

The Photolysis of Carbon Suboxide in the Presence of Olefins

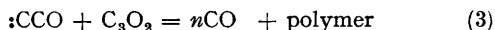
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THE photolysis of carbon suboxide in the presence of olefins has been investigated in the gas phase at

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

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 $\cdot\text{CCO}$ 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, Frey² has found that $\text{CH}_3\text{CH}\cdot$ 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 $\cdot\text{CCO}$ radicals, ethylidene radicals show very little tendency to insert into a $\text{C}-\text{H}$ bond.


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

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

[illegible]

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