chloride was added. After the mixture had stood at room temperature for twelve hours, it was refluxed for two hours, the benzene was evaporated and the residue was hydrolyzed with 45% potassium hydroxide solution. The dicarboxylic acid (2.55 g.) was heated at 160–180° for one-half hour and the resulting acid (VI) was sublimed under reduced pressure (1.5 mm.) and then recrystallized from benzene–petroleum ether, from which it was obtained as colorless crystals melting at 140–141°; yield, 1.4 g. (44%, based on the chloride).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.6. Found: C, 80.2; H, 6.8.

1-Keto-*as*-hexahydropyrene (VII).—To a solution of 0.5 g. of the aforementioned acid, 4 cc. of ether and 1 drop of pyridine was added 0.5 cc. of thionyl chloride. After the mixture had stood at room temperature for one-half hour, the ether and excess of reagent were removed under reduced pressure, the acid chloride was dissolved in 4 cc. of benzene and the cooled solution was treated with 1 cc. of stannic chloride. After ten minutes, the mixture was hydrolyzed. The cyclic ketone crystallized from alcohol in light-yellow needles; yield, 0.42 g. (90%); m. p. 124–125.5°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.5; H, 6.3. Found: C, 86.4; H, 6.5.

***as*-Hexahydropyrene.**—A mixture of 5 g. of amalgamated zinc, 6 cc. of concentrated hydrochloric acid, 5 cc. of acetic acid, 4 cc. of toluene and 0.23 g. of VII was refluxed for twenty-four hours; during this time 6 cc. of hydrochloric acid and 5 cc. of acetic acid was added. The hydrocarbon obtained from the toluene layer was sublimed at 0.2 mm. and recrystallized twice from alcohol from which it was obtained as colorless leaflets; yield, 0.14 g. (65%); m. p. 104.5–106°. The picrate crystallized from alcohol in orange needles; m. p. 148.5–150°. Cook and Hewett[9] reported a melting point of 147.5–148° for the picrate of the hydrocarbon (m. p. 105–105.5°) which they obtained by reduction of pyrene.

A mixture of 0.1 g. of the hexahydropyrene and 0.02 g. of palladium–charcoal catalyst was heated at 300–320° for forty-five minutes. The pyrene crystallized from alcohol in colorless diamond-shaped leaflets; yield, 0.05 g. (51%); m. p. 147–148.5° alone and when mixed with authentic pyrene. The picrate of the hydrocarbon was identical with that of pyrene.

1-Methylpyrene (VIII).—To an ice-cold solution of the Grignard reagent prepared from 0.75 cc. of methyl iodide in 8 cc. of ether was added 2 cc. of benzene and 1.04 g. of the cyclic ketone. After standing overnight in the cold, the mixture was hydrolyzed. A crystalline methyl carbinol (0.98 g.) was obtained from the solution.

A mixture of 0.21 g. of the carbinol and 0.02 g. of palladium–charcoal catalyst was heated at 300–320° for one hour. The hydrocarbon after sublimation at 0.8 mm. crystallized from alcohol in colorless leaflets; yield, 0.1 g. (52%); m. p. 142–144°. After three recrystallizations, it melted at 147.5–148.5°. A mixture of the hydrocarbon and pyrene melted at 135–137° (depression).

Anal. Calcd. for $C_{17}H_{12}$: C, 94.5; H, 5.5. Found: C, 94.1; H, 5.6.

The **picrate** crystallized from alcohol in red needles; m. p. 226–227°. Mixed with the picrate of pyrene, the melting point was 219–222° (depression).

Anal. Calcd. for $C_{17}H_{12} \cdot C_6H_3N_3O_7$: N, 9.44. Found: N, 9.35.

Summary

The synthesis of the carcinogenic hydrocarbon 3,4-benzphenanthrene and of 1-methylpyrene from 4-keto-1,2,3,4-tetrahydrophenanthrene is described.

ANN ARBOR, MICHIGAN RECEIVED AUGUST 15, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Absorption and Re-emission of Light by *cis*- and *trans*-Stilbenes and the Efficiency of their Photochemical Isomerization

BY GILBERT N. LEWIS, THEODORE T. MAGEL AND DAVID LIPKIN

For a fuller understanding of the absorption of light by complex molecules we should have more knowledge of the properties of their electronically excited states. If a substance under ordinary conditions exists in two stereoisomeric forms it is possible, when light is absorbed, that they both produce the same electronically excited molecule. In other words, in the state of electronic excitation, the two isomers may lose their individual existence and become merely phases of rotation or vibration belonging to a single state. On the other hand, it is conceivable that even when no isomers exist in the normal state, they may be found in a state of electronic excitation. It is, however, the first possibility with which the present paper is concerned.

