

## Infrared Study of the Selective Oxidation of Toluene and *o*-Xylene on Vanadium Oxide/TiO<sub>2</sub>

A. J. VAN HENGSTUM,<sup>1</sup> J. PRANGER,<sup>2</sup> S. M. VAN HENGSTUM-NIJHUIS,  
J. G. VAN OMMEN, AND P. J. GELLINGS

*Department of Chemical Technology, Twente University of Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands*

Received August 29, 1984; revised February 5, 1986

Infrared spectroscopy was used to obtain information on the mechanism of the selective oxidation of toluene and *o*-xylene over vanadium oxide catalysts. The interaction of these aromatic hydrocarbons and the products benzaldehyde and *o*-tolualdehyde with the surface of a V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> monolayer catalyst was investigated at different temperatures under conditions comparable to those of the catalytic reaction. The infrared results obtained for each of these compounds showed a great resemblance, indicating that their oxidation proceeds along the same reaction path. Coordinatively adsorbed aldehydes, carboxylate-like structures, and benzoate species could be identified as intermediates on the surface of the catalysts. On the basis of the spectroscopic observations a possible reaction mechanism has been proposed. © 1986 Academic Press, Inc.

### INTRODUCTION

The selective gas phase oxidation of hydrocarbons over oxidic catalysts has been extensively studied over the last few decades. A large number of these investigations concern kinetic measurements or tracer experiments, which have been performed to obtain information on the mechanism of the oxidation reaction. Additional and sometimes even more direct evidence can often be obtained by studying the interaction of the reactant and/or its products with the surface of the catalyst using infrared spectroscopy as was, for instance, demonstrated by Davydov *et al.* (1) for the oxidation of propylene. Several intermediate species, such as  $\pi$ -allyl complexes, carboxylates, carbonates, and formates, could be detected on the surface of the catalyst. Infrared spectroscopy has also been used for the identification of reaction intermediates in the oxidation of alkenes, alkynes (2, 3), and alcohols (4-8). Only a limited number

of infrared studies on the identification of surface structures formed in the oxidation of aromatic hydrocarbons have appeared in the literature. Niwa *et al.* (9,10) investigated the adsorption of toluene and xylenes on a V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, as well as the adsorption of the corresponding aldehydes on the uncovered Al<sub>2</sub>O<sub>3</sub> support, as a first step in the elucidation of the mechanism of the ammoxidation of these aromatic hydrocarbons. However, because these adsorption experiments were all performed at a relatively high temperature (400°C) only infrared vibration bands due to adsorbed benzoate species were observed and no information could be obtained on the structure of any of the preceding reaction intermediates.

Sachtler *et al.* (11) studied the oxidation of benzaldehyde to benzoic acid and could detect asymmetric, covalent carboxylate-like structures on the surface of the catalyst after adsorption of the aromatic aldehyde at room temperature. When the temperature was increased this surface complex was converted into the benzoate structure. On the basis of these spectroscopic observations they obtained a much

<sup>1</sup> Present address: Akzo Chemie Nederland B.V., P.O. Box 15, 1000 AA Amsterdam, The Netherlands.

<sup>2</sup> Present address: Hoogovens B.V., P.O. Box 10.000, 1970 CA IJmuiden, The Netherlands.

clearer understanding of the mechanism of the oxidation reaction. We therefore also employed infrared spectroscopy in our research project concerning the selective gas phase oxidation of toluene and *o*-xylene over oxidic monolayer catalysts (12–15). The interaction of toluene, *o*-xylene, benzaldehyde, and *o*-tolualdehyde with a catalyst consisting of a TiO<sub>2</sub> support completely covered with a monolayer of vanadium oxide (2) has been investigated more closely not at relatively high temperatures (> 300°C) *in vacuo* as is usually done, but under conditions similar to those of the catalytic reaction.

