

CONF-840415-17



DE84009146

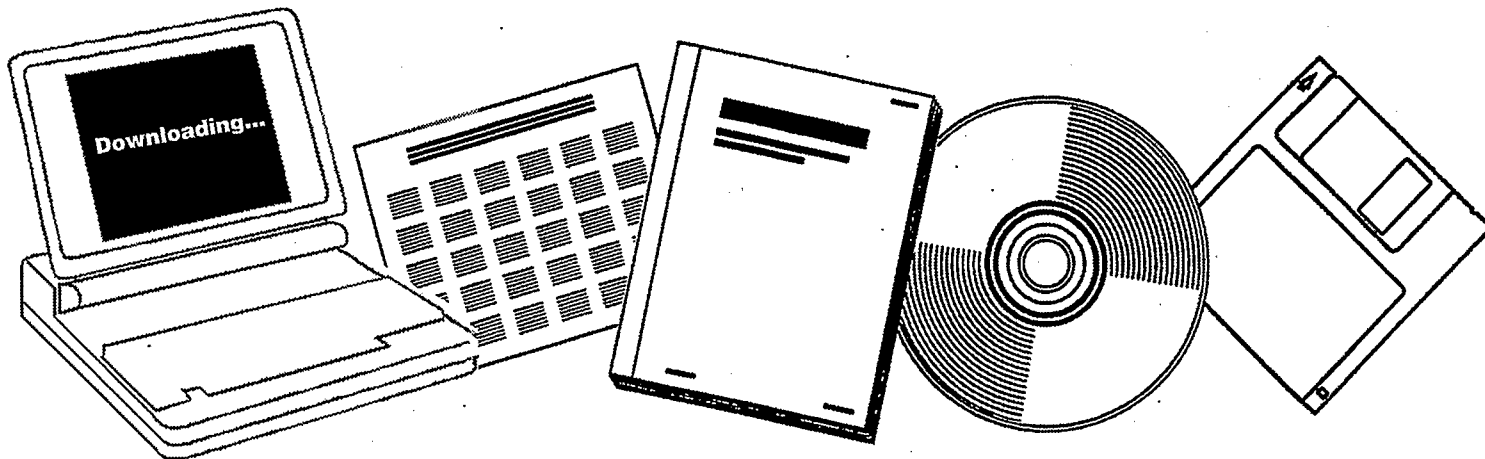
**NTIS**

One Source. One Search. One Solution.

**CO AND CO SUB 2 HYDROGENATION OVER ZRO SUB 2**

TEXAS UNIV. AT AUSTIN. DEPT. OF CHEMICAL  
ENGINEERING

1984



U.S. Department of Commerce  
**National Technical Information Service**



SYMPOSIUM ON MECHANISMS OF SYNGAS AND RELATED REACTIONS  
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.  
AMERICAN CHEMICAL SOCIETY  
ST. LOUIS MEETING, APRIL 8-13, 1984

CO AND CO<sub>2</sub> HYDROGENATION OVER ZrO<sub>2</sub>

BY

Ming-Yuan He and John G. Ekerdt  
Department of Chemical Engineering, University of Texas  
Austin, Texas 78712  
(512) 471-4689

INTRODUCTION

The hydrogenation of CO and CO<sub>2</sub> over ZrO<sub>2</sub> is classified as isosynthesis (the selective formation of branched alkanes and aromatics) when the reaction is conducted at pressures on the order of 50-200 atm (1-3). The reaction is known to produce intermediate oxygenated products, including methanol and dimethyl ether (1, 4, 5), suggesting

that the isosynthesis reaction may proceed via oxygenated intermediates. This paper examines the  $C_1$  intermediates which may initiate the isosynthesis reaction as well as participate in propagation. The presence of intermediates and their interconversion were established at one atm using temperature programmed techniques and FT-IR. The  $C_1$  intermediates formed on  $ZrO_2$  can be expected to be the same at one atm and isosynthesis pressures, however, their relative abundances may differ.

Different mechanisms have been proposed for CO and  $CO_2$  hydrogenation over metal oxides (6-8). Possible  $C_1$  intermediates include: formyl, formate, and molecular formaldehyde as the initial intermediate which forms between  $CO/H_2$  and the metal oxide, and methoxide and hydroxycarbene as precursors to methane or methanol. Our previous work over  $ZrO_2$  (9, 10) has shown that carbonate, bicarbonate, formate and methoxide form upon adsorption of  $CO/H_2$  or  $CO_2/H_2$ . Labeling studies are used to examine the interconversion of these intermediates and assist in establishing the mechanism for CO or  $CO_2$  hydrogenation over  $ZrO_2$ .

## EXPERIMENTAL

The details of the experimental apparatus and techniques are presented elsewhere (9, 10). The IR measurements were taken with the  $ZrO_2$  wafer at  $25^\circ C$ . The temperature programmed desorption/temperature programmed decomposition (TPD/TPDE) experiments were conducted in a

quartz tube using two grams of  $ZrO_2$  (1-3  $\mu$  powder with a  $5.8 \text{ m}^2/\text{g}$  BET area (Alfa-Ventron)). Flushing gas flow rates, during the heating cycle, were low enough to suggest that equilibrated readsorption occurred (11, 12).

The TPD/TPDE studies were conducted by oxidizing the  $ZrO_2$  in flowing  $O_2$  at  $620^\circ\text{C}$  for 0.5 hr followed by cooling in helium to  $25^\circ\text{C}$ , or followed by exposing the  $ZrO_2$  to flowing  $H_2$  at  $620^\circ\text{C}$  for 0.5 hr prior to cooling in flowing He. The surface remained hydroxylated as long as the temperature was kept below  $750^\circ\text{C}$  (13). Following pretreatment, the  $ZrO_2$  was exposed to the gas to be adsorbed as the temperature was increased to  $620^\circ\text{C}$  and cooled back to  $25^\circ\text{C}$  in the adsorbing gas. This procedure was selected to enable those species which may form at elevated temperature to form. The final step for TPD/TPDE involved heating the  $ZrO_2$  at  $1^\circ\text{C}/\text{sec}$  in the presence of a flushing gas, while monitoring the effluent with a mass spectrometer.

