

## Infrared Spectra of Chemisorbed Molecules

### II. Benzene on Silica-Supported Metals

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Infrared spectra of benzene adsorbed on silica-supported nickel, copper, palladium, platinum and iron were studied.

A broad band in the 2760-3060  $\text{cm}^{-1}$  region was obtained for nickel and copper. From this it may be concluded that benzene is chemisorbed with loss of its aromatic character and not by formation of a  $\pi$ -complex as with organometallic complexes. Nor is it probable that, for geometric reasons, benzene is chemisorbed on the surface by a linking of six carbon to six metal atoms. The bonding of the molecule to the surface seems therefore more complex.

No infrared absorption bands due to initially adsorbed species were observed for hydrogen-covered palladium and iron. This may indicate the presence of chemisorbed species of which a large number of the CH-bonds have been dissociated. On platinum, cyclohexane was formed during adsorption.

#### INTRODUCTION

Although the adsorption and catalytic hydrogenation of benzene have been extensively investigated (1), the type of bonding of a benzene molecule to a catalyst surface is still unknown. In 1929, Balandin (2) suggested that in the hydrogenation of benzene, the skeleton of this molecule would lie flat on the catalyst surface and argued that metals active in the hydrogenation reaction would possess both the required lattice spacing and crystal symmetry (2-4). The heats of adsorption of benzene on nickel and copper powders are relatively low (5). The heat of adsorption of diethyl sulfide on platinum is roughly 35 kcal/mole greater than that of thiophen (6). It is therefore generally accepted that aromatic hydrocarbons lose their energy of resonance on adsorption.

Tétényi (7, 8) has reported experiments in which a certain part of  $^{14}\text{C}$ -labeled benzene chemisorbed on nickel could be desorbed by unlabeled benzene at 150°C. Another part of the adsorbed benzene could only be removed by hydrogen treatment at temperatures exceeding 300°C. In

view of this, a certain part of the chemisorption process is assumed to take place through dissociation of CH-bonds. Evidence in support of this assumption is the fact that some hydrogen is liberated after chemisorption of benzene on evaporated nickel, iron and platinum films at room temperature. However, no decomposition is observed for copper and gold (9). Silvent and Selwood (10, 11) concluded from magnetic measurements that up to a temperature of about 130°C, benzene is associatively adsorbed on a nickel surface by the formation of about six bonds. The results obtained by this method may not be quite correct, since no allowance was made for the benzene physically adsorbed on the catalyst support. Suhrmann, Wedler, and Kruger (12) concluded from resistance measurements on nickel films at -183°C that 6.3 electrons were involved per adsorbed benzene molecule.

Since we were of the opinion that the infrared technique might throw more light on the question how benzene is adsorbed on metal surface, we studied its adsorption on nickel, copper, palladium, platinum and

iron catalysts. To our knowledge, the spectrum of benzene adsorbed on metals has not yet been published although there is a reference (11) to unpublished work by Eischens. Recently, Palazov, Andreev, and Shopov (13) reported that their attempts to record the spectrum of adsorbed benzene on a nickel on silica catalyst were unsuccessful. Infrared spectra of benzene and other aromatic compounds adsorbed on silica—with benzene in the gas phase—have been published by Galkin, Kiselev, and Lygin (14–16). The spectrum changes observed during adsorption were ascribed to the interaction between the  $\pi$ -electron system of the aromatic molecules and the hydroxyl groups on the silica surface. Similar work was reported by other authors (17, 18). Karagounis and Peter (19) studied the adsorption of some aromatic molecules on silver iodide and silica gel and their results indicate that the molecules were adsorbed with the plane of the aromatic ring parallel to the surface. A similar conclusion was drawn from the ultraviolet spectrum of adsorbed benzene (20).

After we had finished our investigations we learned that similar work is being done by Prof. N. Sheppard of the University of East Anglia, Norwich, U. K.

#### EXPERIMENTAL

For most catalysts, Aerosil (Degussa) was used as support. Only in the case of palladium, was a wide-pore silica gel, "Wypo", used (prepared according to Ref. 21). Discs (diameter 15 mm, were prepared by pressing the impregnated silica samples at 12–15 tons for 2 min and subsequently reduced in the infrared cell for 16 hr in a stream of hydrogen (see Table 1).

