Kinetics of the oxidation of aromatic *C*-nitroso compounds by nitrogen dioxide

Brian G. Gowenlock,[*,†] **Josef Pfab**[*] **and Victor M. Young**

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh, UK EH14 4AS

The oxidation of nitrosobenzene by nitrogen dioxide in carbon tetrachloride has been re-examined, the rate of reaction exhibiting first-order dependence upon the concentrations of both nitrosobenzene and nitrogen dioxide, with a reactant stoichiometry of 1:1. The rate of reaction is found to be highly sensitive to the presence of trace quantities of water and intensive drying procedures for the solvent have been developed such that the reaction rate could be reduced to a constant level. For nitrosobenzene and a range of substituted nitrosobenzenes the kinetics of the oxidation reaction in carbon tetrachloride have been studied over the temperature range 291–313 K using the stopped flow technique and pseudo-first-order conditions with the nitrogen dioxide in excess. Arrhenius parameters have been obtained for 15 nitrosoarenes and the results obtained are discussed with reference to the Hammett σ constants and the electron population at the nitroso nitrogen as determined by CNDO calculations. It is concluded that the reaction occurs by a radical addition mechanism to the nitroso nitrogen atom giving an unstable aminoxyl intermediate which decomposes rapidly giving the corresponding nitrobenzene and nitric oxide.

The oxidation in solution of *C*-nitroso compounds to *C*-nitro compounds [reaction (1)] is well established for a wide variety

$$\text{R−N=O} + [\text{O}] \longrightarrow \text{R−NO}_2 \qquad (1)$$

of oxidising agents although kinetic studies of such oxidation reactions are confined to the oxidants peroxyacetic acid,[1] peroxychloroacetic acid,[1] Caro's acid,[1] dinitrogen tetroxide,[2] peroxydisulfate anion[3] and nitric acid[4] with a relatively limited range of substituted nitrosobenzenes, *i.e.* *p*-H, Cl, Br, CH_3, OCH_3,[1] 2,5-dimethyl,[2] OH[3] and *p*-Cl, CH_3 and *m*-Cl, NO_2 and CH_3.[4] In the first of these studies it was reported that the oxidation by peroxyacetic acid in aqueous ethanol was second order overall, being first order in each reactant. The reaction was accelerated by electron-releasing *para* substituents, retarded by electron-withdrawing *para* substituents and accelerated also by increasing the water content of the solvent. The authors[1] suggested that the nitroso nitrogen performed a nucleophilic attack on the outer oxygen atom of the peroxyacid, the transition state being made up of the peroxyacid, the nitroso compound, and a solvent molecule. A similar nucleophilic attack was proposed for the nitroso nitrogen in the reaction of the *p*-nitrosophenoxide ion with the peroxydisulfate dianion.[3] Bonner and Hancock[2] suggested the possibility of a 1,3-cycloaddition mechanism when nitrogen dioxide, the reactive species in the equilibrium with dinitrogen tetroxide, reacts with the 2,5-dimethylnitrosobenzene. Ogata and Tezuka[4] suggested that the mechanism of reaction (1) involved addition of the radical species, nitrogen dioxide, to the nitroso group and that this involved addition to the oxygen, producing the radical $\text{PhN}^{\bullet}\text{O-NO}_2$, rather than addition to the nitrogen and production of $\text{PhN(ONO)O}^{\bullet}$.

There is an early report[5] that a small quantity of nitrobenzene was formed when dry chloroform solutions of nitrogen dioxide and nitrosobenzene were allowed to stand at 22 °C for 39 h.

Gas phase studies of reaction (1) have been confined to the case of *C*-nitrosoalkanes. Thus for the case of R = *tert*-butyl it has been shown[6] that the reaction involved transfer of an oxygen atom from the nitrogen dioxide to the nitroso compound, and that the reaction obeyed mixed second-order kinetics.[7]

Experimental

C-Nitrosocompounds

These were all made by standard procedures usually from either the corresponding nitro compound *via* reduction to the *N*-substituted hydroxylamine followed by oxidation using either ferric chloride or aqueous dichromate (Method 1), or by controlled oxidation of the corresponding amino compound using Caro's acid (Method 2). The products were purified by recrystallisation and in some cases this was followed by sublimation. All compounds were stored at −20 °C. The solid compounds were *trans*-dimers with the exception of nitrosobenzene itself which was the *cis*-dimer. The compounds prepared are listed in Table 1.

Nitrogen dioxide–dinitrogen tetroxide

Cylinder nitrogen dioxide (Matheson) was purified by mixing with a stream of dry oxygen and passing slowly through a 2 × 20 cm column of phosphorus pentoxide before cooling and collection. The resultant liquid was then slowly distilled under reduced pressure and a small middle fraction was collected and stored at 0 °C in a glass vessel fitted with a rotaflo tap. Alternatively, excess dry oxygen was mixed with nitric oxide which had been purified by slow distillation at −150 °C. The nitrogen dioxide product was deoxygenated and stored as before. All samples were completely free from dinitrogen trioxide as the solid material produced on cooling to low temperatures was free from blue colour.

