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NEW POTENTIALLY USEFUL CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL

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Final Report for period to December 31, 1979

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The efficiency and selectivity of metal-supported heterogeneous catalysts is closely related to the dispersion of the metal atoms and to the nature of the interaction between the metal and the support. For a particular metal, catalytic activity may be varied by changing the metal dispersion and the support; thus the method of synthesis and any pre-treatment of the catalyst is important in the overall process of catalyst evaluation. Most supported metal catalysts have been prepared by impregnation techniques, e.g. by treating a suitable support such as alumina or silica to "incipient wetness" with an aqueous solution of a metal salt. The material is then dried and pre-treated by heating in hydrogen at an elevated temperature to produce the dispersed metal. Often a "carbiding step" follows the reduction in hydrogen. These procedures result in the formation of small crystallites of the metal or carbide dispersed on the surface of the support. Often a low dispersion of the metal results from incomplete or ineffective reduction of the metal due to relatively large particle size and/or strong interactions between the oxidized form of the metal and the support. Recently, the use of metal carbonyls for the preparation of materials containing supported metal atoms which may serve as potential catalysts have been reported by several authors(1-12). The usual method of preparation of the material, adsorption or impregnation, involves contact between a solution of the metal carbonyl and the support in suspension; the solvent is then removed by evaporation. Howe et al(1) have noted that there were no significant differences between supported molybdenum hexacarbonyl materials prepared by this method and those prepared by dry mixing of the carbonyl and support.

Although the preparation of some supported carbonyls has been reported, with the exception of several IR studies in the $\nu(CO)$ region and the measurement and interpretation of temperature-programmed decomposition spectra by Brenner and coworkers, in depth studies involving the application of physical techniques to the determination of the nature of the interaction between the carbonyl and the support and the chemistry of the supported species have not been undertaken. In order to carry out an effective program of catalyst synthesis and evaluation, correlations between the nature of the catalyst and its activity must be made. This approach has been employed during our investigations in this field and is a continuous theme throughout the whole project.

During the period of the contract, research has been aimed at the synthesis and characterization of some supported transition metal cluster compounds. Some of these materials have been tested as potential catalysts for the hydrogenation of carbon monoxide. Transition metal cluster compounds were chosen for the precursors to the heterogeneous catalysts for several reasons. First, some of these compounds have been shown to behave as homogeneous catalysts for the hydrogenation of carbon monoxide; second, removal of some of the ligands associated with the compounds, e.g. partial decarbonylation of the supported carbonyls, would lead to coordinative unsaturation, a feature which is very important in the function of a catalyst and third, the formation of "naked" metal clusters which are highly dispersed on an inert support (formed by removal of all coordinated ligands under a reducing atmosphere) may produce a material which would readily coordinate carbon monoxide, possibly through a bridging mode, leading to reduction in the CO bond order and a different mechanism for the CO/H_2 reaction than that postulated for the Fischer-Tropsch reaction.

A general procedure for the synthesis of some new, effective heterogeneous catalysts containing highly dispersed transition metal compounds on supports has been developed(13). The initial work involved alumina as the support material although recently the procedure has been applied to the synthesis of materials containing simple and complex oxides as supports. This procedure is different from that used previously by researchers attempting to prepare catalytic materials containing supported metal compounds. The potential catalysts were synthesized from solutions of the carbonyls $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Os_3(CO)_{12}$, $Fe_3(CO)_{12}$, $Co_4(CO)_{12}$ and the supports either as powders, or as 1/8" extrudates or pellets in the case of alumina, by a carefully designed and controlled extraction procedure. The procedure may be conducted in the presence of air or an inert gas such as dry N_2; usually a dried, de-gassed non-polar solvent is employed as the extracting medium. The developed procedures are similar for the synthesis of each potential catalyst, however the solvent and reaction times employed may vary with the carbonyl and support used. Total metal concentration has been determined by X-ray fluorescence or atomic absorption spectroscopy and varies between 1 and approximately 20 percent. The synthesized materials may be handled in air; evidence from optical and scanning electron microscope studies, X-ray diffraction, Raman spectroscopy and chemisorption experiments indicate that the catalysts have an even distribution of highly dispersed, small particle sized metal carbonyls on the support surface and there is no evidence for the presence of crystals or irregular deposits of the carbonyl on the support. (It should be noted that by using previously reported conditions for reactions between some of the carbonyls and alumina(1-11), uneven distributions of crystals of the original carbonyl on the alumina are produced. The physical properties of these materials are identical to those obtained for samples prepared by dry mixing of the reactants; it is concluded that the degree of dispersion of these compounds is not as great as that obtained by the use of our general procedure). The extent of penetration of the metal carbonyl into the alumina extrudate or pellet is dependent on the carbonyl, the alumina, the solvent and the reaction time employed. X-ray fluorescence and scanning electron microscope studies have enabled a distribution profile of the carbonyl through the extrudate or pellet to be determined, see

