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Reactions of Methane and Ethane with Hole Centers O^-

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The reactivities with hydrocarbons of hole centers of the O^- type generated by γ irradiation of V^{5+} and P^{5+} cations deposited on silica gel, and by uv irradiations of V^{5+}/SiO_2 and stoichiometric TiO_2 were studied. In each case reactions of methane and ethane with the hole centers were performed in both the presence and absence of oxygen. The similarities observed in the behavior of these holes is explained by the formation on the surface of stable alkoxide species CH_3O^- or $C_2H_5O^-$. The peculiarities of the V^{5+}/SiO_2 system under uv light are due to the reactive behavior of the reduced stable V^{4+} ion left, in this case, on the surface after completion of the oxidation of hydrocarbon molecule.

INTRODUCTION

Recent works from our laboratory *(1–4)* have been dedicated to the study of holes O^- stabilized on cationic surface impurities (Al^{3+}, B^{3+}, As^{3+}, . . . , V^{5+}, P^{5+}, As^{5+}) in silica gel and generated by γ irradiation, making use mainly of optical and ESR spectroscopies. On the whole, these species have been found to have chemical properties of free radicals rather than of electron acceptors. Under uv light the systems V^{5+} and Mo^{6+}, supported on silica gel as isolated ions, were shown *(5–7)* to give rise to charge transfer complexes, or in other words to nonstable holes O^- whose chemical properties are quite close to those of the γ irradiation-formed O^-.

On the other hand, photocatalytic oxidations of saturated hydrocarbons, taking place on various stoichiometric semiconductors and principally on TiO_2 *(8–11)* have not yet been given a satisfactory explanation, and in particular the role played by surface holes in these reactions is not clear.

Therefore it was thought interesting to study under comparable experimental conditions the reactions of methane and ethane, in the presence as well as the absence of oxygen, with holes of the various types mentioned, namely: (i) stable O^- generated by γ irradiation and stabilized on surface V^{5+}- and P^{5+}-isolated cations deposited on silica gel; (ii) charge transfer complexes formed under uv light on silica gel supporting vanadium pentoxide as surface impurity, and (iii) nonstable surface holes generated by uv light on powdered TiO_2.

In all cases the products of reactions were analyzed by mass spectrometry and in the case of γ-irradiated catalysts a simultaneous ESR study was performed.

EXPERIMENTAL METHOD

Catalysts. As a supporting material for cations V^{5+} and P^{5+}, a high purity silica

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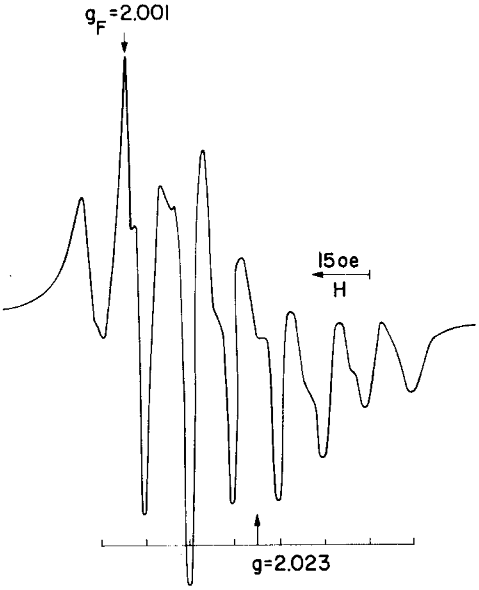


FIG. 1. ESR spectrum of V^{5+}/SiO_2 submitted to γ rays under vacuum and recorded at room temperature.

gel (300 m^2/g), prepared in our laboratory by hydrolysis of silicon chloride, was used. This gel was dried at 150°C for 4 to 5 h and calcined in air at 500°C for 5 to 6 h. Its main impurities were CuO (0.001%), TiO_2 (0.001%), Al_2O_3 (0.003%), and Fe_2O_3 (0.003%). Deposition of vanadium on the silica gel was performed by impregnating the gel with an aqueous solution of NH_4VO_3 and drying. The vanadium content was 2%. The V/SiO_2 γ-irradiated sample weighed 500 mg whereas the weight of the sample used under uv was 250 mg. Phosphorus was deposited on silica gel by impregnation of an aqueous solution of phosphorus pentoxide and drying. The phosphorus content of this catalyst was 1%. The two samples used weighed 500 and 700 mg, respectively.