Dry white fuming nitric acid was prepared by the addition of urea to commercial fuming nitric acid followed by the addition of at least three times its volume of concentrated sulfuric acid and the subsequent slow distillation of a fraction of the nitric acid which was collected and stored at −20 °C in a glass vessel fitted with a rotaflo tap.

Commercial 'white spot' nitrogen was dried by passing it through an activated bed of 5 Å molecular sieve.

Solvents

The carbon tetrachloride used as solvent for kinetic experiments was commercially available and was purified by three methods hereafter named G1, 2 and 3. G1 was purified by distillation only. G2 was the product from G1 obtained by repeated shaking with aliquots of concentrated sulfuric acid, followed by

---

[†] Present address: Department of Chemistry, University of Exeter, Exeter, UK EX4 4QD.

Table 1 Preparation of substituted nitrosobenzenes

Substituent	Method	Ref.	Mp (lit. value)/°C	$\lambda_{max}(CCl_4)$/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}
H	1	8	67 (68[9])	762	50
2,5-di-CH_3	1	10	98 (101.5[11])	*a*	
4-CH_3	1	9	48 (48[12])	760	53
4-OCH_3	*b*	13	32 (32–34[14])	742	56
4-Cl	2	15	90 (90[15])	756	46
4-Br	2	15	94 (94[9])	760	49
4-NO_2	2	16	119 (118–119[17])	788	43
4-CN	2	16	135–136dec (136–137[18])	782	38
4-$COCH_3$	2	16	110 (111[19])	780[c]	42
4-CO_2CH_3	2	16	129.5 (128–129.5[20])	776	45
3-CH_3	2	16	53 (53[12])	764	50
3-OCH_3	2	16	49 (48[21])	758	50
3-Cl	2	16	72 (72[12])	764	28
3-$COCH_3$	2	16	81.5	762	45
3-CN	2	16	107–108 (111[22])	760[d]	23
2-CH_3	*e*	—		760	39

[a] Not measured. [b] Prepared from reaction of 4-nitrosophenol with methanol.[13] [c] Solvent contains added 5% CH_2Cl_2. [d] Solvent contains 10% added CH_2Cl_2. [e] Commercial product.

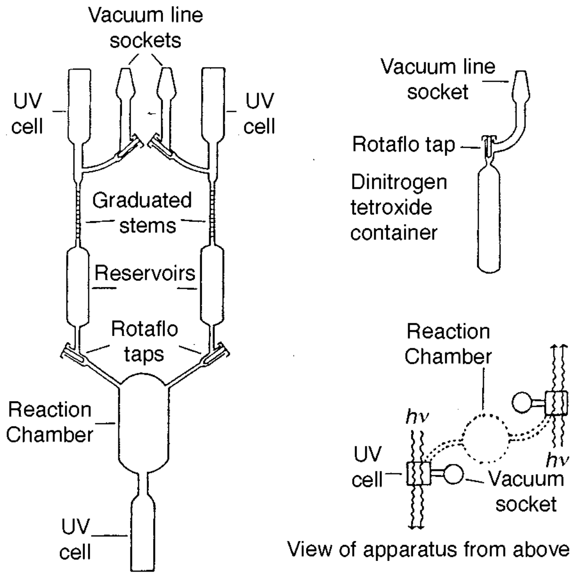


Fig. 1 Vessels used for the spectrophotometric method

passing the separated solvent down a column of commercial alumina under dry nitrogen to remove any suspended acid droplets and any remaining water. It was then stored and used under dry nitrogen. G3 was prepared from G2 by adding a further purification stage. The solvent was passed, under dry nitrogen, down a column of highly activated alumina (previously heated to 250 °C under vacuum and handled under dry nitrogen only), then degassed by repeated freeze–thaw cycles and distilled into a storage vessel on the vacuum line. For all subsequent usage it was vacuum distilled into the reaction vessels and used for reaction under an atmosphere of dry nitrogen. For any case where dichloromethane was used as solvent it was purified as for G3 carbon tetrachloride, stored under vacuum with exclusion of light and used within two days of the purification procedure.

UV–VIS absorption spectra were measured using a Pye-Unicam SP 1800 spectrophotometer. NMR spectra were obtained from a Perkin-Elmer R12, 60 MHz spectrometer and IR spectra were recorded on a Perkin-Elmer 157G grating spectrometer. Kinetic studies were carried out using two techniques: either by optical density measurements with the thermostatted SP 1800 spectrophotometer or by stopped flow spectrometry using a Nortech SF-1A apparatus.

