

Nitrosation of anisole, stability constants of complexes of the nitrosonium ion with aromatic nitroso compounds, and NMR studies of restricted rotation in the complexes

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Received (in Cambridge, UK) 22nd October 1999, Accepted 18th November 1999

Anisole can be nitrosated in good yield under the acidic and anaerobic conditions previously reported for methylbenzenes. The product, 4-nitrosoanisole, is slowly converted into 4-nitrosophenol in acetic–sulfuric acid mixtures. The decrease in the rate constant for this reaction with increasing concentration of nitrosonium ion leads to an estimate of the stability constant of the complex between 4-nitrosoanisole and nitrosonium ion. Stability constants for the similar complexes formed by 4-nitrosotoluene and 1,3-dimethyl-4-nitrosobenzene with nitrosonium ion in trifluoroacetic acid have been determined by UV spectroscopy. Restricted rotation about the bond between nitrogen and aromatic carbon is evident from the ¹H NMR spectra of the complexes; activation parameters for the rotation are reported and compared with similar data in the literature for restricted rotation in uncomplexed aromatic nitroso compounds.

Introduction

Nitrosation of anisole under aqueous or part-aqueous conditions does not give nitrosoanisole but leads directly to 4-nitrosophenol.¹ However a 56% yield of 4-nitrosoanisole has been reported using sodium nitrite in mixtures of dichloromethane and trifluoroacetic acid,² and quantitative formation of 4-nitrosoanisole has been achieved using solutions of nitrosonium tetrafluoroborate in acetonitrile under argon.³ We have reported previously⁴ on the kinetics of nitrosation of *m*-xylene and related compounds in acetic–sulfuric acid mixtures and in trifluoroacetic acid under nitric oxide. The nitroso-products have limited stability, but the strong complexation of the aromatic nitroso compounds with the nitrosonium ion is protective and inhibits their decomposition. We now report that the reaction of anisole is similar, and can give near-quantitative yields of 4-nitrosoanisole if the solution is quenched before the decomposition to 4-nitrosophenol has had time to progress.

The remarkably stable complexes of nitrosoaromatics with nitrosonium ion were first noted by Bosch and Kochi.³ Information about their stability constants is sparse. From a study of the kinetics of the conversion of 4-nitrosoanisole into 4-nitrosophenol in the presence of nitrosonium ion, and information about the extent of protonation of 4-nitrosoanisole under the conditions,⁵ we have been able to estimate the stability constant of the complex between the nitrosonium ion and 4-nitrosoanisole. We have also determined by conventional UV methods the formation constants of the complexes formed by 4-nitrosotoluene and 1,3-dimethyl-4-nitrosobenzene.

Aromatic nitroso compounds exhibit restricted rotation about the bond joining the nitroso compound to the aromatic ring, and activation parameters for such rotations have been deduced from low temperature NMR studies.^{6,7} Similar studies, reported below, show that in the nitrosonium complexes this rotation is much more severely restricted.

Results and discussion

Nitrosation of anisole

“Nitrous acid” is used here to include the N^{III} species HNO₂,

N₂O₃, N₂O₃H⁺, and NO⁺ which may be present in mobile equilibrium in acid solution. The traditional way to introduce nitrous acid is by the addition of sodium nitrite to an acid solution. The slow dissolution of the solid presented difficulties in the present work. As previously we have adopted two alternative methods. For acetic–sulfuric mixtures, commercially available 40% nitrosyl sulfuric acid was used in admixture with acetic and sulfuric acids. Tests showed this gave the calculated concentration of nitrous acid.⁴ In the alternative method, use was made of the purging stream of nitric oxide, the inlet tube for which was fitted with a glass bulb into which oxygen was injected by gas syringe through a septum. This reacts with excess NO to form N₂O₃ (eqn. (1)) which is carried into solution



generating an equilibrium mixture of N^{III} species. Yields of nitrous acid per mol oxygen by this method, which are not quantitative, have been determined.⁴

Trifluoroacetic acid and acetic–sulfuric mixtures have been used as before⁴ because both provide solvent systems of low nucleophilicity in which the predominant N^{III} species is the nitrosonium ion.