## RESULTS AND DISCUSSION

Species evolved during the TPD/TPDE studies at five different temperature regimes depending upon the adsorbed gas and the flushing gas (9). Assignments were made by examining the distribution of the desorbed products and adsorbing formic acid and methanol and desorbing their adsorbed structures, formate and methoxide, respectively. The assignments are listed below along with the TPD/TPDE temperatures.

$\alpha$  - 40 to 60°C; molecular CO.

$\beta$  - 120 to 180°C; carbonate.

$\gamma$  - 380 to 420°C; bicarbonate.

$\delta$  - 460 to 510°C; methoxide.

$\epsilon$  - 580 to 620°C; formate.

The  $\gamma$  species was initially assigned to a carbonate; however, infrared results indicate that bicarbonate forms over  $ZrO_2$  (10) from both CO and  $CO_2$ . Therefore, the  $\gamma$  species is probably a bicarbonate.

The infrared studies confirmed the presence of molecular CO, formate and bicarbonate over  $ZrO_2$ . Carbon monoxide and carbon dioxide interact differently over  $ZrO_2$ . Carbon dioxide adsorbs in the absence of added  $H_2$  to produce the bicarbonate species. Carbon monoxide adsorption results in a formate species. Figure 1a represents the spectrum observed following exposure of  $ZrO_2$  to 200 torr CO as the temperature was raised to 540°C and lowered back to 25°C. The bands at 2880, 1390, 1580, and 1360  $cm^{-1}$  are associated with the C-H stretching, C-H in plane deformation,  $COO^-$  asymmetric and  $COO^-$  symmetric stretching vibrations, respectively (10, 14-17). Continued exposure to 200 torr CO at 25°C for 18 hr produced spectrum b of Figure 1. The formate bands remain and additional bands are observed at 2960 and 1610  $cm^{-1}$ . The 2960  $cm^{-1}$  band is associated with methoxide (10, 16, 18, 19) and the 1610  $cm^{-1}$  band is associated with bicarbonate (10, 13, 20). Similar experiments with  $CO_2$

resulted in the appearance of only one band at  $1610\text{ cm}^{-1}$ , the bicarbonate.

The spectrum in Figure 1b revealed that the formate can be converted into the methoxide at  $25^{\circ}\text{C}$ . Adsorption of methanol at  $25^{\circ}\text{C}$  produces a methoxide species which was found to react at  $25^{\circ}\text{C}$  in the presence of methanol to the formate (10). These observations suggest that formate, methoxide, and any intermediates which are associated with the interconversion of formate and methoxide are reactive at  $25^{\circ}\text{C}$ .

Additional evidence for formate and methoxide species is presented in Figure 2. Spectrum a was recorded after exposing the  $\text{ZrO}_2$  to a flowing 1/1  $\text{CO}/\text{H}_2$  mixture as the temperature was raised to  $540$  and lowered back to  $25^{\circ}\text{C}$ . Methoxide ( $2960\text{ cm}^{-1}$ ) and formate ( $2880, 1580, 1390, 1360\text{ cm}^{-1}$ ) are observed. Evacuation at  $350^{\circ}\text{C}$  (spectrum b) and  $550^{\circ}\text{C}$  (spectrum c) caused the bands to attenuate. Exposure of the  $\text{ZrO}_2$  to formic acid at  $25^{\circ}\text{C}$  produced the formate, as anticipated (14-16), and some methoxide. (The band at  $1720\text{ cm}^{-1}$  correspond to the carbonyl stretch of formic acid.)

Figure 1a demonstrated that formate formation occurred at 200 torr CO. Additional studies at 1 atm flowing CO also show that CO forms the formate. TPD/TPDE reveal that CO adsorption also produces a carbonate when the adsorption occurs over the temperature cycle  $25 \rightarrow 620 \rightarrow 25^{\circ}\text{C}$ . Pulse adsorption of CO on an oxygen/hydrogen treated surface at  $320^{\circ}\text{C}$ ,

which is above the carbonate desorption temperature, reveals that formate does not react to produce the carbonate. Figure 3 presents the TPD/TPDE spectrum that resulted when the pulsed CO was heated in flowing H<sub>2</sub>. The two peaks appear at the  $\delta$  and  $\epsilon$  temperatures, corresponding to the decomposition of methoxide and formate species, respectively. No peaks were observed for the carbonate or bicarbonate species. These results along with previous results (9) suggest that carbonates are not involved in the CO hydrogenation reaction and are not precursors to hydrogenated products.

The formation of methoxide and formate in Figure 1 occurred in the absence of gas phase hydrogen. The ZrO<sub>2</sub> was treated with oxygen and hydrogen at 540°C for 0.5 hr under each gas prior to adsorption of CO. Similar IR spectra are observed if the ZrO<sub>2</sub> is treated only with oxygen. The surface of ZrO<sub>2</sub> contains OH groups (10, 13, 21). These OH groups can be exchanged with gas phase D<sub>2</sub> at temperatures at least as low as 200°C (10) which demonstrates that the OH groups are labile and that hydrogen dissociates over ZrO<sub>2</sub>. Figure 4 represents the TPD/TPDE signals recorded when an oxygen treated surface was heated in the presence of flowing CO. (The surface OH groups had been converted into OD groups with D<sub>2</sub>O prior to oxygen treatment.) Methane was observed at the  $\epsilon$  temperature. The appearance of CH<sub>4</sub> and CHD<sub>3</sub> indicates that OD exchange was incomplete. The appearance of CD<sub>4</sub> and CHD<sub>3</sub> demonstrates that OD groups acted as the deuterium source during these experiments.

