Iodine-photocatalyzed cis-trans Isomerization of Stilbene

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The light absorption of a solution of *cis*- or *trans*-stilbene in an inert solvent such as *n*-hexane and carbon tetrachloride covers a range of wavelength shorter than about 350 mμ[1]. Stilbene in such a solvent undergoes isomerization when irradiated by the light of wavelength shorter than 350 mμ whereas the light of longer wavelength is ineffective. In the presence of iodine, however, it may be possible that the light of longer wavelength becomes effective. Iodine which is known to catalyze the cis-trans isomerization of a number of organic compounds[2] has an absorption maximum at about 520 mμ in the above solvents; in addition, *cis*- or *trans*-stilbene and iodine form a 1:1 molecular complex whose absorption maximum is situated in the neighborhood of 400 mμ in these solvents[3].

In this paper a spectrophotometric study is reported about the kinetics of isomerization of stilbene in *n*-hexane solution with added iodine under the irradiation of light. The range of light wavelength was adjusted by filters in order to investigate the effect of light absorption by iodine and the iodine-stilbene complex.

Experimental

Procedure.—In Fig. 1 the absorption curves of *cis*- and *trans*-stilbene, their iodine-complexes, and free iodine in *n*-hexane solution are shown. The absorption curves of iodine-complexes appear in the shorter wavelength than that of free iodine absorption, indicating the blue shift of the visible band of iodine caused by complex formation. The Mazda SHL-100UV mercury lamp was used for the light source. Taking the above absorption curves into account, the mercury lines to be used for irradiation were filtered out as follows: the use of the Mazda V-03 filter gave the light beam in the range of wavelength 530∼600 mμ which was absorbed practically solely by iodine; by use of the combination of Walz UV and Mazda V-P1.5 filter, the reaction system was irradiated by the light in the range 360∼430 mμ which was absorbed almost solely by the iodine-*cis*-stilbene complex. For the trans→cis isomerization of stilbene the combination of Mazda UV-D2 and an aqueous solution of copper nitrate was used as a filter. This allowed the light in the range of 310∼400 mμ to enter the reaction vessel. The absorbing species in this case are *trans*-stilbene and its iodine-complex. Although there was a little overlap of absorption of the exciting light by the iodine-*cis*-stilbene and iodine-*trans*-stilbene complex on account of some imperfections in the monochromatism of exciting light, the contribution of the reverse process was negligible since the measurements of isomerization rate were confined to the initial low conversion stage. Because of the low concentration of the absorbing species, the rate of absorption of light by the reaction system was taken as proportional to the incident light intensity and to the concentration of the light absorbing entity as in the previous work[4]. Quantum yields were also obtained by the same procedure as that given in the work[4].

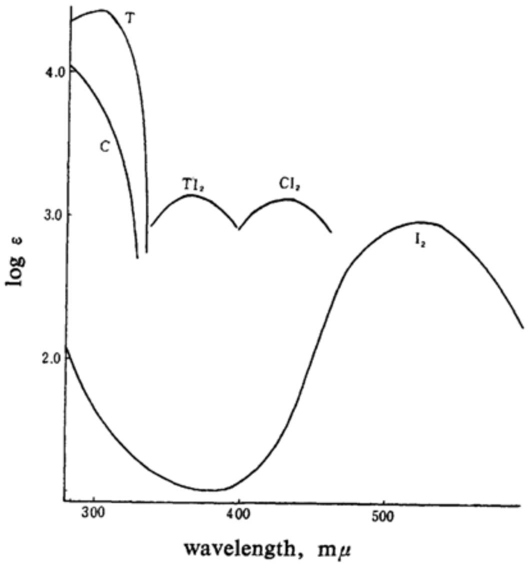

Fig. 1. Molar extinction coefficients. C and T are *cis*- and *trans*-stilbene; CI_2 and TI_2 are respective molecular complexes with iodine.

Results and Discussion

Conversion of *cis*-Stilbene in the Range of Wavelength 530∼600 mμ.—As shown in Figs. 2

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1) G. N. Lewis, T. T. Magel and D. Lipkin, *J. Am. Chem. Soc.*, **62**, 2973 (1940).