Nitrosation in trifluoroacetic acid purged with nitric oxide, with nitrous acid introduced by oxygen injection into the inlet nitric oxide stream, produced good yields of 4-nitrosoanisole together with small amounts of 2- and 4-nitroanisoles (Table 1). Contamination with nitroanisoles increased with the volume of oxygen injected into the nitric oxide stream, perhaps because of incomplete conversion of NO₂ (first formed in the reaction of nitric oxide with oxygen) to N₂O₃. Reaction of anisole was complete within 2 minutes, and there was no change in product yields (in particular no conversion of 4-nitrosoanisole into 4-nitrosophenol) in the following 20 minutes.

Nitrosation in acetic–sulfuric acid mixtures purged with nitric oxide, with nitrous acid introduced either as in the previous paragraph, or by the addition of solid sodium nitrite, or of nitrosyl sulfuric acid, gave rise in each case initially to good yields of 4-nitrosoanisole but the 4-nitrosoanisole was slowly converted into 4-nitrosophenol. A typical time profile is shown

Table 1 Nitrosation of anisole in trifluoroacetic acid

V^a/cm^{-3}	[Anisole]/ mol dm^{-3}	Max yield (%) 4-nitroso- anisole	Yield (%)	
			4-Nitro- anisole	2-Nitro- anisole
180	0.13	64	12	8
180	0.11	70	18	12
90	0.13	90	3	2

^a Volume of oxygen gas at approximately 293 K injected into the inlet stream of NO prior to dissolution of the products in 50 cm³ trifluoroacetic acid. Separate investigation showed that 180 and 90 cm³ gave rise to 0.46 and 0.27 mol dm⁻³ of nitrosonium ion in the trifluoroacetic acid, respectively.⁴

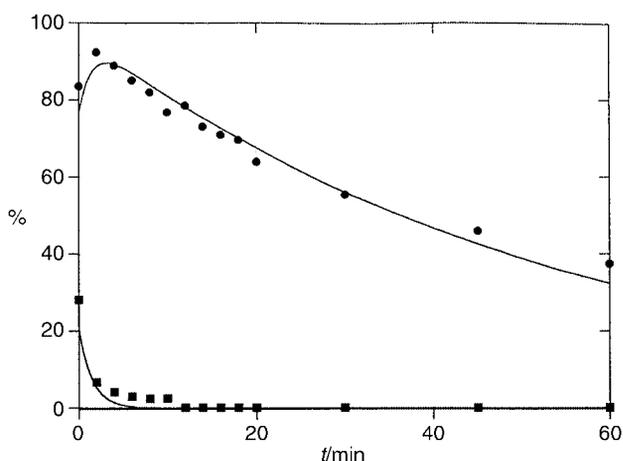


Fig. 1 Concentrations, as they vary with time, of anisole (squares) and 4-nitrosoanisole (circles) expressed as percentages of the initial concentration of anisole (0.116 mol dm⁻³). Points are experimental; curves are best-fitting for two sequential first-order reactions. The solvent was 16% (w/w) of sulfuric acid in acetic acid. The concentration of nitrous acid was 0.26 mol dm⁻³, achieved by injection of oxygen into the inlet stream of purging nitric oxide prior to injection of anisole.

in Fig. 1. Maximum yields of 4-nitrosoanisole were achieved within 3 minutes. With nitrosyl sulfuric acid, or oxygen injection into the nitric oxide inlet, as the source of nitrous acid, these were typically >90%, but somewhat poorer (70–80%) when solid sodium nitrite was used, presumably because the subsequent reaction could occur to a small extent during the time taken for complete dissolution of the solid reagent. Our results showed that neither the maximum yield nor the rate of the subsequent conversion to 4-nitrosophenol were very sensitive to the concentration of sulfuric acid over the range investigated (12–37% sulfuric acid). However the rate of the conversion to 4-nitrosophenol was reduced by high concentrations of nitrous acid, because of protective complexation by nitrosonium ion.⁴ In order to investigate this an independent study was made of the kinetics of conversion of 4-nitrosoanisole into 4-nitrosophenol in the presence of various concentrations of nitrous acid.

