Infrared Studies of the Disproportionation Reaction of Nitric Oxide on Y-Type Zeolites

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Abstract: Infrared spectra produced by adsorbing NO on CaY, NaY, decationated Y, and HY were examined. Except for HY, which is rather inactive, at least eight absorption peaks were observed on each zeolite. The ir absorption peaks were identified by examining the equilibrium which exists between adsorbed molecules and oxides of nitrogen in the gas phase, and by comparing the spectra of the adsorbed species with infrared spectra produced upon adsorbing various oxides of nitrogen on zeolites. The spectra are assigned to adsorbed N_2O, NO_2^+, N_2O_3, NO_3^-, a nitrito complex, and covalently bonded nitrite. The reaction produced N_2O and NO_2 as final gas-phase products. The catalytic activity increases in the following order: HY < decationated Y $\cong$ NaY < CaY. CaY can catalyze the reaction at room temperature, whereas for NaY and decationated Y a temperature of −78° is required. For HY very little reaction occurred even at −78°. Based upon the experimental evidence, a four-step mechanism is proposed for the reaction.

The disproportionation reaction of nitric oxide on zeolites was first reported by Addison and Barrer.[1] From measurements of the specific gravity of the purified degassing products they discovered that the reaction $4NO = N_2O + N_2O_3$ occurred on chabazite, faujasite, and A-type zeolites at 0° or lower temperatures. Later Alekseyev, Filimonov, and Terenin[2] studied the infrared spectra of nitric oxide adsorbed on A- and X-type zeolites. They confirmed the existence of the adsorbed N_2O and assigned peaks at 1940 and 2100 cm^{-1} to coordinatively bonded NO and ionically bonded NO^+.

This reaction is particularly interesting from a practical point of view because NO is a major air pollutant. The zeolite catalysts convert NO into N_2O, which is relatively harmless, and NO_2, which will be retained in zeolites. From a more fundamental viewpoint NO and NO_2 are important probes for understanding the properties of active catalytic and adsorption sites inside zeolites. For example, the paramagnetic property of NO has been used to study electrostatic and magnetic interactions in zeolites by means of epr spectroscopy.[3-6] It is clear from epr and adsorption studies that only a small fraction of the total NO introduced to cationic zeolites remains in a paramagnetic state, and it has been proposed that the products of the disproportionation reaction are able to compete favorably for certain adsorption sites. A clear understanding of this reaction will undoubtedly aid in the interpretation of the epr data.

The purpose of this study was to find the mechanism through which N_2O and NO_2 are produced from NO and to determine the role of the zeolite in this catalytic reaction. The adsorption and infrared studies were carried out on four different Y-type zeolites, CaY, NaY, HY, and decationated Y, in order to establish the role of cations in this reaction.

Experimental Section

The sodium form of the Y-type zeolite was supplied by the Linde Co. (lot no. 11007-73). The calcium form and ammonium form were obtained by exchanging the NaY with cations from a nitrate solution. The exchange procedure was reported in an earlier paper.[5] For CaY 92% of the sodium ions were exchanged for calcium ions, whereas for NH_4Y the extent of exchange was 90%. The NaY and CaY were degassed for 1 hr at 100° increments up to 500° to remove zeolitic water. The HY was prepared by degassing NH_4Y at a maximum of 400° for 1 hr; under such conditions, NH_3 is largely removed, but the H^+ ions are retained as hydroxyl groups.[7] Degassing at 650° for 1 hr removes the H^+ ion with some lattice oxide ions, thus producing the decationated-Y zeolite and water.

The nitric oxide received from a commercial source was repeatedly distilled at the melting point of pentane (−131.5°) until the ir spectrum of the gas at 600 Torr showed no absorption due to N_2O or NO_2. The ^{15}NO was 99% enriched in ^{15}N.

The adsorption isotherms of the zeolites were obtained by measuring by means of a quartz spring balance the weight increase of a zeolite sample of about 0.2 g during the adsorption of NO.

For ir measurements of the adsorbed species, the zeolites were first pressed into plates. The pressures used were 10 and 15 tons/in^2, and the resulting density of the plates varied from 10 to 15 mg/cm^2. The ir cell was constructed according to the design of Peri and Hannan,[8] with a few minor modifications. The sample could be lifted into a rather large side arm for heat treatment, cooling, and for taking an ir spectrum of the gas phase which existed in the cell. The ir path length of the cell was about 5 cm; therefore, the spectra of the gas, even with a moderate pressure, could be easily recorded.

In studying the reaction of NO, infrared spectra were taken after water was removed by degassing, after NO was admitted at 23°, after cooling, after brief evacuation, and after prolonged degassing at 23 and 100°, and in 100° increments up to 500°. All spectra were recorded while the sample was at room temperature.

In order to investigate the equilibrium that exists between the adsorbed reaction products and the gas, the cell which contained the reaction mixture was purged with N_2O, or NO, and the ir spectrum was observed. The purge was carried out by introducing an extra amount of pure gas through an inlet at the lower side of the cell to build up the pressure to several times that of the reaction; then the cell was evacuated to the original pressure. By such batchwise dilution, either N_2O or NO in the mixture was removed.

A Beckman IR 12 spectrophotometer was used for the measurements. The programming of the slit widths was such that a minimum resolution of 3 cm^{-1} was maintained. The maximum transmission for each sample was approximately 30%. The spectra are displayed on a linear scale, and the cutoff point at the lowest wave number corresponds to 0% transmission.

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(1) W. E. Addison and R. M. Barrer, *J. Chem. Soc.*, 757 (1955).