Olson[1] has made a thorough theoretical study of the electronically excited states of *cis* and *trans* isomers, of the type of the substituted ethylenes; and he and his associates[2] have investigated experimentally several such isomeric pairs. He arrived at two main conclusions. The

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(1) Olson, *Trans. Faraday Soc.*, **27**, 69 (1931).

(2) Olson and Hudson, THIS JOURNAL, **55**, 1410 (1933); Olson and Maroney, *ibid.*, **56**, 1320 (1934).

first, which has been accepted by other authors,[3] was that the potential barrier which hinders rotation about the double bond is greatly reduced in the electronically excited molecule, so that the *cis* and *trans* configurations may become only phases in the (non-uniform) rotation of a single state. The second conclusion, which was reached by a quantum-theoretical treatment of pendulum-like motion, was that the molecule spends the greater part of its time in phases of higher potential and, therefore, when the molecule goes back to the normal state, that isomer will preponderate whose configuration corresponds to these phases of higher potential.

When we examine the available experimental data regarding stilbene (*sym*-diphenylethylene), they do not seem to accord with the first of Olson's conclusions. If we assume that *cis*- and *trans*-stilbene absorb light to give approximately the same excited state, then since *cis*-stilbene has a much higher energy content in the ground state than *trans*-stilbene, the absorption of the *cis* isomer should occur at a much lower frequency. In fact, however, the first absorption band of *cis*-stilbene is found at even higher frequencies than that of *trans*-stilbene. This, of course, might be explained by assuming that the absorption by *cis*-stilbene is associated with much greater vibrational and rotational excitation.

However, we must also consider the work of Hausser, Kuhn and Kuhn[4] on the fluorescence spectrum of *trans*-stilbene. In this spectrum they found prominent bands which they could interpret quantitatively as due to transitions from an electronically excited state with no vibration to the normal electronic state with zero, one, or more units of vibration, these vibrations being attributed primarily to a stretching and compressing of the central double bond. If the electronically excited state is essentially the same for the *cis* and *trans* forms, why are there no fluorescence bands corresponding to transitions to the *cis* form? This question leads to another: Would the same fluorescence as is found for *trans*-stilbene be observed when *cis*-stilbene is illuminated?

In order to answer these questions we decided to investigate the fluorescence of *cis*-stilbene. We have also redetermined the absorption curves of both *cis*- and *trans*-stilbenes, since the work of Smakula and Wassermann[5] gives little detail, and the more refined measurements of Smakula,[6] and of Hausser, Kuhn and Seitz[7] were for *trans*-stilbene alone. The results of these studies will be shown to furnish a remarkable example of the "loose bolt" effect of Lewis and Calvin.[8] Finally, we have studied the quantum yield in the photochemical conversion of *cis*- to *trans*- and *trans*- to *cis*-stilbene. Here we find confirmation of the second of Olson's conclusions.

Fluorescence of *cis*- and *trans*-Stilbenes

The *cis*-stilbene was prepared by ultraviolet irradiation of *trans*-stilbene in benzene, using a quartz flask. After a sufficient period the solution was concentrated, and cooled to precipitate the greater part of the *trans*-stilbene. The remaining solvent was then pumped away and the residue was fractionally distilled in a high vacuum at a temperature of about 80°. The middle fraction of the distillate proved to be very pure *cis*-stilbene. A measurement of the refractive index gave $n^{25}D$ 1.6032. The absence of *trans*-stilbene is best shown in the fluorescence experiments which are about to be described.

In investigating fluorescence we have used as exciting source a special type of mercury arc, from which 90% of the light energy is in the line 2537 Å. The solutions of *cis*- and *trans*-stilbene were 0.010 *M*, in a solvent containing 1 volume of ethyl alcohol and 9 volumes of ether, chosen because it has comparatively little fluorescence of its own. A quartz Dewar tube of 750 cc. capacity was the container. The light from the arc was brought to a parallel beam by a lens of crystal quartz and met the wall of the Dewar at an angle of 30° to the horizontal. In the same vertical plane a Hilger E-3 quartz spectrograph viewed the wall in a horizontal direction. The photographic plates were E. K. III-O spectrographic plates (I-B plates in the single case of the solid *trans*-stilbene). Photometric tracings of the photographs are given in Figs. 1 and 2.

