

Studies of Photosensitive Resins. IV. Photosensitization Mechanism of Polyvinyl Cinnamate

Kenichiro NAKAMURA and Shinichi KIKUCHI

The Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo

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The photosensitization mechanism of polyvinyl cinnamate was investigated by measuring the phosphorescence spectra of cinnamic acid and sensitizers. The peak of phosphorescence for *trans*-cinnamic acid was found to be 20100 cm^{-1} , and the triplet energies of the effective sensitizers were found to be situated near or higher than that of cinnamic acid. It was established that the phosphorescences of sensitizers were exceedingly quenched when cinnamic acid was introduced into their solutions. This finding can be understood if it is assumed that the excitation energy is transferred from the triplet state of the sensitizer to that of cinnamic acid. The critical separation of donor and acceptor and the configuration of the triplet state for cinnamic acid are also discussed.

Polyvinyl cinnamate is one of the most common photosensitive resins which become insoluble upon irradiation with light. The sensitized polyvinyl cinnamate is sensitive to visible light, while the non-sensitized resin is sensitive only to ultraviolet light. Many sensitizers, such as aromatic nitro and keto compounds, are reported to have this effect.

The photo-crosslinking mechanism of polyvinyl cinnamate has been made fairly clear. However, the sensitization mechanism of the resin is still the subject of frequent discussion. Tsuda^{1,2} measured the photosensitivities of resins sensitized by mixtures of aromatic compounds, and showed that the mixing effect of a sensitizer can be fairly well understood by assuming a triplet energy transfer. He also measured the phosphorescence spectra of cinnamic acid, and reported that the limit of the spectral sensitization of polyvinyl cinnamate coincided with the wavelength of phosphorescence emitted from cinnamic acid. However, the triplet energy transfer mechanism has not been reported more definitely. Studies of the quenching of sensitizers' phosphorescence would seem to make the mechanism clearer. Therefore, the authors have measured the phosphorescence spectra of various sensitizers and have studied the quenching effect on a sensitizer's phosphorescence of the addition of cinnamic acid.

The photo-crosslinking of polyvinyl cinnamate is a reaction similar to the photo-dimerization of cinnamic acid in a solid phase. Therefore, the authors also studied the photochemistry of cinnamic acid. When cinnamic acid is irradiated with ultraviolet light in a solution, a photoisomerization reaction occurs. The quantum yields of the *cis*→*trans* and *trans*→*cis* isomerization of cinnamic acid were found

by Vaidya³ to be 0.21 and 0.61 respectively. The sum of the two quantum yields was about unity. This fact suggests that the excited states of *cis*- and *trans*-cinnamic acid concerned are the same.

Hammond *et al.*⁴ discussed the *cis*-*trans* isomerization of stilbene in detail, and emphasized that a phantom triplet exists in the lowest triplet state of stilbene. There has, however, been no report which gives information about phantom triplet of cinnamic acid. Therefore, the authors intended to investigate the configuration of the triplet state by measuring the phosphorescence spectra of *cis*- and *trans*-cinnamic acid. The phosphorescence spectrum of *trans*-cinnamic acid was measured by Tsuda,⁵ but that of *cis* isomer has not yet been measured.

Energy transfer from the triplet state has been observed between a number of donor-acceptor pairs.^{6,7} Hammond *et al.*⁸ have shown that the photosensitized *cis*-*trans* isomerization of stilbene is caused by the transfer of the triplet excitation. Porter *et al.*⁹ have studied the quenching of the triplet state by measuring the triplet-triplet absorption spectra; they reported that there is no evidence for long-range resonance transfer of the kind found

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4) G. S. Hammond *et al.*, *J. Am. Chem. Soc.*, **83**, 2396 (1961); *ibid.*, **84**, 4983 (1962); *ibid.*, **86**, 3197 (1964); *ibid.*, **88**, 4769 (1966).

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2) M. Tsuda, *J. Polymer Sci.*, **B2**, 1143 (1964).

in the analogous singlet energy transfer process. In this paper, the distance of the energy transfer between the acceptor and donor molecules will also be discussed.

