CHEMISTRY LETTERS, pp. 957-962, 1972. Published by the Chemical Society of Japan

# A NOVEL ASPECT AGAINST THE "ORBITAL SYMMETRY CORRELATION IN THE SENSITIZATION"

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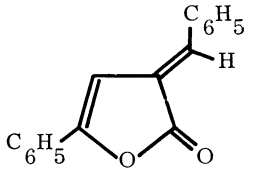
An aspect against Ullman's postulate of "orbital symmetry correlation in the sensitization" for the aromatic hydrocarbon-sensitized reaction of 2-benzylidene-4-phenyl-3-buten-4-olide is now presented, by showing that the lactone efficiently reabsorbes fluorescence emitted from the hydrocarbon sensitizers and its wavelength seems to govern the course of the reaction.

For the photo-irradiation of 2-benzylidene-4-phenyl-3-buten-4-olide(Q) and its related unsaturated lactones in 2-propanol, Ullman and Baumann found that the course of the reaction was varied with the irradiation wavelength; with 313 nm light, the lactone underwent "unselectively" both hydrogen atom abstraction from the solvent and its cis-trans isomerization, whereas, with 365 nm light, the lactone underwent "selectively" only the isomerization.[1)] They also showed that aromatic hydrocarbons sensitized the reaction and some sensitizers "selectively" led to the cis-trans isomerization and other sensitizers "unselectively" led to the hydrogen abstraction in addition to the isomerization, however the "selectivity" of the sensitized reaction course was not dependent at all on the triplet energies of the sensitizers. In order to explain the relation between the selectivity of the reaction course and the structure of the sensitizers employed, they proposed the "orbital symmetry correlation between the sensitizers and the lactones" which implied that close matching of the orbital symmetry between the lowest unfilled molecular orbital of the lactone and a certain part of the highest occupied orbital of the sensitizer led to the "selective reaction", that is, the isomerization.[1)] The present communication reports, based on the observation of the quenching effect of the lactone on fluorescence and phosphorescence of aromatic hydrocarbons, a novel aspect against Ullman and Baumann's "orbital symmetry correlation in the sensitization" by showing that not the triplet but the singlet excited aromatic hydrocarbons play an important role in the reaction; that is, the fluorescence emitted from the excited singlet sensitizers is reabsorbed by the lactone and fluorescence wavelength seems to govern the reported selectivity of the sensitized reaction course.



(Q)

In the present work, fluorescence, measured with a Hitachi MPF-2A fluorescence spectrophotometer,

of the aromatic hydrocarbons ($10^{-3}$ - $10^{-2}$ mol/l) such as biphenyl, fluorene, naphthalene, triphenylene, chrysene, p-terphenyl, phenanthrene and pyrene which had previously been employed as sensitizers by Ullman, was found to be quenched for the intensity by the added lactone (0 - 2 x $10^{-5}$ mol/l) in benzene solution. Plots of the ratio, $I_o/I$, where $I_o$ means the fluorescence intensity of the hydrocarbon in the absence of the lactone and I means the intensity in the presence of the lactone in concentration of [Q], against the concentration of the lactone, [Q], were, for the most cases, linear only in the lower concentration range of the lactone and curved upwards in its higher concentration range. A typical example is shown for chrysene in Figure 1. If, in the lower concentration range of the lactone, the plots are assumed to obey the Stern-Volmer equation (1), the apparent quenching rate constants, $k_q^{app}$, are obtained from their

$$I_o/I = 1 + k_q^{app}\tau_o[Q] \qquad (1)$$

slopes divided by the fluorescence lifetimes as summarized in Table 1 (column 2). In the equations (1)-(3), $\tau_o$ and $\tau$ denote the fluorescence lifetimes of the hydrocarbons in the absence and in the presence of the