Appendix, #1 and 2. Catalysts have been prepared in which the penetration varies from very little (i.e. surface distribution) to complete distribution through to the center of the support. Adsorption/reaction of the carbonyl is accompanied by significant changes in the carbonyl stretching region of the IR spectra of the materials. The alumina-supported carbonyls have been further characterized by a variety of spectroscopic (IR, Raman, ESCA, SEM, X-ray fluorescence, X-ray diffraction) and thermogravimetric techniques, see Appendix, #3, 4, 5, 6, 8. The physical properties of these species are significantly different from those obtained for species prepared by the equivalent of the dry mixing procedures reported by other workers. We conclude from the characterization studies that a strong interaction between the alumina and the carbonyl is present; depending upon the conditions of the preparation, reaction is accompanied by partial or complete decarbonylation of the metal carbonyl and oxidation of the metal to form metal-surface oxygen bonds. When the alumina-supported carbonyls are heated, both in air and in an inert gas medium by using thermogravimetric analysis equipment, decarbonylation results which is accompanied by marked changes in both the appearance and spectroscopic properties of the product. By careful choice of the temperature and conditions, partially or completely decarbonylated species can be prepared, see Appendix, #5. These species have also been characterized by the techniques mentioned above; it is concluded that decarbonylation is accompanied by oxidation of the metal. (Recently, an EPR study of an alumina-supported ruthenium carbonyl prepared by our general procedure has indicated the presence of ruthenium(III) on the support surface(14), see Appendix, #7. Further investigations concerning the application of EPR spectroscopy to the study of adsorbed species are in progress.) Decarbonylation achieved by heating the supported carbonyls in flowing H_2 at temperatures up to 450° produces distributions of the unoxidized metal on the surface. For catalysts derived from $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$ and $Rh_6(CO)_{16}$ by this treatment, chemisorption experiments (H_2 adsorption) indicate a high degree of dispersion of the metal on the alumina support. Preliminary experiments for evaluation of the catalytic activity of some of the species prepared by our procedure have demonstrated that effective methanation catalysts can be derived from the $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$ and $Rh_6(CO)_{16}$ supported carbonyls after prior reduction in flowing H_2 at temperatures up to 450°, (reaction conditions 3:1 H_2:CO at approximately 4 atm pressure; temperature 400°)(15). Deactivation of the catalysts occurs after several hours, however reactivation can be achieved by reheating in hydrogen.

Recently, we(16) have applied our general synthesis procedure to reactions between the carbonyls $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Rh_6(CO)_{16}$ and the simple oxides MgO, ZnO and TiO_2 and to reactions between $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$ and the complex oxides, ZSM-5, silicalite and nu-1. In all cases, the products obtained are similar to those obtained from the syntheses with alumina, i.e. they contain even distributions of highly dispersed, small particle sized metal compounds on the support surface. With the simple oxides as supports the metal compounds are carbonyls, although the infrared spectra of these species indicate that they are different from the original carbonyls. With the complex oxides, complete decarbonylation of the carbonyls accompanies adsorption/interaction with the support. Application of the general procedure has enabled us to prepare potential catalysts containing more than one supported metal ion. For example, potential catalysts consisting of iron and cobalt on the complex oxides have been prepared by successive use of $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$ as sources of the metal ions. No evidence for removal of the first metal was obtained when depositing the second metal. This procedure is rapid, simple to carry out, versatile and has advantages over the conventional impregnation method for the synthesis of multimetallic catalysts(17). Characterization of these materials by the techniques mentioned earlier is in progress. Evaluation of the catalytic activity of iron on ZSM-5 (10-20% Fe) prepared by our procedure for the hydrogenation of carbon monoxide is currently underway, preliminary data indicate that these materials are quite different from those obtained by using aqueous solutions of iron nitrate and incipient wetness techniques(18). Further investigations are necessary to determine if the product distribution obtained is different from that resulting from the use of conventionally prepared iron on ZSM-5 catalysts(19,20) and if so to correlate the nature of the catalyst with the product distribution.

Thus, during the period of the contract, we have developed a new, general procedure which has been used for the synthesis of highly dispersed metal compounds on a variety of supports and demonstrated that some of these species form effective catalysts for the hydrogenation of carbon monoxide. The application of a variety of physical techniques has enabled us to draw conclusions concerning the nature of the supported species and the interaction between the compounds and the support.

The Principal Investigator acknowledges with gratitude the assistance provided by scientists at the Pittsburgh Energy Technology Center for some of the characterization studies and preliminary data concerning catalytic ability of synthesized materials.

