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## The Photochemical Behavior of Adsorbed Stilbene

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THE PHOTOCHEMICAL BEHAVIOR  
OF ADSORBED STILBENE

BY

JEFFREY L. JENSEN

A thesis submitted  
in partial fulfillment of the requirements for the  
degree Master of Science, Major in  
Chemistry, South Dakota  
State University

1977

THE PHOTOCHEMICAL BEHAVIOR  
OF ADSORBED STILBENE

Introduction


Historical

Experimental


Results and

References

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

  
Thesis Adviser

Date

  
Head, Chemistry Department

Date

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## INTRODUCTION

Only limited study has been conducted in the area of photoirradiation of trans-stilbene adsorbed on silica gel or alumina. These previous studies were characterized by the immediate removal of the resultant irradiation products from the solid matrix. Hecht, however, has noted that if an irradiated system was left on alumina and monitored by reflectance spectroscopy the irradiation products did not produce a stable system, but a return of trans-stilbene was noted. The purpose of this work has been to investigate this behavior.

## HISTORICAL

Stilbene

Stilbene occurs as two known geometric isomers, trans-stilbene (M.P. 124-125°C)<sup>1</sup> and cis-stilbene (M.P. 5-6°C)<sup>1</sup>. Trans-stilbene is planar with the phenyl rings lying in the plane of the ethylene double bond, while cis-stilbene is nonplanar due to the twisting of one phenyl ring by approximately 30 degrees<sup>2</sup> to relieve steric hindrance between the ortho hydrogen atoms. Both compounds undergo photoisomerization and cis-stilbene thermally isomerizes to trans-stilbene.

The photochemical behavior of trans and cis-stilbene in solution (Figure 1) depends upon the wavelength of irradiation, concentration, presence of oxygen and temperature. Irradiation of trans-stilbene at concentrations of less than 0.05 M with 313 nm light in an oxygen-free solution at 0°C results in the formation of a photostationary state comprised of 7% dihydrophenanthrene (DHP), 86% cis-stilbene, and 7% trans-stilbene<sup>3,4</sup>. DHP is a thermally unstable product with a solution half life of approximately 2 hours at 30°C<sup>3,5</sup>. The thermal decay of DHP results exclusively in the formation of cis-stilbene<sup>3,6</sup>. This gives a final solution concentration of 93% cis-stilbene and 7% trans-stilbene<sup>7</sup>. If oxygen is present in the solution during irradiation, or admitted afterwards,

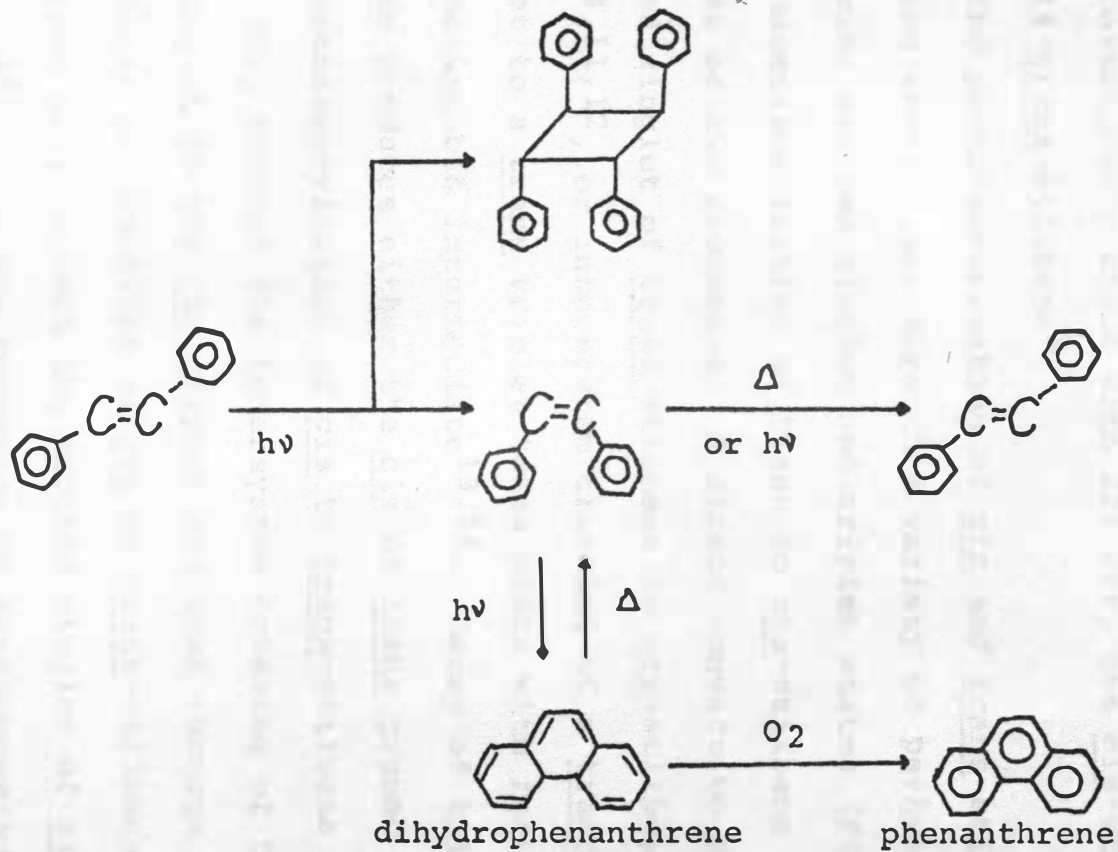


Figure 1. Photochemical behavior of stilbene in solution.

DHP is converted to phenanthrene with 90% efficiency<sup>8</sup>. With starting concentrations of trans-stilbene in excess of 0.05 M, approximately 7% tetraphenylcyclobutane is formed<sup>9,10</sup>. The irradiation of cis-stilbene at 280 nm in an oxygen-free solution at 0°C results in the formation of a photostationary state with 22% DHP, 56% cis-stilbene and 21% trans-stilbene<sup>3</sup>.

The photoisomerization of cis and trans-stilbene in solution takes place through a variety of pathways involving excited singlet and triplet states (Figure 2). The photoisomerization of trans to cis-stilbene appears to consist of two processes. A direct conversion of the excited singlet of trans-stilbene to cis-stilbene can occur<sup>4,11,12</sup>, or intersystem crossing of a trans excited singlet to a trans triplet takes place with further decay to a metastable intermediate<sup>13,14</sup>. Decay of this intermediate produces either the cis or trans ground state<sup>13,14</sup>. The photoisomerization of cis to trans-stilbene appears to occur only through the intersystem crossing of the excited cis singlet to the cis triplet and then through the common metastable intermediate to cis or trans-stilbene<sup>13,14</sup>. DHP is formed only through the excited singlet of cis-stilbene<sup>14</sup>, while the formation of tetraphenylcyclobutane takes place through the excited singlet of trans-stilbene<sup>10,15</sup>.

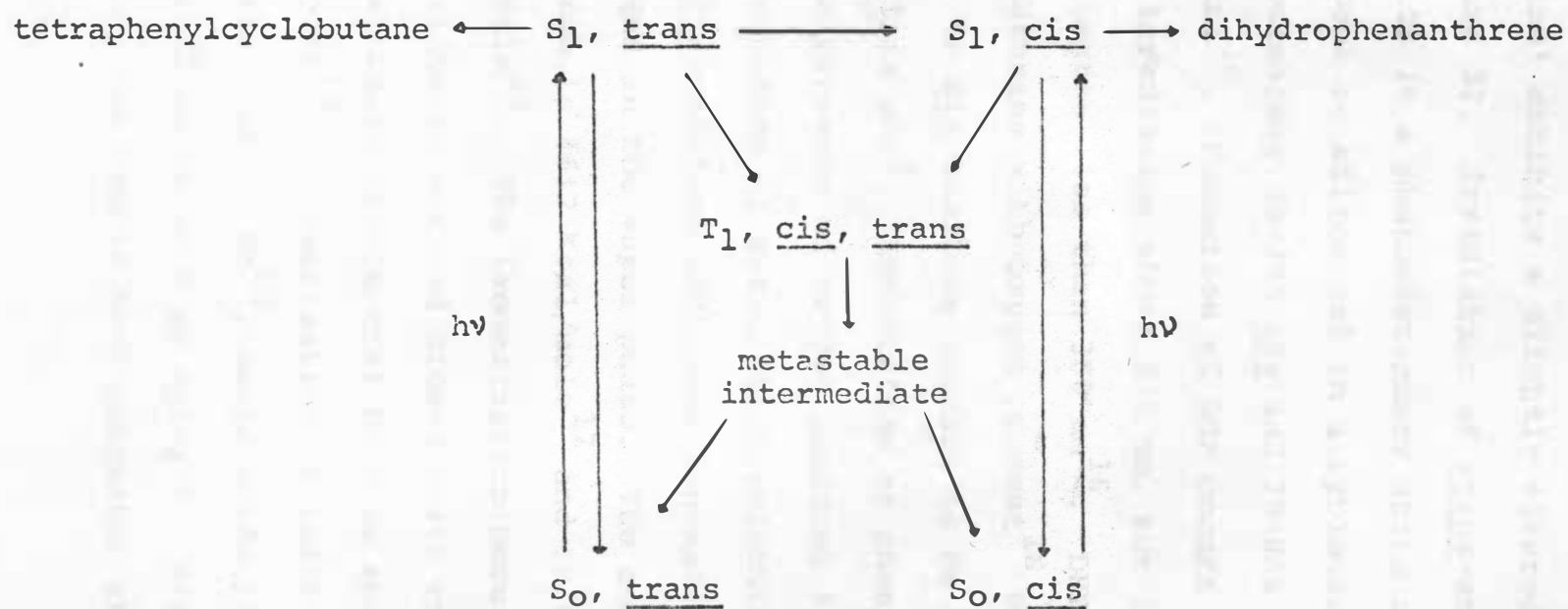


Figure 2. Schematic of excited state behavior of stilbene (energy levels not drawn to scale).

Stilbene adsorbed on a solid matrix (silica gel or alumina) exhibits a slightly altered photochemical behavior (Figure 3). Irradiation of trans-stilbene at 313 nm results in a photostationary state containing 60% cis-stilbene on silica gel in a cyclohexane slurry<sup>7</sup>, or approximately 20-30% cis and 70-80% trans-stilbene on alumina<sup>16</sup>. Formation of DHP occurs to a limited extent with irradiation above 300 nm, but is more significant at wavelengths less than 300 nm<sup>16</sup>. DHP is converted to phenanthrene with oxygen present<sup>16</sup> even though its thermal decay to cis-stilbene appears to be accelerated by alumina or silica gel<sup>3</sup>. Irradiation of phenanthrene below 300 nm in the presence of oxygen produces 9,10 phenanthroquinone<sup>16</sup>. The formation of tetraphenylcyclobutane is not observed<sup>16</sup>.

Cis-stilbene undergoes thermal isomerization in solution and in the vapor phase. The energy of activation in solution is  $46 \pm 2$  kcal/mole<sup>17</sup> and in the vapor phase  $42.6 \pm 1.0$  kcal/mole<sup>18</sup>. The isomerization occurs through either the vibrationally excited ground state or the first excited triplet where the central bond is reduced in double bond character<sup>19</sup>. Isomerization in solution is catalyzed by radicals such as Br<sup>20</sup>, Lewis acids like AlCl<sub>3</sub><sup>21</sup>, and Brønsted acids such as H<sub>2</sub>SO<sub>4</sub><sup>22</sup>. All have the effect of removing the double bond character at the central bond.

