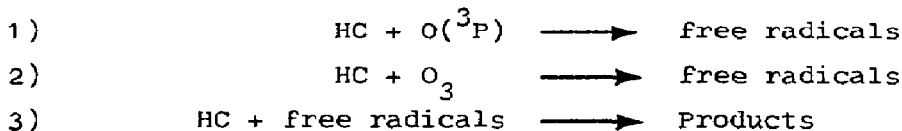


SYNERGISTIC EFFECTS IN THE PHOTOOXIDATION OF ETHYLENE AND VINYL CHLORIDE
INDUCED BY 1-3 BUTADIENE

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Evidence exists that olefins react readily (eq. 3) with free radicals and reactive species generated by the olefin photooxidation processes 1 and 2^{1,4}.



It has been proved that in mixed olefin systems, the less reactive olefins react readily with reactive intermediates (principally $\cdot\text{OH}$ and RO_2) produced by photooxidation involving a more reactive olefins³. Thus, the reactivity of an olefin can be increased by mixing with more reactive olefins. Therefore a smog chamber investigation on mixture effects of polluted industrial atmospheres of know hydrocarbon content seems to be worth while.

The experimental results shown in table I and II were obtained by irradiation of $\text{C}_2\text{H}_4 - \text{C}_4\text{H}_6 - \text{NO}_2$ and $\text{C}_2\text{H}_3\text{Cl} - \text{C}_4\text{H}_6 - \text{NO}_2$ systems. The light intensity expressed as first order rate constant for NO_2 photolysis was $0.29 \pm 0.02 \text{ min}^{-1}$. The photooxidation rate data, obtained from pseudo zero order kinetics of C_2H_4 and $\text{C}_2\text{H}_3\text{Cl}$ decay, show that an increase of the C_4H_6 concentration in both systems causes at first an acceleration and then a slowing down of the C_2H_4 and $\text{C}_2\text{H}_3\text{Cl}$ photooxidation processes. These results indicate the occurrence of positive and negative synergistic effects which depend on the relative concentrations of the hydrocarbons.

In recent studies ^{1,2,3}, it has been demonstrated that the steady-state concentration of OH, HO₂, RO₂ and O(³P) radicals, which are the main responsible of hydrocarbon photooxidation are not strictly dependent from the starting hydrocarbon concentration, but mainly upon the type of hydrocarbon present in the polluted atmosphere.

The behavior of the C₂H₄-C₄H₆-NO₂ and C₂H₃Cl-C₄H₆-NO₂ mixtures shows that two opposing effects exist: the first, which causes an increase in the photooxidation rate of less reactive hydrocarbon, is due to the higher radical concentrations generated by butadiene. This acceleration effect does not work at low C₄H₆ starting concentration, since the time for the attainment at the steady-state of the reactive intermediates appreciably increases at low starting concentration of hydrocarbons.

The second effect, which prevails at higher concentration of C₄H₆ and causes a decrease of the photooxidation rate of C₂H₄ and C₂H₃Cl, results from the competition between the more reactive C₄H₆ and the less reactive C₂H₄ or C₂H₃Cl in the bimolecular scavenging of the free radicals. Owing to this competition, the photooxidation of ethylene and vinyl chloride is quenched by high concentration of butadiene.

Table I

Photooxidation rate of C₂H₄ as a function of C₄H₆ concentration

Photooxidation rate of ethylene in ppb/min	Butadiene ppm
6.6	0.0
8.3	1.4
8.0	2.7
5.9	4.1
3.6	5.9

All experiments were carried out with initial concentration of 3.5 ppm NO₂ and 4.2 ppm C₂H₄ in air.

Table II

Photooxidation rate of C_2H_3Cl as a function of C_4H_6 concentration.

Photooxidation rate of vinyl chloride in ppb/min	Butadiene ppm
4.2	0.0
4.1	0.6
5.7	2.0
5.0	3.3
4.2	6.4
3.4	8.6
2.4	11.4

All experiments were carried out with initial concentration of 3.8 ppm NO_2 and 4.0 ppm C_2H_3Cl in air.

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