#### EXPERIMENTAL

The V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> monolayer catalyst (2.1 wt% V on TiO<sub>2</sub> (Degussa; 50 m<sup>2</sup>g<sup>-1</sup>; 68% Anatase and 32% rutile)), used in all infrared measurements, was prepared by adsorption of vanadyl acetylacetonate from toluene (12). The reactants toluene and *o*-xylene, both of analytical grade, were from Merck and BDH, respectively; the products benzaldehyde and *o*-tolualdehyde were from Baker and Aldrich. The infrared spectra were recorded using a Nicolet MX-S Fourier transform infrared spectrometer. The infrared cell used in this study was constructed according to a description published by Bouwman and Freriks (16). The cell was made of glass and was provided with two vacuum-tight sealed potassium bromide windows, which were cooled by the use of water cooling jackets. The catalyst in the form of a compressed disc (80–100 mg; 20 mm diameter) was mounted in a cylindrical glass sample holder, which was placed in a quartz-clad heating device. This complete device could be raised into the upper part of the cell, making it possible to record the spectrum of the gas phase alone. In the *in situ* measurements, the reactant mixture, which was made by saturating air, purified over molecular sieve 13X, with toluene or *o*-xylene at a temperature of 273 or 290 K, was made to flow through the system at atmospheric pressure.

The products were introduced by a single injection at room temperature into the evacuated infrared cell. After adsorption on the surface of the catalyst the system was continuously flushed with purified air. Spectra recorded from the catalyst in purified air showed only the spectrum of the catalyst.

#### RESULTS AND DISCUSSION

With the Fourier transform instrument used in this study it was possible to subtract the spectrum of the gas and/or the solid phase from that of the catalyst under reaction conditions. In principle this can give more clear information on the nature of the intermediate products formed on the surface of the catalyst during the reaction. However, in most of the cases studied in the present work this compensation procedure had a distinct negative influence on the clearness of the spectra due to an increase in the amount of noise. Furthermore, it often did not give any extra information that could not already be obtained from the original spectra. The spectroscopic results are therefore presented as the original spectra of the catalyst in the reaction medium.

Preliminary adsorption experiments showed that after introduction of benzene into the infrared cell at temperatures of about 90°C followed by evacuation no organic material remained on the catalyst surface. Toluene and *o*-xylene, on the other hand, were both irreversibly adsorbed in these circumstances. This different behavior strongly indicates that the adsorption of toluene and *o*-xylene occurs via the alkyl group(s) and not via the ring. In the present study attention has been focused on infrared absorption bands between 1300 and 1900 cm<sup>-1</sup>. The frequency region around 3000 cm<sup>-1</sup>, where usually C–H vibration bands of both the aromatic ring and its alkyl groups are to be expected, was obscured at low temperatures by the presence of an intense broad band due to adsorbed water. Experiments performed with a catalyst

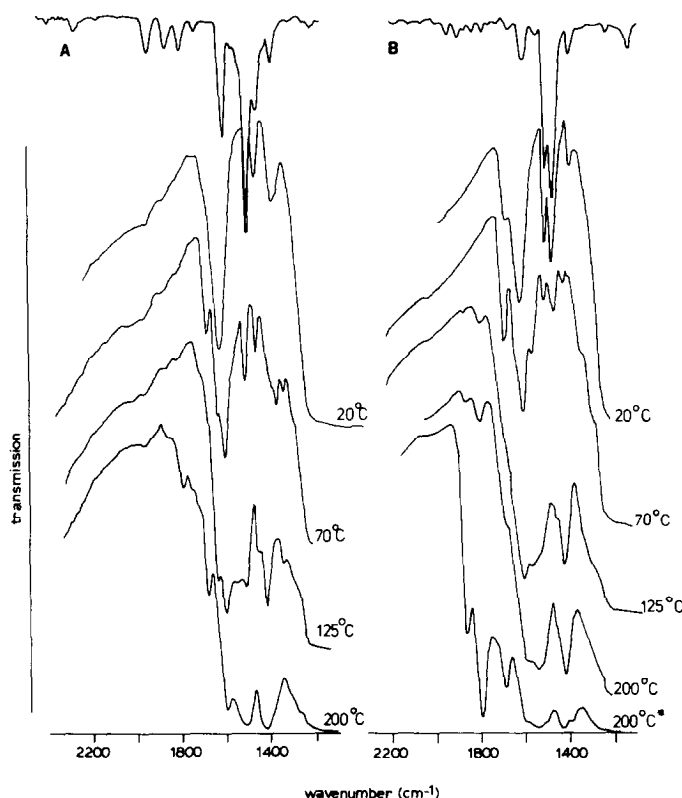


FIG. 1. Infrared spectra recorded during the oxidation of toluene (A) and *o*-xylene (B) on a  $V_2O_5/TiO_2$  monolayer catalyst at different temperatures (\* after 15 h of reaction).

sample preheated at  $450^\circ C$  *in vacuo* to remove adsorbed water gave spectra similar to those obtained after adsorption of the aromatic hydrocarbons on a non-pretreated vanadium oxide catalyst. This indicates that the presence of adsorbed water, probably present in relatively small amounts on the surface of the catalyst, has no effect on the adsorption behavior of the aromatic hydrocarbons.

