CHEMISTRY LETTERS, pp. 1055-1058, 1976. Published by the Chemical Society of Japan

QUENCHING OF THE TRIPLET STATE OF ACETYLENE BY ETHYLENE

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It was confirmed that the excited state of acetylene formed in the mercury photosensitized reaction was quenched by ethylene, the excited state being monitored through phosphorescence of biacetyl mixed as a probe. The results provide an estimate on the relative value of the rate constant for the quenching process.

We have reported previously the role of excited acetylene for the benzene formation, although radical scavengers, such as ethylene, nitric oxide or hydrogen sulfide, inhibit the benzene formation.[1, 2, 3] We wish to discuss here whether the excited state of acetylene is quenched by ethylene, using biacetyl as a prove.

Sensitization of Biacetyl Phosphorescence

In the mercury photosensitization of acetylene, the addition of biacetyl gives a sensitized emission.[4] Figure 1 shows the dependence of sensitized emission at 510 nm on biacetyl pressure when the partial pressures of acetylene, mercury, and nitrogen were kept constant. According to the usual mechanism of the mercury photosensitization of an unsaturated hydrocarbon, the following reaction scheme may be reasonable;

$$Hg + h\nu \longrightarrow Hg^* \quad (1)$$

$$Hg^* + N_2 \longrightarrow Hg^*_o + N_2 \quad (2)$$

$$Hg^*_o + Ac_2 \longrightarrow \text{fragmentation} \quad (3)$$

$$Hg^*_o + A \longrightarrow Hg + A^{*\prime} \quad (4)$$

$$A^{*\prime} \longrightarrow \text{fragmentation} \quad (5)$$

$$A^{*\prime} + N_2 \longrightarrow A^* + N_2 \quad (6)$$

$$A^* + Ac_2 \longrightarrow A + Ac_2^* \quad (7)$$

$$A^* + A \longrightarrow \text{quenching} \quad (8)$$

$$Ac_2^* \longrightarrow Ac_2 + h\nu_p \quad (9)$$

$$Ac_2^* \longrightarrow Ac_2 \quad (10)$$

where Hg^* is $Hg(6^3P_1)$, Hg^*_o is $Hg(6^3P_0)$, A is acetylene, and Ac_2 is biacetyl. The excited state of acetylene, produced via the reaction (4), is thought to be vibrationally excited (indicated by asterisk). But the reaction (6) is probably favored over (5), because of the high pressure of nitrogen used in our experiments.[4] By the steady state treatment, we get

$$\frac{1}{\alpha I_p} = \frac{k_9 + k_{10}}{k_9 I} + \frac{k_8(k_9 + k_{10})}{k_7 k_9 I} \frac{[A]}{[Ac_2]},$$

where I is the light intensity of the mercury lamp, I_p is the intensity of the biacetyl emission, and α represents $(k_3[Ac_2] + k_4[A])/k_4[A]$.