A full description of the infrared cell and the experimental procedure have been given in a previous paper on the subject (22). The advantage of this cell is that the spectrum of the gas phase can be obtained separately by removing the disc from the beam. At elevated temperatures, observation of the spectrum of the adsorbed molecules was not possible. A blank experiment without adsorbent showed that desorption

TABLE 1  
DATA ON DISCS OF SILICA-SUPPORTED  
METAL CATALYSTS

Catalyst	Weight (mg)	Metal content (%)	Reduction temperature (°C)
Copper	17.6	21	350
Nickel	19.4	10	350
Iron <sup>a</sup>	14.0	5	390
Palladium	18.0	5	300
Platinum	13.7	15	300

<sup>a</sup> Prereduced at 600°C for 4 hr and subsequently passivated in a nitrogen/air flow before pressing.

of benzene, probably from the glass wall of the cell, occurred when hydrogen was admitted. It was therefore necessary to heat the cell and the connecting tubing when the gas phase was pumped off after adsorption. The catalyst was kept at room temperature.

All experiments were carried out at room temperature, unless otherwise stated; benzene and hydrogen pressures were about 15 Torr. The spectra were recorded on a Grubb Parsons GS 4 double-beam spectrometer. A beam attenuator was used in the reference beam since the transmission of the discs was only 10–20%.

Benzene (Merck) was purified by distillation and stored over aluminum oxide. It was degassed by repeated freezing, pumping and thawing. Hydrogen was purified over a column of BTS-catalyst (BASF) and dried over a column of molecular sieves (Linde 4 A) followed by a liquid air trap.

#### RESULTS

##### *Adsorption on Nickel and Copper*

The IR-spectrum of benzene adsorbed on a hydrogen-covered nickel surface showed a broad band in the region 2760–3060 cm<sup>-1</sup>. This band was rather weak, even in the presence of gaseous benzene. Apart from bands in the 3000–3100 cm<sup>-1</sup> region (23), the spectrum of gaseous benzene also showed a weak band at about 2888 cm<sup>-1</sup>—observed by other authors at 2856 cm<sup>-1</sup> (24)—which was found by calibration to contribute to only a minor ex-

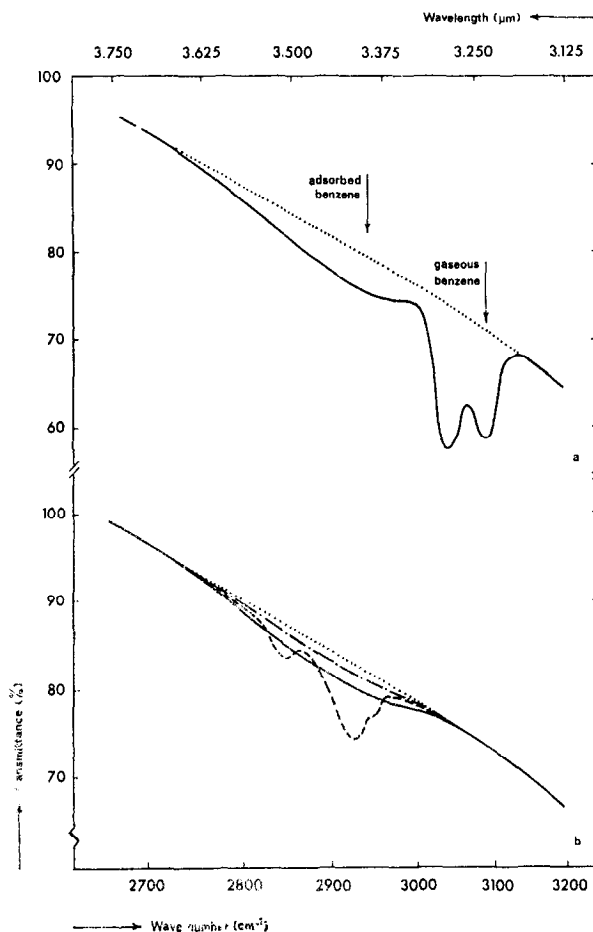


FIG. 1. IR-spectra of benzene adsorbed on a silica-supported nickel catalyst. a. .... background, — benzene admitted, b. .... background, — adsorbed benzene, - - - - 16 hr after hydrogen admission, - . - . - after 20 min pumping.

tent to the broad band of the chemisorbed molecules. GLC-analysis of the gas phase showed the presence of 3% hexane and 1% cyclohexane, the remainder being benzene.

