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Infrared Study of Adsorbed Trans-Stilbene and Azobenzene

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INFRARED STUDY OF ADSORBED TRANS-STILBENE AND AZOBENZENE

BY

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INFRARED STUDY OF ADSORBED TRANS-
STILBENE AND AZOBENZENE

This thesis is approved as a creditable and
independent investigation by a candidate for the degree,
Master of Science, and is acceptable for 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.

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INTRODUCTION

Previous reflectance study in our laboratory has shown that stilbenes and azobenzenes adsorbed on alumina or silica undergo a more-or-less reversible loss of olefinic double bond character upon irradiation at appropriate wavelengths, and an intermediate was proposed. The purpose of this work was trying to characterize the intermediate using infrared technique.

HISTORICAL

Stilbene

Stilbene exists in two isomeric forms. The molecular structure of trans-stilbene was found to be almost planar in the solid state with the phenyl rings only slightly twisted from the general plane of the molecule,[1] and a careful study by Suzuki[2] indicates that it is safe to assume the molecule to be planar in solution as well. The phenyl rings of cis-stilbene are twisted by about 30° to relieve the steric interaction effects in the ortho hydrogens.[3] 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 energy of activation in solution is 46 ± 2.0 kcal/mole[4] and in the vapor phase 42.6 ± 1.0 kcal/mole.[5] 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.[6] Isomerization in solution is catalyzed by radicals such as Br,[7] Lewis acids like $AlCl_3$,[8] and Broensted acids such as H_2SO_4.[9] All have the effect of removing the double bond character from the olefinic bond.

The photochemistry of stilbene adsorbed on solid surfaces, as previously reported,[10,11] exhibits a slightly

altered behavior that is summarized in Figure 1.
Irradiation at 313 nm 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-stilbene. Formation of dihydrophenanthrene
(DHP) occurs to a limited extent with irradiation above
300 nm, but is more significant at shorter wavelengths.
DHP is converted to phenanthrene with oxygen present,
even though the thermal decay to cis-stilbene is
apparently accelerated by alumina or silica gel.[12]
Irradiation of phenanthrene below 300 nm in the presence
of oxygen produces 9,10-phenanthroquinone.

In the above-mentioned studies of adsorbed stilbene,
the resultant irradiation products were all identified
following rapid removal from the surface of the solid
matrix. A careful study by Hecht and Jensen[13] indicates
that trans-stilbene adsorbed on 150°C activated neutral
alumina using vacuum line techniques showed a complete
loss of the trans peak upon irradiation, followed by a
slow return for 22.5 hours at 95°C. The intermediate for
irradiated trans-stilbene adsorbed on alumina was also
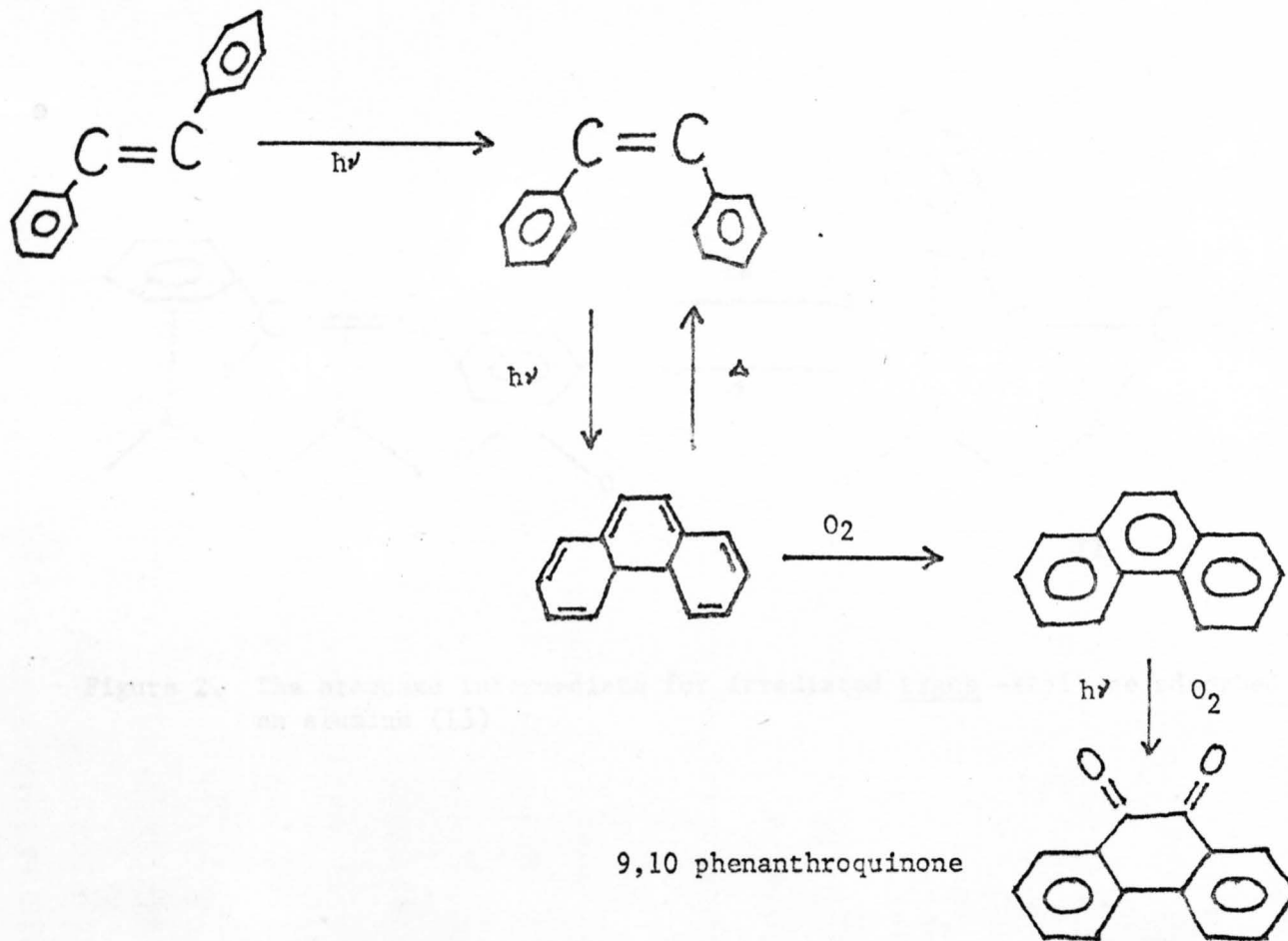proposed (see Figure 2).

9,10 phenanthroquinone

Figure 1. Photochemical behavior of stilbene on a
solid matrix (10,11)

4
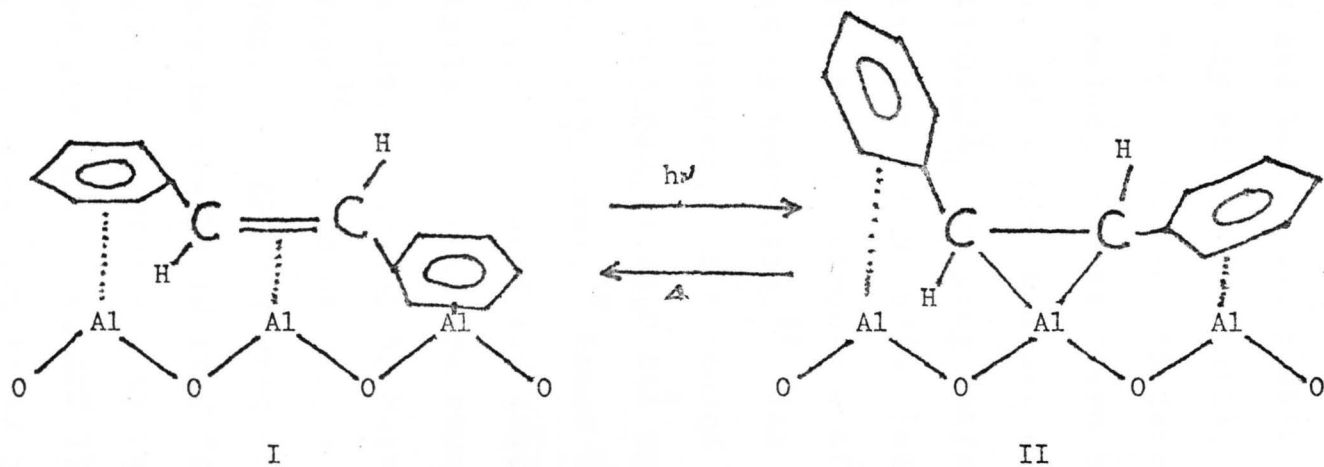
Figure 2. The proposed intermediate for irradiated <u>trans</u> -stilbene adsorbed on alumina (13)

Azobenzene

trans-Azobenzene crystallizes in the monoclinic system and two almost planar centrosymmetrical molecules (which may not be identical) contribute to the asymmetric unit. The structure was described and the mean dimensions of the molecules were given by Robertson.[14] The N = N distance of $1.23 \pm 0.05 \overset{o}{A}$ was determined. The C-N distance is $1.41 \pm 0.03 \overset{o}{A}$, implying conjugation between the benzene ring and the N = N bond. The N = N-C angle is 121.5 ± 3°.

The crystal structure of cis-azobenzene was also studied by Robertson.[14] The system is orthorhombic. The N = N distance, C-N distance and N = N-C valency angle are $1.23 \pm 0.04 \overset{o}{A}$, $1.45 \pm 0.04 \overset{o}{A}$ and 125 ± 4°, respectively.

In 1960, Lewis[15] found that irradiation of azobenzene in 22N sulfuric acid and gives benzo [c] cinnoline (III), and similar results were reported independently and almost simultaneously by Hugelshofer, Kalvoda and Schaffner[16] for solutions in acetic acid containing ferric chloride. In 22N sulfuric acid azobenzene exists almost entirely in the protonated form and it has been shown that cyclization is preceded by rapid trans $\rightleftharpoons$ cis isomerization of the cations (I $\rightleftharpoons$ II).[17] The cyclization in sulfuric acid appears to be a photochemical disproportionation: half the azobenzene undergoes cyclodehydrogenation, the other half undergoes reduction to hydrazobenzene (IV),

which rearranges in acid solution to give benzidine (V).[18] Hence, a sequence of reaction schemes (Figure 3) may be written to describe the photochemical reaction of the parent compound in sulfuric acid. Sometimes the yield of cyclized product exceeds 50%,[19] and it seems likely therefore that the hydrazo compound (IV) also undergoes disproportionation to some extent, yielding the corresponding amine (VI) and the azo compound (I), which then re-enters the cyclization sequence.

Alumina

Infrared studies of hydroxyl groups and adsorbed molecules on solid adsorbents are of wide current interest. Solids imposed serious limitations on such studies. Powders show poor transmission of infrared radiation because of losses from scattering and reflection. Pressed disks give improved transmission, but are poorly permeated by gases and exhibit changes in surface character.

Highly porous alumina aerogel, in transparent plates of essentially uniform thickness and density, has been successfully used by Peri[20] in infrared studies. These plates offer decided advantages in studies of adsorbed molecules at low surface coverages.