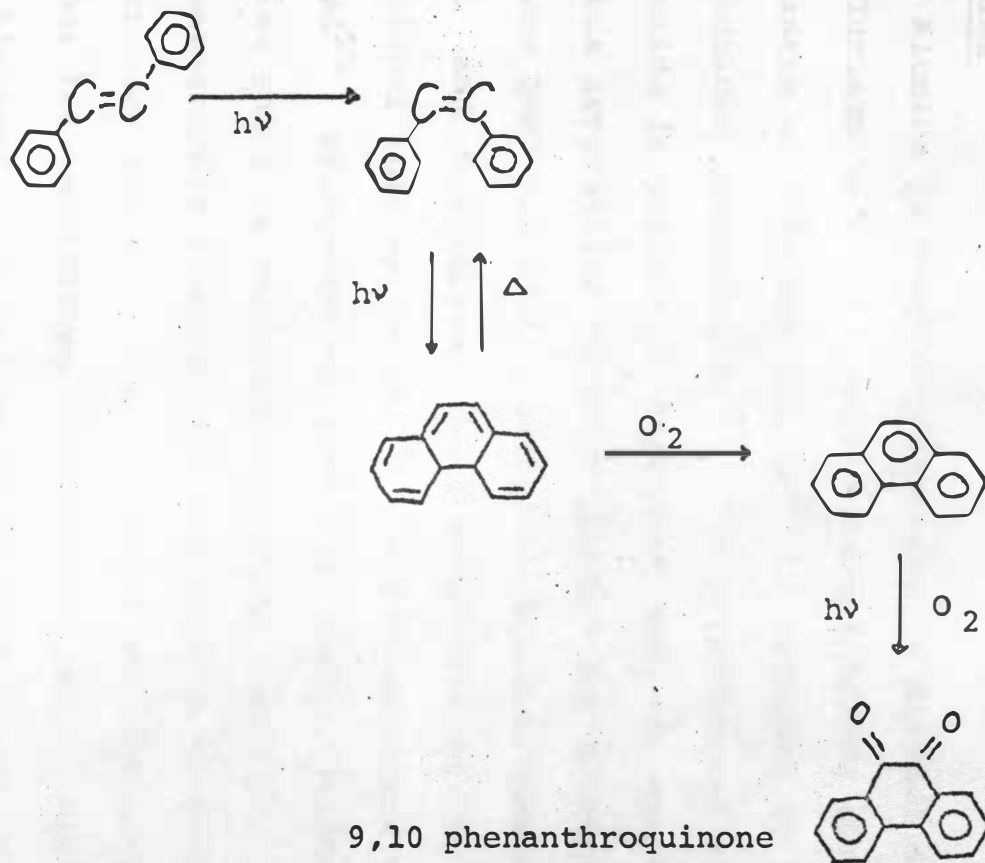


Figure 3. Photochemical behavior of stilbene on a solid matrix.



The energy of activation for  $\text{H}_2\text{SO}_4$ -catalyzed isomerization is  $21.7 \text{ kcal/mole}^{22}$ .

The absorption maximums and molar absorptivities of the molecular species involved in this study are listed in Table 1.

### Alumina

Alumina is generally prepared by partial dehydration of aluminum hydroxide which is precipitated from sodium aluminate with carbon dioxide<sup>23</sup> or obtained by hydrolysis of aluminum isopropoxide<sup>24</sup>. The precipitated aluminum hydroxide is scintered; depending upon the temperature, various crystalline forms of alumina are obtained. Heating between  $200^\circ$  and  $600^\circ\text{C}$  results in the low temperature  $\gamma$ ,  $\lambda$ ,  $\chi$  and  $\rho$  aluminas. At temperatures of 900 to  $1000^\circ\text{C}$  the higher temperature  $\theta$ ,  $\delta$ , and  $\kappa$  aluminas are formed<sup>25</sup>. Scintering at  $1100^\circ\text{C}$  or above results in  $\alpha$  alumina which is chromatographically inactive. Commercial chromatographic aluminas are generally a mixture of the low temperature forms<sup>25</sup>. The structure and properties of the various low temperature aluminas are fairly similar<sup>25,26</sup>.

Aluminas which are prepared from sodium aluminate can be obtained in three different forms characterized by the pH of their aqueous extracts<sup>23</sup>. Basic alumina (pH 9-10) results from the hydrolysis of excess sodium aluminate, while neutral alumina (pH 7.5-8) has the excess sodium



Table 1. Absorption maximums and molar absorptivities for compounds in the study.

	$\lambda$ (nm)	$\epsilon$	Solvent	Ref.
Phenanthrene	252	$6.6 \times 10^4$	cyclohexane	51.
	292	$1.6 \times 10^4$		
	345	$2.1 \times 10^2$		
Tetraphenylcyclobutane	261	$9.5 \times 10^2$	ethanol	46.
Dihydrophenanthrene	297	$2.1 \times 10^4$	methylcyclohexane and isohexane	3.
	310	$2.2 \times 10^4$		
	450	$6.8 \times 10^3$		
9,10 Phenanthroquinone	252	$3.2 \times 10^4$	ethanol	54,55.
	283	$1.0 \times 10^3$		
	427	intense		
<u>Cis-stilbene</u>	283	$1.2 \times 10^4$	ethanol	52.
	222	$2.5 \times 10^4$		
<u>Trans-stilbene</u>	320	$1.6 \times 10^4$	ethanol	52.
	308	$2.5 \times 10^4$		
	295	$2.5 \times 10^4$		
	229	$1.6 \times 10^4$		

aluminate leached out. Acidic alumina (pH 4-5.6) is washed with dilute HCl until the aqueous extract is of the proper pH<sup>23</sup>.

An idealized model of the alumina surface consists of oxide ions ( $O^{2-}$ ) forming a surface layer with aluminum ions ( $Al^{3+}$ ) lying in the next lower plane equidistant from four surface oxide ions. Only three fourths of the aluminum ion positions are filled to maintain charge neutrality<sup>27</sup>. This simple surface is altered by the presence of adsorbed water and five distinct types of hydroxyl groups<sup>28</sup>. The surface concentration of these constituents can be altered by heating. At temperatures less than 300°C, water that has not been adsorbed as a monolayer is removed, while at temperatures greater than this most adsorbed water is lost<sup>25</sup>. With temperatures between 300 and 800°C, hydroxyl formation can also occur depending upon the availability of water<sup>25,29</sup>. Three of the five hydroxyl group types can survive at temperatures up to 800°C<sup>28</sup>. The number of exposed aluminum ions increases with the loss of water and hydroxyl groups from the surface<sup>29</sup>.

The adsorption of olefins on the surface of alumina is thought to occur as the result of electrostatic interaction between the  $\pi$  electrons of the olefin and the positive field of the aluminum ion<sup>27,30</sup>, the positive field being greatest directly over the aluminum ion<sup>27</sup>. The exact

nature of this interaction seems to depend on the specific environment of an exposed aluminum ion<sup>30</sup> and also possibly upon the availability of empty p-type aluminum orbitals on the surface<sup>30,31</sup>. The behavior of butene on  $\gamma$  alumina shows that three distinct types of sites are present on the surface<sup>32</sup>. These sites are associated with strong adsorption, isomerization or D<sub>2</sub> exchange. However, in all cases the sites appear to involve exposed aluminum ions.

### Reflectance Spectroscopy

Reflectance spectroscopy<sup>33</sup> measures the reflected light flux from a sample instead of the light flux which passes through. Measurements are recorded as percent reflectance.

$$\% R = I/I_0 \times 100 \quad (1)$$

I is the intensity of the light reflected, and I<sub>0</sub> is the intensity of the incident beam. The light reflected from the sample is composed of two parts, specular reflectance and diffuse reflectance. Specular reflectance is a mirror type reflection occurring at the surface, while diffuse reflectance occurs as the result of absorption and scattering of the light within the sample. In samples containing weak absorbers, diffuse reflectance is the major component.

The Kubelka-Munk equation, which is an approximation to the equation of radiative transfer, is the most common

means of interpreting diffuse reflectance spectra. The Kubelka-Munk function is a relationship between the concentration of the absorbing species and the diffuse reflectance. The formulation for the Kubelka-Munk function is,

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} \quad (2)$$

where  $R$  is the diffuse reflectance of a sample of infinite thickness,  $k$  is the molar absorption coefficient, and  $s$  is the scattering coefficient of the sample. Usually  $s$  can be assumed constant over a wide wavelength range. The molar absorption coefficient can be replaced by the product  $2.30\epsilon c$  where  $\epsilon$  is the molar absorptivity and  $c$  the molar concentration. Equation (2) then reads

$$F(R) = \frac{2.30 \epsilon c}{s} \quad (3)$$

For the linear dependence between  $F(R)$  and  $c$  to be observed, precautions must be taken to decrease the specular reflectance. The superposition of a large specular component with the diffuse component results in a distortion of the diffuse reflectance. To decrease the specular contribution the particle size of a weakly absorbing sample should be approximately  $1.0\mu$ . The optimum %  $R$  range for concentration accuracy in a system showing no deviation from the Kubelka-Munk equation is between 20 and 80%  $R^{34}$ .

The suitability of reflectance spectroscopy in studying surface phenomena has been demonstrated by Kortuem<sup>35</sup>, who has applied the technique to the determination of surface areas, adsorbent-adsorbate interactions, kinetic studies of surface adsorbed systems and the determination of equilibrium constants for material in the adsorbed state. Successful application of reflectance spectroscopy depends largely upon sample preparation. Key considerations are<sup>36</sup>:

- 1) The ability to obtain small adsorbent particle size through grinding, which gives a small and consistent specular component.
- 2) Prevention of shadows on the surface. Shadows are due to poor packing of the sample, and they can alter the reflectance values from one sample to the next.
- 3) A consistent method of packing the sample, since the reflectance does show a dependence on the degree of packing.
- 4) A sample system which is designed and handled to exclude substances such as water which would displace the adsorbate from the adsorbent.
- 5) A consistent method of introducing the adsorbate to ensure reproducible and homogeneous surface coverages.

If these conditions are observed, reflectance spectroscopy can be used to obtain meaningful data from adsorbed systems.

All reflectance and transmittance measurements were recorded on a Beckman DU-2B ratio recording spectrophotometer fitted with a Beckman DU-2B reflectance attachment. The spectral range was 200-800 mμ. The reflectance attachment was used in the diffuse reflectance mode.

A thin layer of sample was deposited on a glass plate. The plate was held in a holder which was placed in the spectrophotometer. The holder was made of aluminum and was 1.5 cm wide, 1.5 cm high, and 1.5 cm deep. The sample was deposited on the inner surface of the holder.

The holder was completely covered with black paint to eliminate any reflection of light from the holder walls. The holder was placed in the spectrophotometer and the reflectance measurements were taken. The reflectance was measured at 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, and 800 mμ.

The reflectance measurements were taken on a Beckman DU-2B ratio recording spectrophotometer. The spectrophotometer was calibrated with a Beckman DU-2B reflectance attachment. The reflectance was measured at 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, and 800 mμ.

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## EXPERIMENTAL

Ultraviolet and Visible Spectra

All ultraviolet and visible spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer fitted with a Beckman 24500 reflectance attachment. The spectral shift plates were positioned for diffuse reflectance.

Neutral alumina sealed in a container fitted with a quartz optical flat was used as the reference standard. For 100% R adjustment a Beckman BaSO<sub>4</sub> plate was used.

The unit was operated in a completely dark room with the light-emitting electronics shielded. This was necessary because the size of the sample system required the spectra to be recorded with the sample and reference port access door open. When aligning the sample system (Figure 4) at the sample port, the photomultiplier tube was turned off. After placement of the sample system, the photomultiplier tube was reenergized and the spectrum recorded. A Kinderman #22548 safe light with a 15 watt bulb was used to operate the unit after the sample system was in place. The spectra, however, were recorded in complete darkness.

Electron Paramagnetic Resonance Spectra

The electron paramagnetic resonance spectra were recorded on an instrument constructed by Dr. J. R. Tunheim

and David Aaron of the South Dakota State University physics department. The unit consisted of a Varian 0-5 kilogauss field regulated magnet and a microwave bridge operating at 9.48 gigahertz.

#### Irradiation Source

All sample irradiation was done using an Osram 200 watt super pressure mercury lamp (HBO 200W). The power supply was an Oriel model 6240 and the lamp was contained in an Oriel model 6137 housing. The housing was equipped with a 35 mm f/1.0 ultraviolet grade fused silica lens. The source emission was filtered through a 313 nm Barr Associates Inc. interference filter.

#### Adsorbent Grinder

All alumina was ground in a Spex model 8000-11 mixer mill using a tungsten carbide vial and ball.

#### Temperature Control

Temperature control for the sample system was provided by a Poly Science model 73 immersion circulator in an insulated oil bath. Manufacturer specifications list control accuracy as  $\pm 0.01^{\circ}\text{C}$ .

The temperature of the oil bath was monitored by a copper constantan thermocouple used with a Biddle model 72-310 potentiometer. Thermocouple construction was patterned after the design of Adams<sup>37</sup>. The thermocouple



was calibrated at the boiling point of water and temperatures were obtained by interpolation within  $\pm 0.5^{\circ}\text{C}^{38}$ . A crushed ice bath was used for the reference junction.

The sample system was maintained at elevated temperatures by immersing the optical cell portion of the sample system in the oil bath. The sample system was placed in direct contact with the oil and upon removal the quartz optical flat was cleaned using ethanol.