Additional studies have suggested that the OH groups act as the hydrogen source in the presence of gas phase  $H_2$ .

Methane was seen to evolve from the surface of  $ZrO_2$  at both the  $\delta$  and  $\epsilon$  temperatures (Figures 3 and 4). The  $\delta$  species is a methoxide and methane formation involves hydrogenolysis of the C-O bond. The  $\epsilon$  species is a formate and methane formation is thought to occur by the formate reacting to the methoxide, which quickly reacts at the  $\epsilon$  temperature to methane (9).

Methanol is also formed over  $ZrO_2$  at one atm. Figure 5 presents the gas phase spectrum in the infrared cell following exposure of  $ZrO_2$  to 1/1  $CO_2/H_2$  over the temperature cycle  $25 \rightarrow 540 \rightarrow 25^\circ C$ . The characteristic methanol bands at 2960, 2930, and  $2843\text{ cm}^{-1}$  are clearly evident. A previous study (10) showed that  $CO_2/H_2$  reacted to formate, methoxide, and bicarbonate on the  $ZrO_2$  surface. Methanol can also be generated from  $CO/H_2$

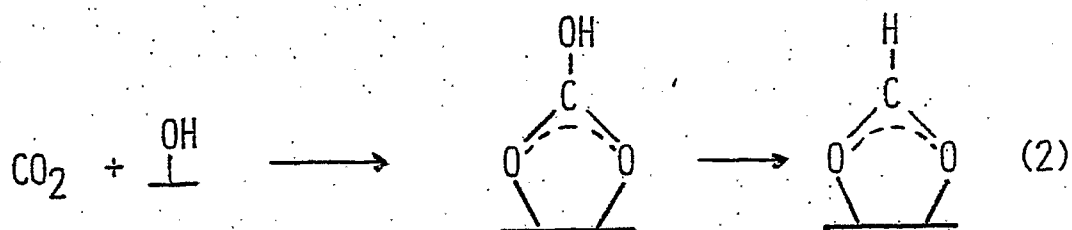
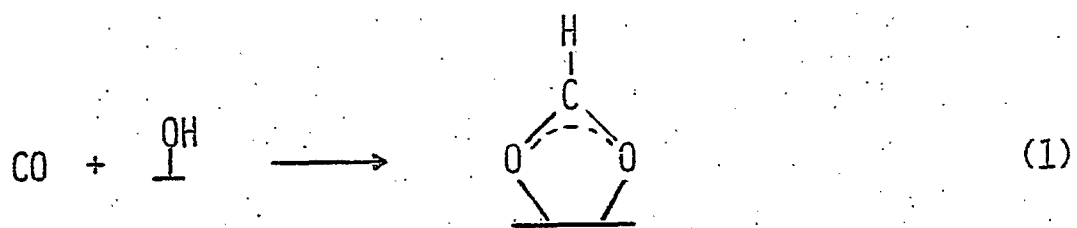
Labeling studies with OD and  $H_2$  (or OH and  $D_2$ ) suggest the mechanism by which methanol is formed as well as the mechanism by which formate converts into methoxide. Adsorption of  $CO_2$  onto a deuteroylated surface followed by TPD/TPDE in  $H_2$  results in  $CD_4$ ,  $CHD_3$ , and  $CH_4$  at the  $\delta$  temperature and  $CD_2HOH$  at  $600^\circ C$ . Adsorption of  $CO_2$  onto a hydroxylated surface followed by TPD/TPDE in  $D_2$  produces methane at the  $\delta$  temperature and  $CH_2DOD$  at  $600^\circ C$ . Carbon dioxide also evolves at



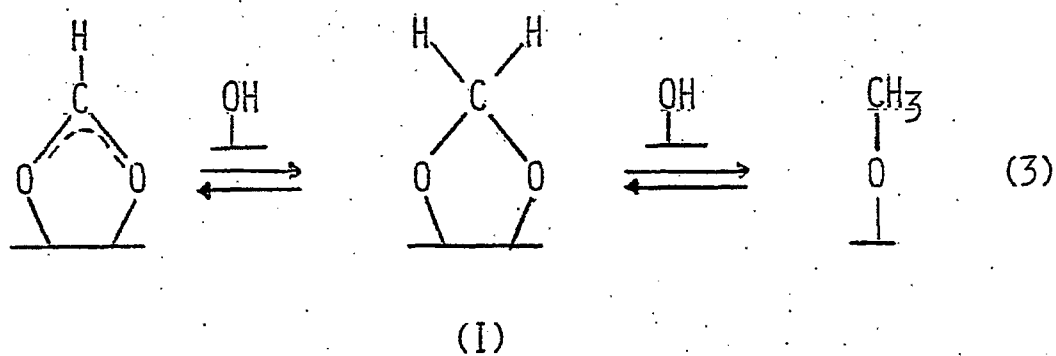
600°C. The species decomposing at 600°C for these experiments is not thought to be the formate. The TPD/TPDE spectrum and labeling studies suggest that an adsorbed form of methylformate is decomposing to give the methanol. Ai (22) has recently shown that methylformate decomposes over metal oxides to produce methanol and CO or CO<sub>2</sub>. Adsorption of methylformate and desorption in H<sub>2</sub> produces methanol at 600°C over ZrO<sub>2</sub>.

