

If CH_3OOCH_3 is produced only by reaction 11, then the relative yield of methyl peroxide in various systems is a qualitative measure of the CH_3O radical abundance. Similarly CH_3OOH is formed only by abstraction of a hydrogen atom from other radicals by CH_3OO , and it is thus a qualitative measure of CH_3OO steady-state concentration. The average relative quantum yields are

Reactant	$\Phi(\text{CH}_3\text{OOCH}_3)$	$\Phi(\text{CH}_3\text{OOH})$
CH_3I	0.037	0.12
CH_3CHO	0.011	0.21

Thus the steady-state concentration of CH_3O is suppressed relative to CH_3OO in this system.

Acknowledgment.—This work was supported by the Division of Air Pollution, Bureau of State Services, Public Health Service, Grant AP-104.

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Effects of γ -Radiation on the Surface Properties of Silica as Studied by the Infrared Spectra of Adsorbed Molecules

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RECEIVED MAY 14, 1964

The effect of γ -radiation on high area oxides has been mainly studied by indirect means. For example, the rate of H_2 - D_2 exchange on silica has been shown to be markedly affected by radiation. The advent of infrared spectroscopy as a tool for the study of adsorbed molecules offers a more direct approach to studying the effect of radiation on surface properties. It is shown that dissociative ethylene chemisorption can be induced in silica by γ -radiation. Careful control experiments showed that no ethylene was adsorbed on the surface, without prior irradiation. The nature of the adsorbed species, the mechanism of growth of the adsorbed species, and the nature of the active sites induced by the radiation are discussed.

I. Introduction

While a considerable literature exists on the effect of radiation on the surface properties of oxides, direct measurements of these effects have been few. For instance, with regard to catalytic properties, many experiments have been reported¹⁻⁴ on the induced H_2 - D_2 exchange activity due to γ -ray bombardment on a series of oxides. However, in most cases the oxides used had some activity before irradiation, and it is possible that the radiation had changed an already existing property of the oxides rather than having induced any new surface properties in the material. Another problem in the interpretation of H_2 - D_2 exchange experiments is that it is unknown what particular surface property, or surface site, is responsible for the exchange. Hence, it is difficult to interpret the effect of radiation on exchange activity in terms of changes in the surface properties of the solid.

This point has been discussed by Taylor,⁵ who has done a great deal of pioneering work in this field, and he had concluded "there is a basic difficulty in the characterization of defects that influence catalysis—namely, physical methods normally see features in the interior of the solid rather than on the surface simply because of the ordinarily much greater number of the former." However, there are exceptions to this rule. For instance, infrared spectroscopy can show directly the existence of some defects (such as OH groups) on the surfaces of oxides. It can also detect the presence of as little as $1/100$ of a monolayer of adsorbed hydrocarbons.⁶

The effect of irradiating silica, *in vacuo*, with Co^{60} γ -rays has been studied by measuring the infrared

spectra of molecules subsequently interacting with the irradiated surface. The majority of work has been done with ethylene. After evacuation of unirradiated silica, ethylene can be left for very long times above the surface, at room temperature, without adsorption. After irradiation, in marked contrast, adsorbed saturated species are very rapidly formed. This provides direct evidence that centers, very active for the strong chemisorption of unsaturated hydrocarbons, have been induced in this oxide by γ -radiation. Experiments to elucidate the nature of these sites, and their relation with the color centers⁵ induced in silica, have been performed and are discussed in detail.

II. Experimental

(a) **Materials.**—Porous glass was obtained from the Corning Glass Works, by the courtesy of Dr. M. E. Nordberg. Tubular material, of varying radii but wall thickness of about 1 to 2 mm., was used, although some experiments were done with flat plates. In an attempt to ensure the maximum degree of uniformity of the samples, they were cut from 15-in. lengths of the tubing. In the preparation of porous glass, an acid-soluble component is leached out, leaving a silica matrix.⁷ The thoroughness of this leaching determines, to a considerable extent, the impurities left on the surface of this material. Although the normal Na content of this material is about 400 parts per million (p.p.m.), we were able to obtain material with 50 p.p.m. of Na. In an effort to reduce the latter still further, we leached this material in boiling 1 *N* nitric acid for 15 hr., then rinsed most of the acid out, and stored the glass in distilled water.⁸ An attempt was made to reduce the boron content of the material by leaching, calcining in air at a higher temperature than subsequently used, and then re-leaching.

Ethylene of 99.0% purity was supplied by the Matheson Co., East Rutherford, N. J. Specially purified ethylene was also used, supplied by the Phillips Petroleum Co., Bartlesville, Okla. This had a purity of 99.92%, and gas chromatographic analyses showed the main impurity to be a small amount of ethane. Hydrogen was obtained from the Linde Co., of Linden, N. J., and had a purity of 99.98%. Deuterium was supplied by the General Dynamics Corp., with a purity of 99.5%. Oxygen, NO , and Ar were supplied by the Matheson Co., with respective purities of 99.6, 99.0, and 99.99%. In the case of the noncondensable gases, they were dried by passage through traps at 77°K.

(7) M. E. Nordberg, *J. Am. Ceram. Soc.*, **27**, 299 (1944).

(8) Leaching procedure suggested by Dr. M. E. Nordberg.

(1) E. H. Taylor and J. A. Wethington, *J. Am. Chem. Soc.*, **76**, 971 (1954).

(2) H. W. Kohn and E. H. Taylor, *J. Phys. Chem.*, **63**, 500 (1959).

(3) H. W. Kohn and E. H. Taylor, *ibid.*, **63**, 966 (1959).

(4) H. W. Kohn and E. H. Taylor, *Trans. Second Intern. Congr. Catalysis*, **2**, 1461 (1961).

(5) E. H. Taylor, *Nucleonics*, **20**, 53 (1962).

(6) N. Sheppard and D. J. C. Yates, *Proc. Roy. Soc. (London)*, **A238**, 69 (1956).