#### Vacuum Line

The vacuum line was constructed of Pyrex with diffusion and fore pump connections being made with Tygon tubing reinforced with coiled nichrome wire. The joints and stopcocks on the vacuum line were greased with Apiezon N. The fore pump was a Welch Duo-Seal model 1400 and the diffusion pump was a CVC VMF-11 with Dow Corning 704 silicone pump fluid. Performance for the system, while cold trapped with liquid nitrogen, was  $5 \times 10^{-6}$  Torr without sample and  $1 \times 10^{-5}$  Torr with sample system. Manifold pressures were monitored by a Kontes/Martin M-403120 cold cathode vacuum gauge system.

#### Sample Cells

Figure 4 illustrates the sample system used for all trials involving reflectance spectroscopy. The cis-stilbene trials were carried out using an adsorbate sidearm

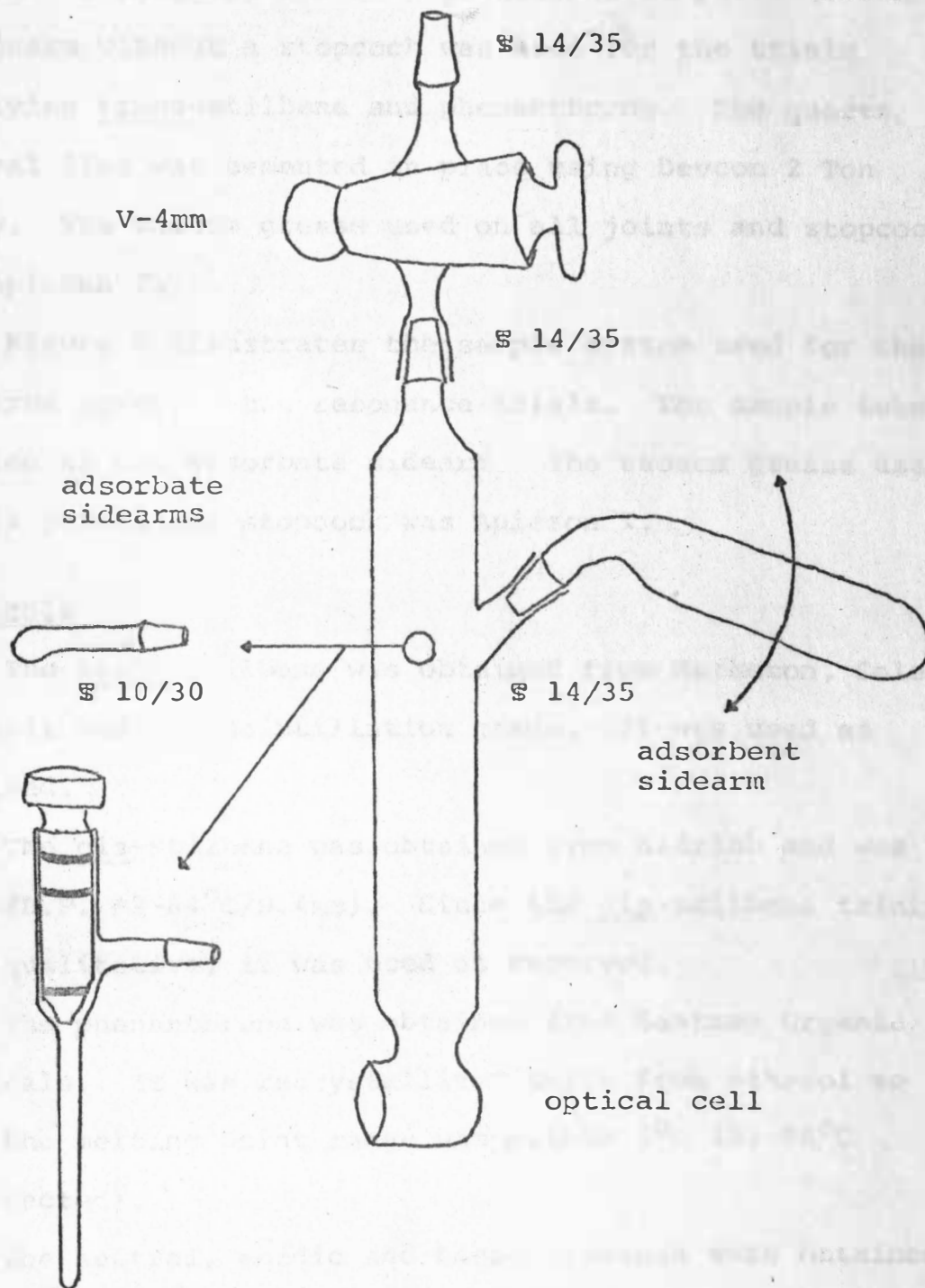


Figure 4. Reflectance sample system.

accessed through an Ace FETE greaseless stopcock (0-3 mm). A sidearm without a stopcock was used for the trials involving trans-stilbene and phenanthrene. The quartz optical flat was cemented in place using Devcon 2 Ton epoxy. The vacuum grease used on all joints and stopcock was Apiezon T.

Figure 5 illustrates the sample system used for the electron paramagnetic resonance trials. The sample tube doubled as the adsorbate sidearm. The vacuum grease used on all joints and stopcock was Apiezon T.

### Chemicals

The trans-stilbene was obtained from Matheson, Coleman and Bell and was scintillation grade. It was used as received.

The cis-stilbene was obtained from Aldrich and was 97% pure (B.P. 82-84°C/0.4mm). Since the cis-stilbene trials were qualitative, it was used as received.

The phenanthrene was obtained from Eastman Organic Chemicals. It was recrystallized twice from ethanol so that the melting point range was within 1°C (97-98°C uncorrected).

The neutral, acidic and basic aluminas were obtained from Fischer Scientific Company. The alumina was chromatography grade with a particle size distribution of 80 to 200 mesh. After 15 minutes grinding in the Spex mixer

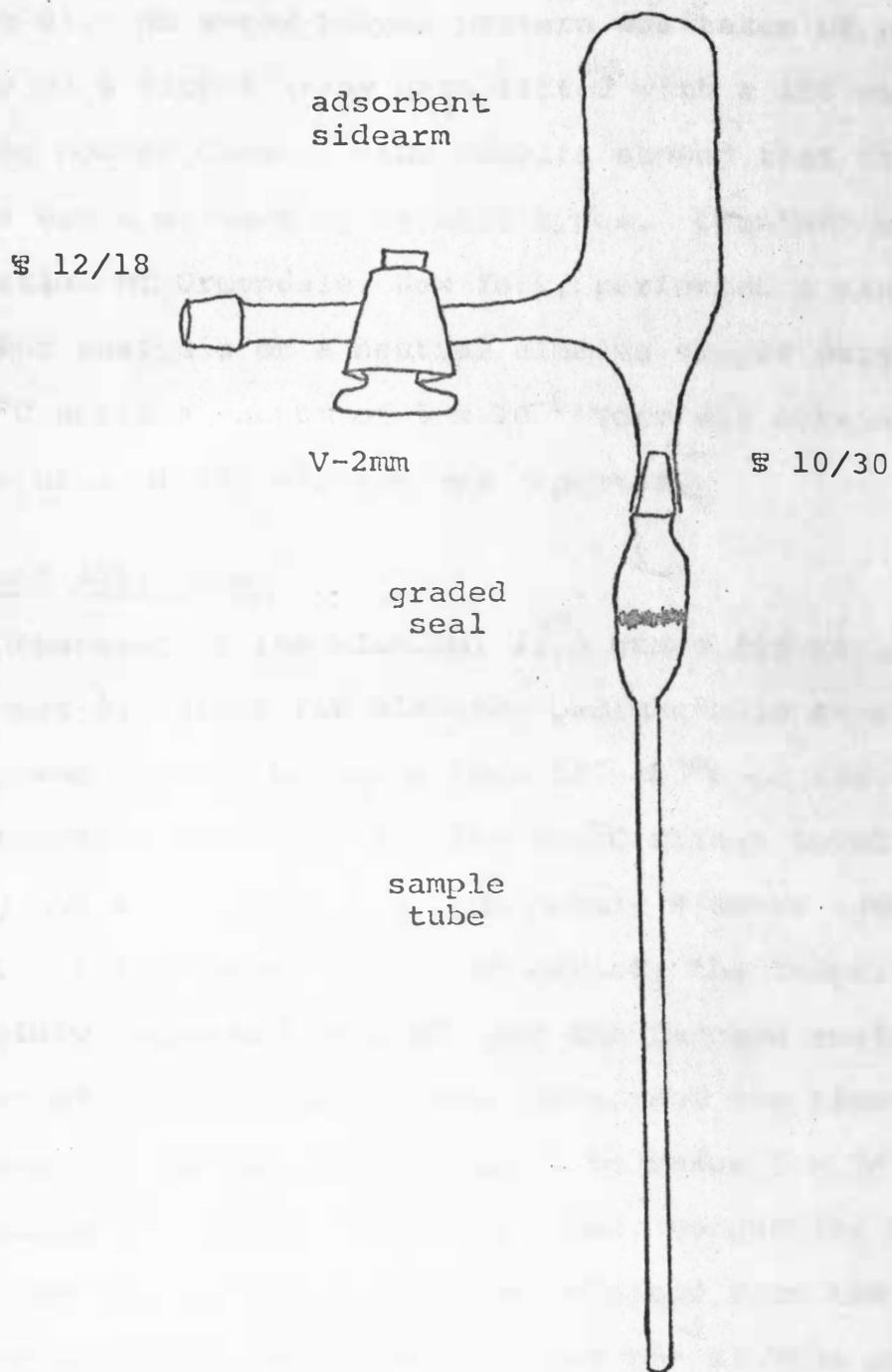
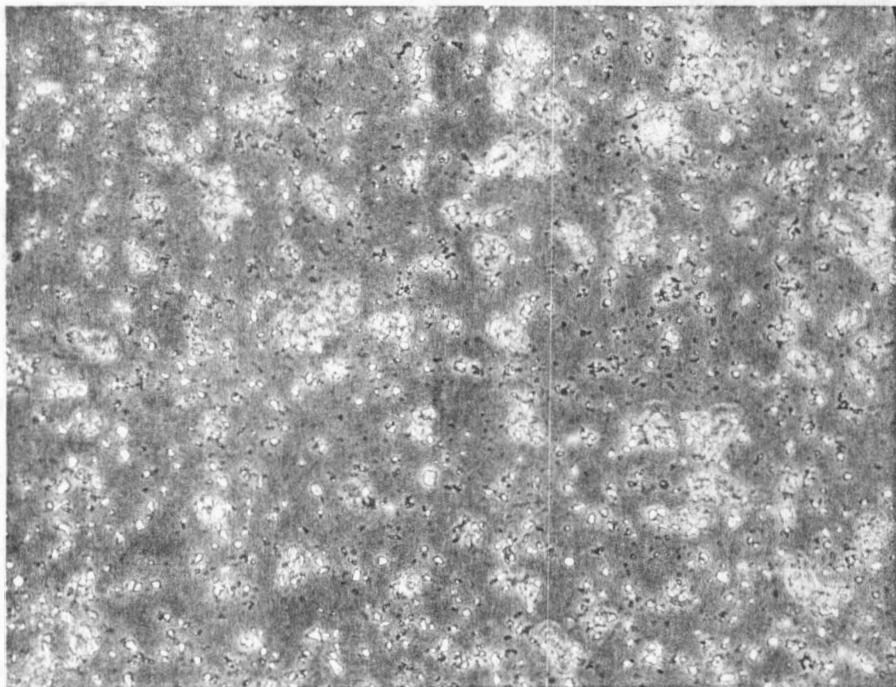


Figure 5. Electron paramagnetic resonance sample system.

mill, a mean particle size of  $1.5 \mu$  was obtained (Figure 6). An x-ray powder pattern was taken of neutral alumina on a Picker x-ray unit fitted with a 180 mm Debye Scherrer powder camera. The results showed that the alumina was a mixture of crystal types. Quantachrome Corporation of Greendale, New York, performed a single point BET analysis on a neutral alumina sample outgassed at  $150^{\circ}\text{C}$  until a vacuum of  $5 \times 10^{-5}$  Torr was obtained. A surface area of  $140 \text{ m}^2/\text{gram}$  was reported.