Kinetics of conversion of 4-nitrosoanisole into 4-nitrosophenol in deuterioacetic acid–sulfuric acid mixtures

Deuterioacetic acid was used to facilitate NMR investigation of the reaction. Two features of the changes of the NMR spectra with time complicated the interpretation. Firstly, except when additional nitrous acid was absent, the aromatic proton signals were very broad (due to the restricted rotation discussed below) rendering estimation of concentration based on the aromatic signals impossible. Secondly, the signal from the methyl group of nitrosoanisole was steadily replaced by two methyl signals, the smaller of which grew then fell whilst the larger one steadily increased. Separate investigation confirmed that these signals

Table 2 Kinetics of decomposition of 4-nitrosoanisole in 12.1% sulfuric acid in deuterioacetic acid

$a^a/\text{mol dm}^{-3}$	$b^b/\text{mol dm}^{-3}$	$10^2 F^c$	$10^2 F_{1/2}^c$	$k_{\text{obs}}/10^{-4}$ s ⁻¹	$k^d/10^{-4}$ s ⁻¹
0.0787	0	100	100	45	45
0.0938	0.0463	54	100	32	59
0.0840	0.111	10.1	11.2	3.0	29
0.110	0.146	8.1	8.8	3.3	41
0.0704	0.131	5.8	6.0	4.1	70
0.1244	0.185	5.6	5.9	1.3	23
0.0513	0.165	3.4	3.4	1.8	53
0.0521	0.169	3.3	3.3	1.7	53
0.0286	0.199	2.3	2.3	1.2	51

^a Initial concentration of 4-nitrosoanisole corrected by subtraction of the observed approximately constant concentration of 4-nitrosophenol.

^b Initial concentration of NO⁺. ^c See text. ^d $k = k_{\text{obs}}/F$, see text.

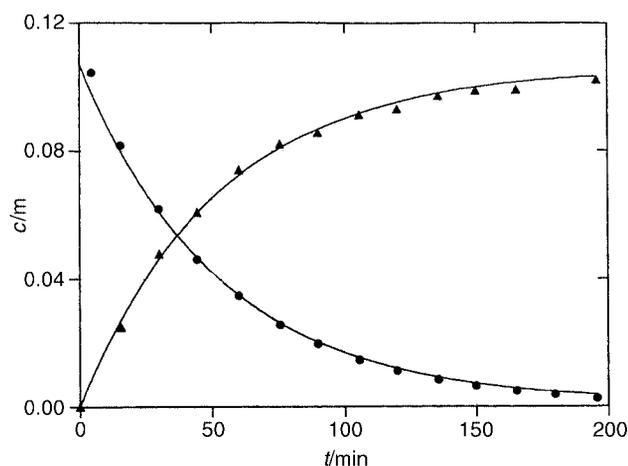


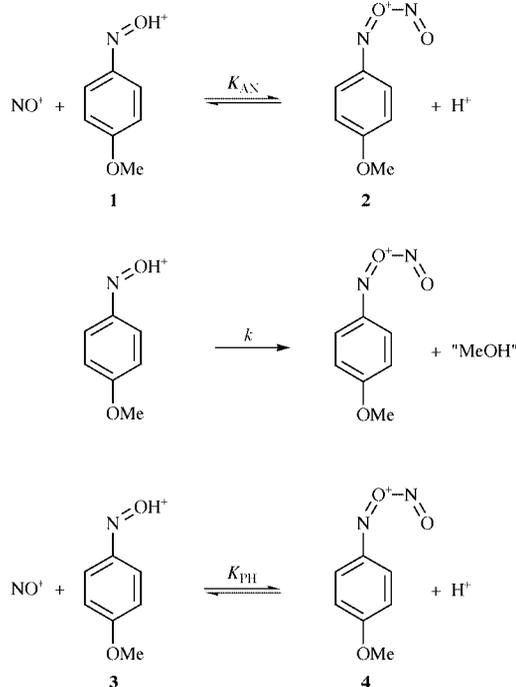
Fig. 2 Concentrations, as they vary with time, of 4-nitrosoanisole (circles) and the sum of methyl acetate and methyl hydrogen sulfate (triangles). Points are experimental; curves are best-fitting for a first-order reaction. For conditions, see Table 2, fourth row.

were due to methyl hydrogen sulfate and methyl acetate respectively and that under the conditions methyl hydrogen sulfate is slowly converted into methyl acetate. (It seems likely by analogy with previous work⁵ that nucleophilic attack on protonated 4-nitrosoanisole at the ring carbon bearing the methoxyl group releases methanol which is immediately converted into a mixture of methyl hydrogen sulfate and methyl acetate, though concurrent S_N2 attack by hydrogen sulfate ion and acetic acid at the methoxyl carbon cannot be ruled out. This aspect of the reaction was not further investigated.)