The titanium dioxide was a sample of TiO_2 Degussa (14 m^2/g) already used by one of us as a catalyst for the photocatalytic oxidation of hydrocarbons (*11*). It weighed 100 mg.

Catalysts treatment and irradiation. All catalysts were submitted to the same preliminary treatment insuring a reproducible surface, free of any hydrocarbon impurity and well oxidized. After 1 hr at 450°C in air (or pure oxygen in some cases) the sample was held for another hour under vacuum (10^{-4} Torr) at the same temperature. The catalyst was then cooled down to 100°C under oxygen before evacuation.

Those catalysts which were to be submitted to γ irradiation were then sealed off under vacuum and brought to the source. Irradiation by the emission of ^{60}Co was performed at room temperature and the dose received by the sample was 40 to 60 Mrad.

For those catalysts to be used under uv the preliminary treatment was performed *in situ* and the sample was maintained under vacuum up to the time of reaction. The uv source was a mercury lamp Model DRSh-1000 equipped with a water filter. In all reported experiments a filter (BS-4) cutting wavelengths shorter than 320 nm was used.

Gaseous reactants. Methane and ethane were first freed from any oxygen impurity by being slowly passed over a column of silica gel-supported divalent chromium and stored. Then before each experiment methane was freed from any trace of ethane by contact with a liquid nitrogen trap at a pressure of the order of the working partial pressure (0.1 to 1 Torr) for more than an hour. Similarly, to avoid any trace of methane, ethane initially at a pressure of the order of 1 Torr was submitted at least to two cycles of condensation to 77 K, evacuation to 10^{-4} Torr, evaporation to room temperature, and condensation to 77 K.

Oxygen from a cylinder was first passed over a trap refrigerated with a mixture of acetone and dry ice and further condensed at 77 K. The liquid oxygen was then slowly warmed up and the middle boiling fraction was stored in a glass container.

Working volume and spectrometer. The

working volume (300 cm^3 in the experiments with γ-irradiated catalysts and 250 cm^3 in uv experiments) consisted of two loops which could be cooled down to liquid nitrogen temperature and the internal volume of a McLeod gauge. The different parts of the volume are separated by metallic valves. This working volume is connected to a mass spectrometer Model UTI 100-C (UTHE Technology international) provided with a titanium sputter ion pump (ULVAC YD21B).

Mass spectra were measured on the range of m/e 2 to 50. An analysis of gaseous products containing CH_4, C_2H_6, and HCHO was conducted using the individual mass spectra of these compounds.

ESR measurements were performed using an X-band ESR spectrometer EPR-3.

RESULTS AND DISCUSSION

ESR Measurements

In agreement with already published data (*3*), the ESR spectrum of γ-irradiated V/SiO_2 (Fig. 1) includes signals with well-defined hyperfine structure from hole centers O^-/V^{5+} at $g = 2.023$ and F-centers at $g = 2.001$, as well as a weaker broad signal corresponding to reduced vanadium ions V^{4+} (not seen in Fig. 1). Accordingly the ESR spectrum of γ-irradiated P/SiO_2 (Fig. 2) consists of a doublet signal from O^-/P^{5+} with a hyperfine splitting constant of $\simeq$50 Oe and F-centers (*4*). By integrations of ESR spectra the concentrations of O^-/V^{5+} and O^-/P^{5+} hole centers were estimated to be 1 to 2×10^{17} g^{-1}.

When methane at $P = 0.1$ Torr is contacted with γ-irradiated V/SiO_2 at 77 K the intensity of the O^- signal decreases slightly, and at 195 K this signal completely disappears after 2 min.

