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A Study of the Mechanisms of Formic Acid Dehydration on TiO_2

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Two different mechanisms have been proposed for the catalytic dehydration of formic acid on TiO_2, depending on the work temperature. The mechanism observed between 150 and 250°C involves the formation of a protonated formic acid molecule which is suggested as being the slowest step in this reaction, which proceeds with an activation energy of 10.5 kcal mol^{-1} on $Ti^{4+}OH^-$ dual sites.

The high temperature mechanism, prevailing at 350–450°C, occurs through formate ions, unstable on the TiO_2 surface at $t > 300°C$. The controlling step for the reaction was in this case the formation of a water molecule from two hydroxyls left on the surface of the catalyst when the formate decomposes. The activation energy for this process was 25.5 ± 0.5 kcal mol^{-1} and 3×10^{14} OH/cm^2 were estimated for the coverage under catalytic conditions.

INTRODUCTION

Different authors (1–3) have previously reported that catalytic dehydration of formic acid takes place on most oxides through formate ions when the reaction is carried out at temperatures higher than 300°C.

However, the reaction has recently been reinvestigated by Tamaru *et al.* (4–6) using Al_2O_3 and SiO_2 at temperatures lower than 200°C, and another mechanism involving gaseous formic acid and surface protons has been proposed.

Although formate ions and water molecules were found on the surface of Al_2O_3 and a very small amount of adsorbed formic acid molecules was detected on SiO_2, it has been shown that neither of these was directly involved in the reaction at $t < 200°C$.

The existence of two mechanisms could be accounted for, using the surface models of these oxides (*7, 8*) and assuming the different states of the active surface according to the range of temperature.

In order to examine this possibility in detail we have studied the reaction on TiO_2, an acidic catalyst whose surface has been widely investigated in our laboratory during recent years (*9, 10*).

EXPERIMENTAL

Materials

The rutile sample (Code No CL/D173/1) was prepared in the laboratory of British Titan Products Co. Ltd. (England) by hydrolysis of redistilled titanium tetrachloride followed by heating in the air at 800°C.

The rutile structure of the sample was established from X-ray and a specific area of 4.5 ± 0.3 m^2/g^{-1} was obtained by the micro-BET method with nitrogen at 78°K (N_2 area 16.2 A^2). A detailed study of the porosity of this sample has been published elsewhere (*11*).

Conductivity water and Schuchard formic acid, redistilled by us on anhydrous SO_4Cu, were outgassed several times until free of dissolved gases.

Apparatus and Procedures

Weighed samples (about 0.5 g) were outgassed before adsorption experiments to a final pressure $<10^{-5}$ Torr and at a temperature of 400 ± 2°C for 3–5 hr. After a series of experiments, the sample was outgassed at 700°C for 15 min and a new set of experiments were performed on this reduced sample. Surface area after this treatment was the same as mentioned previously for a fresh sample.

Water and formic acid isotherms at 18 ± 1°C were normally measured in the range of relative pressures, p/p_0 lower than 0.25 using a volumetric apparatus provided with a silicon fluid manometer of a high sensibility. Formic acid isotherms were corrected using data of Waring (*12*) for the dimerization in the gas phase.

Corrections due to adsorption on the walls of the system and on the free meniscus of the manometer were negligible with regard to the measured values. The equilibrium was established in all cases within 30 min and no further change occurred over a period of up to 2 days.

After a first isotherm, the sample was always outgassed at room temperature and on this surface a new isotherm was obtained. The difference between the amounts adsorbed in both experiments, which remains constant at $p/p_0 > 0.03$, was taken as the irreversible adsorption at room temperature.

This tight adsorption was removed from the surface by Temperature Programmed Desorption (TPD) in a system of design similar to the one described by Amenomiya and Cvetanovic (*13*) using nitrogen as a carrier gas. Detection of the evolved gases was carried out with a TC filament in series with an Aerograph 200 used for the chromatographic analysis of the desorbed species.

After each Adsorption-TPD run, the samples were heated at 400°C in the air for several hours prior to a new evacuation at this temperature. In this way a reproducible initial state was obtained with the same sample in successive experiments.

For infrared studies, rutile was ground and pressed under vacuum into self-supporting discs, which were placed in a small cell with ClNa windows. Infrared spectra were recorded with a Perkin-Elmer mod. 621 double-beam grating spectrometer as previously reported (*14*).

Samples pretreated as in adsorption experiments were used in kinetic studies at temperatures lower than 200°C. A thermally circulating system provided with a silicon fluid manometer was used in this case. The CO evolved during the reaction was measured isolating the silicon gauge and freezing out the water and the formic acid of the mixture with liquid nitrogen in a cold finger. Hydrogen was not detected in the gas phase by GSC in these experiments.