2) a) G. M. Wyman, *Chem. Revs.*, **55**, 625 (1955). b) B. Tamamushi, This Bulletin, **19**, 147 (1944). c) R. E. Wood and R. G. Dickinson, *J. Am. Chem. Soc.*, **61**, 3259 (1939). d) R. G. Dickinson et al., ibid., **71**, 1239 (1949). e) Y. Urushibara and O. Simamura, This Bulletin, **12**, 507 (1937).

3) S. Yamashita, ibid., **32**, 1212 (1959).

4) S. Yamashita, ibid., **34**, 487, 490 (1961).

and 3, the rate of isomerization is proportional to the square root of light intensity, to the *cis*-stilbene concentration and to the square root of iodine concentration. Accordingly, when I_o represents the intensity of the incident light, (C) the initial concentration of *cis*- stilbene, and (I_2) the initial concentration of iodine, the rate of conversion is given by

$$-d(C)/dt=kI_o^{1/2}(C)(I_2)^{1/2} \qquad \text{(a)}$$

Fig. 4 shows the Arrhenius plot of the values of k obtained at 10, 15, 20, 25 and 30°C which yields the activation energy of 7.6±0.1 kcal./mol. The quantum yield referred to free iodine as the absorbing entity was found to be about 0.08 at 25°C under the condition that $(C)=5.0\times10^{-5}$ mol./1., $(I_2)=5.0\times10^{-5}$ mol./1., $I_o=2.2_3\times10^{-8}$ Einstein/sec.

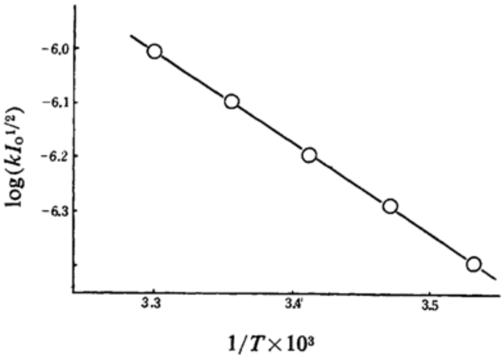

Fig. 4. Temperature dependence of the rate constant. Wavelength, 530~600 mμ; I_o, 6.6×10^{-9} Einstein/sec.

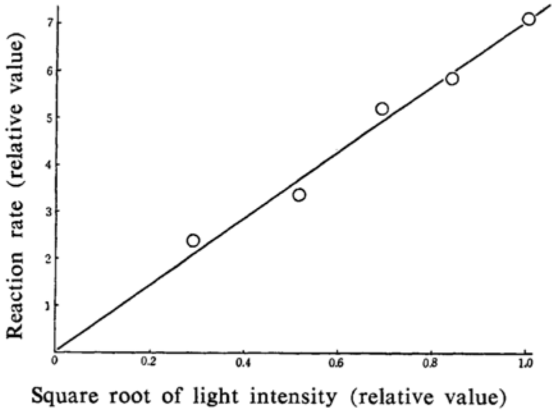

Fig. 2. Dependence of the rate of cis→trans isomerization on light intensity. Wavelength, 530~600 mμ; temperature, 25°C; (C), 5.0×10^{-5} (mol./1.); (I_2), 5.0×10^{-5} (mol./1.).

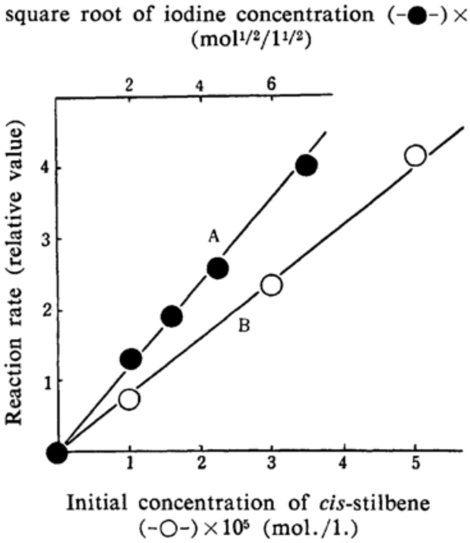

Fig 3. Dependence of the rate of cis→trans isomerization on the concentration of *cis*-stilbene and iodine.
Wavelength, 530~600 mμ; temperature, 25°C
Curve A is for $(C)=5.0\times10^{-5}$(mol./1.)
Curve B is for $(I_2)=5.0\times10^{-5}$(mol./1.)