Plates were made by controlled slow gelation with ammonia vapor of layers of alumina sol suspended on a
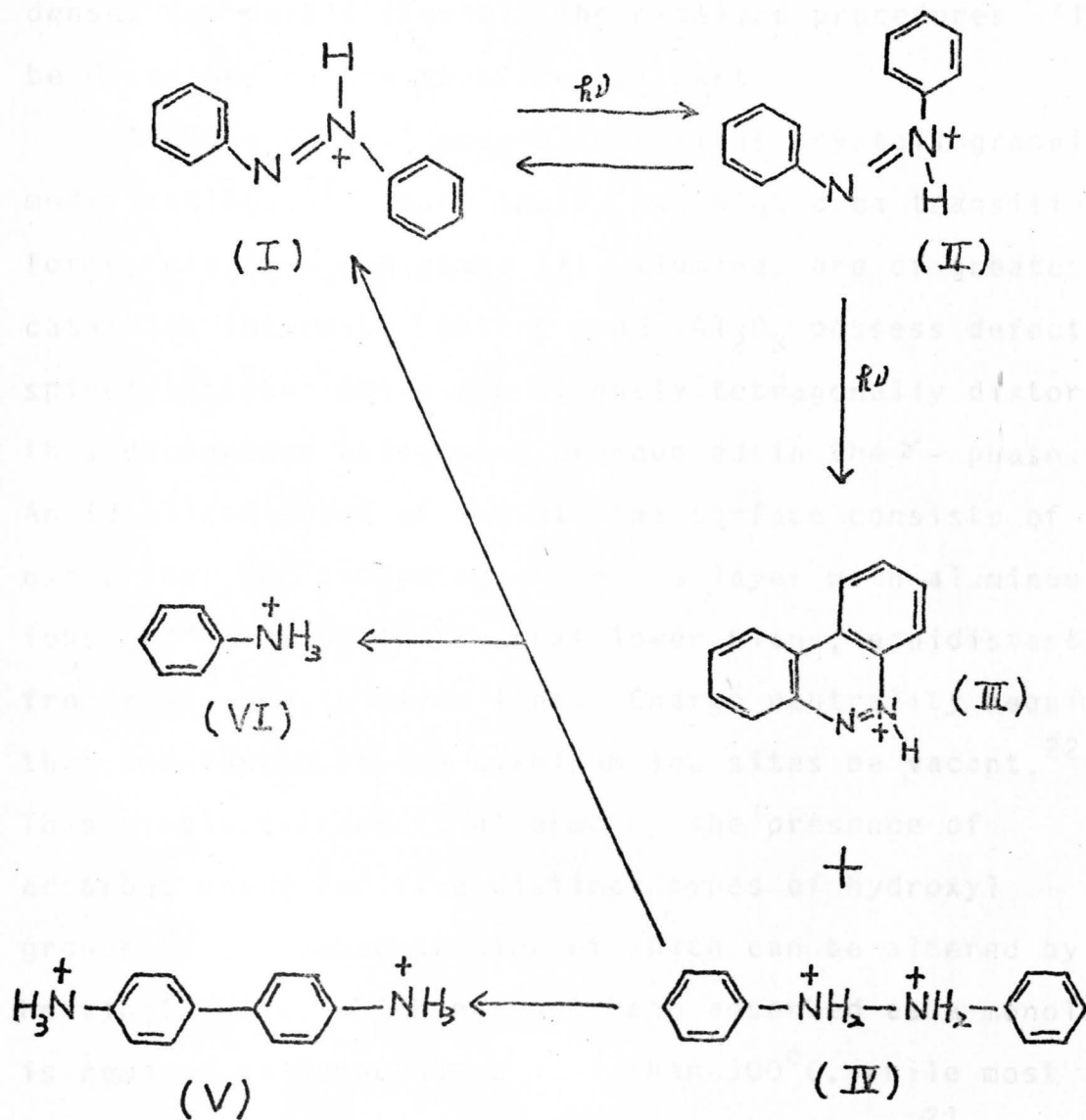
Figure 3. Photochemical reaction of the azo compound in sulfuric acid

dense, immiscible liquid. The detailed procedures will be described in the experimental part.

Alumina (Al_2O_3) occurs in various crystallographic modifications.[21] Among these, two high-area transition forms, eta (η)- and gamma (γ)- alumina, are of greatest catalytic interest. Both η and γ-Al_2O_3 possess defect spinel lattices which are slightly tetragonally distorted, this distortion being more pronounced in the γ- phase. 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. Charge neutrality requires that one-fourth of the aluminum ion sites be vacant.[22] This simple surface is altered by the presence of adsorbed water and five distinct types of hydroxyl groups,[23] the concentration of which can be altered by heating. Water which has not been adsorbed as a monolayer is removed at temperature less than 300°C, while most adsorbed water is lost at higher temperatures.[21] With temperatures between 300° and 800°C, hydroxyl formation can also occur depending upon the availability of water.[24] Three of the five hydroxyl group types can survive at temperatures up to 800°C.[23] The number of exposed aluminum ions increases with the loss of water and hydroxyl groups from the surface.[24]

The adsorption of olefins on the surface of alumina is thought to occur as the result of electrostatic interaction between the π electrons of the olefin and the positive field of the aluminum ion,[22,25] the positive field being greatest directly over the aluminum ion.[22] The exact nature of this interaction seems to depend on the specific environment of an exposed aluminum ion[25] and also possibly upon the availability of empty p-type aluminum orbitals on the surface.[25,26]

Rosynek and Hightower[27] have postulated the existence of four different types of sites on a γ-Al_2O_3, namely A- and B-sites for chemisorption of 1-butene, an I-site for isomerization of 1-butene and an E-site for D_2 exchange. In all cases the sites appear to involve exposed aluminum ions. The alumina surface is extremely complicated. However, for most chemisorption and catalytic processes highly charged defect sites are required.

Silica

Silica occurs in three "common" crystalline forms and in an amorphous form. The three common crystalline forms of silicon dioxide are[28] quartz, which is thermo-dynamically stable below 870°C; tridymite, which is stable from 870 to 1470°C; and cristobalite, which is stable above 1470°C. All three forms are found in nature,

the latter two being in thermodynamically unstable
states. Silica gels are usually obtained by the poly-
condensation of orthosilicic acid, formed from sodium
silicate in aqueous solution, or by hydrolysis of esters
or halides of these acids ($SiCl_4$); porous glasses (96%
silica) are produced by leaching sodium borosilicate
glasses with aqueous solutions of acids or ammonia;
Aerosols (e.g., Aerosil and Cabosil) are formed by the
hydrolysis of $SiCl_4$ at a high temperature in a hydrogen
flame. In 1966 Peri[29] developed a way to prepare strong,
clear silica aerogel plates for infrared study. The
detailed procedures of preparing the plates will also
be described in the experimental part.

McDonald's work[30] represents some of the earliest
infrared studies on surfaces. He studied the infrared
spectra of silanol groups on the surface of Cabosil.
After degassing at $300^{\circ}C$, Cabosil showed three different
frequencies, 3750 cm^{-1} for isolated silanol groups,
3660 cm^{-1} for hydroxyl groups with weak hydrogen bonds,
and 3520 cm^{-1} for strong hydrogen bonds. When the sample
was heated, the absorption at 3520 cm^{-1} receded first;
outgassing at $940^{\circ}C$ led to the disappearance of the peak
at 3660 cm^{-1}, and the intensity of the absorption at
3750 cm^{-1} increased at the same time. The single sharp
band that is observed at 3750 cm^{-1} after the drastic

dehydration at 940°C is attributed to the fundamental stretching vibration of a hydroxyl group attached to a silicon atom on the surface of the silica. The frequency of the band is typical of freely vibrating OH groups, and its symmetrical appearance indicates that there are no interactions between it and other molecules or surface groups. These groups are variously referred to as "free hydroxyl groups" or "isolated silanol groups." The hydration and dehydration of transparent silica plates were studied by Van Roosmalen and Mol.[31] They proposed a mechanism for the hydration of silica gel degassed at 875°K: (1) physical adsorption of water on residual hydrogen-bonded vicinal silanol pairs; (2) formation of more vicinal pairs by hydrolysis of surface siloxanes reached by the growing water aggregates; (3) additional water adsorption on these new hydroxyls. Isolated surface silanols appeared to be hardly involved in water vapor adsorption. In 1962 new chemical methods for the determination of surface hydroxyls were described,[32] using the reaction either with CH_3MgI or CH_3Li, and volumetric measurement of the CH_4 evolved.[33] The amount of methane produced has been used to estimate the number of surface hydroxyl groups per unit surface area. Peterson and co-workers[34] have postulated three kinds of adsorption sites on silica aerogel; namely A sites which

are probably oxygen vacancies on the surface, B sites
which are assigned to paired hydroxyl groups on the
surface, and C sites which comprise 80% of the occupied
surface and are primarily isolated hydroxyl groups.

The nature of the interaction between the surface
hydroxyl groups and the adsorbate has been related to
the electronic nature (ionization potential, polarizabil-
ity) of the adsorbate.[35] In such an interaction, however,
it is clear that the electron distribution in the surface
OH bond must be equally as important as the nature of the
adsorbate. The acidity of the surface hydroxyl groups
is of some importance in the elucidation of the mechanism
of catalytic cracking reactions. The acid hydroxyl
groups have been termed Brønsted sites in order to
distinguish these protonic acids from the electron-
abstracting or Lewis acid sites that exist on many
surfaces.

Infrared Spectroscopy

Infrared spectroscopy has been of great value in
the structural determination of molecules. Its applica-
tion to the study of surface chemistry has provided one
of the most direct means of observing the interactions
and perturbations that occur at the surface during
adsorption, and of determining the structure of the
adsorbed species.

The range from 0.75μ to 200μ, namely, from just out-side the visible region and extending up to the micro-wave region is called the infrared. However, the so-called infrared region usually only covers the range between 2.5 to 16μ; the shorter and longer wavelength regions are called, respectively, the near- and far-infrared regions. Infrared light is also described in terms of wave-numbers, which are the reciprocal of wavelengths expressed in centimeter units.

The absorption is quantized. Therefore, only the infrared beam with a frequency exactly corresponding to that required to raise the energy level of a bond will be absorbed. Actually, vibrational spectra appear as bands rather than lines because a single vibrational energy change is accompanied by a number of rotational energy changes. There are two types of molecular vibrations: stretching and bending. A stretching vibration is a vibration along the bond axis such that the distance between the two atoms is increased or decreased. A bending vibration involves a change in bond angles. Only those stretching and bending vibrations which result in a change in the dipole moment of the molecule are observed in the infrared.

Several considerations for infrared spectroscopic study of surfaces are:[36]

1. The adsorbent must be included in the infrared beam in addition to the requisite number of adsorbed molecules.

2. Most finely divided metal adsorbents show intense absorption of infrared radiation, and are not thermally stable. It is necessary to support these metals on high surface area material of greater stability.

3. The adsorbent particle size is reduced below the wavelength of the radiation used for the purpose of reducing the scattering.

EXPERIMENTAL

Adsorbents

1. Alumina aerogel plate:

The Infrared-transparent alumina aerogel plates have been developed.[37,38] A solution required for making the alumina sol consists of 3.5 l of distilled water and 45 ml of glacial acetic acid contained in a 4 l beaker and heated by a water bath to maintain the temperature at about 122°F. The acetic acid solution was stirred slowly by a mechanical device.

To prepare aluminum amalgam, 0.01115 g of red mercuric oxide was added to 2.5 ml of distilled water and the product was then quickly poured onto 60 g of granulated aluminum metal. Sufficient water was added to cover the metal and the mixture was stirred vigorously to insure uniform amalgamation of the aluminum. The reaction was rapid and before it becomes too violent and after the amalgamation is substantially complete, 50 ml of water was added with stirring and the bulk of the liquid was immediately decanted. The aluminum was then repeatedly rinsed by adding water three times. The resulting aluminum amalgam must be transferred immediately to the acetic acid solution already prepared for converting it into the alumina sol.

The alumina sol was stirred constantly for about 24 hours. After the reaction was completed the resulting sol was centrifuged for settling any suspended particles.

For the purpose of making alumina catalyst, the sol may be coagulated to gel by the addition of ammonium hydroxide. The ordinary 27° Baumé ammonium hydroxide was diluted with an equal volume of water and sufficient was added to adjust the pH value to about 6.8 to 7.8. The liquid was stirred rapidly while the ammonium hydroxide was added until a gelatinous, thick mass was obtained making further stirring practically impossible.

The product may be filtered immediately to remove the bulk of the water. The plates were broken into suitable pieces and carefully transferred to a crystalliz-ation dish containing methanol. The dish was gently swirled once or twice a day, and the methanol was replaced at 2- to 4-day intervals; it was changed at least four times over a 2-week period.

