

A REFLECTANCE STUDY OF THE PHOTOEXCITATION OF STILBENE ADSORBED ON ALUMINA

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Summary

It has been found that the prominent near-UV absorption characteristic of chemisorbed *trans*-stilbene on alumina is entirely removed by irradiation at $31\,950\text{ cm}^{-1}$. The absorption is regenerated in a dark reaction, the reversibility and the time scale of which can be varied over wide limits depending on the activation conditions. It is shown that the process does not involve isomerization. An intermediate is proposed which involves dative sigma bonding to an active aluminum site.

1. Introduction

Stilbene exists in two isomeric forms. The *trans* molecule is planar but it is thought that the phenyl rings of *cis*-stilbene are twisted by about 30° to relieve the steric hindrance between the *ortho* hydrogen atoms [1]. The *trans* form is more stable than the *cis* form by a few kilocalories per mole [2]. Both thermal and photoinduced isomerizations are known to occur.

Thermal isomerization of *cis*-stilbene takes place both in solution and in the vapor phase, the activation energies being $46 \pm 2\text{ kcal mol}^{-1}$ [3] and $42.6 \pm 1.0\text{ kcal mol}^{-1}$ [4] respectively. The isomerization can occur either through the vibrationally excited ground state or the first excited triplet, where the olefinic bond has less double bond character [5]. Isomerization in solution is catalyzed by radicals such as Br [6], Lewis acids like AlCl_3 [7] and Brønsted acids such as H_2SO_4 [8]. All have the effect of removing the double bond character from the olefinic bond.

The photochemical behavior of stilbene adsorbed on solid surfaces, as previously reported [9, 10], is summarized in Fig. 1. Irradiation at $31\,950\text{ cm}^{-1}$ of *trans*-stilbene adsorbed on silica gel in a cyclohexane slurry results in a photostationary state containing 60% *cis*-stilbene, while similar studies on alumina give approximately 20 - 30% *cis*-stilbene and 70 - 80% *trans*-

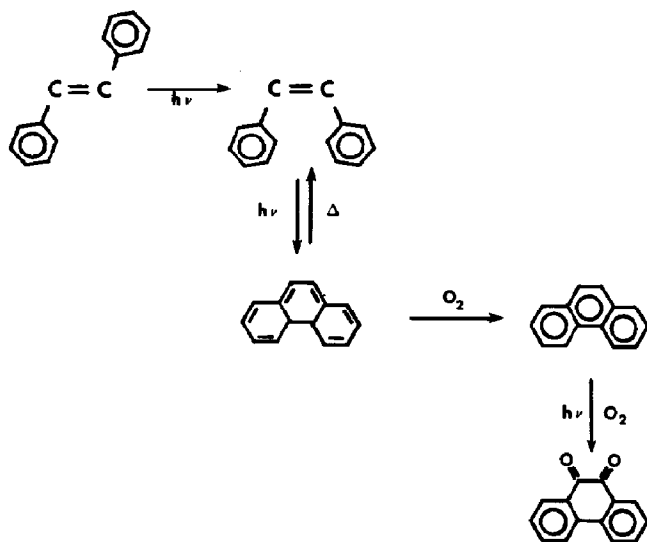


Fig. 1. The photochemical behavior of stilbene on a solid matrix [9, 10].

stilbene. Dihydrophenanthrene (DHP) is formed to a limited extent with radiation below $33\,000\text{ cm}^{-1}$, but is more significant at higher energies. In the presence of oxygen DHP is converted to phenanthrene, even though the thermal decay to *cis*-stilbene is apparently accelerated by alumina or silica gel [11]. Irradiation of phenanthrene above $33\,000\text{ cm}^{-1}$ in the presence of oxygen produces 9,10-phenanthroquinone.

The behavior of adsorbed stilbene described above was inferred by identification following rapid removal of the irradiation products from the surface of the solid matrix. Reflectance studies show the existence of a reactive surface-bound intermediate whose presence was not detected by study of the reaction products alone. The results of some preliminary experiments designed to uncover the nature of the surface-bound intermediate are reported here.