The Gibbs free energies of formation of methanol from CO or CO<sub>2</sub> and H<sub>2</sub> are sufficiently positive that, over the temperature range studied, direct synthesis was unlikely at one atmosphere. Methylformate formation from CO/H<sub>2</sub> is favored at temperatures below 125°C and is unfavored from CO<sub>2</sub>/H<sub>2</sub> at any temperature. Methylformate decomposition into methanol and CO or CO<sub>2</sub> is highly favored (large negative free energies of formation). If the adsorbed form of methylformate follows similar trends, it may be possible to form the adsorbed structure at low temperatures and have it decompose during the TPD/TPDE cycle in H<sub>2</sub>.

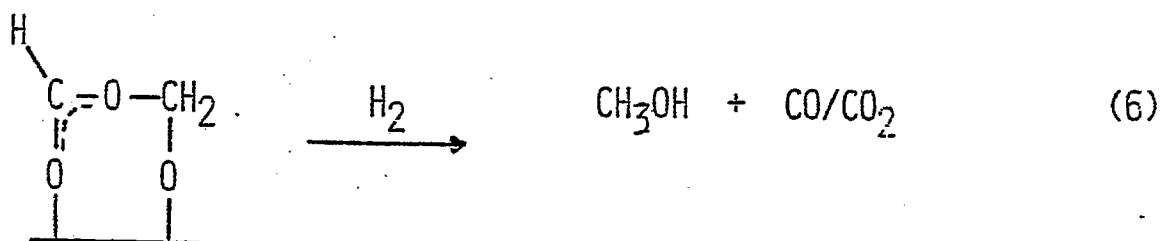
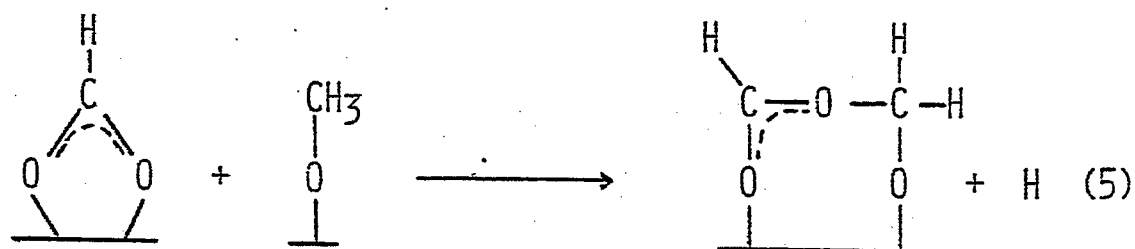
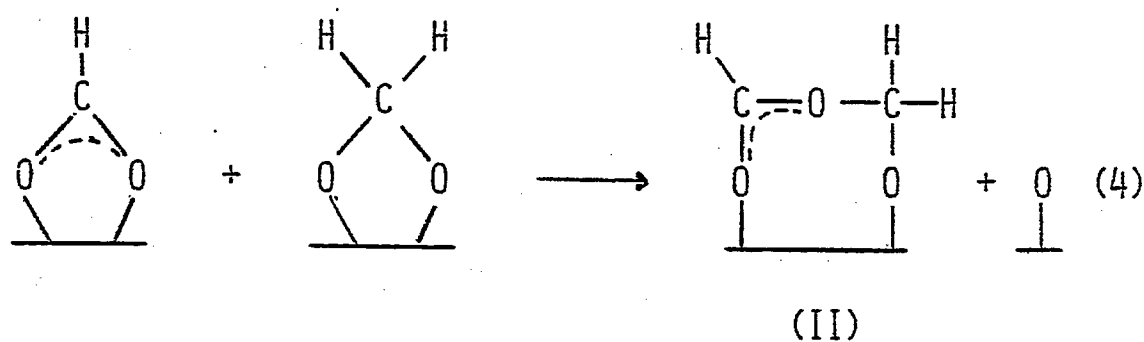
Possible mechanisms for this formation utilize the formate and methoxide species and their interconversion intermediate, H<sub>2</sub>COO<sup>-</sup> (1). Carbon monoxide reacts directly with the surface to produce formate, whereas CO<sub>2</sub> reacts to a bicarbonate which subsequently reacts to a formate (10). These steps are shown below with only one of the possible adsorbed structures shown for both formate and bicarbonate.



The formate was shown to convert into methoxide and did this at a temperature as low as  $25^{\circ}\text{C}$  in Figure 1. We propose that the reaction involves the  $\text{H}_2\text{COO}^-$  intermediate.



The methoxide can be hydrogenated to methane at atmospheric pressure but it is unlikely that it produces methanol at one atm. Methanol may form according to the following schemes, (4) to (6).



The CH<sub>2</sub> group on species II would explain the formation of CH<sub>2</sub>DOD when CO or CO<sub>2</sub> adsorption was followed by TPD/TPDE in D<sub>2</sub>. The

interconversion of formate and methoxide at 25°C revealed that the reactants for reactions 4 and 5 were present at temperatures where species II may be favored thermodynamically. Experiments are in progress to verify this mechanism.

#### ACKNOWLEDGEMENTS

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under Contract DE-AS05-80ER1072.