After the adsorbed species had been allowed to react for 16 hr with admitted hydrogen, two bands occurred at 2849 and 2928  $\text{cm}^{-1}$  due to the symmetric and asymmetric  $\text{CH}_2$ -vibrations respectively. A weak band due to the asymmetric  $\text{CH}_3$ -vibration was observed as well. After evacuation for 20 min, the  $\text{CH}_2$ -bands had disappeared but the broad band in the 2760–3060  $\text{cm}^{-1}$  region was still present, although its intensity had decreased. The gas phase now consisted of 15% cyclohexane, 33% hexane and 52% benzene (GLC). Fig. 1 shows the spectra observed. The presence of hexane

obviously indicates a cleavage of some C–C-bonds.

In a blank experiment with an Aerosil disc, no IR-spectrum due to physically adsorbed benzene was obtained after evacuation.

When benzene was adsorbed on a reduced silica-supported copper catalyst, a broad band due to chemisorbed benzene was again observed in the 2760–3060  $\text{cm}^{-1}$  region (Fig. 2). After admission of hydrogen (25 Torr), weak bands appeared due to  $\text{CH}_2$  and aromatic  $\text{CH}$ -stretching vibrations. No infrared bands were observed in the spectrum of the gas phase when the disc was removed from the beam. When the disc had been heated at 180°C in hydrogen for 15 min, the spectrum of the

adsorbed species and gas phase clearly showed weak bands at 3091, 3062 and 3038 cm<sup>-1</sup> due to adsorbed or gaseous benzene, or possibly to a chemisorbed C<sub>6</sub>H<sub>5</sub>-group, at 2857 and 2933 cm<sup>-1</sup> due to CH<sub>2</sub>-groups, and at 2889 cm<sup>-1</sup> caused by the tertiary CH-group. After the disc had been heated at 350°C in hydrogen for another 25 min, the CH<sub>2</sub>-bands disappeared and the broad band was formed again instead, obviously caused by dehydrogenation of saturated products. The bands due to aromatic CH-stretching vibrations were still present. GLC-analysis carried out at the end of the experiments showed that about 1% of cyclohexane was present.

#### *Adsorption on Iron, Palladium and Platinum*

When benzene was admitted to hydrogen-covered, silica-supported iron and palladium catalysts, no absorption band due

to adsorbed material was observed in the IR-spectrum after evacuation of the gaseous benzene. When hydrogen was admitted, weak bands due to aromatic CH-stretching vibrations and weak CH<sub>2</sub>-bands were observed in the spectrum of the gas phase.

When benzene was adsorbed on a bare palladium surface, which had been evacuated at 250°C for 2.5 hr, CH<sub>3</sub> and CH<sub>2</sub> absorption bands were observed in the spectrum of the gas phase while, after evacuation, weak CH<sub>2</sub>-bands were still observed in the spectrum of the surface species. GLC-analysis of the gas phase showed the presence of a number of non-aromatic products which were not further identified. After admission of hydrogen, the spectrum of the adsorbed species showed bands due to the aromatic CH-stretching vibrations in addition to the CH<sub>2</sub>-bands. All adsorption bands gradually appeared in the spectrum of the gas phase. After 20 hr, GLC-

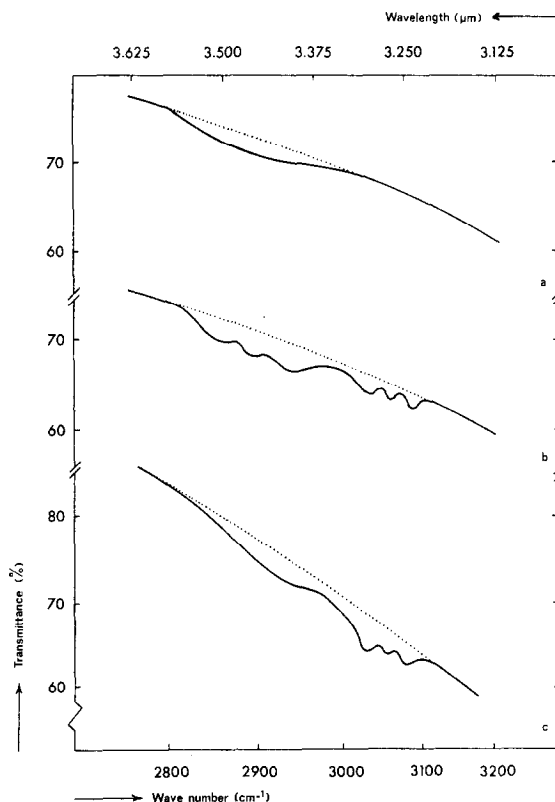


Fig. 2. IR-spectra of benzene adsorbed on a silica-supported copper catalyst. a. . . . . background, — adsorbed benzene, b. . . . . background, — heated in hydrogen at 180°C for 15 min, c. . . . . background, — heating for additional 25 min at 350°C.

analysis of the gas phase showed the presence of 3% cyclohexane and traces of lower hydrocarbons in addition to benzene.