2. Experimental

The initial experiments described in the following section were carried out at the University of Tübingen using a Zeiss PMQ II spectrophotometer equipped with a model RA2 diffuse reflectance attachment. All other experiments were carried out at South Dakota State University with a Beckman DK-2A ratio recording spectrophotometer fitted with a 24500 reflectance attachment. Quartz containers were used, and the pure adsorbent material was used in each case as the reference standard. The Kubelka-Munk function $f(R) \equiv (1 - R)^2/2R$ is used as a measure of the absorbance [12].

Scintillation grade *trans*-stilbene from Matheson, Coleman and Bell was used as received. Qualitative studies were made using 97% pure (boiling

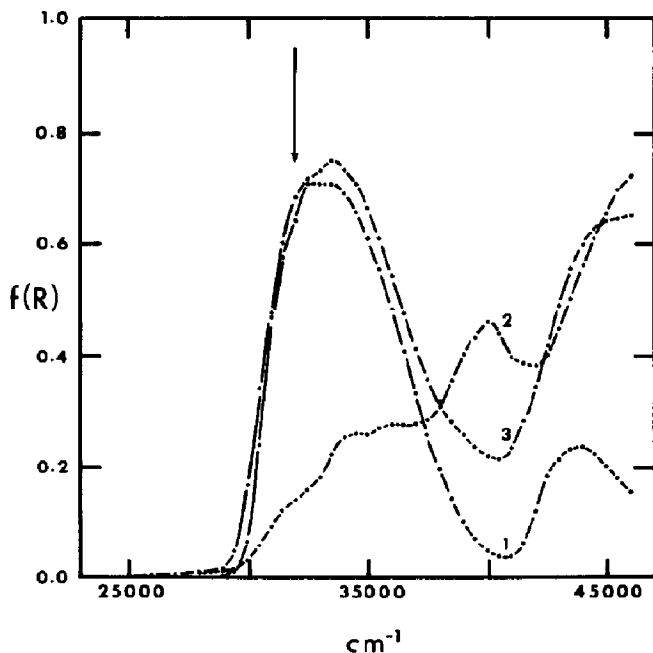


Fig. 2. Reflectance spectra of *trans*-stilbene ground with 120 °C activated neutral alumina: curve 1, before irradiation; curve 2, after 31 950 cm^{-1} irradiation (indicated by the arrow); curve 3, after 22.5 h.

point, 82 - 84 °C/0.4 mm) *cis*-stilbene from Aldrich Chemical Company. Phenanthrene obtained from Eastman Organic Chemicals was recrystallized twice from ethanol (melting point, 97 - 98 °C uncorrected). Neutral, basic and acidic aluminas were all 80 - 200 mesh Brockman Activity I materials obtained from the Fisher Scientific Company.

2.1. *trans*-Stilbene dispersed on neutral alumina by grinding

Neutral alumina (about 3 g) was activated at about 120 °C in a drying oven and rapidly transferred with 0.008 g *trans*-stilbene to a tightly closed agate ball mill vessel. Grinding was continued for approximately 24 h, following which the sample was transferred in the dark to a quartz cuvette and placed in the reflectance attachment. The spectrum labeled curve 1 in Fig. 2 was recorded. The cuvette was then placed in the beam of a filtered quartz radiation source and irradiated at 31 950 cm^{-1} for 1 h with periodic agitation. The spectrum was immediately recorded and is shown as curve 2 of Fig. 2. The material was allowed to stand in the dark for 22.5 h, following which curve 3 of Fig. 2 was recorded. These measurements were all made at room temperature.

