yond the amount predicted by eq 1. This indicates that the product aldehydes are able to effectively compete with the alcohols for the sulfate radical ion. The former enter into the chain and are subsequently oxidized to the corresponding carboxylic acids which can be titrated along with the strong acid HSO_4^- . On the basis of these facts, we postulate the additional steps

$$RCHO + SO_4 \cdot \overline{\longrightarrow} R\dot{C}O + H^+ + SO_4^{2-}$$
(9)

$$\dot{RCO} + S_2O_8^{2-} \xrightarrow{k_6}_{H_2O} RCOOH + H^+ + SO_4^{2-} + SO_4^{--}$$
 (10)

$$\dot{RCO} + \dot{RCHOH} \xrightarrow{k_7} \text{products}$$
 (11)

When the steady-state approximation is applied to the sequence of steps 4–6 and 9–11, one obtains the equation

$$\frac{-\mathrm{d}[\mathrm{S}_{2}\mathrm{O}_{8}^{2-}]}{\mathrm{d}t} = \left(\frac{k_{1}k_{3}k_{6}}{k_{7}}\right)^{1/2} [\mathrm{S}_{2}\mathrm{O}_{8}^{2-}]^{4/2} \left[\left(\frac{k_{2}[\mathrm{RCH}_{2}\mathrm{OH}]_{0}}{k_{5}}\right)^{1/2} + \left(\frac{k_{5}}{k_{2}}\frac{[\mathrm{RCHO}]_{0}}{[\mathrm{RCHO}]_{0}}\right)^{1/2}\right] (12)$$

Two conditions are necessary for inhibition: (1) the aldehyde must react at a comparable or faster rate than the alcohol with SO_4 .⁻; and (2) the radical derived from the aldehyde must participate in chain termination. According to (12), a plot of $k_{1/3}$ [RCH₂OH]₀/[RCHO]₀)^{1/2} vs. [RCH₂OH]₀/[RCHO]₀, where $k_{1/2}$ is the initial three-halves-order rate constant, should be linear. The points of Figure 1 (R = H) fit a straight line (correlation coefficient = 0.994) and are thus consistent with the model. The ratio of intercept to slope of Figure 1 gives $k_5/k_2 = 11$ which agrees with condition 1 above.

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- (11) NASA Fellow, 1965-1966.
- (12) Metcalf Fellow, 1965-1966.

John O. Edwards, Andrew R. Gallopo,¹¹ John E. McIsaac¹² Metcalf Chemical Laboratories, Brown University Providence, Rhode Island 02912 Received May 2, 1966 The figures below were inadvertently omitted from the Communication to the Editor that was published on p 3665 of the August 5, 1966 issue.

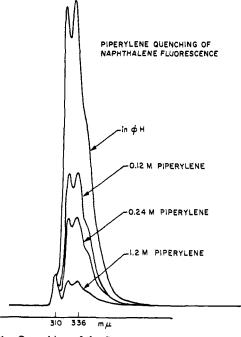


Figure 1. Quenching of the fluorescence of naphthalene by piperylene.

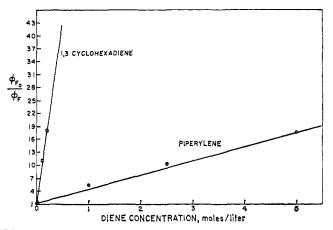


Figure 2. Quenching of 1-methylnaphthalene fluorescence by 1,3cyclohexadiene and piperylene, $\phi_{to}/\phi_t vs.$ diene concentration.

Leonard M. Stephenson, David G. Whitten George F. Vesley, George S. Hammond