The best guide to the progress of the nitrosoanisole-to-nitrosophenol reaction was thus the decrease in the methoxyl signal from the 4-nitrosoanisole or, equivalently, the increase in the sum of the methoxyl signals from methyl acetate and methyl hydrogen sulfate. These fitted a first-order rate law, as exemplified in Fig. 2. The first-order rate constants k decreased with the concentration of nitrous acid, as shown in Table 2.

The interpretation of the kinetic results is based on the mechanism shown in Scheme 1, ("MeOH" in Scheme 1 represents methyl acetate plus methyl hydrogen sulfate) in which account is taken of the complexation of both 4-nitrosoanisole and 4-nitrosophenol with nitrosonium ion, and the fact that the conditions are sufficiently acidic for both 4-nitrosoanisole and 4-nitrosophenol to be predominantly protonated,⁵ and for nitrous acid to be present predominantly as NO⁺.⁴

The equilibria are rapid and reversible. The equilibrium constants K_{AN} and K_{PH} represent values of $[2]/([1][\text{NO}^+])$ and $[4]/([3][\text{NO}^+])$ respectively, $[\text{H}^+]$ being constant. A vast excess of nitrous acid was not present, so to account for the observation of good first-order kinetics it is necessary to postulate that the



Scheme 1

fraction F of nitrosoanisole which is uncomplexed (eqn. (2)) does not change significantly during the reaction. If K_{PH} were

$$F = [1]/([1] + [2]) \quad (2)$$

equal to K_{AN} , $[\text{NO}^+]$ and F would be constant through a run, the reaction would be truly first-order, and the rate constant k (Scheme 1) which is independent of the nitrous acid concentration, would be related to the observed first-order rate constant, k_{obs} , by $k = k_{\text{obs}}/F$. It is likely that K_{PH} is equal to or greater than K_{AN} and it is possible to calculate the value of F at one half-life ($F_{1/2}$) on the limiting assumption that $K_{\text{PH}} = \infty$. If even on this extreme assumption $F_{1/2}$ differs only slightly from its initial value F , then close to first-order kinetics would still be observed. Values of F and $F_{1/2}$ were calculated from eqns. (3) and (4), where a is the initial stoichiometric concentration of

$$F = (a - x)/a \quad (3)$$

$$K_{\text{AN}} = x/((a - x)(b - x)) \quad (4)$$

4-nitrosoanisole and x is the concentration of the nitroso complex formed initially, and where b is the stoichiometric concentration of NO^+ . The value of x and thence of F can then be calculated for an assumed value of K_{AN} by solving a quadratic equation. The value of $F_{1/2}$ can be calculated using the same quadratic equation but with a replaced with $a/2$ and b replaced with $b - a/2$.

It was found that, whatever the assumed value of K_{AN} , for most runs $F_{1/2}$ differed insignificantly from F . Thus the first-order kinetic form is consistent with the mechanism if as seems likely K_{PH} is of similar magnitude to or greater than K_{AN} . It is then possible to estimate the value of K_{AN} , seeking that value which leads to a constant value of k ($k = k_{\text{obs}}/F$) for various initial concentrations of both reagents. A value of $K_{\text{AN}} = 250 \text{ dm}^3 \text{ mol}^{-1}$ was found to be optimal in this regard; results are in Table 2 and are arranged in order of decreasing values of F .

The values of k show considerable scatter, but no trend, and it seems reasonable to conclude that the interpretation is correct. The scatter arises because the reaction is not quite quantitative and some side-products were also formed in small but variable amount. These included 4-nitroanisole (usually present in small and nearly constant concentration throughout the run

Table 3 Formation constants K for complexes of nitrosoaromatics with nitrosonium ion

Nitrosoaromatic	Solvent	$K/10^3 \text{ dm}^3 \text{ mol}^{-1}$	Ref.
4-Nitrosoanisole	CH_3CN	>40	3
4-Nitrosoanisole	$\text{CH}_3\text{COOH}-\text{H}_2\text{SO}_4$	50	This work
4-Nitrosotoluene	CF_3COOH	58	This work
1,3-Dimethyl-4-nitrosobenzene	CF_3COOH	38	This work
Nitrosomesitylene	CH_3CN	2	3

and possibly at least in part a contaminant of the 4-nitrosoanisole used) and 4-nitrophenol formed later in the run possibly due to incomplete removal of oxygen in the purging procedure.

