

# An FTIR Spectroscopic Study of the Selective Oxidation of Nitrosobenzene to Nitrobenzene by Metal Oxides

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Catalytic conversion of nitro- into nitrosobenzene by transition metal oxides is of considerable practical and theoretical interest. Therefore, the surface chemistry of nitrosobenzene on various metal oxides has been studied using IR spectroscopy. The main products of surface reactions are nitrobenzene and azoxybenzene. Findings of this study are compared with the results of a mass spectroscopic study carried out with nitrosobenzene on the same oxides. Molecularily adsorbed nitrosobenzene is found to be coordinated to metal cations by  $\sigma$ -N as well as  $\sigma$ -O bonds. Also the *cis*-dimer of nitrosobenzene is detected. As a reference, the spectra of adsorbed nitrosobenzene were compared with the spectra of monomeric nitrosobenzene dissolved in benzene and dimeric nitrosobenzene dissolved in ethanol. Some IR absorptions not reported earlier are assigned to C-N stretching and ring vibrations of  $\sigma$ -O coordinated and dimeric nitrosobenzene. The coordination modes of nitrosobenzene observed with the different oxides, and the reverse relationship found between  $\nu(\text{N}=\text{O})$  and  $\nu(\text{C}-\text{N})$  are in agreement with the observations made with nitroso compounds coordinated as ligands in organometallic complexes. A link to the catalytic behavior of nitrosobenzene on oxides is indicated. © 1996 Academic Press, Inc.

## INTRODUCTION

The selective reduction of nitrobenzene ( $\Phi\text{-NO}_2$ ) to nitrosobenzene ( $\Phi\text{-NO}$ ) and the surface chemistry of  $\Phi\text{-NO}_2$  have already been studied on many transition metal oxides (1-8). This reduction, which is believed to proceed via a reversed Mars-van Krevelen mechanism (9), is of considerable practical importance because  $\Phi\text{-NO}$  is used as an intermediate in the synthesis of many industrial products. The conventional way to synthesise  $\Phi\text{-NO}$  comprises two steps (1), each of them producing inorganic salts in stoichiometric amounts. In contrast, the catalytic selective reduction of  $\Phi\text{-NO}_2$  over transition metal oxides is an almost waste-free reaction. Since the Mars-van Krevelen mechanism occurs in many selective oxidation reactions, it is desirable to achieve a better understanding of the oxygen transfer between adsorbed molecules and oxidic catalysts. The selective oxidation of  $\Phi\text{-NO}$  has been studied earlier by Grootendorst and Ponec (10), using mass spectrometry (MS). A surprising result of his investigation was that  $\Phi\text{-NO}$

can be transformed to  $\Phi\text{-NO}_2$  also by the nontransition metal oxide  $\text{Al}_2\text{O}_3$ . The Mars-van Krevelen mechanism cannot account for the formation of  $\Phi\text{-NO}_2$  on alumina, since the creation and replenishment of oxygen defects in the catalyst surface require variable valence cations to compensate for the varying degree of surface oxidation. On the other hand, vanadia, which has shown a substantial activity in the selective reduction of  $\Phi\text{-NO}_2$  (4), is completely inactive in the oxidation of  $\Phi\text{-NO}$ . In this paper the oxides investigated by Grootendorst and Ponec (10) are studied by FTIR spectroscopy, in an attempt to gain the lacking information concerning the relation between redox properties and activity in the oxidation of  $\Phi\text{-NO}$ . Additionally, the nontransition metal oxides  $\text{MgO}$  and  $\text{ZnO}$  were studied.

Since one can expect that  $\Phi\text{-NO}$  dimers could be observed in the IR spectra, the spectra of the monomer and the dimer dissolved in benzene and ethanol, respectively, were taken as references for assignment. In most solvents an equilibrium exists between the monomeric and the dimeric form of nitroso compounds, but in benzene nitrosobenzene is present for almost 100% as a monomer, due to  $\pi$ -complexation between the molecule and the solvent (11). Most dimers of nitroso compounds occur in the *cis* as well as in the *trans* form. In the dimer a conjugated six  $\pi$ -electron system is formed by the two NO groups. However, dimerization is less favored with nitrosobenzene than with other nitroso compounds because of a conjugation between the nitroso group and the phenyl ring. Therefore, of nitrosobenzene only the *cis*-dimer has been found. The existence of this dimer can be explained by removal of the conjugation between the NO group and the ring due to steric hindrance: in the *cis*-dimer the rings are twisted out of the plane of the ON · NO system (12a-c). According to Dietrich *et al.* (12c) twisting occurs round *b* and *b'* by  $64.8^\circ$  and  $111.7^\circ$  (Fig. 1). The torsion angle around *a* is  $17.9^\circ$ .

It has to be noted that the IR spectroscopic study presented here was carried out at temperatures below  $0^\circ\text{C}$ , whereas the MS study mentioned above was carried out between 0 and  $300^\circ\text{C}$ . Furthermore, most oxides used here have been prepared following the same methods as those used for the MS study, but in the case of  $\text{Fe}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$

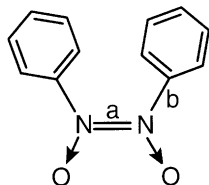


FIG. 1. The *cis*-dimer of nitrosobenzene.

somewhat different methods had to be used in order to obtain IR transparent samples.

## METHODS

The titania used was Eurotitania-1 from TiOxide, UK. MgO and ZnO were from Merck. V<sub>2</sub>O<sub>5</sub> was prepared by decomposition at 500°C in air of NH<sub>4</sub>VO<sub>3</sub> from Baker Chemicals. The  $\gamma$ -alumina was Aluminiumoxid C from Degussa. Cr<sub>2</sub>O<sub>3</sub> was obtained by decomposition of (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> from Merck, in a flow of air. Because of the possible explosive decomposition of the ammoniumbichromate, it was slowly heated to 200°C, followed by heating at 300°C for 2 h.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was made by decomposition in a flow of He at 200°C of FeO(OH), which was prepared from iron nitrate (J. T. Baker Chemicals BV) according to Ref. (13). Co<sub>3</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> were made by decomposition of their hydroxides at 500°C in air. The nitrosobenzene used was from Ega Chemie. Benzene was from Merck, and ethanol was from J. T. Baker Chemicals BV.

