.0	NO ₂ 0.5 → 5.0	SO ₂ 0.75 → 15.0	HI 0.8 → 7.0	H ₂ S 0.4 → 12.0
C ₂ H ₂ (±0.02)	0.29	0.30	0.32	0.32	0.28	0.29
C ₂ H ₄ (± 0.01)	0.07	0.09	0.06	0.06	Fig. 4	— ^b
C ₃ H ₆ (± 0.01)	0.26	0.26	0.25 ₄	0.20	0.25	Fig. 4
C ₃ H ₄ ^d (± 0.01)	0.09 ₅	0.07	0.10	0.10	0.09 ₄	0.10
1,3-C ₄ H ₆ (±0.02)	0.43	0.35	0.38	0.36	0.38	0.40
C ₄ H ₈ ^f (± 20%)	0.14	<0.10	<0.02	0.5	2 ± 1 ^g	0.6

^a Relative to $\Phi(\text{allene}) = 0.085$; ^b Ref. [18] ^c Not measured ^d Propyne ^e Ref. [15].
^f *trans*-2-Butene ^g SO₂ isomerizes *cis*-2-butene, see also ref. [13].

$$\text{C}_2\text{D}_3\text{H}/\text{C}_2\text{D}_4 = 20/80(\pm 5)$$

The analyses were obtained with an electronic beam of energies 70, 10 and 9 eV. In the case of propylene at 10 eV, the only fragment observed corresponds to the ratio $m/e = 30$ indicating that the vinyl fragment is fully deuterated and therefore corroborates the structure indicated as above.

Discussion

Choice of a radical scavenger

From earlier photolytic studies of 2-methyl-1-butene at 147 nm [1c] we have noted that at low pressures it is difficult to prevent the formation of ethane completely. We have revived this aspect in comparing the efficiencies of various radical scavengers (Fig. 1). In these systems ethane originates essentially from the combination of two methyl radicals;



Figure 1 clearly demonstrates that 10% of O₂ is insufficient to suppress the process of ethane formation whereas 5% of NO₂ and 3% of NO is sufficient: $\Phi(\text{C}_2\text{H}_6) \leq 0.003$. Probably the main reason for its inability is due to the low pressure of the reaction mixture. The total pressure of 2 Torr is insufficient for the complete effectiveness of O₂ [2] as it is sufficient for stabilization of about 50% of ethane formed in the process (3) [3].

HI and H₂S are admittedly peculiar. In these two cases there is an additional contribution to ethane formation by a hydrogen atom transfer from the radical scavenger to the ethyl radical formed as indicated by the process (5):



where X is I or HS. In only comparing the decrease in the relative yield of ethane with increasing percentage of the scavengers, the efficiency of the latter towards methyl radicals decrease in the order $HI > NO_2 > NO > H_2S > O_2 > SO_2$.

In the presence of low percentages of scavengers, the yields of ethane rapidly increase as the scavengers are used up. Figure 2 demonstrates that the efficiency of O_2 and SO_2 decreases rapidly with the time of irradiation. It is very difficult here to compare the specific efficiencies of each of the scavengers because several radicals are formed in the photolysis of *cis*-2-butene and all of them consume radical scavengers with different degrees. On the whole NO [4] is more efficient than O_2 and SO_2 [5].

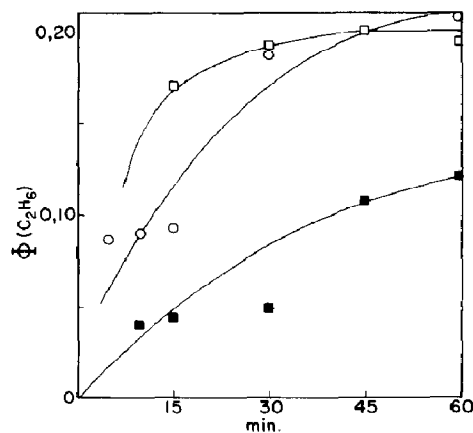
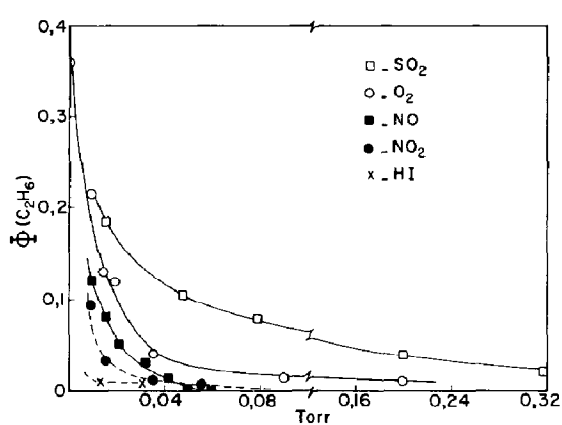


Fig. 1. Photolysis of *cis*-2-butene (2.0 Torr) vs. the pressure of additive.