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APPENDIX

Examples of data obtained for some alumina-supported transition metal carbonyls

1. Penetration profile for $Ir_4(CO)_{12}/Al_2O_3$ extrudate/THF

2. Penetration profile for $Ru_3(CO)_{12}/Al_2O_3$ extrudate/$CHCl_3$

3. Infrared spectra (2300-1900 cm^{-1}) for
    - (a) $Ir_4(CO)_{12}$
    - (b) Dry ground $Ir_4(CO)_{12}/Al_2O_3$ mixture
    - (c) Conventional "impregnation" product from $Ir_4(CO)_{12}/Al_2O_3$
    - (d) Product from extraction procedure, $Ir_4(CO)_{12}/Al_2O_3$/THF

4. Infrared spectra (2300-1900 cm^{-1}) for
    - (a) $Ru_3(CO)_{12}$
    - (b) Dry ground $Ru_3(CO)_{12}/Al_2O_3$ mixture
    - (c) Conventional "impregnation" product from $Ru_3(CO)_{12}/Al_2O_3$
    - (d) Product from extraction procedure, $Ru_3(CO)_{12}/Al_2O_3/CHCl_3$

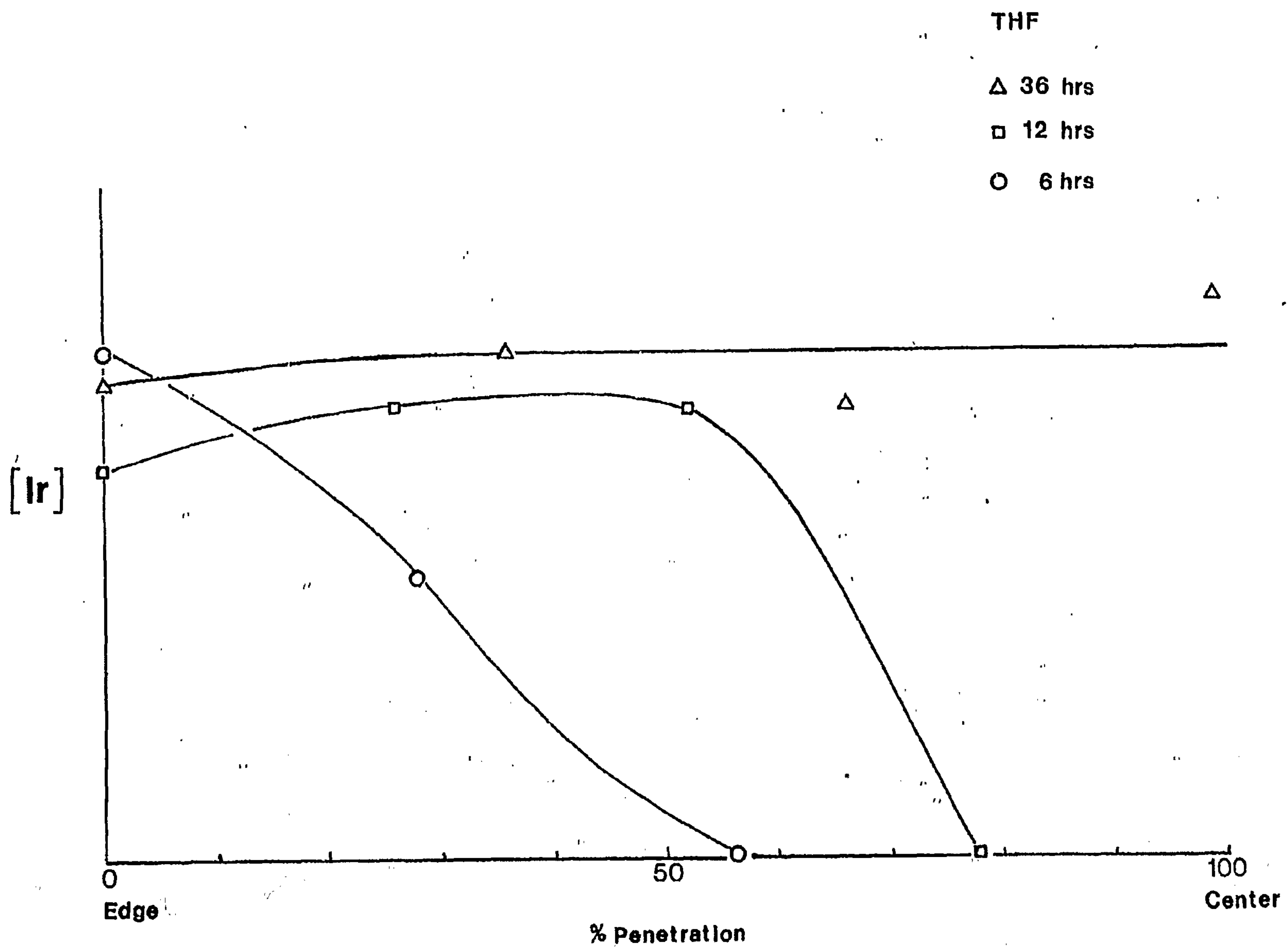
5. Infrared spectra (2300-1900 cm^{-1}) for $Ru_3(CO)_{12}/Al_2O_3$ samples prepared by extraction procedure
    - (a) Using $CHCl_3$ as solvent
    - (b) Sample (a) after heating @ 150°
    - (c) Further heating @ 150° - eventually complete decarbonylation

6. Infrared spectra (2200-1700 cm^{-1}) for $Rh_6(CO)_{16}/Al_2O_3$ samples prepared by extraction procedure
    - (a) Using $CHCl_3$ as solvent for 24 hours
    - (b) Using $CHCl_3$ as solvent for 48 hours
    - (c) Using THF as solvent for 24 hours