For the IR spectroscopic measurements, about 50 mg of each sample was pressed to pellets of 2.8 cm diameter using a pressure of  $1 \times 10^7$  Pa. The pellets were placed in an infrared transmission cell equipped with CaF windows and connected to a conventional vacuum system. Since  $\Phi$ -NO is very reactive after adsorption on most metal oxides, the interaction of the molecule with the oxide samples was followed between  $-40^\circ\text{C}$  and room temperature. Spectra were recorded with a resolution of  $2\text{ cm}^{-1}$ , between 1800 and 1100 (sometimes 1000)  $\text{cm}^{-1}$  on a Mattson Galaxy 3000 FTIR spectrometer. The samples were activated by outgassing in vacuum at 350°C. However, Co<sub>3</sub>O<sub>4</sub> (as a p-type semiconductor with a surplus of oxygen) was pretreated by a mild reduction with H<sub>2</sub> in order to obtain an IR transparent sample (14).

To prevent condensation of  $\Phi$ -NO on the cool parts of the cell, the compound was admitted from a glass bulb attached directly to the IR cell, with the outlet placed as near as possible to the catalyst pellet.

The path length of the liquid phase IR cell used to record the spectra of dissolved  $\Phi$ -NO is 0.1 mm. The windows are NaCl.

## RESULTS

### *Nitrosobenzene Dissolved in Benzene and Ethanol*

The spectra of  $\Phi$ -NO dissolved in benzene and ethanol are shown in Fig. 2. The spectrum of the monomer in benzene can be interpreted according to the Wilson notation

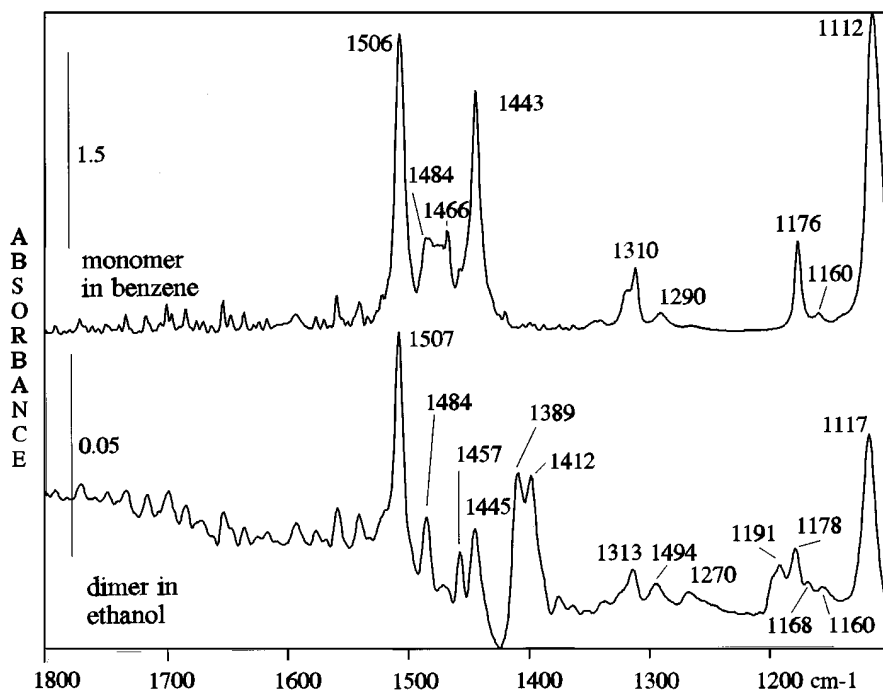
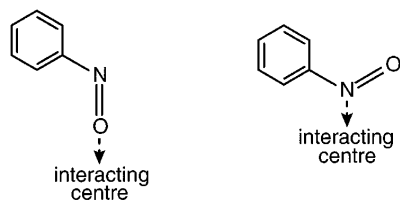


FIG. 2. Spectra of monomeric  $\Phi$ -NO dissolved in benzene (about 3 mg in 5 ml) and a mixture of monomeric and dimeric  $\Phi$ -NO dissolved in ethanol (saturated solution) both at room temperature.

FIG. 3.  $\sigma$ -N and  $\sigma$ -O bound nitrosobenzene.

(15) in the same way as the gas phase spectrum assigned by Bradley and Strauss (16). Some bands are shifted in comparison with the gas phase and the overall spectrum is very similar to the spectrum of  $\Phi$ -NO adsorbed on  $\text{Mn}_3\text{O}_4$  reported by Angevaere (3). In both cases the  $\text{N}=\text{O}$  stretching band is shifted to lower frequency by  $17\text{ cm}^{-1}$ . This has been explained by hydrogen bonding between the nitroso group O atom and a surface hydroxyl group of  $\text{Mn}_3\text{O}_4$  (3). This is in agreement with the observation of Vasopollo *et al.* (17), that the  $\text{N}=\text{O}$  stretching band of nitroso ligands coordinated by a  $\sigma$ -O bond to a low-valent metal center occurs around  $1500\text{ cm}^{-1}$  (Fig. 3). Since the solvent used was not absolutely water free, it is likely that a similar kind of interaction occurs here with  $\Phi$ -NO dissolved in benzene and with  $\Phi$ -NO adsorbed on  $\text{Mn}_3\text{O}_4$ , namely hydrogen bonding, to dissolved water molecules in the first case and to surface  $-\text{OH}$  groups in the second case.