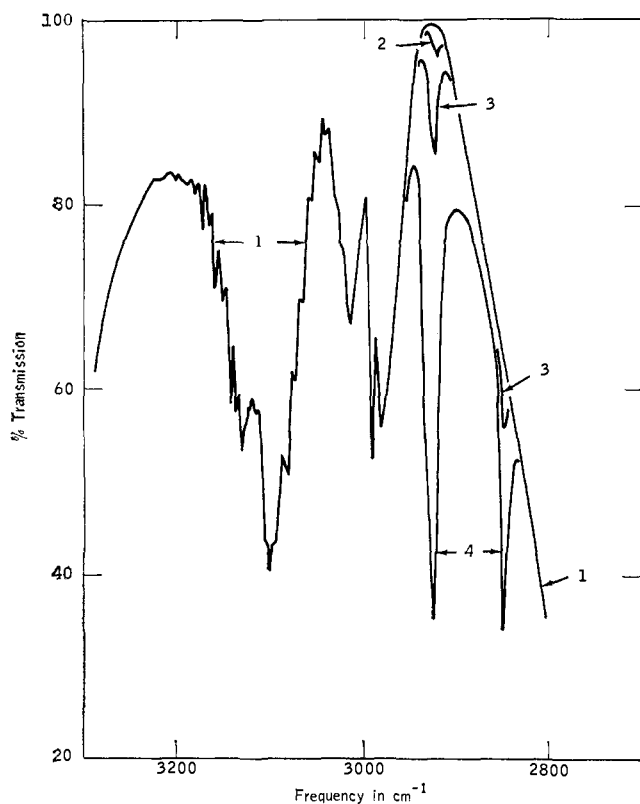


Fig. 1.—Transmission spectra of evacuated porous glass in a silica cell. Curves: 1, background soon after adding 16.6 cm. of ethylene; 2, 3, and 4 taken 1.55, 3.42, and 20.25 hr. after adding the ethylene.

The condensable gases were frozen at 77°K., and the middle fraction was retained for use.

(b) **Apparatus.**—The vacuum system consisted of a mechanical backing pump, an oil-diffusion pump (speed 80 l./sec.), and a trap cooled with solid carbon dioxide. Dynamic vacua in the 10^{-7} torr region were reached, as measured by an Alpert-type ionization gauge. A Beckman IR-7 double-beam grating spectrometer was used, with mirror systems providing external foci. The cell was placed at one of these, and wire gauzes were placed in the other beam to balance the energy in the two beams. In some cases, two cells were used, one containing a reference porous glass sample which had been evacuated, but not irradiated.

The cells used varied. In the work with the flat samples of glass, the dual cell with barium fluoride windows was used.⁹ In other cases, cells were used consisting of a tube of silica, joined with a graded seal to a Pyrex tube. This in turn was joined to a stopcock by a 29/42 cone joint sealed with Apiezon W40 wax. In some of these cells, the gas phase optical path was reduced by a re-entrant silica finger which went up the inside of the tubular sample.

All irradiations were carried out with Co^{60} γ -rays at room temperature. The radiation cave and handling system have been described elsewhere.¹⁰ During long irradiations the cell warmed up to about 35° owing to the γ -heating effect.¹¹ Four plate sources were used, each having an average activity of 2000 c., two placed on each side of the cell. The samples were placed in a fixed relation to the four sources so that the dose rate was about 10^6 roentgens/hr. However, no attempts were made in this work to measure the dose rate accurately. As the half-life of Co^{60} is 5.3 years, the doses received by the samples are proportional to the time of radiation.

(c) **Procedure.**—The samples were evacuated between 400 and 600°, final vacua being in the 10^{-6} torr region. For our system, the temperature of evacuation had minor effects on the behavior of the material after irradiation. The cells were then transferred to the radiation source. After irradiation, they were

(9) D. J. C. Yates and P. J. Lucchesi, *J. Chem. Phys.*, **35**, 243 (1961).

(10) J. F. Black, J. F. Kunc, and G. B. Clark, *Intern. J. Appl. Radiation Isotopes*, **1**, 256 (1956).

(11) D. S. Billington and J. H. Crawford, "Radiation Damage in Solids," Princeton University Press, Princeton, N. J., 1961.

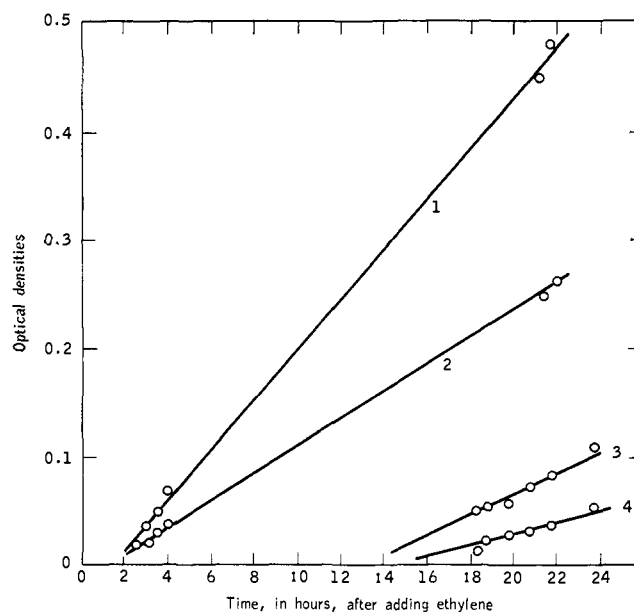


Fig. 2.—Rate of adsorption of ethylene on unirradiated porous glass, as shown by the peak optical densities of bands at 2922 cm^{-1} (1, 3) and at 2850 cm^{-1} (2, 4). Curves 1 and 2 were measured using sample A; typical spectra are shown in Fig. 1, ethylene pressure 16.6 cm. Curves 3 and 4 were obtained with sample B, with an ethylene pressure of 14 cm. Sample A contained about 400 p.p.m. of sodium, B contained less than 50 p.p.m.

attached to the spectrometer and the background spectrum run. The gas to be studied was added and the pressure change followed with time. The sample was removed from the manometers after a fixed period of time and transferred to the spectrometer. In most cases, spectra were not measured while the gas was being adsorbed, but the pressures used were such that there was an excess of gas in the cell while spectra were being run, and thus the rate of adsorption was not limited by the supply of gas to the surface. In the cases where more than one gas was used, the procedure will be given in section III. The surface areas of the samples were determined by a B.E.T. analysis of argon isotherms run at 77° and were in the region of 100–120 m^2/g .

III. Results and Discussion

(a) Adsorption of Ethylene on Unirradiated Samples.