The value, $K_{\text{AN}} = 250 \text{ dm}^3 \text{ mol}^{-1}$, has therefore considerable uncertainty (estimated as $\pm 50 \text{ dm}^3 \text{ mol}^{-1}$). It represents the equilibrium value of $[2]/([1][\text{NO}^+])$ in this medium. For direct comparison with formation constants K of similar complexes (see below), where the uncomplexed nitroso compound is predominantly unprotonated, it is necessary to estimate the ionisation ratio, $I = [1]/[4\text{-nitrosoanisole}]$.

Since the value⁸ of H_0 for this medium is -3.0 , and the $\text{p}K_{\text{a}}$ of 4-nitrosoanisole⁵ is -0.69 the best estimate I is $10^{(3.0-0.69)} = 200$ and therefore $K = [2]/([4\text{-nitrosoanisole}][\text{NO}^+]) = K_{\text{AN}}I = 50000 \text{ dm}^3 \text{ mol}^{-1}$. It is noteworthy that Kochi *et al.*³ state that K is greater than $40000 \text{ dm}^3 \text{ mol}^{-1}$ in acetonitrile.

Formation constants, K , for nitrosonium ion complexes of 4-nitrosotoluene and 1,3-dimethyl-4-nitrosobenzene in trifluoroacetic acid

These nitroso compounds are insufficiently basic to be significantly protonated in trifluoroacetic acid.^{5,9} The formation constants (eqn. (5)) were measured directly, conventionally by UV.



Their values were so large that it was necessary to work with very low concentrations of both nitrosoaromatic and nitrosonium ion. This and the small difference in molar absorption coefficient between the complexed and uncomplexed nitrosoaromatic severely limited the accuracy of the measurements.

It was nevertheless possible to achieve meaningful results and these are in Table 3, where they are compared with the value for 4-nitrosoanisole and with the only literature values. The results so far on the formation constants of these complexes indicate quite unusual stability. There is at present no clear evidence as to the structure of these complexes, but our NMR studies, reported below, cast some light on this.

Variable temperature dynamic NMR studies of nitrosoaromatic-nitrosonium ion complexes

The restricted rotation about the bond between aromatic ring carbon and nitrogen in the complexes was investigated using dynamic NMR. Spectra were collected at 10 K intervals over the range 263 to 323 K. Each showed a static spectrum at 263 K from which chemical shifts for the individual rotamers were deduced. The peaks broadened and coalesced as the temperature was raised. Appropriate parts of the spectra were simulated using a computer package.¹⁰ The aromatic proton signals were simulated in the case of the 4-nitrosotoluene complex as illustrated in Fig. 3. In the cases of the nitrosonium ion complexes of 1,2-dimethyl-4-nitroso and 1,3-dimethyl-4-nitrosobenzenes, the methyl signals were used. Activation parameters for the rotations are in Table 4, where they are compared with literature data for the rotation of the nitroso group in the uncomplexed nitrosoaromatics.

Table 4 Activation parameters for rotation about the bond joining nitrogen to the aromatic ring in nitrosoaromatic–nitrosonium ion complexes compared with, where available, literature values⁷ for the parent nitrosoaromatic (figures in parentheses)

Nitrosonium complex of	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$
4-Nitrosotoluene	85 ± 3 (39 \pm 1)	80 ± 8 (12 \pm 5)
1,2-Dimethyl-4-nitrosobenzene		
Major to minor isomer	79 ± 2 (40 \pm 1)	48 ± 6 (16 \pm 4)
Minor to major isomer	80 ± 2 (39 \pm 1)	53 ± 5 (16 \pm 4)
1,3-Dimethyl-4-nitrosobenzene		
Major to minor isomer	94 ± 4	89 ± 11
Minor to major isomer	94 ± 4	102 ± 12