Curve 1, Fig. 1, shows the fluorescence spectrum of *trans*-stilbene in solution at −90°, the interruptions in the photometer tracing being due to the mercury lines of the exciting source. It is very similar to the curves obtained by Hausser, Kuhn and Kuhn.[4] Attempts to go to lower temperatures were abandoned because of the tendency of the stilbene to crystallize, especially since we found that the fluorescence of solid *trans*-stilbene is of a quite different character. The fluorescence in the crystalline state at liquid air temperature (powder pressed between a glass plate and a quartz cover glass) is shown in Curve 2, Fig. 1. The different structure of the fluorescence bands

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[3] Bonhoeffer and Harteck, "Grundlagen der Photochemie," T. Steinkopff, Dresden, 1933; Rollefson and Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, New York, N. Y., 1939.

[4] Hausser, R. Kuhn and E. Kuhn, *Z. physik. Chem.*, **B29**, 417 (1935).

[5] Smakula and Wassermann, *ibid.*, **A155**, 353 (1931).

[6] Smakula, *ibid.*, **B25**, 90 (1934).

[7] Hausser, Kuhn and Seitz, *ibid.*, **B29**, 391 (1935).

[8] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

in the crystalline state is presumably due to transitions from the excited state to a state which involves not only the normal vibrations of the stilbene molecule, but also vibrations associated with the crystal as a whole. A similar phenomenon was observed by Hausser, Kuhn and Kuhn[4] in the case of solid 1,4-diphenylbutadiene.

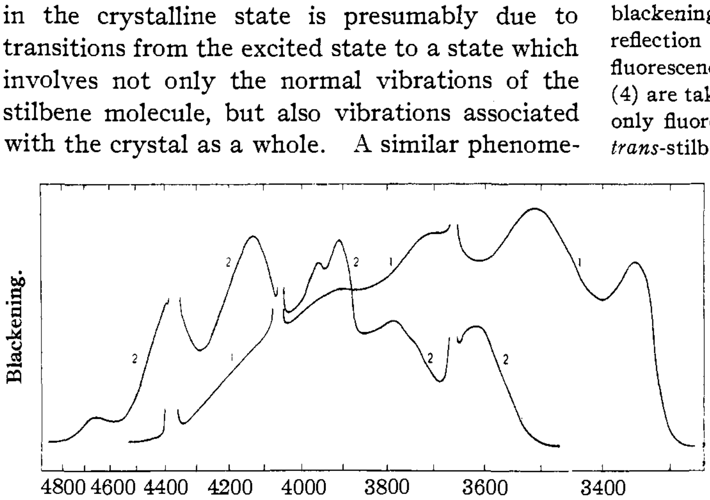

Fig. 1.—Fluorescence spectrum of *trans*-stilbene (1) in ether–alcohol at −90°; (2) crystalline at −180°.

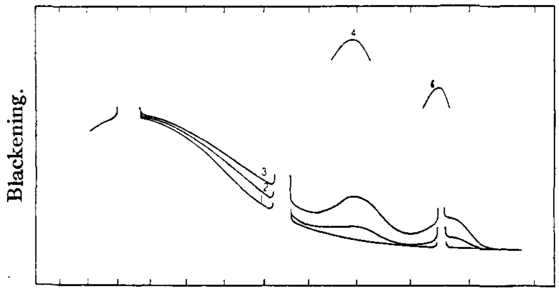

Fig. 2.—The building up of *trans*-stilbene fluorescence in solutions of *cis*-stilbene.

The first experiments on *cis*-stilbene were made at the temperature of liquid air in a solvent containing 2.5 parts by volume of isopentane, 2.5 of ether and 1.0 of absolute alcohol, the dissolved air having been removed. This solvent, which has been of great use to us in other experiments on light absorption at low temperatures, remains clear on cooling and becomes glass-like at the temperature of liquid air. In an exposure lasting one hour, the fluorescence spectrum was entirely similar to that which had been obtained for *trans*-stilbene. It soon became evident, however, that owing to the extreme viscosity of the solvent, which prevented mixing, the surface layer had been sufficiently illuminated to produce a considerable amount of *trans*-stilbene. The next experiments were made in the alcohol–ether solvent at −90°. In Fig. 2, Curves 1, 2, and 3 are reproductions of the photometric tracings of the photographic plates after thirty minutes exposure, (1) of the fresh solution, (2) after preliminary irradiation of one hour, and (3) after preliminary irradiation of three hours. The solution was then replaced by the pure solvent and a curve was obtained identical with Curve 1. In this case blackening of the plate is due to the combined effects of reflection and scattering of the primary source and the fluorescence of quartz and solvent. The two peaks marked (4) are taken from Curve 1, Fig. 1. It is evident that the only fluorescence characteristic of the solution is that of *trans*-stilbene, which is continually produced in small amounts during the irradiation.[8a]

Various other attempts were made to obtain fluorescence from *cis*-stilbene, such as by increasing the slit width, and the conclusion was reached that if *cis*-stilbene has fluorescence, it must be less than 1% of that from *trans*-stilbene under similar conditions.