(i) **Effect of Acid Leaching.**—When unirradiated samples were exposed to ethylene after evacuation at 420°, a saturated chemisorbed species¹² was observed on the surface. The spectrum is shown in Fig. 1 together with the spectrum of gaseous ethylene. A series of spectra were taken, and the rate of growth of the adsorbed species is shown in Fig. 2, where peak optical densities of the 2922- and 2850- cm^{-1} bands are shown. In addition to the above bands, a band at 2970 cm^{-1} , weaker than the 2922- cm^{-1} band, was also found on removing the gaseous ethylene from the cell. These species are quite strongly held as evacuation for 1 or 2 min. affected their intensity only to a small degree, and evacuation for a further 50 min. only removed small amounts. Figure 2 also shows optical density data with sample B. Sample A (used in the experiment shown in Fig. 1) was normal production porous glass, but sample B was specially prepared for this work, and contained less than 50 p.p.m. of Na. Bands identical with those found on sample A were obtained with sample B after longer times.

Figure 2 shows that lowering the Na content markedly decreased the amount of ethylene adsorbed

(12) P. J. Lucchesi, J. L. Carter, and D. J. C. Yates, *J. Phys. Chem.*, **66**, 1451 (1962).

and increased the induction period. Further acid leaching should remove this contaminant. A piece from the same batch as sample A was leached and evacuated, and 17 cm. of C_2H_4 was added. No chemisorbed species were observed after 90 hr. Finally, a piece was taken from a specially calcined batch. This batch was prepared by cutting a 15-in. length into 1.5-in. pieces. This was acid leached overnight, rinsed, and then dried. The pieces were air-calcined at 760° for 1.5 hr. cooled, and then leached again overnight. One of these pieces was evacuated at 450° , and then 9.5 cm. of C_2H_4 was added. This was checked carefully during the first few days, and then at weekly intervals. No chemisorbed ethylene was found even after 3×10^3 hr. This showed conclusively that some acid-soluble surface impurity was responsible for the slow chemisorption of ethylene, and the impurity could all be removed within the limits of detectability used here, giving a surface which was, for all practical purposes, incapable of chemisorbing C_2H_4 . The shortest time that spectra were taken of irradiated samples, after adding C_2H_4 , was 10 min. Well-developed bands were seen. Extrapolation of optical density plots over the first 10 min. showed that there was no detectable induction period. If correct, this means that the glass chemisorbs C_2H_4 about six orders of magnitude faster after irradiation than before it. Using data with no extrapolation (10 min. and 3000 hr.), the ratio of enhancement of chemisorption is 1.8×10^4 .

Earlier work showed that ethylene only physically adsorbed on porous glass.⁶ The glass used then had not been specially treated, and probably contained 400 p.p.m. of Na. The reasons that chemisorbed species were not detected are (a) the exposure time was only a few hours (Fig. 2 shows induction times of from 1.5 to 15.5 hr.), and (b) the C_2H_4 pressure used was lower than in the present work.

(ii) **Effects of Adding Back Known Surface Impurities.**—While Na seemed the most likely impurity responsible for the chemisorption of ethylene, B was another possibility, as this glass contains about 3% boric oxide. A piece of glass from the 50 p.p.m. Na content batch was taken, acid-leached, and evacuated, and C_2H_4 was added at a pressure of 19.5 cm. After standing for 90 hr. at room temperature, no chemisorbed species were detected. The glass was then immersed for 1 hr. in 20 cc. of a solution containing 10 p.p.m. of Na (as NaOH). The sample was removed from the solution and dried overnight at room temperature. It was then inserted into the same cell and evacuated under the same conditions. Then 19.3 cm. of ethylene was added. After standing for 40 hr., strong bands were detected (the 2922-cm.^{-1} band had an optical density of 0.39). The piece was then taken out of the cell, leached in acid overnight again, and re-evacuated. Ethylene was added at a pressure of 20.3 cm., and spectra were run at intervals. No chemisorbed species were detected during the 120 hr. the C_2H_4 was in contact with the sample.

These experiments on one sample show that leaching prevents C_2H_4 chemisorption, and that added Na causes a slow adsorption of C_2H_4 . Finally, a second leaching removes the Na again and prevents the adsorption of C_2H_4 .

Similar experiments were done by adding a boric

acid solution (concentration 0.62% by weight) to a sample of leached glass. After evacuation, 19 cm. of C_2H_4 was added to the cell. No adsorbed species were detected after 160 hr.

(b) **Multiple Irradiations and Reproducibility of Radiation-Induced Chemisorption.**—The initial experiments were done with samples which contained Na. The unleached glass which had an optical density (O.D.) of the 2850-cm.^{-1} band of 0.028, 3.5 hr. after adding C_2H_4 , and an induction period of about 1.3 hr. After irradiation *in vacuo* for 60 hr., the same glass chemisorbed C_2H_4 very rapidly with no measurable induction period. The 2850-cm.^{-1} band had an O.D. of 1.74 when measured 3.5 hr. after adding the C_2H_4 , hence about 60 times more were adsorbed after irradiation. The data could not be plotted on Fig. 2, as the O.D. was 0.73 when measured after 30 min.

After the acid-leaching procedure had eliminated the adsorption of C_2H_4 on unirradiated samples, clearly defined data could be obtained. All subsequent work was done with leached material, unless noted otherwise. Initial studies of the reproducibility of this effect were made using one piece of glass for a series of irradiations. The C_2H_4 was removed (presumably with the radiation effects) by heating to $400\text{--}500^\circ$ between irradiations. However, the second overnight irradiation on one leached piece gave more C_2H_4 adsorbed than the first, but the third irradiation gave less than the first. It was thought possible that some of the problems might have been due to some B diffusing to the surface during the intermediate evacuations.

To avoid this, we took a piece from the sample which had been leached, calcined in air at 760° for 1.5 hr., and re-leached. One of the pieces from this batch (as used in the long blank run) was placed in a re-entrant cell, evacuated at 450° , and irradiated for 16.1 hr. The area of this sample (piece 10) was $108\text{ m.}^2/\text{g}$. Ethylene was then added, and the spectra were recorded over a period of 3 hr. The C_2H_4 was then evacuated, and air let into the cell. The sample was then heated to 480° and left at this temperature overnight. This treatment both oxidized all the chemisorbed hydrocarbon off the surface and removed the purplish color resulting from the irradiation. The adsorption of ethylene on this silica did not remove the color due to radiation, which is a property in which our silica differs from that used by earlier workers.¹³ This difference in ethylene adsorption and the quite large chemical differences between porous glass and silica gel make it inadvisable to compare the effect of radiation on the two solids. Hence, we have not attempted to compare our data with that obtained on silica gel.^{1-5,13} However, in agreement with the earlier work, we find that H_2 (and D_2) bleaches the color immediately. The sample was then evacuated a second time at 450° , and then given a second irradiation of 16.1 hr. Ethylene was then added, and a series of spectra taken. After the second calcination overnight, and subsequent evacuation, the third irradiation was performed for 15.7 hr. Ethylene was added, and the spectra were run as before. These three experiments were run during a period of 6 days, so that there was a negligible variation in activity of the cobalt sources during this time.