After alcohol exchange, the plates were packed loosely in a glass autoclave liner filled with pure methanol. The liner was placed in a stainless steel autoclave, and methanol was added to fill the autoclave completely, which was then sealed and heated slowly to 260° while the methanol was bled off slowly, as necessary, to keep the pressure below 1500 p.s.i. Between 260°

and 280° bleeding was continued for about 2 hr to maintain the pressure as long as possible in the range from 1200 to 1500 p.s.i. Ultimately, the clear aerogel was removed from the autoclave and calcined in air at 600°C to remove impurities. The plates had specific surface areas of 300 to 350 m^2/g as measured by nitrogen adsorption, and were shown by X-ray analysis to be γ-alumina.[20]

2. Silica Aerogel plate:

The 50 ml of stock solution containing 40 vol% tetraethyl orthosilicate (Fisher Purified) in methanol was mixed with 30 ml of concentrated HCl, filtered, and poured onto mercury in a crystallization dish.[29] The dish was then covered. Within 3 hr, a glass-clear sheet of gel was formed. After an additional 16 hr, the gel was broken into smaller pieces and transferred to a 400 ml bath of 50% aqueous methanol. The following day the bath was changed to 25% aqueous methanol, and later in the day to distilled H_2O. During the following week, the H_2O was changed four times. The gel plates were then aged for 4 hr in H_2O at 100°C in a closed autoclave. They were then transferred to 50% aqueous methanol, and after a few hours, to absolute methanol. After three successive changes of methanol (400 ml each) during the next week, the plates were transferred to a glass autoclave liner.

Methanol was added to fill the liner completely, and the plates were autoclaved at 250-300°C while methanol was vented slowly to maintain pressure between 1200 and 1500 p.s.i. until most of the methanol had been vented. After the pressure had dropped to 1 atm, the autoclave was then cooled for two hours.

The final plates were relatively flat, transparent, and free from cracks. Surface areas, after calcination in air at 600°C for 2 hr, were 750-850 m^2/g as measured by N_2 adsorption.[29]

Adsorbates

The trans-stilbene was obtained from Eastman Organic Chemicals and was scintillation grade. It was used as received.

The azobenzene was obtained from Matheson, Coleman and Bell. It was used as received.

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 10^{-6} Torr without sample and 10^{-5} Torr with unheated sample system. Manifold pressures were monitored by a Kontes/Martin M-403120 cold cathode vacuum gauge system.

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 Oriel interference filter.

Infrared Cell

The pictures of the infrared cell, which was con-structed of Pyrex, are shown in Figures 4 and 5. Calcium fluoride windows were sealed with the mixture of 3120 RTV encapsulant and RTV catalyst F (Dow Corning). The "Sealit" from Fisher was used to seal any pinholes found in the cell, and Apiezon T grease was used for the ground joints and stopcock. Furnace area was made by winding nichrome wire.

The sample disks were mounted in a sample holder at the other end of a long glass rod from the remotely

to vacuum system

℥ 14/35

CaF$_2$
window

℥ 34/45

furnace
area

thermocouple
well

℥ 19/22

−magnet

adsorbate
bulb

sample
holder

glass rod
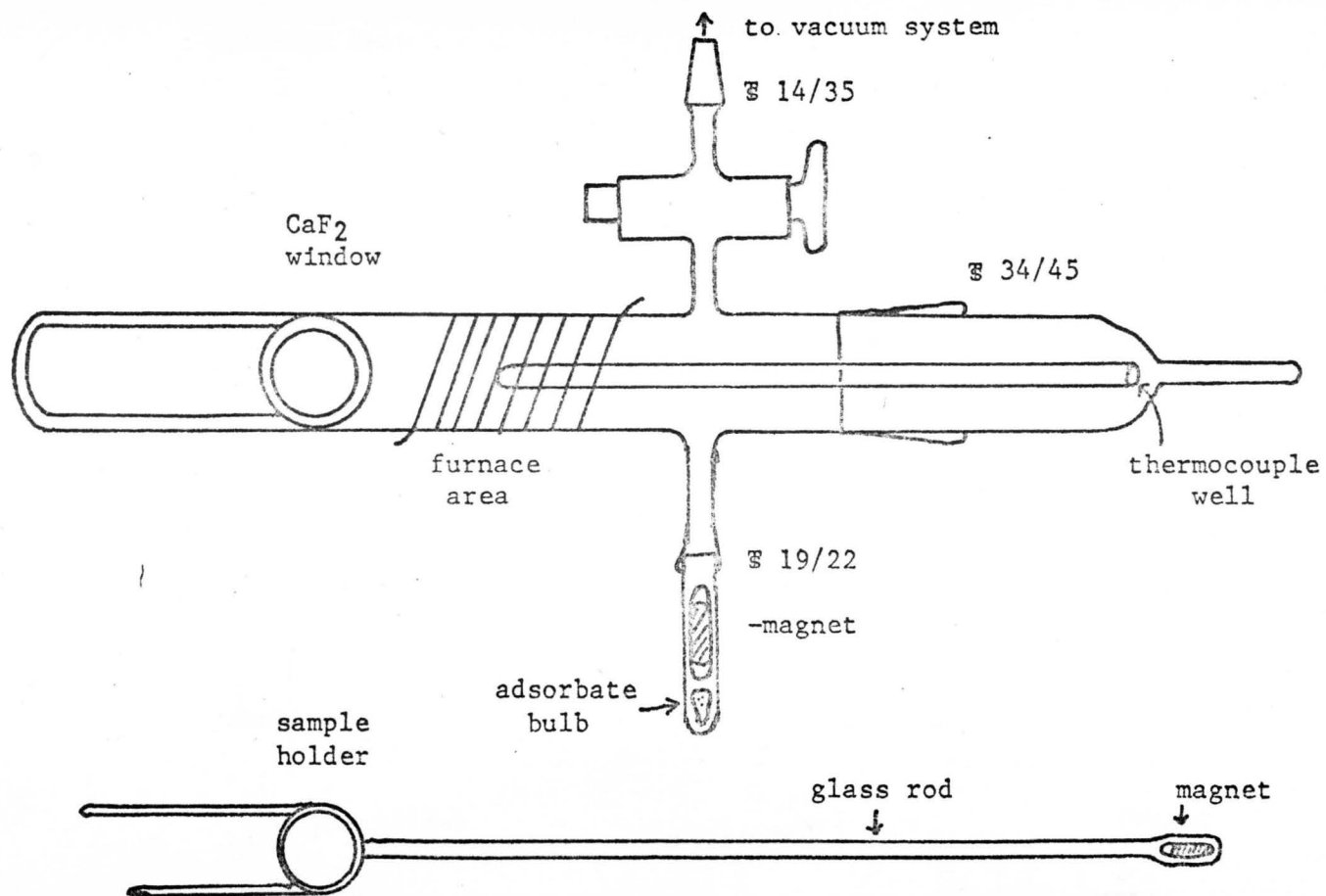
magnet

Figure 4. The side view of the infrared cell

infrared beam

↓

CaF$_2$ window

furnace area

thermocouple well

sample holder

glass rod

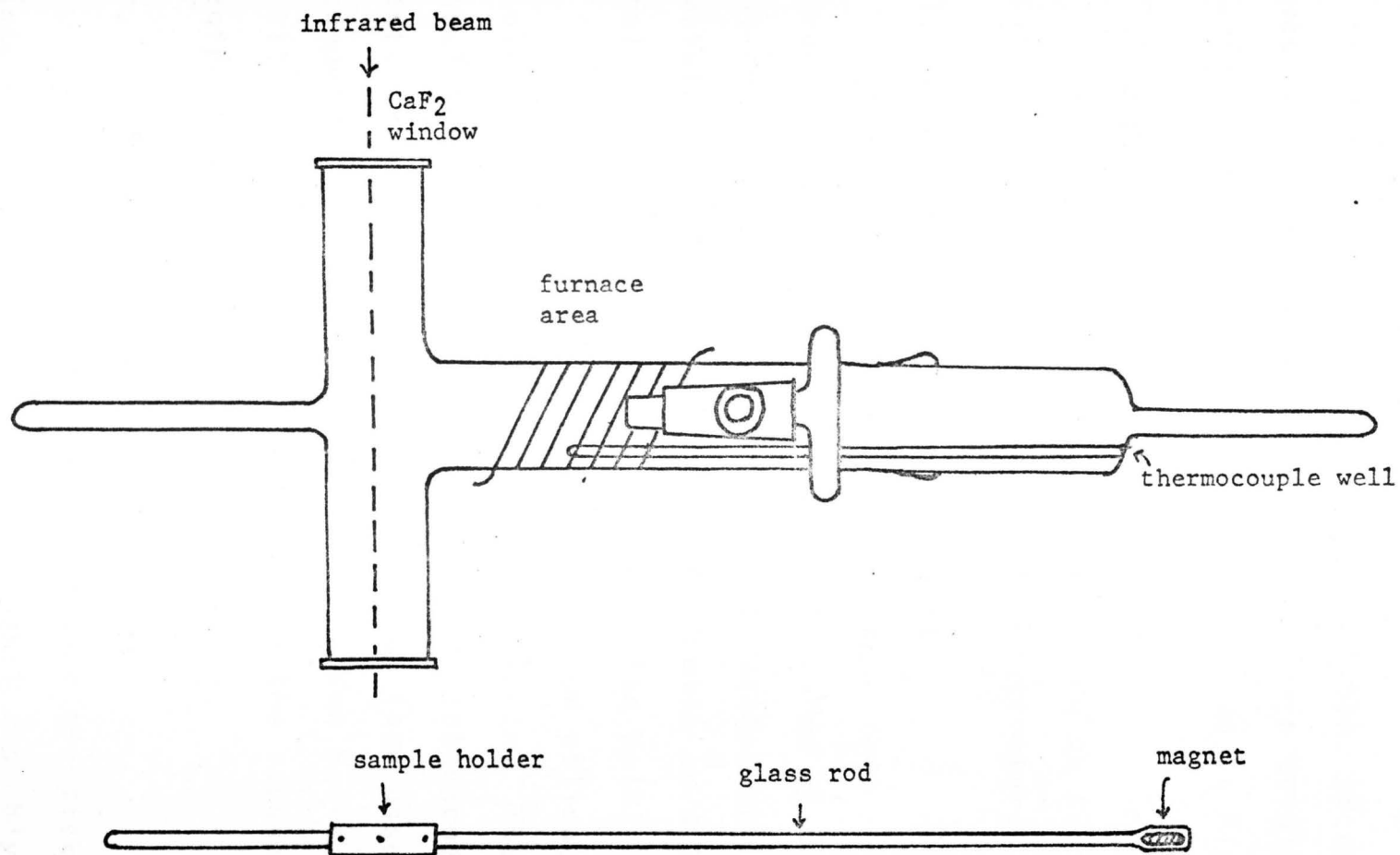magnet

Figure 5. The top view of the infrared cell

controlled magnet, and could be moved between the furnace section and the infrared beam.

The adsorbate, either trans-stilbene or azobenzene, was sealed into a small bulb before each trial, and the bulb was then put into the tube as shown in Figure 4.

Procedures

The infrared spectra were recorded on the Perkin-Elmer 521 grating infrared spectrophotometer.

1. Before Activating the Adsorbent:

The trans-stilbene, approximately 1.80×10^{-3} moles/gram of alumina or 3.73×10^{-4} moles/gram of silica, was placed in the bulb. In the case of azobenzene, approximately 1.24×10^{-3} moles/gram of alumina or 4.74×10^{-4} moles/gram of silica, was placed in the bulb.

A suitable disk, either alumina or silica, was selected and mounted in the sample holder. The bulb sealed with either trans-stilbene or azobenzene was put into the tube. The infrared cell was then assembled and connected with the vacuum system. A few hours later the cell was closed-off and removed from the vacuum line for infrared recording.

2. Adsorbent Activation:

Reconnecting with the vacuum line the disk was moved into the furnace via the remote magnet assembly. The cell

was evacuated, and then flushed with oxygen several times. For the purpose of calcining the disk, oxygen was admitted to the cell until a pressure of 200 mm was reached, and the cell was closed-off immediately. The aerogel disk was heated for 1 to 5 hours at a given temperature which was measured by a chromel-alumel thermocouple gauge (Assembly Products). A crushed ice bath was used for the reference junction.

Subsequently, the disk was heated at the given temperature for 15 minutes with the opening of the cell. After cooling to room temperature, the cell was closed-off and detached from the vacuum line before the spectra were recorded.

3. Adsorbate Introduction:

The cell was returned to the vacuum line and out-gassed until the pressure of 10^{-6} Torr was reached with the trapping of liquid nitrogen. Adsorption of various adsorbates was carried out at low pressures.

At the pressure of 10^{-6} Torr, the cell was closed-off and the bulb was broken by dropping the magnet. The adsorbate was diffused on the surface of aerogel disk either with the help of heatgun or placing the whole cell into the oven to facilitate the volatilization. The spectra were recorded after the cell was evacuated for a half hour to remove the excess amount of adsorbate.