The Absorption of Light by *cis*- and *trans*-Stilbene.—In studying the absorption of the two stilbenes, carefully purified iso-octane was chosen for the solvent, as having very little absorption of its own in the region being investigated. The measurements were made in a quartz cell 1.2 cm. thick, with parallel walls. The source of light was a hydrogen arc of the type recently described by Allen and Franklin,[9] which gives a very satisfactory continuum. .The plates were E. K. I-O spectroscopic plates. This proved to be a fortunate combination since the blackening, as will be seen in the calibration spectra, was found to be linear and nearly constant with changing wave length. These calibration spectra were obtained with the cell and pure solvent, by the aid of calibrated screens. The exposure time in each experiment was two seconds. The experiments were made at −90°. The temperature was maintained in our quartz Dewar tube by placing the cell over liquid air and regulating the electric current through a resistance coil in the liquid air (more heating produces lower temperature).

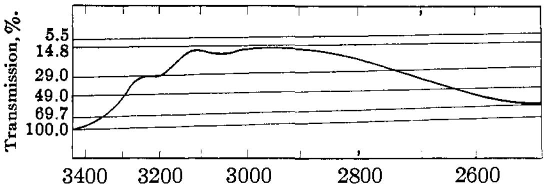

Fig. 3.—Photometric tracing from spectrogram of *trans*-stilbene in iso-octane at −90°.

Figure 3 shows the blackening of the plate as a function of the wave length for 3×10^{-5} M *trans*-stilbene, and for pure solvent with various calibrated screens. Figure 4 is for 6.5×10^{-5} M *cis*-stilbene and the same calibrations. From these figures Fig. 5 was constructed, showing the absolute extinction coefficients (moles per liter,

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[8a] Since this paper was written we have seen a paper by Ley and Specker (*Z. wiss. Phot.*, **38**, 13 (1939)) describing the fluorescence of *cis* and *trans* stilbenes. They found the same fluorescence in both cases. It is evident from our work that their *cis*-stilbene must have contained *trans*-stilbene, either initially or after illumination.

[9] Allen and Franklin, *J. Optical Soc. Am.*, **29**, 453–455 (1939).

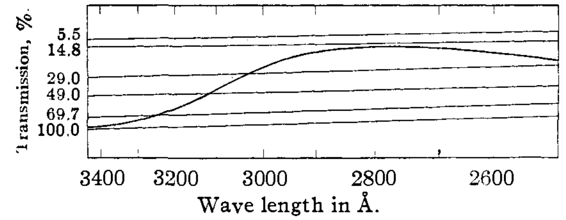

Fig. 4.—Photometric tracing from spectrogram of *cis*-stilbene in iso-octane at −90°.

logarithm to base ten) of the two isomers between 2530 and 3340 Å. The structure which is so noticeable in the spectrum of *trans*-stilbene is absent, or at least unnoticeable, in the spectrum of *cis*-stilbene.

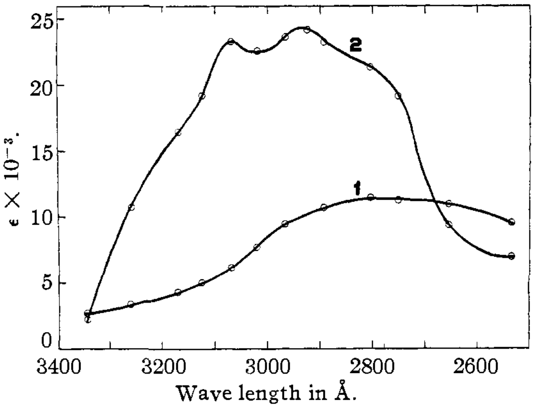

Fig. 5.—Molal extinction coefficients of *cis*-stilbene (1) and *trans*-stilbene (2) in iso-octane at −90°.

Quantum Yields in the Photochemical Conversion of One Isomer into the Other

Smakula[6] has made an extensive investigation of the photochemical efficiency in the isomerization of *trans*-stilbene. He obtained 100% quantum yield at 3130 Å. and decreasing yields at higher frequencies. He also states that *cis*-stilbene "does not go by irradiation into *trans*-stilbene, but into a substance with an absorption maximum at 2470 Å." These results must be erroneous. In the case of *trans*-stilbene, 100% quantum yield would mean that no light could be emitted as fluorescence, yet Smakula himself observes that "*trans*-stilbene fluoresces strongly," and we have seen that in fluorescing the substance returns to the *trans* state. Furthermore, the quantum yield in the isomerization of *cis*-stilbene must be considerable, as we have seen, for example, in Fig. 2. We decided, therefore, to reinvestigate this problem, and we are very thankful to Dr. R. W. Stoughton and Mr. K. Atwood, who helped us to become oriented in the technique of quantum yield determinations.