(13) H. W. Kohn, *Nature*, **184**, 630 (1959).

Figure 3 shows that drastic changes in the nature of the species formed took place with the above series of successive irradiations. For the first (curve 2), the ratio of the optical densities of the 2970-cm.⁻¹ band to the 2922-cm.⁻¹ band was 0.94. The former band is due to the asymmetrical stretching vibration in CH₃ groups in saturated hydrocarbons, while the latter is the corresponding vibration in CH₂ groups. For ethyl groups, such as those found in ethyl bromide, *n*-C₄H₁₀, and in adsorbed species,¹² this ratio is about 1.30. For longer chain species, such as physically adsorbed *n*-C₇H₁₆, the ratio drops¹² to about 0.8. Thus in general terms, curve 2 in Fig. 3 is the spectrum of a saturated hydrocarbon with about two CH₂ groups for every CH₃ group. Curve 3 (after the second irradiation) had a ratio of 0.58, hence fewer CH₃ groups. This trend is even more extreme after the third irradiation (curve 4), where very few CH₃ groups seemed to be present, the ratio being 0.15.

Evidently, there is some residual effect of the irradiation, and the glass is not being restored to its initial state by the calcining and evacuation at elevated temperatures. This is unexpected, as most defects induced in silica by high energy radiation are either trapped electrons or trapped holes.¹¹ These can be thermally bleached in the 350–400° temperature region in pure silica.¹⁴ The removal of interstitial defects (such as displaced atoms) by thermal treatment is much more difficult, as shown¹⁴ by the effects of γ -ray bombardment after a neutron bombardment, with an intermediate annealing at 700°. Little appears to be known about the number of displaced atoms in silica produced by 1.3 Mev. γ -rays. However, the number of displacements produced by such γ -rays is very small in Cu and Ge.¹⁵

In view of the fact that the nature of color centers in irradiated silica of very high purity is still uncertain,¹⁶ it is evident that relatively impure high area materials are very much more complex and difficult to study. It is concluded that, at least for our form of high area silica, multiple irradiations of one sample cannot lead to reproducible data, owing to some form of radiation "memory." All subsequent work was done with pieces that were only irradiated once, and which were cut from the same long sample of tubing in an effort to ensure the maximum degree of homogeneity of the samples.

(c) Effects Due to the Adsorption of Ethylene.—

Pieces 10 and 11 were used from the same batch of glass which was calcined at 760°, as discussed in IIIb. Both were evacuated at 500°. Piece 10 was irradiated for 16.1 hr., and the spectrum has been given in Fig. 3 (curve 2). Piece 11 was irradiated for 13.4 hr. Both the absolute amount adsorbed and the CH₃/CH₂ ratio were in close agreement, as shown by the data in Table I. The absolute amount adsorbed, which is directly proportional to the optical density, shows slight differences in the 2922-cm.⁻¹ band between the two experiments. However, no differences, within experimental error, were detected in the 2970-cm.⁻¹ band.

(14) C. M. Nelson and J. H. Crawford, *J. Phys. Chem. Solids*, **13**, 296 (1960).

(15) See ref. 11, pp. 95 and 96.

(16) See, for example, the proceedings of a conference on defect structures in quartz and silica, held at the Mellon Institute, Pittsburgh, Pa., in 1957, published in *Phys. Chem. Solids*, **13** (1960):

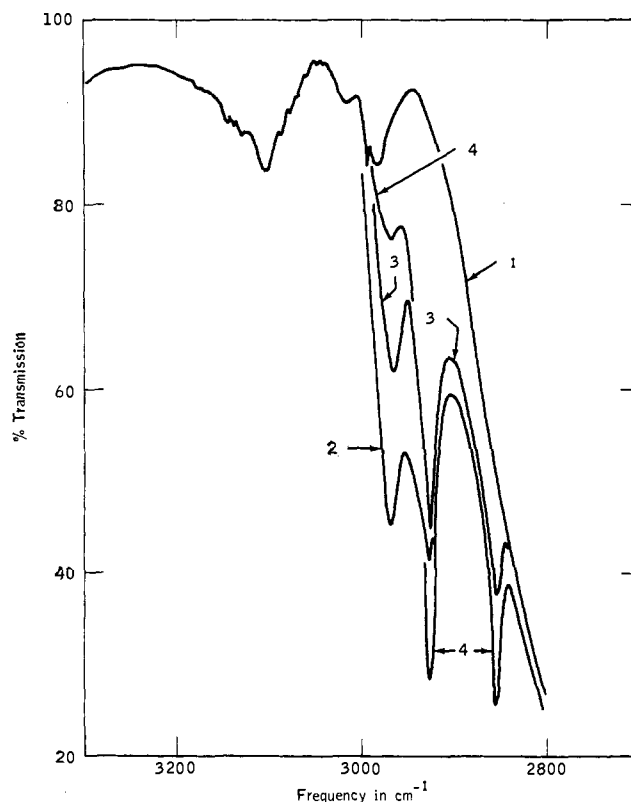


Fig. 3.—Effects of a series of irradiations on one piece of porous glass. Curve 1: background spectra after adding ethylene (pressure 8.8 cm.) to the unirradiated sample after evacuation at 450°. Curve 2: evacuation at 450°, irradiation for 16.1 hr., ethylene added (pressure 15 min. after addition was 8.65 cm.). The spectrum shown was recorded 2 hr. after adding ethylene. Curve 3: after second irradiation (16.1 hr.). Spectrum run 2 hr. after adding ethylene (pressure 15 min. after addition was 9.22 cm.). Curve 4: after third irradiation (15.7 hr.). Spectrum run 2 hr. after adding ethylene (pressure 15 min. after addition was 9.2 cm.).

For both pieces, a series of spectra were run over a period of 3 hr. The above optical densities were both measured from spectra taken 1.9 hr. after adding C₂H₄.