When the temperature was increased, the intensity of the interfering water band decreased. The only band that could be observed in this region at elevated temperatures was due to the C-H vibration of the aromatic ring, suggesting that in these circumstances normal alkyl groups were no longer present in the intermediate species adsorbed on the surface of the catalyst. The infrared spectra recorded during the selective gas phase oxidation of toluene and *o*-

xylene are shown in Fig. 1. These measurements have been performed at temperatures lower than those used in the catalytic reaction ( $250\text{--}300^\circ C$ ) (13–15) in order to obtain information on especially the first reaction steps. Furthermore, at higher temperatures a range of products can be formed (17, 18) and this will definitely make interpretation of the spectra more complex. The spectra given in Fig. 1 contain not only bands due to species adsorbed on the surface of the catalyst, but also bands produced by toluene or *o*-xylene present in the gaseous reactant mixture. The spectra of the reactants, toluene and *o*-xylene, are also included in Fig. 1 for clarity.

The results of the infrared measurements performed with the products benzaldehyde and *o*-tolualdehyde are presented in Fig. 2. The relatively broad band present in the

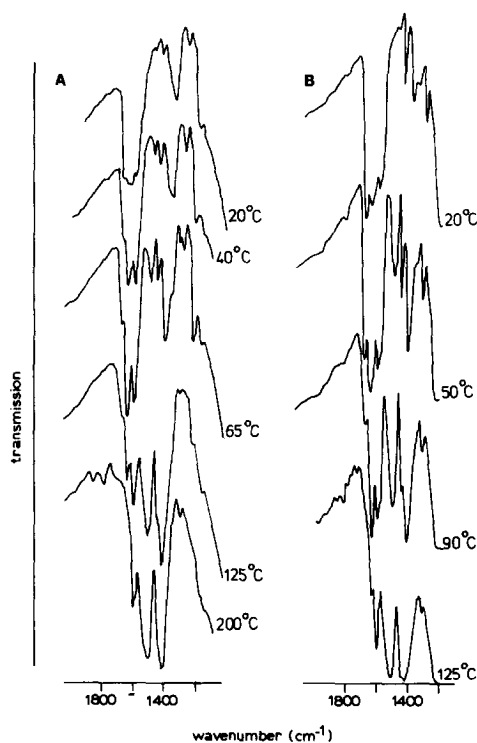


Fig. 2. Infrared spectra of benzaldehyde (A) and *o*-tolualdehyde (B) adsorbed at 20°C on a  $V_2O_5/TiO_2$  monolayer catalyst and subsequently oxidized at different temperatures.

spectra recorded during the experiments performed with toluene, benzaldehyde, and *o*-tolualdehyde at 1385, 1351, or 1361  $cm^{-1}$  was found to be due to an unknown contaminant irreversibly adsorbed on the KBr windows of the infrared cell.

A typical ring vibration around 1600  $cm^{-1}$  was observed in all spectra. This strongly indicates that during the adsorption/oxidation of the hydrocarbon the aromatic nucleus remains unaffected. The frequencies of the characteristic bands, produced by the side chain of the aromatic hydrocarbon in direct contact with the surface of the catalyst, are summarized in Table I. It can be seen that the spectroscopic results obtained for toluene, *o*-xylene, benzaldehyde, and *o*-tolualdehyde show a clear resemblance. The adsorption/oxidation of these four aromatic hydrocarbons thus leads to the for-

mation of similar intermediate species on the surface of the  $V/TiO_2$  catalyst. Adsorption of benzaldehyde or *o*-tolualdehyde did not give the two typical aldehyde C–H absorption bands between 2700 and 2850  $cm^{-1}$  or bands due to the C=O stretching vibration of the free aldehyde around 1710  $cm^{-1}$ , which are both usually relatively intense. This is in agreement with the observations of Sachtler *et al.* (11), who studied the adsorption/oxidation of benzaldehyde on a  $V_2O_5-SnO_2$  catalyst. After the adsorption of both benzaldehyde and *o*-tolualdehyde at room temperature two intense bands were observed around 1680/1690 and 1650  $cm^{-1}$ . These bands are most likely to be due to the C=O group of different surface species.