Experimental

The phosphorescence spectra of sensitizers were measured in an EPA solution at 77°K. The concentration of the sensitizer was 10^{-3} M, and 0.01–0.2 M *trans*-cinnamic acid was added to the sensitizer's solution. In the quenching measurements, the concentration of the sensitizer was kept at a constant value.

cis-Cinnamic acid was prepared from phenyl propiolic acid by the hydrogen reduction method described by Paal.¹⁰⁾ Colloidal palladium¹¹⁾ was used as a catalyst in the reduction. The synthesized product was slightly colored, but the product recrystallized three times from ligroin was white, mp 68°C. *trans*-Cinnamic acid, guaranteed reagent, was purified two times by recrystallization from ethanol. The phosphorescence spectra were measured by an Aminco-Bowman spectrophotofluorometer.

Results and Discussion

Phosphorescence Spectra of Cinnamic Acid.

The phosphorescence spectrum of *trans*-cinnamic acid in an EPA solution is shown in Fig. 1. The 0–0 band (20100 cm^{-1}) and the 0–2 band (18600 cm^{-1}) are strong in this phosphorescence spectrum, while 0–1 band is rather weak. The excitation wavelength was 280 $\text{m}\mu$; it corresponds to the K-absorption band of cinnamic acid.

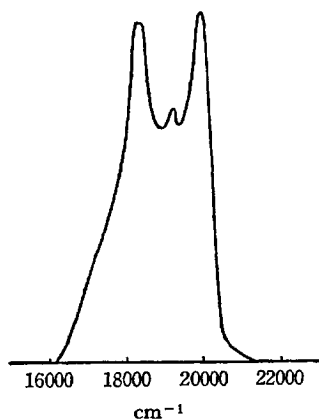


Fig. 1. Phosphorescence spectrum of *trans*-cinnamic acid.

In order to study the solvent effect on the phosphorescence, the authors also measured it in petroleum ether. However, no change in spectra could be found between EPA and petroleum ether. It may, therefore, be concluded that the phosphores-

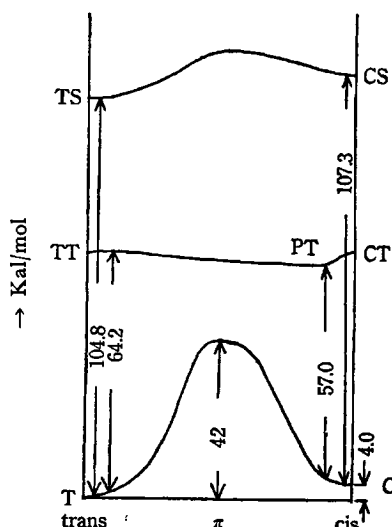


Fig. 2. Possible potential function for rotation in cinnamic acid.

cence of cinnamic acid is not affected by the solvent.

The phosphorescence spectra of *cis*-cinnamic acid in EPA and in petroleum ether were also measured; They were the same as those of *trans*-cinnamic acid. This fact suggests that the triplet state of *trans*-cinnamic acid is the same as that of *cis*-cinnamic acid, and that the phantom triplet state proposed by Hammond *et al.*⁴⁾ exists in the triplet state of cinnamic acid. Therefore, the configuration of the potential function for rotation in cinnamic acid may be as is shown in Fig. 2.

The energies necessary for exciting *trans*- and *cis*-cinnamic acid are 104.8 kcal/mol (273 $\text{m}\mu$) and 107.3 kcal/mol (266 $\text{m}\mu$) respectively. The energy difference between the ground state of *trans*-cinnamic acid and that of *cis*-cinnamic acid was estimated to be 4.0 kcal/mol from the difference in hydrogenation energy between the two compounds.¹²⁾

The activation energy for the thermal isomerization of cinnamic acid has not been measured, because the decomposition reaction takes precedence over the isomerization reaction at higher temperatures. However, its esters are stable for heat and they thermally isomerize. The activation energy for the thermal isomerization of methyl cinnamate has been reported to be 41.6 kcal/mol. A similar activation energy, about 41.6 kcal/mol, is necessary to cause the isomerization of styryl compounds.¹³⁾ Consequently, the activation energy of cinnamic acid may not be very different from that of cinnamic acid.

At a photostationary state, the ratio of the *cis* product to the *trans* product is about 3.0.³⁾ The

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12) R. B. Williams, *J. Am. Chem. Soc.*, **64**, 1395 (1942).

