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Photodecomposition of Adsorbed Ethanoic Acid over Silica Gel Catalyst in a Flow System

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The photodecomposition of ethanoic acid adsorbed on silica gels from various sources was studied at wavelengths greater than 300 nm. The experiments were carried out in a flow apparatus. A few photoreactivity tests using acetone or ethanol were also performed. The photodecomposition of ethanoic acid and acetone produced mainly carbon dioxide and methane, in the ratio 2 : 1, and traces of ethane and methanol. Adsorbed ethanol was not affected at all by the radiation. Infrared and UV–vis reflectance spectra of ethanoic acid adsorbed on silica gels as well as UV–vis reflectance spectra of acetone and ethanol adsorbed on silica gels were recorded. The spectra show the presence of a variety of adsorbed species. It is suggested that the origin of photoreactivity for ethanoic acid is due to a chromophore $>C{=}O$ group of surface esters. A reaction mechanism which accounts for the ratio 2 : 1 of carbon dioxide to methane is proposed. © 1986 Academic Press, Inc.

INTRODUCTION

The behavior of many compounds adsorbed on solids, including varieties of silica, has been extensively investigated by spectroscopic methods, especially IR spectroscopy. Problems such as spectral shifts, changes in absorption coefficients, behavior of vibrational frequencies, appearance of new bands, and other features have been addressed and reviewed (*1*, *2*).

Much less attention has been paid to the photochemical reactions of adsorbed species. Few such studies, for instance, are reported in the review by Nicholls and Leermakers (*2*). There have been studies related to the photolysis of alkyl ketones adsorbed on porous Vycor glass in the presence of a quencher such as nitric oxide and also photolysis of mixtures of ketones adsorbed on Vycor glass (*3*, *4*). The photoisomerization of 2-butenes adsorbed on porous Vycor glass in the presence and in the absence of sensitizers was also reported (*5*, *6*).

The main scope of our investigation is an attempt to understand the reasons why silica gel exhibits catalytic activity when adsorbed species are irradiated. In this paper we report the results of an investigation devoted to the study of the photodecomposition of ethanoic acid adsorbed on silica gel. The choice of ethanoic acid is related to the interest in its photodecomposition for the field of photoelectrochemical and photocatalytic investigations at semiconductor surfaces (*7–11*).

METHODS

Apparatus. The catalytic experiments were carried out in a flow apparatus using a fixed-bed flat reactor, whose internal dimensions (width, thickness, and height) were 3.7, 0.2, and 9 cm, respectively. The photoreactor walls, 0.3 cm thick, and the gas distributor were made of Pyrex glass. It was vertically mounted inside a thermostated chamber whose internal surfaces were painted black. A circular aperture, made on a wall of the chamber and also covered by Pyrex glass (0.3 cm thick), allowed the reactor to be irradiated on one side by a 1000-W Hg–Xe lamp (Hanovia

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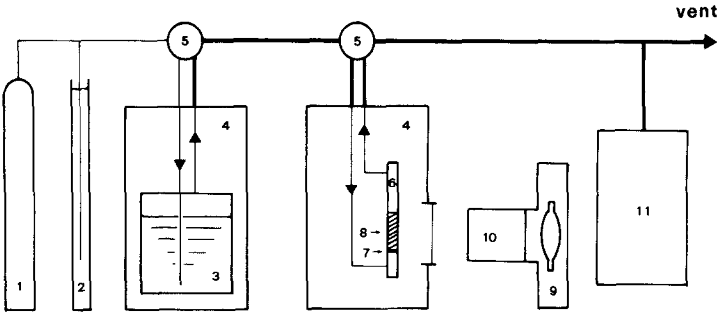


FIG. 1. Setup of the experimental apparatus. (1) He cylinder, (2) water valve, (3) bubbling bottle, (4) thermostated chamber, (5) four-way valve, (6) flat photoreactor, (7) gas distributor, (8) fixed bed, (9) lamp housing, (10) water filter, (11) gas chromatograph. Thick lines were electrically warmed.

L5173). The approximate distance between the reactor and the lamp was 50 cm. A water filter, 10 cm in thickness, was placed in the lamp housing to absorb the infrared radiation. The increase in temperature on the catalyst due to the radiation was measured and found to be negligible.