The O^- signal on γ-irradiated P/SiO_2 also diminishes when contacted with 2 Torr of methane but less rapidly than in the case of V/SiO_2. After 2 min at 195 K the signal had decreased 50% of its initial value. It completely disappears instantaneously at room temperature.

When brought into contact with a mixture containing 0.1 Torr of methane and 0.1 Torr of oxygen at 77 K the ESR signal of O^- on γ-irradiated V/SiO_2 slightly decreases. In 30 sec at 195 K a very intense new signal appears which can be attributed to O_3^- (*3*) and this signal disappears suddenly after some minutes at 195 K.

With γ-irradiated P/SiO_2 under the action of a mixture of methane (1 Torr) and oxygen (1 Torr) the O_3^- signal was obtained at 77 K and it instantly disappeared at the temperature of 195 K.

Thus it seems that the hole centers O^- under study can react with methane in both the presence and absence of oxygen giving nonparamagnetic products. Also note that in none of the described experiments was the characteristic signal of O_2^- observed.

Reactions in the Absence of Oxygen

Results of Reactions with Pure Methane

Table 1 presents the results from the mass spectrometric analysis of the products of reactions of pure methane, expressed in moles per gram of catalyst used, with the various kinds of hole centers under study.

In Experiment 1, pure methane (approximately 1 Torr) was contacted with γ-irradiated V/SiO_2 at room temperature. Analysis of the gas phase at this temperature showed that only a small amount of ethane was produced. The whole working volume was then evacuated and the catalyst was gradually heated. The table gives the additional amount of each product which appeared on the reported ranges of temperature. Methane and carbon monoxide desorbed in relatively large quantities, as well as very small amounts of ethane and carbon dioxide. Experiment 1b is a

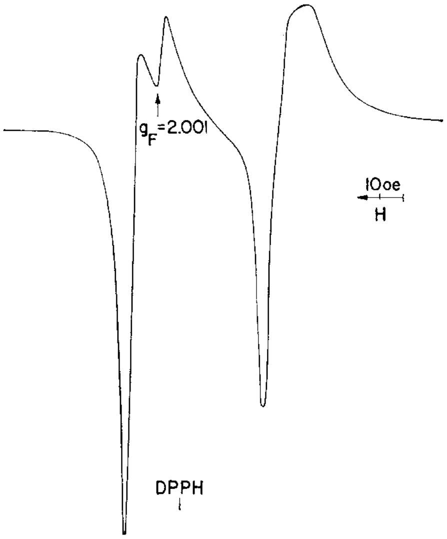


FIG. 2. ESR spectrum of P^{5+}/SiO_2 submitted to γ rays under vacuum and recorded at room temperature.

typical blank experiment with a nonirradiated catalyst.

During Experiment 2, as long as V/SiO_2 was under the uv lamp, one of the loops of the working volume was plunged in liquid nitrogen. The reported negative number corresponds to the amount of methane which disappeared after 2.5 h under these conditions. To analyze the products of reaction, the loop is isolated from the catalyst before being warmed to room temperature. The reported amounts of ethane and formaldehyde are found. It is interesting to note that after this period of reaction the catalyst displays a blue-gray color, which is observed as long as it remains isolated from the loop. When the corresponding valve is opened and the produced ethane and formaldehyde are readmitted at room temperature on the catalyst in the absence of uv, the V/SiO_2 catalyst returns to its original white color. Analysis shows that a large proportion of the product disappears upon this readmission, and after heating only methane is evolved.

The results of Experiment 3, conducted with TiO_2 under uv, show that this system is comparable to the γ-irradiated catalyst of Experiment 1. The oxidation products obtained are CO and CO_2 as well as some ethane.

Results of Reactions with Pure Ethane

Table 2 shows the results of experiments analogous to those of Table 1, but conducted with pure ethane instead of methane.

The results in both tables are quite similar. Methane and ethane are desorbed on heating in Experiments 4 to 7, and oxidation product CO is obtained in Experiments 4, 5, and 7. In Experiments 6 and 7 conducted under uv, the liquid nitrogen trap was not used since ethane would condense at this temperature.