Chromatographic techniques

Thin layer chromatographic plates used were commercial Merck Kieselgel GF_{254} precoated plates. Columns for preparative liquid chromatography were slurry packed with Merck Kieselgel 60, 0.040–0.063 mm (230–400 mesh ASTM). HPLC was carried out using a Haskell pressure multiplying pump and the eluted fraction was monitored with a Cecil CE 212 variable wavelength UV detector connected to a Servoscribe 1s chart recorder. The HPLC columns were 5 mm bore, internally polished, stainless steel tubes with a septum injector bolted to the top and a fine sintered frit at the bottom. A 25 cm column was filled with 5 μm Spherisorb silica gel by slurry packing from a reservoir under a pressure of 3000 psi. Disturbance of the surface of the column was avoided by use of a fine wire disc on top of the packing. Samples were added through the septum, directly onto the top of the column. The column was packed using methanol and this was gradually changed to the required solvent for analyses, namely isooctane–diethyl ether in a 9 : 1 ratio.

Following identification of the compounds present in a sample, the HPLC was calibrated by injection of these compounds in known concentrations at a fixed wavelength. The amount of compound eluted was determined from the recorded peak area and a previously determined response factor.

Experimental method for the spectrophotometric technique

The dried solvents and reactants were introduced into and handled in an all-glass reaction vessel as shown in Fig. 1. The complete reaction vessel was evacuated and the interconnecting taps were closed. The two reservoirs had known capacities and any volume of solvent which filled the graduated stems could be accurately read. The approximate weight of nitrosoarene was weighed into one of the reservoir socket stems and then degassed on a vacuum line. Solvent was then distilled in from a storage bulb on the vacuum line and condensed into the socket stem. The reservoir tap was then opened and all the reactant was washed into the reservoir. More solvent was distilled in until the level had reached an appropriate point on the graduated stem. The reservoir tap was then closed and the other side-arm connected to the vacuum line and evacuated. Solvent was distilled into the reservoir until just below the graduated stem. The reservoir tap was closed and the socket stem evacuated. An approximate amount of nitrogen dioxide was distilled in from a small container, as shown in Fig. 1, and condensed into the socket stem. The top of the nitrogen dioxide reservoir was cooled using a cotton wool pad dipped in liquid nitrogen and the reservoir tap was opened allowing the condensed nitrogen dioxide to flow in rapidly. The volume of the solvent in the reservoir plus the dissolved nitrogen dioxide now filled the reservoir to a point on the graduated scale and its volume was read off after thermostatting to 20 °C. The concentrations of both

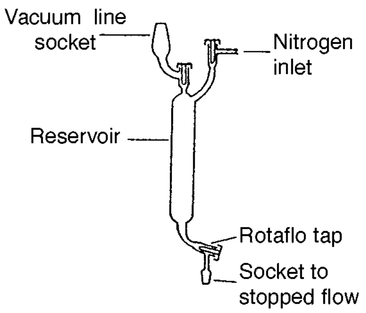


Fig. 2 Reactant storage vessel for the stopped flow apparatus

reactants were now measured spectrophotometrically by measurement of their UV–VIS absorbances at the appropriate wavelengths, the extinction coefficients being known from previous determinations. The apparatus was inverted to fill the two upper UV cells, the spectrometer being fitted with a shaped cover to exclude any outside light. To obtain the concentration of nitrogen dioxide it was necessary to consider the equilibrium with dinitrogen tetroxide; from knowledge of the volumes of both reactant solutions it was possible therefore to calculate the equilibrium concentrations of both NO_2 and N_2O_4 in the mixed solutions as well as the initial concentration of the nitrosoarene in the reaction chamber. The mixing of the thermostatically controlled solutions (20 °C) was carried out by opening the taps connecting the sidearms to the reaction chamber, timing the start of the reaction, shaking the apparatus to ensure thorough mixing of the reactants, followed by rapid insertion into the spectrophotometer where the disappearance of the nitrosoarene was monitored using the absorption in the range 700–800 nm where neither the nitrogen dioxide–dinitrogen tetroxide nor the nitroarene product absorb light. This technique enables the rate constant for the bimolecular reaction between nitrogen dioxide and the nitrosoarene to be determined, but the stopped flow technique is both more accurate and more convenient to use and the description of this technique follows.

Experimental method for the stopped flow technique

The reactant storage vessels used in our experiments were designed to avoid moisture and air contact and are shown in Fig. 2. A storage vessel was connected to the vacuum line and evacuated. It was then weighed and a known weight of nitrosoarene was inserted into the stem of the connection to the vacuum line and the connection stem was evacuated. Dried solvent was then distilled in from a storage bulb and the upper tap opened allowing the nitrosoarene to be washed completely into the storage vessel. Solvent was then distilled in until the vessel was approximately three-quarters full. The taps were then closed and the vessel allowed to warm to room temperature after which it was weighed. The volume of solvent contained in the reservoir could then be calculated from its initial weight and the weight of added nitrosoarene. Alternatively the nitrosoarene concentration could be determined from the absorbance of the nitrosoarene at its λ_{max} in the 750 nm region using the stopped flow spectrophotometer. The agreement between these two measurements showed that any loss by sublimation of the nitrosoarene in its introduction procedure was negligible.