The measurements were made in the following manner. In order to obtain nearly monochromatic radiation, light from the same mercury lamp that was used before was passed through a chlorine filter (12 mm. layer at 1 atmosphere). It was focussed upon a quartz cell, 1.0 cm. thick, and the number of photons entering the cell per second was determined by placing in the cell an aqueous solution of uranyl oxalate of sufficient concentration to absorb all of the light. After irradiation for a definite time, while the solution was thoroughly stirred, the oxalate was titrated with standard permanganate and the number of entering photons calculated[10] by assuming a quantum yield of 60%. The number of photons per second entering the cell in all of our experiments was 3.95×10^{15}. Without changing anything else, and while the constancy of the light source was repeatedly checked by a photocell, the stilbene solutions were irradiated. The temperature was about 20°.

In the first experiment, 2×10^{-5} *M* *cis*-stilbene in iso-octane was exposed for a certain time, and then the absorption was determined with light of 3130 Å. This process was repeated for each point in Curve 1, Fig. 6, which shows the change in the absorption of light at 3130 Å., with time of exposure to light of 2537 Å. The ordinates show the common logarithm of the ratio of incident light intensity to the intensity after the light has passed through the cell. Since the absorption at 3130 Å. is much higher for *trans* than *cis*, the curve rises rapidly at the start, but instead of approaching the horizontal asymptotically the curve reaches a maximum and then descends. This shows that some new substance, of small absorption at 3130 Å., is being formed. In fact, whenever a solution containing *cis*-stilbene is irradiated, a yellow substance is gradually formed. There is no evidence that *trans* molecules, as

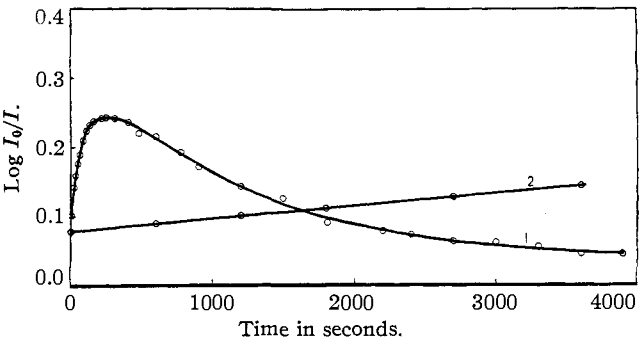

Fig. 6.—Rate of change of the absorption of *cis*-stilbene (at 3130 Å.) with exposure to light of 2537 Å.

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(10) Leighton and Forbes, THIS JOURNAL, 52, 3139 (1930).

such, undergo such a change. From the shape of the curve, we roughly estimate that 10% of the *cis*-stilbene molecules that absorb light at 2537 Å. go over into this yellow substance.

A similar set of experiments was made with *trans*-stilbene and here the curve drops rapidly at first and then continues to fall far below the value for *cis*-stilbene, for the *cis* molecules that are formed are later converted into the new substance.

From the initial slopes of the two curves it is possible to determine the two quantum yields. Since, however, the solutions were so dilute that the cell contents absorbed only a part of the light, it was necessary to make use of the absorption coefficient of the contents of the cell in making the calculation. Moreover, in these experiments the percentage change was so rapid at the beginning of the experiment that the initial slope of the curve is a little uncertain.

For these reasons we next employed solutions so concentrated (0.005 M) that all of the entering light was absorbed, and with the same light source the percentage change in composition was $^1/_{80}$ as rapid. The solutions were irradiated constantly, while thoroughly stirred, and at intervals a small pipet removed a sample of the contents. Each sample was diluted with 125 parts by volume of iso-octane and the absorption of light of 3130 Å. was determined. The results for *cis*-stilbene are given in the straight line (2) of Fig. 6, in which the last point corresponds to about the fourth point of Curve 1. Since the accuracy of the curves of Fig. 5 is limited by the small number of calibration spectra, we have redetermined at 3130 Å. the molal extinction coefficients of the two stilbenes by the same method used for obtaining Fig. 6, namely, a quartz monochromator and photoelectric cell. The value found for *trans*-stilbene was $\epsilon = 16{,}300$ which falls on our previous curve. The value for *cis*-stilbene was $\epsilon = 2280$ which falls below Curve 1, Fig. 5.