TABLE I
REPRODUCIBILITY OF RADIATION-INDUCED CHEMISORPTION
OF ETHYLENE ON POROUS GLASS

Date of irradiation	Piece	Time of irradiation, hr.	Ethylene pressure (15 min. after admission), cm.	Optical density—		Ratio A/B
				2922 cm. ⁻¹ (A)	2970 cm. ⁻¹ (B)	
26 April	10	16.1	8.65	0.356	0.334	1.065
3 May	11	13.4	8.64	0.346	0.334	1.036

The above pair of irradiations showed that reproducible data could be obtained by using adjacent samples from a single rod. Further experiments were done to determine the effect of dosage on the system. A piece (no. 5) from the batch calcined at 760° was evacuated at 500° and then irradiated for 16 hr. A series of spectra were taken, and one is shown in Fig. 4, curve 2. Another piece, which had been cut from the adjacent portion of the original tube (no. 6), was then prepared exactly as piece 5, but irradiated for 64 hr. In Fig. 4, curve 3 shows that much more ethylene is adsorbed after the longer irradiation.

From all the spectra which were taken in the two experiments, the rate of growth of the adsorbed species

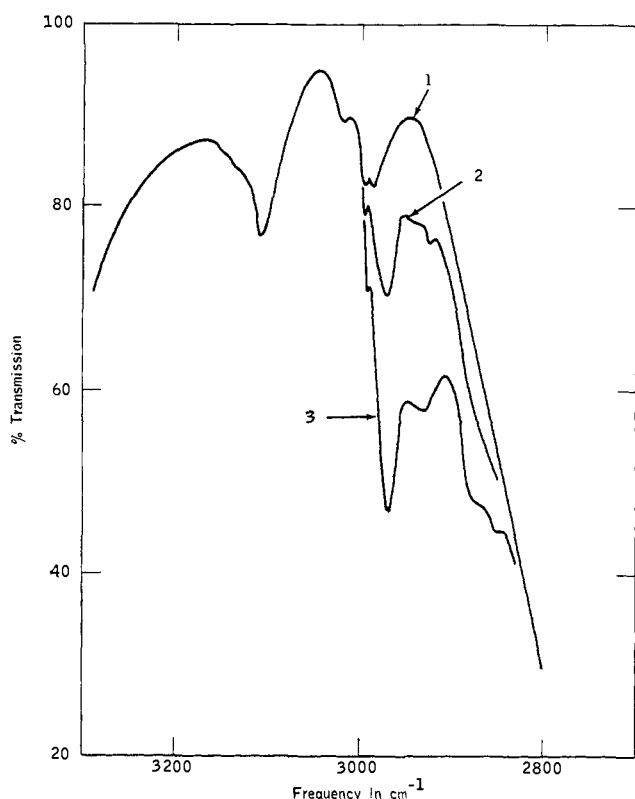


Fig. 4.—Effect of time of irradiation on rate of adsorption of ethylene. Curve 1: background spectrum with ethylene in the cell, but no adsorbed species. Curve 2: spectrum of piece 5, after evacuation at 500° , irradiation for 16.1 hr., and ethylene added (pressure 15 min. after addition was 9.52 cm.). The spectrum shown was recorded 1.83 hr. after adding the C_2H_4 . Curve 3: spectrum of piece 6, treated as piece 5, but irradiated for 63.8 hr. Spectrum run 2.12 hr. after adding ethylene (pressure 15 min. after addition was 9.09 cm.).

was determined by measuring the peak optical density of the 2970-cm.^{-1} band. Figure 5 shows that, 20 min. after adding the ethylene, there is about 2.7 times as much adsorbed material for the longer irradiation. This is similar to the ratio of the time of irradiation (3.96). It should be noted that varying surface coverages were used in this work. For the longer irradiations, blackouts were observed in the infrared spectra of adsorbed molecules. This means that at least a monolayer, and probably more, of the chemisorbed species was present. Other experiments produced quite weak bands, so that the over-all coverage is from less than 0.2 to greater than 1.0.

However, the effects of radiation on this system are extremely complex. Although the ratio of amounts adsorbed at short times is comparable to the ratio of the times of γ -ray exposure, the subsequent growth of the bands is quite different. With the 16-hr. experiment, only about 40% more was adsorbed after waiting 3 hr. beyond the first spectrum. The comparable percentage for the long radiation is 70%. As similar pressures of C_2H_4 were used in the two experiments, it is probable that the cause of the differences in the two rates of growth is due to the different way in which the glass has been affected by the radiation. Moreover, the kinetics of this system are extremely complex. Rather than investigate in detail either the variation in amount adsorbed by varying the γ -ray dosage at constant ethylene pressure, or by varying the ethylene pressure at given dosage, we attempted to

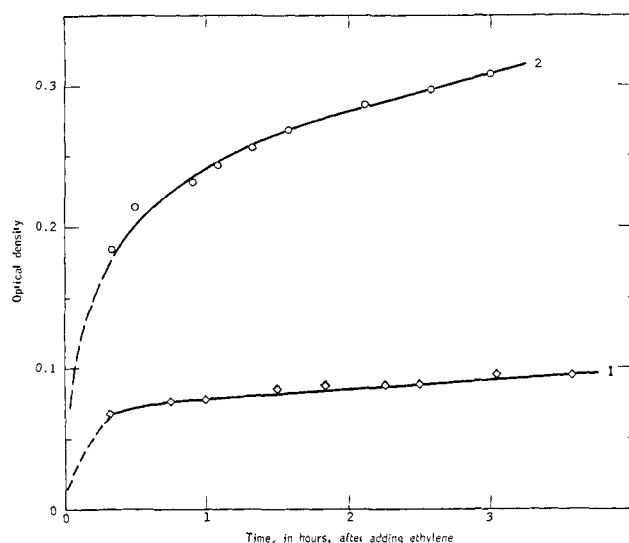


Fig. 5.—Rate of growth of the 2970-cm.^{-1} band in adsorbed ethylene as a function of time of irradiation. Curve 1: piece 5, irradiated 16.1 hr. Curve 2: piece 6, irradiated for 63.8 hr. Ethylene pressure 15 min. after admitting gas: 9.52 cm. for curve 1 and 9.09 cm. for curve 2.

learn more about the properties of those sites which cause the ethylene to be chemisorbed.