At temperatures higher than 350°C the reaction was studied in a conventional flow system, using the Herbo method (*15*), which enables the evaluation of the true energy of activation for the reaction.

RESULTS

Infrared Study of Hydroxyls and Adsorbed Formic Acid

The infrared spectrum of a sample evacuated at 10^{-6} Torr and 400°C for 10 hr has been recorded in the range 4000–3500 cm^{-1}, and is shown in Fig. 1.

Bands at 3725, 3670, and 3650 cm^{-1} are easily resolved and have been ascribed (*16*) to OH-groups on the surface of this oxide with a different level of hydrogen bonding. A prolonged outgasing at 400°C completely removes bands at 3670 and 3650 cm^{-1}, but the one at 3725 cm^{-1} remains almost unchanged after this treatment.

Reoxidation of the 400°C outgassed discs in oxygen or dry air at the same temperature does not change the intensity and shape of these bands. However, outgassing at $t \geqslant 550°C$ releases oxygen from the oxide, increasing the absorbance of the disc in this range. In such a case, OH-bands could only be recorded after heating the disc in oxygen at 400°C until the white color of TiO_2 was restored.

On the other hand, leakage of minor amounts of wet air at room temperature into the infrared cell leads to an increase in the intensity of both the 3670 and 3650 cm^{-1} bands (Fig. 1(b)), while the other band remains unchanged and so too the region of the spectrum between 1500 and 1700 cm^{-1} in which molecular water, if present, must

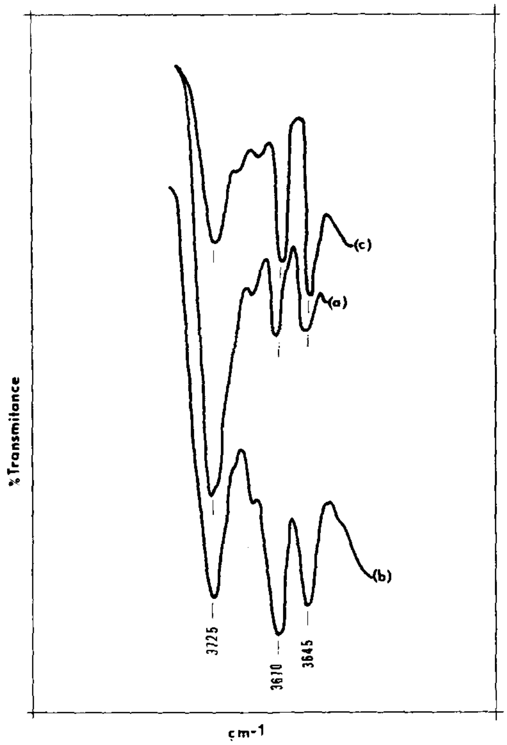


FIG. 1. Infrared spectra of hydroxyls on TiO_2 outgassed at 400°C for 10 hr: (a) in the vacuum after outgassing; (b) after leakage of traces of wet air; (c) after formic acid adsorption.

give a band at 1600–1630 cm^{-1} due to the bending vibration of the molecule. However, when the TiO_2 pellet remained in contact with wet air for several hours, a broad band at 1620 cm^{-1} could be observed. The infrared spectra of this sample were similar to those obtained with a fresh disc before any pretreatment in vacuum.

The new band at 1620 cm^{-1} was completely removed by evacuation at $t \geqslant$ 250°C while regeneration of the three hydroxyl bands was achieved by outgassing at 400°C.

Adsorption of formic acid at room temperature on the 400°C evacuated sample, followed by removal of the gas phase and physical adsorption, leads to smaller hydroxyl bands as can be seen in Fig. 1(c). A broad band due to complex hydrogen bonding between OH-groups and formic acid on the surface, was recorded at 3450 cm^{-1} in these conditions.

The infrared spectra recorded between 2000 and 1200 cm^{-1} show a band at 1690–1700 cm^{-1} due to molecular adsorption, which cannot be removed by outgassing at room temperature for 3 hr, but disappears by heating at 150°C. On the contrary, the bands due to formate ions (1580 and 1365 cm^{-1}) decreased very slowly at these temperatures but they did so very quickly above 300°C. Evacuation in the usual way at 400°C gives the OH-bands as in the initial sample.

Adsorption and TPD Analysis

Figure 2 shows water isotherms on the TiO_2 sample. The knee at $p/p_0 \simeq 0.03$ in the first isotherm represents the irreversible adsorption at room temperature. Table 1 includes adsorption data of a series of experiments with the same sample.