(2) A. V. Alekseyev, V. N. Filimonov, and A. N. Terenin, *Dokl. Akad. Nauk. SSSR*, **147**, 1392 (1962).

(3) J. H. Lunsford, *J. Chem. Phys.*, **46**, 4347 (1967).

(4) J. H. Lunsford, *J. Phys. Chem.*, **72**, 2141 (1968).

(5) J. H. Lunsford, *ibid.*, **72**, 4163 (1968).

(6) B. M. Hoffman and N. J. Nelson, *J. Chem. Phys.*, **50**, 2598 (1969).

(7) J. B. Uytterhoeven, L. G. Christner, and W. K. Hall, *J. Phys. Chem.*, **69**, 2117 (1965).

(8) J. B. Peri and R. B. Hannan, *ibid.*, **64**, 1526 (1960).

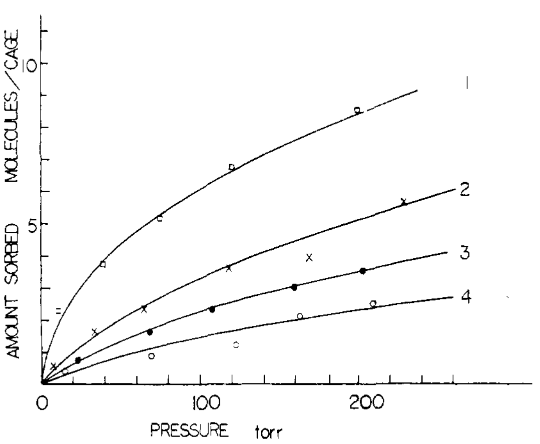

Figure 1. Sorption of NO on Y-type zeolites at −78°: (1) CaY, (2) NaY, (3) decationated Y, (4) HY.

Results

Sorption of NO in Zeolites. The adsorption isotherms of NO at −78° in four Y-type zeolites are presented in Figure 1. The adsorptivity of zeolites depends on the cation that they possess. It is clearly shown in the figure that the equilibrium adsorption follows the order: CaY > NaY > decationated Y > HY. Most of the ir studies were carried out at the coverage of about three NO molecules per supercage.

Infrared Studies of Adsorbed Species. 1. NaY. Figure 2 shows the ir spectrum of NaY at various stages of adsorption of NO. Curve 1 is the spectrum of NaY itself after the degassing procedure. Except for a small window between 800 and 900 cm^{-1} (not shown in the figure), zeolites are infrared opaque in the region below 1200 cm^{-1}. Curve 2 gives the spectrum of the system after 105 Torr of NO was added to the cell at room temperature. The absorption peak of gas-phase NO at 1876 cm^{-1} can be seen clearly, but no peaks due to adsorbed species appeared. Curve 3 gives the spectrum after the sample had been cooled to −78° for 1.5 hr. The spectrum was taken at room temperature. New peaks at 1260, 1305, 1555, 1920, 2000, 2100, 2224, and 2240 cm^{-1} appeared. The 2224-cm^{-1} and part of the 1260-cm^{-1} peaks are due to gas-phase N_2O; this was shown by taking a spectrum with the sample lifted into the side arm. The remaining peaks are due to adsorbed species. Curve 4 shows the spectrum after evacuating for 15 sec at 23°; all of the peaks in curve 3 disappeared, except a fraction of the one at 1260 cm^{-1}. A new doublet centered at 1400 cm^{-1} and another new peak at 3650 cm^{-1} were observed. Curve 5 shows that the 1260- and 3650-cm^{-1} peaks could be removed by degassing the sample at 200° for 1 hr. The doublet at 1400 cm^{-1} could be removed completely only by degassing at 400° or higher temperatures (curve 6).

In order to establish the identity of those ir absorption peaks produced by the reaction, known molecules were put onto NaY and their ir spectra were observed. These spectra are shown in Figure 3, where the first curve is N_2O on NaY. If the N_2O was put on at room temperature, only peaks at 2240 and 1260 cm^{-1} showed up. If the sample was cooled to −78°, another rather weak peak at 2360 cm^{-1} also appeared. According to the gas-phase ir spectrum, degassing of this sample only produced N_2O. Curve 2 is a spectrum of a NaY sample doped with 0.2 molecule of nitrate ion per supercage. It shows a doublet at 1400 cm^{-1}. A very large amount of NO_2 can be adsorbed by NaY. Curve 3 shows the ir

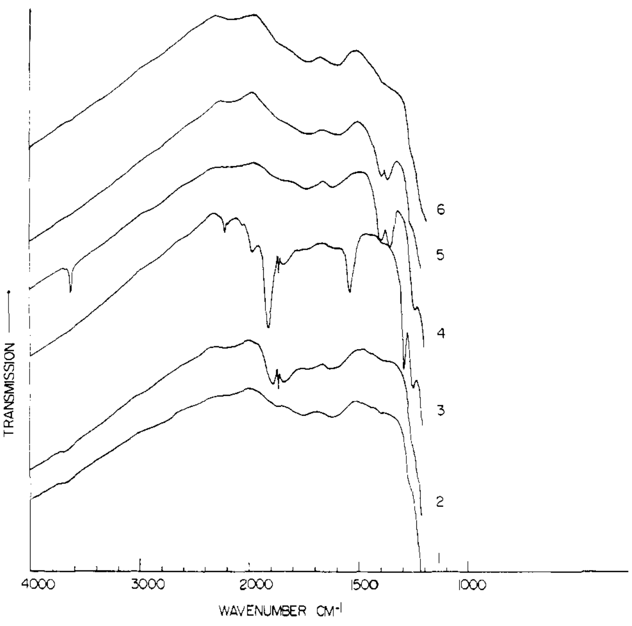

Figure 2. Spectra produced when NO is adsorbed on NaY: (1) degassed to 500°, (2) 105 Torr of NO added at 23°, (3) −78° for 1.5 hr, (4) degassed for 15 sec at 23°, (5) degassed at 200° for 1 hr, (6) degassed at 400° for 1 hr.