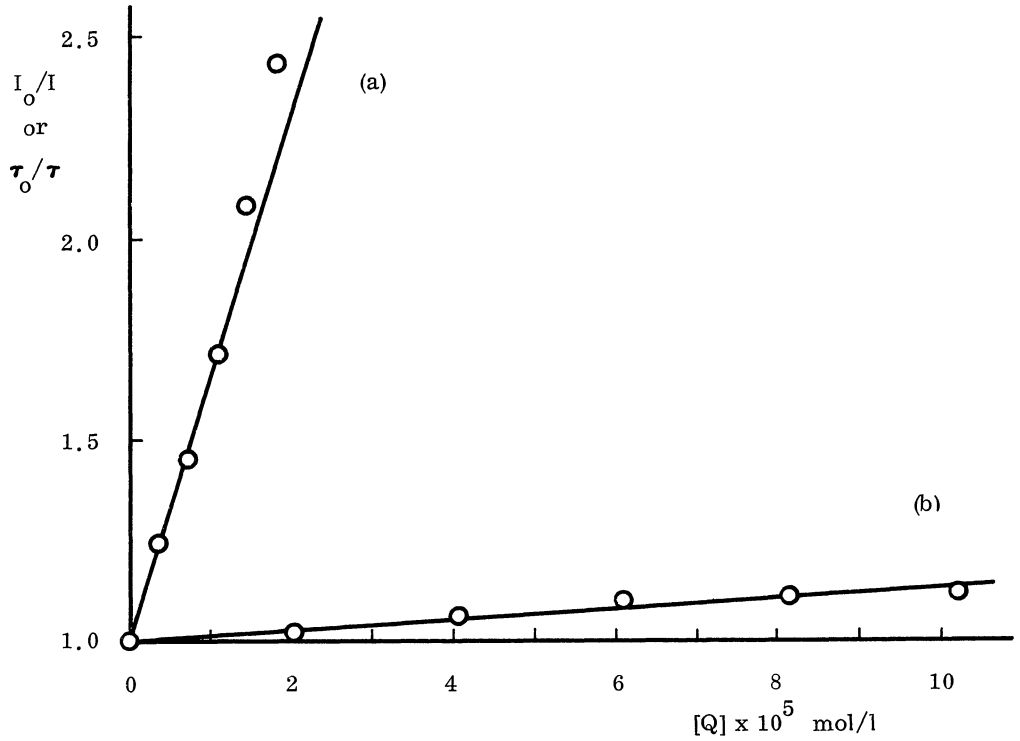



Figure 1. Quenching of Fluorescence of Chrysene for Intensity (curve a) and for Lifetime (curve b) by 2-Benzylidene-4-phenyl-3-buten-4-olide(Q) in Benzene (under the aerated condition).
(a) Concentration of chrysene: 5.00 x $10^{-4}$ mol/l; Excitation at 344 nm; Emission intensity observed at 383 nm. (b) Concentration of chrysene: 5.67 x $10^{-4}$ mol/l; Excitation at 338 nm.

Table 1. Quenching of Hydrocarbon Fluorescence by 2-Benzylidene-4-phenyl-3-buten-4-olide in Benzene[a)]

| Hydrocarbons | $k_q^{app}$ b) | $k_q$ b) | $I_o/I$ c) | $\tau_o/\tau$ c) |
|---|---|---|---|---|
| Biphenyl | $1.4 \times 10^{12}$ | $1.4 \times 10^{10}$ | $1.2_6$ | $1.00_3$ |
| Fluorene | $4.7 \times 10^{12}$ | $2.6 \times 10^{11}$ | $1.5_2$ | $1.0_3$ |
| Naphthalene | $6.3 \times 10^{11}$ | $3.2 \times 10^{10}$ | $1.3_0$ | $1.0_1$ |
| Triphenylene | $2.3 \times 10^{12}$ | $7.8 \times 10^{10}$ | $1.9_2$ | $1.0_2$ |
| Chrysene | $4.4 \times 10^{12}$ | $1.2 \times 10^{11}$ | $2.4_3$ | $1.0_4$ |

a) Conducted under the aerated condition; the concentration of the hydrocarbons and the lactone: $10^{-3}$ - $10^{-2}$ mol/l and 0 - $2 \times 10^{-5}$ mol/l, respectively, for the intensity measurement, and $10^{-4}$ - $10^{-2}$ mol/l and 0 - $5 \times 10^{-4}$ mol/l, respectively, for the lifetime measurement. b) In $mol^{-1}$ l $sec^{-1}$. c) Value at the lactone concentration of $2 \times 10^{-5}$ mol/l.

lactone in concentration of [Q], respectively. Also $k_q$ [eq. (2) and (3)] means the bimolecular rate constant for the quenching process of the excited singlet hydrocarbon by the lactone, and notation of $k_q^{app}$ is specially used to treat the apparent quenching of the fluorescence intensity in the form of the usual Stern-Volmer equation (1) as described later.