Upon heating the two bands both shifted to lower frequencies. The subtraction of the spectrum of a catalyst, which contained only adsorbed water, from that of the same catalyst after adsorption of the aromatic aldehyde revealed that this shift in frequency was not due to a decrease in the intensity of the interfering water band around 1630  $cm^{-1}$ , but could be attributed to a weakening of the C=O bond. Sachtler *et al.* (11) reported only a strong band at 1632  $cm^{-1}$ , which was assigned to a covalent carboxylate-like structure formed during the dissociative adsorption of benzaldehyde.

The band observed in this study at somewhat higher frequencies was not mentioned in their paper. Miyata *et al.* (8) studied the oxidation of ethanol and isopropanol on a vanadium–titanium oxide catalyst. Adsorption of these alcohols as well as adsorption of ethanol and acetone resulted in an infrared absorption band around 1680  $cm^{-1}$ . This band was, according to them, due to coordinatively adsorbed aldehyde or ketone species. Grabowski and Haber (19) reported a band at 1675  $cm^{-1}$  in their study of the interaction of propylene with the surface of a CoO–MgO solid solution, which was also assigned to aldehyde species bonded to the surface of the catalyst through the carbonyl group. The band observed in the present work at a frequency

TABLE 1

Positions of Characteristic Infrared Absorptions (in  $\text{cm}^{-1}$ ) Produced by the More or Less Oxidized Side Chain(s) of Toluene, *o*-Xylene, Benzaldehyde, and *o*-Tolualdehyde in Contact with  $\text{V}_2\text{O}_5/\text{TiO}_2$

<i>T</i> (°C)	1410	1500 <sup>a</sup>	1545	1632	1674	
20						
70				1625(sh)	1674(s)	Toluene
125	1411(s)		1544(w)	1632(w)		
200	1414(vs)	1500(vs)			1673(s)	
20					1672(sh)	<i>o</i> -xylene
70	1415(w)		1545(w)		1675(s)	
125	1409(s)		1542(br)			
200	1408(vs)		1526(s)		1676(sh)	
200 <sup>b</sup>	1412(vs)		1532(vs)		1681(s)	
20		1495(w)		1651(vs)	1691(vs)	Benzaldehyde
50	1408(s)	1500(s)		1641(vs)	1684(s)	
90	1411(vs)	1504(vs)		1637(vs)	1682(sh)	
125	1413(vs)	1498(vs)		1635(w)		
20		1495(w)		1651(s)	1691(s)	<i>o</i> -tolualdehyde
40		1493(w)		1643(vs)	1680(sh)	
65	1404(s)	1495(s)		1641(vs)	1678(sh)	
125	1412(vs)	1504(vs)		1634(s)	1672(sh)	
200	1418(vs)	1500(vs)				

Note. s = strong, w = weak, sh = shoulder, br = broad.

<sup>a</sup> The band observed at low temperatures for toluene and *o*-xylene was produced by the gaseous reactant mixture.

<sup>b</sup> After 15 h of reaction.

between 1670 and 1690  $\text{cm}^{-1}$  is most probably produced by similar surface structures.

The absence of vibration bands between 2700 and 2850  $\text{cm}^{-1}$  strongly indicates that the adsorbed aldehyde species do not contain a typical aldehyde C–H bond. Hence, not only the carbonyl group but also the hydrogen atom of the aldehyde interacts with the surface of the vanadium oxide catalyst. The results presented in Fig. 2 furthermore clearly show that at increasing temperatures the coordinatively adsorbed complex (1670–1690  $\text{cm}^{-1}$ ) and at a later stage also the complex with the carboxylate-like structure (1630–1650  $\text{cm}^{-1}$ ) are both converted into another species with two absorption bands around 1500 and 1410  $\text{cm}^{-1}$ . These bands were assigned respectively to the asymmetric and symmetric vi-