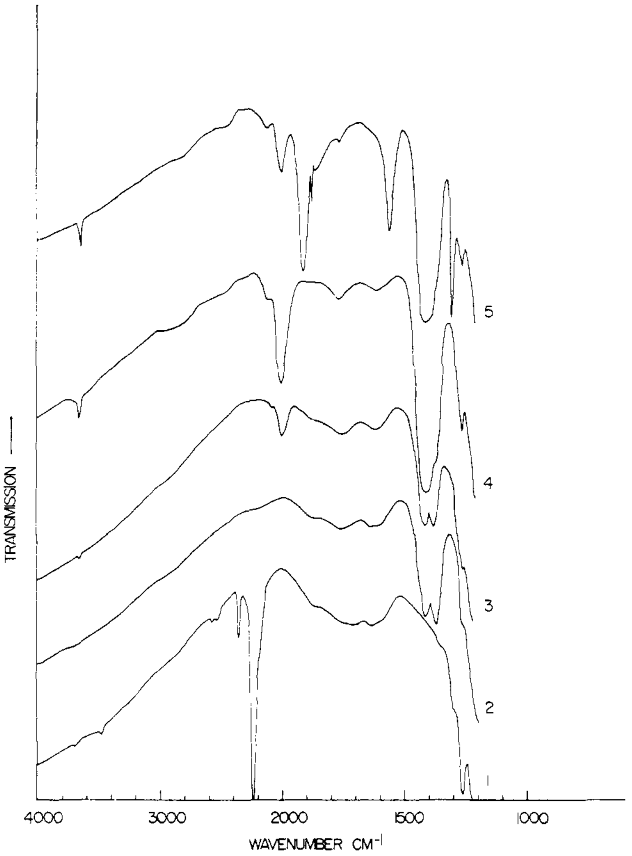

Figure 3. Spectra produced by adsorbing oxides of nitrogen on NaY: (1) N_2O at −78° for 1 hr; (2) $NaNO_3$, 0.2 molecule/cage; (3) NO_2, 0.2 molecule/cage; (4) NO_2, 0.5 molecule/cage; (5) sample in (4) + 180 Torr of NO at 23°.

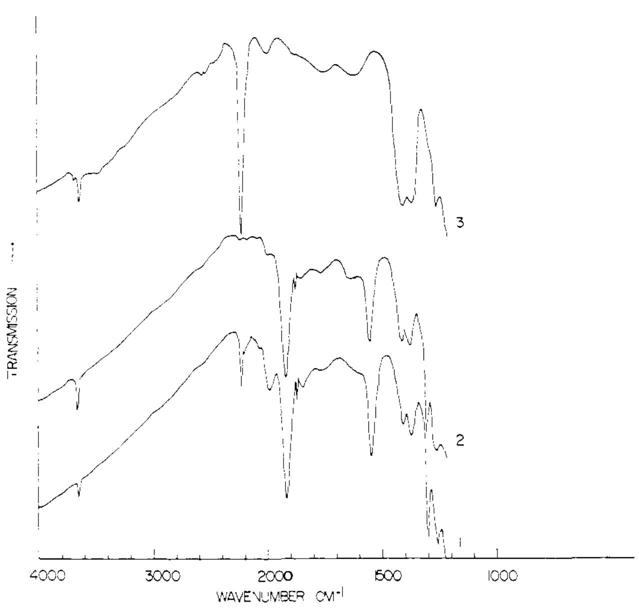

Figure 4. Equilibrium between oxides of nitrogen adsorbed on NaY and the gas phase: (1) reaction products of NO on NaY, (2) purged with NO, (3) purged with N_2O.

spectrum of a sample in which only 0.2 molecule of NO_2 per supercage was adsorbed. It has a doublet at 1400 cm^{-1} and a singlet at 2000 cm^{-1}. Curve 4 shows a spectrum after the NO_2 concentration was increased to 0.5 molecule of NO_2 per supercage. The peak at 1400 cm^{-1} is no longer a doublet, the 2000-cm^{-1} peak becomes more intense, and new peaks show up at 1260 and 2100 cm^{-1}. Curve 5 shows a spectrum of the sample after 180 Torr of NO was added into the system which gave curve 4. New peaks at 1305, 1555, and 1920 cm^{-1} emerged at the expense of the 2000- and 2100-cm^{-1} peaks.

The equilibrium between the adsorbed species produced by the disproportionation reaction and NO or N_2O gas was explored. Figure 4, curve 1, depicts the spectrum of adsorbed molecules produced by the disproportionation reaction. Curve 2 is a spectrum of the sample after the gas-phase mixture was purged with NO. The result of purging is that the peaks at 2000, 2100, and 2240 cm^{-1} have been removed. Curve 3 shows a spectrum of the sample after purging with N_2O gas. As one can see, the doublet at 1400 cm^{-1} and the singlet at 2240 cm^{-1} were greatly enhanced by this latter treatment. The peaks at 1305, 1555, and 1920 cm^{-1} disappeared.