Figure 3 shows characteristic desorption chromatograms of tightly adsorbed water

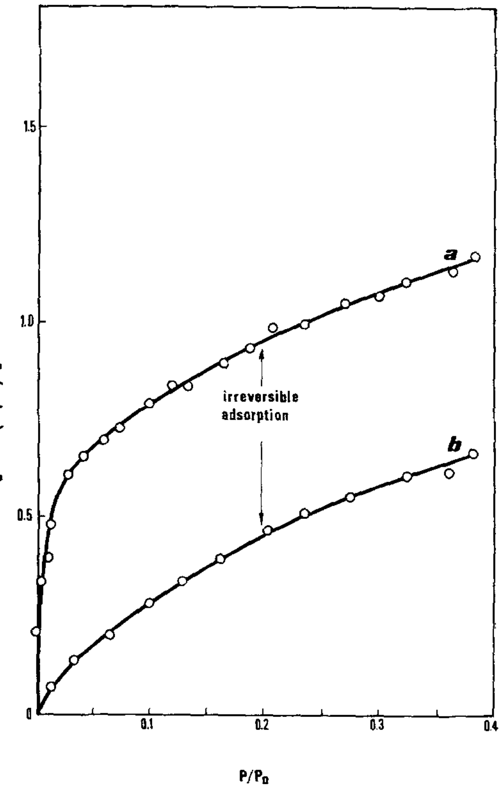


FIG. 2. Isotherms of water at room temperature: (a) on a sample outgassed at 400°C for 3–5 hr; (b) on the same sample outgassed at room temperature after isotherm (a).

TABLE 1
Adsorption of Water and Formic Acid on TiO_2 (in ml(n.p.t.)g^{-1})

Expt. No.	Adsorbate	Irreversible adsorption
1 (fresh sample)	water	0.47
2	"	0.52
3	"	0.50
4	formic acid	0.30

on TiO_2 (Table 1). After the first heating up to 650°C using a fresh sample, successive runs with the same sample did not show the maximum at 500°C while a slight increase in the maximum at 370°C was observed. A chromatogram of an aged sample, heated in air at 400°C and evacuated at the same temperature, has been included in Fig. 3(c). The shape of the peak, with a long tail, suggests a process with increasing heat of activation for the release of these residual hydroxyls.

Four types of adsorbed water have been distinguished according to their release from the surface. The amount of water corresponding to each of these forms has been obtained assuming that type III plus IV represent the irreversible adsorption measured from the isotherms. Calculations on this basis leads to the values in Table 2. The number of OH-groups in this table has

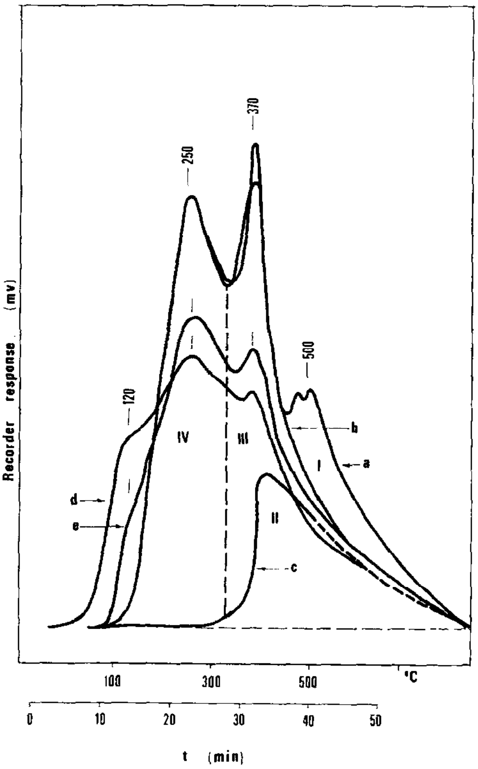


Fig. 3. TPD chromatograms of adsorbed water on a 400°C evacuated sample: (a) run 1, 0.47 ml(n.p.t.)g^{-1}; (b) run 2, 0.52 ml(n.p.t.)g^{-1}; (c) residual water on the 400°C outgassed sample; (d) water adsorbed on reduced TiO_2 (pretreated at 700°C in the vacuum for 15 min); (e) on the above sample reoxidized at 400°C.