13) G. B. Kistiakowsky and W. R. Smith, *ibid.*, **57**, 269 (1935).

irradiated solution contains more of the *cis* isomer than that of the *trans* isomer. Therefore, the phantom triplet state may be located near the *cis* position, as is shown in Fig. 2. It may be seen in this figure that, when cinnamic acid at the phantom triplet is degraded to the ground state, the *cis* isomer may be mainly produced.

In a previous paper,¹⁴⁾ the present authors calculated the electronic structure and energy levels of *trans*-cinnamic acid by the LCAO-SCF-MO method. The calculated energy of the first triplet, 2.79 eV, corresponds to the T-TT energy in Fig. 2. In Fig. 3, all the energy levels are the calculated values.

The fluorescence of cinnamic acid was measured, but no fluorescence could be detected. This may be due to the intersystem-crossing from the singlet state to the triplet state. The intersystem-crossing from the first excited singlet state to the second triplet state is probable, because the second triplet state is located near the first excited singlet state, as is shown in Fig. 3.

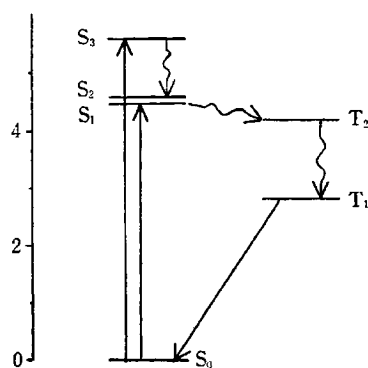


Fig. 3. State diagram for cinnamic acid.

Phosphorescence Spectra of Sensitizers. All the effective sensitizers for polyvinyl cinnamate emit phosphorescence near the 20000 cm^{-1} region, as is shown in Table 1. In this table, the wavelengths for the phosphorescence and absorption peaks and the values of the photosensitivities of the sensitized resins are shown. The triplet state energy of phenol is larger than that of cinnamic acid, but it is not an effective sensitizer for the resin. In photosensitization, phosphorescence is not the only important factor; the absorption of a sensitizer is also essential. For the irradiation of the resin, a mercury lamp is generally used. The photosensitivities shown in Table 1 are those obtained by irradiation with a mercury lamp. The wavelength of the emission peak of a mercury lamp is about 350 $\text{m}\mu$. Therefore, the effective sensitizers must have absorption peaks near this region. In this table the intersystem-crossing efficiency from the singlet state to the triplet state is also shown. The efficiencies of 5-nitroacenaphthene and *p*-nitroaniline have not yet been reported. However, their efficiency may be about 1 because their absorptions are caused by $\pi-\pi^*$ and the efficiency for the $\pi-\pi^*$ compound is generally large. The efficiency of Michler's ketone is about 1, and its photosensitivity is very large. These results can be understood if the excitation energy is transferred from the triplet state of the sensitizer's molecule to that of the resin.

In order to make the triplet energy transfer more clear, the quenching of a sensitizer's phosphorescence was studied. The phosphorescence spectra of 2-nitrofluorene are shown in Fig. 4. The spectrum was measured at 77°K in a 10^{-3} M EPA solution. The uppermost curve in this figure is the spectrum of 2-nitrofluorene alone. The other curves are the spectra of 2-nitrofluorene, which includes 0.01–0.2 M cinnamic acid. It may be seen in this figure

TABLE 1. PHOTOSENSITIVITIES OF SENSITIZED RESINS

Sensitizer	Abs. cm^{-1}	Phos. cm^{-1}	Intersystem ¹⁶⁾ crossing efficiency	Photosensitive ^{1, 17)} value
Naphthalene	36400	22000	0.39	2.6
Phenanthrene	26700	19000		7.7
Chrysene	27800	19800	0.67	18
Phenol	37000	28600		1.8
2-Nitrofluorene	30300	20600		113*
5-Nitroacenaphthene	27000	19800		84*
<i>p</i> -Nitroaniline	27000	19700		110
Michler's ketone	25600	21300	1.01	650

* The method employed for these two values is different from that for other values.

5-Nitroacenaphthene is about 10 times more sensitive than *p*-nitroaniline.

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15) T. Forster, *Discussions Faraday Soc.*, **27**, 1 (1959).

16) M. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York (1965), p. 131.

17) L. M. Minsk, J. S. Smith, W. P. VanDeusen and J. F. Wright, *J. Appl. Pol. Sci.*, **2**, 302 (1959).