A flow diagram for the overall experimental apparatus is presented in Fig. 1. He (99.5% purity), at a constant rate of 0.1 cm^3 s^{-1} under standard conditions, was bubbled through a bottle containing, according to the requirements, glacial ethanoic acid, acetone, and ethanol (Carlo Erba reagent grade). A water valve was inserted into the gas line just after the He cylinder in order to guarantee that the pressure in the line did not exceed 10^4 Pa, since pressures higher than this rapidly damage the flat photoreactor. The gaseous mixture from the bubbler was then fed to the photoreactor; its composition could be varied by changing the temperature of the saturator. Finally, the gas from the reactor outlet was passed to a gas chromatograph (Varian, Vista 6500), equipped with FID and TCD detectors, to monitor the mixture composition. A Porapak QS column, 3 m in length, was used to separate gases. Two four-way valves, inserted in the gas line, allowed both the saturator and the photoreactor to be bypassed and the gas mixtures to be analyzed at various points in the flow system. Owing to the overall arrangement of the experimental apparatus, the presence of traces of water and air in the gaseous mixture feeding the photoreactor was unavoidable.

Reactor temperatures used T_R were 30, 50, 70, 80, and 110°C; saturator temperatures T_S used were 16, 40, 51, and 62°C. Obviously, no experiment was performed with a saturator temperature higher than that of the reactor. To avoid vapor condensation, the gas line was electrically warmed at 110°C during all runs.

The run procedure was as follows: The photoreactor was filled with catalyst and time was allowed for thermal equilibrium to be reached in the whole system. Then, feeding of the gaseous mixture and irradiation of the reactor started simultaneously; this time is considered the zero time for the run. Analyses of gas leaving the reactor were performed a few minutes after the start and then after about every 3 h. The runs lasted 16 to 69 h and were stopped when no changes in catalytic activity were observed.

Catalysts. The catalysts used were silica gel powders of various sources (BDH, Grace, Carlo Erba, Johnson–Matthey Chemicals Specpure, Bioglass Silica Foam), and were used without any preliminary chemical treatment. Powders were crushed and sieved and those particles in the size ranges 37–90, 90–180, and 125–250 μm were used. For all runs the same amount of catalyst was used (1.5 g), and,

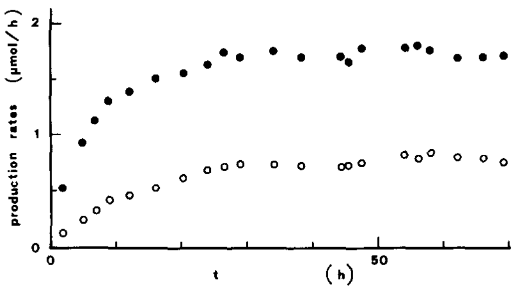


FIG. 2. Reaction rates versus time for a silica gel catalyst not saturated with ethanoic acid before the run. ●, Carbon dioxide; ○, methane.

independently of the particle size, the fixed bed always had the same height of 4 cm. Much care was taken to avoid the possibility of fortuitous contamination of catalysts before and during runs.

One catalyst was also prepared as follows. Silica gel (BDH) was completely dissolved in a strong alkaline solution of NaOH. To this solution, vigorously stirred, HCl (37%) was then added until a pH value of about 3 was reached. The white precipitate, held at room temperature for 1 day, was filtered and washed with distilled water until there was complete elimination of chloride ions. Finally the catalyst was dried in air at 120°C for 24 h.

A preliminary heating treatment at 120°C for 24 h was performed on all catalysts before use. Three specimens, all from the Grace 113 batch, were also tested after a heating treatment in air for 1 day at 200, 400, and 600°C, carried out just before the experiments. The loss of weight due to heating was 3, 3.5, and 5.5%, respectively.

Catalysts were tested according to two procedures. In the first, the powder was placed into the photoreactor after the heating treatment and then the run was started as described above. In the second, before the run was carried out, the powder was held for 1 week in an atmosphere of an organic compound selected for the experiment and then the run was started as above.

Typical plots of experimental results of reaction rates versus time, obtained by using the first and the second methods, are reported in Figs. 2 and 3, respectively.