Assuming that $\log_{10} I_0/I$ for a mixture of *cis*- and *trans*-stilbenes is linear with the percentage composition, we find from the slope of Curve 2, Fig. 6, and from the measured number of entering photons, that 29% of the excited *cis* molecules are converted into *trans* molecules. Since, however, 10% are converted into something which is neither *cis*- nor *trans*-stilbene, we find that of the molecules which do not suffer this change, 32% go to the *trans* state and 68% return to the *cis* state.

Similar experiments were now made starting with *trans*-stilbene. Owing to some fluctuations in the source of light at 3130 Å., the observed points are not as regular as those shown in Curve 2, Fig. 6, but the quantum yield obtained from this experiment, namely, 35%, is only a little higher than two values (29 and 31%) obtained by the method in which dilute solutions were employed, and may be regarded as approximately correct.

Discussion

In examining the known difference in energy between various pairs of *cis–trans* isomers, we have noticed that this difference is small except when two groups in the *cis* molecule are near enough to exert a large repulsion upon one another. In such cases the *cis* form always possesses far more energy than the *trans*. In the case of the stilbenes this difference has been found calorimetrically to be 10 kcal.[11] For the purpose of illustration we shall use this figure, although chemical evidence indicates that it is too high.[12]

This difference in energy may be explained, as Lewis and Calvin[8] explained the difference in optical properties of the two stilbenes, by assuming that the repulsion of two ortho hydrogens of the phenyl groups forces the molecule out of a plane and thus diminishes resonance. Thus while *trans*-stilbene lies wholly in a plane, the molecule of *cis*-stilbene must be approximately as represented in Fig. 7. Owing to the large amount of double bond character in the ethylene group, and the small amount between the ethylene carbons and the first phenyl carbons, these four carbon atoms must lie almost, but not quite, in a plane. The chief departure from planarity must be obtained by turning the two phenyl groups around their 1,4 axes.

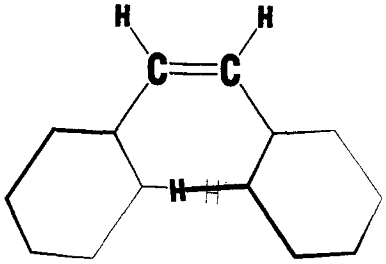

Fig. 7.—The non-planar character of *cis*-stilbene.

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[11] Berner, *Arch. Math. Naturvidenskab*, **39**, No. 6, 5 (1927).

[12] For example, see Kistiakowsky and Smith, THIS JOURNAL, **56**, 638 (1934).

With this picture in mind we may now interpret some of our experiments by means of the "loose bolt" theory of Lewis and Calvin.[8] According to that theory, the energy of electronic oscillation, that characterizes the electronically excited state, will be quickly changed to atomic vibrations and dissipated in the form of heat if (1) there is some radical which is capable of low energy vibrations (because of large mass or small constraints), (2) that radical is a part of the resonating system associated with the electronic oscillation, and (3) the direction of motion of the electronic oscillation has a component in the direction of the possible vibrations of the radical. Such a radical, in dissipating the electronic energy, acts like a loose bolt in a machine.

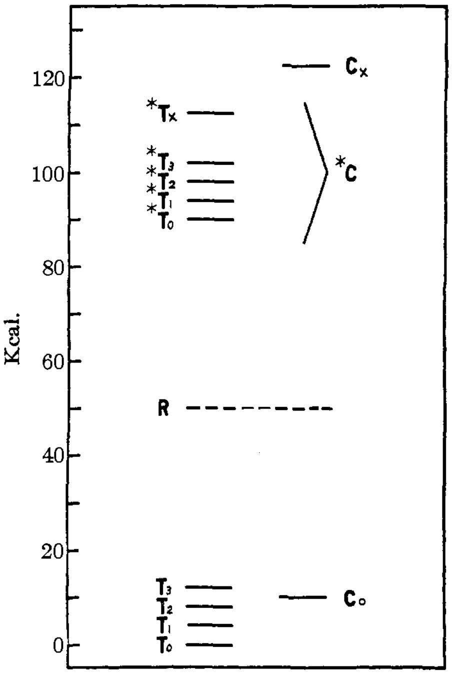

Fig. 8.—Energy diagram of stilbene.

When such a "loose bolt" effect is present, the molecule may exist in the electronically excited state so short a time that it has no opportunity to fluoresce. Also (by the principle of uncertainty) the short life of the electronically excited state so blurs the finer energy levels, corresponding to the chief atomic vibrations of high energy, that the smaller bands of which an electronic band is ordinarily composed become greatly broadened or completely obliterated. It may be remarked parenthetically that the converse of this proposition does not hold; the existence of broad bands or the lack of fluorescence does not necessarily indicate a "loose bolt" effect.