#### LITERATURE CITED

1. Pichler, H., and Ziesecke, K-H., Bureau of Mines Bull. 448 (1950).
2. Storch, H. H., Golumbic, N., and Anderson, R. B., "The Fischer-Tropsch and Related Synthesis", Wiley, New York, 1951.
3. Cohn, E. M., in "Catalysis" (P. H. Emmett, Ed.), Vol. 4, p 443, Reinhold, New York, 1956.
4. Barker, M. A., "Conversion of Synthesis Gas Over Zirconia",

- M. S. thesis, Department of Chemical Engineering, University of Texas, Austin, 1983.
5. Chang, C. D., Lang, W. H., and Silvestri, A. J., *J. Catal.* 56, 268 (1979).
  6. Klier, K., *Advances in Catalysis* 31, 243 (1982).
  7. Kung, H. H., *Catal. Rev. - Sci. Eng.* 22 (2), 235 (1980).
  8. Denise, B., Sneeden, R. P. A., and Hamon, C., *J. Mol. Catal.* 17 (2/3), 359 (1982).
  9. He, M.-Y., and Ekerdt, J. G., "Temperature Programmed Studies of the Adsorption of Synthesis Gas on Zirconium Dioxide", submitted for publication to *J. Catal.*
  10. He, M.-Y., and Ekerdt, J. G., "Infrared Studies of the Adsorption of Synthesis Gas on Zirconium Dioxide", submitted for publication to *J. Catal.*
  11. Ibok, E. E., and Ollis, D. F., *J. Catal.* 66, 391 (1980).
  12. Gorte, R. J., *J. Catal.* 75, 164 (1982).
  13. Tret'yakov, N. E., Pozdyakov, D. V., Oranskaya, O. M., and Filiminov, V. N., *Russ. J. Phys. Chem.* 44, 596 (1970).
  14. Trillo, J. M., Munuera, G., Criado, J. M., *Catal. Rev.* 7, 51 (1972).
  15. Noto, Y., Fukuda, K., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* 67, 3585 (1971).
  16. Busca, G., and Lorenzelli, V., *J. Catal.* 66, 155 (1980).
  17. Nakano, K., "Infrared Spectra of Inorganic and Coordination Compounds", p.231, Wiley, New York, 1978.

18. Ueno, A., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* 67, 3585 (1971).
19. Greenler, R. G., *J. Chem. Phys.* 37, 2094 (1962).
20. Little, L. H., "Infrared Spectra of Adsorbed Species", Academic Press, New York, 1966.
21. Yamaguchi, T., Nakano, Y., and Tanabe, K., *Bull. Chem. Soc. Japan* 51, 2482 (1978).
22. Ai, M., *J. Catal.* 83, 141 (1983).

## LIST OF FIGURES

- Figure 1. Adsorption of CO on  $ZrO_2$ : (a) spectrum recorded immediately after adsorption; (b) after 18 hr.
- Figure 2. Adsorption of CO/ $H_2$ , and HCOOH: (a) CO/ $H_2$  1/1; (b) evacuation at  $350^\circ C$  for 0.5 hr; (c) evacuation at  $550^\circ C$  for 0.5 hr; and, after (d) 10 torr HCOOH was admitted at  $25^\circ C$ .
- Figure 3. Mass signals characteristic of the indicated molecules during the TPD/TPDE of oxygen/hydrogen treated  $ZrO_2$ , with CO pulse preadsorption at  $320^\circ C$ , into  $H_2$ .
- Figure 4. Mass signals characteristic of the indicated molecules during the TPD/TPDE of oxygen/ $D_2O$  treated  $ZrO_2$ , without preadsorption into CO.
- Figure 5.  $CO_2/H_2$  1/1 adsorbed on  $ZrO_2$ , spectrum of the gas phase of the IR cell.