The presumed  $\pi$ -bonding between  $\Phi$ -NO and benzene (11) is not reflected by the IR spectrum. No new IR absorptions, in comparison with the gas phase spectrum, are observed in the spectrum of  $\Phi$ -NO dissolved in benzene. The band at  $1484\text{ cm}^{-1}$  is assigned to another adsorption mode of  $\Phi$ -NO, namely the  $\sigma$ -N coordinated molecule. Vasopollo *et al.* (17, 18) locate the  $\text{N}=\text{O}$  stretching of N coordinated nitroso ligands in metal complexes between  $1505$  and  $1465\text{ cm}^{-1}$ . Thus, the influence of benzene as a solvent on the equilibrium between monomeric and dimeric  $\Phi$ -NO should probably be related to the interaction of benzene with the phenyl ring, but not with the  $-\text{NO}$  group.

In ethanol an equilibrium exists between monomeric and dimeric  $\Phi$ -NO, giving rise to an IR spectrum containing bands of both species. The  $\text{N}=\text{O}$  stretching bands at  $1507$  and  $1484\text{ cm}^{-1}$  show the presence of  $\sigma$ -O as well as  $\sigma$ -N coordinated  $\Phi$ -NO. In ethanol hydrogen bonding might occur either with the solvent or with dissolved water. The most obvious difference between the pure monomer in benzene and the mixture of monomer and dimer in ethanol is a strong doublet in the latter spectrum with absorption maxima at  $1412$  and  $1389\text{ cm}^{-1}$ . This absorption has been assigned by Gowenlock and Lüttke (12a) to the symmetric and antisymmetric  $\text{N}=\text{O}$  stretching frequencies of *cis*-dimeric  $\Phi$ -NO.

Another new, weak band is observed at about  $1270\text{ cm}^{-1}$ . Two interpretations could be suggested for the  $1270$  band:

(A) The  $\text{N}=\text{O}$  stretching band of the  $\Phi$ -NO *trans*-dimer

TABLE 1  
Assignments of the IR Absorption Bands (in  $\text{cm}^{-1}$ ) of the Nitrosobenzene Monomer Dissolved in Benzene and the Dimer Dissolved in Ethanol (Room Temperature)

Gas (15)	Monomer (benzene)	Monomer + dimer (ethanol)	Assignment
$\sim 1615$			8a or 8b
1523	1506	1507	$\nu\text{N}=\text{O}$ ( $\sigma$ -O)
	1484	1484	$\nu\text{N}=\text{O}$ ( $\sigma$ -N)
1477	1466	1457	19a
1455	1443	1445	19b
		1389, 1412	$\nu\text{N}=\text{O}$ <i>cis</i> -dimer
1314	1310	1313	14
1290	1290	1294	3 monomer
		1270	3 dimer
		1191	13, C-N dimer
1176	1176	1178	9a
1159	1160	1160	15
1112	1112	1117	13, C-N monomer

is expected between  $1290$  and  $1190\text{ cm}^{-1}$ . If the interaction with a solvent could remove the above mentioned conjugation between the  $\text{NO}$  group and the phenyl ring, the formation of the *trans*-dimer might be possible.

(B) Ring vibration 3 (C-H in-plane bending) of monosubstituted benzenes, which is found at  $1294\text{ cm}^{-1}$  in the case of the monomer, is expected to shift to lower wavenumber with increasing weight of the substituent. The *cis*  $\Phi$ -NO dimer can be considered as a system of two heavily monosubstituted phenyl rings and therefore ring vibration 3 might occur between  $1275$  and  $1253\text{ cm}^{-1}$  (19), thus offering a more likely explanation for the band at  $1270\text{ cm}^{-1}$ .

In the  $1200$ – $1100\text{ cm}^{-1}$  range, the differences observed between the pure monomeric and the mixed spectrum are a new band at about  $1190\text{ cm}^{-1}$  and a decrease in intensity of the C-N stretching band at  $1117\text{ cm}^{-1}$ . The C-N stretching band (ring vibration 13 of monosubstituted benzenes) can vary between  $1280$  and  $1100\text{ cm}^{-1}$  depending on the weight and nature of the substituent (19). Most likely, the new band at  $1190\text{ cm}^{-1}$  arises from the C-N stretching of the  $\Phi$ -NO dimer at the expense of some intensity of the monomeric C-N stretching band. The assignments of the bands observed in the spectra of  $\Phi$ -NO dissolved in benzene and ethanol are given in Table 1.

#### Nitrosobenzene Adsorbed on Metal Oxides

The spectra of  $\Phi$ -NO adsorbed on various oxides are shown in Figs. 4–7. The assignments of the bands observed are given in Table 2. Band intensities are not presented since they change upon heating of the sample and representative spectra obtained with various oxides are included in this paper. Considerable variation in the quality of the spectra is due to different oxide transparencies, to different

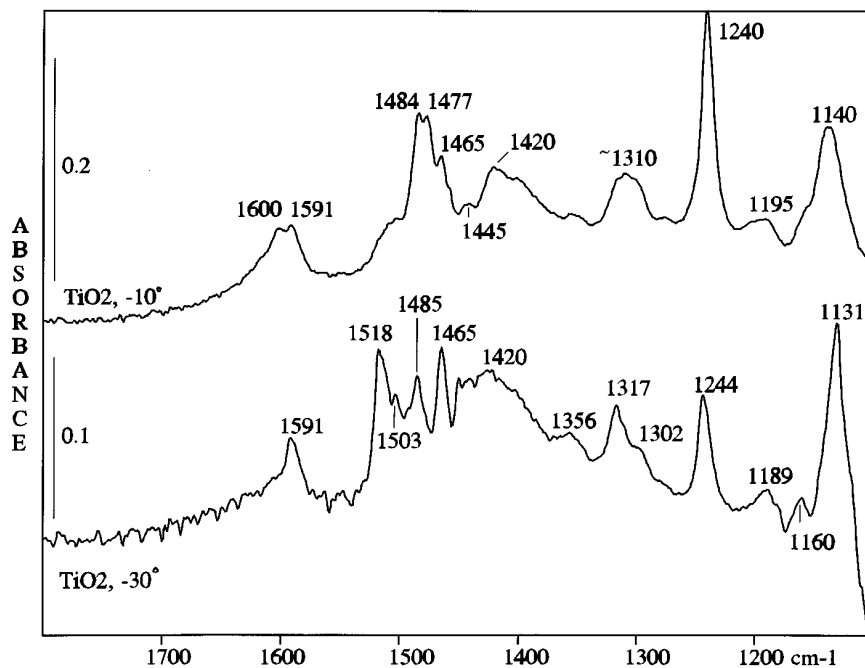


FIG. 4. Spectra of  $\Phi$ -NO adsorbed on  $\text{TiO}_2$  at  $-30$  and  $-10^\circ\text{C}$  and  $10^{-4}$  Torr.

strengths of  $\Phi$ -NO adsorption, and to a strong temperature dependence of some of the oxidic background IR spectra, leading to artifacts in the spectra generated by subtraction.