4. Irradiation:

The sample was 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 spectra were recorded after the irradiation.

5. Dark Reaction:

It is known that under certain conditions irradiating a sample of adsorbed stilbene or azobenzene on the surface of alumina or silica causes a change in the sample. The change is reversible when the sample is allowed to sit for a period of time. The reverse reaction following irradiation is known as the dark reaction.[13,40]

The infrared spectrum was measured after a period of time to see if a dark reaction had occurred.

RESULTS AND CONCLUSIONS

trans-stilbene adsorbed onto alumina trials

Trial 1. alumina activated at $400^{\circ}C$:

The band at 3700 cm^{-1} attributed to isolated hydroxyl groups disappeared by the adsorption of trans-stilbene and a broad absorption band appears between 3640-3520 cm^{-1}. The band at 1330-1270 cm^{-1} corresponding to olefinic CH = CH in-plane bending is unchanged after irradiation. The irradiation, however, did somewhat decrease the intensity of the bands which are attributed to aromatic C = C stretching. The dark reaction has not been observed at this trial. The characteristic bands are summarized in table 1 and infrared spectra are attached in the Appendix.

Trial 2. alumina activated at $300^{\circ}C$:

Similarly, the band at 3700 cm^{-1} attributed to isolated hydroxyl groups disappeared by the adsorption of trans-stilbene and a broad absorption band appears around 3640-3540 cm^{-1}. The band at 1330-1290 cm^{-1} corresponding to olefinic CH = CH bending disappeared by irradiation. The band intensity of aromatic C = C stretching vibration is decreased upon irradiation. The detailed information can be obtained from table 2 and the infrared spectra in the Appendix.

Table 1. Characteristic peaks of infrared spectra.

position, cm^{-1}	1	2	3	4	designation
3700	x	-	-		isolated hydroxyl group stretch
2910, 2840	x	x	x		?
2330	x	x	x		?
1590-1560	x	x	x		
1470	x	-	-		alumina's peaks and -OH bend
1365	x	-	-		
3640-3520		x	x		hydroxyl group stretch
3050, 3020		x	x		aromatic CH stretch
2500		x	-		? noise
1590-1550		x	x		
1490		x	x		aromatic C = C stretch
1450-1420		x	x		
1330-1270		x	x		olefinic CH = CH in plane bend
1960			x		
1870			x		aromatic C
1800			x		

Remarks:

1 = activated alumina at 400°C for 1.5 hours
2 = trans-stilbene adsorbed onto alumina
3 = after irradiation
4 = dark reaction (not observed)
x = appearance
- = disappearance

Table 2. Characteristic peaks of infrared spectra

position, cm^{-1}	1	2	3	4	designation
3700		x	-	-	isolated hydroxyl group stretch
2960-2920		x	x	x	?
2330		x	x	x	?
1570		x	x	x	
1460		x	x	x	alumina's peaks and hydroxyl group bend
1350		x	-	-	
1260		x	x	x	?
3640-3540			x	x	hydroxyl group stretch
3060, 3030			x	x	aromatic CH stretch
1600-1570			x	x	
1495			x	x	aromatic C = C stretch
1455			x	x	
1380			x	x	?
1330-1290			x	-	olefinic CH = CH in plane bend

Remarks:

1 = activated alumina at 300°C for 2 hours

2 = trans-stilbene adsorbed onto alumina

3 = after irradiation

4 = dark reaction (not observed)

x = appearance

- = disappearance

Trial 3. alumina activated at $103^{\circ}C$:

From table 3, it will be observed that the broad band at 3600-2980 cm^{-1} is unchanged during this trial. This broad band is attributed to the combination of molecular water and hydroxyl groups. The bands at 1330 cm^{-1} and 1290 cm^{-1}, corresponding to olefinic CH = CH bending, disappeared upon irradiation. The decreased intensity was also observed for the bands of aromatic C = C stretching vibration after irradiation. There are no significant changes which have been observed for the bands corresponding to dark reaction.

From the results of these three trials we can draw five possible conclusions. First, the band at 3700 cm^{-1} disappears by the adsorption of trans-stilbene and a broad absorption band appears at lower frequency. Th:s phenomenon indicates that only weak interaction occurs between the hydroxyl groups and the adsorbate. Peri[39] observed the same situation when butene adsorbed on the surface of alumina aerogel.

Second, the band of olefinic CH = CH bending of trial 1 does not disappear after irradiation. There is one possible explanation for this. As the surface is activated at temperatures higher than $400^{\circ}C$, adjacent hydroxyl ions are considered to condense and eliminate water, leaving oxide ions on the surface. Underlying

Table 3. Characteristic peaks of infrared spectra.

position, cm^{-1}	1	2	3	4	designation
3600-2980	x	x	x	x	molecular water and hydroxyl group stretch
2830	x	x	-	-	?
2330	x	x	x	x	?
1590-1450	x	x	x	x	alumina's and hydroxyl group bend
several peaks between 2000-1800	x	x	x		aromatic C
1590-1550	x	x	?		
1495	x	x	x		aromatic C = C stretch
1450	x	x	x		
1380	x	-	-		?
1330, 1290	x	-	-		olefinic CH = CH in plane bend

Remarks:

1 = activated alumina at 103°C for 5 hours

2 = trans-stilbene adsorbed onto alumina

3 = after irradiation

4 = dark reaction observed after 16 hours

x = appearance

- = disappearance

aluminum ions are considered to be exposed to the surface by spaces, too narrow for the adsorption of molecules, between the superimposed oxide ions in the outer layer. Peri[23,39] suggested that if the surface hydroxyl content decreases below 33 percent of the original value, these results either the formation of (a) adjacent aluminum ions exposed to the surface, or (b) an oxide ion with four nearest neighbors of its own kind in the outermost layer. Peri considered that the defect structure of the type (a) might possibly accommodate olefins by coordinating their π-electrons in a manner similar to that in metal-olefin coordination complexes. The complex for irradiated trans-stilbene adsorbed on 400°C activated alumina is possibly the structure I of Figure 2 which was proposed by Hecht and Jensen.[13] The formation of the dative sigma bond forces a change in the SP^2 hybridization which lifts the phenyl rings from the surface (structure II). 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 maintain the phenyl rings in the planar configuration. The result is a weakening of the dative sigma bond. Therefore, in this complex the double bond is preserved and

there is no significant change of the olefinic CH = CH bending during this trial.

Third, the band corresponding to olefinic CH = CH bending disappeared upon irradiation for alumina activated at lower temperatures. When alumina is heated at lower temperature, some of the adsorbed water is desorbed while some reacts to form hydroxyl groups. It is believed that either molecular water or hydroxyl groups are involved in this reaction. Hecht[40] suggested a kind of reaction which might be concerned with this case (Figure 6). The radiation possibly leads to the formation of surface peroxides, which are known to yield epoxides through interaction with olefins.

Fourth, from the infrared spectra it is obvious that the intensity of the bands corresponding to aromatic C = C stretching is decreased less for the trial 1 than that for the other two trials upon irradiation. The intensity of an infrared band is proportional to the square of the derivative of the dipole moment with respect to distance along a normal coordinate associated with a particular vibrational mode. This indicates that the interaction between phenyl rings and surface aluminum ions of trial 1 is strongly bonded. The fact that the band intensity of trials 2 and 3 decreases upon irradiation is suggested to be an indication of a
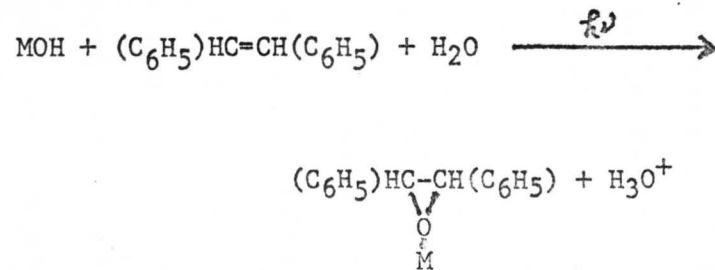
$$\text{MOH} + (C_6H_5)HC=CH(C_6H_5) + H_2O \xrightarrow{\hspace{0.3cm} h\nu \hspace{0.3cm}}$$

$$(C_6H_5)HC-CH(C_6H_5) + H_3O^+$$
$$\underset{\underset{M}{\overset{\dot{O}}{|}}}{\vee}$$

Figure 6. The suggested reaction when <u>trans</u>-stilbene adsorbed onto
lower activated alumina

weakening of the bond between the phenyl groups and the surface.

Fifth, there is no dark reaction which has been observed for these three trials.

Azobenzene adsorbed onto alumina trials

Trial 1. alumina activated at $400^{o}C$ (table 4):

The bands at 1364 cm^{-1} and 1345 cm^{-1} are attributed to the aromatic C-N stretching. These bands disappeared by irradiation, but the recovery was not observed after 15 hours.

Trial 2. alumina activated at $105^{o}C$ (table 5):

The anticipated band of aromatic C-N stretching can not be observed after the adsorption of azobenzene, and there is no significant change during this trial.

In conclusion, it is believed that the N = N double bond character is changed by irradiation, but the actual situation remains unknown. The investigator considers two kinds of intermediate, where either an aluminum ion or an oxide ion is bonded to both nitrogen atoms. In either case the N = N double bond character can not be preserved. The reverse reaction has not been observed. The bands of aromatic C-N stretching have not been observed on trial 2 which is possibly due to the perturbation by the bands of molecular water and/or hydroxyl groups.

Table 4. Characteristic bands of infrared spectra.

position, cm^{-1}	1	2	3	4	designation
3720		x	-	-	-	isolated hydroxyl group stretch
2330	x	x	x	x	?
1557	x	x	x	x	
1480, 1465, 1445	x	x	x	x	alumina's band and hydroxyl group bend
1380-1374	x	-	x	x	
3670		x	x	-	hydroxyl group stretch
3050, 2960, 2930		x	x	x	aromatic CH stretch and alumina's
1557, 1480, 1455		x	x	x	aromatic C = C stretch
1364, 1345		x	-	-	probably C-N stretch
1295, 1270		x	x	x	?
3580				x	hydroxyl group stretch

Remarks:

    1 = alumina activated at 400°C for 2 hours

    2 = azobenzene adsorbed onto alumina

    3 = after irradiation

    4 = dark reaction

    x = appearance

    - = disappearance

Table 5.   Characteristic bands of infrared spectra.

position, cm^{-1}	1	2	3	4	designation
broad band 3600-3000	x	x	x	x	molecular water and hydroxyl groups stretch
2330	x	x	x	x	?
broad peak 1560-1540	x	x	x	x	?
1500, 1450-1430	x	-	-	-	?
1560		x	x	x	
1475		x	x	x	aromatic C = C stretch
1450		x	x	x	
several peaks between 2000-1800		x	x	x	aromatic C

Remarks:

1 = alumina activated at 105° for 2.5 hours

2 = azobenzene adsorbed onto alumina

3 = after irradiation

4 = dark reaction

x = appearance

- = disappearance

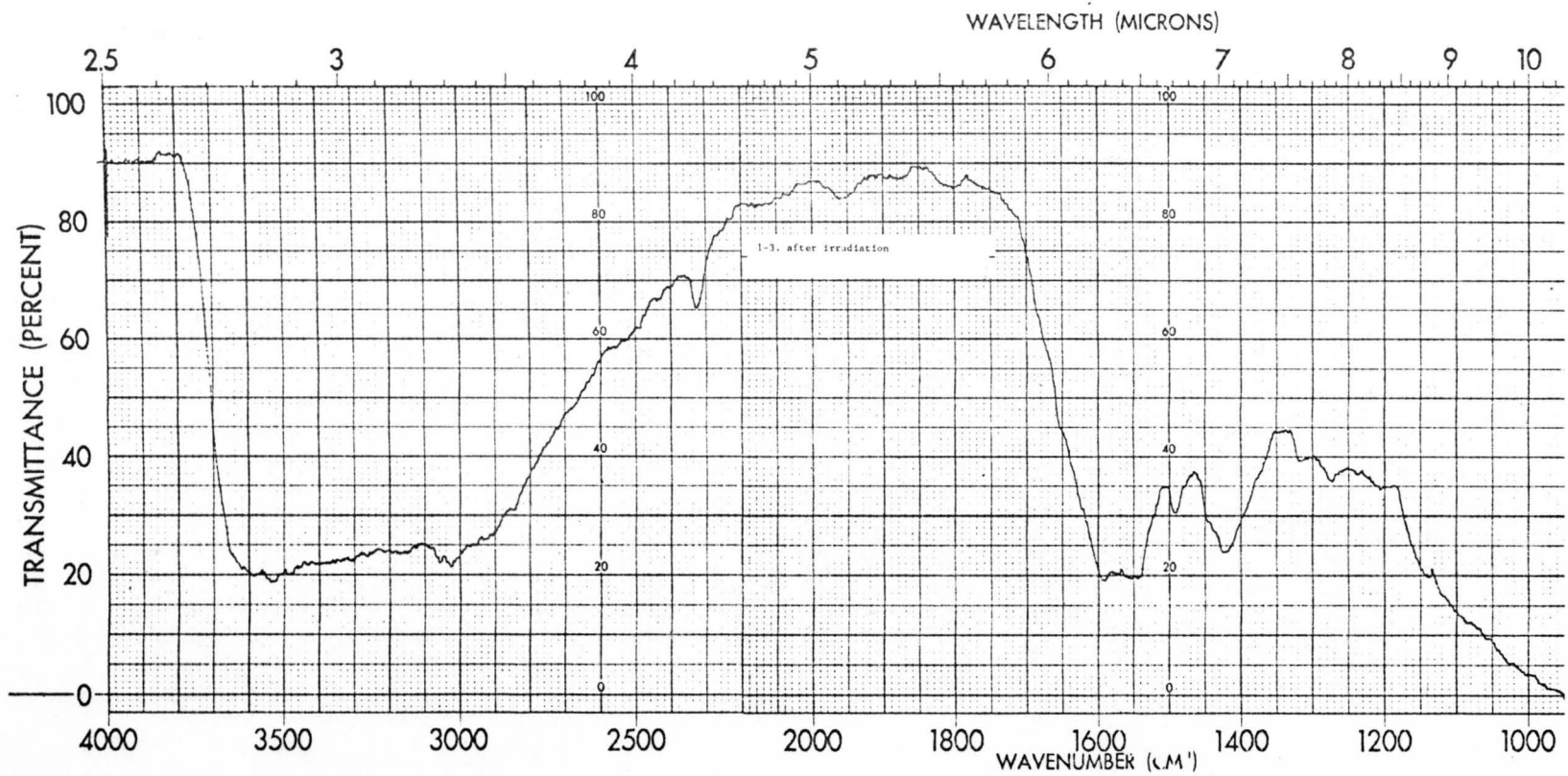trans-stilbene or azobenzene adsorbed onto silica trials

From table 6, table 7 and infrared spectra, it will be observed that intense absorption bands of silica exclude frequencies below 2000 cm^{-1} from study. Therefore, similar observations can not be made for aliphatic bands of adsorbed trans-stilbene or azobenzene.

Catalytic studies show that the surface of alumina is more active toward chemical interaction with electron-donor molecules than a silica surface. Since the properties of the hydroxyl groups of an alumina surface with reference to interaction with adsorbed molecules do not appreciably differ from those of the hydroxyl groups of silica, the difference in chemical activity may be due to the existence of other, more active adsorption centers on the alumina surface.

Table 6.   Characteristic bands of <u>trans</u>-stilbene adsorbed onto silica aerogel.

position, cm^{-1}	1	2	3	4	designation
broad band 3680-3580	x	x	x	x	Hydrogen bonded OH stretch
2950	x	x	x	x	?
2850	x	x	x	x	?
1875	x	x	x	x	SiO combination
1630	x	x	x	x	HOH bend
3060		x	x	x	aromatic CH stretch
3030		x	x	x	
2990		x	x	x	?
2250				x	probably SiH stretch

Remarks:

1 = silica activated at 300°C for 2 hours

2 = <u>trans</u>-stilbene adsorbed onto silica

3 = after irradiation

4 = dark reaction observed after 5 days

x = appearance

Table 7. Characteristic bands of azobenzene adsorbed
           onto silica aerogel.

position, cm^{-1}	1	2	3	4	designation
broad band 3740-3620	x	x	x		Hydrogen bonded OH stretch
2950	x	x	-		?
2850	x	x	x		?
2240	x	x	x		probably SiH stretch
3050		x	x		aromatic CH stretch
2310, 2370		x			?

Remarks:

1 = silica activated at $300^{o}C$ for 2 hours

2 = azobenzene adsorbed onto silica

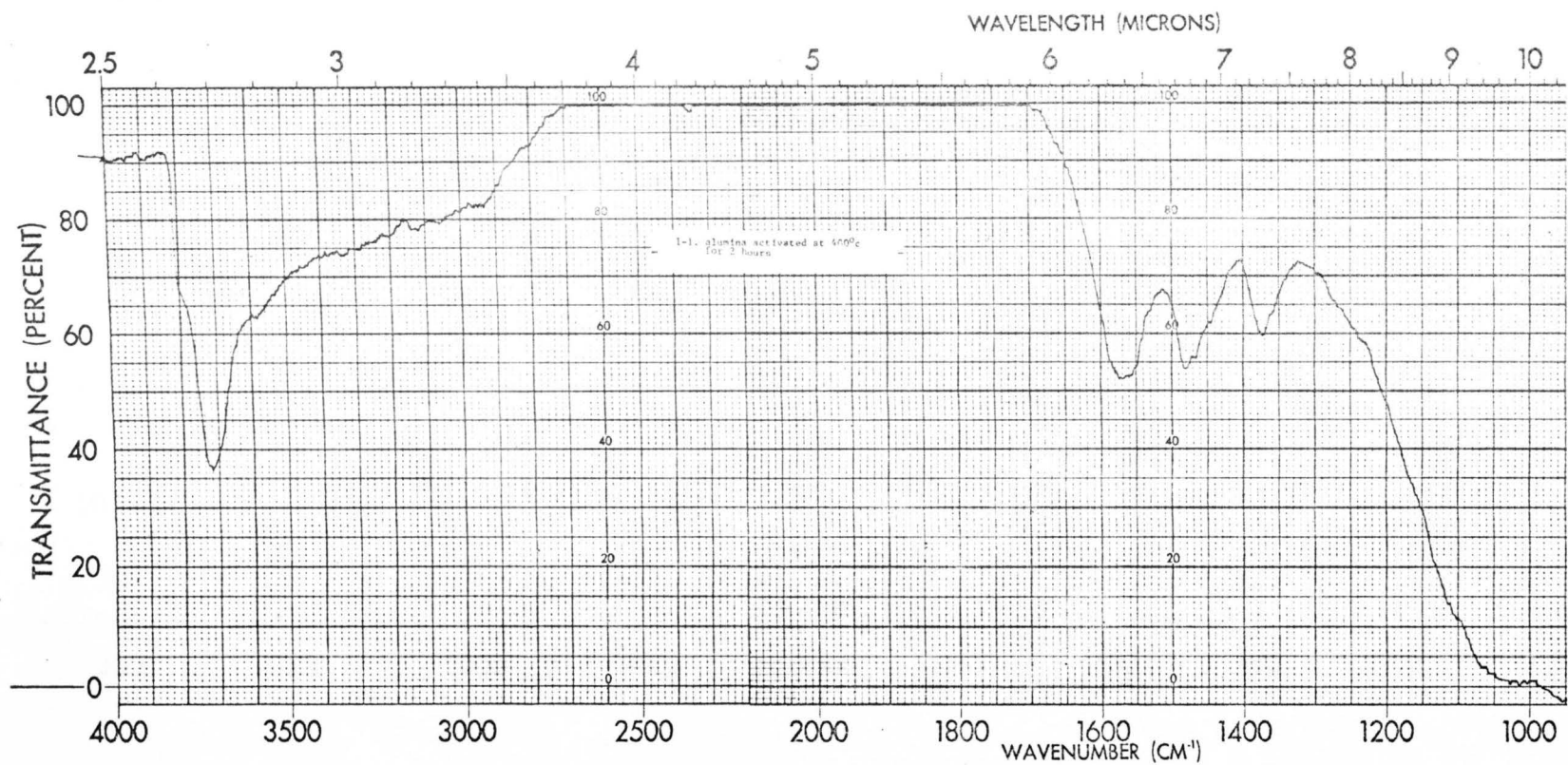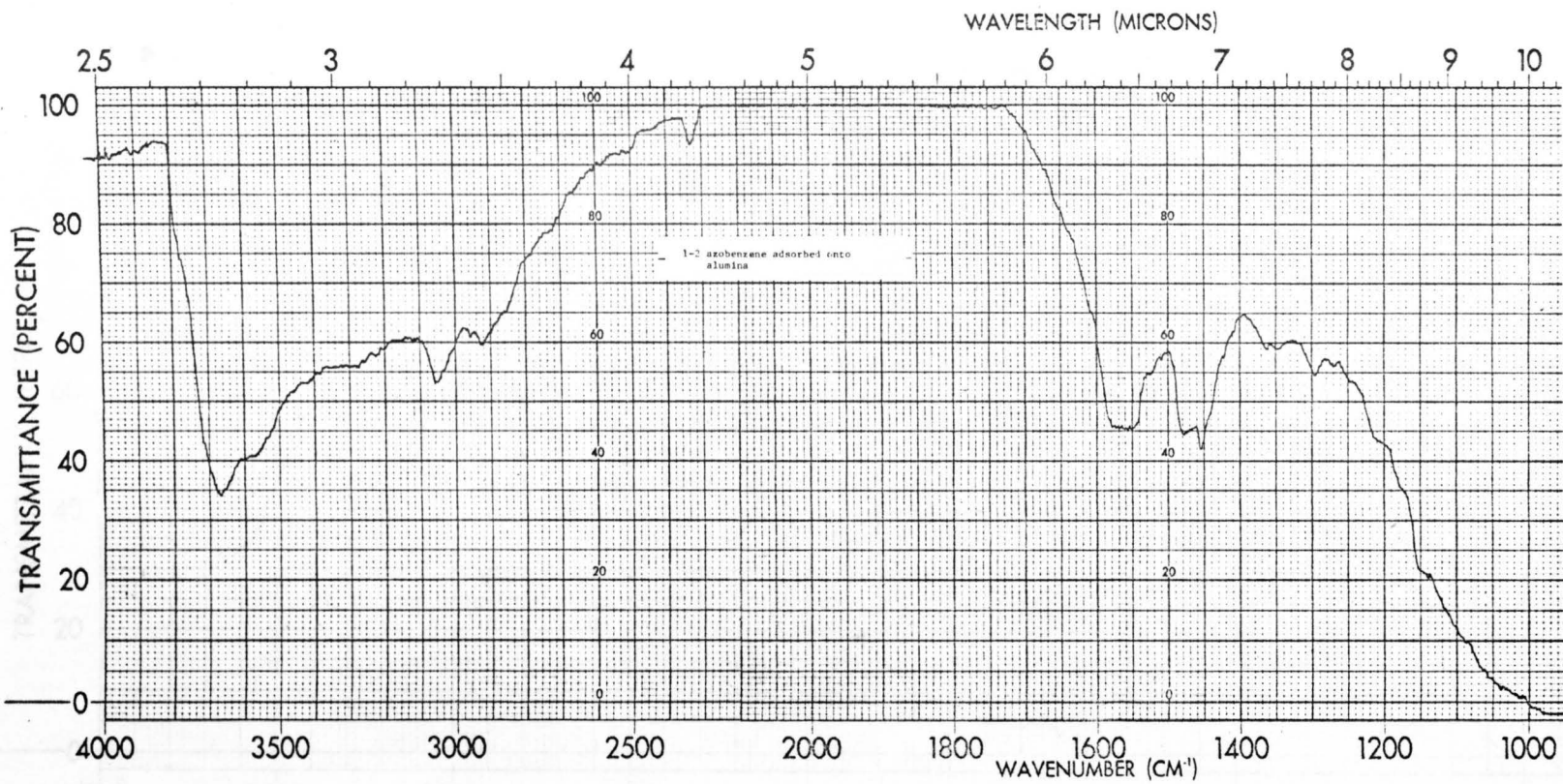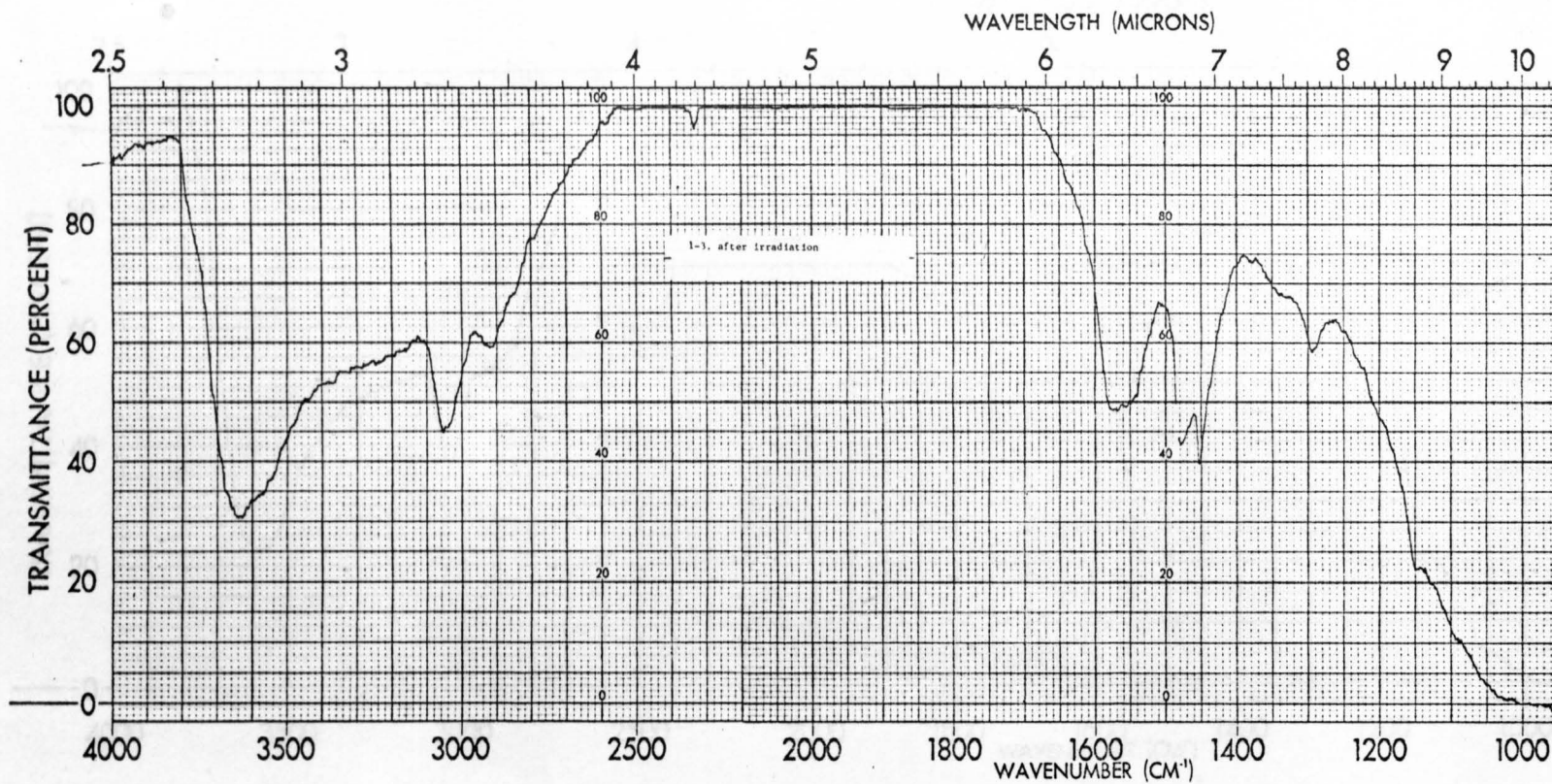3 = after irradiation