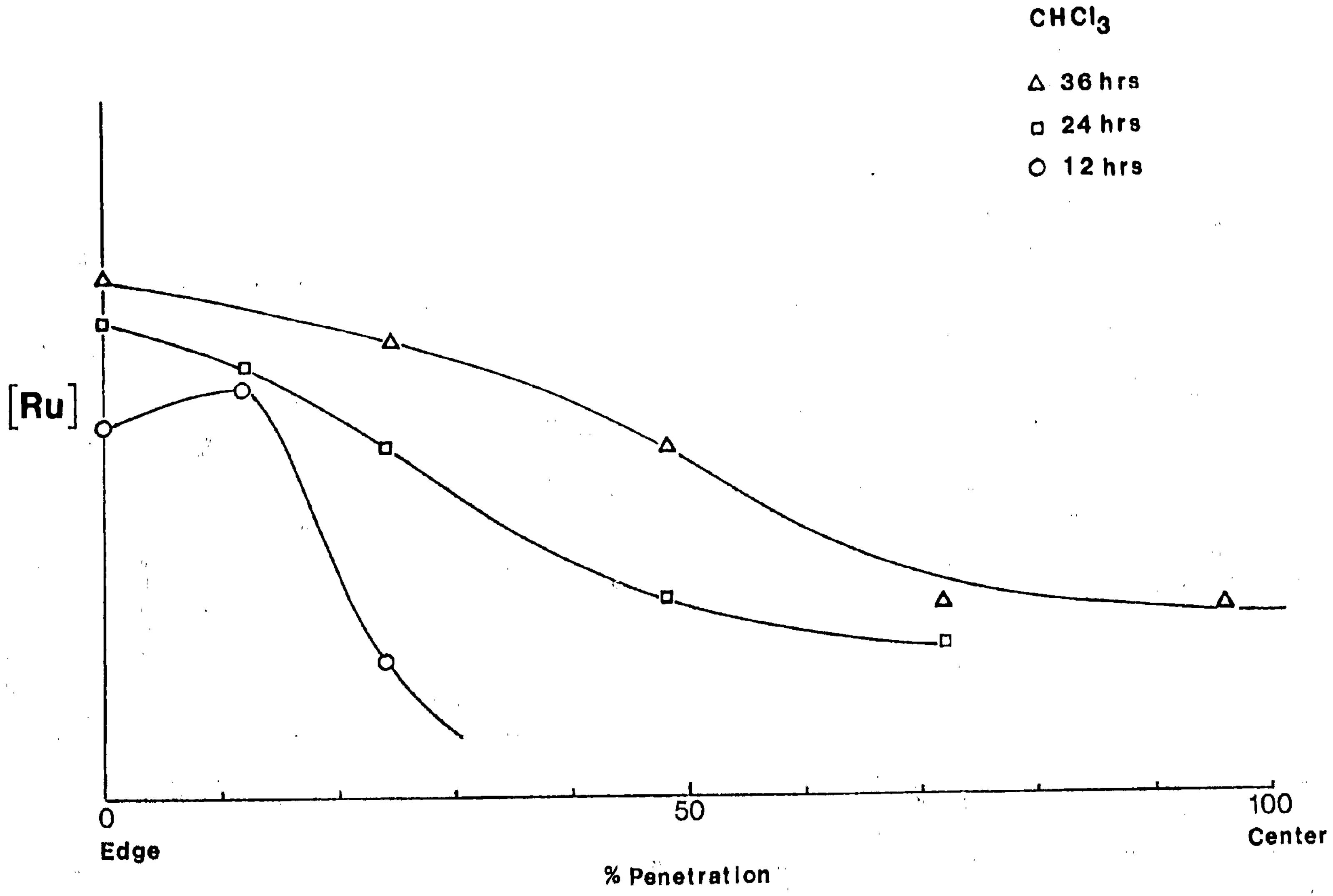
    Note in (b) and (c) disappearance of 1800 cm^{-1} (bridging CO) band indicating breakdown of cluster on alumina surface.