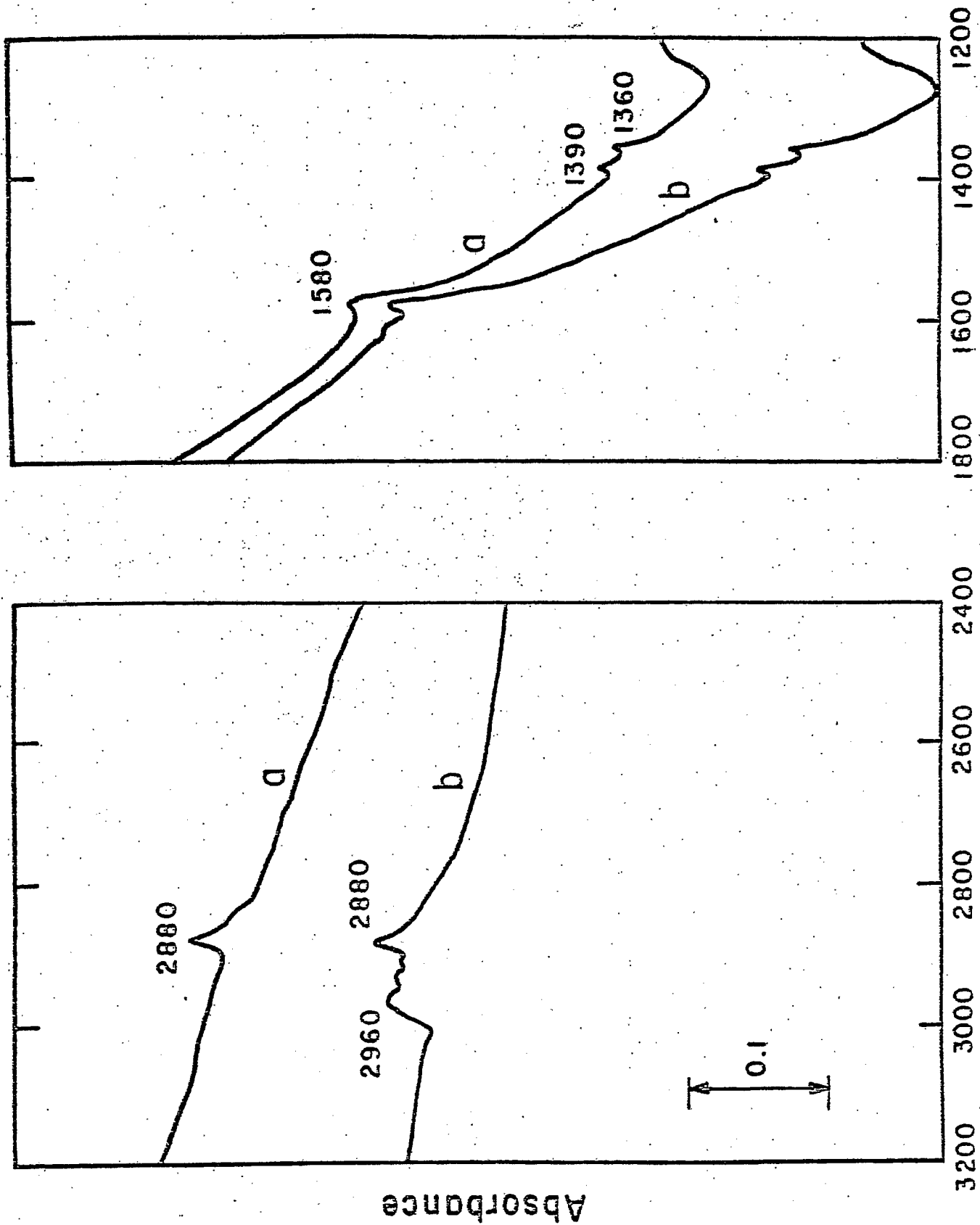


FIGURE 1 Wavenumber ( $\text{cm}^{-1}$ )



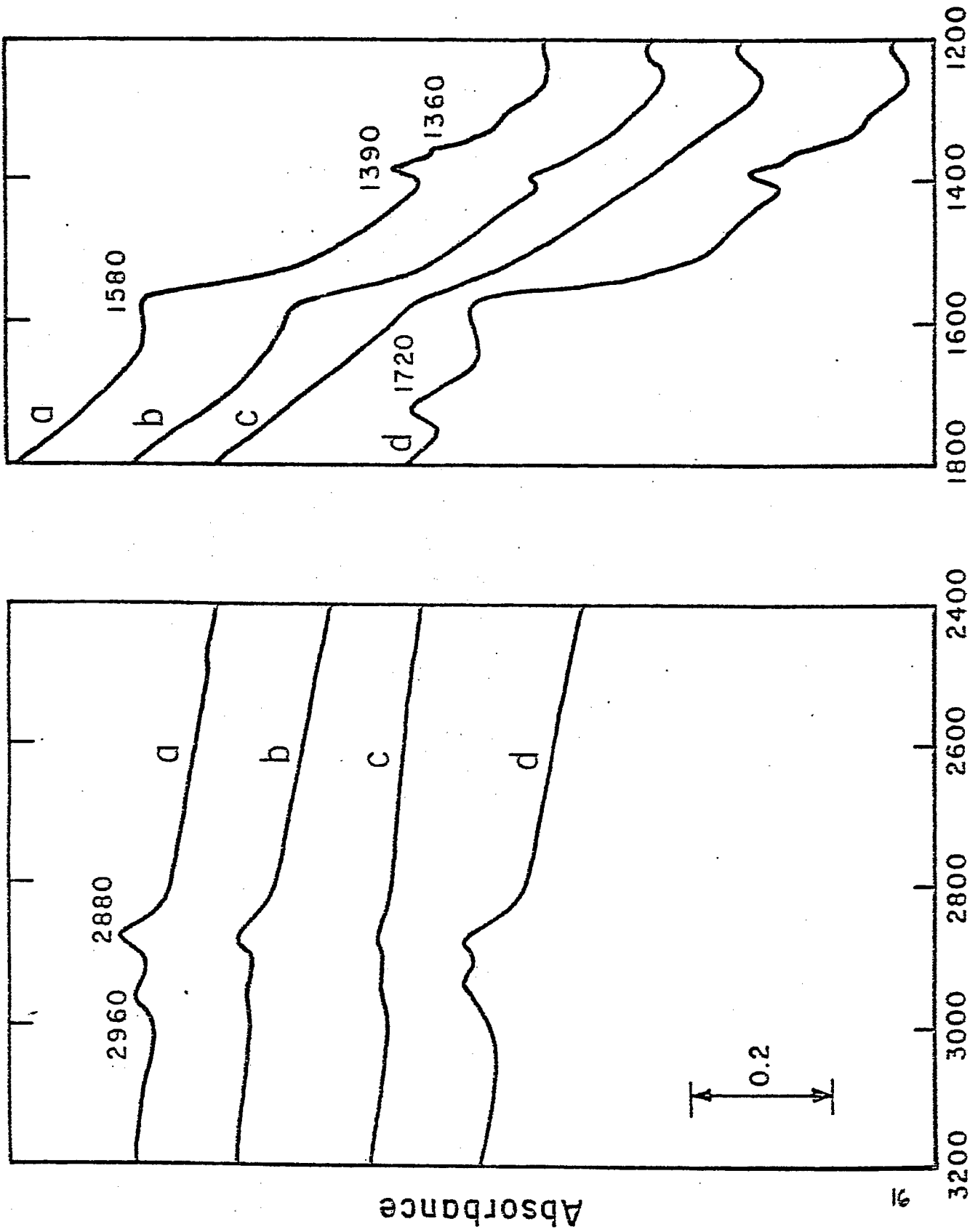


FIGURE 2 Wavenumber ( $\text{cm}^{-1}$ )

INTENSITY (arbitrary units)