For the transition as well as the nontransition metal oxides most bands observed by this study are assignable to the

$\sigma$ -O and  $\sigma$ -N coordinated  $\Phi$ -NO monomer, the *cis*-dimer, and the products reported already by Angevaere upon  $\Phi$ -NO adsorption on  $\text{Mn}_3\text{O}_4$ , namely  $\Phi$ - $\text{NO}_2$  and azoxybenzene ( $\Phi$ -N( $\rightarrow$ O)N- $\Phi$ ). Most  $\Phi$ -NO bands are only weakly perturbed by adsorption. The only band that shows considerable shifts, compared with the spectra of gaseous and

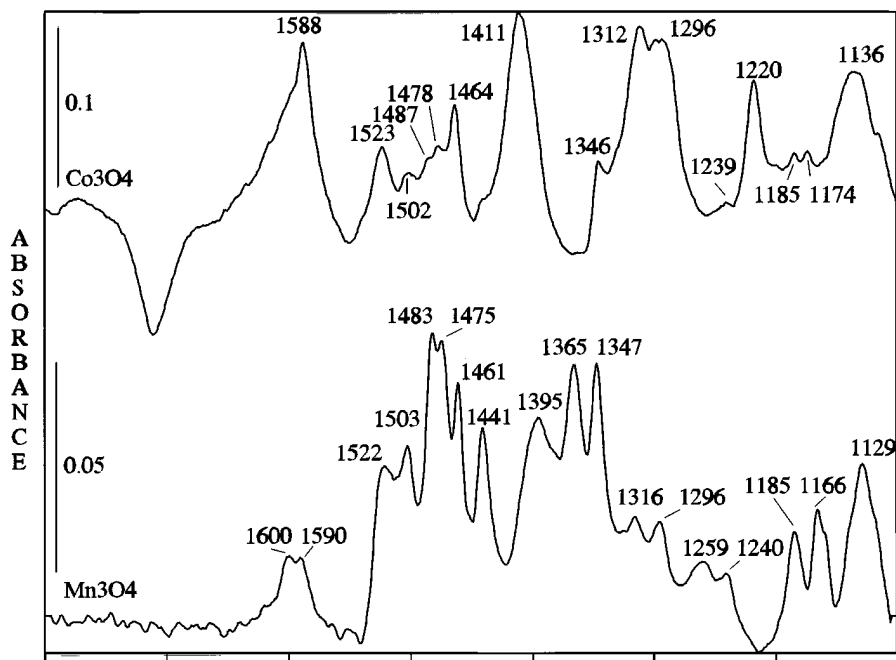


FIG. 5. Spectra of  $\Phi$ -NO adsorbed on  $\text{Mn}_3\text{O}_4$  at  $-30^\circ\text{C}$  and on  $\text{Co}_3\text{O}_4$  at  $-40^\circ\text{C}$  at  $10^{-4}$  Torr.

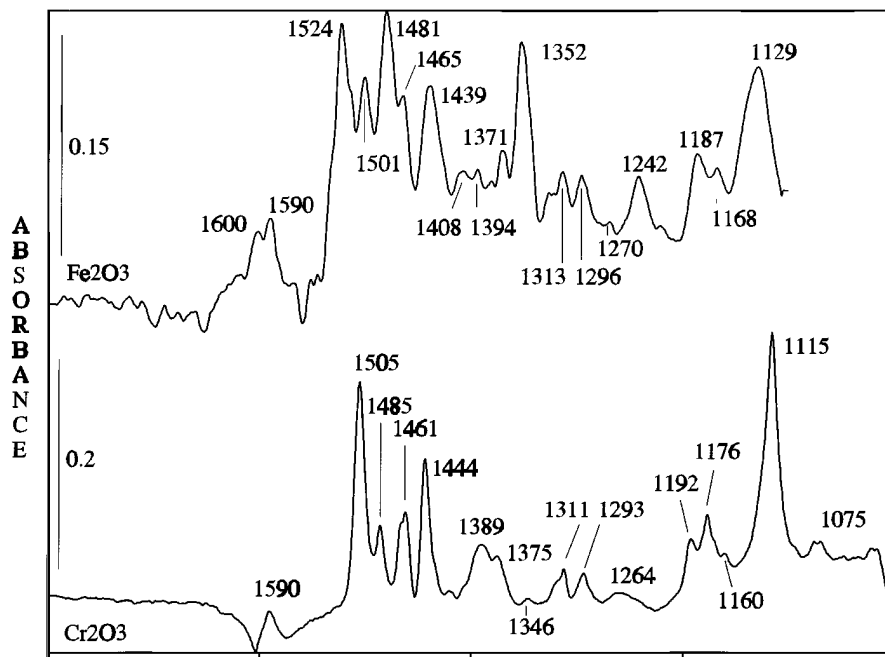


FIG. 6. Spectra of  $\Phi$ -NO adsorbed on  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  at  $-30^\circ\text{C}$  and  $10^{-4}$  Torr.

dissolved  $\Phi$ -NO, is the  $\nu(\text{C-N})$  (ring vibration 13) of the monomer, which is found around  $1130\text{ cm}^{-1}$  on the transition metal oxides and  $1112\text{ cm}^{-1}$  in the vapor. The shift to higher frequency is possibly caused by a partial delocalization of the nonbonding electrons on nitrogen. A new band is found at  $1240\text{ cm}^{-1}$ . This band is strong on  $\text{TiO}_2$  and

$\text{Fe}_2\text{O}_3$ , weak on  $\text{Al}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ , and  $\text{Co}_3\text{O}_4$ , and absent on  $\text{ZnO}$ ,  $\text{MgO}$ , and  $\text{Cr}_2\text{O}_3$ . The assignment of this band is not straightforward and will be discussed below. Adsorption of  $\Phi$ -NO could not be detected by IR spectroscopy with the two lead oxides and with vanadia. This would explain the lack of  $\Phi$ -NO<sub>2</sub> formation from  $\Phi$ -NO by these oxides.