7. EPR spectrum for sample from $Ru_3(CO)_{12}/Al_2O_3/CHCl_3$ extraction procedure.

8. X-ray diffraction data for metal carbonyls.


THF
△ 36 hrs
□ 12 hrs
○ 6 hrs
[Ir]
0
Edge
50
100
Center
% Penetration

2



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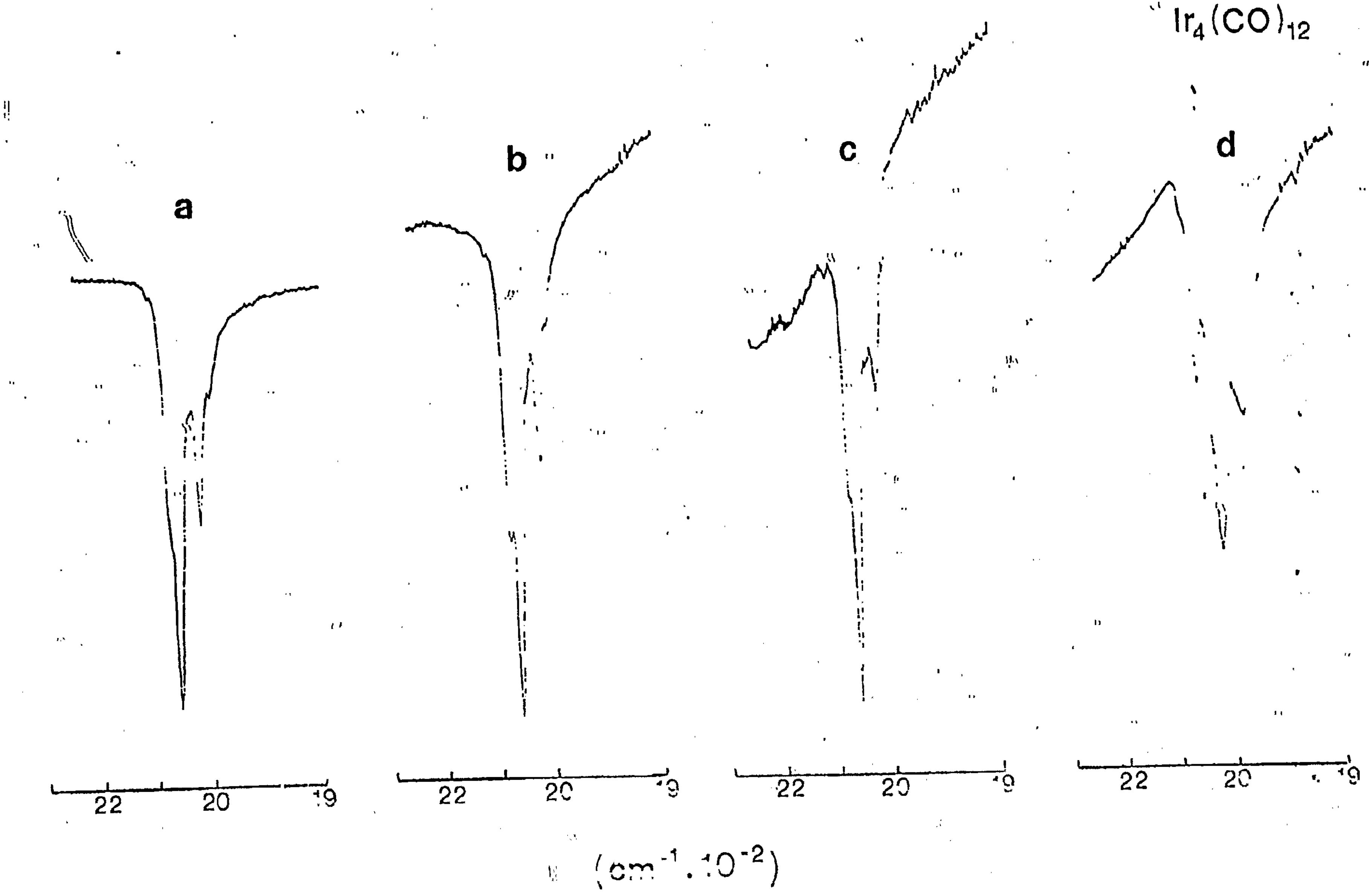