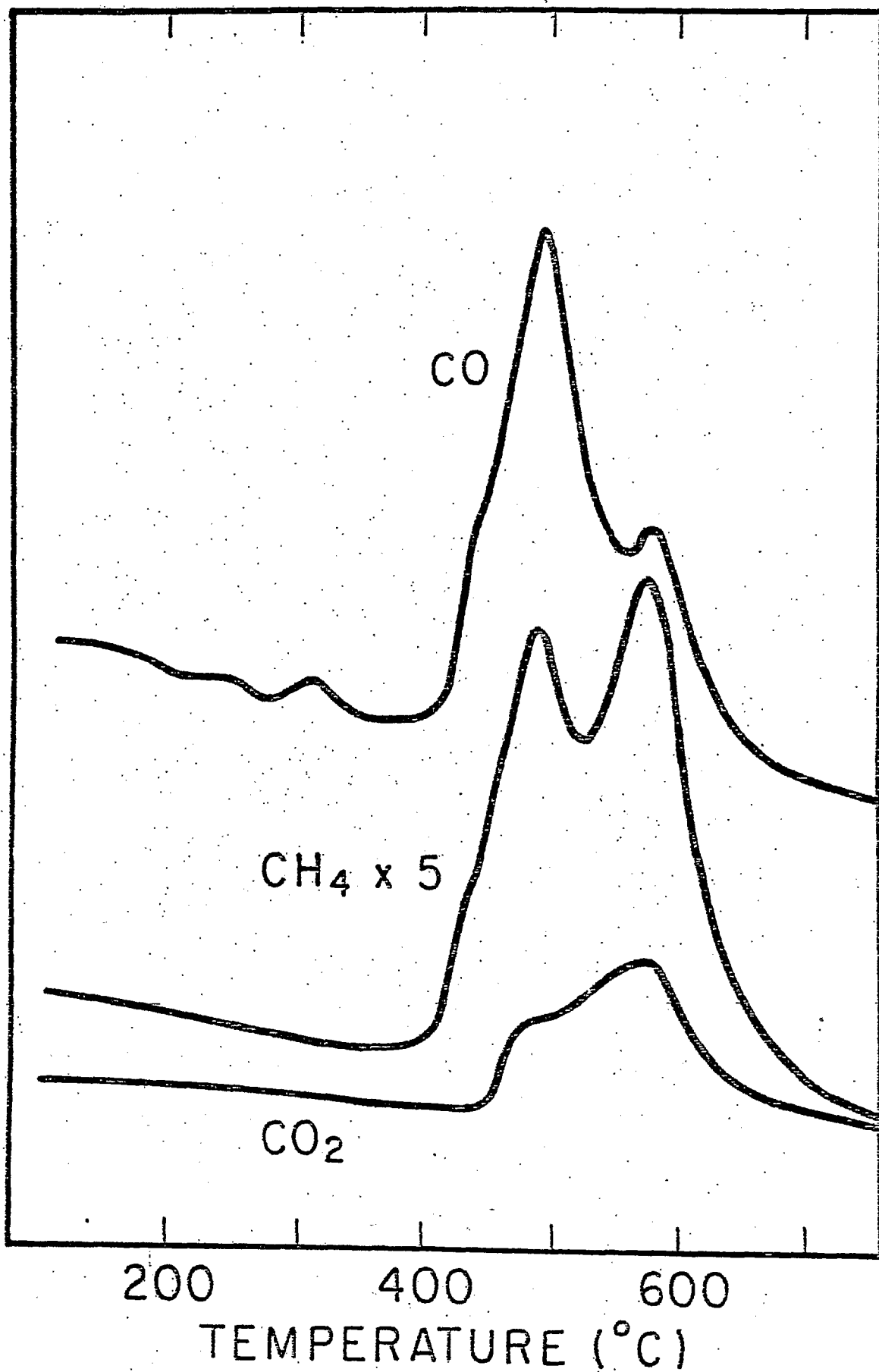


FIGURE 3

INTENSITY (arbitrary units)