Fig. 2. Photolysis of *cis*-2-butene (2.0 Torr) vs. photolytic time; \square , SO_2 ($0.75 \pm 0.05\%$); \circ , O_2 ($0.62 \pm 0.10\%$); \blacksquare , NO ($0.51 \pm 0.04\%$).

In the photolysis the absorption coefficients of the radical scavengers were also taken into consideration. At 147 nm the absorption coefficient of oxygen [6] is closer to that of *cis*-2-butene [7]: $\epsilon(O_2, 147 \text{ nm}) = 540 \text{ atm}^{-1}\text{cm}^{-1}$. One does not therefore add large quantities of O_2 without modifying the nature of the system. The absorption coefficients of H_2S [8] and SO_2 [9] are weaker and that of HI [10] and NO [11] are moderate on the whole: $\epsilon(HI, 147 \text{ nm}) = 50$ and $\epsilon(NO, 147 \text{ nm}) = 6.2 \text{ atm}^{-1}\text{cm}^{-1}$.

Another drawback in using certain scavengers is of the observable secondary reactions. Particularly the *cis-trans* isomerization of *cis*-2-butene in the presence of NO_2 [12], SO_2 [13], HI [14] and above all H_2S [15]. The mechanisms responsible for the isomerization are already discussed in each of the cases. It is also noted that the disappearance of 1,3-butadiene was observed when the irradiation was made in the presence of H_2S [15].

Finally, the substantial drawback in using SO_2 , H_2S , and HI as radical scavengers is that they cause a progressive diminution in transmission of the window. In the first two cases a deposit of S on the window was observed

which can be removed easily by CS_2 . In the case of HI, it produces a deposit of iodine which can be cleaned by CCl_4 . The deposit of S is formed by direct photolysis of SO_2 and H_2S and partly from the dismutation reaction of thiyl radicals formed in the process (6) [16].



Iodine is evidently formed by the combination of iodine atoms which originate from the photolysis of HI and from process (5). It is observed (Fig. 3) that H_2S is more efficient in diminishing the transmission of the window.

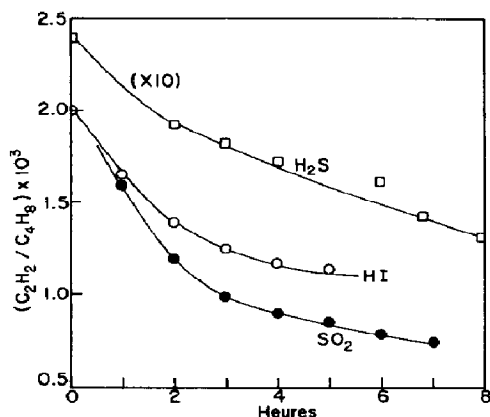


Fig. 3. Photolysis of *cis*-2-butene (2.0 Torr) in the presence of additive (0.1 Torr) vs. photolytic time.

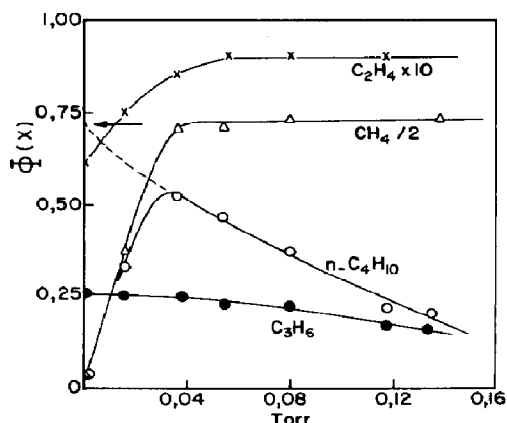


Fig. 4. Photolysis of *cis*-2-butene (2.0 Torr) vs. the pressure of added HI. The arrow shows the quantum yield of *s*-butyl radicals formed in the absence of HI.