The nitrogen dioxide solution was made up in a similar fashion by first evacuating a reactant storage vessel, weighing it, then three-quarters filling it with dried solvent and reweighing it. Nitrogen dioxide was then distilled into a small storage vessel as described for the spectrophotometric method and accurately weighed. It was then carefully and quantitatively transferred to the carbon tetrachloride in the reaction storage vessel using liquid nitrogen cooling of the storage vessel neck to ensure complete transfer. This vessel and the small nitrogen dioxide storage vessel were then reweighed to ensure that transfer was complete. Both reaction storage vessels with their respective solutions of reactant in carbon tetrachloride were then filled with dry nitrogen to atmospheric pressure from the vacuum line and transferred to the stopped flow apparatus. At this point the glass tubes of the stopped flow apparatus were filled with carbon tetrachloride.

The oscilloscope scales were then adjusted with reactant injections so as to obtain a full scale trace on the screen of nitrosoarene disappearance with time. All traces and light levels were then stored on the storage oscilloscope and recorded using a Polaroid camera (black and white film) for future measurement. A reaction run was thus performed at the designated temperature, the trace recorded, and the flow cell flushed out with either reactant. The temperature was then adjusted and allowed to stabilise at the next desired temperature. Following recalibration of the intensity levels a reaction run was performed as before and then further repeated at additional temperatures. The reaction storage vessels were attached to a supply of dry nitrogen and as each aliquot of sample or reactant was drawn off into the thermostatted coils it was replaced by a corresponding volume in the storage vessels.

From the photographic record the absorbance (A) of the nitrosoarene was measured at various reaction times thereby enabling the pseudo-first-order rate constant to be calculated. The nitrogen dioxide concentration was obtained from the known values[23] for the equilibrium constant and enthalpy of dissociation of the dinitrogen tetroxide–nitrogen dioxide system and the concentration of dinitrogen tetroxide calculated from its known[24] extinction coefficient of 200 $dm^3\ mol^{-1}\ cm^{-1}$ at λ_{max} 342 nm and its measured absorbance. The nitrogen dioxide concentration remains constant throughout each experimental run due to the large 'reservoir' of dinitrogen tetroxide and the very fast re-establishment of equilibrium. From the nitrogen dioxide concentration and the pseudo-first-order rate constant the second-order rate constant k_2 was obtained.

Results

The stoichiometry of reaction (2) was established by Bonner

$$RNO + NO_2 \longrightarrow RNO_2 + NO \qquad (2)$$

and Hancock[2] for the case of 2,5-dimethylnitrosobenzene: they showed that the ratio of $RNO:NO_2:RNO_2$ was 1:1:1. We have confirmed this for nitrosobenzene using quantitative HPLC analysis and assume that it is operative for all the substituted nitrosobenzenes which we have studied. Support for this assumption is afforded by our observation that in all cases TLC analysis of the products of reaction revealed only one product.

In the Experimental section we have drawn attention to the different levels of purification of solvent that we have employed. These considerations are exemplified by the rate constant data collected in Table 2 which relate to the influence of solvent dryness and influence of air upon the values obtained for the nitrosobenzene–nitrogen dioxide reaction. Because of its importance as the only case in the literature where a rate constant value had been obtained for the oxidation by nitrogen dioxide of a substituted nitrosobenzene, a rate constant measurement was made for 2,5-dimethylnitrosobenzene using G3 solvent under nitrogen and UV spectrophotometry at 292 nm as in ref. 2. The reaction was so slow as to be almost unobservable and the maximum possible value for the rate constant at 20 °C was 0.028 $dm^3\ mol^{-1}\ s^{-1}$. Discussion of the difference between this value and that reported by Bonner and Hancock[2] (1.86 $dm^3\ mol^{-1}\ s^{-1}$) is deferred to the Discussion section.

A preliminary study of the reaction of nitrosobenzene with a six-fold excess of dry fuming nitric acid in G3 solvent was made using spectrophotometric monitoring of the nitrosobenzene concentration. An initial small drop in the nitrosobenzene concentration was followed by no change in absorbance over a period of 16 hours. A slow increase in absorbance followed over

Table 2 Dependence of rate constant values at 20 °C upon experimental conditions

Experimental conditions				k/dm^3 mol^{-1} s^{-1}
Solvent	Gas phase	Other	Apparatus	
G1	Air		*a*	0.79
G1	Air		*b*	0.97
G1	Air		*b*	1.02
G1	Air	*c*	*b*	0.81
G1	Air	*d*	*b*	0.74
G2	N_2		*a*	0.42
G3	N_2		*a*	0.18
G3	N_2		*a*	0.27
G3	N_2	*e*	*a*	0.27
G3	N_2	*f*	*b*	0.13
G3	N_2	*g*	*b*	0.21