#### Adsorbent Activation

Outgassing of the alumina, 11.5 grams for reflectance trials and 3.0 grams for electron paramagnetic resonance trials, was carried out at either  $150-155^{\circ}\text{C}$  or  $400-410^{\circ}\text{C}$ . The activation procedure for the  $150^{\circ}\text{C}$  trials involved heating the adsorbent for approximately 8 hours under vacuum. At the end of this time period, the temperature was rapidly increased to  $350^{\circ}\text{C}$  and the furnace control was then turned back to  $150^{\circ}\text{C}$ . This decreased the time necessary for the manifold pressure to reach  $5 \times 10^{-5}$  Torr (approximately 1 hour). At this point, outgassing was stopped and the sample system was isolated from the vacuum line for adsorbate introduction. For the alumina activated at  $400-410^{\circ}\text{C}$ , this temperature was maintained until the manifold pressure reached  $5 \times 10^{-5}$  Torr (approximately 60 hours).



measured particle size (app. mean): .6mm

magnification: 383

mean particle size:  $\frac{600\mu}{383} = 1.5\mu$

Figure 6. Particle size distribution for neutral alumina ground 15 minutes.



### Adsorbate Introduction

For trans-stilbene or phenanthrene approximately  $5.6 \times 10^{-5}$  moles/gram of alumina was placed in the adsorbate sidearm and mounted on the sample system with the adsorbent sidearm. After the alumina had been outgassed, the sample system was removed from the vacuum line and placed in a 95°C oven for 15 minutes to facilitate the volatilization of the adsorbate. The trans-stilbene trials were returned to the vacuum line and outgassed at 125°C until the manifold reached  $2.5 \times 10^{-5}$  Torr (approximately 15 minutes).

For cis-stilbene an assumed excess was placed in the sealable adsorbate sidearm and evacuated to  $2 \times 10^{-4}$  Torr prior to placement on the sample system. The volatile nature of the cis-stilbene prevented further evacuation. With the adsorbate system evacuated, the sidearm was sealed off and mounted on the sample system with the adsorbent sidearm. The system was then treated as in the trans-stilbene trials.

### Loading of Optical Cell

The adsorbed system was transferred from the adsorbent sidearm to the optical cell or sample tube by inverting the sidearm and tapping. The samples for reflectance measurements were then placed on the base of the vacuum rack overnight and the vibration from the fore pump packed the powder.

### Irradiation

The reflectance samples were irradiated for 30 minutes at a distance of 55 mm. The power supply setting for the irradiation source was 52 volts and 3.0 amps. The electron paramagnetic resonance sample was irradiated for 50 minutes at a distance of 30 mm. The sample tube was repositioned every 5 minutes to allow direct irradiation of all portions of the adsorbed system. The power supply setting was 52 volts and 3.0 amps.

### Kinetic Measurements

Kinetic data was obtained by placing the sample system in the constant temperature oil bath and then removing at later time periods to record the spectra. The spectra were recorded at a fixed time interval after removal from the oil bath. This was necessary because stilbene exhibits a temperature dependent hyperchromic shift. The time out of the oil bath was not included in the recorded time. Monitoring continued until no appreciable change was noted in the spectrum.



## RESULTS AND CONCLUSIONS

With trans-stilbene adsorbed onto a 150°C activated neutral alumina, irradiated at 313 nm, and then allowed to stand for a period of time at an elevated temperature, the behavior shown in Figure 7 was noted. Upon irradiation the initial trans absorptions at 315 and 235 nm were replaced by absorptions at 293 and 252 nm, coinciding with the spectra of cis-stilbene<sup>3</sup> and phenanthrene (Figure 8). No absorptions in the visible region (360-800 nm) were observed. After approximately 72 hours at 95°C a distinct return in the area of the major trans absorption (320 nm) was noted, accompanied by a decrease in the cis-stilbene and phenanthrene region. Reirradiation of the return product (Figure 9) behaved in the same manner as the initial trans-stilbene system inferring that the return product was in fact trans-stilbene. The red shift seen for the return peak implied that the return trans-stilbene was subject to a strong adsorbent interaction<sup>39</sup>. The low return yield of trans-stilbene was assumed to be due to the loss of weakly adsorbed molecules from the surface by irradiation, or the formation of phenanthrene.

Previous work done on the irradiation of adsorbed stilbene<sup>7,16</sup> did not consider the post-irradiation behavior of the system. A study<sup>40</sup> using a substituted stilbene (4-nitro-4'-hydroxy- $\alpha$ -cyanostilbene) adsorbed onto

Figure 7. Reflectance spectrum of trans-stilbene adsorbed on 150°C activated neutral alumina 1) before irradiation, 2) after irradiation, and 3) after approximately 72 hours at 95°C.

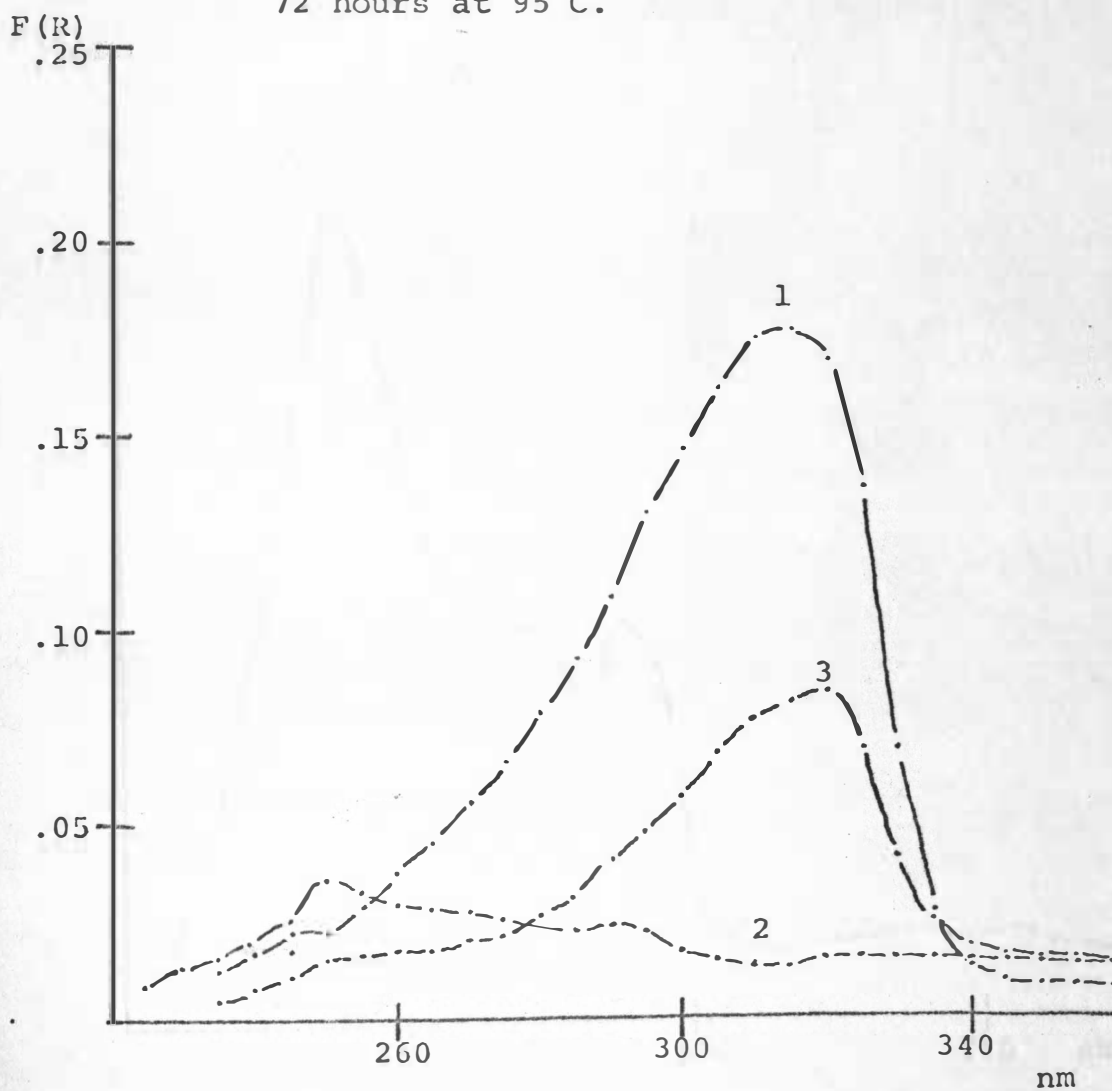


Figure 8. Reflectance spectrum of phenanthrene adsorbed on 150°C activated neutral alumina.

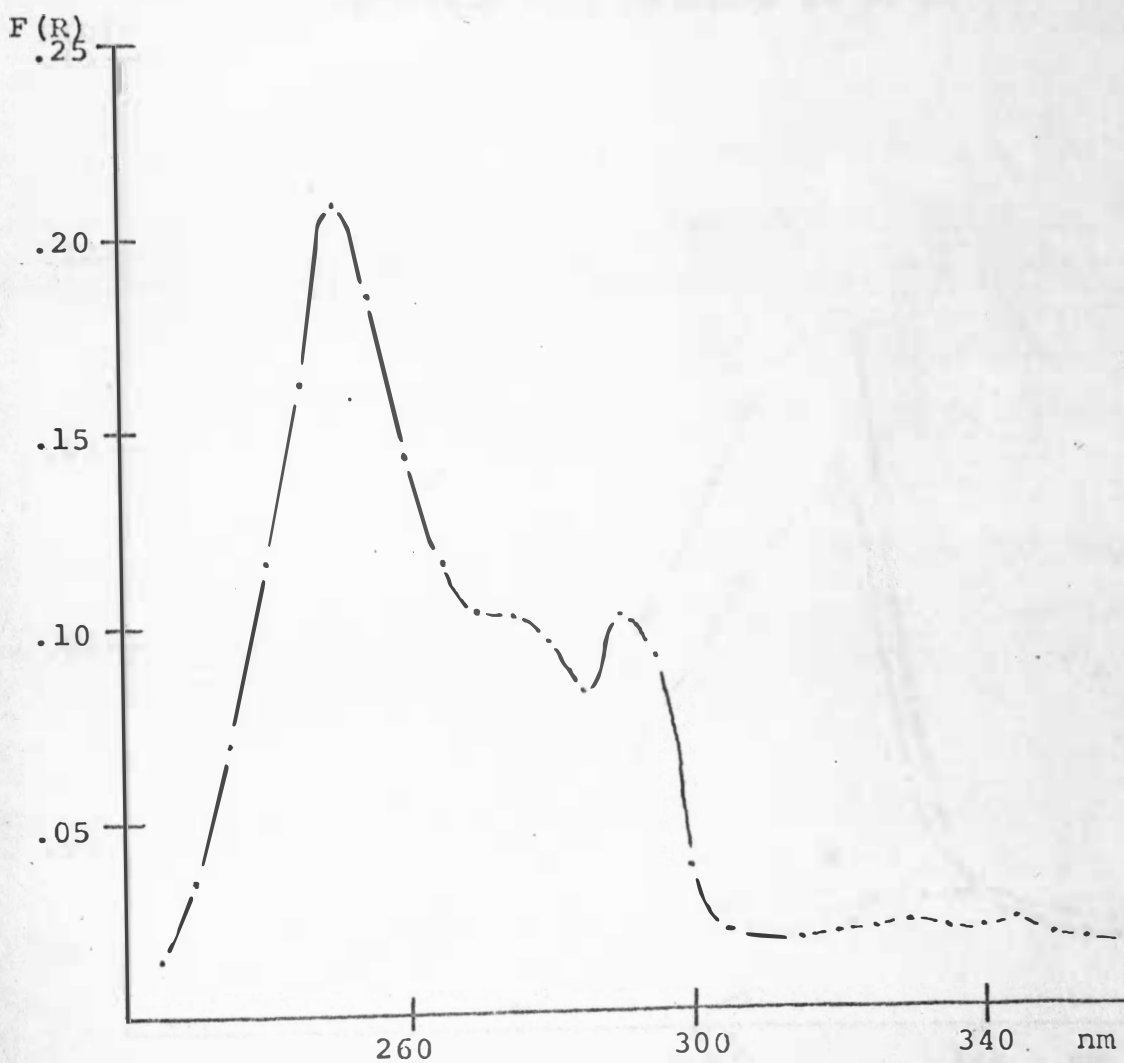
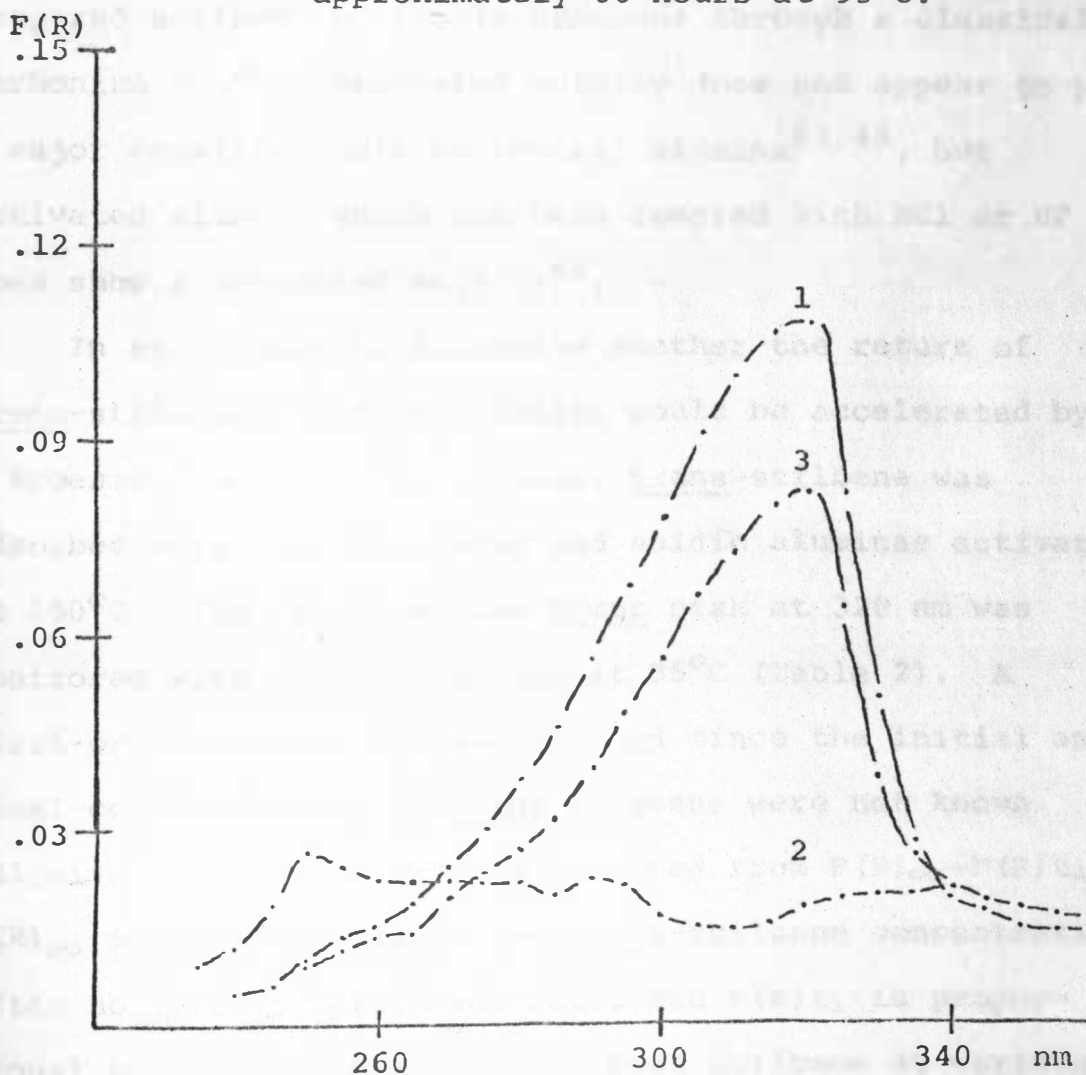