It will be noted that the strong peak at about 33 000 cm^{-1} , which is characteristic of the *trans*-stilbene, is greatly reduced by irradiation. The process is apparently reversible with the return being complete in less than 22.5 h at room temperature. Some very crude kinetic measurements at 31 000

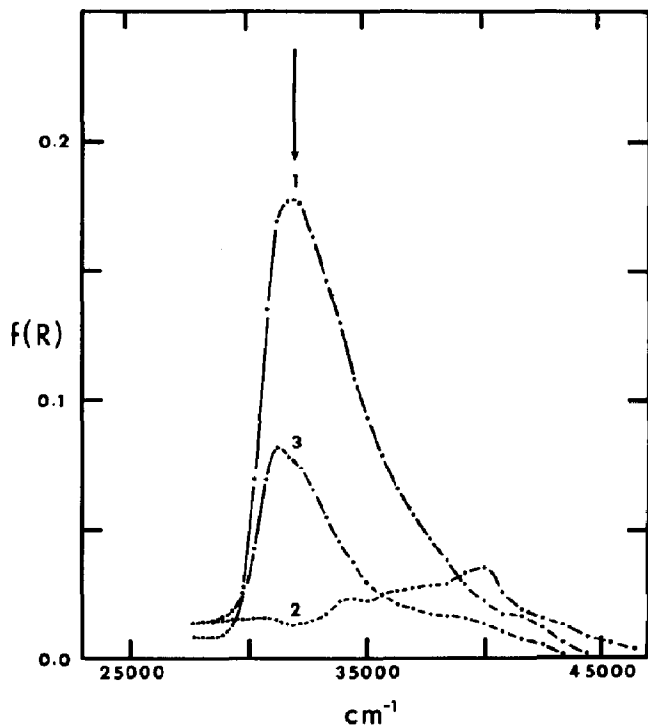


Fig. 3. Reflectance spectra of *trans*-stilbene adsorbed on 150 °C activated neutral alumina: curve 1, before irradiation; curve 2, after 31 950 cm^{-1} irradiation (indicated by the arrow); curve 3, after 22.5 h.

cm^{-1} showed that the room temperature dark reaction can be approximated as a first order process with a rate constant $k \approx 0.002 \text{ min}^{-1}$. This suggests a room temperature half-life of approximately 6 h.

2.2. Stilbene adsorbed on alumina from the vapor phase

The experiment described above did not allow for accurate control and monitoring of the preparation conditions, and it is likely that the sample contained both chemisorbed and physically adsorbed stilbene. Thus, the remaining samples used in the study were all prepared using vacuum line techniques.

A given sample typically contained about 5×10^{-5} mol adsorbate per gram of adsorbent. The adsorbate side arm was evacuated and closed, after which the previously ground adsorbent was activated by heating and pumping. After the alumina had been outgassed for about 8 h the evacuated cuvette was removed from the vacuum line and the adsorbate side arm was opened. The entire assembly was placed in a warming oven at about 95 °C to facilitate adsorbent volatilization. It was then returned to the vacuum line and outgassed at 125 °C until the manifold pressure reached 2.5×10^{-5} Torr (about 15 min). The last step was taken to ensure the removal of the physically adsorbed material.

Curve 1 of Fig. 3 shows a sample of *trans*-stilbene on neutral alumina prepared in this way, and curve 2 shows the same sample following irradiation at $31\,950\text{ cm}^{-1}$. After the dark reaction had proceeded for 22.5 h at $95\text{ }^{\circ}\text{C}$, the sample was cooled to room temperature and curve 3 was recorded.

Kinetic data were obtained by placing the cuvette in a constant temperature oil bath for certain periods of time, after which the sample was cooled and the spectrum was recorded. Such techniques were necessary because the adsorbed stilbene exhibits a temperature-dependent hypsochromic shift.

3. Discussion

A comparison of Figs. 2 and 3 provides considerable evidence that the former sample contained a significant amount of physically adsorbed *trans*-stilbene. The overall absorbance represented by $f(R)$ was about four times as large, and the major peak at about $33\,000\text{ cm}^{-1}$ was much broader. It is also noted that the peak at about $43\,000\text{ cm}^{-1}$ is almost totally absent in Fig. 3; this indicates that this feature is not attributable to chemisorbed *trans*-stilbene. Finally the $31\,700\text{ cm}^{-1}$ peak of chemisorbed *trans*-stilbene is totally removed by irradiation (Fig. 3), whereas there is a residual absorbance in this region in Fig. 2. Thus curve 1 of Fig. 3 is thought to be characteristic of chemisorbed *trans*-stilbene, while curve 1 of Fig. 2 is the resultant of some combination of spectra from both chemisorbed and physically adsorbed molecules.