[a] Spectrometer. [b] Stopped flow. [c] PhNO : NO_2 = 2 : 1. [d] PhNO : NO_2 = 1 : 2. [e] Highly purified commercially available NO_2. [f] Highly purified NO_2 prepared from NO–O_2. [g] Highly purified NO_2 containing traces of white fuming HNO_3.

a two hour period followed by a decrease accompanied by evolution of nitrogen dioxide. In order to test the assumption of an initial protonation of nitrosobenzene followed by a long induction period during which decomposition of the nitric acid takes place, the experiment was repeated with addition of crystalline sodium nitrite to the mixture. A yellow coloration appeared followed by slow evolution of nitrogen dioxide accompanied by a more rapid diminution of the nitrosobenzene concentration.

Discussion

The effect of water upon the reaction is exemplified by the progressive lowering of the rate constant as more stringent experimental conditions for the removal and exclusion of moisture are introduced. Once the effect had been recognised for nitrosobenzene itself it was necessary to carry out a study of the nitrogen dioxide–2,5-dimethylnitrosobenzene reaction as this was the only reaction of nitrogen dioxide with a nitrosoarene which had previously been subjected to a kinetic investigation. The very large difference in the values of the rate constant obtained is due to the differences in the experimental techniques employed. In the method adopted by Bonner and Hancock,[2] the reactants, each dissolved in ‘reasonably dry’ carbon tetrachloride and thermostatted in flasks, were pipetted together into a reaction cell. Our technique emphasises rigorous drying, handling the reactants under dry nitrogen and strict exclusion of the atmosphere. The apparatus used for the stopped flow technique permits these conditions to be better achieved than does the use of the spectrophotometric cell method and consequently our discussion of results obtained relates entirely to the stopped flow kinetic data. We consider that we have reduced any water effect to negligible proportions. The reaction with 2,5-dimethylnitrosobenzene was not investigated further by the stopped flow method because it is too slow to yield accurate results by this method, as back diffusion of the reactants into the reaction cell would be considerable over the necessary reaction time.

There are several studies of the kinetics of bimolecular reactions of substituted nitrosobenzenes[1–4,12,25–31] and all of these, studied over a range of temperatures, have large negative entropies of activation. Thus the oxidation reactions[1,25] have $\Delta S^\ddagger$ values in the range -109 to -138 J mol^{-1} K^{-1}, the condensation reactions[12,26] have $\Delta S^\ddagger$ values in the range -227 to -264 J mol^{-1} K^{-1}, the Diels–Alder reactions[29,30] have $\Delta S^\ddagger$ values in the range -123 to -145 J mol^{-1} K^{-1} and the radical addition reactions[31] have $\Delta S^\ddagger$ values in the range -93 to -129 J mol^{-1} K^{-1}. Our values for $\Delta S^\ddagger$ are similar to those for the oxidation, Diels–Alder and radical addition reactions. Extending these considerations to the $\Delta H^\ddagger$ values it can be seen that our values are similar to those obtained for the *m*-chloroperbenzoic acid oxidation of nitrosobenzene in a variety of solvents (44–60 kJ mol^{-1}) and Diels–Alder addition reactions of 2,3-dimethylbutadiene to *para*-substituted nitrosobenzenes (49–60 kJ mol^{-1}), but higher than those for the addition of alkyl radicals to nitrosocompounds (4–8 kJ mol^{-1}).

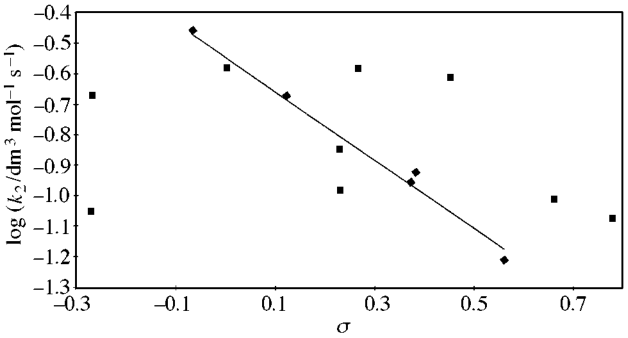
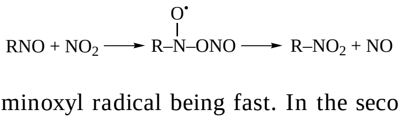


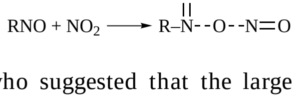
Fig. 3 Variation at 298 K of $\log_{10}$ (k_2/dm^3 mol^{-1} s^{-1}) with Hammett σ constant of substituent X in XC_6H_4NO, *p*-X (■), *m*-X(◆)