However, measurement of the fluorescence lifetime, with the use of a JASCO FL-10 phase fluorimeter, of the hydrocarbons ($10^{-2}$ - $10^{-4}$ mol/l) with varied concentration of the lactone (0 - $5 \times 10^{-4}$ mol/l) showed that the quenching of the fluorescence lifetime fitted the following linear Stern-Volmer relationships over the concentration range of the lactone as depicted in Figure 1 for chrysene:

$$1/\tau = 1/\tau_o + k_q[Q] \qquad (2)$$

or

$$\tau_o/\tau = 1 + k_q\tau_o[Q] \qquad (3)$$

Values of $k_q$ for the typical hydrocarbons employed were obtained from the slope of the equation (2) as listed in Table 1 (column 3) and it is clearly seen that $k_q^{app}$ values are ten to a hundred times higher than $k_q$ values. In Table 1 are also listed (column 4 and 5) $I_o/I$ and $\tau_o/\tau$ values at [Q] = $2.0 \times 10^{-5}$ mol/l, indicating that $I_o/I$ values are significantly higher than the corresponding $\tau_o/\tau$ values which are close to unity.

The difference between $I_o/I$ and $\tau_o/\tau$ values seems reasonably understood to result from the decrease in fluorescence intensity due to the reabsorption of the fluorescence emitted from the excited singlet hydro-

carbons by the lactone. Thus, if the added lactone in concentration of [Q] acts only to quench the excited singlet hydrocarbon with a rate constant of $k_q$, the fluorescence intensity of the hydrocarbon should be decreased by the same extent as the fluorescence lifetime, so $I_o/I$ should be equal to $\tau_o/\tau$. However, when the fluorescence emitted from the hydrocarbon is reabsorbed by the lactone in the surrounding medium, the actually observed fluorescence is to be further reduced in intensity, accordingly $I_o/I$ value is to be higher than $\tau_o/\tau$ value by the extent corresponding to the efficiency of the reabsorption, and this aspect is supported by the following findings.

In the first place, the lactone has high molar extinction coefficient ($\varepsilon$: 5,000 - 27,000) in the wavelength region (300 - 430 nm) where the hydrocarbons employed fluoresce, suggesting that the emitting fluorescence can be efficiently reabsorbed by the lactone leading to the decrease of the observed fluorescence intensity. Secondly, the fluorescence spectra of some hydrocarbons were changed in the shape with the increase in the concentration of the added lactone. A typical example is shown for naphthalene in Figure 2; the intensity of a maximum at 336 nm where the lactone has higher molar extinction coefficient ($\varepsilon$: 8,000) decreased more remarkably than another maximum at 322 nm where the lactone has lower molar extinction