The rate expression (a) is identical with that obtained for the iodine-catalyzed thermal cis→trans conversion of stilbene in the previous work⁴⁾ except for the light intensity term. It seems therefore most probable that the iodine atoms produced by photodissociation of iodine molecules catalyze the conversion reaction with the same mechanism as in the case of thermal reaction, since in the wavelength range concerned here iodine is the only light-absorbing entity. The reaction is thus represented by the following scheme:

$$I_2+h\nu \rightarrow I+I \qquad (1)$$
$$C+I \rightarrow CI \qquad (2)$$
$$CI \rightarrow C+I \qquad (3)$$
$$CI \rightarrow TI \qquad (4)$$
$$TI \rightarrow T+I \qquad (5)$$
$$I+I \rightarrow I_2 \qquad (6)$$

Here, C and T represent *cis*- and *trans*-stilbene respectively. Provided that the concentration of transient complexes CI and TI are sufficiently small, this scheme leads to the following expression for the reaction rate in the steady state:

$$-d(C)/dt=\{\alpha_i^{1/2}k_2k_4/(k_3+k_4)k_6^{1/2}\} \times I_o^{1/2}(C)(I_2)^{1/2} \qquad \text{(b)}$$

where α_i is equal to $\phi_i a_i l$; ϕ_i, a_i and l denoting the quantum yield of the photodissociation of iodine, its molar absorption coefficient and the light path length, respectively.

Eq. b is consistent with the experimental rate expression (a) and hence

$$k=\alpha_i^{1/2}k_2k_4/(k_3+k_4)k_6^{1/2}$$

or

$$k \cdot k_6^{1/2}/\alpha_i^{1/2} = k_2k_4/(k_3+k_4) \qquad \text{(c)}$$

It has previously been found that the term $k_2k_4/(k_3+k_4)$ has a temperature dependence corresponding to an activation energy of 7 kcal./mol. in the iodine-catalyzed thermal cis→trans isomerization of stilbene in *n*-hexane[4]. Since the temperature dependence of α_i and k_6 are reasonably supposed to be small, the fact[5] that the rate constant k in Eq. c has an almost identical activation energy of 7.6 kcal./mol. may be taken as evidence in favor of the reaction scheme given above. The relatively low value of the quantum yield obtained here may be ascribed to the recombination of iodine atoms in reaction 6 and to the small quantum yield of iodine photodissociation ϕ_i[6]. According to the results reported by Meadows and Noyes[7], the values of ϕ_i observed under irradiation of 546 and 577∼579 mμ mercury lines are respectively 0.46 and 0.36 in *n*-hexane solution at 25°C.

It has been suggested by the present author that the photoisomerization of *cis*-stilbene may involve a triplet state[4]. It is generally accepted from the studies of phosphorescence phenomena that the internal conversion between the singlet and triplet state is facilitated in the presence of heavy atoms such as lead or iodine[8]. Eyring and Harman[9] explained the catalytic activity of paramagnetic substances observed in cis-trans isomerization reactions by such an internal conversion mechanism. Hence, as described in the previous study of the iodine-catalyzed thermal cis-trans conversion of *cis*-stilbene[4], it is likely that a triplet state plays a role in the process 4 although the present work provides no definite evidence for such an interpretation[10].

Conversion of *cis*-Stilbene in the Range of Wavelength 360∼430 mμ.—Effect of concentrations and light intensity on the conversion velocity are shown in Figs. 5 and 6. The rate of reaction is therefore represented by an equation of the same form as Eq. a.