In order to investigate the origin of the observed photoactivity, IR transmittance and UV–vis reflectance spectra have been recorded for catalyst samples. An IR spectrophotometer (Perkin–Elmer, Model 580) was used to obtain spectra in the range 4000–1200 cm^{-1} on a disk obtained by pressing silica gel powder at a pressure of 1.3×10^9 Pa. The cell containing the sample was equipped with a CsI window and was connected to a high-vacuum system equipped with suitable traps.

Reflectance spectra in the range 600–300 nm were obtained by using a UV–vis spectrophotometer (Varian, Model DMS 90) equipped with quartz cells. $BaSO_4$ was used as reference sample. The silica gel powder used for reflectance measurements was ground until no influence of the particle size on the reflectance spectrum was observed. To obtain silica gel saturated with the organic reactants used, the powder was held at room temperature in an atmosphere of ethanol, ethanoic acid, or acetone for 2 weeks before performing the spectra reported in Fig. 4 and indicated as 1, 2, and 4, respectively. By contrast, the reflectance spectrum indicated as 3 in Fig. 4 was obtained for a silica gel powder taken from the photoreactor just after the run.

Specific surface areas, S, of all the catalysts used were determined by applying the BET method to the adsorption isotherms of nitrogen at −196°C. Analyses performed by

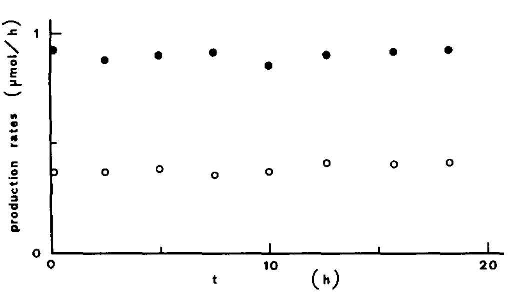


FIG. 3. Reaction rates versus time for a silica gel catalyst saturated with ethanoic acid before the run. ●, Carbon dioxide; ○, methane.

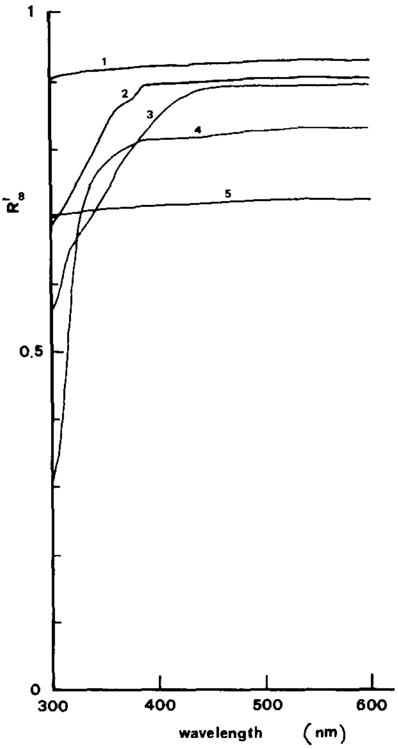


FIG. 4. UV-vis reflectance spectra. (1) Pure silica gel and silica gel saturated with ethanol, (2) silica gel saturated with ethanoic acid, (3) silica gel powder after a catalytic run, (4) silica gel saturated with acetone, (5) silica gel with liquid ethanol.

X-ray diffractometry showed that all the silica catalysts were completely amorphous.

RESULTS

Catalytic Results

For all catalytic runs performed using ethanoic acid and acetone as reactants, the main reaction products were carbon dioxide and methane, but traces of ethane and methanol were also detected. When ethanol was used as reactant, no reactivity was observed.

Results obtained from catalytic experiments are reported in Tables 1–4. The production rate values (μmol h^{-1}), reported in these tables refer to the mean value or to the asymptotic value achieved during the run. In fact, for catalysts saturated with the organic reactant before the run, constant values of reaction rate appeared after the start of the run. On the contrary, for catalysts free of organic reactant, the reaction rate always started from zero and asymptotically reached the same constant value after a period of time ranging from 10 to 30 h. As previously stated, typical plots illustrating these different behaviors are reported in Figs. 2 and 3.