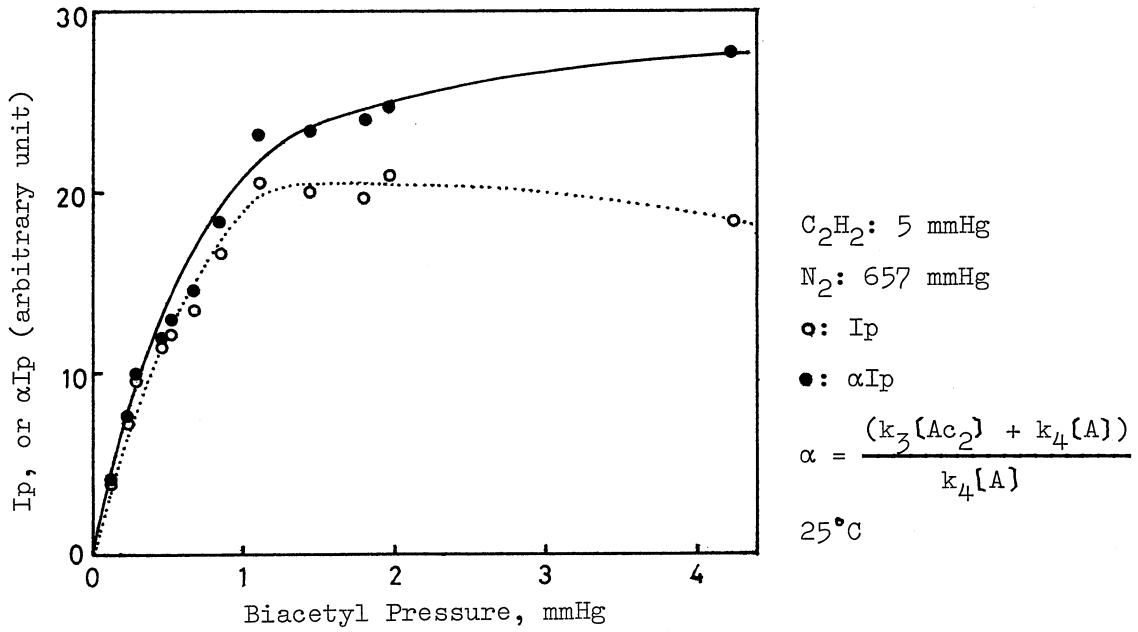

Fig. 1. Dependence of sensitized emission at 510 nm on biacetyl pressure.

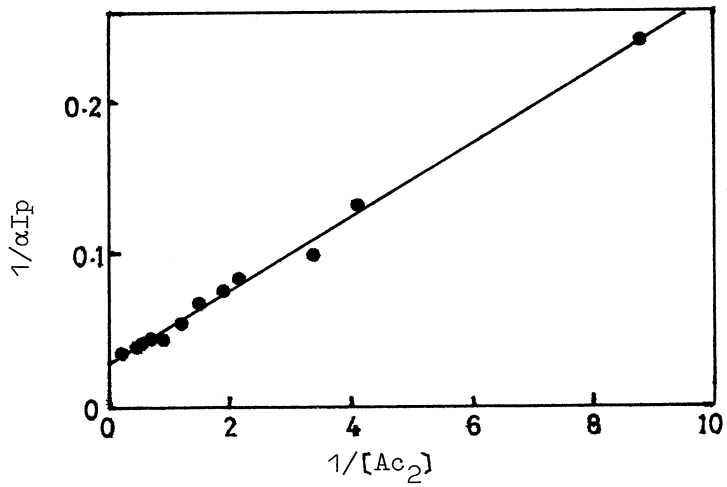

Fig. 2. Variation of the reciprocal of emission intensity vs. reciprocal of biacetyl pressure.

The quenching cross section for $Hg(^3P_0)$ with acetylene or biacetyl was measured to be 48 Å^2 or 45 Å^2 by Burton and Hunziker.[4] While, Horiguchi and Tsuchiya proposed the cross section of 36 Å^2 and 41 Å^2 for acetylene and ethylene.[5] In this study, α or β(next section) has been calculated on the estimated values of cross section 36 Å^2, 41 Å^2, and 34 Å^2 for acetylene, ethylene, and biacetyl respectively. Figure 2 shows the relation of $1/\alpha I_p$ against $1/[Ac_2]$. From the ratio of the intercept and the slope of Figure 2, we obtain $k_8 = 0.17\ k_7$.

Effect of Ethylene on the Biacetyl Emission

Figure 3 shows the effect of ethylene on the biacetyl emission. When ethylene was added to the mixture, the partial pressures of acetylene and biacetyl were kept constant.