$$-d(C)/dt = k' I_0^{1/2}(C)(I_2)^{1/2} \qquad \text{(d)}$$

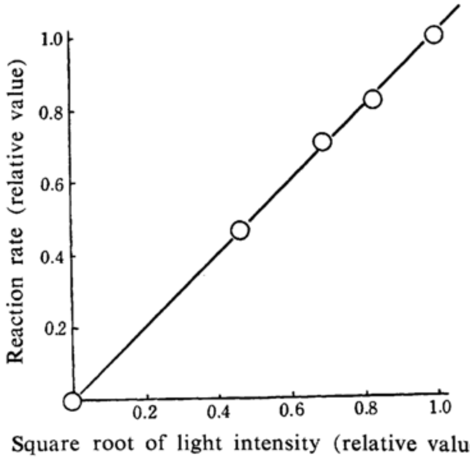

Fig. 5. Dependence of the rate of cis→trans isomerization on light intensity. Wavelength, 360∼430 mμ; temperature, 25°C; (C), 5.0×10^{-5}(mol./l.); (I_2), 5.0×10^{-5}(mol./l.)

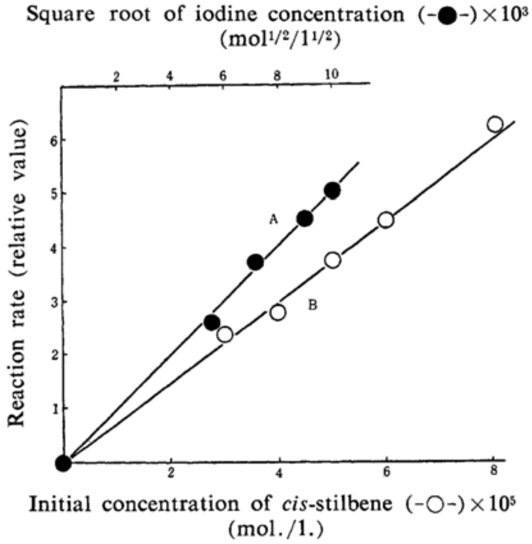

Fig. 6. Dependence of the rate of cis→trans isomerization on the concentration of *cis*-stilbene and indine.
Wavelength, 360∼430 mμ; temperature, 25°C
Curve A is for (C) = 5.0×10^{-5} (mol./l.)
Curve B is for (I_2) = 5.0×10^{-5} (mol./l.)

The reaction mechanism, however, can not be supposed to be identical with that given above for the reaction under irradiation of light 530∼600 mμ: the quantum yield of conversion obtained by assuming the absorbing species again to be free iodine proves to be almost

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[5] This fact implies that the activation energy for the iodine-catalyzed isomerization of *cis*-stilbene under irradiation of light in this range of wavelength is lower than that for the iodine-catalyzed thermal isomerization by half the dissociation energy of molecular iodine as it should be (see Ref. 4).

[6] a) R. L. Strong and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 2098 (1957). b) E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **31**, 547 (1935).

[7] a) L. F. Meadows and R. M. Noyes, *J. Am. Chem. Soc.*, **82**, 1872 (1960). b) R. M. Noyes, *Z. Elektrochem.*, **64**, 153 (1960).

[8] a) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949). b) E. Clement and M. Kasha, ibid., **26**, 956 (1957).

[9] R. A. Harman and H. Eyring, ibid., **10**, 557 (1942).

[10] In the course of the present work phosphorescence was studied with a phosphoroscope similar to that described by Kasha[8]. The results obtained with *cis*-stilbene in isopentane - methylcyclohexane rigid solvent at liquid nitrogen temperature showed that the lifetime of the phosphorescent state was remarkably shortened by the presence of iodine.

100 times[11] as great as that found in the range 530～600 mμ, and such a large variation can not be explained merely by the difference between the quantum yields of iodine dissociation in the two ranges of wavelength. The only absorbing species, which explains reasonably the conversion in the range 360～430 mμ, is therefore the iodine-complex of *cis*-stilbene[12]. The quantum yield of conversion referred to this complex was found to be about 1.2 at 25°C under the condition that $(\mathrm{C})=5.0\times10^{-5}$ mol./l., $(\mathrm{I_2})=5.0\times10^{-5}$ mol./l., $I_o=1.99\times10^{-9}$ Einstein/sec. In Fig. 7 the Arrhenius plot of the values of the rate constant k' obtained at 15, 20, 25 and 30°C, is shown which yields an activation energy of 4.1±0.2 kcal./mol. Such a lower activation energy, compared to 7.6 kcal./mol. as found for the conversion in the range 530～600 mμ, also seems to indicate that the mechanism of conversion is not the same in the two ranges of wavelength.

