Kinetic studies of the reaction of some nitrosoalkanes with nitrogen dioxide

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The rates of the oxidation of some nitrosoalkanes $(CH_3)_2C(CH_2X)NO$ by nitrogen dioxide in carbon tetrachloride have been studied by stopped-flow techniques, and have been found to exhibit second order kinetics. Arrhenius parameters have been determined for the cases of X = H, CH_3, $C(CH_3)_3$, C_6H_5, NO_2, Cl and $OCOCH_3$. Electron withdrawing substituents are found to decrease significantly the rates, which are generally much faster than the corresponding oxidation of nitrosoarenes. The results obtained are discussed with reference to the Hammett σ constants of the substituents X, and the atomic charges at the nitrogen atom as given by the TNDO/2 method, the geometries of the molecules having been optimised by the PM3 semi-empirical method.

The oxidation in solution of aromatic nitroso compounds by nitrogen dioxide has been the subject of kinetic studies by Bonner and Hancock[1] for 2,5-dimethylnitrosobenzene and by ourselves[2] for nitrosobenzene and several *meta*- and *para*-substituted nitrosobenzenes. Studies of the corresponding reaction (1) for nitrosoalkanes are limited to two gas phase

$$RNO + NO_2 \longrightarrow RNO_2 + NO \qquad (1)$$

reactions. In the first of these[3] it was shown that for the case of R = *tert*-butyl the reaction involved transfer of an oxygen atom from the nitrogen dioxide to the nitroso compound, and secondly[4] that the reaction followed mixed second order kinetics over the temperature range 291–318 K with the Arrhenius parameters $\log(A/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = 8.83$ and $E = 47.5$ kJ mol^{-1}. We have demonstrated[2] that for R = phenyl the rate of reaction (1) in carbon tetrachloride is greatly reduced by intensive drying of the solvent and consequently it is of interest to see whether the same feature operates for the case of nitrosoalkanes. It is also of interest to compare the relative rate parameters for the nitrogen dioxide oxidations of nitrosoarenes and nitrosoalkanes.

Experimental

Preparations of dimeric nitroso compounds $[(CH_3)_2CCH_2XNO]_2$

All of these compounds appear in the chemical literature. Modification or amplification of preparations are given where necessary, together with any previously unreported spectroscopic data.

X = H. This was prepared from 2-nitro-2-methylpropane by Emmons' method[5] and from 2-methyl-2-aminopropane by oxidation using sodium tungstate–hydrogen peroxide following Stowell's method.[6]

X = CH_3 and $(CH_3)_3C$. These were prepared by the oxidation of the corresponding amine by Stowell's method.[6]

X = C_6H_5. 2-Methyl-3-phenylpropan-2-ol was prepared from reaction of benzylmagnesium chloride with acetone and converted to 2-methyl-3-phenyl-2-*N*-formylaminopropane by the following method. To 42 cm^3 glacial acetic acid, cooled in ice, was added 19 g sodium cyanide under vigorous stirring at <20 °C. 45 cm^3 conc. sulfuric acid in 42 cm^3 glacial acetic acid was added slowly followed by the addition, with stirring, of 50 g 2-methyl-3-phenylpropan-2-ol over a 10 minute period. The reaction mixture was heated to 75 °C and maintained at this temperature for 30 min. After standing at room temperature for 2 h, 500 cm^3 water was added to the reaction mixture, which was then neutralised with sodium hydrogen carbonate. The solid product was extracted with diethyl ether, dried and concentrated to give 55% yield of the 2-methyl-3-phenyl-2-*N*-formylaminopropane, mp 60–62 °C. This product was then hydrolysed to the amine hydrochloride by refluxing with 3 M HCl for 1 h followed by liberation of the free base using 2 M NaOH. Oxidation by sodium tungstate–hydrogen peroxide[6] gave the dimeric nitroso compound in 13% yield, mp 76–77 °C, ν_{max}(KBr)/cm^{-1} 1605, 1495, 1448, 1270, 1240, 1205, 1165, 1120, 779, 740, 704; $\lambda_{max}(CCl_4)$/nm 683, ε/dm^3 mol^{-1} cm^{-1} 24; $\delta_H(CDCl_3)$ monomer 1.1 (6H, s), 3.38 (2H, s), 7.2 (5H, s); dimer 1.55 (6H, s), 3.4 (2H, s), 7.2 (5H, s).