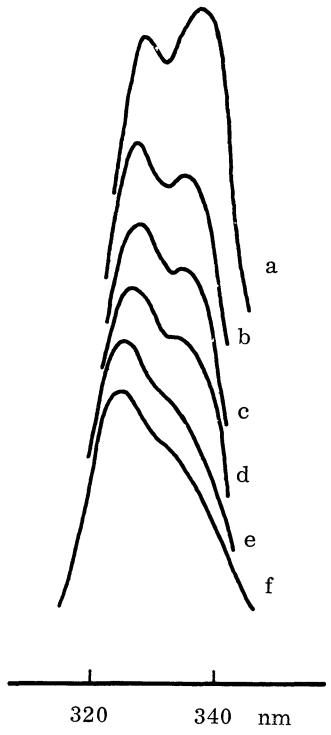



Figure 2. Change of Fluorescence Spectrum of Naphthalene with the Concentration of Added 2-Benzylidene-4-phenyl-3-buten-4-olide(Q) in Benzene (under the aerated condition). Concentration of naphthalene: $1.09 \times 10^{-3}$ mol/l. Concentration of Q: a, 0; b, $2.22 \times 10^{-5}$; c, $4.44 \times 10^{-5}$; d, $6.66 \times 10^{-5}$; e, $8.88 \times 10^{-5}$ and f, $1.11 \times 10^{-4}$ mol/l.

coefficient ($\varepsilon$: 6,000). Thirdly, the fact that the hydrocarbons were used in sufficient concentration to absorb most of the excitation light excludes a possibility that the lactone in increasing concentration would be excited in more effective competition with the hydrocarbons resulting in the decrease of the latter's fluorescence intensity. Fourthly, in the absorption spectra of mixtures of lactone with the hydrocarbons

in ethanol, appearance of no absorption band other than those of each component eliminates a possibility that complexing between both the components in their ground states would reduce the fluorescence intensity. Therefore, it is reasonable to conclude that the apparent decrease of the hydrocarbon fluorescence intensity in the presence of the lactone in the concentration range employed is partly due to the quenching of the excited singlet hydrocarbon by the lactone but mainly due to the reabsorption of the emitted fluorescence by the lactone.

Furthermore, a possibility of the sensitization by the excited triplet hydrocarbons on the lactone, which was postulated by Ullman,[1] appears to be scarce. Thus, for phosphorescence of triphenylene ($3 \times 10^{-3}$ mol/l) in degassed EPA at 77°K, its lifetime was only slightly reduced by the addition of the lactone ($1.5 \times 10^{-3}$ mol/l) from 17.4 to 15.8 sec although its intensity was remarkably decreased. This fact indicates that the lactone does not effectively quench the triplet triphenylene and the apparent decrease of the phosphorescence intensity is attributable to the quenching of the excited singlet triphenylene accompanied by the reduction of the efficiency of its intersystem crossing to the triplet state.

It should be mentioned that the present result can explain Ullman's observation concerning the dependence of the "selectivity" of the sensitized reaction course on the structure of the sensitizers employed, that is, the use of biphenyl, fluorene and naphthalene as sensitizers led to the "unselective reaction", whereas the use of triphenylene, phenanthrene, o- and p-terphenyl, chrysene, fluoranthene, pyrene and 1- and 2-phenylnaphthalene brought about the "selective reaction".[1,2] It is noticiable that among these hydrocarbons, those leading to the "unselective reaction" fluoresce in shorter wavelengths (for example, $\lambda_{max}$: 305 and 315 nm for biphenyl, 303 and 310 nm for fluorene, and 322 and 336 nm for naphthalene)[3] than those leading to the "selective reaction" (for example, $\lambda_{max}$: 324 and 340 nm for p-terphenyl, 346 and 364 nm for phenanthrene, 355 and 371 nm for triphenylene, and 361, 382 and 403 nm for chrysene).[3] Dependence of the "selectivity" of the sensitized reaction course on wavelength of the fluorescence emitted from the hydrocarbons accords well with difference in the "selectivity" of the unsensitized reaction course observed between 313 and 365 nm irradiation. Therefore, irrespective of the excitation procedure of the lactone, by direct absorption of the incident light from a light source or by reabsorption of the emitted fluorescence, light of nearly 313 or 365 nm is supposed to cause respectively "unselective" or "selective" reaction of the lactone. Finally, it should be stressed that reabsorption mechanism, though often called "trivial mechanism",[4] takes an important role in the energy transfer process in some organic photochemical reactions.

Acknowledgements. Professor O. Simamura is thanked for his interest in this work and Dr. M. Takakusa, Electrotechnical Laboratory, for the use of a phase fluorimeter in his laboratory. Grants from the Mitsubishi Foundation and from the Ministry of Education are acknowledged for partial support of this work.

## References

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( Received July 20, 1972 )