Photolysis of *cis*-2-butene in the presence of HI and H_2S

Addition of HI (Fig. 4) in small quantities to *cis*-2-butene scavenges the free radicals according to the reaction (5). Thus from the increase in the yield of methane and ethylene, one can deduce the yield of methyl and vinyl radicals:

$$(\Delta\text{CH}_4) = \Phi(\text{CH}_3) = 1.35 \pm 0.10$$

and

$$(\Delta\text{C}_2\text{H}_4) = \Phi(\text{C}_2\text{H}_3) = 0.02$$

Similarly the yield of butyl radicals is determined from the yield of *n*-butane based on the following mechanism:





As the total pressure of HI varied is small, addition of small percentage of HI does not change the ratio Φ (process 11)/ Φ (process 12). Thus the decrease in the yield of n-butane is accounted for by the competition reaction between HI and *cis*-2-butene for the interception of H atoms. From this decrease one can thus calculate the ratio $k_{10}/k_9 = 21.2 \pm 1.2$. In comparing this with different values obtained in different systems by other workers one can obtain from the literature a value for the above ratio of about 28 [16a, 17]. This agreement is excellent considering that the latter value is obtained in more indirect way than that obtained here.

At 4.3% of HI, the n-butane yield is reduced by 50%, and the yield in propylene should also be diminished by the same proportion since both of them originate from the same precursor. It is observed that indeed the yield of propylene is diminished but is not compatible with the above indicated value. The possible explanation for the difference is due to the interception of C_3H_5 radicals formed in the direct photolysis of *cis*-2-butene by HI;



The difference between the decrease in n-butane yield and that in propylene leads to a value for the yield of C_3H_5 radical which can be given as $\Phi(\text{C}_3\text{H}_5) = 0.08 \pm 0.02$. The process (14) was not observed in the previous studies [1] for analytical reasons, and it must therefore be added to that already observed. Knowing the structure of butene and assuming that it does not undergo a major modification on photoexcitation, it is probable that the fragment C_3H_5 is of vinylic structure. It is necessary finally to note the yields of methane in the presence of HI. In addition to the methyl radicals formed in the primary process (14), they are also produced in the secondary process (12), and thus the calculated yield of total CH_3 radical is of the value $\Phi(\text{CH}_3) = 1.14 \pm 0.15$. The difference between this value and one that obtained experimentally in the presence of HI is large, but within the limits of experimental uncertainties. An almost similar value for the yield of methyl radical was observed in the presence of H_2S [18]: $\Phi(\text{CH}_3) = 1.25$ at 1.32 Torr of *cis*-2-butene. Table 2 summarizes the fragmentation processes of the photoexcited molecule of *cis*-2-butene at 8.4 eV.

Photolysis of 1-pentene-d₁₀ in the presence of HI

Figure 5 summarizes the yields of several products obtained. From the increased yields observed in the presence of HI, one can deduce the radical yields as follows:

$$\Phi(\text{C}_5\text{H}_{11}) \approx 0.75; \quad \Phi(\text{C}_2\text{H}_5) = 0.51; \quad \Phi(\text{C}_3\text{H}_5) = 0.34;$$

$$\Phi(\text{CH}_3) = 0.32; \quad \Phi(\text{C}_2\text{H}_3) = 0.20 \text{ and } \Phi(\text{C}_3\text{H}_7) = 0.07$$

Here too 2% of HI is sufficient for scavenging all the radicals except in the case of propylene where a stable value is not attained even at relatively

TABLE 2

Fragmentation of the photoexcited *cis*-2-butene molecule at 8.4 eV (147 nm)

<i>(cis</i> -2-C ₄ H ₆) ^{**}	Φ
C ₄ H ₆ + 2 H	0.38 ± 0.02
C ₂ H ₂ + 2 CH ₃	0.29 ± 0.02
C ₃ H ₄ + CH ₃ + H	0.18 ± 0.02
C ₃ H ₅ + CH ₃	0.08 ± 0.02
C ₄ H ₇ + H	< 0.05
C ₂ H ₅ + C ₂ H ₂ + H	0.03
C ₂ H ₃ + C ₂ H ₄ + H	0.02
C ₃ H ₆ + CH ₂	< 0.02
C ₂ H ₄ + C ₂ H ₄	< 0.02
isomerization	0.02
Total	0.98 < Φ < 1.09

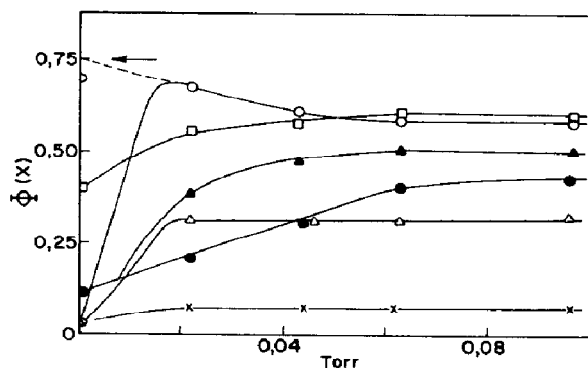


Fig. 5. Photolysis of 1-pentene-*d*₁₀ (2.0 Torr) vs. the pressure of added HI; ○, n-pentane; □, ethylene; ▲, ethane; ●, propene; △, methane; ×, propane. The arrow shows the quantum yield of *s*-pentyl radicals formed in the absence of HI.