bration of a benzoate group. Similar bands have been reported in a number of investigations concerning the adsorption of toluene, benzaldehyde, benzoic acid, or xylenes on oxidic materials (9–11, 20). The exact frequencies of the two vibration bands depend on the catalytic material used in the adsorption experiments. For instance, we observed two bands at 1430 and 1552  $\text{cm}^{-1}$  upon adsorption of benzaldehyde on  $\gamma\text{-Al}_2\text{O}_3$ , which is in agreement with the results published by Niwa *et al.* (9) and Deflin *et al.* (20). Adsorption of benzaldehyde on a  $\text{V}_2\text{O}_5\text{-SnO}_2$  catalyst, on the other hand, produces a benzoate species with vibration bands at 1415 and 1520  $\text{cm}^{-1}$ . When benzaldehyde or orthotolualdehyde is adsorbed on a  $\text{V}_2\text{O}_5/\text{TiO}_2$  monolayer catalyst the asymmetric vibration band is ob-

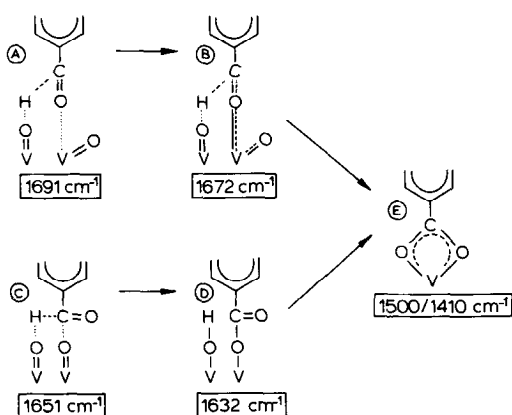


FIG. 3. Intermediate species identified on the surface of the  $V_2O_5/TiO_2$  monolayer catalyst after adsorption/oxidation of an aromatic aldehyde.

served at an even lower frequency (i.e.,  $1500\text{ cm}^{-1}$ ).

The species identified with infrared spectroscopy on the surface of the  $V_2O_5/TiO_2$  catalyst after adsorption of the aldehydes are summarized in Fig. 3.

Some of these complexes could also be detected in the oxidation of toluene and *o*-xylene. At low temperatures an absorption band around  $1675\text{ cm}^{-1}$ , appeared for both oxidation reactions, indicating the formation of a coordinatively bonded aldehyde (= species B) on the surface of the catalyst. Complexes with a covalent carboxylate-like structure (= species D) were observed only in the oxidation of toluene. At increasing temperatures two bands appeared around  $1545$  and  $1410\text{ cm}^{-1}$ , which were assigned to the asymmetric and symmetric vibration of a benzoate ion. However, these frequencies are not completely identical to the values mentioned above, suggesting a somewhat different structure of the adsorbed benzoate species. The bands observed around  $1545$  and  $1410\text{ cm}^{-1}$  are close to the free ion values ( $1548$  and  $1391\text{ cm}^{-1}$  (21) which, according to Itoh and Bernstein (22), points to a so-called bridging structure in which the carboxylate ion is coordinated with two metal atoms (Fig. 4). The formation of this structure on the surface of a

vanadium oxide monolayer catalyst indicates that the two oxygen atoms which have to be inserted during the conversion of a methyl side chain into a benzoate group are supplied by two neighboring vanadium-oxygen sites. In the oxidation of the corresponding aldehydes, however, this bridging structure is not formed as is clear from the infrared results presented in Fig. 2 and Table 1. This is due to the fact that an aldehyde molecule already contains one oxygen atom. The oxidation of such a species into a benzoate complex, therefore, requires only a single vanadium-oxygen site, which explains the formation of bidentate benzoate instead of bridging structures.

The so-called bidentate benzoate complexes are also formed in the oxidation of toluene at somewhat higher temperatures, as can be concluded from the appearance of two intense infrared bands around  $1500$  and  $1410\text{ cm}^{-1}$ . In the oxidation of *o*-xylene, on the other hand, the asymmetric vibration band remains at a higher frequency, suggesting a higher stability of the bridging structure of the adsorbed species.

The electron donating inductive effect of the second methyl group in the *o*-xylene molecule might be responsible for this different behavior. Due to this inductive effect the carbon atom of the oxidized side chain adsorbed on the surface of the catalyst will bear a somewhat smaller positive charge, resulting in an increase in the strength of the vanadium-oxygen band, as illustrated in Fig. 5. In the oxidation of *o*-xylene the bridging structure will therefore be more stable, whereas in the oxidation of toluene it is converted into the bidentate benzoate complex.