In *trans*-stilbene the phenyl groups are able to vibrate out of the plane, but since the electronic oscillation is entirely in the plane it is unable to stimulate these transverse vibrations. It exhibits, as we have seen, strong fluorescence and structure in the absorption spectrum.

In *cis*-stilbene, on the other hand, we have found no evidence of fluorescence nor of structure. While we cannot state the exact axis of the electronic oscillation, it must have a component in the direction of one of the possible vibrations of the phenyl groups, and is thus able to couple with and lose its energy to such vibrations. It seems probable that this change from the electronically excited molecule to a molecule in the normal electronic state, but with enormous vibrational and rotational excitation, occurs in less than 10^{-14} second. A half-life of this magnitude is associated with a broadening of bands amounting to about 3000 wave numbers. We may refer to a comparison of perylene and dinitroperylene in the paper of Lewis and Calvin.[8] The almost instantaneous destruction of the electronic oscillation in an excited *cis* molecule may be looked at in a different way. The phenyl groups are constrained between the tendency of resonance to make them lie in a plane and their mutual repulsions. At the time of electronic excitation the resonance forces change, and therefore the phenyl groups start toward an altered equilibrium position. This motion will in itself set up the transverse vibrations which we regard as responsible for the early dissipation of the electronic energy.

We shall attempt to interpret what happens to our two isomers, when they absorb light, by the energy diagram of Fig. 8, drawn as nearly as possible to scale. T_0 represents the lowest level of the *trans* molecule in iso-octane. C_0, some 10 kcal. higher, shows the energy level of the *cis* molecule in its lowest state. In order to convert *cis*- to *trans*-stilbene thermally, without a catalyst, an activation energy of about 40,000 cal. is required.[12,13] This, presumably, is about the height of the potential barrier which opposes rotation about the central double bond, and is indicated in the diagram by the level R. Below this level each isomer will have its own set of levels (not shown in the diagram) corresponding to *torsional* vibrations about the ethylene bond.

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(13) Taylor and Murray, *J. Chem. Soc.*, 2078 (1938).

Above the level R these torsional vibrations change to a halting sort of rotation in which the two isomeric configurations are merely phases in the rotation of a single type of molecule.

In the figure, the lines T_0, T_1, ..., show the chief levels of ordinary *trans*-stilbene with respect to *longitudinal* vibrations along the ethylene bond. Corresponding levels of longitudinal vibration in the electronically excited state are represented by $^*T_0$, $^*T_1$, ... At room temperature and below, nearly all the molecules are in a state T_0, and when they absorb light they go to the several levels $^*T_0$, $^*T_1$, ..., thus giving the several peaks shown in Fig. 5, Curve 2.

$^*T_x$ shows the energy after the T_0 molecule has been excited by the line 2537 Å. These electronically excited molecules are still co-planar and, as we shall see presently, about half of them, without departing from the co-planar condition, fall rapidly to the state $^*T_0$ and then drop by fluorescence[4] to the states T_0, T_1 ..., corresponding to the peaks of Fig. 1, Curve 1. Judging by similar cases where measurements have been made, we may assume the half-life in the state $^*T_0$ to be of the order of 10^{-9} second. The rest of the molecules that have gone to the $^*T_x$ state do not fluoresce, but exchange their electronic energy for rotational and vibrational energy.

The behavior of the *cis* molecules is very different. The molecules of state C_0 are carried by light of 2537 Å. to the level C_x, and by light of the wave length corresponding to the maximum of the absorption band to $^*C$, but there are no discrete levels, only a broad continuum of states. The excited molecule almost instantly changes its electronic energy to energy of vibration and rotation, corresponding to enormous excitation of a state of no electronic oscillation.

We assume, as in Olson's theory, that if ordinary *cis* and *trans* molecules are given increasing torsional vibration about the ethylenic double bond, the distinction between the two isomers will persist until this torsional energy approaches the value R, above which true rotation will occur. It seems certain that *cis* molecules, which have been excited to the level C_x, and it seems probable that *trans* molecules which have fallen just below the level $^*T_0$ will, before they have lost too much energy, at some time acquire enough torsional energy to lose their identity as *cis* or *trans* molecules. From this "no-man's land" they eventually fall by loss of energy, a certain fraction to the *cis* state, and the remaining fraction to the *trans* state.

From our measurements on the quantum yield, we have seen that 32% of the *cis* molecules which are carried to the state C_x (and which are not destroyed) return as *trans* molecules, while 68% return to the *cis* state. In other words, the chance that a molecule in the "no-man's land" will fall into the *cis* state is about two out of three. This confirms Olson's conclusion that the configuration of highest potential in the rotating state corresponds to the isomer that is produced in largest amount when the rotational energy is lost.