Figure 9. Reflectance spectrum of return product adsorbed on 150°C activated neutral alumina 1) return product, 2) after irradiation, and 3) after approximately 60 hours at 95°C.



nylon 6.6 demonstrated that thermal isomerization occurred in this system by first order kinetics. Assuming the return process witnessed to be a thermal isomerization, it was felt this process might be speeded up through selection of adsorbent pH. The ability of cracking catalysts (aluminosilicates) to protonate surface species has been substantiated<sup>41,42</sup> and butene isomerization on a suitably prepared surface apparently proceeds through a classical carbonium ion<sup>41</sup>. Broensted acidity does not appear to play a major catalytic role on neutral alumina<sup>43,44</sup>, but activated alumina which has been treated with HCl or HF does show a Broensted acidity<sup>45</sup>.

In an attempt to determine whether the return of trans-stilbene after irradiation could be accelerated by a Broensted acid on the surface, trans-stilbene was adsorbed onto neutral, basic and acidic aluminas activated at 150°C. The return of the trans peak at 320 nm was monitored with respect to time at 95°C (Table 2). A first-order process was assumed and since the initial and final concentrations of trans-stilbene were not known relative concentrations were obtained from  $F(R)_\infty - F(R)t_i$ ,  $F(R)_\infty$  is proportional to the trans-stilbene concentration after no further return was noted and  $F(R)t_i$  is proportional to the concentration of trans-stilbene at various times prior to  $F(R)_\infty$ . A least squares fit was used to

Table 2. Kinetic data for the return of trans-stilbene on 150°C activated aluminas.

	F(R)	ln( $\Delta F(R)$ )	t (min)
Acidic alumina (95°C):			
	.01976	-3.112	60.
slope = $-1.26 \times 10^{-3}$	.02672	-3.282	195.
intercept = -3.06	.03435	-3.509	315.
	.04013	-3.723	495.
	.05444	-4.621	1335.
	.06429	-	$\infty$ (>60 hr)
Neutral alumina (95°C):			
	.02228	-2.780	45.
slope = $-1.21 \times 10^{-3}$	.02791	-2.874	105.
intercept = -2.81	.03435	-2.995	195.
	.04651	-3.274	305.
	.05585	-3.557	485.
	.07186	-4.381	1355.
	.08438	-	$\infty$ (>60 hr)
Basic alumina (95°C):			
	.02643	-3.079	60.
slope = $-1.16 \times 10^{-3}$	.03167	-3.200	120.
intercept = -3.10	.04167	-3.482	300.
	.04609	-3.637	420.
	.05538	-4.072	710.
	.06325	-4.691	1445.
	.07299	-	$\infty$ (>60 hr)
Neutral alumina (115°C):			
	.02335	-3.170	40.
slope = $-2.59 \times 10^{-3}$	.03103	-3.372	80.
intercept = -3.24	.03645	-3.544	120.
	.04245	-3.777	160.
	.04651	-3.972	220.
	.06223	-5.775	1030.
	.06533	-	$\infty$ (>48 hr)



give the best straight line through the data points  $\ln (F(R)_\infty - F(R)t_i)$ ,  $t_i$ . The effective rate constant,  $k_{\text{eff}}$ , was obtained as the slope of the least squares line. The results showed all three  $k_{\text{eff}}$ 's to be within  $\pm 0.1 \times 10^{-3}$  of each other:

$$k_{\text{eff}} \text{ acidic} = 1.3 \times 10^{-3} \text{ min}^{-1}$$

$$k_{\text{eff}} \text{ neutral} = 1.2 \times 10^{-3} \text{ min}^{-1}$$

$$k_{\text{eff}} \text{ basic} = 1.2 \times 10^{-3} \text{ min}^{-1}$$

This result suggests one of two possibilities. Either the acidic alumina does not have significant Brønsted acidity after activation, or the return of trans-stilbene has not been affected by the availability of surface protons.

The plots of  $\ln (F(R)_\infty - F(R)t_i)$  versus time (Figure 10, 11 and 12) also suggest that the systems are not correctly defined by first-order kinetics. A trial performed on neutral alumina activated at 150°C and monitored at 115°C (Figure 13) accentuated the nonlinearity. This nonfirst-order behavior raises the question whether the deviation is due to surface effects, or the decay of irradiation side products. The surface effect envisioned is one which, due to a possible nonhomogeneity of surface sites, results in parallel return processes. Interference from irradiation side products points to the thermal decay of DHP creating a consecutive return process.

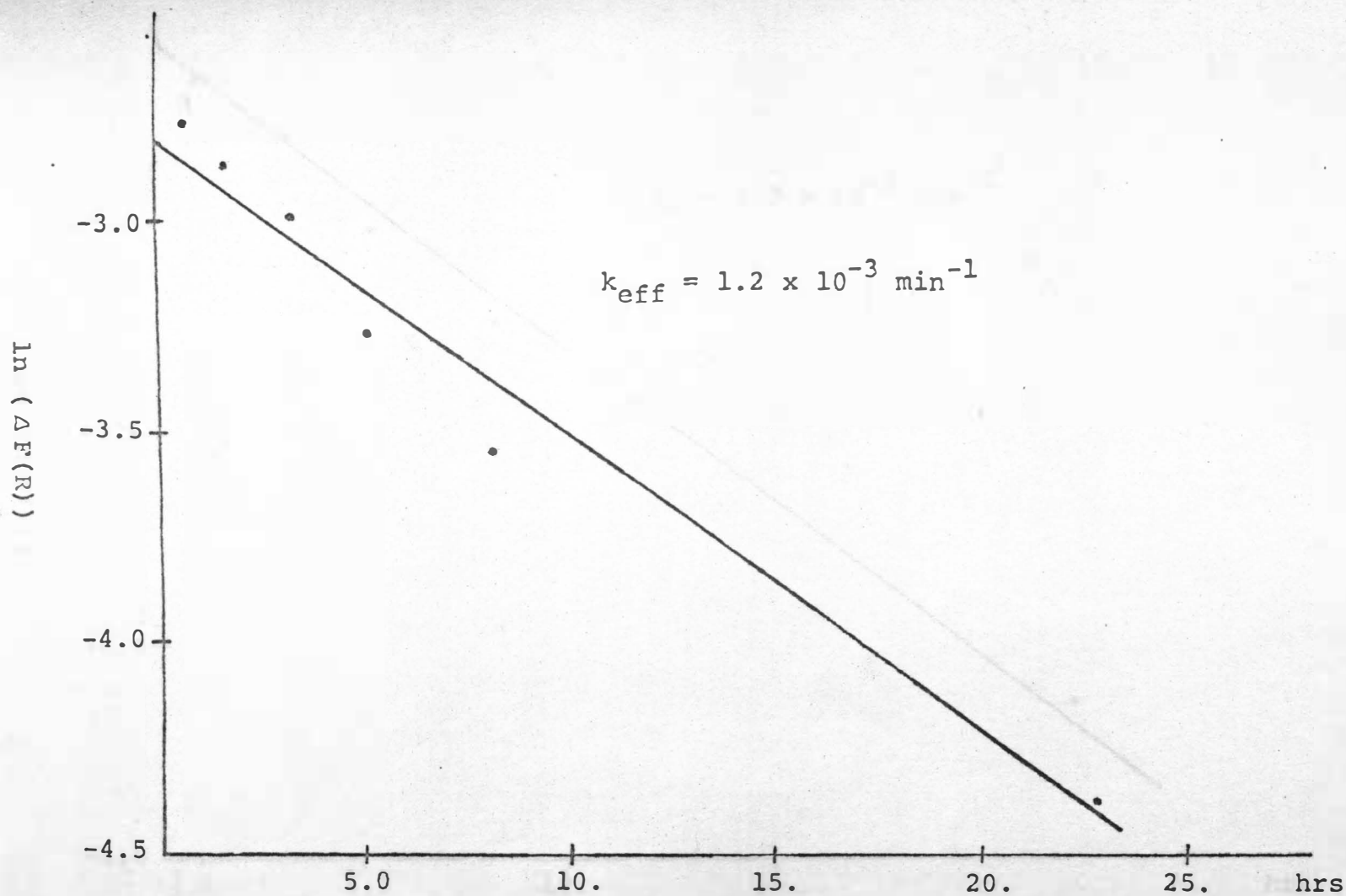


Figure 10.  $k_{\text{eff}}$  plot for trans-stilbene on 150°C activated neutral alumina at 95°C.