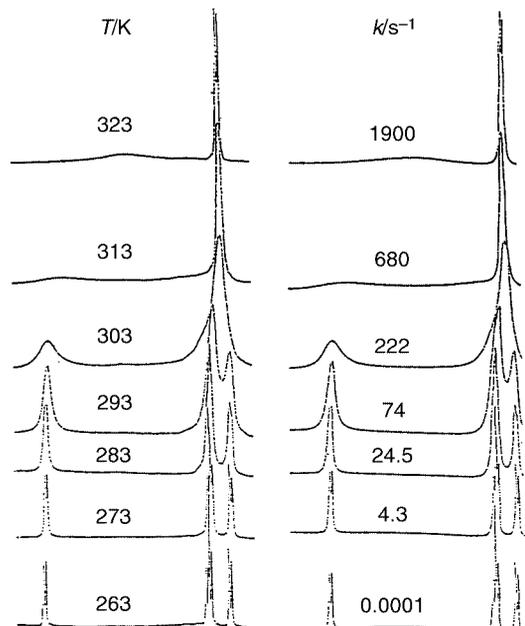
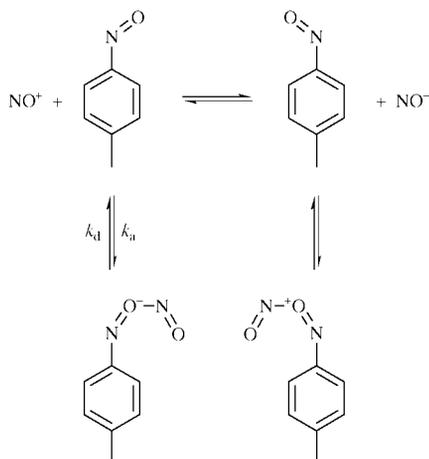


Fig 3 ¹H NMR spectra at various temperatures of the aromatic region of the 4-nitrosotoluene–nitrosonium ion complex. Actual spectra and temperatures on the left, simulated spectra and exchange rate constants on the right.

Enthalpies and entropies of activation are both considerably greater than in the uncomplexed materials. The much more positive entropies of activation indicate that the mechanism of rotation is different, and are more consistent with a mechanism in which isomerisation is achieved, not by rotation in the complex, but by rate determining dissociation, rotation of the uncomplexed nitrosoaromatic, and reassociation, as in Scheme 2.

If this is the mechanism it is possible to deduce rate constants



Scheme 2

for dissociation and association, k_d and k_a respectively, of the complex, because they are related to the observed rate constant for isomerisation, k_{obs} , and the formation constant K for the complex (value in Table 3), by eqns. (6) and (7).

$$k_d = 2k_{\text{obs}} \quad (6)$$

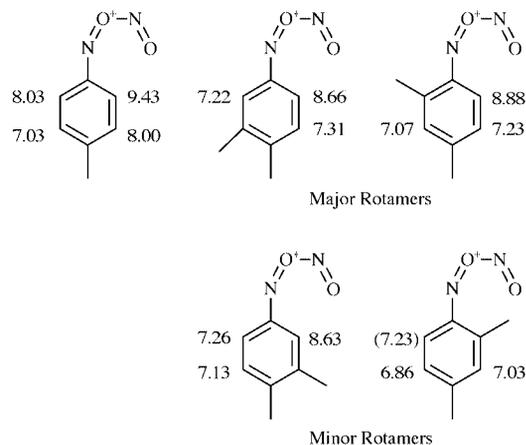
$$k_a = 2K k_{\text{obs}} \quad (7)$$

Thus, $k_d = 256 \text{ s}^{-1}$, and $k_a = 1.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The latter value does not exceed that for encounter, so the mechanism is feasible. If it is correct then the free energy barriers to direct rotation must be even higher than those indicated by the activation parameters in Table 4.