TABLE 2
TPD Analysis of the Irreversible Adsorbed Water on TiO_2

Experiment No.		Original OH-groups (I)	Residual OH after evac. 400° (II)	Reformed OH groups (III)	Water molecules (IV)	Total adsorption
1	peak area	40	60	70	100	
fresh sample	ml(npt)g^{-1}	0.11	0.17	0.19	0.28	0.47
	species/100 A^2	1.3	2.0	2.2	1.7	
2	peak area	—	57	74	100	
	ml(npt)g^{-1}	—	0.17	0.22	0.30	0.52
	species/100 A^2	—	2.0	2.6	1.8	
3	peak area	—	60	80	100	
	ml(npt)g^{-1}	—	0.17	0.22	0.28	0.50
	species/100 A^2	—	2.0	2.6	1.7	

been estimated assuming a maximum density of 9 OH/100 A^2 on the face 110 of the rutile, the most likely to be exposed (*17*). On the other hand, water molecules remaining on the surface after outgassing at room temperature (Table 2.IV) are on sites of a decreasing strength, as suggested by TPD chromatograms in Fig. 4.

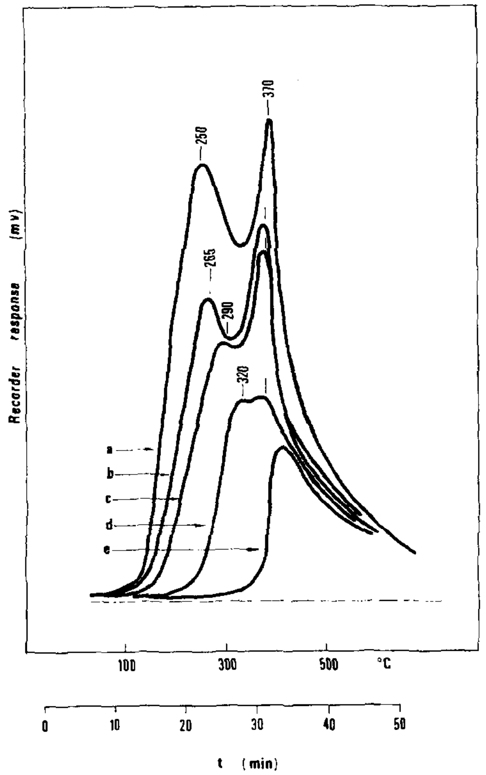


Fig. 4. TPD chromatograms of decreasing amounts of water readsorbed on TiO$_2$: (a) 0.52 ml(n.p.t.)g^{-1}; (b) 0.25 ml(n.p.t.)g^{-1}; (c) 0.15 ml (n.p.t.)g^{-1}; (d) 0.08 ml(n.p.t)g^{-1}; (e) residual water on the 400°C outgassed surface.

Surface reduction decreases the irreversible adsorption of water molecules and hydroxyls and leads to a new form of adsorption giving a peak at 120°C (Fig. 3(d)). Reoxidation at 400°C of this sample removes the peak at 120°C and increases the peaks at 250°C and 370°C.

Finally, Fig. 5 shows TPD chromatograms of formic acid irreversibly adsorbed at room temperature on the 400 and 700°C evacuated samples.

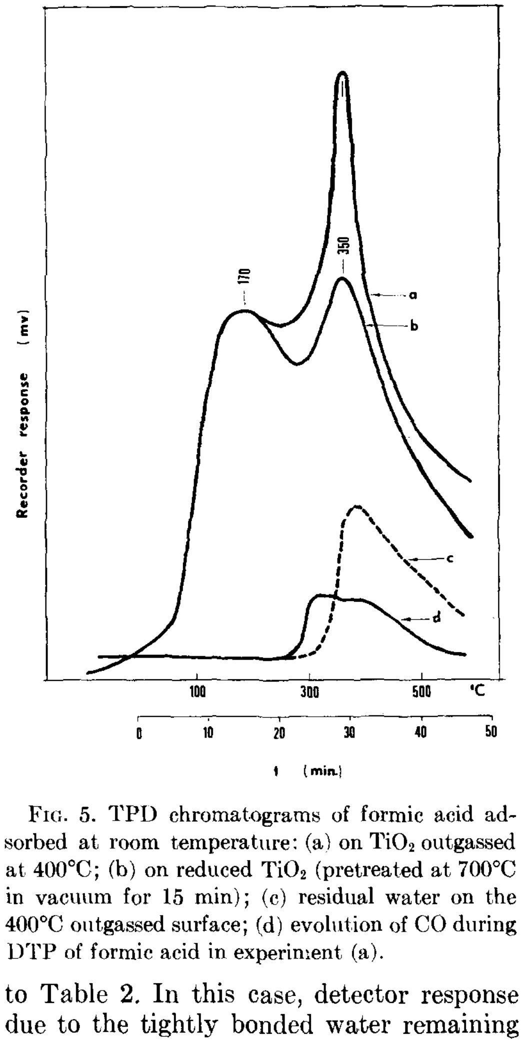


Fig. 5. TPD chromatograms of formic acid adsorbed at room temperature: (a) on TiO$_2$ outgassed at 400°C; (b) on reduced TiO$_2$ (pretreated at 700°C in vacuum for 15 min); (c) residual water on the 400°C outgassed surface; (d) evolution of CO during DTP of formic acid in experiment (a).