Some of these studies of the rate constants of reactions of substituted nitrosobenzenes have also claimed correlations with Hammett substituent constants.[4,12,27,28,30] The major feature of any such correlation is the expectation that there will be a smooth correlation between the rate constant and the electron-donating and -accepting characteristics of the substituents. In our studies all of the *para*-substituents (with the exception of $COCH_3$) show rate constants lower than for nitrosobenzene including both negative and positive values of σ. A linear relationship ($\rho = -1.14$) is found for the *meta*-substituents, there being no evidence for a linear plot for the *para*-substituents or for the two sets combined (see Fig. 3). For some other reactions of substituted nitrosobenzenes the values of ρ are negative *e.g.* -0.5 (nitric acid oxidation[4]), -1.58 (peroxyacetic acid oxidation[1]), -1.74 (formaldehyde addition to give *N*-phenylhydroxamic acids[32]), although $\rho = +1.22$ for the condensation reaction of aniline with substituted nitrosobenzenes in acid solutions.[12] For the *para*-substituents in this study, there is an unusual feature in that all of them, excepting acetyl, have rate constants lower than for nitrosobenzene itself. This contrasts with all other studies of rates of reaction of *para*-substituted nitrosobenzenes. There is however a possible parallel in the ^{13}C NMR spectroscopy of *para*-substituted nitrosobenzenes[33] where it is found that the π-electron accepting property of the nitroso group is such that it can turn other π-electron acceptor groups in the *para*-position into π-electron donors. It is clear from previous studies[6] that in the overall reaction (2) an oxygen atom from the nitrogen dioxide is transferred to the nitrogen of the nitroso compound as distinct from the nitrogen dioxide molecule displacing the nitroso group. We suggest that this transfer can be achieved in three ways compatible with the second-order kinetics that we have established. In the first of these nitrogen dioxide, itself a free radical, adds to the nitrogen atom of the nitroso compound to give an intermediate aminoxyl radical as in reaction (3), the decomposition



$$\text{RNO} + \text{NO}_2 \longrightarrow \text{R–}\overset{\text{O}^\bullet}{\overset{|}{\text{N}}}\text{–ONO} \longrightarrow \text{R–NO}_2 + \text{NO} \qquad (3)$$

of the aminoxyl radical being fast. In the second of these the addition of the nitrogen dioxide gives a transition state as in reaction (4). The third mechanism is provided by Bonner and



$$\text{RNO} + \text{NO}_2 \longrightarrow \text{R–}\overset{\text{O}}{\overset{||}{\text{N}}}\text{- -O- -N=O} \qquad (4)$$

Hancock[2] who suggested that the large negative entropy of activation for reaction (2) was consistent with nitrogen dioxide

Table 3 Rate constant values and Arrhenius parameters for the reaction of XC_6H_4NO with NO_2 at 298 K using the stopped flow technique and G3 solvent under N_2

X	k_{298}/dm^3 mol^{-1} s^{-1}	E_a/kJ mol^{-1}	A/dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J mol^{-1} K^{-1}
H	0.263	48.1	7.0×10^7	45.6	−102.9
p-CH_3	0.214	49.4	9.3×10^7	46.9	−100.8
p-OCH_3	0.089	49.8	4.4×10^7	47.3	−106.7
p-Cl	0.105	56.8	8.4×10^8	54.0	−82.4
p-Br	0.144	45.6	1.5×10^7	43.1	−115.6
p-CN[a]	0.098	54.4	3.3×10^8	51.9	−90.4
p-CO_2CH_3[b]	0.247	46.4	3.4×10^7	43.9	−109.2
p-NO_2[c]	0.085	67.4	4.5×10^{10}	64.9	−47.7
p-$COCH_3$[d]	0.264	43.5	1.1×10^7	41.0	−118.4
m-CH_3	0.345	40.2	3.8×10^6	37.7	−127.2
m-OCH_3	0.211	34.3	2.0×10^5	31.8	−151.9
m-Cl	0.110	43.9	5.8×10^6	41.4	−123.8
m-CN[e]	0.062	32.6	3.1×10^4	30.1	−166.9
m-$COCH_3$	0.119	51.0	1.1×10^8	48.5	−99.2
m-$COCH_3$[f]	0.142	41.4	2.5×10^6	38.9	−131.0
o-CH_3[g]	0.098	46.1	1.3×10^8	43.6	−98.0

[a] Solvent contains 8.0% CH_2Cl_2. [b] Solvent contains 4.0% CH_2Cl_2. [c] Solvent contains 6.3% CH_2Cl_2. [d] Solvent contains 4.4% CH_2Cl_2. [e] Solvent contains 7.1% CH_2Cl_2. [f] Solvent contains 5.5% CH_2Cl_2. [g] We are indebted to Dr B. King for these measurements.