Experiments were also carried out in which NO or N_2O was sorbed at room temperature onto a NaY sample which showed only the spectrum of the 1400-cm^{-1} doublet. Regardless how the doublet was produced, whether by removing the gas after the disproportionation reaction of NO, by doping NaY with $NaNO_3$, or by putting NO_2 on NaY followed by degassing, no new absorption peaks were produced except the gas-phase peaks and the 2240- and 1260-cm^{-1} peaks.

2. CaY. The ir peaks produced by adsorbing NO on CaY are basically the same as those produced on NaY, only peak positions are shifted slightly to the higher energy side. However, CaY can catalyze the reaction much better. Upon using a higher pressure of NO (for example 200 Torr), the reaction occurred at room temperature to give a very intense spectrum of the products. If the zeolite is cooled to −78°, then 20 Torr of NO is enough compared to the 100 Torr or more required for NaY.

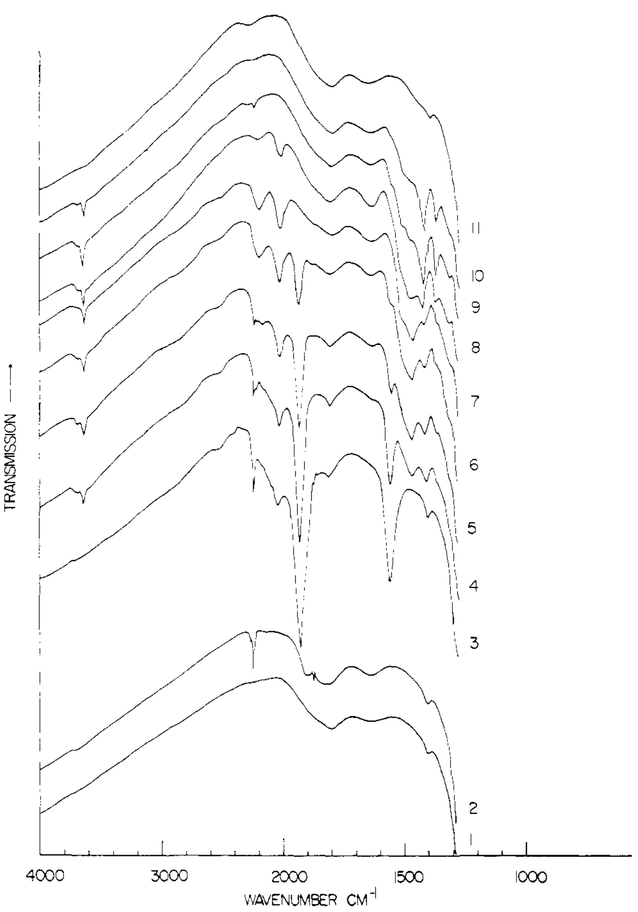

Figure 5. Spectra produced when NO is adsorbed on CaY: (1) degassed to 500°, (2) 30 Torr of NO at 23°, (3) −78° for 1 hr, (4) degassed at 23° for 16 sec, (5) degassed at 23° for 40 sec, (6) degassed at 23° for 3 min, (7) degassed at 23° for 1.5 hr, (8) degassed at 100° for 1 hr, (9) degassed at 200° for 8 hr, (10) degassed at 300° for 8 hr, (11) degassed at 400° for 1 hr.

The first curve in Figure 5 is the ir spectrum of CaY which had been degassed to 500°. In the 1250–1300-cm^{-1} region CaY is less transparent than the NaY. Curve 2 was recorded after the addition of 30 Torr of NO at 23°. One can see that a sharp absorption peak appeared at 2250 cm^{-1}. After cooling the sample to −78°, many new peaks appeared, as shown in curve 3. The peak in the 1305-cm^{-1} region is not well resolved from the CaY absorption. The other peaks are at 1565, 1935, 2040, 2200, and 2224 cm^{-1}. The peak at 2250 cm^{-1} is enhanced. Curve 4 is a spectrum which was taken after the reaction mixture was pumped for 8 sec. The 2040- and 2200-cm^{-1} peaks remained the same, whereas the peaks at 1305, 1565, 1935, 2224, and 2250 cm^{-1} diminished or disappeared. Meanwhile, new peaks at 1400, 1470, and 3640 cm^{-1} grew. In CaY the concomitant growth of the 1400- and 1470-cm^{-1} peaks with the decrease of the 1305-, 1565-, and 1935-cm^{-1} peaks can be clearly demonstrated by following their intensity change during the degassing process, as shown by curves 5, 6, 7, and 8. Curve 9 shows that degassing at 200° removed the 2040- and 2200-cm^{-1} peaks. It also diminished the peak at 1470 cm^{-1}; thus the doublet at 1400 cm^{-1} can be clearly seen.

Table I. Ir Absorption Peaks Induced by Adsorbing NO on Zeolites

	23°	Cooled to −78°	Degassed at 23°	Degassed at 200°	Degassed at 300°	Degassed at 400°
NaY	None	1260, 1305, 1555, 1920, 2000, 2100, 2240	1260, 1400, 3650	1400	1400	None
CaY	1305 (unresolved), 1565, 1935, 2040, 2200, 2250	1305, 1565, 1935, 2040, 2200, 2250	2040, 2200, 3640	1400, 1470	1400, 1470	None
Dec Y	None	1300, 1570, 1910, 1980, 2120, 2240	1585, 1650, 2000, 2120	1585, 1650	None	None
HY	None	2200	None	None	None	None

In a separate experiment ^{15}NO was adsorbed on CaY and the sample was cooled to −78°. The spectrum was essentially the same as shown in Figure 5, curve 3, except all of the peaks were shifted to lower wave numbers (1530, 1900, 2000, 2060, and 2170 cm^{-1}). Upon purging the sample at room temperature with ^{14}NO, all of the peaks shifted back to the higher wave numbers except the 2170-cm^{-1} peak which was due to N_2O. Evacuation of the gas phase resulted in a spectrum which had the usual doublet centered at 1400 cm^{-1} and the 1470-cm^{-1} peak.