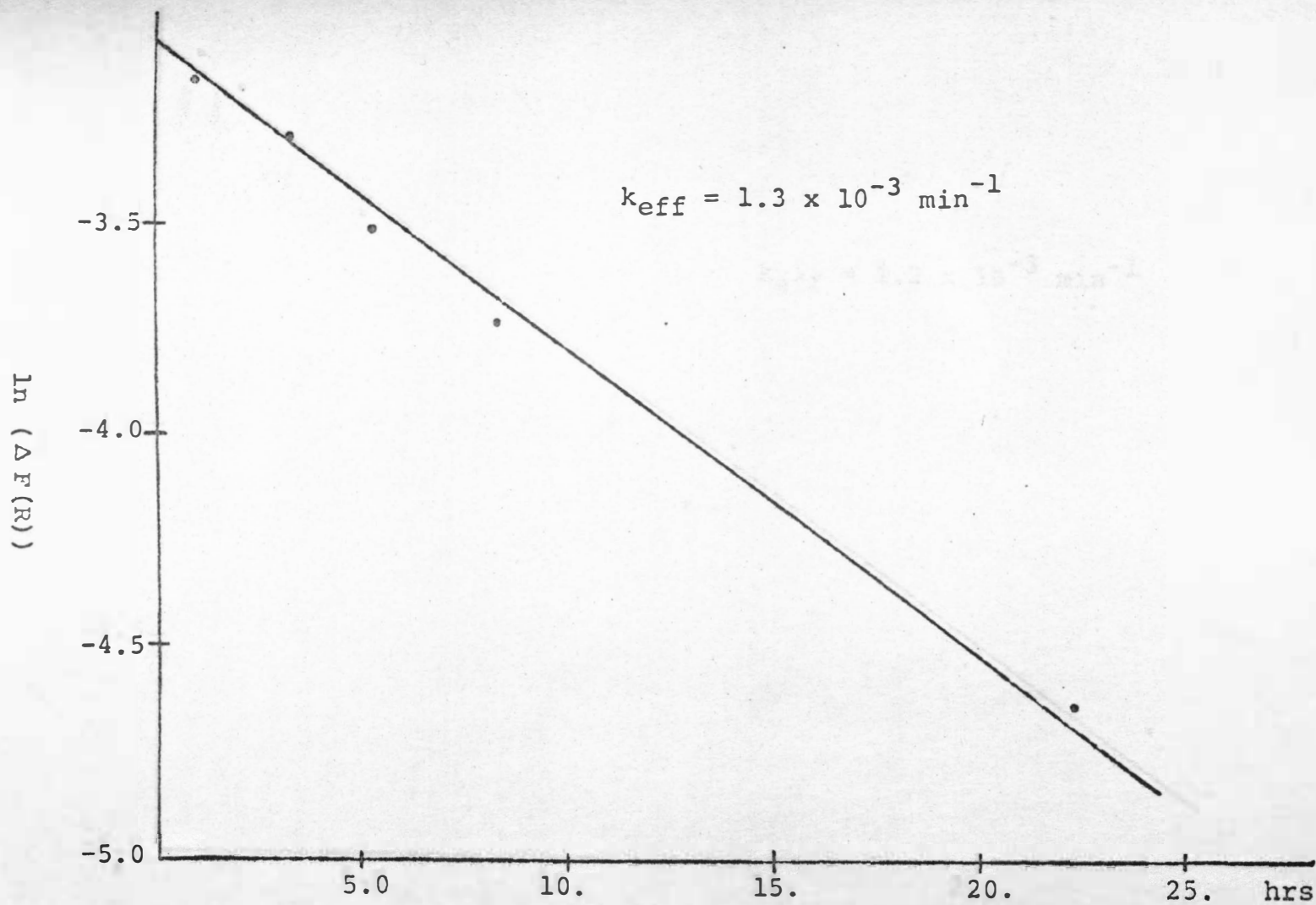


Figure 11.  $k_{\text{eff}}$  plot for trans-stilbene on 150°C activated acidic alumina at 95°C.

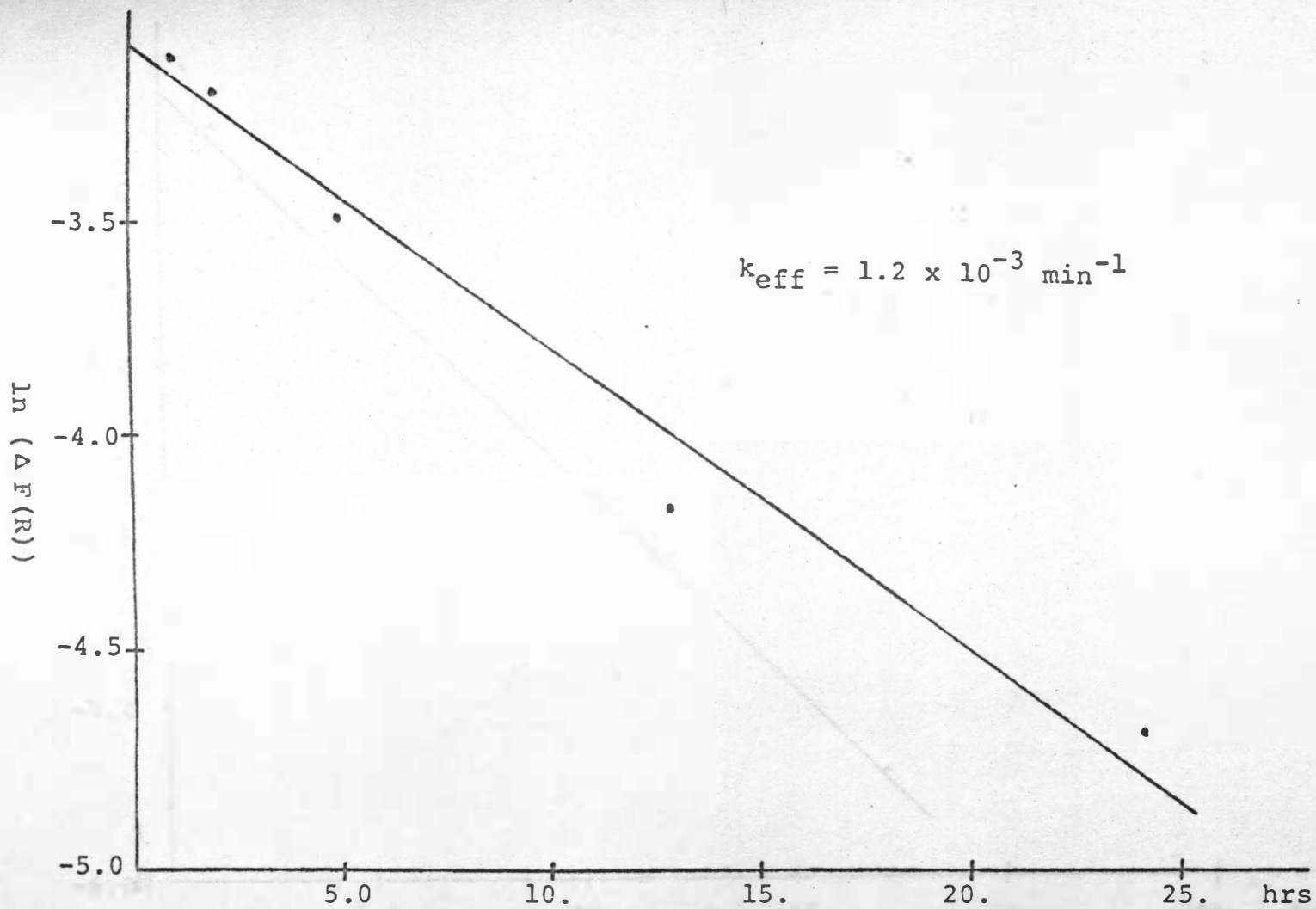


Figure 12.  $K_{\text{eff}}$  plot for trans-stilbene on 150°C activated basic alumina at 95°C.

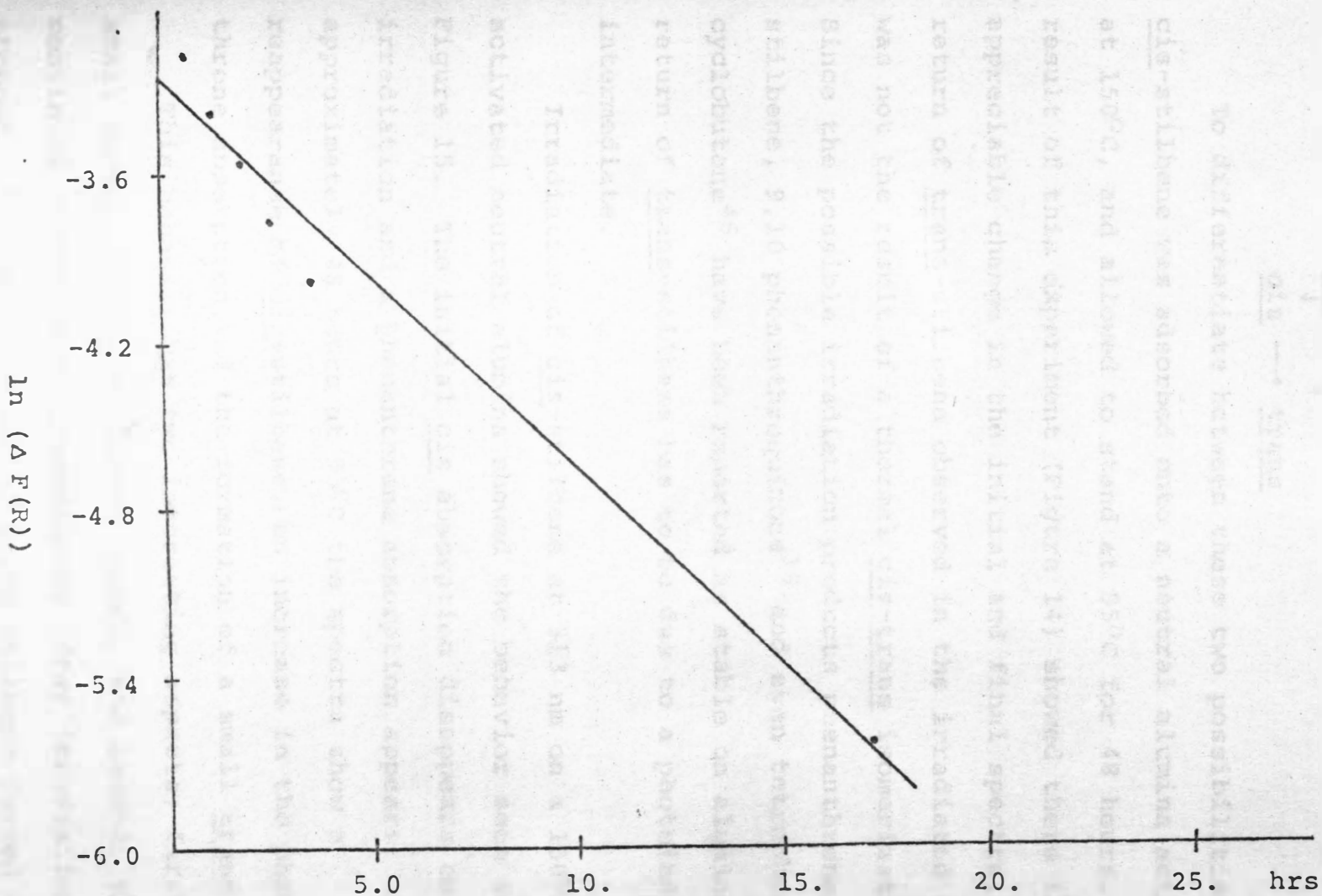
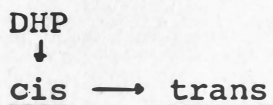


Figure 13.  $K_{eff}$  plot for trans-stilbene on 150°C activated neutral alumina at 115°C.



To differentiate between these two possibilities cis-stilbene was adsorbed onto a neutral alumina activated at 150°C, and allowed to stand at 95°C for 48 hours. The result of this experiment (Figure 14) showed there is no appreciable change in the initial and final spectra. The return of trans-stilbene observed in the irradiated trial was not the result of a thermal cis-trans isomerization. Since the possible irradiation products phenanthrene, cis-stilbene, 9,10-phenanthroquinone<sup>16</sup> and even tetraphenylcyclobutane<sup>46</sup> have been reported as stable on alumina the return of trans-stilbene has to be due to a photoinduced intermediate.

Irradiation of cis-stilbene at 313 nm on a 150°C activated neutral alumina showed the behavior seen in Figure 15. The initial cis absorption disappears on irradiation and a phenanthrene absorption appears. After approximately 48 hours at 95°C the spectra show a reappearance of cis-stilbene, an increase in the phenanthrene absorption and 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 stopped. The small amount of trans-stilbene formed after

Figure 14. Reflectance spectrum of 1) *cis*-stilbene adsorbed on 150°C activated neutral alumina, and 2) after approximately 48 hours at 95°C.