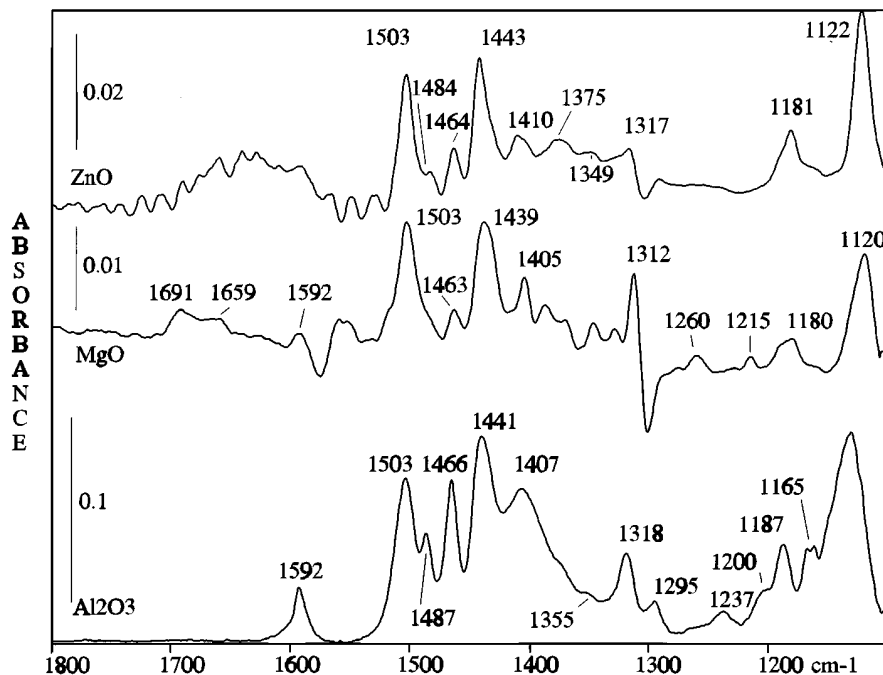


FIG. 7. Spectra of  $\Phi$ -NO adsorbed on  $\text{MgO}$ ,  $\text{ZnO}$ , and  $\text{Al}_2\text{O}_3$  at  $-30^\circ\text{C}$  and  $10^{-4}$  Torr.

TABLE 2

Assignments of the IR Absorption Bands (in  $\text{cm}^{-1}$ ) of Nitrosobenzene and Its Products Adsorbed on Various Oxides at  $-40^\circ\text{C}$  and  $10^{-4}$  Torr

TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Co <sub>3</sub> O <sub>4</sub>	Mn <sub>3</sub> O <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub>	ZnO	MgO	Cr <sub>2</sub> O <sub>3</sub>	Assignment
1591	1600, 1590	1588	1600, 1590	1592		1592	1590	8a
1518	1524	1523	1522					$\nu_{\text{as}}\text{NO}^a$
1503	1501	1502	1503	1503	1503	1503	1505	$\nu\text{NO}(\sigma\text{-O})$
1485	1481	1487	1483	1487	1484		1485	$\nu\text{NO}(\sigma\text{-N})$
1477		1478	1475					19b <sup>b</sup>
1465	1465	1464	1461	1466	1464	1463	1461	19a
1444	1439	1441sh	1441	1441	1443	1439	1444	19b $\nu\text{N}=\text{N}^b$
~1420	1408, 1394, 1371	1411	1395, 1365	1407, 1373sh	1410, 1375	1405	1389, 1375	$\nu\text{NO}$ dimer
1356	1352	1346	1347	1355	1349		1346	$\nu_s\text{NO}^a$
1317	1313	1312	1316	1318	1317	1312	1311	14
1302	1296	1296	1296	1295	<sup>c</sup>	<sup>c</sup>	1293	3
	1270		1259			1260	1264	3 dimer
1244	1242	1239	1240	1237				$\nu\text{CN}(\sigma\text{-N})$
		1220				1215		
1189		1200		1200			1192	$\nu\text{CN}$ dimer
	1187	1185	1185	1187	1181	1180	1176	9a
1160	1168	1174	1166	1165			1160	15
1131	1129	1136	1129	1131	1122	1120	1115	$\nu\text{CN}(\sigma\text{-O})$

<sup>a</sup> Nitrobenzene.

<sup>b</sup> Azoxybenzene.

<sup>c</sup> Nitrosobenzene bands can not be identified here due to spectral artifacts resulting from temperature dependent changes in the oxidic background spectra.

(NB: These oxides are, however, active in the oxidation of the phenyl ring (4)). On MgO and ZnO the dimer and traces of  $\Phi\text{-NO}_2$  are observed.

A comparison of the data presented here with the findings of Ref. (10) reveals a good agreement between the IR spectroscopic and the MS study. The only exception is TiO<sub>2</sub>, where a small amount of (chemisorbed)  $\Phi\text{-NO}_2$  was found in the IR spectrum, in contrast to the mass spectrum (of the gas phase).

## DISCUSSION

First, it is remarkable that similar positions of the  $\text{N}=\text{O}$  stretching band are found with  $\Phi\text{-NO}$  dissolved in benzene, adsorbed on metal oxides, and coordinated as a ligand in metal complexes. This suggests that  $\nu(\text{N}=\text{O})$  depends only on the bonding mode of  $\Phi\text{-NO}$  (about  $1505\text{ cm}^{-1}$  for  $\sigma\text{-O}$  and about  $1485\text{ cm}^{-1}$  for  $\sigma\text{-N}$ ) and not on the nature of the interacting center. The latter may be a dissolved water molecule, a Lewis acidic surface ion, or a metal center in an organometallic complex.