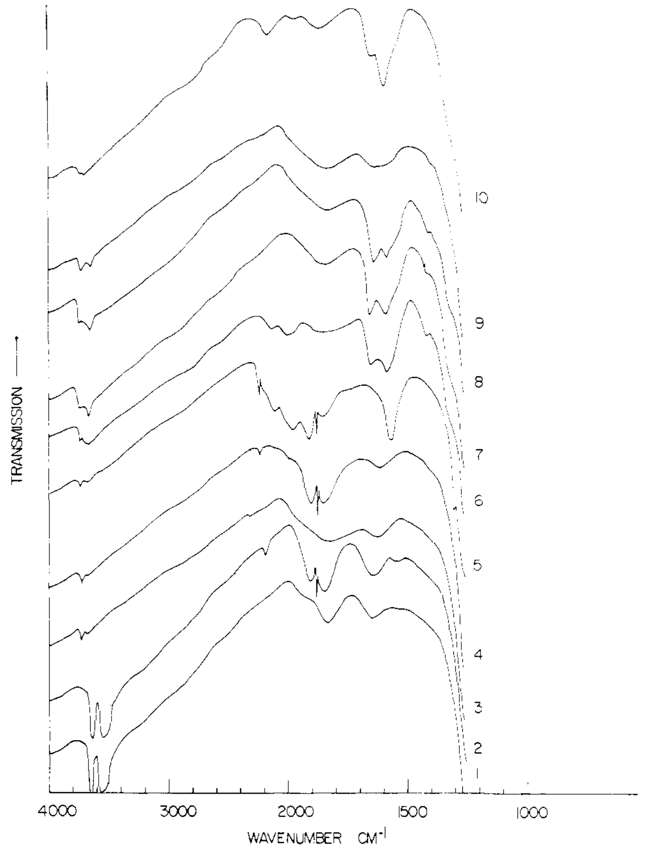

Figure 6. Spectra produced when oxides of nitrogen are adsorbed on HY and decationated Y zeolites: (1) NH_4Y degassed to 400°; (2) 285 Torr of NO at −78° for 1 hr; (3) NH_4Y degassed to 650°; (4) 130 Torr of NO added at 23°; (5) −78° for 1 hr; (6) degassed at 23° for 5 min; (7) degassed at 100° for 1 hr; (8) degassed at 200° for 1 hr; (9) degassed at 300° for 1 hr; (10) NO_2 on decationated Y, concentration = 0.2 molecule/cage.

3. HY and Decationated Y. As a catalyst for the disproportionation reaction, HY is relatively inactive and cannot induce much reaction even upon cooling the sample in 285 Torr of NO. In Figure 6, the first curve shows that upon degassing a NH_4Y sample to 400° one indeed obtains HY, since the hydroxyl groups absorb strongly at 3550 and 3650 cm^{-1}. Curve 2 is a spectrum of the zeolite after 285 Torr NO was added and the sample was cooled to −78°. Very little of the adsorbed species was produced, as indicated by the weak ir absorption.

Curve 3 is a spectrum of a NH_4Y sample which had been degassed to 650° to produce decationated Y. This zeolite has about the same activity as NaY. The ir absorptions of hydroxyl groups are rather weak here since heating at high temperature removed them as water. Curve 4 shows that decationated Y is much like NaY in that no reaction can be catalyzed at room temperature. Cooling the sample to −78° induced a reaction which resulted in ir absorption peaks at 1300, 1570, 1910, 1980, 2120, 2224, and 2240 cm^{-1} (curve 5). Subsequent degassing removed all the peaks in curve 5 and produced new peaks at 1585 and 1650 cm^{-1}. Unlike the cases of NaY and CaY, no doublet at 1400 cm^{-1} was produced. The peaks at 1585 and 1650 cm^{-1} resisted the degassing up to 200°, but the adsorbed species could be removed by degassing at 300° (curve 9). Adsorption of NO_2 on decationated Y at 23° produced ir absorption at 1585, 1650, and 2160 cm^{-1}, as shown in curve 10.

Positions of ir peaks of adsorbed species on the four zeolites at various stages are summarized in Table I.

Discussion

Identification of Infrared Absorption Peaks Introduced by Adsorbing NO on Zeolites. A large volume of work has been carried out in the field of infrared absorption of nitrogen–oxygen compounds.[9-12] The vibrational frequencies of nitrogen–oxygen groups, however, are very much dependent on the manner in which the group is connected to the rest of the molecule. For example, in $Co(NH_3)_5(NO)^{2+}$ the NO is anionic and absorbs at 1195 cm^{-1}, while the free NO absorbs at

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(9) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(10) L. J. Bellamy, "Infrared Spectra of Complex Molecules," Methuen, London, 1958.

(11) G. Blyholder and M. C. Allen, *J. Phys. Chem.*, 70, 352 (1966).

(12) M. Shelef and J. T. Kummer, Symposium on Important Chemical Reactions in Air Pollution Control, AIChE 62nd Annual Meeting, 1969.