It is interesting that in Experiments 1 to 7 butane is not produced in any appreciable quantity. In the mass spectra of the products which desorbed on heating we never found the peak with $m/e = 43$ which is the most intense in the spectrum of butane (*13*). Nor was ethylene produced in any of these experiments.

Discussion

Examination of the results obtained with γ- and uv-irradiated catalysts leads to two important qualitative conclusions which must be kept in mind.

(1) On those catalysts submitted to preliminary γ irradiation, as well as on the catalysts we studied under uv light, an important chemisorption (photosorption) of methane and ethane takes place.

(2) An important part of the hydrocarbons desorbs from the surface of the catalyst only on heating, and hydrocarbons predominate in the products of reaction.

When methane is contacted at room temperature with stable hole centers O^- produced by γ irradiation of vanadium supported on SiO_2 (Experiment 1), the

TABLE 1

Analysis for the Products of Reaction of Pure Methane with Hole Centers O^{-}[a]

Expt	Catalyst	P_{CH_4} (Torr)	Temperature	CH_4	C_2H_6	HCHO	χ	CO	CO_2
1	V/SiO_2, γ-Irradiated	$\simeq 1.0$	RT[b]		0.4				
			RT to 88°C	17.6	2.3			3.6	tr[c]
			88 to 144°C	13.0				12.0	1.0
			144 to 200°C	11.4				10.2	
			Total	42.0	2.7			25.8	1.0
1b	V/SiO_2	1.41×10^{-1}	RT to 295°C	3.2	tr			<1	
2	V/SiO_2 + uv for 2.5 h with liquid nitrogen trap	6.63×10^{-2}	During uv irradiation	−135	47.4	6.0			
			After readmission of products on the catalyst	2.5	−43.1	−5.4			
			RT to 300°C	43.7					
3	TiO_2 + uv for 1.25 h with nitrogen trap	1.35×10^{-1}	During uv irradiation	−135.5	5.1				0.3
			RT to 210°C	18.1	tr			3.0	1.9
			210 to 350°C	71.9				27.5	2.7
			Total	90.0	5.1			30.5	4.9

[a] Moles per gram $\times 10^{18}$.

[b] Room temperature.

[c] Traces.

reaction responsible for the disappearance of the O^- ESR signal, as already postulated in Ref. (*6*) is

$$CH_4 + O^- \rightarrow CH_3^\bullet + OH^-. \quad (1)$$

The small amounts of ethane observed in the gas phase at room temperature can then be the result of

$$2CH_3^\bullet \rightarrow C_2H_6. \quad (2)$$

Since, however, most of the products desorb only on heating, it is quite likely that the methyl radicals formed by Reaction (1) further react with oxygen surface species. As supposed by Aika and Lunsford (*12*), in the case of O^- on MgO reacting with methane under similar conditions, this reaction could be

$$CH_3^\bullet + O^{2-} \rightarrow CH_3O^- + e. \quad (3)$$

In that case, most of the electrons resulting from Reaction (3) recombine with hole centers O^-,

$$e + O^- \rightarrow O^{2-}, \quad (3a)$$

instead of interacting with V^{5+} ions,

$$e + V^{5+} \rightarrow V^{4+}. \quad (3b)$$

This assertion is supported by the observation that the ESR spectra did not show any significant increase in the V^{4+} concentration, as would follow from Reaction (3b).

Apparently another reaction could lead to alkoxide (CH_3O^-) formation:

$$CH_3^\bullet + O^- \rightarrow CH_3O^-. \quad (4)$$

In both cases, Reactions (3) and (3a) or Reaction (4) would succeed Reaction (1) and compete with it for O^-.