The absence of  $\Phi\text{-NO}$  adsorption on the lead oxides has been predicted by Grootendorst and Ponec (10) and attributed to the presence of a nonbonding electron pair on the  $\text{Pb}^{2+}$  ions. On vanadia the absence of  $\Phi\text{-NO}_2$  production has been explained by the immediate combustion of  $\Phi\text{-NO}$  to CO and CO<sub>2</sub> on the highly reactive V<sub>2</sub>O<sub>5</sub> surface (10). However, with IR spectroscopy neither adsorption of

$\Phi\text{-NO}$  nor combustion products like carbonates have been observed. Obviously  $\Phi\text{-NO}$  is on vanadia not adsorbed in detectable amounts, perhaps for a similar reason as with the lead oxides. Vanadium (V) bears a doubly bonded oxygen and may be inaccessible for  $\Phi\text{-NO}$ . Unlike the lead oxides, V<sub>2</sub>O<sub>5</sub> has a considerable activity in the selective reduction of nitrobenzene. This might be explained by a positive electrostatic potential (attractive toward negative charges) above and below the ring plane of  $\Phi\text{-NO}_2$  (20). This could enhance the adsorption of the molecule on the vanadia surface, whereas  $\Phi\text{-NO}$  has a negative potential above and below the ring (21), which is probably repelled by the vanadia surface. A definitive explanation of all phenomena observed is not yet available, but the following consistent picture of  $\Phi\text{-NO}$  can be suggested.

$\Phi\text{-NO}$  can be  $\sigma\text{-N}$  or  $\sigma\text{-O}$  bound, either to a surface  $-\text{OH}$  group or to a cation. Lead oxides and vanadia induce the reduction of  $\Phi\text{-NO}$  to aniline (albeit in a small extent) and it is known that this reaction consumes hydrogen from  $-\text{OH}$  groups (10). In this situation one can assume that on PbO and V<sub>2</sub>O<sub>5</sub> the  $\Phi\text{-NO}$  is only very weakly bound to  $-\text{OH}$  groups.

However, with oxides like Mn<sub>3</sub>O<sub>4</sub> or Co<sub>3</sub>O<sub>4</sub> the adsorption of  $\Phi\text{-NO}$  can be detected by IR spectroscopy and they are active in the selective oxidation of  $\Phi\text{-NO}$  to  $\Phi\text{-NO}_2$ . We suggest that this is due to the coordination of  $\Phi\text{-NO}$  to a metal cation, which facilitates the transfer of oxygen in the  $\Phi\text{-NO} \leftrightarrow \Phi\text{-NO}_2$  couple.

TABLE 3

Absolute Intensities of the Strongest Bands, Specific Surface Area of the Oxides, Relative Amounts of N Coordinated and O Coordinated Nitrosobenzene, Relative Intensities of the Band Assigned as  $\nu\text{CN}(\sigma\text{-N})$ , Spectral Position (in  $\text{cm}^{-1}$ ) of  $\nu\text{CN}(\sigma\text{-O})$ , and Electronic Configuration of the Oxides.

Oxide	Specific surface area ( $\text{m}^2/\text{g}$ )	$I$ (strongest band)	$I\nu\text{NO}(\sigma\text{N})/I\nu\text{NO}(\sigma\text{-O})$	$I_{\text{rel}}$ $\nu\text{CN}(\sigma\text{-N})$	$\nu\text{CN}(\sigma\text{-O})$ ( $\text{cm}^{-1}$ )	Cation el. conf.
TiO <sub>2</sub>	47	0.2	>1	very strong	1131 1140 (RT)	$d^0$
Fe <sub>2</sub> O <sub>3</sub>		0.15	>1	strong	1129	$d^5$
Co <sub>3</sub> O <sub>4</sub>	18	0.1	>1	weak	1136	$d^{6a}$
Mn <sub>3</sub> O <sub>4</sub>	25	0.05	>1	weak	1129	$d^{4a}$
Al <sub>2</sub> O <sub>3</sub>	95	0.1	<1	weak	1131	$p^6$
ZnO	10	0.02	<1	—	1122	$d^{10}$
MgO		0.01	0	—	1120	$p^6$
Cr <sub>2</sub> O <sub>3</sub>	36	0.2	<1	—	1115	$d^3$

Note. Nitrosobenzene adsorbed at  $-30^\circ\text{C}$  and  $10^{-4}$  Torr.

<sup>a</sup> Based on results presented in (1–7) it is assumed that only  $\text{Co}^{3+}$  and  $\text{Mn}^{3+}$  are exposed in the surface of  $\text{Co}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4$ , respectively.

Several assignments can be proposed for the band at  $1240\text{ cm}^{-1}$  found in the spectra of  $\Phi\text{-NO}$  adsorbed on TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub>. Azobenzene ( $\Phi\text{-N=N-}\Phi$ ), azoxybenzene, and various other possible reaction products of adsorbed  $\Phi\text{-NO}$  like diphenylhydrazine ( $\Phi\text{-NH-NH-}\Phi$ ) or the  $\text{NO}_2^-$  ion have IR adsorption bands near  $1240\text{ cm}^{-1}$  (22–24). However, adsorption of these compounds on TiO<sub>2</sub>, which showed the strongest  $1240\text{ cm}^{-1}$  band, did not produce the same spectral feature. We know that the band belongs to a stable species, since it remains visible upon heating the oxide to room temperature and in the case of TiO<sub>2</sub> it even increases in intensity with increasing temperature (Fig. 4). Thus, it can be excluded that a *trans*-dimer is responsible for the  $1240\text{ cm}^{-1}$  band.