Table 3 was obtained in a similar way to Table 2. In this case, detector response due to the tightly bonded water remaining on the 400°C evacuated surface has been substracted from the total area of the peak at 350°C and corrections were made to take into account the partial decomposition of the formate.

It has been shown that molecular formic acid (maximum at 170°C) desorbs without decomposition while the strongest adsorption (formate) is partially recovered as H$_2$O and CO. The amount decomposed was about 30–35% of the adsorbed formate.

Kinetics of Hydroxyl and Formate Desorptions

The shape and the half-width of our TPD peaks of water and formic acid at 370 and 350°C, respectively, were compared with the standard maxima calculated

TABLE 3
TPD ANALYSIS OF HCOOH ADSORBED ON TiO_2

Experiment No.		Residual OH after evac. 400°	Dissociative Ads. of HCOOH H^+ ions	 $HCOO^-$ ions	HCOOH molecules
1 aged sample	peak area ml(npt)g^{-1}	(see Table 2.II)	150 0.18		100 0.12
	$\frac{\text{species}}{100\ A^2}$	2.0	1.1	1.1	0.7

by Amenomiya and Cvetanovic (*13*). Agreement was found when a monomolecular desorption without readsorption from an homogeneous surface was assumed. An activation energy of 25.5 ± 0.5 kcal mol^{-1} was estimated for the desorption of both species.

When the surface becomes partially dehydroxylated during the heating run, the peaks show a long tail suggesting that in these conditions another process is controlling the rate of desorption, probably with a high activation energy.

Applying different linear heating programs ($\beta = 2.5$; 4.5 and 14.5°C/min) and according to equation:

$$2 \log T_M - \log \beta = E_d/2.303\,RT_M + \log E_d/A_oR. \quad \text{(Eq. 1)}$$

Values of E_d and A_o were calculated from the straight lines in Fig. 6. These data were recompiled in Table 4 for the desorption of both species from the surface of our sample, together with the values of the entropy of activation obtained from the expression:

$$A_o = (kT/h) \exp(\Delta S^{\ddagger}/R). \quad \text{(Eq. 2)}$$

The Formic Acid Dehydration on TiO_2

It was found that a fast adsorption occurs at 165°C when formic acid at 8.06 Torr contacts the 400°C evacuated surface of the oxide. The 0.19 ml(n.p.t.)g^{-1} adsorbed in this way represent the dissociative adsorption of formic acid on our sample. Fig. 7 shows the changes in the gas phase and in the adsorbed state in this experiment.

Water generated in an initial stage up to 0.20 ml(n.p.t.)g^{-1} also remains irreversibly adsorbed on the surface. The rate of evolu-

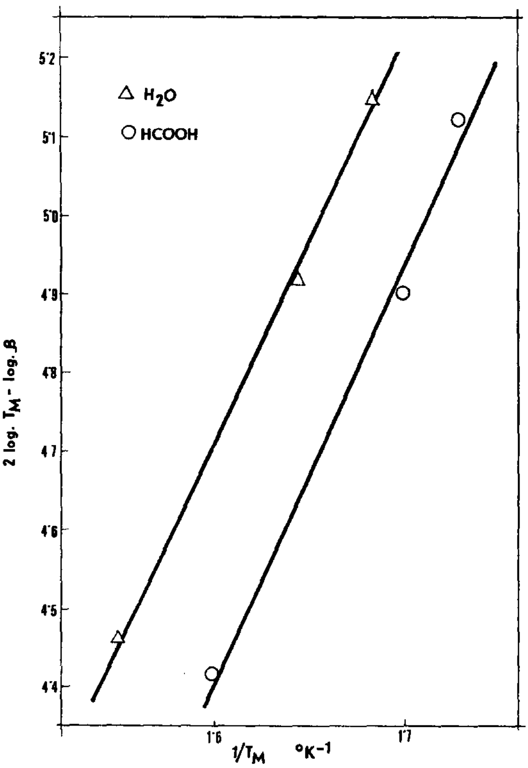


FIG. 6. Data from DTP chromatograms with different linear heating programs ($\beta = 2.5$; 4.5 and 14.5°C/min) plotted according to Eq. 1.