4 = dark reaction (not observed)

x = appearance

- = disappearance

trans-Stilbene adsorbed onto alumina trials

trial 1

WAVELENGTH (MICRONS)

APPENDIX

1-?, trans-stilbene adsorbed onto
alumina

WAVELENGTH (MICRONS)

TRANSMITTANCE (PERCENT)

WAVENUMBER (CM⁻¹)

41

WAVELENGTH (MICRONS)

1-3. after irradiation

TRANSMITTANCE (PERCENT)

WAVENUMBER (CM⁻¹)

42

trial 2

WAVELENGTH (MICRONS)

2-1. alumina activated at 300°c
for 2 hours

TRANSMITTANCE (PERCENT)

WAVENUMBER (CM⁻¹)

43

2-2. trans-stilbene adsorbed onto alumina

WAVELENGTH (MICRONS)

2-3. after irradiation

trial 3

46

WAVELENGTH (MICRONS)

3-2, trans-stilbene adsorbed onto alumina

WAVELENGTH (MICRONS)

1-3, after irradiation

WAVELENGTH (MICRONS)

3-4. dark reaction observed
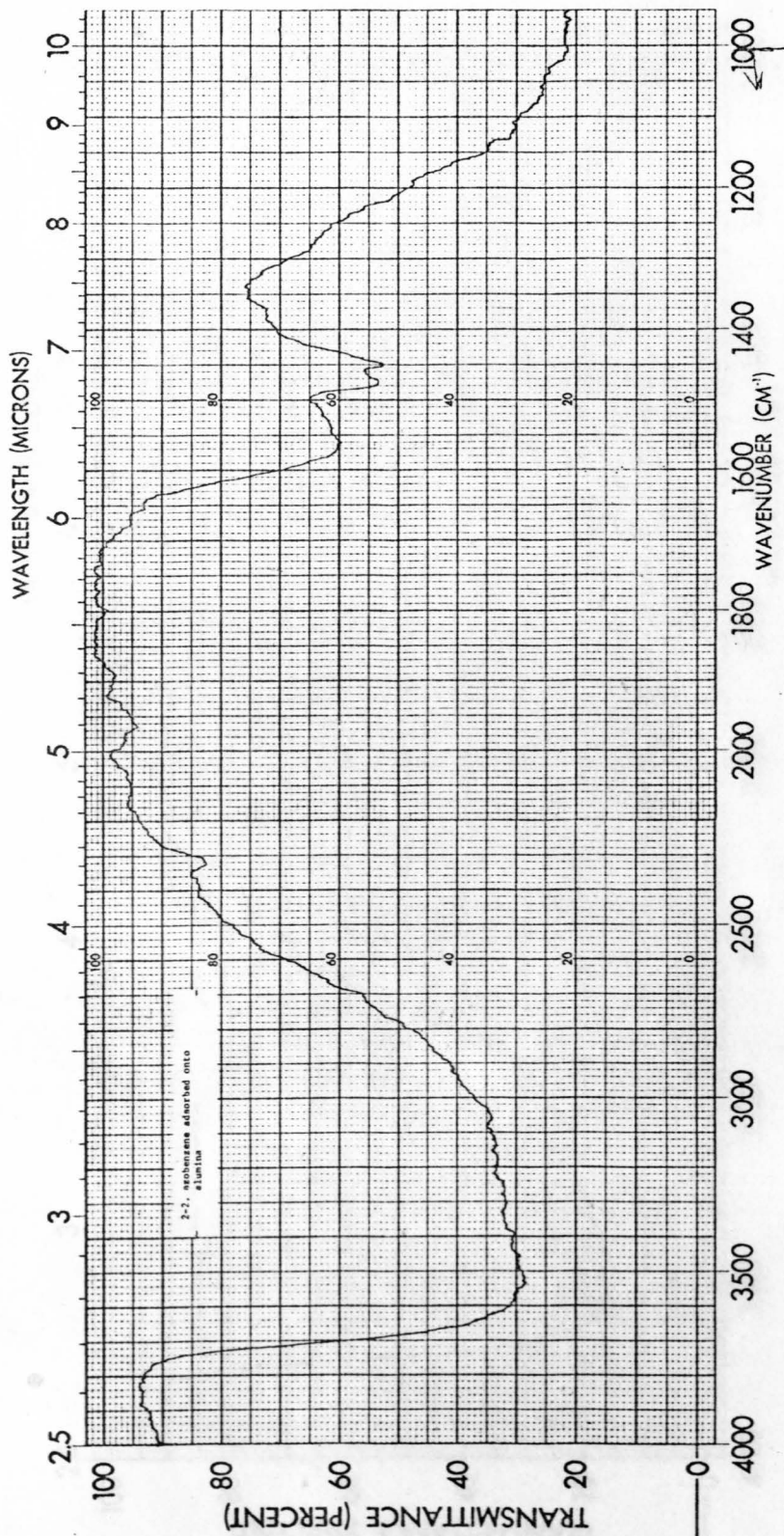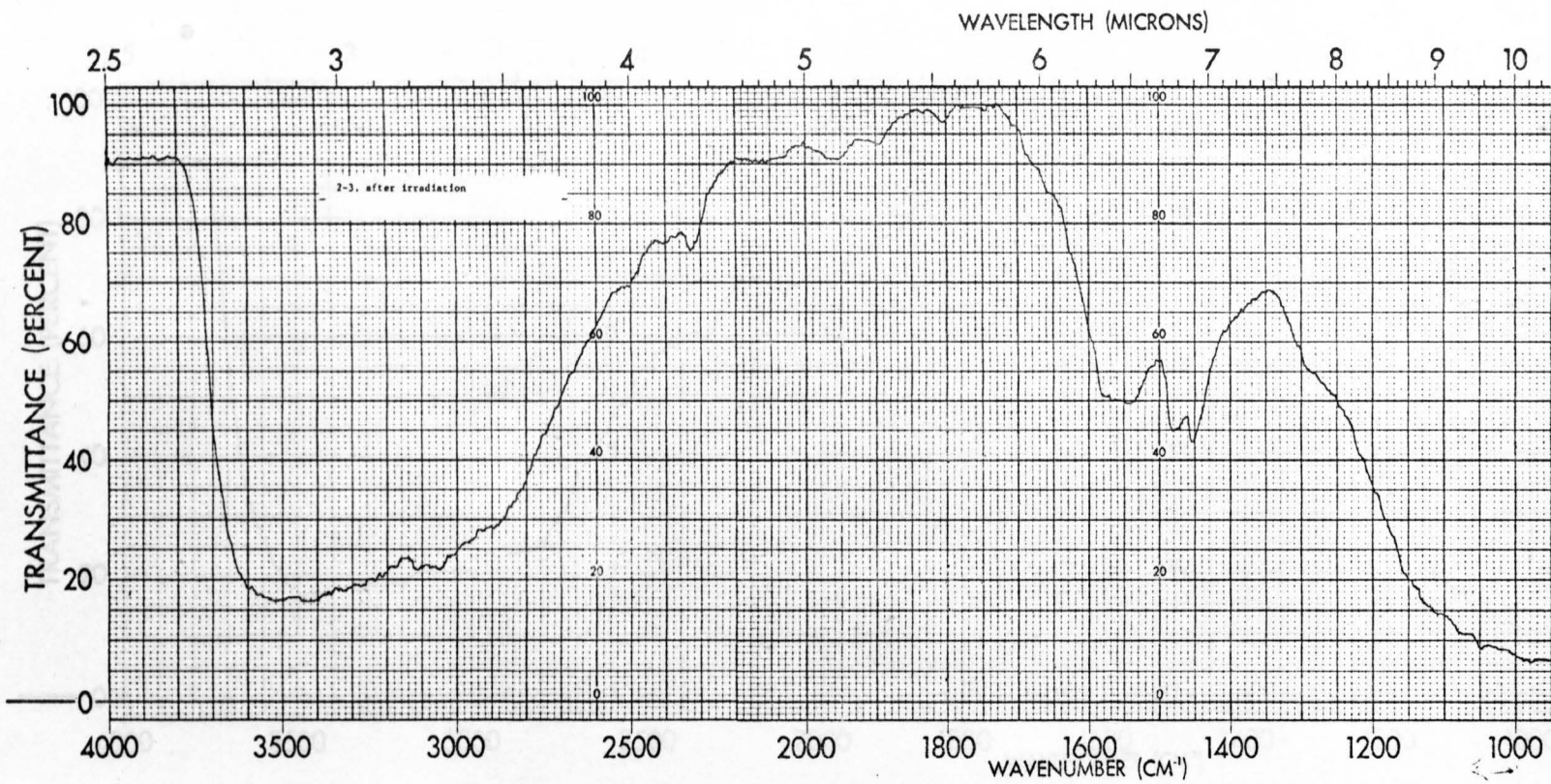after 16 hours