A platinum on silica catalyst—hydrogen-covered or bare (achieved by evacuating the cell at 275°C for 2.5 hr)—showed a somewhat different behaviour. During the adsorption of benzene for 2.5 hr, CH<sub>2</sub>-bands were formed, the intensity of which increased linearly as a function of time. After removal of the gas phase, a weak band caused by aromatic CH-stretching vibration and bands due to CH<sub>2</sub>-groups were present. GLC-analysis showed the presence of about 2% cyclohexane. After admission of hydrogen, the intensity of the CH<sub>2</sub>-bands, which appeared in the spectrum of the gas phase, increased during a reaction time of 1 hour. After removal of the gas phase, which contained 17% cyclohexane, CH<sub>2</sub>-bands were still observed in the spectrum of the adsorbed species.

#### DISCUSSION

The principal result of our investigations is the broad band observed in the 2760–3060 cm<sup>-1</sup> region for benzene adsorbed on nickel or copper. This band is in the range of the CH-stretching vibrations at a saturated carbon atom. Benzene obviously loses its aromatic character during adsorption on these two metals, which is in agreement with literature data (5, 6).

The position of the band due to adsorbed benzene has also been compared with those of some benzene-metal complexes, using the data collected by Fritz (25). Benzene-metal  $\pi$ -complexes, such as (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>M (in which M is Cr, Mo, W and V) and (C<sub>6</sub>H<sub>6</sub>)M'(CO)<sub>3</sub> (in which M' is Cr and Mo), all have a band above 3000 cm<sup>-1</sup> and some have also a band in the 2900–2930 cm<sup>-1</sup> region. From the absence of a band above 3000 cm<sup>-1</sup> in the spectrum of benzene adsorbed on nickel or copper, it may be concluded that the adsorbed benzene molecule does not form such a  $\pi$ -complex.

The extreme broadness of the adsorption band observed points to a mixture of adsorbed species differing widely as regards CH-stretching vibrations. Bonding of the six carbon atoms of benzene to six transition

metal or copper atoms on the hexagonal plane by an associative mechanism is hardly possible since the interatomic distances concerned do not favour such a configuration. A less defined type of bonding to the surface would be more probable. The interatomic distances on a nickel or copper surface, for instance, allow each carbon atom of the benzene ring to interact equally with three metal atoms. It is, however, hardly to be expected that the frequency of the CH-stretching vibration would be greatly influenced by differences in the way of bonding of the carbon atom to the surface.

In the adsorbed molecule, rupture of some CH-bonds may occur and therefore the bonding character of the molecule may be changed. This might influence the frequencies of the CH-stretching vibrations.

The presence of weak bands caused by aromatic CH-stretching vibrations observed in some experiments in the spectrum of the adsorbed species obviously points to the presence of benzene, possibly physically adsorbed on the support.

The band due to benzene chemisorbed on nickel or copper was not observed in the case of iron, platinum or palladium. Although it is dangerous to draw any conclusions from the absence of absorption bands, it may be possible that on hydrogen-covered iron and palladium, an extensive dissociation of CH-bonds occurs. This could give rise to an adsorbed product having the structure of the carbon skeleton of benzene, which cannot be observed in the infrared spectrum in the region investigated. This suggestion is in agreement with the fact that when hydrogen was admitted to the adsorbed species, mainly benzene was present in the gas phase.

The reaction of benzene on platinum, yielding cyclohexane, may be due to a strong dissociation of the CH-bonds, giving rise to self-hydrogenation. It is also possible that benzene reacts with adsorbed hydrogen, which was still present after evacuation at elevated temperature for several hours. Literature data (26) indeed indicate that even at temperatures of 300°C or higher, part of the hydrogen is

irreversibly adsorbed on platinum surfaces.

For bare palladium, the formation of various gaseous products, including those with CH<sub>3</sub>-groups, points to a cleavage of the ring.

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