THE 7.1 AND 7.6 eV PHOTOLYSIS OF METHYLBUTENES

G. J. Collin, H. Gagnon-Deslauriers (Mme) and S. Auclair

Département des Sciences Pures, UQAC, Chicoutimi, Québec G7H 2B1 (Canada)

We have studied the 7.1 and 7.6 eV photolysis of the three methylbutenes, using a nitrogen lamp and a bromine resonance lamp. The quantum yield of the fragmentation of the photoexcited molecule is close to one. The observed fragmentation is simpler than the one observed at 8.4 eV. The pressure dependence effect as well as the use of O_2, NO, H_2S and HI as radical scavengers display the main fragmentation processes. The quantum yield of the split of the β(C-C) bond is the main primary process ($\Phi \approx 0.8$), in both the 2-methyl-1-butene and 3-methyl-1-butene systems. The formed allylic C_4H_7 radical may decompose further, depending on the total pressure of the sample. The α-methylallyl radical leads to the formation of 1,3-butadiene plus a hydrogen atom, and the β-methylallyl radical leads to the formation of allene plus a methyl radical. In the 2-methyl-2-butene system, where there is no C-C bond in the β position to the double bond, there are two major processes of nearly equal importance for the decomposition of the photoexcited molecule: *i* - the split of a C-H bond in the β position and *ii* - the split of a C-C bond in the α position. The allylic C_5H_9 radicals decompose further at low pressure into isoprene plus a hydrogen atom. The vinylic C_4H_7 radicals also decompose at low pressure into either propyne plus a methyl radical or 1,3-butadiene plus a hydrogen atom, depending on its original structure.

1) $C_5H_{10} + h\nu \rightarrow C_5H_{10}^{**}$

2) $C\text{-}C(C)\text{-}C{=}C^{**} \rightarrow C\text{-}\dot{C}\text{-}\dot{C}\text{-}\dot{C}^{*} + CH_3$

$C\text{-}\dot{C}\text{-}\dot{C}\text{-}\dot{C}^{*} \rightarrow C{=}C\text{-}C{=}C + H$

$C\text{-}\dot{C}\text{-}\dot{C}\text{-}\dot{C}^{*} \xrightarrow{(M)} C\text{-}\dot{C}\text{-}\dot{C}\text{-}\dot{C}$

3) $C{=}C(C)\text{-}C\text{-}C^{**} \rightarrow \dot{C}\text{-}\dot{C}(C)\text{-}\dot{C}^{*} + CH_3$

$\dot{C}\text{-}\dot{C}(C)\text{-}\dot{C}^{*} \rightarrow C{=}C{=}C + CH_3$

$\dot{C}\text{-}\dot{C}(C)\text{-}\dot{C}^{*} \xrightarrow{(M)} \dot{C}\text{-}\dot{C}(C)\text{-}\dot{C}$

4a) $C\text{-}C(C){=}C\text{-}C^{**} \rightarrow C\text{-}\dot{C}(C)\text{-}\dot{C}\text{-}\dot{C}^{*} + H$

or

$\dot{C}\text{-}\dot{C}(C)\text{-}\dot{C}\text{-}C^{*} + H$

$C\text{-}\dot{C}(C)\text{-}\dot{C}\text{-}\dot{C}^{*} \rightarrow C{=}C(C)\text{-}C{=}C + H$

$C\text{-}\dot{C}(C)\text{-}\dot{C}\text{-}\dot{C}^{*} \xrightarrow{(M)} C\text{-}\dot{C}(C)\text{-}\dot{C}\text{-}\dot{C}$ ... etc.

4b) $C\text{-}C(C){=}C\text{-}C^{**} \rightarrow C\text{-}C(C){=}\dot{C}^{*} + CH_3$

$C\text{-}C(C){=}\dot{C}^{*} \rightarrow C\text{-}C{\equiv}C + CH_3$

$C\text{-}C(C){=}\dot{C}^{*} \xrightarrow{(M)} C\text{-}C(C){=}\dot{C}$

$C\text{-}C(C){=}C^{*} \rightarrow \dot{C}\text{-}C(C)\text{-}\dot{C}$ ... etc.

4c) $C\text{-}C(C){=}C\text{-}C^{**} \rightarrow C\text{-}\dot{C}{=}C\text{-}C^{*} + CH_3$

$C\text{-}\dot{C}{=}C\text{-}C^{*} \rightarrow C\text{-}C{\equiv}C + CH_3$

$C\text{-}\dot{C}{=}C\text{-}C^{*} \xrightarrow{(M)} C\text{-}\dot{C}{=}C\text{-}C$

$C\text{-}\dot{C}{=}C\text{-}C^{*} \rightarrow C\text{-}\dot{C}\text{-}\dot{C}\text{-}\dot{C}^{*}$ ... etc.