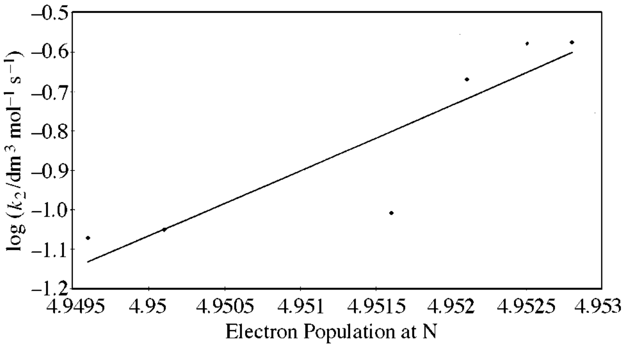
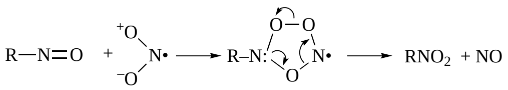


Fig. 4 Variation at 298 K of $\log_{10}$ (k_2/dm^3 mol^{-1} s^{-1}) with electron population at nitroso N in p-XC_6H_4NO as calculated by the CNDO method

acting as a 1,3 dipole leading to a cyclic transition state as in reaction (5) followed by oxygen transfer and formation of nitric oxide.



(5)

We have noted however that large negative entropies of activation are experienced for other bimolecular reactions of nitrosobenzenes without cyclic transition states and that this includes radical addition reactions. It is difficult to envisage the oxidation of the nitrosoarene taking place without the attachment of at least one of the oxygen atoms of the nitrogen dioxide onto the nitroso nitrogen in the rate-determining step. The long established ability of *C*-nitroso compounds to act as radical trapping agents lends further support for radical attack by nitrogen dioxide at nitroso nitrogen and we suggest that the first of these possible mechanisms is the most likely. Support is provided by CNDO calculations of the electron populations at the nitrogen atom of *para*-substituted nitrosobenzenes[34] which demonstrate that as this electron population increases so does the rate constant for reaction (2), (see Fig. 4) and that the relative order $COCH_3 > H > CH_3 > CN > OCH_3 > NO_2$ is consistent for the two variables. The figure is drawn with a linear relationship between log k_2 and the electron population at the nitrogen: a curvilinear relation may equally be appropriate. Whatever the interrelationship may be, we have no knowledge of any other substituent parameter that will produce the relative order given above. The possibility of a correlation with the substituent constant[35] for radical reactions, $\sigma^\bullet$, has been explored but found to be inoperative. (The $\sigma^\bullet$ values fall in the order $COCH_3 > CN > OCH_3 > CH_3 > H$). If our explanation of radical addition to nitroso N is correct then it seems likely that a similar effect would hold for addition reactions of other radicals to *para*-substituted nitrosobenzenes.

It has been shown that when nitrogen dioxide reacts with excess nitrosobenzene in methylene chloride[36] the reaction products are nitrobenzene and benzenediazonium nitrate, the latter product having been formed by reaction of the nitric oxide produced in the oxidation process reacting further with the excess nitrosobenzene as established by Bamberger.[5] Our reaction conditions (excess nitrogen dioxide) avoid this secondary reaction of the nitric oxide produced.

The influence of nitric acid and water upon the reaction systems requires consideration. The observation that addition of purified anhydrous nitric acid to nitrosobenzene in carbon tetrachloride led to an initial drop in the absorbance of the nitrosobenzene is probably due to the formation of a hydrogen bonded association complex [equilibrium (6)] followed by the reaction sequence (7)–(10).

$$PhNO + HNO_3 \rightleftharpoons PhNO{\cdot}HNO_3 \qquad (6)$$

$$PhNO + HNO_3 \xrightarrow{\text{slow}} PhNO_2 + HNO_2 \qquad (7)$$

$$HNO_2 + HNO_3 \rightleftharpoons H_2O + 2NO_2 \qquad (8)$$

$$PhNO + NO_2 \longrightarrow PhNO_2 + NO \qquad (9)$$

$$NO + HNO_3 \rightleftharpoons HNO_2 + NO_2 \qquad (10)$$

After an induction period of some 16 hours the nitrosobenzene concentration began to decrease due to reaction (7) and the resultant nitrogen dioxide produced in equilibrium (8) reacts by reaction (9). Equilibrium (10) is pushed to the right by the excess of nitric acid and by the reaction of the nitrogen dioxide in reaction (9). Similarly equilibrium (8) is also pushed to the right and the production of water also accelerates reaction (9). Addition of sodium nitrite removes the induction period by production of nitrous acid followed by equilibrium (8). On the other hand, addition of trace amounts of nitric acid to a reaction mixture of nitrosobenzene–nitrogen dioxide has no observable effect upon the rate of removal of the nitrosobenzene.

