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[1] found that the following mechanism described the photolysis with ethylene:

$$C_3O_2 + h\nu = :CCO + CO \quad (1)$$

$$:CCO + C_2H_4 = CO + C_3H_4 \quad (2)$$

$$:CCO + C_3O_2 = nCO + \text{polymer} \quad (3)$$

The C_3H_4 was a mixture of allene and propyne, n was found to be 1. Assuming a steady concentration of :CCO and at low conversions,

$$(CO/C_3H_4) - 2 = 2(k_3/k_2)\,[C_3O_2]/[C_2H_4]$$

A plot of $[(CO/C_3H_4) - 2][C_2H_4]$ against $[C_3O_2]$ is a straight line through the origin of slope $2k_3/k_2$. For ethylene, Bayes found $k_3/k_2 = 1{\cdot}4$ against 1·3 in this work. The results in the table which are independent of pressure between 15 and 200 torr show that the reactivites of olefins with :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[2] has found that CH_3CH:radicals produced from the photolysis of diazoethane react much faster with the C=C bond in propene than with either *cis*- or *trans*-but-2-enes. Also like :CCO radicals, ethylidene radicals show very little tendency to insert into a C–H bond.

Relative Reactivity of Olefins with Biradicals

Olefin	:CCO		:CBr_2	:CCl_2	:O	:S	:Se
	Diene/Alkyne						
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[a]	0·023[a]	5·8	3·6	7·1
Isobutene	0·096	19·2	1·00	1·00	25·0	—	44·7
cis-But-2-ene	0·155	29·5	—	—	23·8	—	2·40
trans-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

[a]Hex-1-ene

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