X = NO_2. This was prepared by reaction of dinitrogen trioxide with 2-methylpropene.[7]

X = Cl. To a solution of 60 g 2-methyl-2-nitropropan-1-ol, prepared according to Parham and Ramp,[8] and 40 g pyridine in 200 cm^3 CCl_4 at 5 °C a solution of 63 g thionyl chloride in 100 cm^3 CCl_4 was added dropwise with stirring. The stirring was continued for a further 30 min, the solvent distilled off, 100 cm^3 water added and steam distilled. The oily distillate was then fractionally distilled under reduced pressure to give 60 g 2-methyl-2-nitro-1-chloropropane. The nitro compound was then reduced to the hydroxylamino compound, followed by acidified dichromate oxidation to the nitroso compound, which was recrystallised from benzene–light petroleum (bp 40–60 °C) to give the crystalline dimer, mp 50–51 °C; $\delta_H(CDCl_3)$ monomer 1.2 (6H, s), 4.25 (2H, s); dimer 1.65 (6H, s), 4.18 (2H, s); ν_{max}(KBr)/cm^{-1} 1550, 1470, 1440, 1430, 1385, 1370, 1280, 1250, 1220, 1160, 1115; $\lambda_{max}(CCl_4)$/nm 680, ε/dm^3 mol^{-1} cm^{-1} 31.

X = $OCOCH_3$. This was prepared by Schwartz's method.[9]

Purification of nitrogen dioxide

Commercially available nitrogen dioxide was purified and stored as before.[2]

Purification of carbon tetrachloride

Intensive purification and drying of this solvent together with its storage under dried nitrogen followed the procedure for the G3 solvent (*i.e.* the most intensively purified) as before.[2] Preparation of the reactant solutions followed our previous practice. The nitrogen dioxide solutions were approximately 0.8 M and

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Table 1 Kinetic parameters for the reaction $(CH_3)_2C(NO)CH_2X$ with NO_2

X	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J mol^{-1} K^{-1}	k_2 (298 K)/ dm^3 mol^{-1} s^{-1}
H	22.9	−141	24.05
CH_3	22.7	−147	13.45
$C(CH_3)_3$	15.5	−179	5.12
C_6H_5	16.2	−175	6.76
Cl	22.9	−164	1.90
$OCOCH_3$	24.2	−155	2.71
NO_2	38.9	−126	0.23

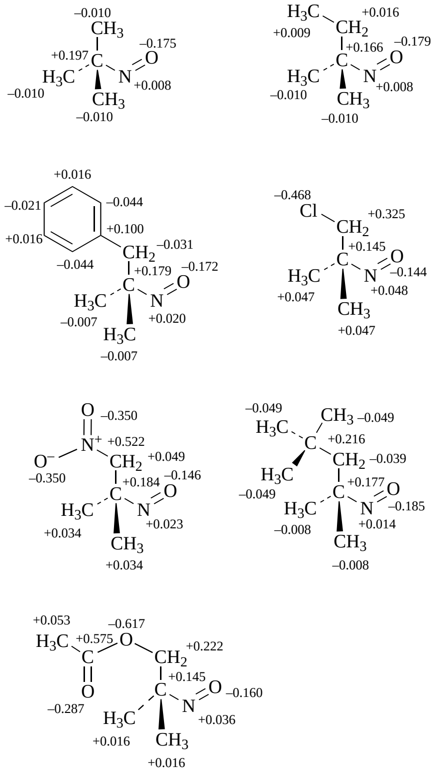


Fig. 1 Calculated atomic charges for nitrosoalkanes in this study

those of the nitroso compound were approximately 0.05 M at which concentration dissociation to monomer is ⩾99%.