TABLE 1

Results for Ethanoic Acid Decomposition Obtained by Using the "Home-Prepared" Silica Gel Catalyst (Particle Size 37–90 μm, S = 287 m^2/g)

T_R (°C)	T_S (°C)	CO_2 (μmol/h)	CH_4 (μmol/h)	t (h)
80	62	0.94	0.45	40
80	51	0.91	0.41	18
80	40	0.98	0.53	24
110	40	0.98	0.50	23
50	40	0.93	0.43	20

Tables 1–3 report the experimental results of ethanoic acid decomposition obtained from all the silica gel catalysts used. In Table 1 the results obtained from our own prepared catalyst at different reactor temperatures and at different ethanoic acid partial pressures clearly indicate the independence of reaction rates from these two variables in the range used. These results seem to indicate that the activation of some species adsorbed on the catalyst may be the

TABLE 2

Results for Ethanoic Acid Decomposition Obtained by Using Grace 113 Silica Gel (Particle Size 125–250 μm, S = 240 m^2/g, T_R = 30°C, T_S = 16°C) at Different Temperatures of Heating Treatment, T_{HT}

T_{HT} (°C)	CO_2 (μmol/h)	CH_4 (μmol/h)	t (h)
120	1.73	0.85	69
200	1.82	0.92	45
400	1.80	0.92	41
600	1.76	0.90	68

TABLE 3

Results for Ethanoic Acid Decomposition on Silica Gel Powders from Different Sources (T_R = 70°C, T_S = 62°C)

Source	Particle size (μm)	S (m²/g)	CO_2 (μmol/h)	CH_4 (μmol/h)	t (h)
Bioglass Silica Foam	90–180	312	1.81	0.86	20
Johnson–Matthey Specpure	37–90	39	0.88	0.38	16
Carlo Erba	90–180	261	0.95	0.44	26

rate-determining step of the process. Table 2 reports the results obtained from Grace silica catalysts with different heating treatments. For these runs the powders were used without preliminary saturation with ethanoic acid and the results indicate that the heating treatment does not affect the final catalyst reactivity. The achievement of the asymptotic value for the reaction rates was faster for powders with a higher temperature of heating treatment. In Table 3 the results obtained from different sources of silica gel, including a certified specpure material, indicate that the activity must be attributed to silica gels and not to a fortuitous presence of impurities. Finally Table 4 reports the results obtained by using ethanol, acetone, and ethanoic acid with a Grace 113 catalyst. The results indicate the absence of any reactivity for ethanol.

From the reported results one may observe that for all catalysts the ratio between production rates of carbon dioxide and methane is about 2 to 1. This feature suggests that the system involves intermediate products which can be eventually oxidized to carbon dioxide.

TABLE 4

Results Obtained by Using Grace Silica Gel (Particle Size 125–250 μm, S = 240 m²/g, T_R = 50°C, T_S = 40°C)

Reagent	CO_2 (μmol/h)	CH_4 (μmol/h)	t (h)
Ethanoic acid	1.96	1.03	48
Acetone	0.26	0.17	65
Ethanol	—	—	50

No reactivity was detected, at any temperature, when light was turned off or when a 0.5-cm-thick sheet of polymethylmethacrylate was inserted between the lamp and the photoreactor. In Fig. 5 the reflectance spectrum of this sheet is reported together with that of the Pyrex glass used in the apparatus. When the light was turned on or the sheet was removed, reaction rates immediately returned to their previous values.

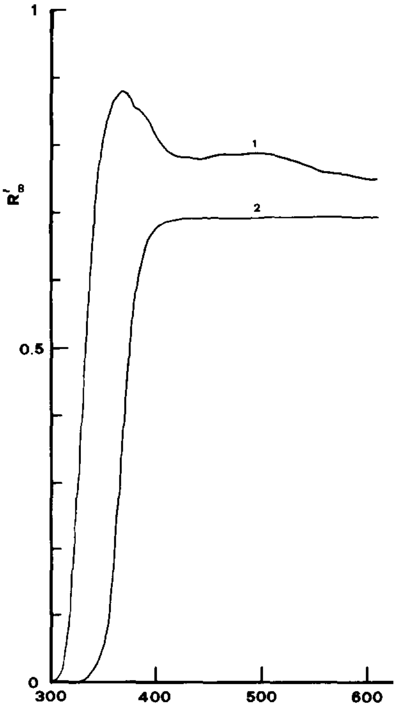


FIG. 5. UV–vis reflectance spectra of Pyrex glass (1) and of polymethylmethacrylate (2).