It will be observed that the product of the dark reaction for chemisorbed *trans*-stilbene (curve 3 of Fig. 3) is typified by an absorption peak which is bathochromically shifted relative to the initial material. This suggests that the dark reaction product is subjected to a stronger adsorbent interaction than the initial adsorbate (see p. 209 of ref. 12).

The dark reaction product is *trans*-stilbene. This was confirmed by observing identical behavior upon re-irradiation of the product. A greater degree of reversibility was noted for the re-irradiated product although there was still some loss, possibly due to a small amount of volatilization of more weakly adsorbed molecules from the surface or to the formation of phenanthrene. The spectrum of phenanthrene adsorbed on neutral alumina shows prominent absorption bands at $34\,100\text{ cm}^{-1}$ and $39\,700\text{ cm}^{-1}$, and these features are observable to a certain degree in curve 3 of Fig. 3.

It was assumed in the initial phases of the present investigation that we might be dealing with a *cis-trans* isomerization. The post-irradiation behavior had not been considered in previous studies of *trans*-stilbene on silica gel [9] and alumina [10], although a study [13] of 4-nitro-4'-hydroxy- α -cyanostilbene adsorbed on nylon 6.6 showed that thermal isomerization occurs in this system by first order kinetics.

If thermal isomerization were involved, the process would probably be accelerated through an increase of the surface acidity or basicity. The ability of aluminosilicates to protonate adsorbed molecules has been demonstrat-

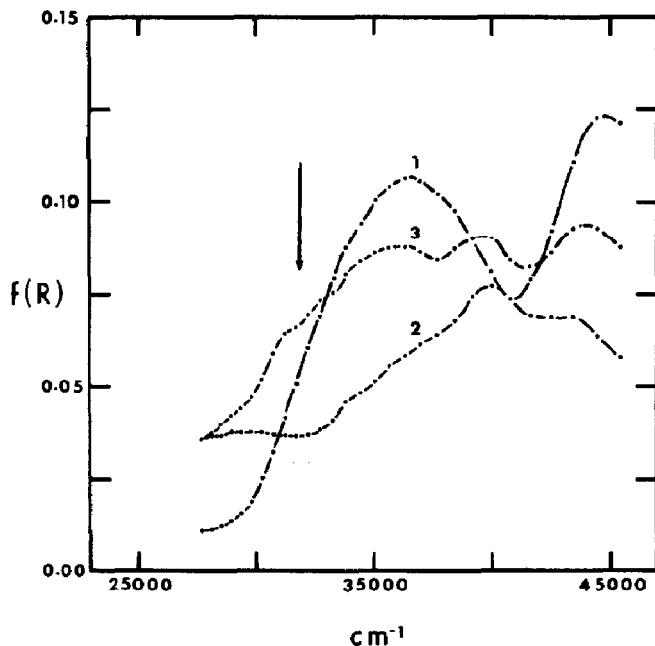


Fig. 4. Reflectance spectra of *cis*-stilbene adsorbed on 150 °C activated neutral alumina; curve 1, before irradiation; curve 2, after 31 950 cm^{-1} irradiation (indicated by the arrow); curve 3, after 48 h at 95 °C.

ed [14, 15], and butene isomerization on a suitably prepared surface apparently proceeds through a classical carbonium ion [14]. Brønsted acidity does not appear to play a major catalytic role on neutral alumina [16, 17], but activated alumina which has been treated with HCl or HF does show Brønsted acidity [18].

In an effort to determine the effect of surface acidity on the dark reaction *trans*-stilbene was adsorbed from the vapor phase onto neutral, basic and acidic aluminas which had been activated at 150 °C as described above. The *trans* peak was monitored with respect to time at 95 °C and interpreted in terms of a first order rate constant. A least squares fitting of the first order plots of $\log \{F(R)_\infty - F(R)_t\}$ versus t_t gave the following rate constants:

$$k_{\text{eff, acidic}} = (1.3 \pm 0.1) \times 10^{-3} \text{ min}^{-1}$$

$$k_{\text{eff, neutral}} = (1.2 \pm 0.1) \times 10^{-3} \text{ min}^{-1}$$

$$k_{\text{eff, basic}} = (1.2 \pm 0.1) \times 10^{-3} \text{ min}^{-1}$$

It may be concluded that, either the alumina has no appreciable surface acidity or basicity following activation, or the dark reaction rate is unaffected by the surface acidity.