The high intensity of this band indicates that it is a C–N or N=O stretching absorption. A C–N stretching mode seems to be the most likely for the following reasons. First, according to Varsanyi (19) the position of  $\nu(\text{C-N})$  (ring vibration 13) in  $\Phi\text{-NO}$  may vary between  $1280$  and  $1100\text{ cm}^{-1}$ . Second, there is a correlation between the intensity of the  $1240\text{ cm}^{-1}$  band and the relative intensities of  $\nu(\text{N=O})$  ( $\sigma\text{-N}$ ) at  $1485\text{ cm}^{-1}$  and  $\nu(\text{N=O})$  ( $\sigma\text{-O}$ ) at  $1505\text{ cm}^{-1}$  (see Table 3). On TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> the  $1240$  band is strong and  $\nu(\text{N=O})$  ( $\sigma\text{-N}$ ) is stronger than  $\nu(\text{N=O})$  ( $\sigma\text{-O}$ ). On MgO, ZnO, and Cr<sub>2</sub>O<sub>3</sub> where the  $1240\text{ cm}^{-1}$  band is absent,  $\nu(\text{N=O})$  ( $\sigma\text{-N}$ ) is weaker than  $\nu(\text{N=O})$  ( $\sigma\text{-O}$ ) or, in case of MgO it is not observed at all. Thus, a reasonable assignment for the  $1240\text{ cm}^{-1}$  band is the C–N stretching mode of  $\sigma\text{-N}$  coordinated  $\Phi\text{-NO}$ . In Table 3 an indication of the intensity ratio between  $\nu(\text{C-N})$  ( $\sigma\text{-N}$ ) and  $\nu(\text{C-N})$  ( $\sigma\text{-O}$ ) is given for each oxide. It is not possible to establish an exact value for this ratio since the two bands overlap often with each other and with neighboring bands. However, the trend is obvious.

The location of  $\nu(\text{C-N})$  of the  $\sigma\text{-N}$  coordinated  $\Phi\text{-NO}$  at  $1240\text{ cm}^{-1}$  agrees with an empirical relationship established by Talberg (25) and Cameron *et al.* (26). It relates the N=O stretching frequency and the  $r(\text{C-N})$  and  $r(\text{N-O})$  bond lengths in nitroso compounds:

$$r(\text{N=O}) [\text{\AA}] = k_1 - k_2\nu(\text{N=O}) [\text{cm}^{-1}]$$

$$r(\text{N=O}) [\text{\AA}] = k_3 + k_4/[r(\text{C-N}) [\text{\AA}] - k_5].$$

Although these relationships have been obtained with solid nitroso compounds, Cameron *et al.* (26) have shown recently that they hold for dimers and for  $\sigma\text{-N}$  and  $\sigma\text{-O}$  coordinated nitroso compounds too, provided that the compounds are *aromatic*. Thus, a decrease in  $\nu(\text{N=O})$  should be accompanied by a decrease in the C–N bond length and, accordingly, an increase in  $\nu(\text{C-N})$ . Compared with the  $\sigma\text{-O}$  coordinated molecule,  $\nu(\text{N=O})$  is lower, and  $\nu(\text{C-N})$  is higher in  $\sigma\text{-N}$  coordinated  $\Phi\text{-NO}$  on metal oxides.

The observation of the  $\sigma\text{-O}$  coordinated  $\Phi\text{-NO}$  on so many metal oxides is remarkable, since  $\Phi\text{-NO}$  ligands in organometallic complexes are only known to be coordinated by  $\sigma\text{-N}$  bonding. The  $\sigma\text{-O}$  coordinated nitroso ligands (not  $\Phi\text{-NO}$ ) have been found in  $\text{Sn}(\text{Me})_2\text{Cl}_2$  (*p*-nitrosodimethylaniline)<sub>2</sub> and  $\text{ZnCl}_2$ (*p*-nitroso-dimethylaniline)<sub>2</sub>, both complexes of  $d^{10}$  metal ions (26). However, the behavior of  $\Phi\text{-NO}$  on metal oxides agrees very well with this: the IR absorption bands assigned by us to the  $\sigma\text{-O}$  coordinated  $\Phi\text{-NO}$  are prevailing on ZnO ( $d^{10}$ ), MgO ( $p^6d^0$ ), and Al<sub>2</sub>O<sub>3</sub> ( $p^6d^0$ ). The bands assigned to the  $\sigma\text{-N}$  coordinated  $\Phi\text{-NO}$  have maximal intensity on TiO<sub>2</sub> ( $d^0$ ). The oxides Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, and Mn<sub>3</sub>O<sub>4</sub> with partly filled *d*-orbitals are between the extremes. An exception is formed by Cr<sub>2</sub>O<sub>3</sub>, that will be discussed separately. Although it is sometimes difficult to discriminate between the  $\sigma\text{-O}$  and  $\sigma\text{-N}$  coordinated  $\Phi\text{-NO}$

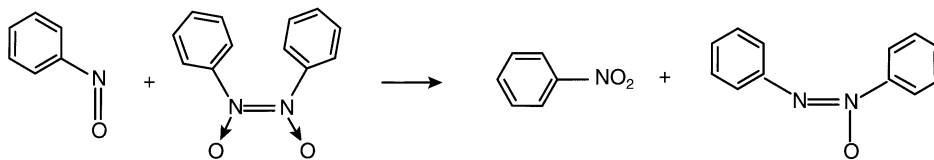


FIG. 8. The reaction of a nitrosobenzene molecule with a nitrosobenzene dimer to nitrobenzene and azoxybenzene.

in organometallic complexes (26), the *simultaneous* observation of IR bands from both species on various metal oxides supports our assignment of the  $1503\text{ cm}^{-1}$  absorption to  $\sigma$ -O coordinated, and the  $1485\text{ cm}^{-1}$  absorption to the  $\sigma$ -N coordinated  $\Phi$ -NO.