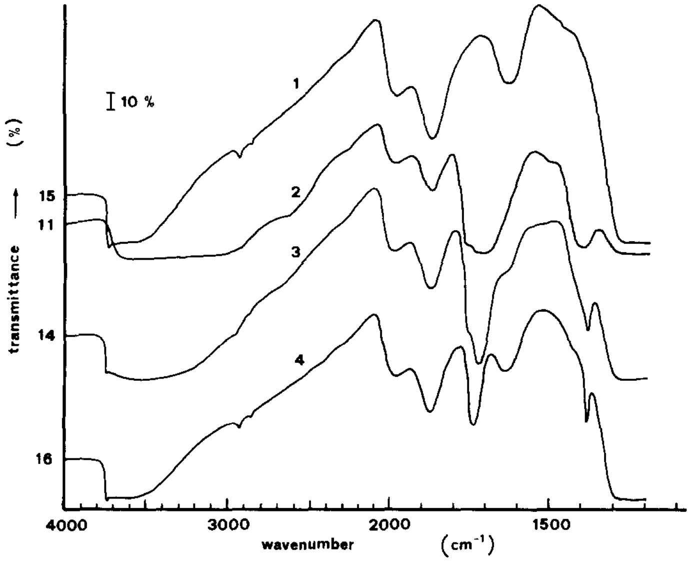


FIG. 6. IR transmittance spectra. (1) Silica gel after evacuation at 393 K for 1 h, (2) silica gel after subsequent exposure to ethanoic acid (0.5 Torr, 293 K), (3) silica gel after subsequent evacuation at 293 K for 30 min, (4) silica gel after subsequent evacuation at 353 K for 1 h.

Blank experiments under the usual experimental conditions were also performed with the empty reactor. Negligible amounts of carbon dioxide and methane were detected. By considering that the Pyrex glass used does not transmit at wavelengths shorter than 300 nm, which could directly excite the organic molecules used as reactants, this very small photoactivity can be attributed to the reactor itself.

IR and UV–Vis Spectra Results

IR spectra are presented in Fig. 6. Spectrum 1 refers to silica gel evacuated at 393 K for 1 h. This spectrum shows a complex absorption in the region 3800–3400 cm^{-1}, attributable to the stretching vibration of free (3750 cm^{-1}) and H-bonded hydroxyl groups on the surface.

Spectrum 2 was recorded on the previous specimen after exposure, at 293 K, to 0.5 Torr ethanoic acid vapor. One may note that the band due to free OH groups has disappeared and that the high frequency region is dominated by a very broad and intense absorption ranging from 3680 down to 2500 cm^{-1}, assignable to H-bonded hydroxyl groups of the surface and of adsorbed molecules. The C–H stretching vibrations are submerged in this absorption (*12–15*). The broad and complex absorption from 1675 to 1760 cm^{-1} may be attributed to ν(C=O) of species containing this group (*13, 16*). The broad band centered at 1400 cm^{-1} is due to CH_3 deformation modes (*13, 16*).

Spectrum 3 was recorded on the previous specimen outgassed for 30 min at 293 K. Its main features are that the band near 3750 cm^{-1}, due to isolated OH groups, is partly restored and that there is a decrease in the continuous band previously attributed to ν(OH) interacting with adsorbed ethanoic acid species. The band attributed to species containing C=O groups is still well visible, although reduced and partly modified. The same pattern applies to a broadband due to $\delta(CH_3)$ absorption.

Spectrum 4 was recorded on the previous specimen after a further outgassing at 353 K for 1 h. The ν(OH) absorption region almost overlaps that of spectrum 1, indicating that most of the adsorbed species are reversible at this temperature. However, the band at

1740 cm^{-1} is still clearly observable, although weaker and sharper. The sharpness and symmetry of the 1740 cm^{-1} band imply the likely existence of a single C=O-containing species. The sharpness of the residual $\delta_s(CH_3)$ band is also in favor of a single species containing the CH_3 group.

UV–vis reflectance spectra are reported in Fig. 4. The ordinate, R'_∞, is defined as the ratio between the sample reflectance and that of the reference sample (*17*). Spectrum 1 refers to a very fine powder of pure silica gel. As expected, there is no significant absorption between 600 and 300 nm.

Spectrum 2, recorded for the previous specimen exposed at room temperature to ethanoic acid vapor, shows a marked absorption starting from 390 nm.