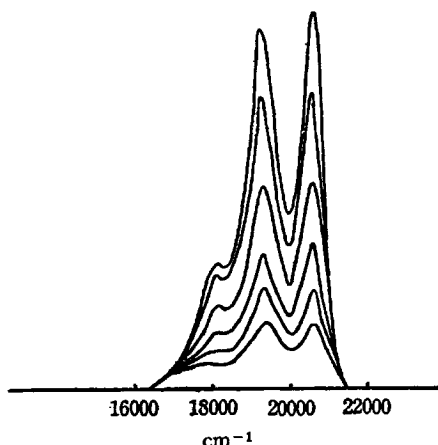


Fig. 4. Phosphorescence spectra of 2-nitrofluorene. the uppermost curve: added 0 M cinnamic acid the second curve: added 0.01 M cinnamic acid the third curve: added 0.05 M cinnamic acid the fourth curve: added 0.1 M cinnamic acid the fifth curve: added 0.15 M cinnamic acid the lowest curve: added 0.2 M cinnamic acid

that the phosphorescence of 2-nitrofluorene is remarkably quenched by the addition of cinnamic acid. The solutions were irradiated by a 350-m μ light. There is no absorption of cinnamic acid in this region, while 2-nitrofluorene has an intensive absorption band there. Therefore, the addition of cinnamic acid does not affect the phosphorescence spectrum. The quenching of the phosphorescence is considered to be due to the energy transfer from the triplet state of 2-nitrofluorene to cinnamic acid.

In Fig. 5, the intensities of the 0-0 bands of the sensitizers' phosphorescence are plotted against the concentrations of cinnamic acid. The quenching curves of other bands of 2-nitrofluorene are uniformly quenched. The concentration of the acceptor molecule, $[A]_{1/2}$, is estimated when the decay of the donor's phosphorescence, in the presence of the acceptor, is equal to one-half of its value in the absence of the acceptor. Thus, it is found from this

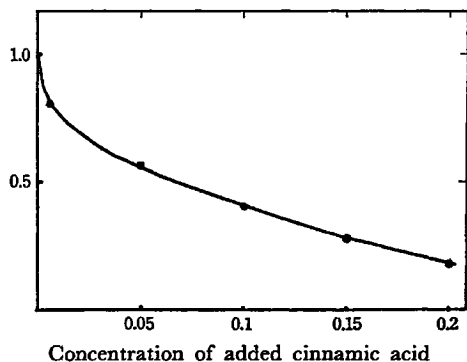


Fig. 5. The decay curve of phosphorescence of 2-nitrofluorene with addition of cinnamic acid.



Fig. 6. Phosphorescence spectra of *p*-nitroaniline. the uppermost curve: added 0 M cinnamic acid the second curve: added 0.01 M cinnamic acid the third curve: added 0.05 M cinnamic acid the fourth curve: added 0.1 M cinnamic acid the fifth curve: added 0.15 M cinnamic acid the lowest curve: added 0.2 M cinnamic acid

figure that the concentration of $[A]_{1/2}$ is 0.063 M.

The phosphorescence spectra of *p*-nitroaniline are shown in Fig. 6. The samples were irradiated with a 350 m μ light. The remarkable quenching of the phosphorescence occurs just as in the case of 2-nitrofluorene. The 0-0 band of *p*-nitroaniline was found to be 19700 cm $^{-1}$. Therefore, the triplet state of *p*-nitroaniline is also an effective sensitizer of polyvinyl cinnamate. However, *o*-nitroaniline is not effective for sensitizing the resin. The intensity of the phosphorescence of *o*-nitroaniline was found

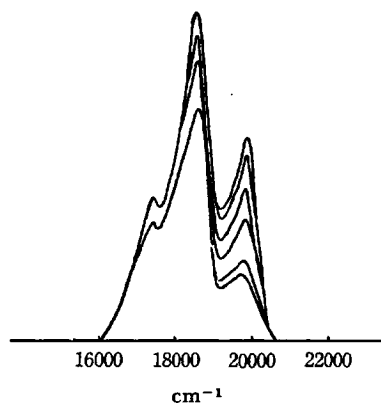


Fig. 7. Phosphorescence spectra of 5-nitroacenaphthene.