1876 cm^{-1}; however, in $NOBFCl_3$ the NO is cationic and absorbs at 2335 cm^{-1}.[9] The same situation occurs with other nitrogen–oxygen groups. Since one is dealing with adsorbed nitrogen–oxygen compounds, there are many possible types of bonding between the surface and the molecules. In addition to comparing the band frequencies observed in this work to frequencies of known compounds and complexes, further information is needed before a meaningful assignment can be made. The major approach which has been taken here is to explore equilibria that exist between adsorbed species and molecules in the gas phase.

Starting with the assignment of the 2240-cm^{-1} peak of NaY, an analysis of the spectra will be made. It is known that N_2O is stable in zeolites[1] and that the 2240- and 1260-cm^{-1} peaks are the major peaks produced by putting N_2O on NaY (Figure 3, curve 1). Therefore, there is little question that these peaks are due to adsorbed N_2O.

Terenin, *et al.*,[2] assigned the peaks at 2100 and 2000 cm^{-1} to ionically and coordinatively bonded NO^+, since this is the region where NO^+ absorbs. They explained the observation that these two peaks also can be produced by adsorbing NO_2 on zeolites (Figure 3, curves 3 and 4) by postulating that NO_2 can be decomposed on zeolites. However, a particular reaction occurs which strongly suggests that the species is NO_2^+ instead of NO^+. If a small, measured quantity of NO_2 is added to the NaY sample, as was done to produce Figure 3, curve 4, the NO_2 gas is completely adsorbed and the resulting spectrum absorbs at 2000 and 2100 cm^{-1}. Furthermore, if 180 Torr of NO is added to that sample at *room temperature*, the 2000- and 2100-cm^{-1} peaks are diminished and new peaks grow at 1305, 1555, and 1920 cm^{-1} (Figure 3, curve 5). These new peaks, as will be shown later, are due to N_2O_3. Since it is known that NaY does not catalyze the disproportionation reaction of NO at room temperature, it is concluded that the adsorbed NO_2^+ is reacting with NO to produced adsorbed N_2O_3.

As an additional point, it should be recalled that the 2000- and 2100-cm^{-1} peaks, produced by the disproportionation reaction of NO, can be removed by purging the system with pure NO at higher pressures (Figure 4, curve 2). It is unlikely that NO would remove NO^+ from the zeolite.

The vibrational frequencies of free NO_2 are 1621, 1320 (ir inactive), and 750 cm^{-1}. The tremendous frequency shift to 2000 or 2100 cm^{-1} is probably due to the partial loss of one electron to the surface. It is known that NO_2^+ in N_2O_5 has vibrational frequencies at 2350, 1400 (ir inactive), and 538 cm^{-1}.[13]

The 1920-, 1555-, and 1305-cm^{-1} peaks can be identified by comparison with the spectrum of free N_2O_3 which absorbs at 1863, 1589, and 1297 cm^{-1}.[14] In addition, it is known that at comparable temperatures N_2O_3 is in equilibrium with NO and NO_2. Likewise, the spectrum attributed to adsorbed N_2O_3 appears to be in equilibrium with NO and NO_2, since it disappears upon removing NO from the gas phase. The doublet at 1400 cm^{-1} which rises with the uniform disappearance of these three peaks can be produced by adsorbing NO_2 on NaY (Figure 3, curve 3). In addition, in the last section it was shown that these three peaks can also be produced by reaction of adsorbed NO_2^+ with gas-phase NO. Based on the above reasoning the 1920-, 1555-, and 1305-cm^{-1} peaks are assigned to adsorbed N_2O_3.

The doublet at 1400 cm^{-1} is assigned to the NO_3^- ion since it is known that free nitrate ions absorb in the region of 1400 cm^{-1}.[9] This doublet at 1400 cm^{-1} can also be produced by doping NaY with small amounts of $NaNO_3$ (Figure 3, curve 2). The fact that this doublet can be produced by adsorbing NO_2 on NaY indicates that there are some easily extractable oxygen ions in NaY.

The peak at 1260 cm^{-1} is attributed to nitrite ions and nitrous oxide molecules which are present in the zeolite under various conditions. This is the usual absorption region for the nitrite ion,[9] and a single peak at this wave number was produced by doping NaY with $NaNO_2$. Nitrous oxide also absorbs at this wave number, as cited earlier. The ir absorption at 1260 cm^{-1} in Figure 2, curve 3, is probably due to N_2O but may include some NO_2^-; however, the absorption at this wave number in Figure 2, curve 4, indicates only NO_2^-, since the N_2O has been removed.

The peak at 1420 cm^{-1}, which was clearly observed only when 0.5 molecule per cage or more of NO_2 was adsorbed on the NaY, appears to be the spectrum of a nitrito complex, M–ONO. These complexes are known to have an ir absorption band at 1465 cm^{-1}.[9] The formation of this species can be interpreted upon realizing that there are only a limited number of oxygens which can be easily extracted to form the nitrate ion, and the excess NO_2 molecules must remain covalently bonded to the lattice. As will be shown subsequently, the formation of the nitrito complex is more obvious in the CaY case.

Adsorption of NO on CaY and decationated Y basically produces the same adsorbed species, except that the positions of the peaks are slightly shifted and there are no nitrate ions formed in the decationated Y. The assignment of the spectra follows the same reasoning which was used for the adsorbed species on NaY. The assignments are summarized in Table II, and only some special features will be discussed.