high percentage of HI. We observed a diminution in the yield of n-pentane, much less pronounced than in the yield of n-butane observed in the photolysis of *cis*-2-butene. The reactivity of 1-pentene towards H atoms is nearly twice that of *cis*-2-butene and HI is therefore less efficient in intercepting H atoms in this system compared to the *cis*-2-butene system:

$$k(\text{H} + 1\text{-pentene})/k(\text{H} + \textit{cis}\text{-2-butene}) = 1.9 \text{ [17c].}$$



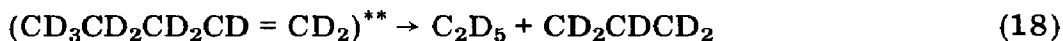
From the decrease in the yield of n-pentane one obtains a value for $k_{17}/k_{16} = 10 \pm 2$. This value is compared with the product:

$$\frac{k_{10}}{k_9} \times \frac{k(\text{H} + \text{cis-2-butene})}{k(\text{H} + 1\text{-pentene})} = \frac{21.2}{1.9}$$

$$= 11.2 = \frac{k_{10}}{k(\text{H} + 1\text{-pentene})}$$

The two values k_{17}/k_{16} and $k_{10}/k(\text{H} + 1\text{-pentene})$ are in good agreement taking into account the experimental uncertainty involved and the ratio k_{17}/k_{16} reported here is derived from the deuterated species.

The radical yields obtained in the presence of HI are similar to those observed in the presence of H_2S [1b] except for the C_3H_5 radical. In the presence of H_2S we have only observed a small increase in the yield of propylene: $\Phi(\text{C}_3\text{H}_6) = 0.05$; indeed the suggested mechanism requires an appreciable yield of C_3H_5 [1b]. The structure of 1-pentene suggests that the C_3H_5 radicals formed are of allylic nature. They are not intercepted by H_2S , but are effectively intercepted by HI [19]. The structure of propylene obtained in the mixture 1-pentene: HI (see results) confirms this result. In addition the ratio of $\text{C}_3\text{D}_5\text{H} : \text{C}_3\text{D}_6$ is compatible with the increase in propylene in the presence of HI:



In the same way the isotopic analysis of ethylene has confirmed the interception of vinyl radical (C_2D_3) by HI and the importance of $\text{C}_2\text{D}_3\text{H} : \text{C}_2\text{D}_4$ ratio is confirmed from the increase in the yields of ethylene in the presence of HI. In the presence of H_2S we had some difficulties in intercepting vinyl radicals except at high pressures. The results presented here and those published earlier indicate the modes of fragmentation of the photoexcited molecule as shown in Table 3. The calculated yield of ethyl radi-

TABLE 3

Fragmentation of the photoexcited 1-pentene molecule at 8.4 eV (147 nm).

$(1\text{-C}_5\text{H}_{10})^{**} \rightarrow$	Φ
$\text{C}_2\text{H}_4 + \text{C}_3\text{H}_5 + \text{H}$	0.24
$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_3 + \text{CH}_3$	0.16
$\text{C}_4\text{H}_6 + \text{CH}_3 + \text{H}$	0.15
$\text{C}_3\text{H}_4 + \text{C}_2\text{H}_5 + \text{H}$	0.14
$\text{C}_3\text{H}_5 + \text{C}_2\text{H}_5$	0.10
$\text{C}_2\text{H}_2 + \text{C}_3\text{H}_7 + \text{H}$	0.06 ₅
$\text{C}_5\text{H}_8 + 2\text{H}$	0.06
$\text{C}_3\text{H}_6 + \text{C}_2\text{H}_3 + \text{H}$	0.04
Total	0.95 ₅

calcs from Table 3, increased by the contribution from the excited $s\text{-C}_5\text{H}_{11}$ radical [1b], is 0.3 as compared with 0.51 that is observed in the presence of HI. The difference is outside the experimental error. It must nevertheless be added that other minor processes are not accounted and probably the yields of C_3H_5 (process 18) are underestimated.

Acknowledgements

We express our gratitude to the National Research Council of Canada for encouragement and providing financial support to one of us (K. B.) through UQAC presidential funds.

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