There is other more conclusive evidence that the dark reaction is not an isomerization. *cis*-Stilbene was adsorbed onto neutral alumina which had been activated at 150 °C and the spectrum was monitored as a function of

time at 95 °C. No appreciable difference was found over a period of 48 h. A sample of *cis*-stilbene irradiated at $31\,950\text{ cm}^{-1}$ showed a decrease of the *cis* absorption with the appearance of phenanthrene peaks (see Fig. 4). After approximately 48 h at 95 °C the *cis* spectrum reappeared and there was an increase in the phenanthrene absorption along with the formation of a small *trans* peak.

This behavior has two interesting aspects: first, the small amount of *trans*-stilbene formed, and second, the continued formation of phenanthrene after irradiation has ceased. The small amount of *trans*-stilbene formed suggests that the intermediate formed by irradiation does not undergo configurational rotation. The *trans*-stilbene obtained shows a strong adsorbent interaction and was probably present before irradiation but was overshadowed by the large absorption of *cis*-stilbene. The continued formation of phenanthrene has interesting implications, since solution studies have shown that phenanthrene is formed only from the excited *cis* singlet [19]. Only a very weak electron paramagnetic resonance (EPR) signal, probably due to a minor constituent, was found at room temperature in irradiated samples of *trans*-stilbene adsorbed on 150 °C activated neutral alumina.

An attempt was made to study the dark reaction involved in these adsorbed stilbene samples as a function of temperature so that an activation energy could be determined. It was found that the first order plots became very curved at elevated temperatures, indicating that the kinetics are in fact more complicated.

It was found that the rate of the dark reaction was increased by increasing the temperature used to activate the alumina. For example, at 95 °C no detectable change took place after 16 h for *trans*-stilbene on a neutral alumina which had been activated at 400 °C, but it took approximately 30 h to achieve this same stable endpoint for a 150 °C activation. It is assumed that the reaction rate is increased by a more complete removal of the water monolayer, resulting in a more active surface. The vacuum system had a very slow pumping speed, however, and it is likely that hydroxyl formation occurred [20, 21]. This is suggested by the fact that even with the vacuum activation the rate is very slow compared with that observed when *trans*-stilbene was ground with alumina, in which case the stilbene molecules are presumably chemisorbed on freshly cleaved sites which are very active.

4. Summarizing remarks

The various observations defining the nature of the photoinduced intermediate thus far observed can be summarized as follows.

- (1) It does not have a visible or UV absorption except perhaps in the region of the *cis*-stilbene and phenanthrene absorptions.
- (2) It does not have a significant EPR signal.
- (3) It does not appear to depend upon Brønsted acidity.
- (4) It does not appear to undergo configurational rotation.

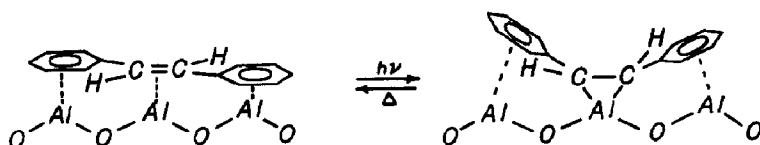


Fig. 5. The proposed intermediate for irradiated *trans*-stilbene adsorbed on alumina.

(5) The decay results in *trans*-stilbene which is subject to a strong adsorbent interaction.

(6) The stability appears to be inversely related to surface activity.

(7) The decay does not follow a first order rate law.

(8) Phenanthrene formation continues to occur after irradiation of *cis*-stilbene has ceased.

These characteristics can be interpreted as ruling out several possible intermediates. The lack of a visible or noticeable UV spectrum along with a negligible EPR signal precludes a non-classical carbonium ion as the intermediate. Such a species should show a significant EPR signal and major absorption bands in the visible and UV regions [22]. A classical carbonium ion is not a satisfactory intermediate because formation of the intermediate does not appear to depend upon the Brønsted acidity of the surface. Finally, the formation of a carbene is not consistent with the continued formation of phenanthrene, owing to the ability of the carbene to withdraw electron density from the phenyl rings.