The process of methane chemisorption on the previously γ-irradiated samples, whether occurring through Reactions (1), (3), and (3a) or through Reactions (1) and (4), can be described by the stoichiometric

TABLE 2

Analysis for rhe Products of Reaction of Pure Ethane with Hole Centers O^-[a]

Expt	Catalyst	$P_{C_2H_6}$ (Torr)	Temperature	CH_4	C_2H_6	HCHO	χ	CO	CO_2
4	V/SiO_2, γ-Irradiated	3.29×10^{-1}	RT[b]						
			RT to 77°C	17.1	56.8			5.8	
			77 to 141°C	0.8	27.6			—	
			141 to 199°C	—	15.1			1.6	tr[c]
			Total	17.9	99.5			7.4	
5	P/SiO_2, γ-Irradiated	1.63×10^{-1}	RT	—				—	
			RT to 218°C	22.8	21.7			15.7	1.0
			218 to 298°C	49.9				7.2	
			298 to 341°C	28.9				4.6	
			Total	101.6	21.7			27.5	1.0
6	V/SiO_2 + uv for 2 h	4.53×10^{-1}	Under uv	85.4	−607				
			RT to 320°C	136.0	148		tr		
			Total	221.4	148				
7	TiO_2 + uv for 2 h	6.25×10^{-2}	Under uv	1.3	−216.7				
			RT to 258°C	6.8	40.6			1.3	tr
			258 to 348°C	94.8	36.6			16.2	1.3
			Total	102.9	87.2			17.5	1.3

[a] Moles per gram $\times 10^{18}$.

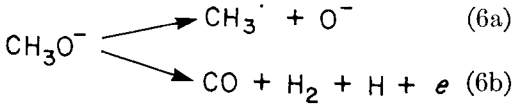
[b] Room temperature.

[c] Traces.

equation:

$$CH_4 + 2O^- \rightarrow CH_3O^- + OH^-. \quad (5)$$

In such a case if the CH_3O^- and OH^- particles are adsorbed in neighboring positions, the reverse reaction can take place on increasing the temperature, leading to methane desorption. However in addition to this desorption process, thermal decomposition of the alkoxides on the surface can also occur leading to new products of reaction:



$$CH_3O^- \rightarrow CH_3^{\cdot} + O^- \quad (6a)$$

$$CH_3O^- \rightarrow CO + H_2 + H + e \quad (6b)$$

Recombination of methyl radicals explains the formation under these conditions of the small quantities of ethane observed in addition to the main product CO. It is also possible that part of the desorbed methane results from the addition of some methyl radicals with atomic hydrogen.

Similar reactions quite probably occur during the interaction of ethane with γ-irradiated catalysts (Experiments 4 and 5); the only difference is that the decomposition of the surface alkoxide $C_2H_5O^-$ leads in this case to methane:

$$C_2H_5O^- \rightarrow CH_4 + CO + H + e. \quad (7)$$

The absence of butane in the products could be linked to the fact that ethyl radicals would be very reactive toward O^{2-} or O^- leading to $C_2H_5O^-$, and as a result the proportion of $C_2H_5^{\bullet}$ recombining to give butane would be very small. It is also possible that a noticeable desorption of butane from the catalyst surface occurs only for temperatures higher than 350°C. This however would be in contrast to the desorption of ethane, say in Experiment 1, which occurs at low temperature.

An analogous representation of the interactions between paraffins and the short-lived electron-excited complexes with charge transfer, formed under uv irradiation (Experiment Nos. 2 and 6), is:

$$V^{5+}O^{2-} \xrightarrow{h\nu} [V^{4+}O^-]^*. \qquad (8)$$

$$[V^{4+}O^-]^* + CH_4 \rightarrow V^{4+} + CH_3{}^{\bullet} + OH^-. \qquad (9)$$

$$CH_3{}^{\bullet} + CH_3{}^{\bullet} \rightarrow C_2H_6. \qquad (2)$$

Radical recombination (*2*) seems to be more important here since a rather large quantity of ethane is evolved at room temperature, thus suggesting a less rapid oxidation:

$$V^{5+}O^{2-} + CH_3{}^{\bullet} \rightarrow V^{4+} + CH_3O^-, \qquad (10)$$

$$[V^{4+}O^-]^* + CH_3{}^{\bullet} \rightarrow V^{4+} + CH_3O^-. \qquad (11)$$

Reaction (10) would correspond to Reactions (3) and (3b). Here the stable holes O^- responsible for Reaction (3a) in Experiment 1 are not present and therefore Reaction (3a) cannot occur. Reaction (11) would correspond to Reaction (4). Definitively the whole process of photosorption can be described as:

$$2V^{5+} + 2O^{2-} + RH \rightarrow 2V^{4+} + OH^- + RO^-. \qquad (12)$$

The occurrence of Reaction (12) is further demonstrated by the blue-gray color appearing on the samples after uv irradiation. This color is linked to the reduction of pentavalent to tetravalent vanadium.

