

## The Photolysis of Carbon Suboxide in the Presence of Olefins

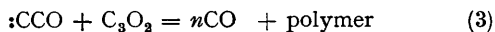
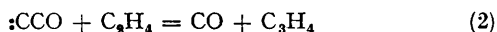
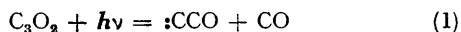
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THE photolysis of carbon suboxide in the presence of olefins has been investigated in the gas phase at

0°. The reaction vessel was quartz and the light from a medium-pressure mercury arc was filtered to

remove radiation below 2200 Å. Bayes<sup>1</sup> found that the following mechanism described the photolysis with ethylene:



The  $\text{C}_3\text{H}_4$  was a mixture of allene and propyne,  $n$  was found to be 1. Assuming a steady concentration of  $\text{:CCO}$  and at low conversions,

$$(\text{CO}/\text{C}_3\text{H}_4) - 2 = 2(k_3/k_2) [\text{C}_3\text{O}_2]/[\text{C}_2\text{H}_4]$$

A plot of  $[(\text{CO}/\text{C}_3\text{H}_4) - 2][\text{C}_2\text{H}_4]$  against  $[\text{C}_3\text{O}_2]$  is

a straight line through the origin of slope  $2k_3/k_2$ . For ethylene, Bayes found  $k_3/k_2 = 1.4$  against 1.3 in this work. The results in the table which are independent of pressure between 15 and 200 torr show that the reactivities of olefins with  $\text{:CCO}$  vary with structure in a way exactly opposite to that for other biradical species, for which similar data have been published. The variation is also different from that found with monoradicals. However, Frey<sup>2</sup> has found that  $\text{CH}_3\text{CH}$  radicals produced from the photolysis of diazoethane react much faster with the  $\text{C}=\text{C}$  bond in propene than with either *cis*- or *trans*-but-2-enes. Also like  $\text{:CCO}$  radicals, ethylidene radicals show very little tendency to insert into a C-H bond.

*Relative Reactivity of Olefins with Biradicals*

Olefin .. .. .	Diene	Alkyne	$\text{:CBr}_2$	$\text{:CCl}_2$	$\text{:O}$	$\text{:S}$	$\text{:Se}$
Ethylene .. .. .	1.00	3.7	—	—	1.00	1.00	1.00
Propene .. .. .	0.313	12.8	—	—	5.8	3.6	2.6
But-1-ene .. .. .	0.101	31.0	0.07 <sup>a</sup>	0.023 <sup>a</sup>	5.8	3.6	7.1
Isobutene .. .. .	0.096	19.2	1.00	1.00	25.0	—	44.7
<i>cis</i> -But-2-ene .. .. .	0.155	29.5	—	—	23.8	—	2.40
<i>trans</i> -But-2-ene .. .. .	0.091	140	—	—	28.3	—	56.0
Trimethylethylene .. .. .	0.040	45.0	3.20	2.90	79.3	—	—
Tetramethylethylene .. .. .	0.020	∞	3.50	6.60	101.8	—	—
References .. .. .	This work		3	4	5	6	7

<sup>a</sup>Hex-1-ene

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