A definite assignment has not yet been made for the intermediate structure, but the experimental evidence in conjunction with olefinic adsorption characteristics suggests a possibility. An intermediate is proposed in which the photoexcited ethylenic π electrons interact with the vacant p-type aluminum orbitals to form a dative σ bond (see Fig. 5). The formation of this species would appear to be reasonable in that the ethylenic carbons contain the greatest π electron density [23] and would preferentially adsorb over an exposed aluminum ion. It is suggested that the irradiation process makes these π electrons available to the vacant p orbitals on the aluminum ion and bonding results.

A somewhat analogous model system has been dealt with in $X\alpha$ calculations by Roesch and Rhodin [24]. These workers made a comparison of calculated π orbital bonding shifts with photoemission spectra for chemisorbed ethylene on nickel, and showed that the configuration in which both π -bonded carbon atoms are bonded to a single metal atom is favored over that in which each carbon atom is individually bonded to a surface atom. Calculated charge distributions of the various molecular orbitals indicate that the C=C double bond of C_2H_4 is weakened when chemisorbed on nickel, analogous to our suggestion for the adsorbed stilbene on alumina. In the present case, however, we are suggesting a complete loss of double bond character through photoexcitation.

Qualitatively, this species can account for the experimental behavior of the intermediate as follows. The lack of a visible or noticeable UV

spectrum is due to the loss of conjugation across the central bond. This results in a spectrum similar to benzene with only one weak absorption maximum above $44\,000\text{ cm}^{-1}$ ($39\,060\text{ cm}^{-1}$, $\epsilon = 1.99 \times 10^2$ in cyclohexane [25]). The return of the *trans*-stilbene absorption in a thermal dark reaction should coincide with a loss of absorption in this region and this is observed. The lack of configurational rotation and strong adsorbent interaction of the return *trans*-stilbene is consistent with the proposed species.

The decrease in stability of the intermediate as surface activity increases can be accounted for with this species by considering the surface interaction with the phenyl rings. The normal configuration for *trans*-stilbene is planar. The formation of the dative σ bond forces a change in the sp^2 hybridization which lifts the phenyl rings from the surface. With increased surface activity the concentration of exposed aluminum ions increases on the surface and the electrostatic interaction with the electrons of the phenyl ring also increases. The greater the surface activity the more significant is the interaction which tends to restore the phenyl rings to a planar configuration. The result is a weakening of the dative σ bond dependent upon surface activation. This model also satisfactorily explains the deviation from first order kinetics, since it is difficult to obtain a homogeneous surface interaction for all the phenyl rings owing to site variations, residual hydroxyl groups and adsorbed water.

The continued formation of phenanthrene after irradiation of *cis*-stilbene can also be accounted for by the change in hybridization owing to the formation of a dative σ bond. The loss of sp^2 character in the *cis* configuration places the phenyl rings in closer proximity, allowing for bond formation across the rings when the surface bond is broken. It is also possible that the photoexcited ethylenic π electrons bond with the oxygen ions surrounding the aluminum ion rather than with the aluminum ion directly, although we feel that this is less likely. One of the reasons is that the samples prepared using vacuum line techniques in this study probably contained an excess of Al^{3+} sites. The experimentally determined Brunauer-Emmett-Teller surface area was $140\text{ m}^2\text{ g}^{-1}$. Assuming a density of $5 \times 10^{13}\text{ Al}^{3+}\text{ sites cm}^{-2}$ [26] gives $7 \times 10^{19}\text{ sites g}^{-1}$, compared with $3 \times 10^{19}\text{ stilbene molecules g}^{-1}$.

Although the structure proposed for the photoexcited intermediate appears to be quite plausible and consistent with the available data, it is still regarded as tentative. Experimental IR studies and theoretical $X\alpha$ calculations will be used to probe further the nature of the chemisorbed stilbene and will be reported elsewhere.

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