Chemical shifts of the aromatic protons of the rotamers of the complexes

These were determined from the low-temperature spectra of the complexes. There is no firm evidence available at present as to the structure of the complexes. However the following points are indicative. Firstly, the severely restricted rotation about the carbon–nitrogen bond (see above) indicates that this bond has some double bond character and therefore that conjugation between the ring and the nitrogen is possible. This supports the view³ that complexation is through the oxygen rather than the nitrogen atom of the nitroso compound. Secondly, whereas the rotamers of 1,2-dimethyl-4-nitrosobenzene complexes are nearly equally abundant, with the 1,3-dimethyl-4-nitrosobenzene complexes one rotamer is much preferred. This, and the fact that nitrosomesitylene forms much weaker complexes than either (Table 3), indicates that there is hydrogen bonding between the terminal oxygen of the complex and the nearest *ortho* aromatic proton which provides stability and additional resistance to rotation. Where the *ortho* proton is replaced by methyl (minor rotamer of the complex of 1,3-dimethyl-4-nitrosobenzene, and the complex of nitrosomesitylene) stability is much reduced. With these thoughts in mind the structures are drawn, rather tentatively, as in Scheme 3, which



also shows the chemical shifts of the aromatic protons. (One value is in parentheses because of imprecision caused by peak overlap.) The relatively large chemical shifts of the *ortho* protons nearest to the terminal oxygen of the complexes are consistent with some hydrogen-bonded interaction. The double bond character of the carbon–nitrogen bond, presumably greater than in the uncomplexed nitroso compound, must confer some positive charge to the *para* position and thus enhance susceptibility to nucleophilic attack but this effect must be less than in the protonated nitroso compound because complexation provides protection towards nucleophilic attack.

Experimental

Materials

Trifluoroacetic acid (99%) was distilled from 10% (v/v) sulfuric acid, under nitrogen. Dichloromethane (Fischer) was distilled from calcium hydride. Oxygen was dried by passing through a column of diphosphorus pentoxide prior to use.

4-Nitrosoanisole. 50 cm³ of a mixture of aristar grade glacial acetic acid (100.0 g), 40 wt.% nitrosyl sulfuric acid (14.8 g) and sulfuric acid (45.5 g) were placed in a thermostatted vessel at 25 °C and nitrogen was allowed to flow for 30 minutes. The gas flow was then changed to nitric oxide. After a further 30 minutes anisole (0.9 g, 8.3 mmol) was added by injection. The solution turned opaque dark red/brown. After 1 minute the gas flow was changed back to nitrogen for 1 minute. The solution was then quenched in saturated sodium hydrogen carbonate solution (1000 cm³), the crude product was extracted using dichloromethane (3 × 150 cm³), the organic layers were collected, dried (MgSO₄), filtered and the solvent removed on a rotary evaporator. The crude product was purified by column chromatography (60 g flash silica, 20% v/v dichloromethane in hexane). The blue fraction was collected, 0.6 g, 53%. Mp (19–21 °C, lit.¹¹ 21 °C) $\nu_{\max}/\text{cm}^{-1}$ (CH₂Cl₂) 1501 (N–O), δ_{H} (300 MHz, CDCl₃) 7.92 (2H, bd, *J* 7.9 Hz, C(3)H, C(5)H), 7.03 (2H, d, *J* 7.9 Hz, C(2)H, C(6)H), 3.95 (3H, s, OCH₃).

4-Nitrosotoluene, 1,2-dimethyl-4-nitrosobenzene, and 1,3-dimethyl-4-nitrosobenzene. These were prepared as described.⁴

Nitrosation of anisole in acetic–sulfuric acid mixtures using oxygen injection into the nitric oxide purging gas

1,2-Dinitrobenzene (GC reference standard, 0.6087 g, 3.62 mmol) was dissolved in 50 cm³ of 16.3% sulfuric acid in acetic acid (by mass). The vessel was placed in a water bath at room temperature (22 °C), nitrogen was then passed through the reaction vessel for 2 hours; after this time the gas flow was changed to nitric oxide. Oxygen (90 cm³) was then injected into the nitric oxide flow. On injection the gas flow turned brown and on being carried into solution the colour of the solution turned green. After a further 15 minutes, anisole (0.63 g, 5.83 mmol) was added by injection into the reaction vessel. Aliquots (≈1 cm³) taken at intervals were quenched in a mixture of 30 cm³ saturated sodium hydrogen carbonate solution and 5 cm³ dichloromethane, the solutions were shaken and the dichloromethane layers extracted, washed with water and then analysed by gas chromatography. Results are shown in Fig 1.