Since the vibrational frequency of the nitrito complex in CaY is further away from that of the nitrate ion, it can be clearly seen that the nitrito group was produced by decomposition of N_2O_3 (Figure 5, curve 4). Both the nitrito complex and the nitrate ion have to be decomposed before they can be removed from the surface as NO_2. One would expect that the nitrito complex is less stable than the nitrate ion. Indeed, we do find that the peak at 1470 cm^{-1} can be completely removed by heating the sample at 300°, but the doublet at 1400 cm^{-1} is removed only after heating the sample to 400° (Figure 5, curves 10 and 11).

Another unique feature of CaY is that it holds N_2O_3 more strongly, and it is harder to decompose the N_2O_3 by removing the NO in the gas phase. Thus it is possible to take spectra consecutively during degassing to illustrate dramatically that the decomposition of N_2O_3 and the formation of the nitrito group and the nitrate ion occur simultaneously (Figure 5, curves 6, 7, 8, and 9).

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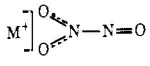
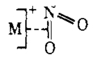
(13) R. Teranishi and J. C. Decius, *J. Chem. Phys.*, **22**, 896 (1954); **21**, 1116 (1953).

(14) I. C. Hisatsune and J. P. Devlin, *Spectrochim. Acta*, **16**, 401 (1960); **17**, 218 (1961).

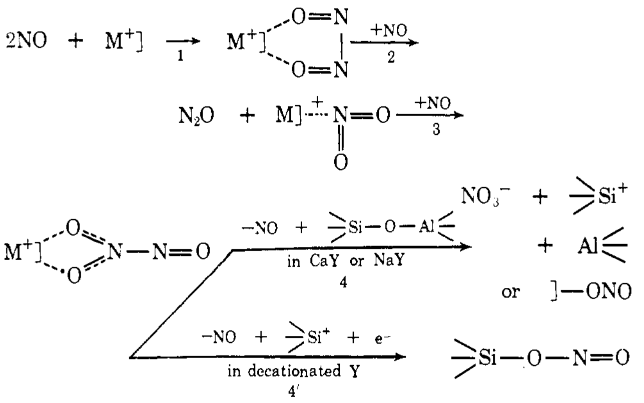
Table II. Assignments of Ir Absorption Peaks Produced by Disproportionation Reactions of NO on Zeolites

	Zeolite			
Adsorbed species	NaY	CaY	Dec Y	HY
$]-(N_2O)$	2240, 1260	2250	2240	2200
	1305, 1555, 1920	1305 (unresolved), 1565, 1935	1305, 1570, 1910	
	2000, 2100	2040, 2200	1980, 2120	
Si—O—N=O			1585, 1650	
]—ONO		1470		
NO_3^-	1400	1400		
NO_2^-	1260			

In the case of decationated Y, the disappearance of peaks at 1305, 1570, and 1910 cm^{-1}, which are assigned to N_2O_3, is accompanied by the appearance of peaks at 1585 and 1650 cm^{-1}. Meanwhile, nothing appeared in the 1400–1500-cm^{-1} region. It is known that organic nitrites absorb in the 1580–1680-cm^{-1} region.[10] It is also known that in decationated Y there exist trigonal Si^+ centers.[7] Since the decationated-Y lattice has an oxygen deficiency, the 1585- and 1650-cm^{-1} peaks probably are centers formed due to adsorption of NO_2 without extraction of an oxygen from the lattice. They are assigned to nitrites which are covalently bonded to silicon as Si—O—N=O.

Active Sites and Reaction Mechanisms. A comparison of the four zeolites studied here shows that CaY is clearly the most active in the disproportionation of nitric oxide. This zeolite not only adsorbs more nitric oxide but also is more active for a specific amount adsorbed. Both adsorption[15] and epr[16] data indicate that the electrostatic field in CaY is greater than in NaY. The least active zeolite, HY, should have relatively small electrostatic fields because the proton actually forms a hydroxide ion by reacting with a lattice oxide ion. In essence there is no region of positive charge in HY as there is in the other cationic forms. Removal of these hydroxide ions during the dehydroxylation process leaves lattice defects which expose positively charged silicon and aluminum ions to the surface. The positive charge is formally placed on the silicon atom; however, it is undoubtedly shared with the aluminum. In any event these defect centers give rise to electrostatic fields that are comparable to those found in cationic zeolites.[17]

As a first step in the disproportionation mechanism, it seems most probable that two NO molecules are brought together on a positively charged site. Yet, it is not clear at the present time whether this results in an adsorbed N_2O_2 or immediate decomposition to produce N_2O and an adsorbed O atom. However, since the zeolite has the ability to stabilize N_2O_3 as compared to the stability of N_2O_3 in the gas phase it is reasonable to assume that N_2O_2 dimers are also stabilized on the zeolite surface at −78°. The next step involves an interaction between N_2O_2 and a third NO molecule which causes a rearrangement to produce N_2O and NO_2^+. Both of these products have been identified by the ir spectra. Next, NO_2^+ reacts with NO gas to produce adsorbed N_2O_3. For this step, not only has adsorbed N_2O_3 been identified on the surface, but also this reaction has been carried out independently; *i.e.*, adsorbed NO_2^+ was prepared by adsorbing a small amount of NO_2 on a zeolite and NO was treated with it to produce adsorbed N_2O_3. When the excess NO gas is removed from the reaction mixture the adsorbed N_2O_3 will decompose to give NO and NO_2. In NaY and CaY the NO_2 reacts with lattice oxygen to produce nitrate ions or a covalent nitrito complex. In decationated Y the NO_2 bonds to a trigonal Si^+ to produce covalently bonded nitrite. The reactions are summed up in the following scheme.