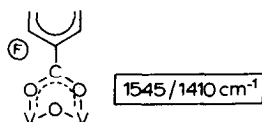


FIG. 4. Bridging benzoate complex on vanadium oxide monolayer catalyst.

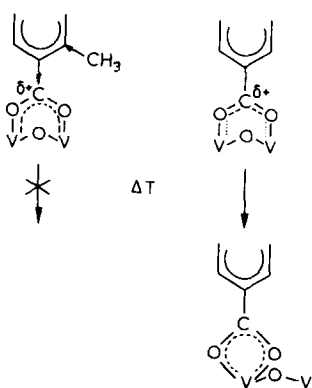


FIG. 5. Influence of second methyl group on the structure of adsorbed benzoate species.

From Fig. 1 it can furthermore be seen that at these relatively high temperatures the band around  $1675\text{ cm}^{-1}$  reappeared. Under these conditions this band can probably be assigned to cyclic anhydride complexes (i.e., maleic anhydride or phthalic anhydride) bonded to the surface of the catalyst through one of their carbonyl groups (analogous to the coordinatively adsorbed aldehyde species). In the oxidation of *o*-xylene two more bands appeared at  $1786$  and  $1854\text{ cm}^{-1}$ , which were also observed in the infrared spectrum of phthalic anhydride. These bands were therefore assigned to phthalic anhydride species physically adsorbed on the surface of the catalyst.

*Proposal for a reaction mechanism.* On the basis of the spectroscopic results discussed above a possible mechanism is proposed for the selective oxidation of the methyl group of toluene or *o*-xylene on a vanadium oxide monolayer catalyst (Fig. 6). The first step in this mechanism is, as is often suggested in the literature (23, 24), an abstraction of a hydrogen atom followed by the adsorption of the aromatic hydrocarbon via its methyl group on the vanadium oxide. It was not possible to obtain direct evidence for this reaction step from the infrared spectra presented in this study. After abstraction of a second hydrogen atom an aldehyde complex is formed which is coordinatively adsorbed on the surface of the

catalyst (= species B). Water is desorbed and the vanadium oxide species, which has been transformed from V(V) into V(III), is readily reoxidized with molecular oxygen.

Abstraction of the last hydrogen atom will give the bridging benzoate complex (= species F), which in the case of the oxidation of toluene is converted via a covalent carboxylate-like complex (= species D) into the bidentate benzoate complex (= species E). Benzoic acid is formed in the oxidation of toluene upon desorption of the benzoate complexes, whereas in the oxidation of xylene two neighboring carboxylate groups react to give phthalic anhydride.

It is obvious that the reaction mechanism proposed in Fig. 6 is far from complete since only the selective oxidation of the

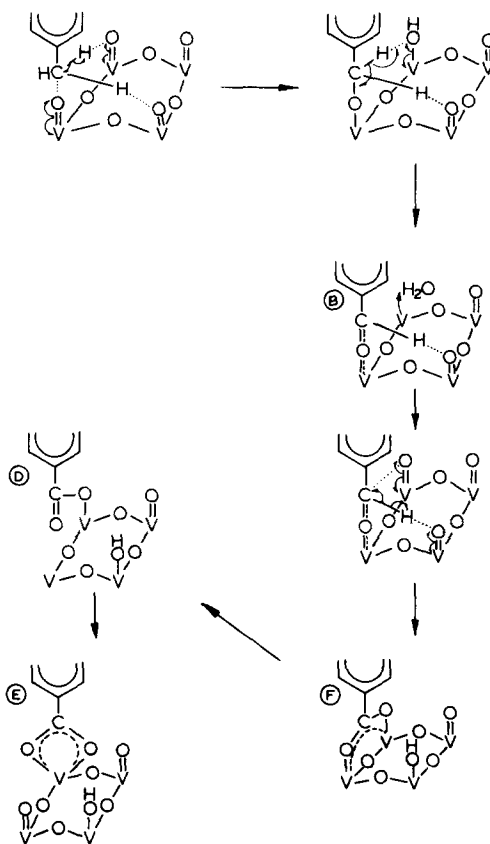


FIG. 6. Possible reaction mechanism for the oxidation of the methyl group of toluene or *o*-xylene on a vanadium oxide monolayer catalyst.

methyl group of the aromatic hydrocarbons was considered and no attention has been given to possible side or parallel reactions. It must furthermore be remembered that highly reactive intermediate species or intermediates which are present only at relatively low concentrations remain undetected and therefore in order to obtain a more complete insight into the course of the catalytic oxidation of the aromatic hydrocarbons toluene and *o*-xylene other experimental techniques, such as for instance tracer experiments, will have to be used.