The nature of the surface species formed from adsorbed ethylene is a very variable entity, containing varying CH_3/CH_2 ratios. In the case of those experiments where predominantly CH_2 groups were found, infrared spectra cannot readily distinguish between a saturated species lying flat on the surface, such as previously observed on an alumina,¹² and a long CH_2 chain extending from the surface. As such a chain could have only one CH_3 group, at the end remote from the surface, this species would be consistent with the observed spectra. Attempts were made to desorb the chemisorbed material and analyze the products by gas chromatography. These did not succeed, nor could we find any suitable chemical means of separating the adsorbed material from its substrate. Finally, we transferred one of the samples, in its cell, to a high resolution mass spectrometer. At room temperature, little was desorbed from the sample. However, on evacuating and heating to temperatures of 100, 200, 300, 400, and 500° , the adsorbed material could be removed. An extremely complex range of products was obtained, with low molecular weight paraffinic materials dominating. The olefinic, and also some aromatic, material was found mostly at temperatures above 200° . The higher the temperature, the higher the mass of the material removed, although C_5 species were present after desorption at 100° . However, the most pertinent observation for our purposes was that a small amount of material containing up to 13 carbon atoms was present. This indicates that one way in which ethylene chemisorbs on this material may be by a chain type of growth, forming long alkyl chains which probably extend outward from the surface.

(d) **Effect Due to Adsorption of Gases Other than Ethylene.** (i) **Gases Pre-adsorbed before Ethylene.**—These experiments were performed with the aim of elucidating the nature of the sites responsible for the radiation-induced chemisorption of ethylene. The first gases investigated were H_2 and D_2 . The

following sequence of experiments were performed. A sample (400 p.p.m. of Na) was evacuated and irradiated for 16 hr. Then 6.5 cm. of D_2 was added, and the purple color disappeared a little more slowly than after adding H_2 . (Earlier experiments had shown that for all samples, the addition of H_2 removed the color within 5 sec.) The spectrum was run from 2400 to 4000 cm^{-1} . No OD groups were detected. The gaseous D_2 was then removed and 29.9 cm. of C_2H_4 added. This pressure was close to that previously used with this glass, after it had been irradiated but not exposed to D_2 . The amount of C_2H_4 adsorbed was similar to that found previously. These experiments showed that: (a) the defects responsible for the formation of color centers are not the centers responsible for ethylene chemisorption; (b) the adsorption of D_2 , on color centers, or on any other sites, does not prevent the subsequent adsorption of C_2H_4 ; (c) it is unlikely that any form of OH group is responsible for the radiation-induced chemisorption of C_2H_4 . If they were, it would be thought that such OH groups would readily exchange with D_2 at room temperature. No such exchange was detected. For that matter, a similar argument leads to the conclusion that initiation by $H\cdot$ formed by irradiation is also unlikely.

Nitric oxide was also pre-adsorbed. This gas is noted for its reactivity toward free radicals.¹⁷ It was thought that if the sites responsible for ethylene adsorption behave chemically like free radicals, the pre-adsorbed NO would totally inhibit the adsorption of ethylene. A sample, from the batch containing less than 50 p.p.m. of Na, was evacuated and irradiated for 40 hr. (It is unlikely that any NO is on the surface of the glass during irradiation. Any small amounts of NO left on the glass from acid leaching would be all removed by the evacuation at high temperature.) After removal from the source, NO was added at a pressure of 5 cm. The purple color changed to yellow within 10 sec., but the sample did not decolorize as occurred with H_2 and D_2 . The NO was then evacuated until the pressure was 5×10^{-5} torr, and 17.3 cm. of C_2H_4 was then added. No adsorption of the ethylene whatever could be detected while the spectra were run (22 hr.). This shows that pre-adsorption of NO entirely stops the chemisorption of ethylene on irradiated silica.

The effect of O_2 was studied for a similar reason. An acid-leached sample was put in a cell, evacuated as usual, and irradiated for 64 hr. Then oxygen (passed through a trap at 77°K.) was added, at a pressure of 34 cm., and left in the cell for 1 hr. It is of considerable interest to note that, in marked contrast with NO, H_2 , and D_2 , no color change took place in the sample of adding O_2 . The oxygen was then evacuated and 21 cm. of ethylene added. The rate of growth of the adsorbed species was slower than usual, but after 23 hr., the 2970- cm^{-1} band in the adsorbed species had an optical density of 0.25. Thus, the pre-adsorption of O_2 has no effect on the color centers and only slowed down the subsequent chemisorption of C_2H_4 .

(ii) **Gases Adsorbed after Exposure to Ethylene.**—As a further check on the inhibiting effect of NO,

an experiment was performed to see if a similar effect occurred when the NO was added to the ethylene while the surface species were growing. Another sample of unleached, low Na glass from the same batch as that previously used for the NO experiment was evacuated and irradiated for 40 hr. Ethylene was then added, and 40 min. later the pressure was 14.4 cm. The growth of the chemisorbed species was followed with time, by taking a series of spectra. Figure 6 shows the rate of

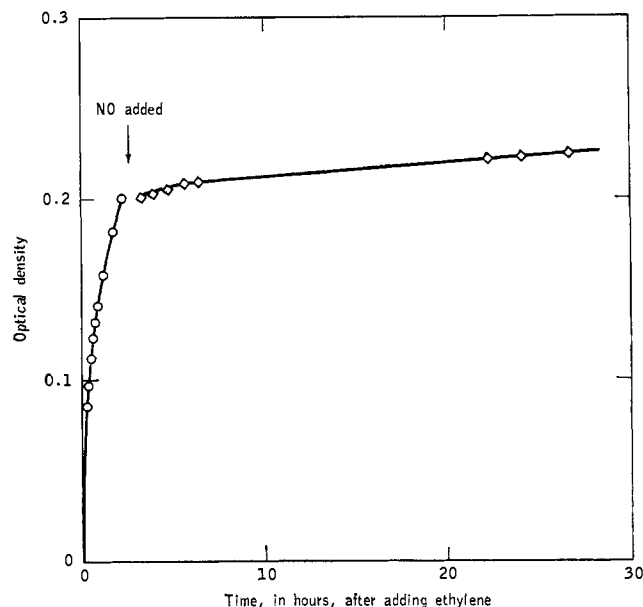


Fig. 6.—Rate of growth of adsorbed species from ethylene (shown by the optical density of the 2922 cm^{-1} band) as affected by the addition of nitric oxide. Pressure before adding the nitric oxide, 14.4 cm.; after, 14.7 cm.

growth of the 2922- cm^{-1} band in the adsorbed species. Then, 3.5 hr. after adding the ethylene, a small amount of NO was added to the sample, *without* removing the ethylene from the cell. It will be seen that the growth of chemisorbed ethylene was drastically reduced, despite the small amount of NO added. This observation confirms, in an even more positive fashion, that the centers responsible for the radiation-induced chemisorption of ethylene are poisoned rapidly by NO when added either before or during the C_2H_4 chemisorption.