Finally, formation of formaldehyde at room temperature in Experiment 2 can be explained by the photodecomposition of the surface alkoxide ions (CH_3O^-), which form in the vicinity of V^{4+} ions [Reactions (10) and (11)]:

$$V^{4+}CH_3O^- \xrightarrow{h\nu} HCHO + H^{\bullet} + V^{4+}. \qquad (13)$$

Reactions (9) to (11) all leave on the surface trapped electrons (V^{4+}), which apparently can react with both HCHO and C_2H_6 to some extent at room temperature to yield methane, for example:

$$2V^{4+} + HCHO \rightarrow 2V^{5+} + CH_2 + O^{2-}, \qquad (14)$$

$$2V^{4+} + CH_2 + 2OH^- \rightarrow 2V^{5+} + CH_4 + 2O^{2-},$$

$$\left.\begin{aligned} &C_2H_6 + V^{4+} \rightarrow C_2H_6{}^- + V^{5+}, \\ &C_2H_6{}^- + OH^- \rightarrow CH_4 + CH_3 + O^{2-}. \end{aligned}\right. \qquad (15)$$

These reactions would lead to surface reoxidation, followed by the disappearing of the sample's blue color, and on heating only methane would desorb.

Since in TiO_2 under uv the photoelectrons are raised to the conduction band and migrate through the crystal lattice, no species similar to $V^{4+}CH_3O^-$ exists, so that no formaldehyde is found in Experiment 3. On the other hand, the similarities between the results of Experiments 3 and 1 and between Experiments 7 and 4 or 5 suggests that the unstable holes O^- on TiO_2 do take part in Reactions (1) and (4). In Reactions (1) to (3) or in (4) the hole would be stabilized, since the alkoxides CH_3O^- and $C_2H_5O^-$ seem quite stable in both Experiments 3 and 7.

REACTIONS IN THE PRESENCE OF OXYGEN

Results of Reactions of Methane

Experiment 8 (Table 3) was conducted under conditions close to those of Experiment 1, except that the reacting gas was approximately a 1/1 mixture of methane and oxygen. On heating of the catalyst after reaction, a rather large quantity of methane is evolved as well as some ethane. The oxygenated products contained appreciable amounts of CO and CO_2 as in Experiment 1 but in addition here a rather large quantity of formaldehyde was observed as well as traces of a product labeled χ which could be acetaldehyde.

Similar results were obtained with γ-irradiated P/SiO_2 (Experiment 9), except that in this case no formaldehyde was formed.

TABLE 3

Analysis for the Products of Reaction of Methane with Hole Centers O^- in the Presence of Oxygen[a]

Expt	Catalyst	P_{CH_4} (Torr)	P_{O_2} (Torr)	Temperature	CH_4	C_2H_6	HCHO	χ	CO	CO_2
8	V/SiO_2, γ-Irradiated	1.50×10^{-1}	1.08×10^{-1}	RT[b]		0.7				0.7
				RT to 80°C	52.2	1.3			tr[c]	0.7
				80 to 165°C	110		8.0		12.7	3.0
				165 to 200°C	116		52.2	tr	51.2	5.7
				Total	278.2	2.0	60.2		63.9	10.1
9	P/SiO_2, γ-Irradiated	1.76×10^{-1}	1.59×10^{-1}	RT		4.6		tr		13.8
				RT to 80°C	15.4	1.3		tr	20.3	1.5
				80 to 166°C	14.3	2.8		tr	30.2	2.3
				166 to 238°C	15.4			tr	9.6	
				Total	45.1	27			60.1	17.6
10	V/SiO_2 + uv for 1 h, 10 min with liquid nitrogen trap	5.1×10^{-2}	2.3×10^{-1}	RT under uv	−217	tr	tr	tr		198
				RT to 310°C	37.7	2.7	3.2	tr	16.8	1.8
				Total	37.7	2.7	3.2		16.8	200
11	TiO_2 + uv for 1.5 h with liquid nitrogen trap	9.7×10^{-2}	1.52×10^{-1}	RT under uv	−452	24.1				0.8
										19.6
				RT to 150°C	27.0			tr		17.7
				150 to 280°C	40.8	tr		tr	38.5	
				280 to 350°C	98.9	tr			49.6	
				Total	166.7	24.1			88.1	38.1