Here, M^+ refers to Na^+ and Ca^+ for NaY and CaY, respectively. In the latter case it has been shown that the bivalent cation has an apparent charge which is less than two because of the coordination of the cation to either a hydroxyl or an oxide ion.[15] For the decationated zeolite, M^+ refers to the trigonal Si^+ which results from the dehydroxylation of the zeolite.

Both steps 4 and 4′ are irreversible since addition of NO back to the nitrate ions and the nitrito complex did not produce N_2O_3. The rapid exchange of ^{15}N in $^{15}NO_2^+$ with ^{14}N in gas-phase ^{14}NO may occur *via* the reverse of reaction 3.

It is interesting to note that a hydroxyl band at 3650 cm^{-1} appeared upon dissociation of the N_2O_3. This band, which is generally attributed to an SiOH stretching vibration,[7] also appeared when rather large amounts of NO_2 were added to the NaY zeolite. Addison and

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Barrer[1] have speculated that nitrite and nitrate ions result from the reaction of NO_2 with residual intracrystalline water to produce HNO_2 and HNO_3. Although such a reaction may be the source of protons and nitrite ions, it does not appear to be the major source of nitrate ions, since (a) the disproportionation reaction on decationated zeolites produced SiOH groups, but very few nitrate or nitrite ions, and (b) very few SiOH groups were produced when 0.2 molecule per cage of NO_2 was adsorbed on CaY. At this NO_2 level the nitrate ion concentration was comparable to that from the disproportionation reaction.

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Oxygen-17 Nuclear Magnetic Resonance and Oxygen Exchange in Aqueous Solutions of Iodate

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Abstract: Oxygen-17 nmr measurements on aqueous solutions of $LiIO_3$ are reported. The iodate resonance, having a line width $1/T_2 = 995 \pm 20$ sec^{-1}, lies 206.4 ± 1 ppm downfield from the solvent $H_2{}^{17}O$ line. Relative intensity, as well as shift, measurements indicate that the iodate is present as IO_3^- in the solution. Addition of acid results in line broadening of both the iodate and water resonances due to oxygen exchange with the solvent water. Analysis of the results indicates that in addition to the first-order acid-catalyzed exchange reaction studied previously there is a second-order oxygen-exchange reaction (with respect to acid) which predominates when $[H^+]$ is above 0.1 *M*. This reaction involves presumably the double-protonated iodate, and its rate law is rate = $k[IO_3^-][H^+]^2$, with $k = 1.5 \pm 0.5 \times 10^6$ sec^{-1} M^{-2}.

A number of experimental findings have suggested that the iodate ions in aqueous solution are strongly hydrated. For example, the ionic mobility of iodate is significantly lower than the value expected from comparison with the ionic mobilities of chlorate and bromate.[2] Also, the acid-catalyzed isotopic oxygen-exchange rate of iodate is much higher than that of chlorate and bromate and, contrary to the latter, is also general-base catalyzed.[3] These observations brought Anbar and Guttmann to propose that the iodate ion in solutions exists mainly in the hydrated form $H_2IO_4^-$ through the equilibrium

$$IO_3^- + H_2O \rightleftharpoons H_2IO_4^- \qquad (1)$$

Oxygen-17 nmr (omr) seems to be an ideal tool[4] to study this problem, since the resonance signal of the iodate can be directly observed.[5] In this paper we report the results of such a study and show that the *dominant iodate species in aqueous solutions is* IO_3^-. It is also shown that at high acid concentration oxygen exchange between water and iodate becomes sufficiently fast to affect the omr line width of both the water and IO_3^- resonances. The kinetics of this reaction is studied and it is found that in addition to the reaction studied by Anbar and Guttmann[3] there is an additional reaction, second order with respect to acid, which dominates the exchange rate at high acid concentrations.

Experimental Section

$LiIO_3$ and $HClO_4$ were obtained as the purest available grades from Alfa Inorganic Chemicals and Fluka Chemicals, respectively. The $LiIO_3$ was dried in a vacuum oven at 60° for 10 hr. Water enriched with ^{17}O was obtained from the Institute's enrichment plant and distilled before use. Omr measurements were carried out on a Varian DP-60 nmr spectrometer operating at 8.13 MHz. For the relative intensity as well as for the shift measurements, the absorption mode was recorded using the side band of a 2-kHz field modulation. For the kinetic measurements, both the absorption mode and the derivative of the absorption mode were used. Appropriate corrections were applied to account for broadening due to saturation and modulation effects.

Acidified aqueous solutions were prepared by adding, using a micropipet, small amounts of either a 2.50 or 12.5 *M* $HClO_4$ solution to the $LiIO_3$ solutions.

Results and Discussion

(a) Description of Omr Spectrum and Identification of the Iodate Species. The omr spectrum of a neutral solution of $LiIO_3$ consists[5] of two resonances, the bulk water line and the line due to iodate, lying at -206.4 ± 1 ppm (relative to solvent water) with width of 317 ± 5 Hz. The iodate signal can be observed immediately after preparation of the solution. Its shift was found to be independent of temperature and $LiIO_3$ concentration. In order to identify the iodate species, *i.e.*, whether it is IO_3^- or $H_2IO_4^-$, two experiments were performed. One consisted of direct intensity measurements of the water and the iodate signals and the other involved measurements of the difference in the chemical shift of the solvent water line under conditions of slow and fast exchange, respectively.

(i) Intensity Measurements. These measurements were performed using the high-frequency side-band

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