Azobenzene adsorbed onto alumina trials

trial 1

WAVELENGTH (MICRONS)

TRANSMITTANCE (PERCENT)

WAVENUMBER (CM⁻¹)

1-1. alumina activated at 400°c
for 2 hours

1-2 azobenzene adsorbed onto
alumina

51

WAVELENGTH (MICRONS)

1-3, after irradiation

WAVELENGTH (MICRONS)

1-4, dark reaction observed
after 15 hours

WAVELENGTH (MICRONS)

2-1. alumina activated at 105°c for 2.5 hours
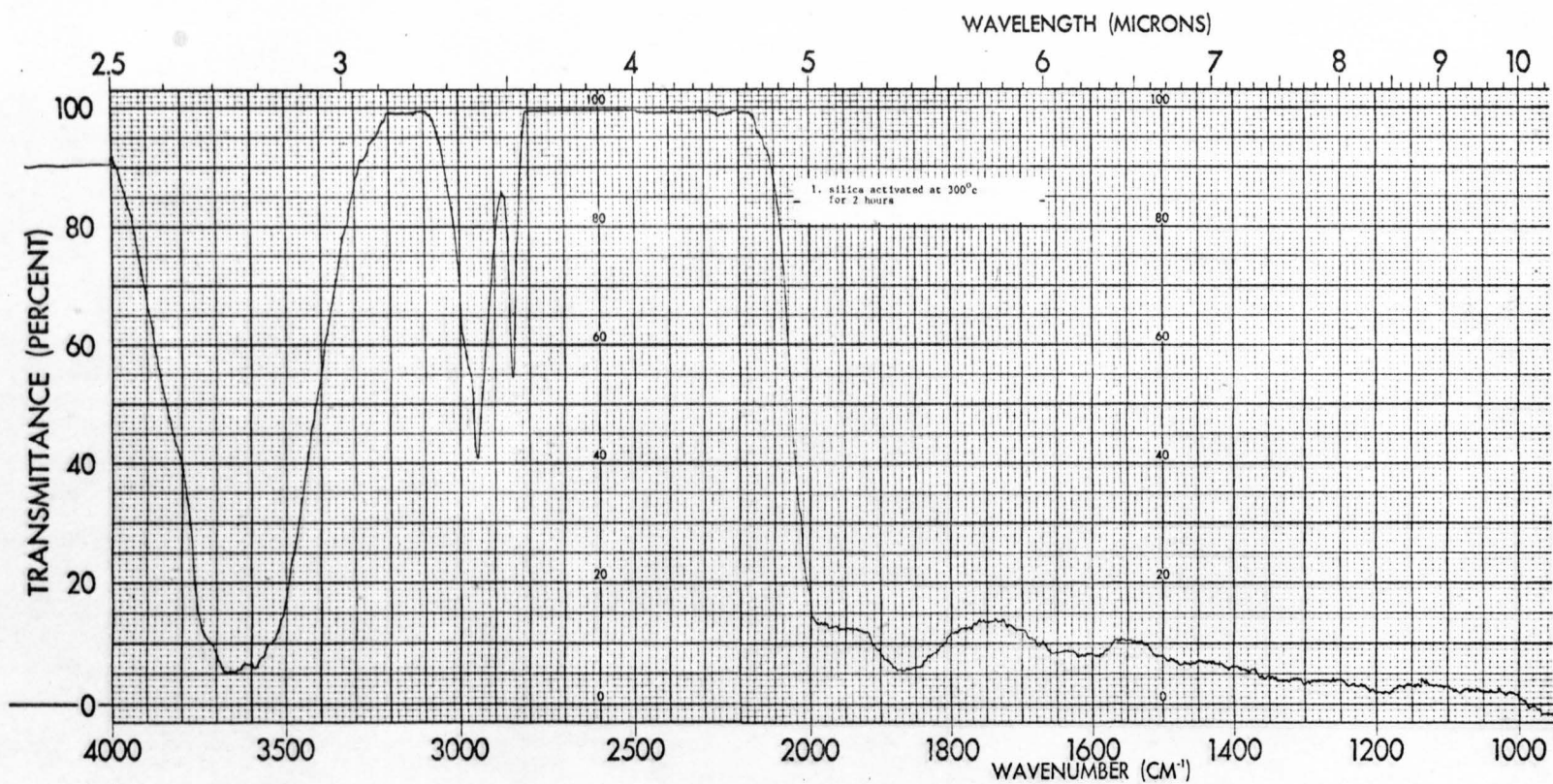
2-2, azobenzene adsorbed onto alumina

2-3. after irradiation

56
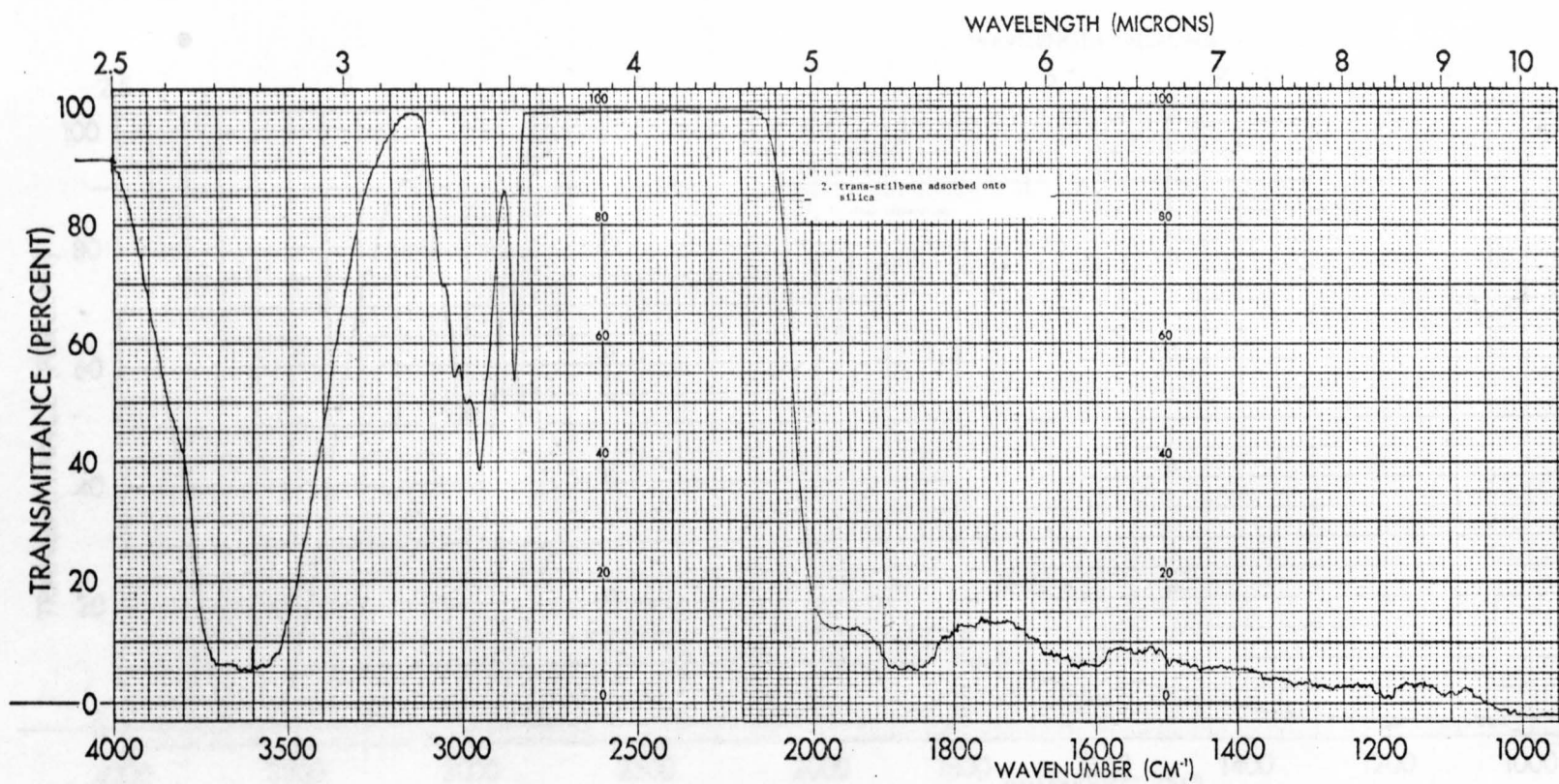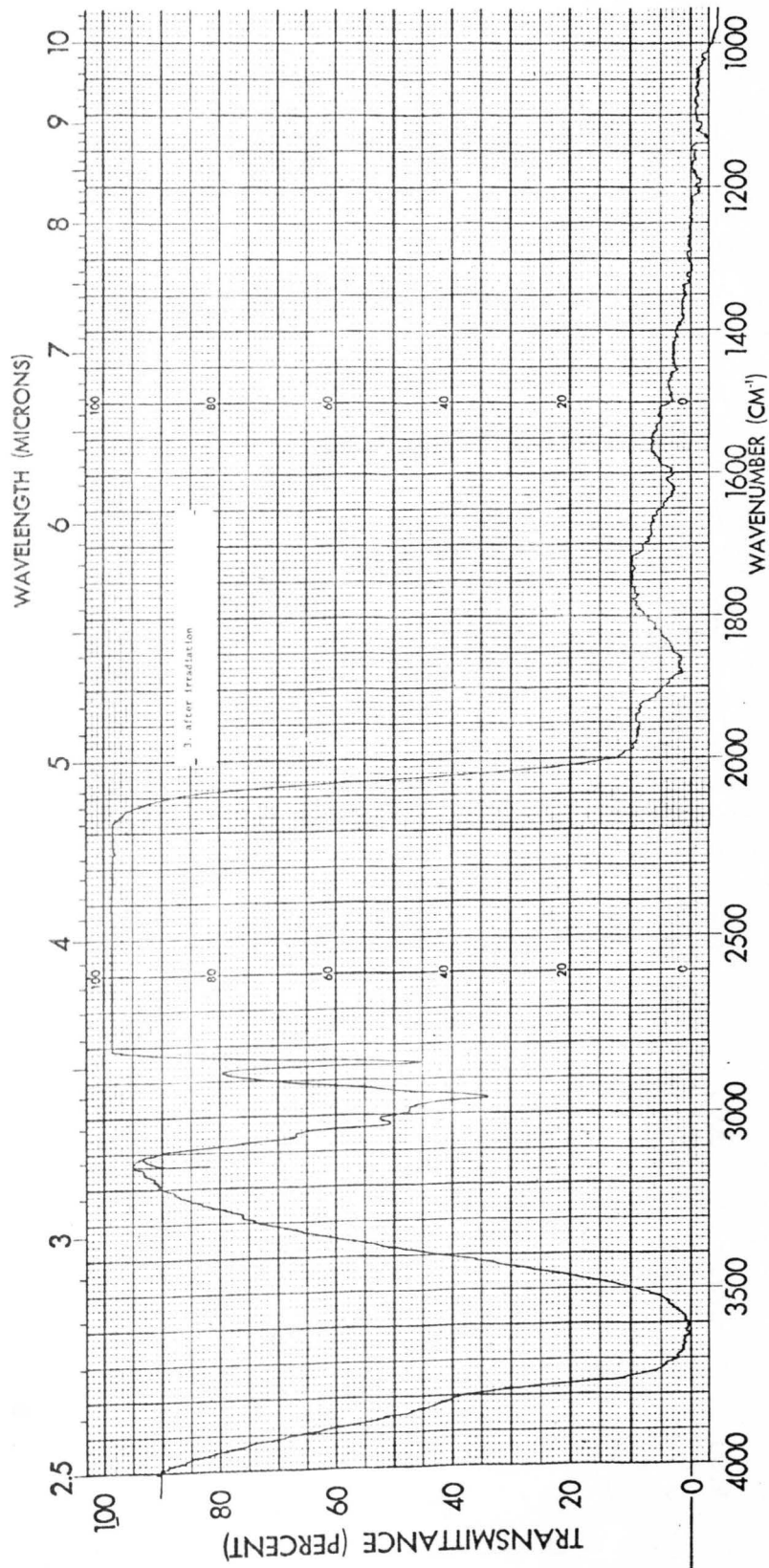
trans-Stilbene adsorbed onto silica gel.