TABLE 4
KINETIC OF HYDROXYL AND FORMATE DESORPTION FROM TiO_2

Adsorbed species	A_o (sec^{-1})	E_d (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)
hydroxyl groups	2.7×10^8	25.7	−21.5
formate ions	3.2×10^8	25.1	−21.0

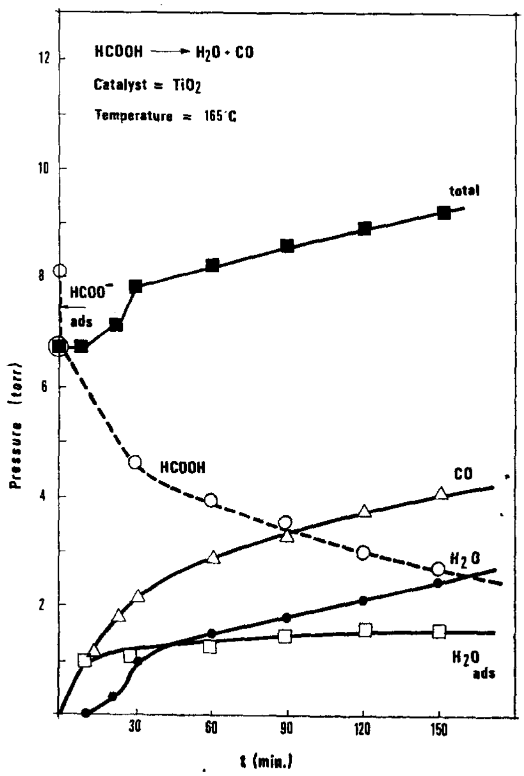


FIG. 7. Evolution of HCOOH, H_2O, and CO during the decomposition of formic acid on TiO_2 at $t \leqslant 200°C$.

tion of CO in the gas phase during this stage decreased sharply as might be expected if adsorbed water poisons a fraction of the active centers. In a second stage the evolution of H_2O and CO in the gas phase occurs in the ratio 1:1, although a small amount of water now remained weakly adsorbed in equilibrium with the gas phase. This adsorption produced a progressive decrease in the rate of reaction.

In successive runs with the same sample, evacuation of the surface was only carried out at room temperature. Initial adsorption of formic acid and water were not observed in these conditions while the evolution of water vapor in the gas phase started immediately after admission of the formic acid in contact with the catalyst. By trapping the gas phase in liquid nitrogen the evolution of CO drops immediately, which indicates that formic acid in the gas phase is involved in the reaction.

At a pressure of 6.64 Torr the activation energy for the reaction was found to be 10.5 kcal mol^{-1}, and a first order for the pressure of formic acid was observed in the range between 1 and 25 Torr, for which the initial rate of reaction can be written:

$$d(CO)/dt = 4.3 \times 10^{15} \cdot p^1_{HCOOH} \cdot \exp(-10.5/RT) \text{ molecules/cm}^2\text{sec}, \quad (Eq. 3)$$

p_{HCOOH} being in Torr.

When, after this series of experiments, the system was evacuated at room temperature and the sample heated slowly up to 350°C, about 0.17 ml(n.p.t.)g^{-1} of CO were evolved. This amount agrees quite well with the value of the formic acid adsorbed as formate on the 400°C evacuated surface (TPD), and indicates that formate initially adsorbed on the sample does not decompose at $t \leqslant 200°C$ under catalytic conditions.

Catalytic activity at temperatures higher than 350°C was measured in a flow system and values of E_r and A were obtained from the Arrhenius plots in this range (*18*). The rate of reaction in these conditions can be written as follows:

$$d(CO)/dt = 1.9 \times 10^{23} \cdot p^0_{HCOOH} \cdot \exp(-25.0/RT) \text{ molecules/cm}^2\text{sec}. \quad (Eq. 4)$$

Dehydrogenation of some of the formic acid could be detected in the upper limit of temperatures at which the reaction was studied in this work. However, this form of decomposition is far more difficult, as suggested by the 46.5 kcal mol^{-1} calculated for the energy of activation for this process.

DISCUSSION

Adsorption on TiO_2 Surfaces

A study of the surface structure of TiO_2 has been published (*9, 10*) together with a model of TiO_2 surface which account for the behavior of this oxide in adsorption and catalysis.

The maximum of TPD at 500°C was ascribed in this model to free OH-groups from the original hydroxide, which remain isolated or clustered in small patches, after sintering of the sample at 800°C in the air. These hydroxyls give a band at 3725 cm^{-1}.

which is removed by evacuation at $t \geqslant 550°C$ or by heating at $t \approx 1000°C$ in the air.

Evacuation of a fresh sample at 400°C for about 3 hr leads to a surface holding 3.3 OH/100 A^2, though this amount decreased to 2.0 OH/100 A^2 in successive runs after the first TPD analysis up to 650°C. The difference is easily explained if we take into account that evacuation at 400°C of the fresh sample does not remove free OH-groups (peak at 500°C in TPD), which are released during the first TPD analysis.