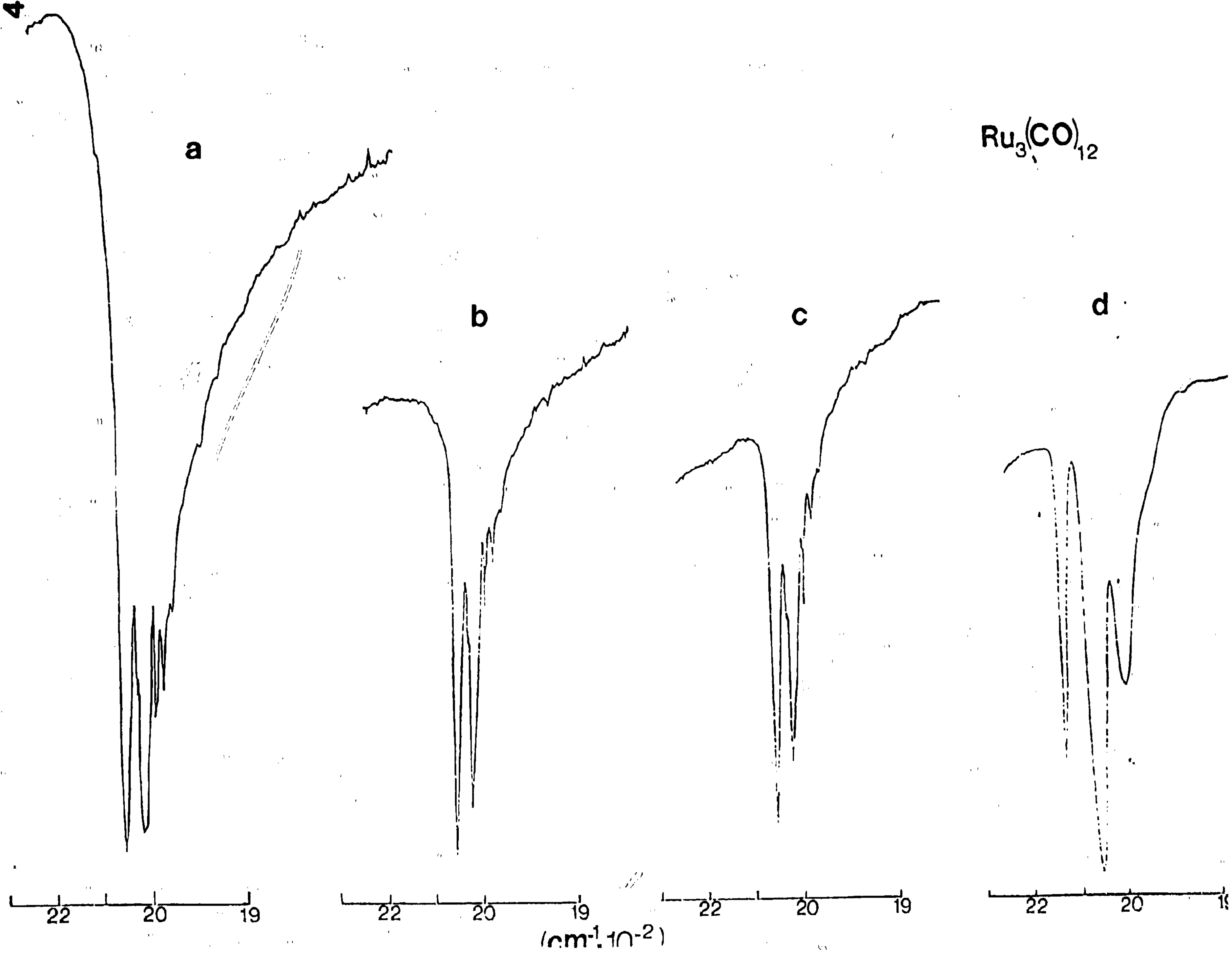
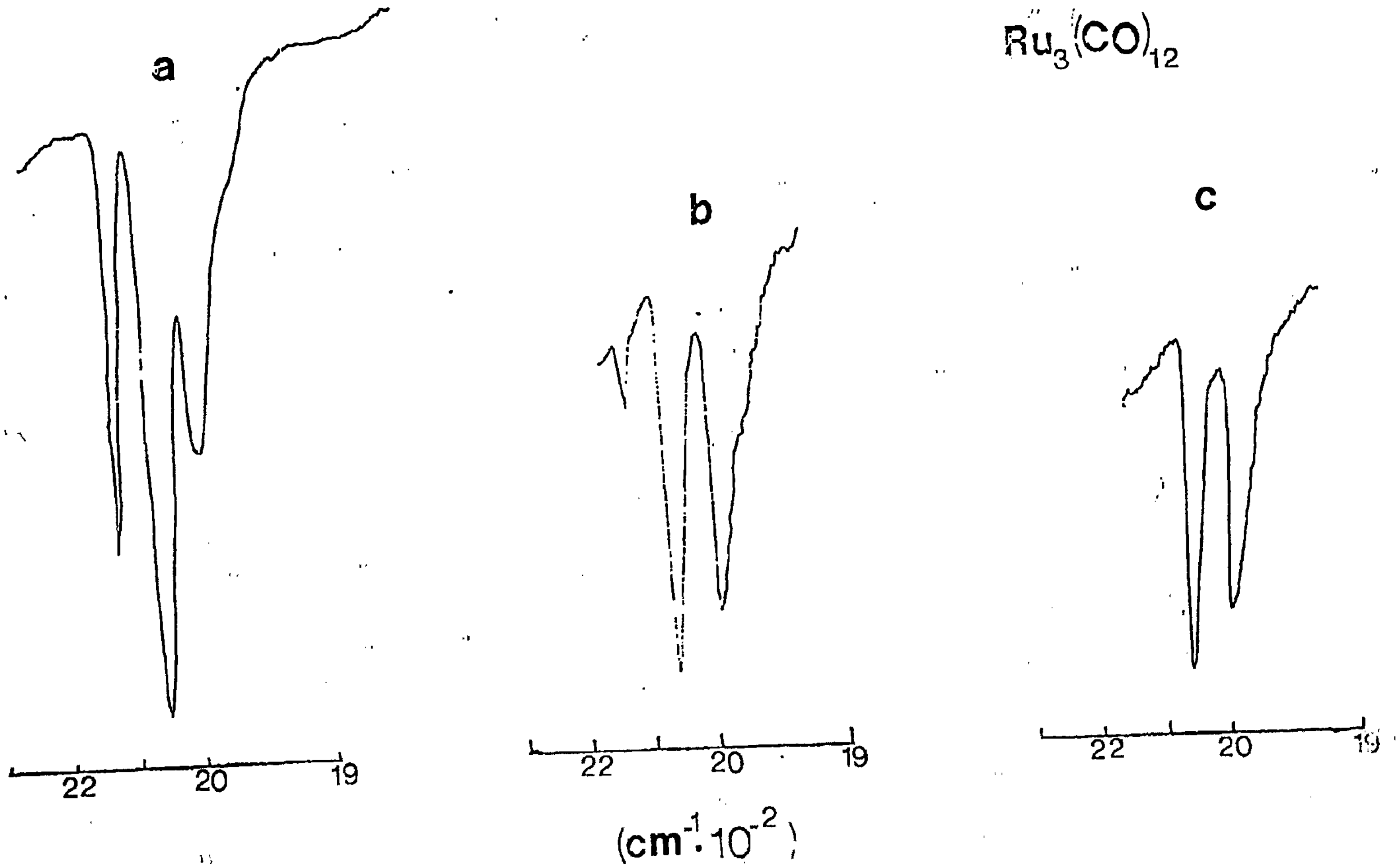
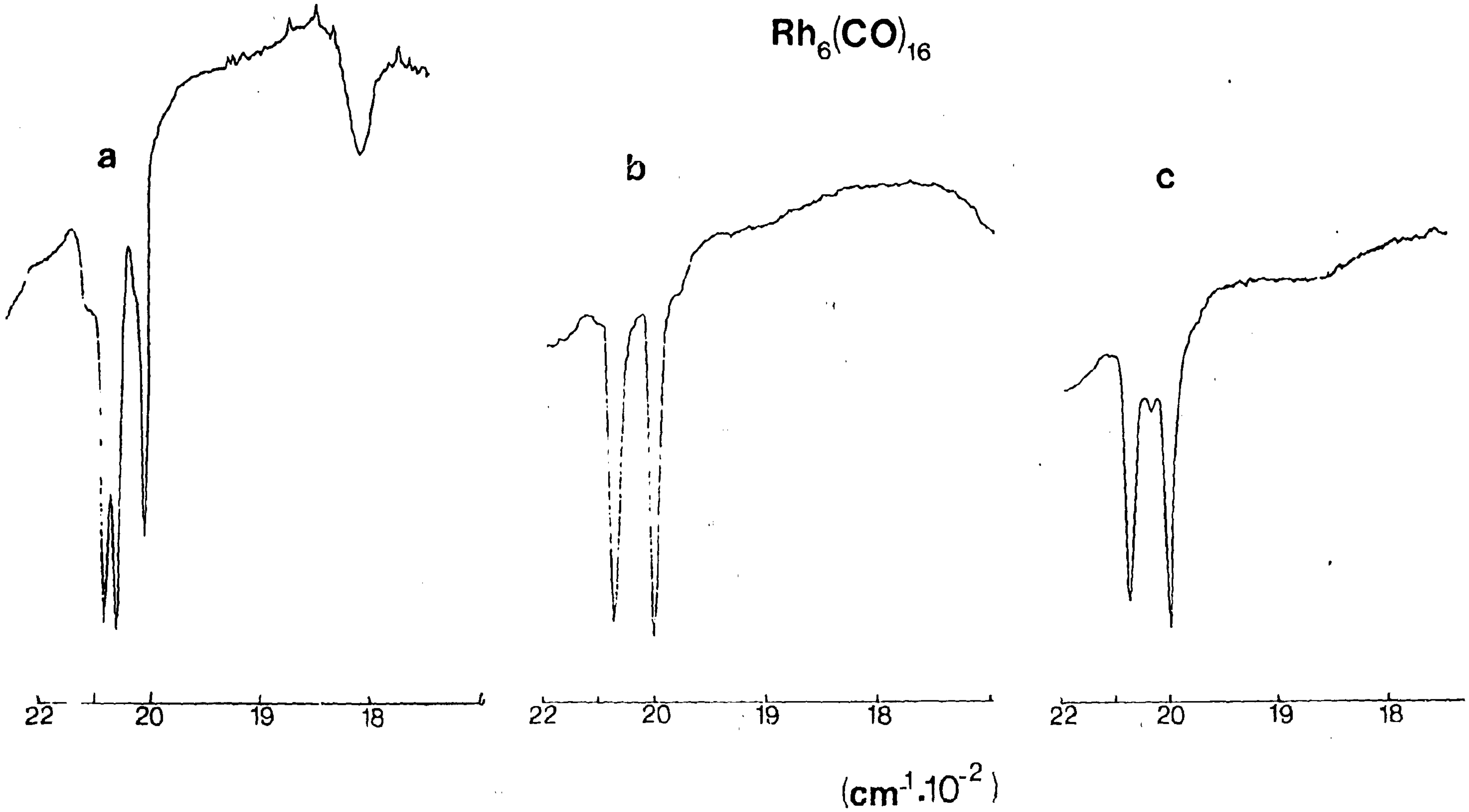