[a] Moles per gram $\times 10^{18}$.

[b] Room temperature.

[c] Traces.

When supported vanadium under uv radiation is contacted with a mixture of methane and oxygen (Experiment 10) the results are quite different from those observed in the absence of oxygen (Experiment 2). Large amounts of oxygenated products are readily obtained, and in particular CO_2 is produced at room temperature and condensed in the liquid nitrogen trap.

With TiO_2 under uv (Experiment 11) the results are once again comparable to those obtained with γ-irradiated V/SiO_2 (Experiment 8) and P/SiO_2 (Experiment 9). No formaldehyde is found in the products in agreement with Ref. (*9*).

Results of Reactions of Ethane

As can be seen by comparing Tables 3 and 4 the results obtained with ethane–oxygen mixtures confirm those results from experiments with methane–oxygen mixtures. Here again formaldehyde is obtained only with γ-irradiated V/SiO_2 (Experiment 12) and not with P/SiO_2 (Experiment 13). Under uv in both cases of V/SiO_2 (Experiment 14) and TiO_2 (Experiment 15) much CH_4 is formed, whereas the oxygenated products CO and CO_2 are in smaller amounts than in the corresponding experiments with methane (Experiments 10 and 11).

Discussion

Since in almost all cases studied, oxygenated products are obtained in the absence of gaseous oxygen and since one of the main effects of the presence of oxygen is to increase the amounts of reacted hydrocarbons, surface oxygen atoms from the lattice play the role described in the first part of the discussion, but oxygen from the gas phase has an additional effect in these reactions.

First, it could be supposed that the difference observed in the behavior of γ-irradiated catalysts in the presence and absence of oxygen is linked to the inter-

TABLE 4

Analysis for the Products of Reaction of Ethane with Hole Centers O^- in the presence of Oxygen[a]

Expt	Catalyst	$P_{C_2H_6}$ (Torr)	P_{O_2} (Torr)	Temperature	CH_4	C_2H_6	HCHO	χ	CO	CO_2
12	V/SiO_2, γ-Irradiated	2.24×10^{-1}	1.53×10^{-1}	RT[b]	—				—	
				RT to 91°C	2.7	53.2				
				91 to 150°C		106.7			3.6	
				150 to 202°C		74.5	38.7	tr[c]	33.1	
				Total	2.7	234	38.7		36.7	
13	P/SiO_2, γ-Irradiated	1.95×10^{-1}	1.22×10^{-1}	RT	—				—	
				RT to 95°C	0.5	9.2			5.0	0.5
				95 to 195°C	11.5				26.0	1.7
				Total	12	9.2			31	2.2
14	V/SiO_2 + uv for 50 min	8.4×10^{-2}	2.80×10^{-1}	RT under uv	83.2	−390				5.2
				RT to 290°C	81	44.2		tr	13.2	4.6
				Total	164	44.2			13.2	9.8
15	TiO_2 + uv for 2 h	2.07×10^{-1}	1.06×10^{-1}	RT under uv	96.2	−2290				
				RT to 105°C	9.5	39.3		tr		17.6
				105 to 283°C	420	19.0		tr	9.5	21.6
				283 to 356°C	119.2	203.2			17.6	
					644.9	261.5			27.1	39.2

[a] Moles per gram $\times 10^{18}$

[b] Room temperature.