We found the quantum yield from *trans*- to *cis*-stilbene to be 35%. Accompanying this process, as we have seen in the preceding paragraph, there must have been a little less than half this amount, namely, 17%, which returned to the *trans* state from the "no-man's land." The sum of these two is 52%; thus leaving 48% for the excited *trans* molecules which have never lost their identity. This 48% represents the upper limit of the fluorescence efficiency when pure *trans*-stilbene is illuminated; and it is equal to the fluorescence efficiency if we assume that all of the molecules which do not fluoresce enter the "no-man's land."

In interpreting the facts that are before us, a sharp distinction must be made between two conversion processes. The first is the conversion of one isomer into the other; the second is the sudden conversion of an electronically excited state into a state with no electronic but with very large atomic energy. In the latter process there is an abrupt transition from a state in which the electron cloud is oscillating along a single axis, to one in which this energy is transferred to violent agitation among the various modes of atomic motion. It is to be expected that under the conditions of our experiments such a process will be almost entirely irreversible. This proves experimentally to be the case. Many of the excited *cis* molecules, namely, those which have energy of rotation around the double bond higher than the level R, are constantly passing through phases which are nearly identical in atomic configuration with molecules corresponding to $^*T_0$, $^*T_1$, ... If they ever went over into these electronically excited *trans* states, we should get some characteristic *trans* fluorescence when pure *cis*-stilbene is illuminated.

On the other hand, if an electronically excited *trans* molecule ever gets far out of the planar state, we may conclude that it will rapidly lose for good its electronic vibration.

Since *trans* molecules when excited by light of 2537 Å. have an internal energy of more than 20 kcal. above the state $^*T_0$, and yet nearly half of these molecules fall to the state $^*T_0$ and then fluoresce, we cannot avoid the conclusion that a high potential barrier, against rotation about the double bond, is present in the electronically excited *trans* states. This barrier, however, as far as our experiments show, may be considerably less than it is in the normal state.

Summary

The fluorescence and absorption spectra of *cis* and *trans*-stilbenes have been studied. The quantum yield in the conversion of each isomer into the other by light of 2537 Å. has been determined. These experiments permit a calculation of the upper limit to, and the probable value of, the fluorescence yield of *trans*-stilbene. The results are interpreted in terms of the "loose bolt" theory of Lewis and Calvin, and of Olson's theories regarding the electronically excited states of *cis* and *trans* isomers.

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[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

The Oxidation of Nitrogen in an Ozonizer Discharge at High Temperatures[1]

BY J. F. SHULTZ[1a] AND OLIVER R. WULF[1b]

Introduction

Much work has been done during the last fifty years on the oxidation of nitrogen in various forms of electrical discharges, and a portion of this work has been given to the study of the oxidation in discharges of the form occurring in ozonizers. The general field has been covered recently by Glockler and Lind[2] in their book on the electrochemistry of gases. Since a comprehensive survey of this subject is available, no attempt to cover the field will be made in this paper. The object of the present research was to study the oxidation of nitrogen in the silent electrical discharge under conditions for which the existing data were either insufficient or lacking, namely, at atmospheric pressure and over a range of temperatures extending sufficiently high that, if possible, the naturally limiting thermal decomposition of nitric oxide should be reached. These conditions should favor high reaction rates in the secondary chemical reactions involved, and would tend to prevent any of these being limiting factors in the oxidation. Fischer and Hene[3] had found that the amount of oxidized nitrogen formed in air flowing at a constant rate through a quartz ozonizer became greater at higher temperatures, increasing up to 700°, the highest temperature they give.

It is notoriously difficult to measure electrically the power dissipated in an ozonizer and no attempt to do this was made in the present work. Nor was any direct attempt made to study the primary electrical process occurring in the gas. The results of this work concern the relative rates of the reactions of formation and of decomposition of oxidized nitrogen in the discharge and not the electrical efficiency, though they bear upon the latter. However, certain observations made in the course of this and related work,[4] together with the results of an oscillographic study of the ozonizer discharge described in a recent paper by Klemenc, Hintenberger, and Höfer,[5] have led the authors to some conclusions concerning the physical behavior of an ozonizer which will be included in the discussion of the results.

Experimental

The principal arrangement of apparatus employed is shown in Fig. **1**. Mixtures of nitrogen and oxygen in varied proportions were passed through an ozonizer at known rates of flow, the gases coming from tanks, through flowmeters, and through drying spirals immersed in a mixture of solid carbon dioxide and alcohol. After passing through the ozonizer, the gases were mixed with a small amount of ozonized oxygen from an auxiliary water-cooled ozonizer

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[1] Not subject to copyright

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[2] Glockler and Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, Inc., New York, N. Y., 1939.

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