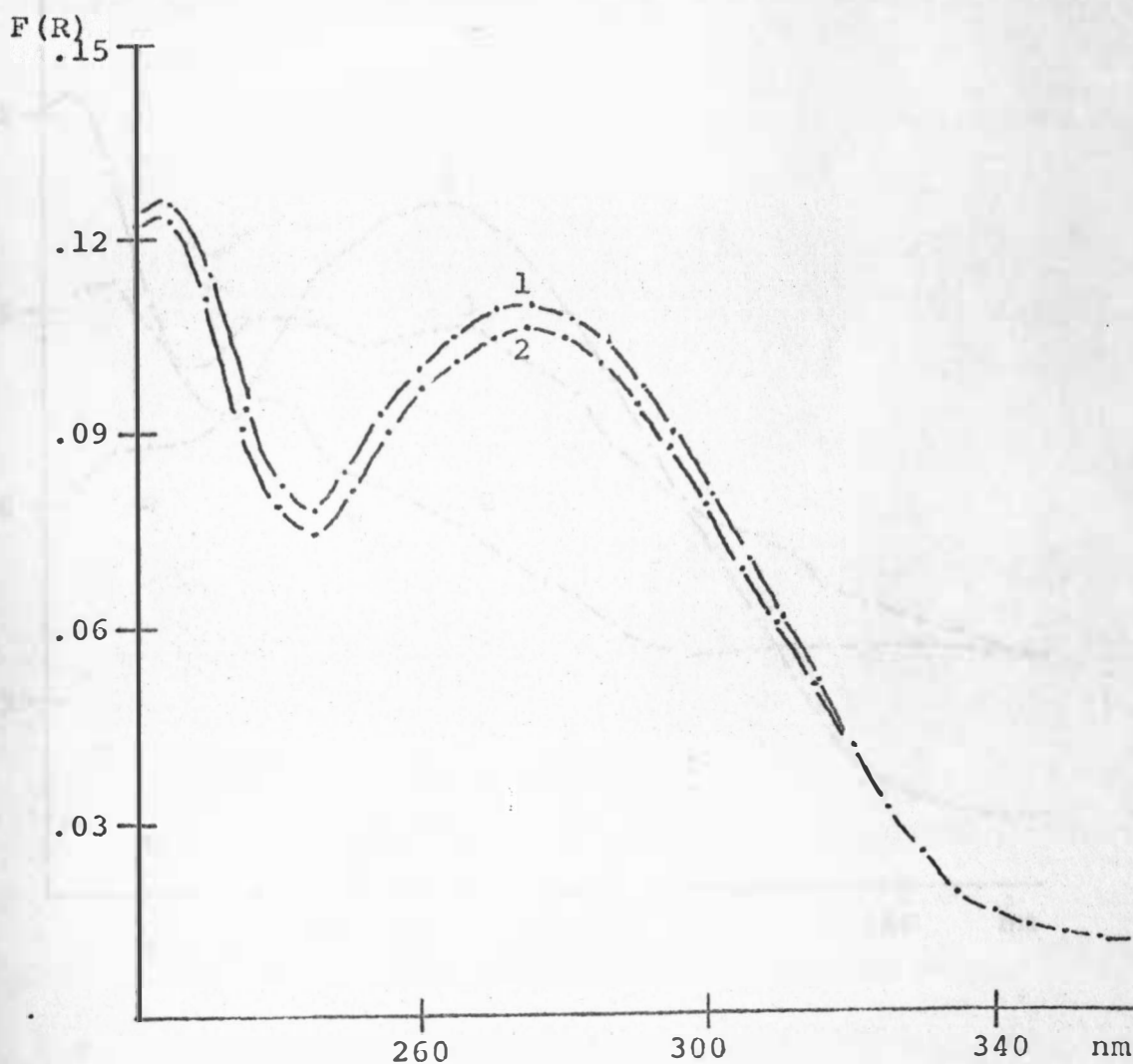
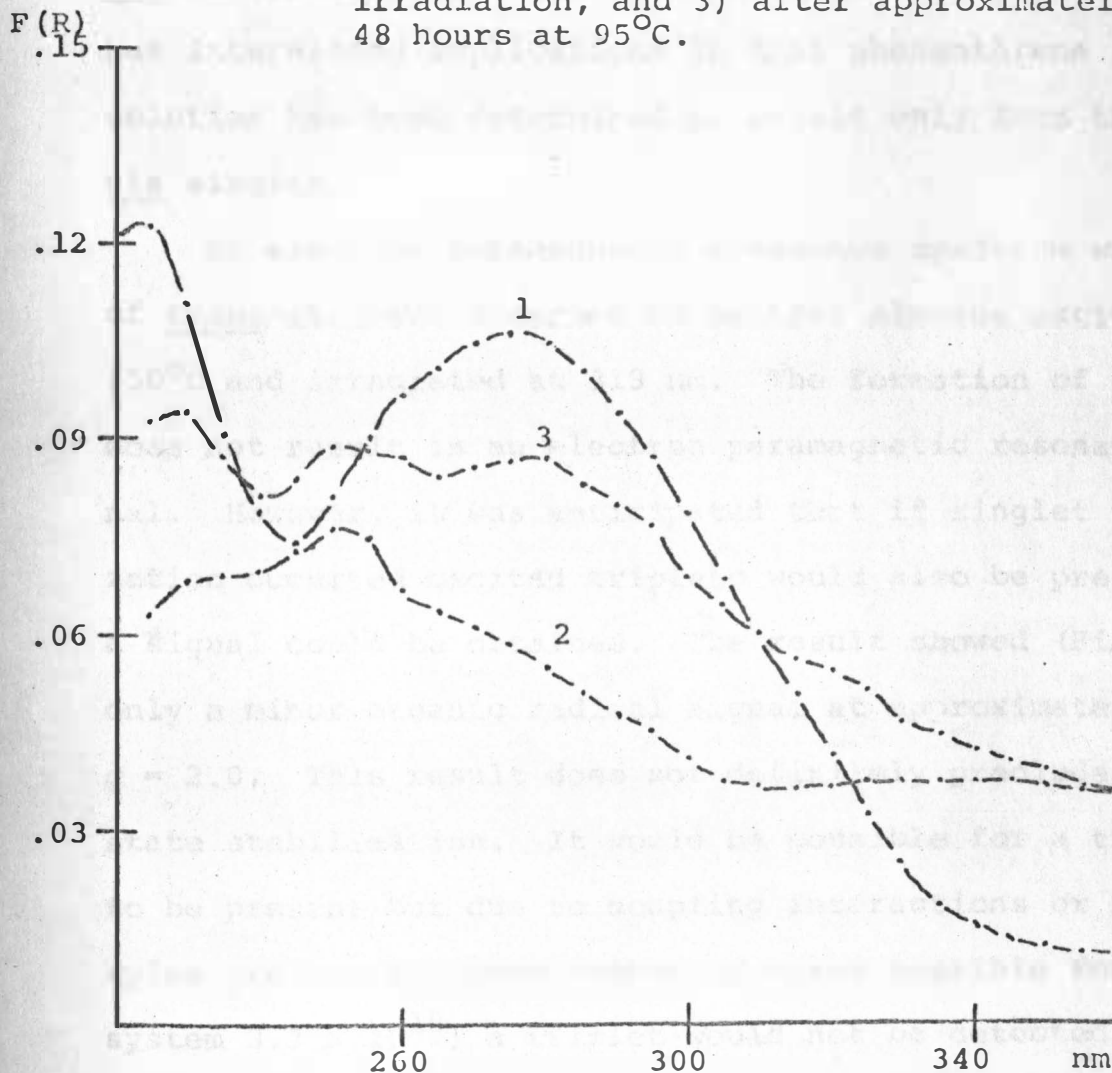


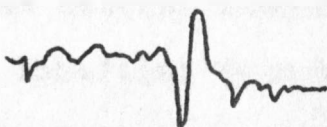
Figure 15. Reflectance spectrum of cis-stilbene adsorbed on 150°C activated neutral alumina 1) before irradiation, 2) after irradiation, and 3) after approximately 48 hours at 95°C.





irradiation suggests that the intermediate does not undergo configurational rotation. The trans-stilbene obtained shows a strong adsorbent interaction which suggests that it was present prior to irradiation but overshadowed by the large cis absorption. The continued formation of phenanthrene has interesting implications in that phenanthrene in solution has been determined to result only from the excited cis singlet.

An electron paramagnetic resonance spectrum was taken of trans-stilbene adsorbed on neutral alumina activated at 150°C and irradiated at 313 nm. The formation of a singlet does not result in an electron paramagnetic resonance signal. However, it was anticipated that if singlet stabilization occurred excited triplets would also be present and a signal could be obtained. The result showed (Figure 16) only a minor organic radical signal at approximately  $g = 2.0$ . This result does not definitely preclude excited state stabilization. It would be possible for a triplet to be present but due to coupling interactions or number of spins present (maximum number of spins possible for this system  $3.3 \times 10^{18}$ ) a triplet would not be detected. The solution behavior of excited state singlets and triplets<sup>47</sup> though, does not tend to support stabilization. In general one would also expect to see an absorption spectrum for this type of intermediate.



signal to noise ratio = 5

$$g = \frac{h\nu}{\beta H_0} = 2.006 \quad (56)$$

$$\beta = \text{Bohr magneton} = 9.2732 \times 10^{-21} \text{ erg/gauss}$$

$$H_0 = \text{field strength} = 3.375 \times 10^3 \text{ gauss}$$

$$h = \text{Planck constant} = 6.6256 \times 10^{-27} \text{ erg sec}$$

$$\nu = \text{frequency of radiation} = 9.48 \times 10^9 \text{ Hz}$$

Figure 16. Electron paramagnetic resonance spectrum of irradiated trans-stilbene adsorbed on 150°C activated neutral alumina.

The behavior of the intermediate with respect to increased surface activity was also investigated, surface activity being associated with the number of exposed aluminum ions. The surfaces envisioned for the 150°C and 400°C activated neutral alumina both have exposed  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  ions resulting from the grinding process. Prior to activation both have adsorbed water from atmospheric handling. The activation process at 150°C in vacuum removes only weakly adsorbed water, presumably leaving a surface with exposed  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  ions in a framework of an incomplete adsorbed monolayer of water. The vacuum activation at 400°C removes the monolayer of water, but due to slow pumping speed of the vacuum line hydroxyl formation probably occurs. Such activation likely gives a surface with an increased concentration of  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  ions in a framework of adsorbed hydroxyl groups.

The time required for no further return of trans-stilbene on 150°C activated alumina is approximately 30 hours at 95°C. For the 400°C activation no further return is noted at 95°C after approximately 16 hours. In preliminary work performed by Hecht<sup>48</sup>, the surface was prepared by grinding the trans-stilbene onto the alumina in an air tight container. This procedure should have resulted in a high surface concentration of  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  ions, relatively free of adsorbed water and hydroxyl groups. The irradiated

system showed nearly a complete return of trans-stilbene in less than 24 hours at 25°C. A 150°C activated neutral alumina system showed virtually no return at 25°C within this same time period (Figure 17). This data suggests that the stability of the intermediate decreases with increased surface activity.

A final aspect of the intermediate noted was that after no further return of trans-stilbene was seen at 95°C, increasing the temperature to 125°C created a further return of trans-stilbene on 400°C activated neutral alumina (Figure 18). Of concern at this point was whether the kinetic studies had been terminated too soon to reflect first-order behavior. The data from the 95°C and 115°C trials on 150°C activated neutral alumina were analyzed using a nonlinear least squares program<sup>53</sup> in an attempt to answer this question. This program allowed the slope, intercept, and  $F(R)_\infty$  values to vary giving the best linear fit to the  $\ln (F(R)_\infty - F(R)t_i)$ ,  $t_i$  data points. If the computed value of  $F(R)_\infty$  was greater than the experimentally determined value the process could indeed be first-order in that a correct end point had not as yet been reached. However, if the computed  $F(R)_\infty$  was less than that experimentally determined, the process would not be first-order in that an end point had to be reached prior to that recorded experimentally. The computed  $F(R)_\infty$  values

Figure 17. Reflectance spectrum of trans-stilbene adsorbed on 150°C activated neutral alumina 1) before irradiation, 2) after irradiation, and 3) after approximately 24 hours at 25°C.