the uppermost curve: added 0 M cinnamic acid the second curve: added 0.01 M cinnamic acid the third curve: added 0.05 M cinnamic acid the fourth curve: added 0.1 M cinnamic acid the fifth curve: added 0.15 M cinnamic acid the lowest curve: added 0.2 M cinnamic acid

to be very weak, in comparison with that of the *p*-isomer, although the phosphorescences of the two compounds are quite similar in shape and are equally quenched by the addition of cinnamic acid. In the case of *o*-nitroaniline, the same energy transfer could be found as in the *p* isomer. This suggests that the structural effect on the triplet transfer is small, and that the smaller sensitization effect of *o*-nitroaniline can be correlated with the weak intensity of the phosphorescence in comparison with that of *p*-nitroaniline.

The phosphorescence spectra of 5-nitroacenaphthene are shown in Fig. 7. The exciting light was 350 m μ . The remarkable quenching by cinnamic acid could also be observed. The triplet state of 5-nitroacenaphthene is situated near that of cinnamic acid, and the effect of the sensitization on the resin is very large.

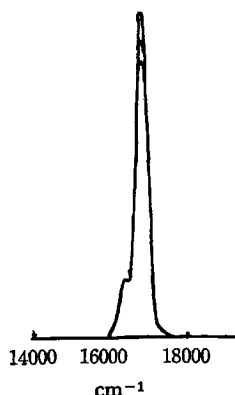


Fig. 8. Phosphorescence spectra of 1,2-benzanthracene.

the uppermost curve: added 0M and 0.01M cinnamic acid

the second curve: added 0.05M and 0.1M cinnamic acid

the lowest curve: added 0.15M and 0.2M cinnamic acid

The phosphorescence spectra of acenaphthene were also measured. It was found that its phosphorescence is greatly quenched by the addition of cinnamic acid. However, this compound is not an effective sensitizer. This lack of effectiveness is at-

tributable to the absorption wavelength. The wavelength of the absorption peak for 5-nitroacenaphthene is about 320 m μ .

As is shown in Fig. 8, the phosphorescence of 1,2-benzanthracene is not quenched by the addition of cinnamic acid. The triplet energy of this compound is 16700 cm $^{-1}$, much smaller than that of cinnamic acid. Therefore, it is impossible for the triplet energy of 1,2-benzanthracene to be transferred to cinnamic acid.

The above quenching measurements make it clear that sensitization is due to the triplet-energy-transfer mechanism. The authors also tried to detect the sensitized phosphorescence of cinnamic acid. However, it could not be detected. The strength of the phosphorescence of cinnamic acid is smaller than that of the sensitizer, and the wavelengths of the two phosphorescence peaks are similar. Therefore, it seems reasonable to say that it is covered by that of the sensitizer.

In the measurement of the quenching of the sensitizer's phosphorescence, the authors could estimate $[A]_{1/2}$. Once $[A]_{1/2}$ is known, the experimental value of R_0 may be calculated by the equation:¹⁵⁾

$$R_0 = \frac{7.35}{\sqrt{[A]_{1/2}}} \quad (\text{\AA})$$

The critical separation estimated from the above equation is shown in Table 2. There is no evidence for a long-range resonance transfer of the kind found in the analogous singlet-energy-transfer process. Therefore, the exchange transfer mechanism may be applied to the triplet energy transfer from the sensitizer molecule to cinnamic acid.

The rate of the production of the triplet state can be written by:

$$\frac{d[T]}{dt} = \phi I_{abs} - (k_1[T] + k_q[Q][T]) \quad (1)$$

where I_{abs} is the number of the absorbed photons, ϕ is the quantum yield which represents the efficiency of the absorbed photon in creating the triplet state, k_1 is the first-order rate constant of the decay of the triplet donor T, k_q is the bimolecular-quenching rate constant, and $[Q]$ is the concentration of the quencher, cinnamic acid.

