

C. THE VACUUM ULTRAVIOLET PHOTOCHEMISTRY OF TETRAHYDROTHIOPHENE
AND SULFOLANE¹

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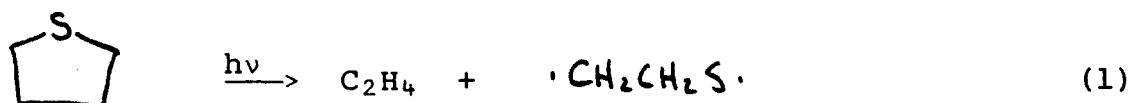
by

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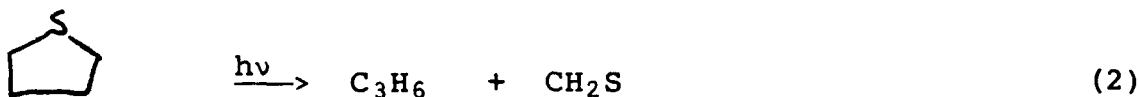
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The vacuum ultraviolet photochemistry of tetrahydrothiophene, THT, is closely related to the fragmentation pattern of the tetrahydrothiophene ion in the mass spectrometer. This is true despite the observation that the vacuum ultraviolet photolyses of ethylenesulfide and thietane are considerably more complicated than their mass spectra would indicate.²

As with most of the heterocycles which have been studied, the products are best interpreted by mechanisms which involve as the initial step the breaking of the heteroatom to α -carbon bond. Reaction 1 is the predominant primary process. Quantum yield measure-



ments at 147 nm indicate that secondary decomposition of the products of reaction 1 is minimal, $\phi=1$; however at 123.6 nm there is considerable secondary decomposition. At least 90% of the ethylene produced originates from the α and β carbon atoms. Reactions 2 and 3



are the next most significant primary processes. At 147 and 123.6 nm their quantum yields are each about 0.1. The C_3H_6 produced in reaction 2 is the trimethylene diradical since it forms both cyclopropane

EXB

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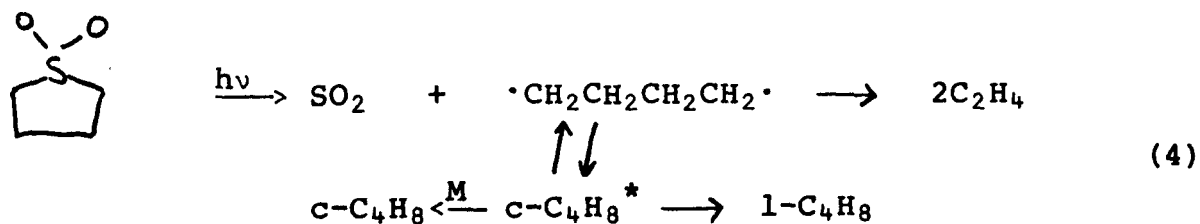
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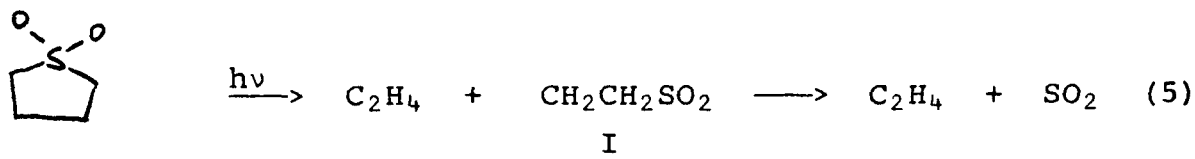
and propylene. The formation of 1,3-butadiene in reaction 3 is a unique process which has no precedent in any of the heterocycles we have studied. There is no evidence for the formation of 1,3-butadiene in either the oxygen or nitrogen analogs of THT. Both tetrahydrofuran and pyrrolidine produce very small yields of 1-butene but no 1,3-butadiene. Except for the production of 1,3-butadiene and the larger quantum yields observed from THT, the photolyses of THT, THF and pyrrolidine are quite similar.

The THT ion, which is formed with an ionization efficiency (η) of 0.11, 0.45, and 0.35 at 147, 123.6 and 106.7 nm respectively, forms a dimer ion at a rate which is close to that predicted by the ADO Theory. There is no evidence of any proton transfer reaction from THT ion.

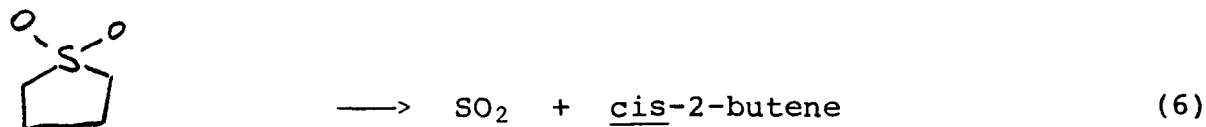
The close similarity between THF, THT and pyrrolidine suggested that we extend this study by examining the vacuum ultraviolet photochemistry of tetramethylene sulfone, sulfolane, which was expected to behave similarly to cyclopentanone whose photochemistry we had already studied.³⁻⁶ This expectation was based upon the premise that because of the stability of sulfur dioxide it could be extruded from the sulfolane in much the same way as carbon monoxide is extruded from cyclopentanone. The extrusion of sulfur dioxide is an important process in the photochemistry of sulfolane. As shown in reaction 4 the companion product is the tetramethylene diradical which ultimately produces cyclobutane, 1-butene, and ethylene, through competitive reaction channels. There is also evidence for the sequential loss of



ethylene as shown in reaction 5. The sulfinate ester resulting from



the cyclization of I has been identified by mass spectrometry. Sequential loss of ethylene was not observed in the photolysis of cyclopentanone. Another process which has no analog in cyclopentanone photochemistry is the stereospecific formation of cis-2-butene. The absence of any trans-2-butene requires a very specific intramolecular



reaction for the production of trans-2-butene. No cis-2-butene was observed in the mercury sensitized photolysis of sulfolane.⁵

References

1. This work was supported by the U. S. Department of Energy under contract number EY-76-S-02-3569.
2. Unpublished work from this laboratory.
3. Z. Diaz and R. D. Doepker, J. Phys. Chem., 82, 10(1978).
4. D. Salomon and A. A. Scala, Radiat. Phys. Chem., 13, 89(1979).
5. K. Honda, H. Mijuni, M. Takahasi and Y. Morii, J. Photochem., 3, 199(1974).
6. A. A. Scala and D. G. Ballan, Can. J. Chem., 50, 3938(1972).