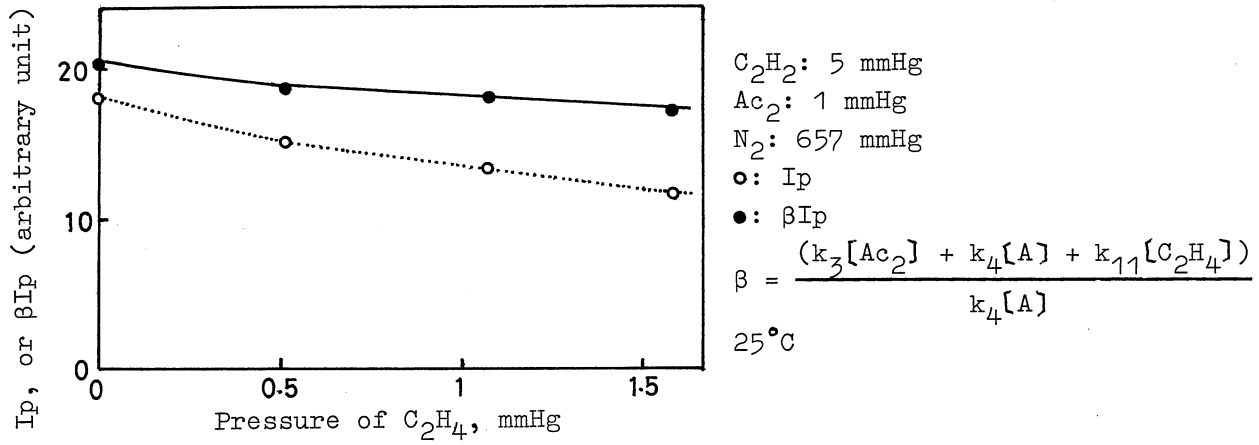

Fig. 3. Effect of ethylene on the biacetyl emission.

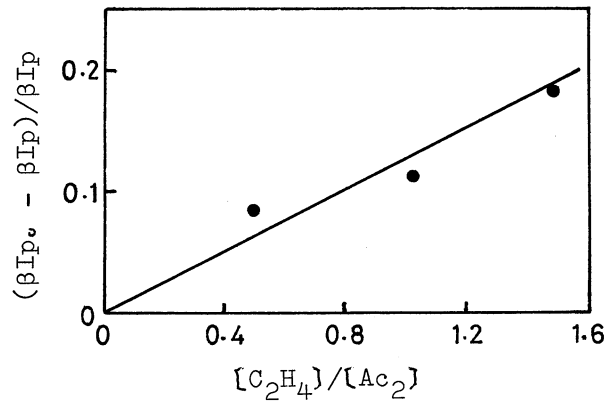

Fig. 4. Variation of $(\beta Ip_o - \beta Ip)/\beta Ip$ vs. $[C_2H_4]/[Ac_2]$.

The emission decreased with ethylene pressure. The decrease of the biacetyl emission in the presence of ethylene is not due to the quenching of biacetyl emitting state by ethylene, because the biacetyl phosphorescence was not quenched by ethylene when the biacetyl was excited directly in the 365 nm region. Furthermore, the biacetyl emission could not be found in ethylene- biacetyl-mercury-nitrogen system. Therefore the next reactions should be added to the above reactions.

$$Hg^*_o + C_2H_4 \longrightarrow Hg + C_2H_4^* \quad (11)$$

$$A^* + C_2H_4 \longrightarrow \text{quenching} \quad (12)$$

The following formula is given by the steady state treatment in which k_8 is equal to 0.17 k_7 and $[A]$ is equal to 4.71 $[Ac_2]$,

$$\frac{\beta I_{p_o} - \beta I_p}{\beta I_p} = \frac{k_{12}[C_2H_4]}{1.81k_7[Ac_2]}$$

here I_{p_o} represents the emission intensity in the absence of ethylene, and β is equal to $(k_3[Ac_2] + k_4[A] + k_{11}[C_2H_4])/k_4[A]$. In Figure 4, the value of $(\beta I_{p_o} - \beta I_p)/\beta I_p$ is plotted against $[C_2H_4]/[Ac_2]$. From the slope of Figure 4, we get $k_{12} = 0.22\ k_7$.

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(Received August 10, 1976)