#### ACKNOWLEDGMENT

We are grateful to the Esso Organization in The Netherlands for financial support.

#### REFERENCES

1. Davydov, A. A., Mikhaltchenko, V. G., Sokolovskii, V. D., and Borekov, G. K., *J. Catal.* **55**, 299 (1978).
2. Hata, K., Kawasaki, S., Kubokawa, Y., and Miyata, H., in "Proceedings, International Congress on Catalysis, 6th (London 1976)," p. 1102. Chem. Soc., London, 1976.
3. Nakajima, T., Sonoda, T., Miyata, H., and Kubokawa, Y., *J. Chem. Soc. Faraday Trans. 1* **78**, 555 (1982).
4. Miyata, H., Wakamiya, M., and Kubokawa, Y., *J. Catal.* **34**, 117 (1974).
5. Miyata, H., Hata, K., Nakajima, T., and Kubokawa, Y., *Bull. Chem. Soc. Japan* **53**, 2401 (1980).
6. Miyata, H., Nakajima, T., and Kubokawa, Y., *J. Catal.* **69**, 292 (1981).
7. Nakajima, T., Miyata, H., and Kubokawa, Y., *Bull. Chem. Soc. Japan* **55**, 609 (1982).
8. Miyata, H., Nakagawa, Y., Ono, T., and Kubokawa, Y., *J. Chem. Soc. Faraday Trans. 1* **79**, 2342 (1983).
9. Niwa, M., Ando, H., and Murakami, Y., *J. Catal.* **49**, 92 (1977).
10. Niwa, M., Ando, H., and Murakami, Y., *J. Catal.* **70**, 1 (1981).
11. Sachtler, W. M. H., Dorgelo, G. J. H., Fahrenfort, J., and Voorhoeve, R. J. H., in "Proceedings, International Congress on Catalysis, 4th (Moscow 1968)," Vol. 1, p. 454. Akadémiai Kiado, Budapest, 1971.
12. van Hengstum, A. J., van Ommen, J. G., Bosch, H., and Gellings, P. J., *Appl. Catal.* **5**, 207 (1983); van Ommen, J. G., Hoving, K., Bosch, H., van Hengstum, A. J., and Gellings, P. J., *Z. Phys. Chem. N.F.* **134**, 99 (1983).
13. van Hengstum, A. J., van Ommen, J. G., Bosch, H., and Gellings, P. J., *Appl. Catal.* **8**, 369 (1983).
14. van Hengstum, A. J., van Ommen, J. G., Bosch, H., and Gellings, P. J., in "Proceedings, International Congress on Catalysis, 8th (Berlin 1984)," Vol. 4, p. 297. Verlag Chemie, Weinheim, 1984.
15. van Hengstum, A. J., Pranger, J., van Ommen, J. G., and Gellings, P. J., *Appl. Catal.* **11**, 317 (1984).
16. Bouwman, R., and Freriks, I. L. C., *Appl. Surf. Sci.* **4**, 11 (1980).
17. Germain, J. E., and Laugier, R., *Bull. Soc. Chim. Fr.* **2**, 650 (1971).
18. Bernardini, F., and Ramacci, M., *Chim. Ind. (Milan)* **48**, 9 (1966).
19. Grabowski, R., and Haber, J., *React. Kinet. Catal. Lett.* **21**, 455 (1982).
20. Deflin, M., Eltantawy, I. M., and Baverez, M., *J. Catal.* **54**, 345 (1978).
21. Dunn, G. E., and McDonald, R. S., *Canad. J. Chem.* **47**, 4577 (1969).
22. Itoh, K., and Bernstein, H. J., *Canad. J. Chem.* **34**, 170 (1956).
23. Adams, C. R., in "Proceedings, International Congress on Catalysis, 3rd (Amsterdam, 1964)," Vol. 1, p. 240. North-Holland, Amsterdam, 1965.
24. Vanhove, D., and Blanchard, M., *J. Catal.* **36**, 6 (1975).