Spectrum 3 refers to a silica gel catalyst (same batch as that used for spectrum 1) taken from the reactor after a run to test the photoactivity. It shows the same pattern of spectrum 2. Due to different particle size distributions and to the presence of reaction products, spectra 2 and 3 are not completely comparable.

Spectrum 4 refers to a silica gel specimen (same features as that used for performing spectrum 1) exposed to acetone vapor at room temperature. An extensive absorption, starting from 380 nm, can be noted.

The reflectance spectrum of a silica gel specimen (same source as previous ones) exposed to ethanol vapor at room temperature does not appreciably differ from spectrum 1. Spectrum 5 refers to the previous specimen with the addition of a few drops of liquid ethanol. It may be noted that the presence of the liquid had no effect on the spectrum pattern; it had only the effect of shifting the ordinate.

DISCUSSION

From all the experimental results the following general considerations can be drawn:

(a) the reactivity appears only when the catalyst is irradiated;

(b) the photoactivity cannot be attributed to contaminants and/or impurities present on silica but must be attributed to the interaction between silica gel surfaces and organic molecules;

(c) the observed photoactivity occurs at wavelengths higher than 300 nm;

(d) ethanoic acid is adsorbed on silica gel surfaces forming several species and one or more of these species are decomposed under irradiation.

Before discussing the previous points, it is worth pointing out that it is not the purpose of this study to try to give an order of photoreactivity of the various silica gels used. Our concern is to stress the important fact that all the silica gels studied behave in a similar way and to try to give a likely explanation for this behavior.

It is well known that silica glass is completely transparent in the visible and ultraviolet region until a wavelength value of about 190 nm. However, light absorption at wavelengths longer than 190 nm may be exhibited and can be attributed to various phenomena such as light scattering (*17*) by silica powders, presence of constitutional defects and/or contaminants, and presence of photoactive adsorbed molecules. The reflectance spectra indicated as 2, 3, and 4 in Fig. 4, when compared with spectrum 1 of pure silica, show an increase in absorption for wavelength values starting from 390 nm. This implies that molecules of ethanoic acid and acetone adsorbed on this solid affect light absorption in the near UV region. Moreover, the absence of any modification of the absorption spectrum when ethanol is present on silica shows that the species able to absorb radiation is the $\rangle$C=O group.

The main question to be answered now is whether the chromophore $\rangle$C=O group of the adsorbed molecule can exhibit photoreactivity at wavelengths greater than 300 nm.

The pertinent literature reports that radiation at 180 and 210 nm is necessary in order that the $\rangle$C=O group of ethanoic acid undergoes the π–π^* and n–π^* transitions, respectively, in gas phase or in apolar media (*18, 19*). Thus electronic transitions of the $>C{=}O$ group of the adsorbed molecule must undergo a red shift, caused by its interactions with the neighboring system, of, at least, 90 nm.

In a more general sense, silica gel can be considered as acting as a solvent for acetone and ethanoic acid. Solvent polarity has opposite effects on the shifting of n–π^* and π–π^* transitions of the $>C{=}O$ group. In fact, polar solvents, able to form hydrogen bonds with the nonligand electron pairs of oxygen, give rise to blue shifts for the n–π^* transition. On the contrary, the π–π^* transition undergoes red shifts because the solvent polarity stabilizes the charge separation of the excited state (*2, 20, 21*).

On this ground one could exclude for our system the occurrence of the n–π^* transition and conclude that the π–π^* transition occurs with a red shift of more than 120 nm. This conclusion would be completely true if all the chromophore $>C{=}O$ groups existing on the silica surface are bound by hydrogen bonds. This is not the case for our system.

By analyzing the IR spectra reported in Fig. 6, one may note that the adsorption–desorption process of ethanoic acid on silica powder is not completely reversible. A certain degree of irreversibility is present due to the presence of centers of esterification as

$$\geqq Si{-}O{-}CO{-}CH_3.$$

Moreover, the presence of the symmetrical band at 1740 cm^{-1} (Fig. 6, spectrum 4) and the decrease in engaged OH groups at the silica surface, when the outgassing was performed, clearly indicate that the esterified $>C{=}O$ groups maintain their vibrational states unchanged.