The residual hydroxyls on the evacuated sample ($\leqslant 30\%$ of a mono-layer) are strongly bonded to the surface, giving a long tail in the chromatograms. The formation of surface defects with increasing dehydroxylation in this range may be invoked to explain the stability of these hydroxyls.

The TPD maximum at 370°C together with the bands at 3670 and 3650 cm^{-1} indicate that readsorption of water at room temperature occurs in a first stage with heterolytic dissociation of the molecule on a 400°C evacuated surface. The small difference between these bands has been ascribed in our model to the form of interaction between the OH-pairs and the Ti^{4+} ions of the oxide layer underneath, as seen in Fig. 8.

The number of hydroxyls on the surface after readsorption of water at room temperature was about 4.6 OH/100 A^2, except for the first experiment. This represents 50% of a monolayer on the 110 face of the rutile and suggests that readsorption occurs on $Ti^{4+}O^=$ pairs until a surface holding isolated OH-pairs is built up. These acid-basic centers must involve lattice $O^=$ ions, which are irreversibly removed from the surface by heating at 700°C in the vacuum.

Further adsorption of water on this half-hydroxylated surface now occurs without dissociation and with a decreasing heat of adsorption. Thus, about 1.7 H_2O/100 A^2 remain on the surface after pumping (Table 2.IV) while temperatures up to 250°C should be used to obtain a surface free from water molecules.

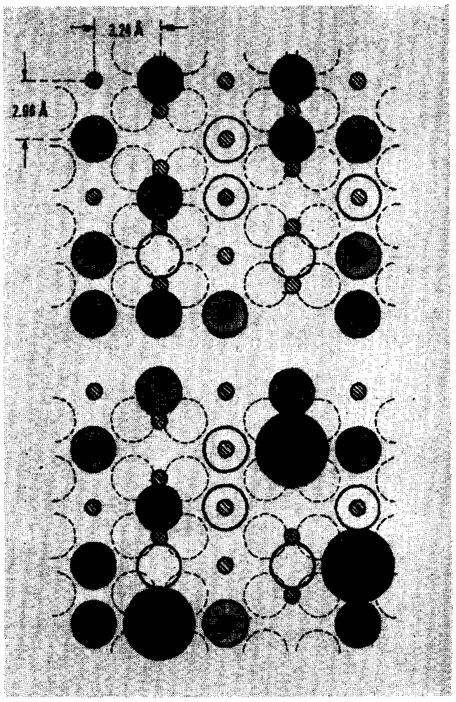


FIG. 8. Rutile surface (110 face) after dissociative adsorption of water and formic acid up to $\theta = 0.5$. Small circles, Ti^{4+} ions; white circles, $O^=$ ions (dashed circles are in a lower plane); grey circles, OH^- and $HCOO^-$ ions.

The study of the stability of the tightly adsorbed water as a function of the reduction state of the surface, suggests that Ti^{4+} ions surrounded by weak basic sites (adsorbed $O^=$ ions) are the most active centers for this type of non-dissociative adsorption.

Using formic acid, adsorption giving formate ions and protons was observed. The number of sites covered in this way, assuming that formate ions are to be found on Ti^{4+} ions, represents nearly 50% of a completely covered surface as in the case of dissociative adsorption of water.

The large size of these formate ions and the lack of OH-pairs on this surface make the adsorption of non-dissociated formic acid very weak; only 0.7 HCOOH/100 A^2 was adsorbed after room temperature outgassing.

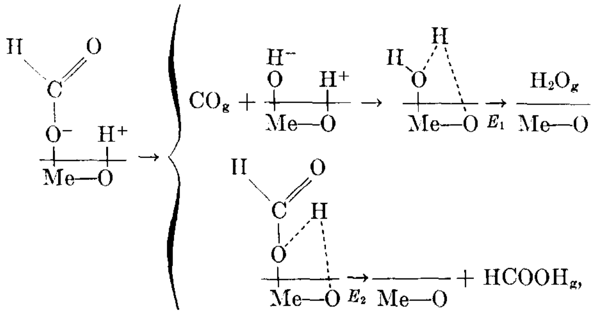
The existence of two types of adsorbed species has been previously reported by Smith (*19*) for several carboxylic acids on this oxide, though dissociative adsorption of formic acid on highly hydroxylated TiO_2 surfaces does not occur (*20*) as could be expected from our TPD studies.

Dehydration of Formic Acid on TiO_2 at $t \geqslant 350°C$

The activation energies for the desorption of hydroxyls and formate ions in Table 4 are the same as for the catalytic dehydration of the acid at high temperatures, given in Eq. 4.