Let us now turn to the C-N stretching mode of the  $\sigma$ -O coordinated  $\Phi$ -NO. The position of this band varies between  $1140\text{ cm}^{-1}$  on  $\text{TiO}_2$  (at room temperature) and  $1115\text{ cm}^{-1}$  on  $\text{Cr}_2\text{O}_3$ . The latter is almost the gas phase frequency of this band ( $1112\text{ cm}^{-1}$ ). In Table 3 the spectral positions of  $\nu(\text{C-N})$  ( $\sigma$ -O) are shown. The specific surface area of the oxides and an indication of the absolute intensities of each spectrum are also included to show that the frequency of  $\nu(\text{C-N})$  does not change due to the increasing amount of  $\Phi$ -NO adsorbed. The trends shown in Table 3 are that both the frequency of  $\nu(\text{C-N})$  ( $\sigma$ -O) and the relative amount of  $\Phi$ -NO( $\sigma$ -N), indicated by the intensity ratio of  $\nu(\text{N=O})$  ( $\sigma$ -N) and the  $\nu(\text{N=O})$  ( $\sigma$ -O) and by the intensity of  $\nu(\text{C-N})$  of the  $\sigma$  bonded molecule, increase, going from the basic  $\text{MgO}$  to the strongly Lewis acidic  $\text{TiO}_2$ . The  $\nu(\text{C-N})$  ( $\sigma$ -O) absorption seems to be the only spectral band that is not only sensitive to the coordination mode, but also to the nature of the oxide surface.

In this series of oxides,  $\text{Cr}_2\text{O}_3$  behaves differently than expected for an oxide having partly filled  $d$  orbitals and being also acidic (27). Its behavior is similar to that of  $\text{MgO}$ . This might be due to the preparation method used, namely the decomposition of ammonium bichromate. The oxide obtained in this way differs in color (greyish green) and structure (Aerosil-like) from commercially available chromic oxide and probably its surface composition differs from other forms of  $\text{Cr}_2\text{O}_3$  too.

Possibly, both types of coordinated  $\Phi$ -NO are intermediates in the formation of  $\Phi$ -NO<sub>2</sub>, since no correlation has been found between the individual adsorption modes of  $\Phi$ -NO observed on metal oxides and their activity in  $\Phi$ -NO oxidation. Concerning the mechanism of  $\Phi$ -NO<sub>2</sub> formation, it is likely that on the most active transition metal oxides  $\Phi$ -NO is oxidized by lattice oxygen, i.e., by the Mars-van Krevelen mechanism, whereas on alumina the only source of oxygen is  $\Phi$ -NO itself. Coordinated monomeric  $\Phi$ -NO could, for example, react with a dimer to yield  $\Phi$ -NO<sub>2</sub> and azoxybenzene as shown in Fig. 8 (12). A reaction of this type might take place on transition metal oxides too, resulting in an additional  $\Phi$ -NO<sub>2</sub> production. Also, the observation made by IR spectroscopy of traces of  $\Phi$ -NO<sub>2</sub> on  $\text{MgO}$  and

$\text{ZnO}$  can be explained by this mechanism. Since these oxides have not been investigated in the MS study (10), their activities in the oxidation of  $\Phi$ -NO are not known, but they are probably less active than  $\text{Al}_2\text{O}_3$ .

The deviating behavior of  $\text{TiO}_2$  (large amounts of  $\sigma$ -N coordinated  $\Phi$ -NO, increasing with time; no substantial  $\Phi$ -NO<sub>2</sub> production) can be explained by a strong bonding of  $\Phi$ -NO to the surface. This could prevent both the reaction of adsorbed  $\Phi$ -NO to  $\Phi$ -NO<sub>2</sub> and the formation of sufficient amounts of the dimer, which might be the required source of oxygen with this oxide: due to the strong Ti-O bond, the Mars-van Krevelen mechanism is probably not operating on  $\text{TiO}_2$  (10). The observation of a small amount of  $\Phi$ -NO<sub>2</sub> in the IR spectrum can be explained by some initial activity according to reaction (I), which is later poisoned by irreversibly adsorbed  $\Phi$ -NO.

## CONCLUSIONS

- Two IR absorption bands observed in the IR spectrum of nitrosobenzene dissolved in ethanol at  $1270$  and  $1190\text{ cm}^{-1}$ , not reported earlier, are assigned to the ring vibrations 3 (C-H in-plane bending) and 13 (mainly C-N stretching) of dimeric nitrosobenzene.

- For the  $\sigma$ -N and  $\sigma$ -O coordinated nitrosobenzene, the same IR bands are obtained when nitrosobenzene is dissolved in benzene (hydrogen bonding with  $\text{H}_2\text{O}$ ), adsorbed on metal oxides (coordination to surface cations), and coordinated in organometallic complexes. The IR spectrum is determined by the coordination mode rather than by the nature of the coordination center. Both species ( $\sigma$ -N and  $\sigma$ -O bound nitrosobenzene) seem to participate in catalytic reactions.

- The strong absorption at  $1240\text{ cm}^{-1}$  in the spectrum of nitrosobenzene adsorbed on  $\text{TiO}_2$  and other oxides containing Lewis acidic sites has been assigned to the ring vibration 13 (mainly C-N stretching) of the  $\sigma$ -N coordinated molecule.

- In agreement with the findings in organometallic complexes, nitrosobenzene is  $\sigma$ -O coordinated to oxide surfaces containing metal ions with completely filled valence orbitals. A large amount of  $\sigma$ -N coordinated nitrosobenzene is found on  $\text{TiO}_2$ , which has  $d^0$  ions at the surface. Both types of coordinated nitrosobenzene are found on transition metal oxides containing cations with partly filled  $d$  orbitals.



5. In agreement with the empirical relationships established by Talberg (25) and Cameron *et al.* (26) for nitroso compounds,  $\nu(\text{C-N})$  increases when  $\nu(\text{N=O})$  decreases.

6. PbO (red and yellow) and V<sub>2</sub>O<sub>5</sub> do not catalyze the selective oxidation of nitrosobenzene to nitrobenzene because nitrosobenzene is not adsorbed on these oxides in sufficient amounts.

7. TiO<sub>2</sub> does not catalyze the oxidation of nitrosobenzene to nitrobenzene due to poisoning of the surface by nitrosobenzene irreversibly bound to Lewis acidic sites.

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