Kinetic measurements

The kinetic measurements were made as before using the same stopped-flow apparatus. The temperature ranges employed fell within the limits 285–318 K and the individual ranges varied between 15 and 31 K.

Calculations

The calculations of optimised PM3 geometries and TNDO/2 atomic charges for $(CH_3)_2CCH_2XNO$ were as carried out previously.[10]

Results

Oscilloscope traces were evaluated as described before[2] to obtain the rate constants k_2. The reaction stoichiometry was established from the observation that when [RNO] > [NO_2] the amount of RNO consumed was identical with the amount of NO_2 added and that there was only one organic product.

Because we had observed[2] a pronounced effect of solvent dryness upon the reaction rates for the corresponding reaction of aromatic nitroso compounds with nitrogen dioxide, a similar study of solvent dryness was conducted for the case of the 2-methyl-2-nitrosopropane–nitrogen dioxide reaction using G1 solvent (distilled but not subjected to intensive drying and purification). In marked contrast to the aromatic compounds, where the rate constant was significantly reduced when using the purified and dried solvent, there was no detectable effect upon the reaction rate. Nevertheless, in order to ensure total comparability with our previous study, all of the kinetic studies reported here were carried out using the G3 solvent.

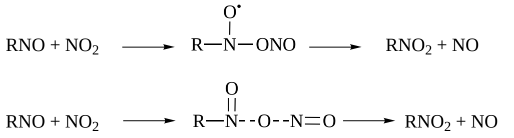
The kinetic data are summarised in Table 1, and the results of the calculations of the atomic charges are displayed in Fig. 1.

Discussion

Reaction (2) is presumed to occur by transfer of an oxygen

$$(CH_3)_2C(CH_2X)NO + NO_2 \longrightarrow (CH_3)_2C(CH_2X)NO_2 + NO \quad (2)$$

atom from the nitrogen dioxide to the nitroso nitrogen. This may be achieved by formation of an aminoxyl radical which then undergoes rapid decomposition to the nitro compound and nitric oxide [see reaction (3)]. Alternatively a transition state is formed as in reaction (4). Because [$(CH_3)_2C(CH_2X)$-



$$RNO + NO_2 \longrightarrow R{-}\overset{O^\bullet}{\overset{|}{N}}{-}ONO \longrightarrow RNO_2 + NO \quad (3)$$

$$RNO + NO_2 \longrightarrow R{-}\overset{O}{\overset{||}{N}}{-}{-}O{-}{-}N{=}O \longrightarrow RNO_2 + NO \quad (4)$$

NO] ⪡ [NO_2] any subsequent reaction of the nitric oxide with the nitroso compound can be ignored.

We have previously suggested[2] that the water effect in the corresponding reaction with nitrosoarenes is related to the formation of nitrous and nitric acids [reaction (5)] and subsequent production of nitric oxide [reaction (6)] which reacts with the nitrosoarene.

$$H_2O + 2NO_2 \longrightarrow HNO_2 + HNO_3 \quad (5)$$

$$NO_2 + HNO_2 \longrightarrow HNO_3 + NO \quad (6)$$

If the reaction (7) is much slower for the cases where R = aliphatic than for R = aromatic then this is a possible explanation.

$$RNO + NO \longrightarrow RN(NO)O^\bullet \xrightarrow{NO} RN(NO)ONO \quad (7)$$

Comparison of the values of the rate constants k_2 and k_8 at 298 K demonstrates that $k_2 \gg k_8$ for X = H and CH_3 and $k_2 > k_8$ for X = Cl and NO_2. The enthalpy of activation is lower for reaction (2) than for reaction (8) and the entropy of activation,

$$XC_6H_4NO + NO_2 \longrightarrow XC_6H_4NO_2 + NO \quad (8)$$

though it is also lower for reaction (2) than for reaction (8), is insufficient to compensate for the drop in $\Delta H^‡$.