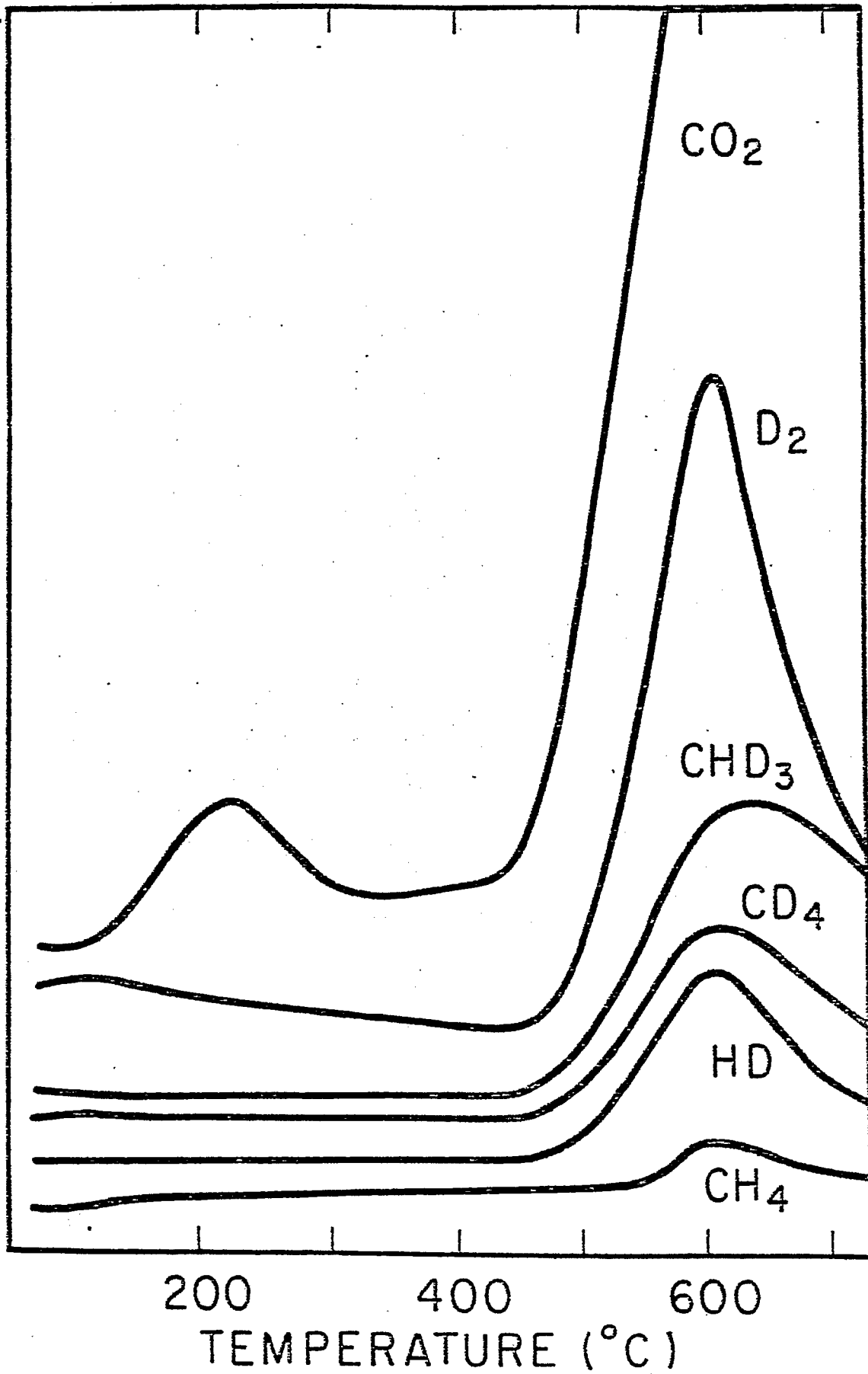


FIGURE 4

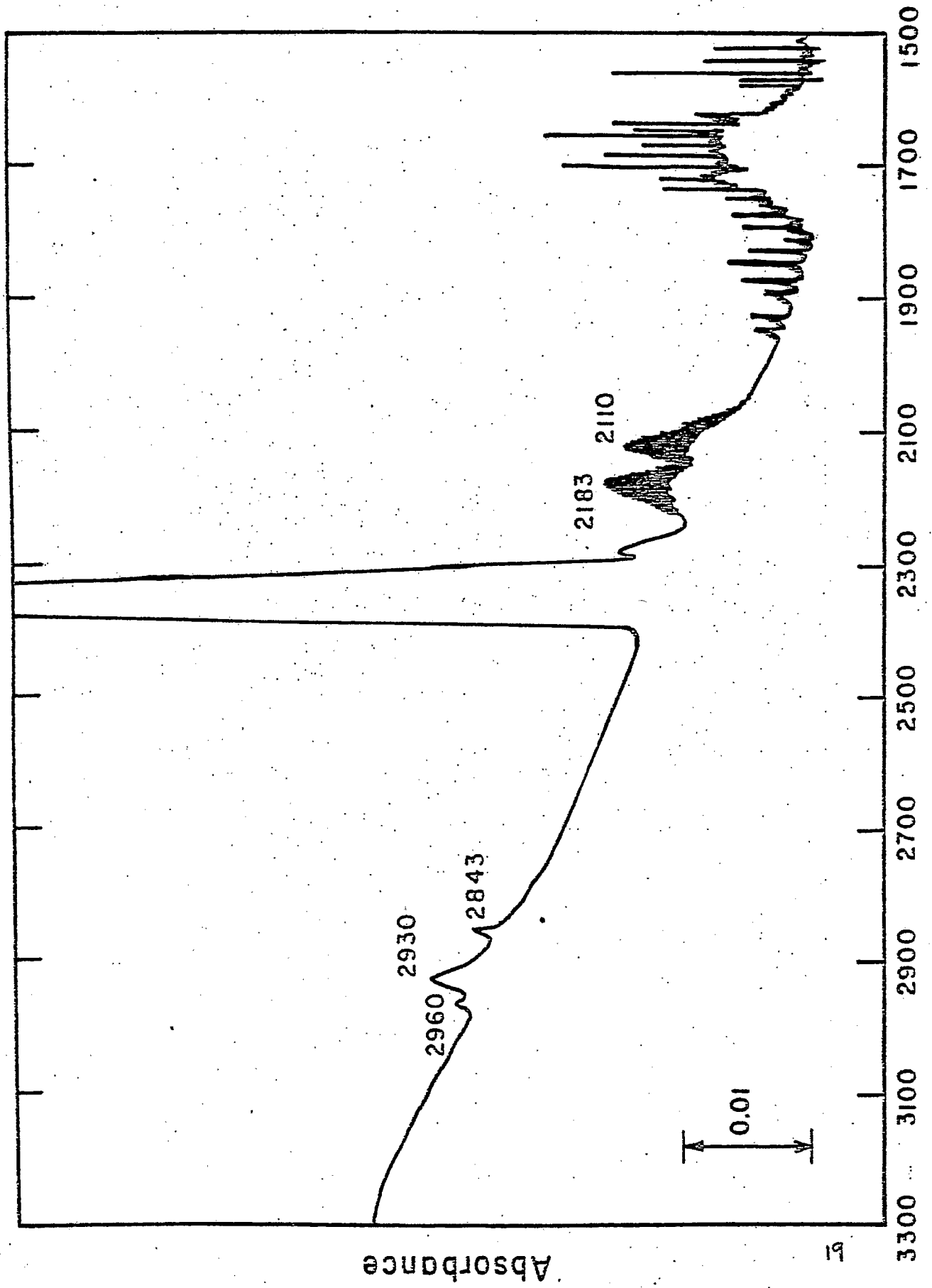


FIGURE 5 Wavenumber (cm<sup>-1</sup>)