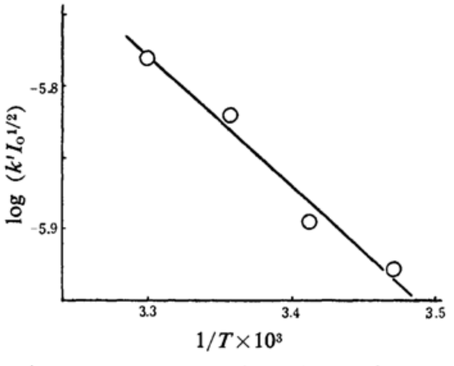

Fig. 7. Temperature dependence of the rate constant. Wavelength, 360～430 mμ; I_o, 1.9×10^{-9} Einstein/sec.

The primary process is therefore assumed to be

$$\mathrm{CI_2}+h\nu \rightarrow \mathrm{CI_2^*} \qquad (1')$$

followed by

$$\mathrm{CI_2^*}+\mathrm{C} \rightarrow \mathrm{CI}+\mathrm{CI} \qquad (1'')$$

Subsequent steps may again be represented by the above-mentioned reactions 2—6. As for the elimination of unstable species, however, Eqs. 7 and 8 will have to be taken into account in addition to Eq. 6 because of the higher concentration of CI compared to the conversion in the range 530～600 mμ.

$$\mathrm{CI}+\mathrm{I} \rightarrow \mathrm{CI_2} \text{ or } \mathrm{C}+\mathrm{I_2} \qquad (7)$$

$$\mathrm{CI}+\mathrm{CI} \rightarrow \mathrm{C}+\mathrm{CI_2} \text{ or } 2\mathrm{C}+\mathrm{I_2} \qquad (8)$$

Rand and Strong[13] have recently found that a transient complex $\mathrm{C_6H_6\cdot I}$, supposed to be a charge-transfer complex, is formed by flashing the benzene solution of iodine, and that it disappears with second order kinetics just as represented by reaction 8. It is well-known that a 1 : 1 molecular complex $\mathrm{C_6H_6\cdot I_2}$ is formed between iodine and benzene as in the case of the iodine-stilbene system. Hence, on flashing the benzene solution of iodine, the transient complex $\mathrm{C_6H_6\cdot I}$ would have been formed by processes similar to 1′ and 1′′ as well as to 1 and 2.

If $k_7=2(k_6k_8)^{1/2}$, as is frequently assumed for radical elimination[14], the following rate expression is derived from reaction 1′, 1′′ and 2—8 for the steady state

$$-\mathrm{d(C)}/\mathrm{d}t=\kappa I_o^{1/2}(\mathrm{C})(\mathrm{I_2})^{1/2} \qquad (e)$$

where

$$\begin{aligned}\kappa= &[\alpha_c^{1/2}k_4K^{1/2}\{2(\alpha_c KI_o(\mathrm{I_2}))^{1/2}+k_2k_6^{-1/2}(\mathrm{C})^{1/2}\}]\\ &\div[k_3+k_4+k_8^{1/2}(\mathrm{C})^{1/2}\{2(\alpha_c KI_o(\mathrm{I_2}))^{1/2}\\ &+k_2k_6^{-1/2}(\mathrm{C})^{1/2}\}] \qquad (f)\end{aligned}$$

K is the equilibrium constant of the process $\mathrm{C}+\mathrm{I_2}\rightleftarrows\mathrm{CI_2}$, and α_c is equal to $a_c l$, a_c representing the molar absorption coefficient of $\mathrm{CI_2}$ complex and l the light path length. If under the experimental conditions of the present work, the quantity represented by κ depends only slightly on the variation of I_o, (C) and $(\mathrm{I_2})$, Eq. e explains the experimental rate Eq. d. When all the molecules of the transient complex CI produced in the process 1′′ are converted into isomeric molecules, the quantum yield of reaction would be equal to 2. The result obtained therefore implies that about a half of CI molecules produced primarily isomerize, if the primary process is Eq. 1′ followed by 1′′.