(iii) **Data Obtained from Electron Spin Resonance Experiments.**—In collaboration with Dr. G. M. Muha, a study has been made of the nature of the trapped electrons produced in the glass; these results will be published elsewhere. As all the e.s.r. spectrum¹⁸ that is observed is due to the radiation-induced changes in the glass, this helps to simplify the interpretation. For purposes of this discussion, it is only pertinent to point out the electrons were trapped at Si, B, or O atoms of the lattice. On adding C_2H_4 , very little change in the e.s.r. spectrum could be detected. This was surprising, but showed conclusively that none of the unpaired electrons, or at least none of the unpaired electrons that were detectable by our e.s.r. techniques, takes part in the chemisorption of ethylene.

The results obtained earlier by infrared spectroscopy showed that the preadsorption of H_2 did not affect the subsequent C_2H_4 adsorption. Similar effects were

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observed in the e.s.r., in that the effects produced by H_2 were different from those produced by C_2H_4 . Although no change in the spectrum was produced by C_2H_4 , substantial changes were found on the adsorption of H_2 and D_2 . These changes were found both when the H_2 was added before the C_2H_4 , and when it was added after the C_2H_4 . This is, therefore, independent confirmation that the sites responsible for H_2 adsorption have no relation to the sites responsible for the chemisorption of C_2H_4 . Adding NO to the samples also produced no change in the e.s.r. spectrum. This is what would be expected in view of the fact that the simplest explanation of the poisoning action of NO is to assume that it strongly adsorbs on the sites responsible for the ethylene adsorption. As the sites for C_2H_4 adsorption are not detectable in the e.s.r. spectrum, it is reasonable that adding NO has no effect on the e.s.r. spectrum of the irradiated glass. However, CO did have an effect on the e.s.r. spectrum, which shows that some of the sites giving rise to e.s.r. bands are accessible to molecules of a size similar to NO.

IV. Conclusions

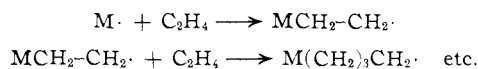
(a) **General.**—The experiments described in this paper show that it is possible to selectively study changes in surface properties of oxides produced by γ -radiation by studying their infrared spectra. This method is useful both as a very sensitive tool for determining the lack of any surface activity before irradiation, and as a means of identifying the surface species formed as a result of the radiation-induced chemisorption. For materials that can be studied by the infrared technique, this approach can give direct information about the effect of radiation on surface properties. As an example, the effect of traces of impurity in the parts per million range should be noted. Such slow adsorptions, at such a low coverage, could not be detected by the normal means of measuring adsorption at the gas-solid interface.

Once the role of radiation in inducing the chemisorption of C_2H_4 on silica had been established, the way was clear for a systematic study of the effect. This proved to be unexpectedly difficult. For bulk high purity SiO_2 , it is known that the trapped electrons responsible for the color centers are readily thermally annealed. Hence, one would suppose that thermal bleaching would enable multiple irradiations to be performed on one sample. This was tried and led to systematic changes in the nature of the adsorbed species with the number of times the given sample was irradiated. Hence, a systematic study of radiation effects can only be done by irradiating a given sample once. Nevertheless, even when each piece was used only once, it proved difficult to obtain reproducible data. This shows, to an even greater extent, the great complexity of the effects of radiation on highly dispersed oxides. Evidently, to obtain any sort of reliable quantitative information on the effects of γ -radiation on such systems, very careful, systematic experiments will be needed. Such experiments do not appear to have been performed to date. Most of the investigations that have been published have been more concerned with demonstrating an effect of radiation, rather than systematically investigating the phenomena. As the effects of the radiation are extremely complex, considerable care must be taken in choosing a suitable

system. If catalytic effects are to be investigated, care must be taken to find a simple enough reaction. For exchange experiments, it is desirable to find a system that has no exchange without irradiation. Similarly, for induced chemisorption, a system must be found where there is no chemisorption in the absence of radiation.

(b) **The Nature of Sites for the Chemisorption of Ethylene on Irradiated Silica.**—The effects of γ -radiation on insulators are extremely complex, even for bulk high-purity silica. This situation is complicated further by the presence of a surface. While the specific sites for ethylene chemisorption, as atomic entities, have not been identified in the course of the experiments described here, one positive attribute of the sites has been determined. In addition, three properties of the irradiated solid have been shown to have no relation to the sites.

The following is known about the sites responsible for the ethylene chemisorption. In chemical terms, ethylene polymerization can occur *via* both radical and ionic mechanisms. Assuming the radiation leads to unpaired electrons in the solid ($M\cdot$) which can react as chemical initiators, a likely radical mechanism would be



Since NO is a well-known inhibitor for free-radical chain reactions for hydrocarbons in the gas phase,¹⁷ NO would be expected to poison the scheme depicted above. Similarly, O_2 would be expected to inhibit the reaction.

The electron spin resonance studies showed the presence of unpaired electrons associated with groups such as Si, O, and B. Since the adsorption of gases such as CO affected the e.s.r. spectrum, the unpaired electrons visible in the e.s.r. must be "accessible" to molecules such as CO, and presumably also to NO. However, NO was observed to have no effect on the e.s.r. spectra of irradiated samples. Therefore, the species observed in the e.s.r. are not chemically similar to hydrocarbon free radicals and do not react with NO. They would not then be expected to initiate the above reactions.

The effect of O_2 is convincing evidence that the reaction cannot be initiated by $H\cdot$ somehow "trapped" in the solid. It is true $H\cdot$ would easily react with NO to form HNO, but it would also surely react with O_2 . It is not possible, however, to be so emphatic about the possibility that the reaction is initiated by species such as $OH\cdot$ formed during the irradiation. Thus, $OH\cdot$ would be expected to react with NO, but not with O_2 . Therefore, the possibility that $M\cdot$ is $OH\cdot$ formed during the irradiation cannot be ruled out. However, the experiment noted previously—the failure of the irradiated solid to exchange with D_2 —would argue against $\cdot OH$ as the initiator assuming the reaction with D_2 is not much slower than the addition to C_2H_4 .