[c] Traces.

action of oxygen with radiation defects. As follows from the data presented in this paper and from data in the literature (*3*), oxygen interacts weakly with hole centers O^-, giving rise at 77 K to complexes O_3^- (or O^-___O_2), which are easily broken up by a small increase in temperature. However, oxygen, a very strong electron acceptor, reacts easily with electron donor centers of the surface or with free electrons forming various charged atomic and molecular oxygen species. Therefore, when mixtures of oxygen with either methane or ethane are brought into contacted with γ-irradiated catalysts, Reactions (1), (3), and (4) are apparently accompanied by trapping of electrons by oxygen molecules with formation of diamagnetic, charged oxygen species adsorbed on the surface. As a consequence of this reaction the rate of recombination of hole centers with electrons (Reaction 3a), essentially is decreased and the concentration of alkoxide radicals is significantly increased. This could probably explain not only the increase in yield in products of partial and total oxidation but also the increase in the quantities of desorbed hydrocarbons on heating of the γ-irradiated catalysts [Reactions (6) and (7)].

Since according to Reactions (1) and (6a) adsorbed methyl radicals would be formed in the system, it would be natural to assume that these radicals react with oxygen from the gas phase,

$$CH_3{}^{\bullet}{}_{ads} + O_2 \rightarrow CH_3{}^{\bullet}OO_{ads}, \quad (16)$$

which could for example yield formaldehyde by thermal decomposition,

$$CH_3{}^{\bullet}OO \rightarrow HCHO + OH^{\bullet}. \quad (17)$$

To check this possibility we have run an experiment using labeled oxygen (^{18}O), under conditions close to those of Experiment 8. Although the atomic fraction of ^{18}O in the gas phase was $\alpha = 0.45$, no ^{18}O was found in any of the oxygenated products, which rules out the mechanism described by Reactions (16) and (17). Therefore more experimental work is necessary to explain the influence of gaseous oxygen on formaldehyde formation.

Let us now examine the results of experiments in which V/SiO_2 and TiO_2 were illuminated with uv light in the presence of mixtures of hydrocarbons with oxygen. In this case oxygen from the gas phase obviously reoxidizes the surface ions V^{4+} or Ti^{3+} formed through Reactions (9) and (11) back to the V^{5+} and Ti^{4+} ions, respectively. This is supported by the fact that the samples of TiO_2 at the end of Experiments 11 and 15 are absolutely white, which is typical of an oxidized TiO_2 surface, whereas at the end of Experiments 3 and 7 they show the blue color characteristic of a reduced TiO_2 surface. This same difference was also observed with V/SiO_2 samples in Experiments 2, 6, 10, and 14. That way, during uv irradiation in the presence of oxygen, each ion, V^{5+} or Ti^{4+}, can participate numerous times in Reaction (8), so that the reactions of photooxidation of CH_4 and C_2H_6 are truly photocatalytic. This also explains the significant increase in the quantity of hydrocarbons consumed in Experiments 10, 11, 14, and 15, as compared to Experiments 2, 3, 6, and 7. In Experiment 10, oxygen probably oxidizes HCHO and C_2H_6 quite effectively to CO and even CO_2, since these products predominate in the products of reaction.

As a general conclusion, the data presented in this paper show quite clearly that hole centers play an important role in the reactions of hydrocarbons with V/SiO_2 and P/SiO_2 previously submitted to γ irradiation, as well as with V/SiO_2 and TiO_2 samples under uv light. In each case the experimental results can be explained by the formation of alkoxide species CH_3O^- or $C_2H_5O^-$ which are quite stable and decompose only on thorough heating.

In the presence of gaseous oxygen, the detailed mechanism of the interactions between paraffins and hole centers is not yet completely clear, and more experimental work is necessary to reach a better understanding of this rather complex system. However, an important conclusion is already clear: It will be impossible to understand the photocatalytic reactions of paraffins, without a thorough study of their specific interactions with hole centers of the O^--type.

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