trans-Stilbene adsorbed onto silica trial

WAVELENGTH (MICRONS)

2. trans-stilbene adsorbed onto silica

WAVELENGTH (MICRONS)

TRANSMITTANCE (PERCENT)

WAVENUMBER (CM⁻¹)

3. after irradiation

WAVELENGTH (MICRONS)

4. dark reaction observed
after 5 days

61

Azobenzene adsorbed onto silica trial

WAVELENGTH (MICRONS)

TRANSMITTANCE (PERCENT)

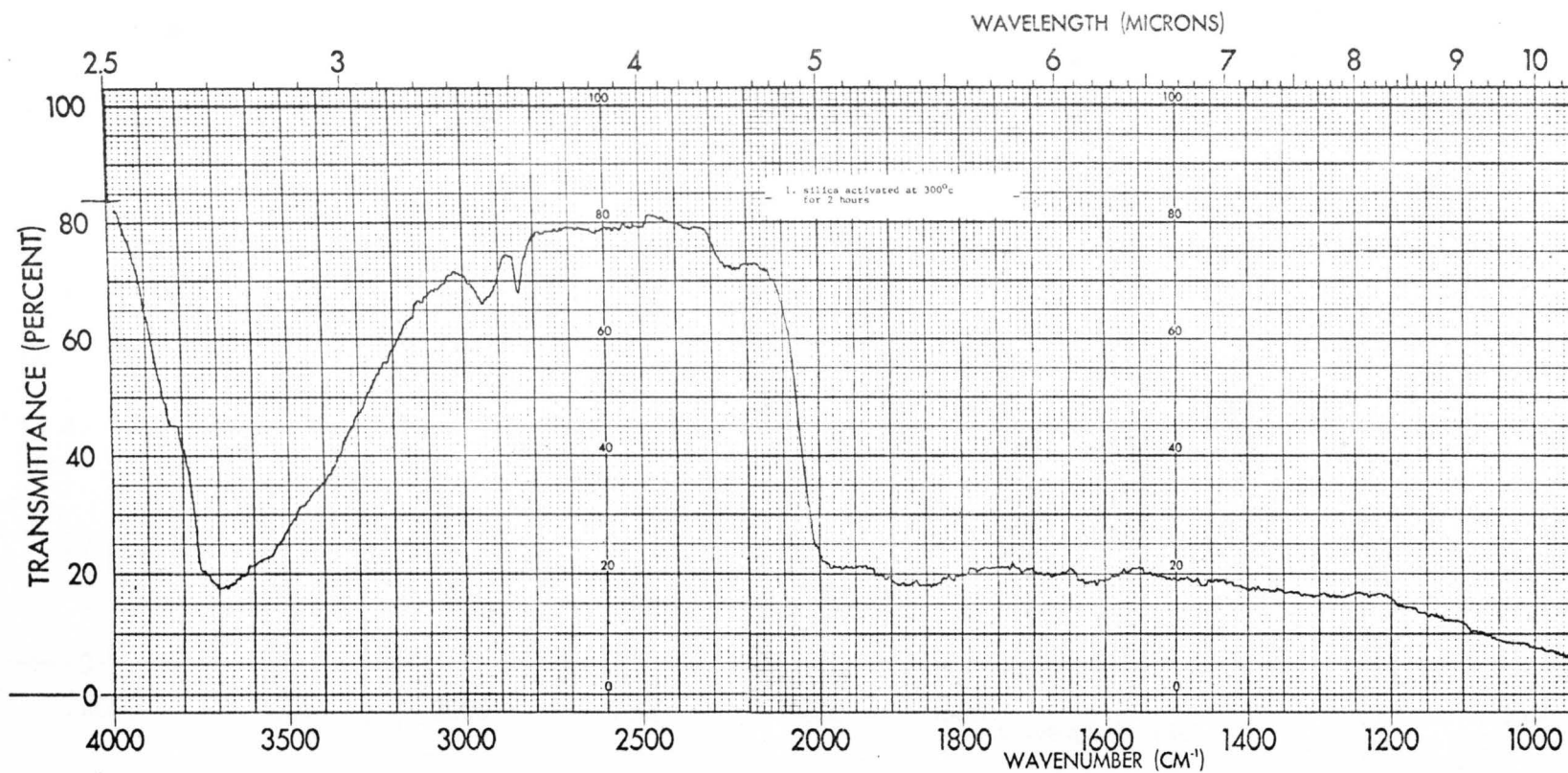WAVENUMBER (CM⁻¹)

1. silica activated at 300°c
   for 2 hours

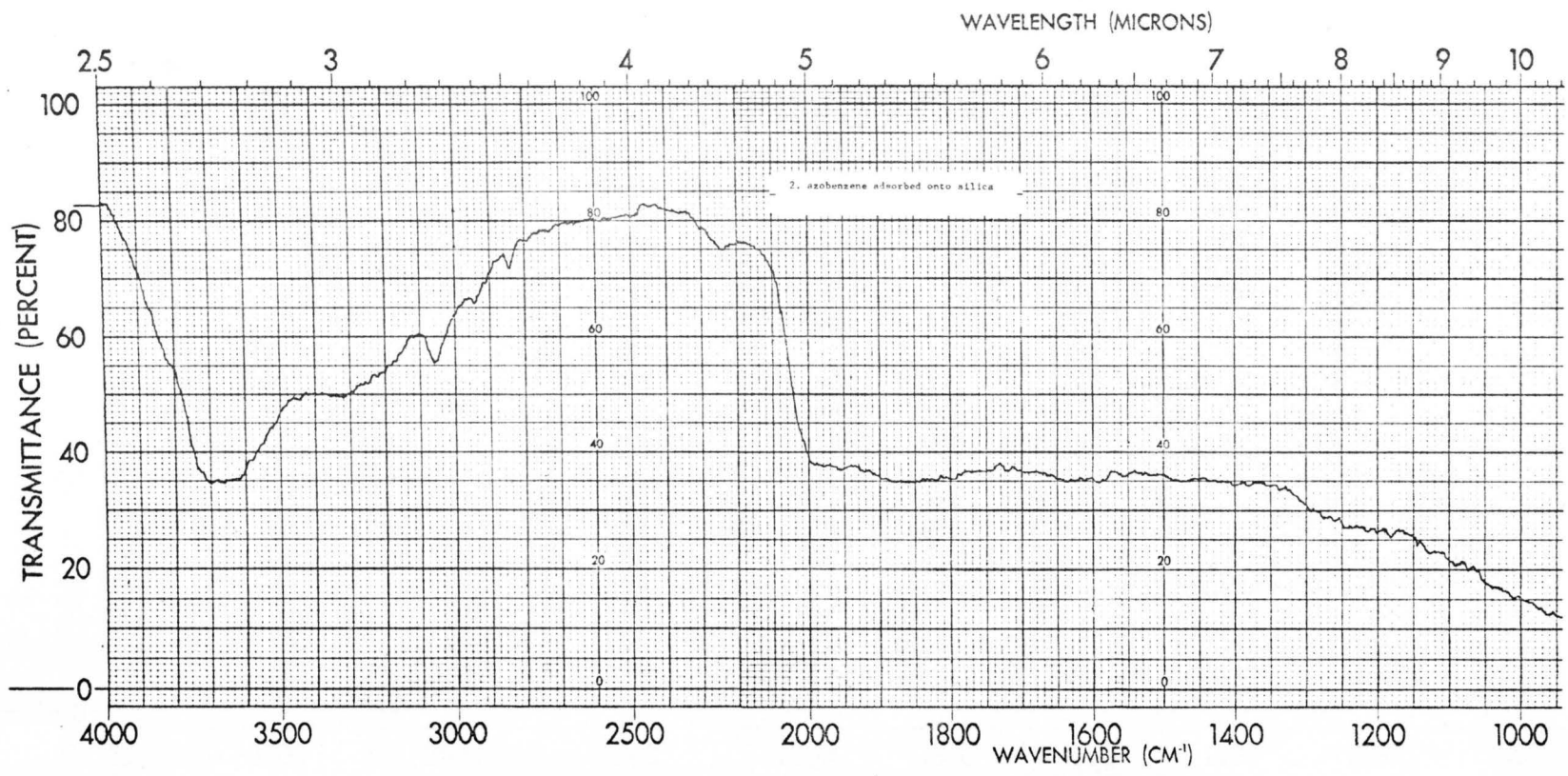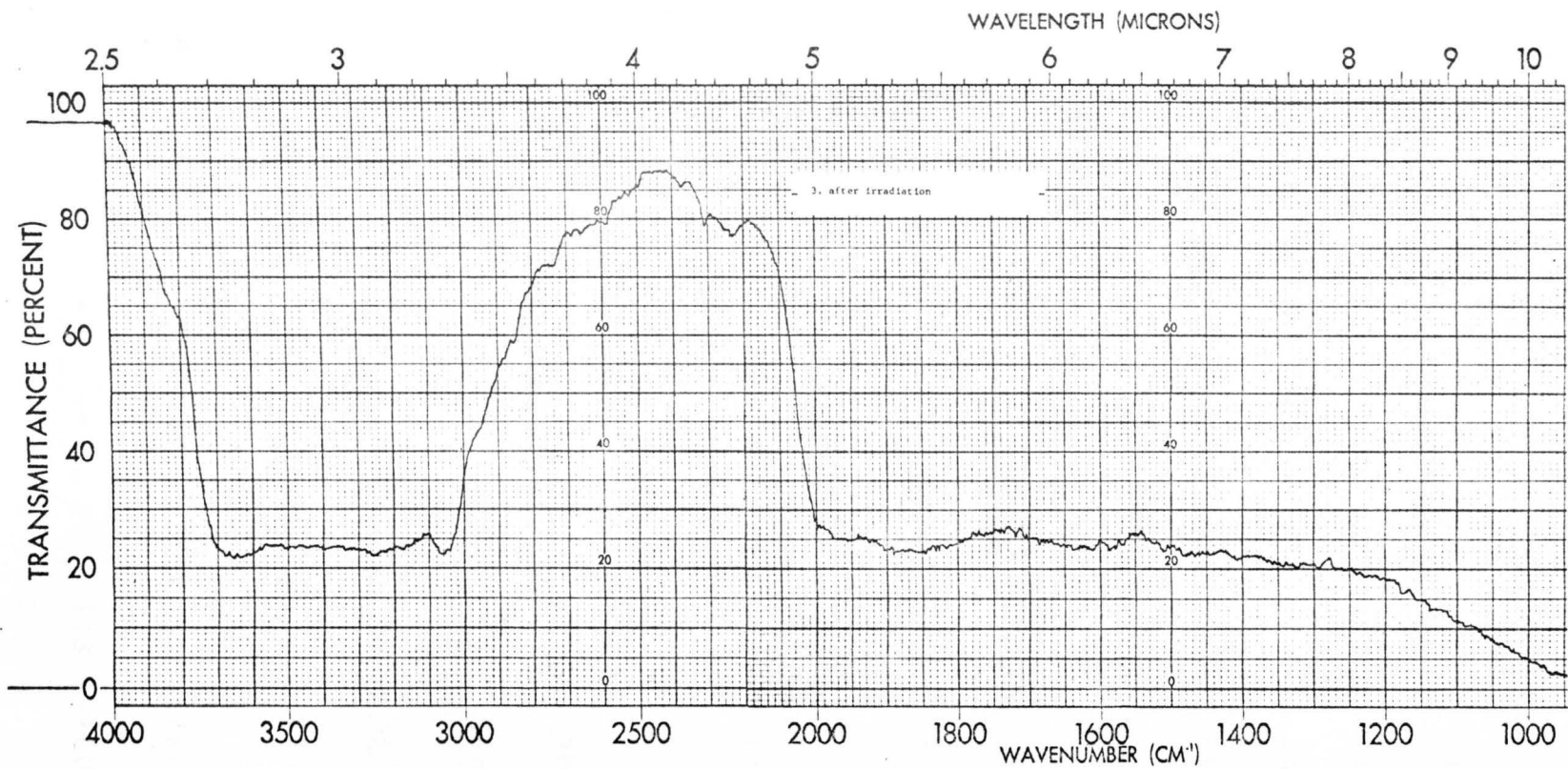2. azobenzene adsorbed onto silica

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