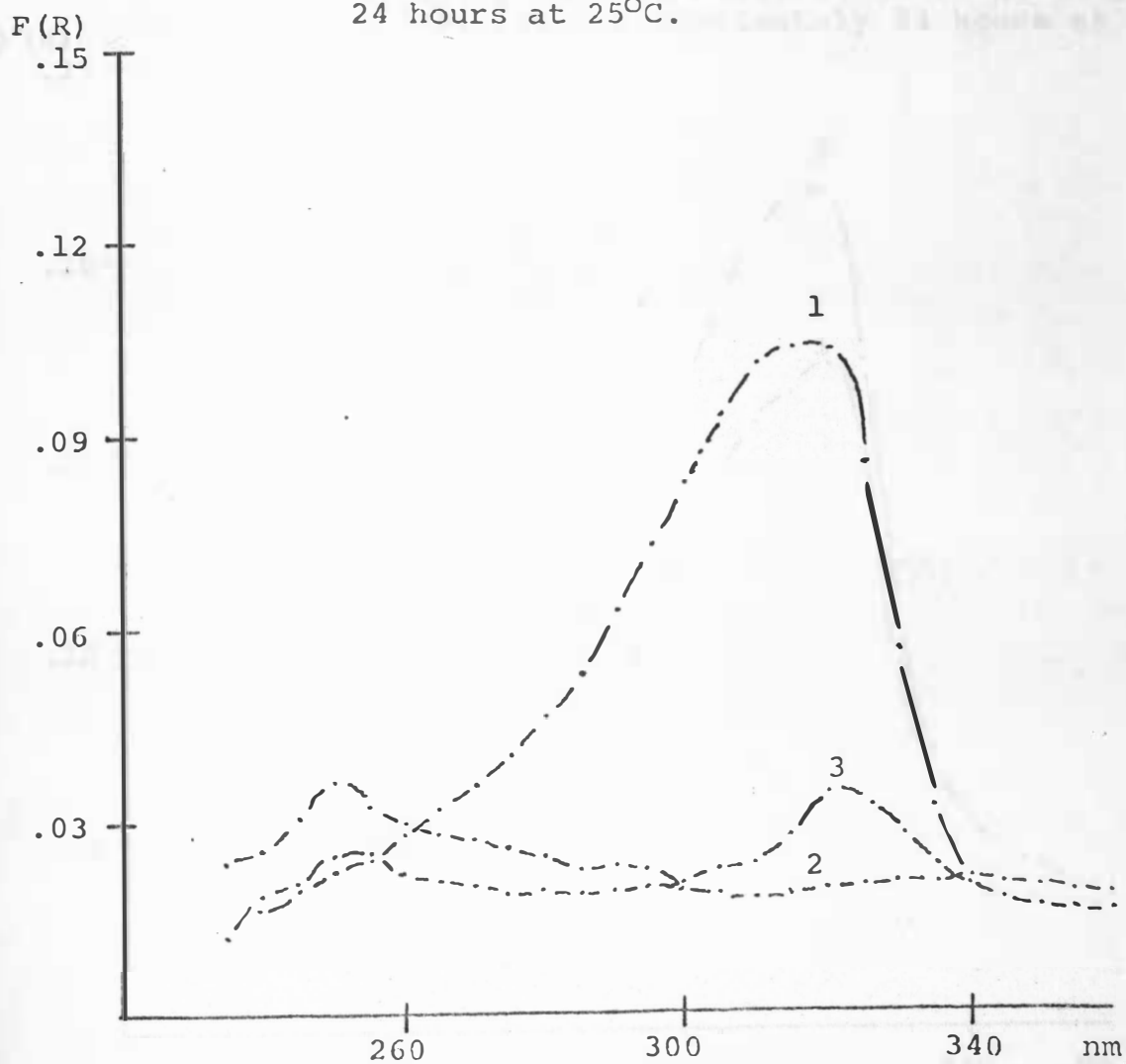
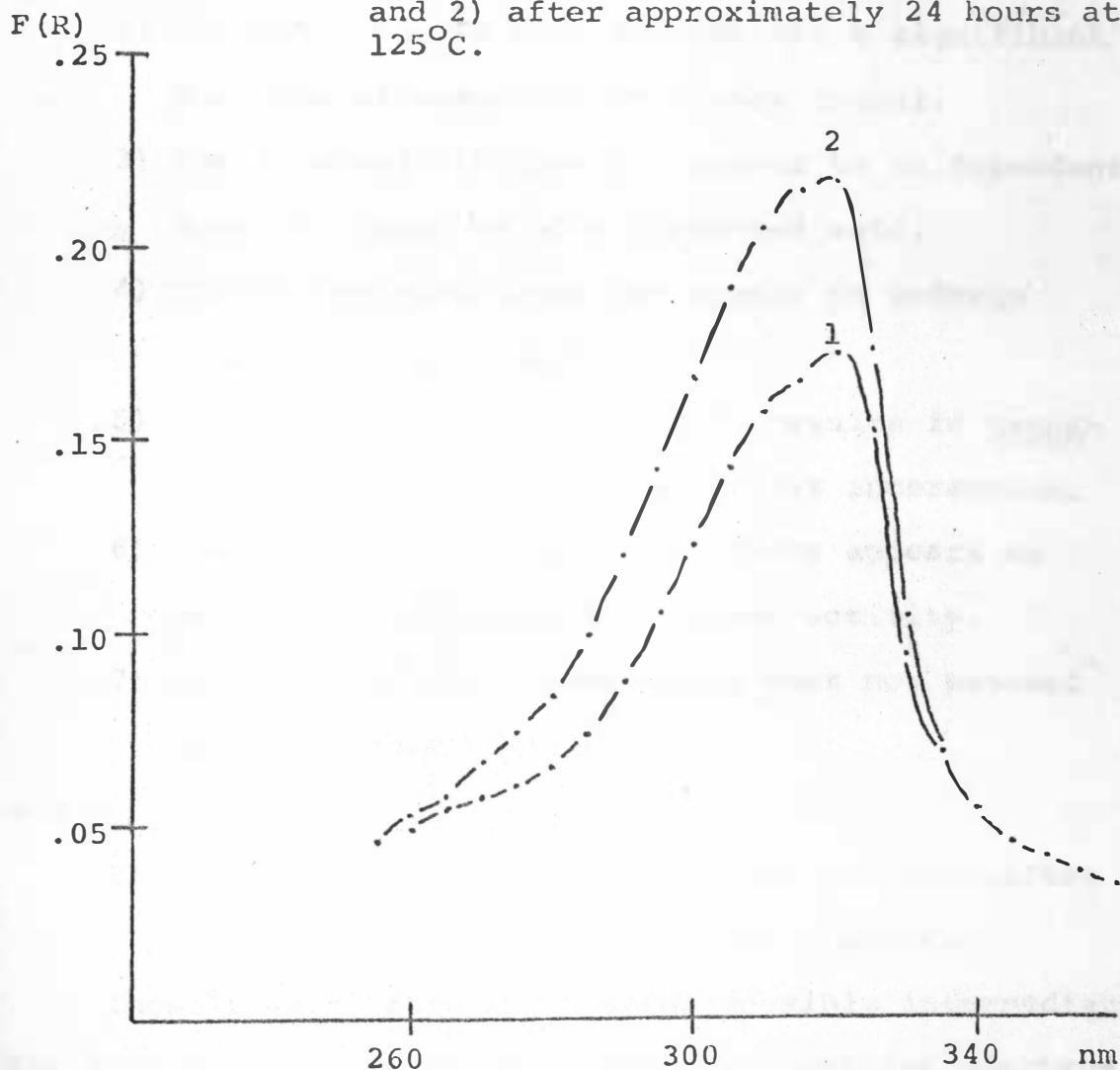


Figure 18. Reflectance spectrum of return product on 400°C activated neutral alumina 1) after approximately 36 hours at 95°C, and 2) after approximately 24 hours at 125°C.





obtained (Table 3) showed that a smaller value was needed and confirmed nonfirst-order behavior.

In summary the photoinduced intermediate has shown the following characteristics.

- 1) The intermediate does not exhibit a visible or ultraviolet spectrum except perhaps in the region of the cis-stilbene and phenanthrene absorptions.
- 2) The intermediate does not exhibit a significant electron paramagnetic resonance signal.
- 3) The intermediate does not appear to be dependent upon the presence of a Broensted acid.
- 4) The intermediate does not appear to undergo configurational rotation.
- 5) The decay of the intermediate results in trans-stilbene showing strong adsorbent interaction.
- 6) The stability of the intermediate appears to be inversely related to surface activity.
- 7) The decay of the intermediate does not proceed by first-order kinetics.

and

- 8) Phenanthrene formation continues to occur after irradiation of cis-stilbene has stopped.

These results rule out several possible intermediates. The lack of a visible or noticeable ultraviolet spectrum along with a small electron paramagnetic resonance signal

Table 3. Nonlinear least square values for return of trans-stilbene on 150°C activated neutral alumina.

	95°C	115°C
slope	$-2.21 \times 10^{-3}$	$-6.35 \times 10^{-3}$
intercept	-2.84	-2.99
$F(R)_{\infty}$	.07482	.06033

precludes a non classical carbonium ion as the intermediate. Such a species should show a significant electron paramagnetic resonance signal and major absorptions in the visible and ultraviolet regions<sup>49</sup>. A classical carbonium ion is not a satisfactory intermediate, because formation of the intermediate does not appear to depend upon the Broensted acidity of the surface. Finally, the formation of a carbene is not consistent with the continued formation of phenanthrene, due to the carbene's ability to withdraw electron density from the phenyl rings.

Although a definite assignment cannot be made for the intermediate structure, the experimental evidence in conjunction with olefin adsorption characteristics does suggest a possible intermediate. This intermediate is based on the photo-excited ethylenic  $\pi$  electrons interacting with the vacant p-type aluminum orbitals to form a dative sigma bond (Figure 19). The formation of this species would appear reasonable in that the ethylenic carbons contain the greatest  $\pi$  electron density<sup>50</sup> and would preferentially adsorb over an exposed aluminum ion. It is felt that the irradiation process makes these  $\pi$  electrons available to the vacant p-type orbitals on the aluminum ion and bonding results.

Qualitatively this species can account for the experimental behavior of the intermediate. The lack of a visible

or noticeable ultraviolet spectrum would be due to the loss of conjugation across the central bond. This should result in a spectrum similar to benzene with only one weak absorption maximum above 220 nm (256 nm,  $\epsilon = 1.99 \times 10^2$  in cyclohexane<sup>51</sup>). The return of the trans-stilbene absorption 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 would be 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 sigma bond would force a change in the  $sp^2$  hybridization which would lift 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 would also increase. The greater the surface activity the more significant the interaction becomes in attempting to restore the phenyl rings to a planar configuration. The result would be a weakening of the dative sigma bond dependent upon surface activation. This approach would also satisfactorily explain the deviation from first-order kinetics since it

would be difficult to obtain a homogeneous surface interaction for all the phenyl rings due 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 due to the formation of a dative sigma bond. The loss of  $sp^2$  character in the cis configuration would place the phenyl rings in closer proximity to each other allowing for bond formation across the rings when the surface bond is broken.

A second intermediate can be proposed which would mimic the behavior of the dative sigma bond species. In this intermediate the photo-excited ethylenic  $\pi$  electrons would bond with the oxygen ions surrounding the aluminum ion (Figure 20).

The confirmation of a surface bond and evidence that the phenyl rings weaken the surface bond through surface interaction are critical aspects for acceptance of either of these intermediate structures. It is felt that this evidence could be obtained by studying the photo-induced behavior of adsorbed ethylene and 1-phenylethylene with infrared reflectance spectroscopy. The ethylene system would be monitored to determine whether the olefinic carbon-hydrogen absorptions shift to saturated carbon-hydrogen absorptions, or if carbon-oxygen absorptions

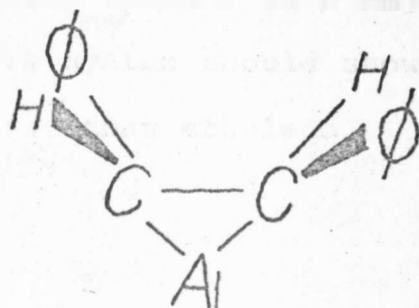


Figure 19. Aluminum bonded intermediate.

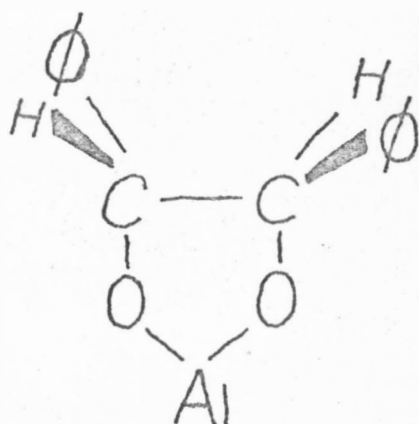


Figure 20. Oxygen bonded intermediate.



occur. The 1-phenylethylene system would be investigated with respect to its post-irradiation stability. If the phenyl ring-surface interaction is a major factor the intermediate for this system should show greater stability than stilbene but less than ethylene.

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