Simultaneously, the activation entropy of desorption agrees for both species, as could be expected if formate are intermediate species in the reaction at these temperatures and decompose giving OH-groups, whose release from the surface is the controlling step of the overall reaction.

On the other hand, TPD of the adsorbed formate shows that only partial decomposition occurs, while a single peak at 350°C is observed. This suggests that both, desorption and decomposition of the formate take place with almost the same activation energy as may be expected from the following scheme:



in which $E_1 = E_2$, represent the outbreak of a Me—O bond in the activated state. This is supported by the linear relationship found in our laboratory (*21*) between the measured activation energies for the reaction on TiO_2, V_2O_3, and Cr_2O_3 catalysts, and the entalpy of formation of these oxides, $\Delta H°$ given by atom-gram of oxygen.

Therefore, under catalytic conditions, formate ions must readily decompose in CO leaving hydroxyl groups on the surface whose protons are likely to move on the oxygen layer at the high temperatures of reaction.

A simple calculation gives a value of —20.6 eu for the decrease of entropy when two of these protons on a surface covered up to $\theta = 0.5$ lose their translational freedom and become bonded to one oxygen, whose link with the surface is simultaneously broken.

About 6 centers/100 A^2 were estimated from the values of A and A_0 in Eq. 4 and Table 4, respectively. These centers can be visualized as the oxygen ions of the top layer of the surface ($O^{=}_{\mathrm{latt.}}$), which are able to accept protons to give a water molecule. The number of such ions on a full dehydroxylated surface is only about 4.5 $O^{=}/100\ A^2$, thus 3 $H^{+}/100\ A^2$ must exist on the sample to account for the other 1.5 $O^{=}/\ 100\ A^2$.

The number of hydroxyls calculated in this way represents 33% of a monolayer, in agreement with the observed coverages in this range of temperatures.

Dehydration of Formic Acid on TiO_2 at $t \leqslant 200°C$

A simple calculation using Eq. 3 shows that the observed rates of reaction in this temperature range are about a hundred times faster than the expected ones for the decomposition of the adsorbed formate at the same temperatures, calculated using Eq. 4 and data in Table 4. On the other hand, decomposition of formate seems to be hindered under reaction conditions at low temperatures.

Although molecular adsorption of formic acid was not detected at $t \geqslant 150°C$, it must be present in the gas phase during the process. Thus we must conclude that in the range 150–250°C the reaction occurs involving gaseous formic acid molecules.

In a first period of up to 30 min, the 400°C outgassed TiO_2 retains water on the $Ti^{4+}O^{=}$ dual sites, poisoning a fraction of the centers for the reaction. In a second stage, as well as in successive runs using the same sample previously outgassed at room temperature, the reaction proceeds on a surface holding formate ions, residual and reformed hydroxyls and water molecules, as previously reported by Tamaru *et al.* (*5*) for Al_2O_3 catalysts.

Moreover, as in the case of Al_2O_3, regenerated hydroxyls on TiO_2 seem to be very acidic (*22*), probably acting as centers for the reaction together with the Lewis acid sites as suggested by the initial poisoning. Thus, it could be thought that $Ti^{4+}OH^-$ (Lewis-Brönsted pairs) are the active centers for the reaction. Some of them, those having a further neighboring $O^=$ ion ($O^=Ti^{4+}OH^-$ groups), become poisoned during the strong adsorption of water on the $Ti^{4+}O^=$ pairs.

On a first approach, taking 1.1 OH/100 A^2 (see Table 3) as the protons involved in active centers on TiO_2, and applying the transition state theory, $\Delta S^\ddagger = -52$ eu is obtained from Eq. 3. However, this value decreases to —47 eu if only about 10% of the reformed hydroxyls have an exposed Ti^{4+} ion in their neighborhood, as is likely to occur after adsorption of water in the first stage.

The large loss of entropy suggests a controlling step in which formic acid molecules in the gas phase and exposed Lewis-Brönsted sites interact leading to an activated state in which the gaseous molecule loses its translational motions ($\simeq$45 eu), becoming protonated.

The small number of active centers and the existence of adsorbed formate and water on the surface of both Al_2O_3 and TiO_2 may prevent the motion of the adsorbed molecule on the surface. Thus making the adsorption step far more difficult than the surface reaction, which proceeds very rapidly.

A different behavior should be expected on SiO_2 catalysts. Peri's surface model for this oxide (*8*) explains the observed lack of dissociative adsorption of formic acid on this oxide, while two types of adsorbed molecules have been reported by NMR (*23*). The weaker of these forms can be described as a mobile adsorption on the hydroxyl pairs covering almost all the surface of this oxide, and seems to be involved in the reaction. In such a case the surface reaction may become the controlling step for the overall reaction.

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