The three properties of the irradiated solid which have no relation to the sites for C_2H_4 adsorption are the following. When either H_2 or D_2 is pre-adsorbed before the ethylene, the growth of the adsorbed ethylene was normal. Thus, the sites on which the H_2 and D_2 adsorb are not those on which the C_2H_4 adsorbs. It is, of course, possible that H_2 adsorbs on the

ethylene sites, and that the subsequent ethylene adsorption displaces the adsorbed H_2 , but this seems unlikely. Secondly, the ethylene sites are not related to the color centers. The latter are bleached very rapidly by the addition of H_2 (and D_2), and yet the C_2H_4 subsequently adsorbs as normal. Furthermore,

if the ethylene is added first, color still remains in the sample, and subsequent addition of H_2 , after removing the gaseous C_2H_4 , bleaches all the color. Finally, none of the unpaired electrons which are observed in the e.s.r. spectrum are related to the sites responsible for C_2H_4 chemisorption.

[CONTRIBUTION NO. 1229 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA]

The Molecular Structure of 1,3,5-Cycloheptatriene in the Vapor Phase as Determined by the Sector Electron Diffraction Method

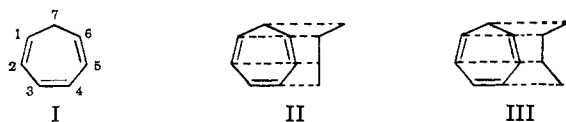
BY MARIT TRÆTTEBERG¹

RECEIVED FEBRUARY 10, 1964

The sector electron diffraction method was used to determine the molecular structure of 1,3,5-cycloheptatriene in the vapor phase. The molecule possesses C_s symmetry, and the most important observed structural results are as follows (for numbering of the atoms, see Fig. 5): $r_g(C_1-C_2)$ (assumed equal to $r_g(C_3-C_4)$) = 1.356, $r_g(C_2-C_3)$ = 1.446, $r_g(C_6-C_7)$ = 1.505, $r_g(C_1-C_6)$ = 2.511, $r_g(C_2-C_5)$ = 2.792, $r_g(C_3-C_4)$ = 2.424, $r_g(C_2-C_7)$ = 2.501, $r_g(C_1-C_3)$ = 2.510, $r_g(C_1-C_5)$ = 2.975, $r_g(C_7-C_5)$ = 3.064, $r_g(C_1-C_4)$ = 3.116, $r_g(C_1-H_1)$ = 1.095, $r_g(C_7-H_7)$ = 1.106 Å.; $l_m(C_1-C_2)$ = 0.044, $l_m(C_2-C_3)$ = 0.047, $l_m(C_6-C_7)$ = 0.050, $l_m(C_1-H_1)$ = 0.083, $l_m(C_7-H_7)$ = 0.085 Å.; $\angle C_1C_2C_3$ = 127.2°, $\angle C_2C_3C_4$ = 119.8°, $\angle C_5C_6C_7$ = 121.8°. The molecule exists in a boat conformation with the methylene group and the opposite carbon-carbon double bond bent out of the plane determined by the carbon atoms 1, 2, 5, and 6. The methylene group is tilted 36.5° away from that plane, and the angle between the planes determined by the carbon atoms 1, 2, 5, 6 and 2, 3, 4, 5 is found to be 40.5°. The estimated standard deviations of the molecular parameters are listed in Table I.

I. Introduction

During the last decade the molecular structure of 1,3,5-cycloheptatriene (CHT) has attracted interest from many scientists in different fields of research. But, so far an unambiguous over-all structure determination of this molecule has not been reported.



Three possible structural conformations of the carbon skeleton in the seven-membered carbon ring system are shown above (models I-III). Model I with planar carbon skeleton possesses C_{2v} symmetry, while the other two models belong to the point group C_s .

On the basis of the n.m.r. spectrum of CHT, Doering, *et al.*,^{2a} in 1956 suggested a pseudo-aromatic structure for the molecule with a planar carbon skeleton. The supposed aromatic structure is reflected in their use of the name tropilidene for CHT.

In 1958 Abel, *et al.*,^{2b} suggested from n.m.r. and vibrational spectra that the six carbon atoms in CHT, other than the methylene group, must be very nearly in the same plane, and that the six π -electrons form a delocalized system which bypasses the methylene group.

Dunitz and Pauling³ found from X-ray analysis that CHT in crystalline $C_7H_8Mo(CO)_3$ has a nonplanar structure and that the methylenic carbon atom does not lie in the plane of the conjugated system. The close similarity between limited regions of the infrared spectra of the complex and of the free CHT makes these

authors suppose that C_s symmetry also holds for the free molecule.

Evans and Lord⁴ have studied the infrared and Raman spectra of CHT and have satisfactorily interpreted the spectra in terms of C_{2v} symmetry (model I). They admit, however, that a slight displacement of the methylene group out of the ring plane is possible, as the selection rules would not be sensitive enough to make such a slight departure apparent.

Recently La Lau and De Ruyter⁵ reported an investigation of the vibrational spectra of CHT in order to determine the molecular symmetry. A comparative study⁶ of the infrared spectra of CHT and 7-D-CHT showed that the methylenic hydrogen atoms occupy geometrically nonequivalent positions, and the authors therefore concluded that the methylene group is tilted out of the plane of the conjugated system.

It should also be mentioned that Davis and Tulinsky⁷ have studied the molecular structure of thujic acid by X-ray crystallography. They found that the CHT ring in this molecule assumes a boat conformation (model III), with the methylene group and the C_3-C_4 double bond tilted 49.7 and 23.7° away from the plane determined by the carbon atoms 1, 2, 5, and 6.

It can be assumed that the energy of the π -electron system will decrease rapidly as the distance between carbon atoms 1 and 6 is decreased and that it will increase if the ring is puckered. These two factors are closely connected with the strain energy of the molecule, since decreasing the distance between carbon atoms 1 and 6 increases the strain, especially on $\angle C_5C_6C_7$ and on $\angle C_1C_2C_6$, and tends to force carbon atom 7 away from the plane of the adjacent double bonds. This would twist the π -orbitals of carbon atoms 1 and 6 out of parallelism of the other π -orbitals in the molecule and there-

(1) (a) The author wishes to thank the United States Air Force Office of Scientific Research for financial assistance; (b) on leave of absence from Norges Laererhogskole, Trondheim, Norway.

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