The acceleration of the reaction rate by trace quantities of water in the solvent is possibly due to the formation of nitrous acid [equilibrium (8)] followed by production of nitric oxide by equilibrium (10) and reaction of these species with the nitroso compound adding to the rate of its removal. The acceleration suggests that in the presence of water a more reactive oxidising agent than nitrogen dioxide is formed. The possible agents may include nitrous acid, nitrogen monoxide and nitrogen trioxide. Whatever the reaction sequences may be, it is clear that only rates of reaction of nitrosobenzenes with nitrogen dioxide obtained under scrupulously dry conditions can be taken as reliable rates for reaction (2).

Acknowledgements

We thank the Ministry of Defence for a research grant and Drs L. Phillips and A. R. Osborn for helpful discussions. We thank Dr J. A. Hunter for carrying out CNDO calculations of *p*-substituted nitrosobenzenes.

References

1 K. M. Ibne-Rasa, C. G. Lauro and J. O. Edwards, *J. Am. Chem. Soc.*, 1963, **85**, 1165; K. M. Ibne-Rasa, J. O. Edwards, M. T. Kost and A. R. Gallopo, *Chem. Ind.*, 1974, 964.
2 T. G. Bonner and R. A. Hancock, *J. Chem. Soc. B*, 1970, 519.
3 Y. Ogata and T. Akada, *Tetrahedron*, 1972, **28**, 15.
4 Y. Ogata and H. Tezuka, *J. Am. Chem. Soc.*, 1967, **89**, 5428.
5 E. Bamberger, *Ber. Dtsch. Chem. Gesell.*, 1918, **51**, 634.
6 P. J. Carmichael, B. G. Gowenlock and C. A. F. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1379.
7 C. A. F. Johnson and C. M. Mechie, *J. Chem. Res. (S)*, 1983, 212.
8 G. H. Coleman, C. M. McCloskey and F. A. Stewart, *Org. Synth.*, 1945, **25**, 80.
9 W. J. Mijs, S. E. Hoekstra, R. M. Ulmann and E. Havinga, *Recl. Trav. Chim. Pays-Bas.*, 1958, **77**, 746.
10 R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, 1938, **2**, 73.
11 E. Bamberger and A. Rising, *Liebigs Ann. Chem.*, 1901, **316**, 289.
12 Y. Ogata and K. Takagi, *J. Am. Chem. Soc.*, 1958, **80**, 3591.
13 F. E. Williams, USP 3 417 147, 1968; *Chem. Abstr.* 1969, **70**, 47 089w.
14 A. Baeyer and E. Knorr, *Ber. Dtsch. Chem. Gesell.*, 1902, **35**, 3034.
15 C. K. Ingold, *J. Chem. Soc.*, 1924, **125**, 93.
16 A. Schors, A. Kraaijeveld and E. Havinga, *Recl. Trav. Chim. Pays-Bas.*, 1955, **74**, 1243.
17 E. Bamberger and R. Hübner, *Ber. Dtsch. Chem. Gesell.*, 1903, **36**, 3803.
18 J. N. Ashley and S. S. Berg, *J. Chem. Soc.*, 1957, 3089.
19 J. H. Hall and F. W. Dolan, *J. Org. Chem.*, 1978, **43**, 4608.
20 F. J. Alway and A. B. Walker, *Ber. Dtsch. Chem. Gesell.*, 1903, **36**, 2312.
21 O. Baudisch and R. Furst, *Ber. Dtsch. Chem. Gesell.*, 1915, **48**, 1665.
22 A. Darchen and C. Moinet, *Bull. Soc. Chim. Fr.*, 1976, 812.
23 T. F. Redmond and B. B. Wayland, *J. Phys. Chem.*, 1968, **72**, 1626.
24 C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 1958, 3142.
25 K. M. Ibne-Rasa and J. O. Edwards, *Int. J. Chem. Kinet.*, 1975, **7**, 575.
26 R. A. Yunes, A. J. Terenzani, O. D. Andrich and C. A. Scarabino, *J. Chem. Soc., Perkin Trans. 2*, 1973, 696.
27 M. D. Corbett and B. R. Corbett, *Biochem. Pharmacol.*, 1986, **35**, 3613.
28 S. Kazanis and R. A. McClelland, *J. Am. Chem. Soc.*, 1992, **114**, 3052.
29 J. Hamer, M. Ahmad and R. E. Holliday, *J. Org. Chem.*, 1963, **28**, 3034.
30 M. Ahmad and J. Hamer, *J. Org. Chem.*, 1966, **31**, 2829.
31 P. Schmid and K. U. Ingold, *J. Am. Chem. Soc.*, 1978, **100**, 2493.
32 S. Ursic, *Helv. Chim. Acta*, 1993, **76**, 131.
33 B. M. Al-Tahou and B. G. Gowenlock, *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 253.
34 J. A. Hunter, personal communication.
35 J. M. Dust and D. R. Arnold, *J. Am. Chem. Soc.*, 1983, **105**, 6531.
36 B. Milligan, *J. Org. Chem.*, 1983, **48**, 1495.

Paper 7/00258K
Received 10*th January* 1997
Accepted 13*th May* 1997