An alternative primary process may be supposed as

$$\mathrm{CI_2}+h\nu \rightarrow \mathrm{CI}+\mathrm{I} \qquad (1''')$$

However, replacing 1′ and 1′′ by reaction 1′′′ produces no substantial alteration in the rate expression e except that a numerical factor of 2 in the numerator and denominator of Eq. f is now eliminated. The quantum yield of 1.2 seems to favor reactions 1′ and 1′′.

Conversion of *trans*-Stilbene.—The conversion of *trans*-stilbene was measured in the presence of iodine under irradiation of mercury lines in the range 310～400 mμ. The rate of

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[11] Such an apparently large quantum yield arises from the very weak absorption of free iodine in this range of wavelength (see Fig. 1).

[12] It has been confirmed that *cis*-stilbene, having negligible absorption in the range of wavelength longer than 350 mμ, is not converted to the trans-form by irradiation of light in the range 360～430 mμ.

[13] S. J. Rand and R. L. Strong, *J. Am. Chem. Soc.*, **82**, 5 (1960).

[14] A factor of 2 is the symmetry number for the collision frequency.

conversion was found to be the same as that obtained in the absence of iodine as shown in Table I. It may therefore be concluded that the trans→cis conversion here observed is solely caused by the direct absorption of light by *trans*-stilbene and that iodine makes no contribution to the conversion process.

TABLE I. EFFECT OF IODINE ADDITION ON THE RATE OF TRANS→CIS PHOTOISOMERIZATION OF STILBENE: INCIDENT LIGHT INTENSITY, 6.6×10^{-9} EINSTEIN/sec.; LIGHT WAVELENGTH, 310～400 mμ; REACTION TEMPERATURE, 25.0±0.1°C.

Run	Initial concn. of *trans*-stilbene mol./l.×10^5	Concn. of iodine mol./l.×10^5	Reaction time, min.	Concn. *cis*-stilbene produced mol./l.×10^5
1	2.0	4.0	60	0.27
2	2.0	2.0	60	0.26
3	2.0	20.0	60	0.27
4	2.0	0.4	60	0.26
5	2.0	0	60	0.27

The thermal equilibrium between cis- and trans-isomer is in general shifted to the trans side, and the thermal isomerization of trans-form can not be observed at low temperatures. Under irradiation of light, however, a photostationary state is brought about. Since in this photostationary state the composition is usually intermediate between 100% cis and 100% trans, conversion occurs on irradiating the trans-form with the light of suitable wavelength. Iodine as a catalyst can not shift the thermal equilibrium between cis- and trans-isomer; even under irradiation, the atomic iodine or TI complex formed from molecular iodine or TI$_2$ complex by light absorption can not shift the equilibrium. Only direct absorption of light by *trans*-stilbene enables it to isomerize. In fact, no conversion was observed in the presence of iodine under irradiation of 546 and 577～579 mμ mercury lines which are strongly absorbed by iodine but not by *trans*-stilbene.

Summary

The rate of isomerization of *cis*- and *trans*-stilbene in *n*-hexane solution has been studied spectrophotometrically over the temperature range 10～30°C in the presence of iodine under irradiation of light. The conversion rate of *cis*-stilbene has been found to be proportional to the square root of light intensity, to the concentration of *cis*-stilbene and to the square root of the iodine concentration in both wavelength ranges 360～430 and 530～600 mμ. The activation energies and quantum yields of conversion are however different in these ranges of wavelength. These results, combined with absorption curves of various components present in solution, show that the primary process in the range 530～600 mμ is $I_2+h\nu\rightarrow2I$ and that in the range 360～430 mμ it is probably $CI_2+h\nu\rightarrow CI_2^*$ followed by $CI_2^*+C\rightarrow2CI$, where CI$_2$ represents a molecular complex formed between iodine and *cis*-stilbene. Secondary reactions, suggested from the kinetics, are $C+I\rightleftarrows CI$ and $CI\rightarrow TI\rightarrow T+I$ with one or more elimination steps for unstable species, T representing *trans*-stilbene. Rate of isomerization of *trans*-stilbene in the presence of iodine under irradiation of light in the range of wavelength 310～400 mμ has been found to be identical with the rate observed in the absence of iodine under the same condition, excepting the absence of iodine. An explanation for this finding has been given.

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