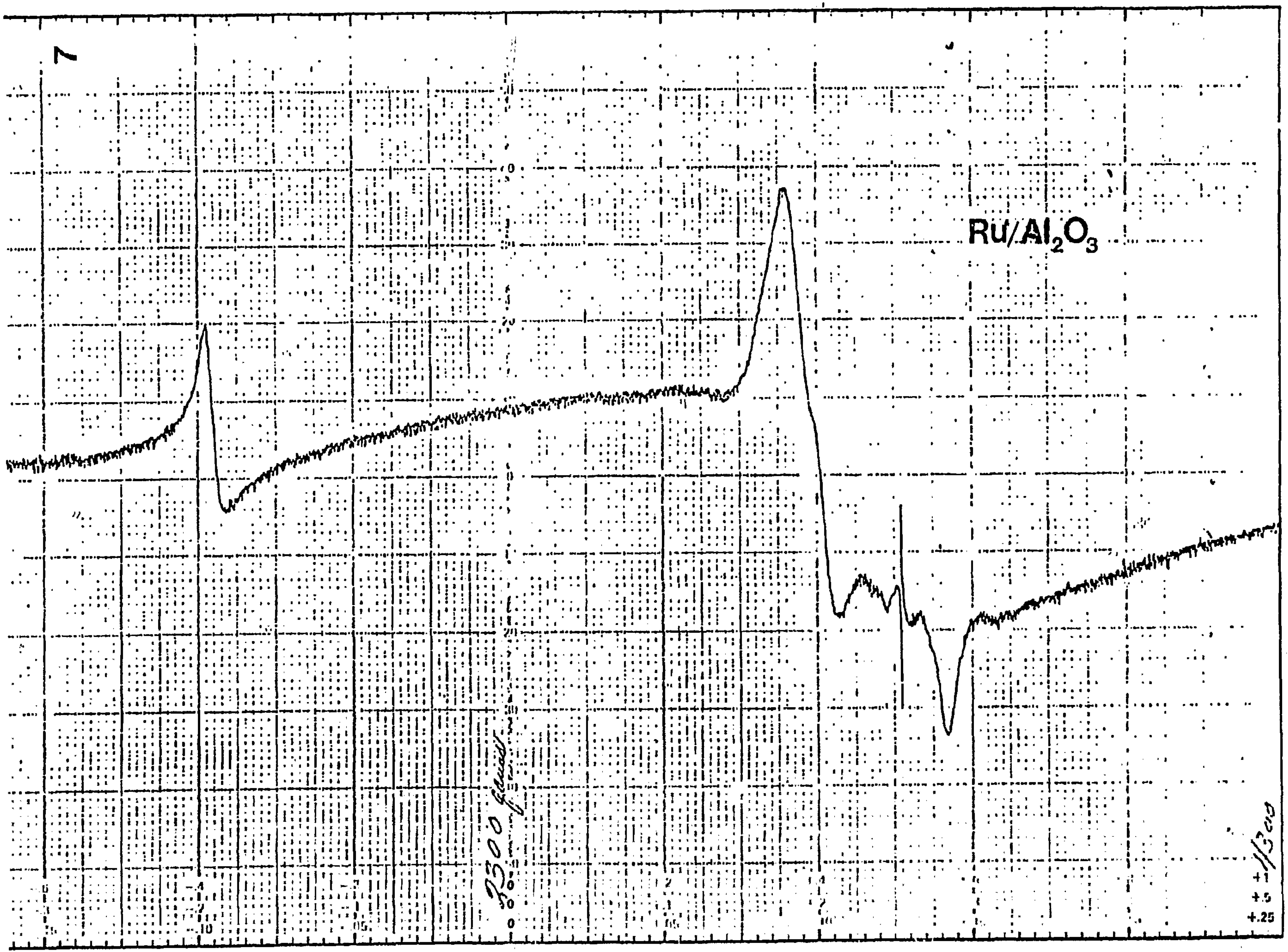

4
a
b
c
d
$Ru_3(CO)_{12}$
22
20
19
22
20
19
22
20
19
22
20
19
(cm⁻¹·10⁻²)


$Ru_3(CO)_{12}$
a
b
c
22
20
19
22
20
19
22
20
19
$(cm^{-1} \cdot 10^{-2})$

6



7



X-RAY DIFFRACTION DATA FOR METAL CARBONYLS

d spacings Å

	Pure Carbonyl	Dry Ground[1]	Adsorption[2]	Extraction[3]
$Ir_4(CO)_{12}$	7.076	7.076	7.076	†
	6.652	6.60	6.60	
		1.97*	1.97*	1.97*
$Os_3(CO)_{12}$	7.132	7.104	7.132	
	6.965	6.965	6.965	
	6.702	6.702	6.702	†
	6.57	6.55	6.55	
	5.47	5.45	5.47	
$Ru_3(CO)_{12}$	7.190	7.132	7.130	
	6.65	6.71	6.70	†
	5.50	5.47	5.50	
$Rh_6(CO)_{16}$	8.110	8.110	8.1	
	7.431	7.431	7.4	†
	7.249	7.190	7.2	

1. Dry Ground refers to a metal carbonyl/Al_2O_3 dry ground mixture.
2. Adsorption refers to a conventional "impregnation" product from metal carbonyl/Al_2O_3.
3. Extraction refers to a product prepared from metal carbonyl/Al_2O_3 by the newly-developed extraction procedure.

* Due to Al_2O_3 support. Observed in all samples containing Al_2O_3.

† No pattern due to supported carbonyl observed.

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