TABLE 2. CRITICAL SEPARATION OF SENSITIZER

Sensitizer	Phos. energy cm $^{-1}$	$[A]_{1/2}$ M	R_0 \AA	α mol $^{-1}$
5-Nitroacenaphthene	19800	0.12	14.9	9
Acenaphthene	20900	0.019	17.5	52
1,2-Benzanthracene	16700	—	—	1
<i>p</i> -Nitroaniline	19700	0.094	16.2	8
<i>o</i> -Nitroaniline	19700	0.105	15.5	7
2-Nitrofluorene	20600	0.063	18.4	21
Pyrene	19700	0.113	15.2	15

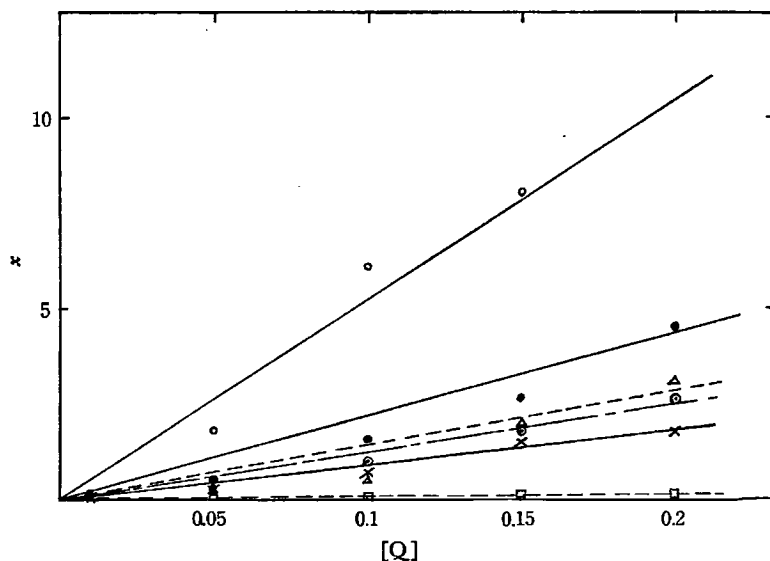


Fig. 9. The quenching effect of sensitizers.

- | | |
|-------------------------|------------------------|
| —○— acenaphthene | —●— 2-nitrofluorene |
| —△— o-nitroaniline | —⊙— p-nitroaniline |
| —×— 5-nitroacenaphthene | —□— 1,2-benzanthracene |

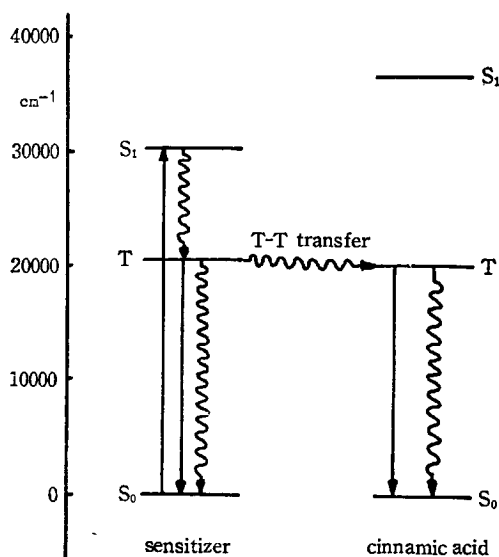


Fig. 10. The electronic levels of the sensitizer, 2-nitrofluorene, and cinnamic acid in the phenomenon of sensitization.

At the stationary state, the following equation can be derived :

$$[T]_q = \frac{\phi I_{abs}}{k_1 + k_q[Q]} \quad (2)$$

The emission strength of the donor phosphorescence is proportional to the triplet concentration $[T]$. Therefore, the ratio of phosphorescences, P_q/P_0 , can be estimated by:

$$\frac{P_q}{P_0} = \frac{1}{1 + \alpha[Q]} \quad (3)$$

where P_0 and P_q are the emission strengths of the phosphorescences of the donor and the quenched donor, and α is k_q/k_1 . From the above equation, the following relation can be derived:

$$x = \alpha[Q] \quad (4)$$

where $x = (P_0/P_q - 1)$.

In Fig. 9, the relations obtained experimentally are shown. The linear relation between them is fairly satisfactory. The inclination of the line shows the value of α . In Table 2 the obtained values of α are presented in the last column.

Finally, the electronic levels of the energy donor and acceptor in the phenomenon of sensitization can be expressed as is shown in Fig. 10. The energy difference in the donor between the lowest singlet and the triplet is much smaller than that in the acceptor, and the phosphorescence of the donor is quenched by the addition of an acceptor.

On the basis of the above results, it can be concluded that the photosensitization of polyvinyl cinnamate is caused by the triplet-state mechanism.