The presence on silica of chromophore $>C{=}O$ groups that are not engaged, but free, may justify a transition, n–π^* and/or π–π^*, with a broad red shift. In fact, by considering that the dissociation equilibrium constants, pK_a, of silica (*22*) and ethanoic acid have values of 10 and 4.78, respectively, silica macromolecules can be seen as electron donor agents with respect to the CH_3CO groups of esterified centers. This action destabilizes the fundamental state of CO groups by increasing the energy levels of the n and π ground states.

It is known that the n–π^* transition of the $>C{=}O$ group shifts from 210 nm for ethanoic acid to 276.5 nm for acetone (*19*). Thus the donor effect of the methyl group, larger than that of the hydroxyl group, is able to induce a red shift of 66.5 nm on the $>C{=}O$ group. Moreover the energy level of the π^* state is stabilized by the high surface potential of silica and also by its polarity. These factors decrease the energy requirement for the n–π^* and π–π^* transitions and therefore they may cause a red shift of the $>C{=}O$ group transitions to wavelengths above 300 nm.

In conclusion, it seems likely that the photoactive center is the chromophore $>C{=}O$ group of surface esters. These groups can be free or engaged with hydrogen bonds. For the first, both the n–π^* and π–π^* transitions are red shifted; for the second, the n–π^* transition is blue shifted while the π–π^* transition is red shifted. The broad red shift can be caused by the following factors:

(a) electron donor effect of silica macromolecule on the $CH_3{-}CO{-}O{-}\!\!\|\!\!{-}Si\leqq$ group;

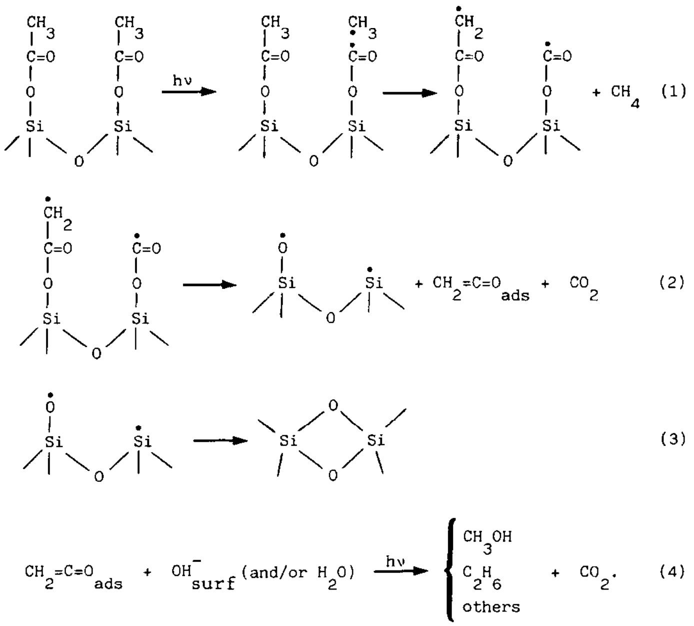
(b) silica polarity;

(c) surface interaction of $>C{=}O$ dipoles;

(d) effect of dispersion forces.

The synergic effect of all the previous factors eventually allows absorption of radiation at wavelengths higher than 300 nm with the final effect of dissociating the CH_3CO group.

On the basis of all the experimental findings, the reaction mechanism shown in Scheme 1 is proposed. This mechanism is able to explain the observed value, of about 2, for the ratio between carbon dioxide and methane production rates and, moreover, to justify the initial zero value of reaction



SCHEME 1

rates found for silica powders not saturated with the organic reactant before the catalytic runs. The formation of ketene, as shown in reaction 2, has been hypothesized by analogy with the thermal decomposition processes of ethanoic acid carried out in the vapor phase and on metallic oxides (*23–25*).

CONCLUSIONS

The chemical adsorption of ethanoic acid molecules on silica gel leads to the formation of surface esterified centers and, as a consequence, a modification of the electronic absorption spectrum of the adsorbed molecule. This modification involves a decrease in the energy requirement for the photodecomposition reaction of the surface ester.

The main scope of this work has been to explain the reasons for the photoreactivity exhibited by this system although, from the experimental results, it has not been possible to discriminate which transition, n–π^* or π–π^*, occurs to effect the reaction.

The work suggests that care must be taken in examining the photoreactivity of organic molecules which have a chromophore group when they are adsorbed on insulating or semiconductor oxides.

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