Nitrosation of anisole in trifluoroacetic acid using oxygen injection into the nitric oxide purging gas

Trifluoroacetic anhydride (3.6–4.0 g) was added to 50 cm³ of 100% trifluoroacetic acid and placed in a jacketed vessel, thermostatted at 28 ± 1 °C with nitrogen passing through under constant stirring for 2 hours. The gas flow was then changed to nitric oxide, and after a further 15 minutes, oxygen (90–180 cm³) was injected into the nitric oxide flow. The gas turned brown, on being carried into solution the solution turned dark apple green. A solution of 1,2,3-trichlorobenzene (GC reference standard) in anisole was added by injection and the solution immediately turned a deep red/brown colour.

Aliquots (≈1 cm³) taken at intervals were quenched in a mixture of 30 cm³ saturated sodium hydrogen carbonate solution and 5 cm³ dichloromethane; the solutions were shaken and the dichloromethane layers extracted, washed with water and then analysed by gas chromatography. Results are shown in Table 1.

Kinetics of conversion of 4-nitrosoanisole into 4-nitrosophenol

A typical experiment is described. Acetonitrile (NMR refer-

ence, 0.0108 g) deuterioacetic acid (CD₃CO₂D, 3.221 g) sulfuric acid (0.329 g) and 40% nitrosyl sulfuric acid (0.128 g) were mixed and purged with nitrogen for 15 minutes. 1 cm³ was then removed and placed in a sealed vessel preflushed with nitrogen for 5 minutes, and weighed. A further 0.5 cm³ was placed in a sealed NMR tube preflushed with nitrogen. This tube was used to preshim the NMR. 40 μl of a solution of 4-nitrosoanisole in deuterioacetonitrile (2.58 mol dm⁻³) was then added by injection into the vessel containing 1 cm³ of the acid mixture and a timer was started. This vessel was shaken and 0.5 cm³ was transferred to a second NMR tube preflushed with nitrogen. This solution was then analysed by NMR over a period of time at a probe temperature of 303 K.

Measurement of equilibrium constants for nitrosoaromatic–nitrosonium ion complexes

4-Nitrosotoluene–nitrosonium ion complex. Solutions of 4-nitrosotoluene (2.7 mmol dm⁻³) in acetonitrile (solution A), trifluoroacetic anhydride (0.106 mol dm⁻³) in trifluoroacetic acid (solution B) and of sodium nitrite (11.5 mmol dm⁻³) in trifluoroacetic acid (solution C) were each prepared under nitrogen.

Appropriate aliquots of solutions B and C were mixed under nitrogen in a UV cuvette. The cuvette was placed into a thermostatted cell compartment at 25.0 ± 0.2 °C. At zero time 20 μl of solution A was injected, the cell shaken and the absorbance measured at 367, 370, 373, 377, 380 and 383 nm over 1 minute intervals for 5 minutes. Initial absorbances were deduced by linear back extrapolation.

4-Nitroso-*meta*-xylene–nitrosonium ion complex. This was investigated in a similar way. The absorbance was measured at 363, 366, 370, 373 and 376 nm.

Variable temperature NMR studies of nitrosoaromatic–nitrosonium ion complexes

4-Nitrosotoluene–nitrosonium ion complex. Into a 5 cm³ graduated flask was placed sodium nitrite (0.0141 g, 0.204 mmol) and the flask was purged with nitrogen for 15 minutes. Into a 5 cm³ graduated flask was placed trifluoroacetic anhydride (0.158 g, 0.752 mmol) and deuterotrifluoroacetic acid (3.060 g). The flask was sealed and purged with nitrogen for 15 minutes. 1 cm³ of this solution was added to the flask and shaken so that the sodium nitrite dissolved. 0.5 cm³ of this was then placed into a sealed NMR tube which had been preflushed with nitrogen. 20 μl of a solution of 4-nitrosotoluene (0.2695 g, 2.22 mmol) in deuterioacetonitrile (0.9 cm³) was then added and the sample studied using variable temperature NMR.

4-Nitroso-*ortho*-xylene–nitrosonium ion complex and 4-nitroso-*meta*-xylene–nitrosonium ion complex. These were studied similarly.

Acknowledgements

We wish to thank the EPSRC and ZENECA for a CASE award for D. R. N., and Drs K. G. Orrell and V. Sik for helpful discussions.

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Paper a908441j