In Table 2 the variation of log k_2 with X is presented together with the substituent properties of X as indicated by Hammett σ_F and σ_χ constants.[11,12] In general k_2 decreases with an increase in both σ_F and σ_χ suggesting that field effects play an important role in the reaction. Also, in addition to field effects, it may be necessary to consider whether an increase in the size of substituent X introduces any hindering of access of the nitrogen dioxide to the nitroso group. In the case of the analogous reaction for nitrosoarenes we showed that there was a correlation of the rate constant with the electron population at the nitroso nitrogen. Recent calculations[10] have demonstrated the effects of electron accepting groups, operating across an aliphatic chain of carbon atoms, on the NO nitrogen shielding in the molecules $(CH_3)_2CRNO$ and this suggested that significant differences in

Table 2 Comparison of $\log(k_2/\mathrm{dm^3\ mol^{-1}\ s^{-1}})$ at 298 K with Hammett σ constants and atomic charges at nitroso N and nitroso O in $(CH_3)_2CCH_2XNO$

X	$\log(k_2/\mathrm{dm^3\ mol^{-1}\ s^{-1}})$	σ_χ[a]	σ_F[b]	Net atomic charge at N	Net atomic charge at O
H	1.381	0.00	0.00	+0.008	−0.175
CH_3	1.1329	0.17	0.00	+0.008	−0.179
C_6H_5	0.830			+0.020	−0.172
$(CH_3)_3C$	0.709	0.16	0.00	+0.014	−0.185
Cl	0.279	0.28	0.45	+0.048	−0.144
$OCOCH_3$	0.433			+0.036	−0.160
NO_2	−0.634	0.40	0.65	+0.023	−0.146

[a] Ref. 12. [b] Ref. 11.

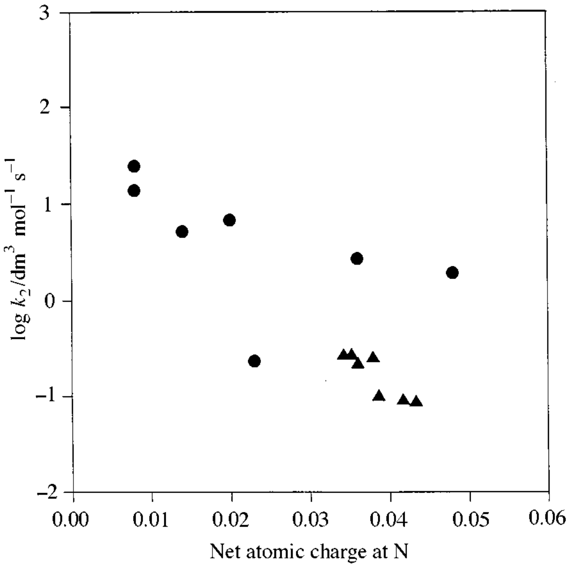


Fig. 2 Interrelationship between $\log_{10} k$ for reaction $RNO + NO_2 \rightarrow RNO_2 + NO$ and net atomic charge at nitroso N from TNDO/2 calculations. $k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ measured at 298 K. $R = (CH_3)_2CCH_2X$ indicated by ●, R = *para*-XC_6H_4 indicated by ▲.

the electronic environment of the nitroso nitrogen may occur also in the series $(CH_3)_2CCH_2XNO$. Inspection of the data in Table 2 shows that there is a general correlation between the atomic charge (as calculated by the semi-empirical TNDO/2 scheme) at both the nitroso N and the nitroso O atoms, and the value of $\log k_2$, which decreases as the atomic charge increases. The two exceptions to this are (a) $X = NO_2$, where the value of k_2 is a factor of about ten lower than would be expected on the basis of the general trend for the other five examples of X [H, CH_3, C_6H_5, $(CH_3)_3C$ and Cl], and (b) $X = OCOCH_3$ where the value of k_2 is a factor of about 10 higher. In Fig. 2 we have extended the treatment which we employed[2] for the interrelation between the rate constant for the nitrogen dioxide oxidation reaction of substituted nitrosoarenes and the electron population at nitroso nitrogen. TNDO/2 calculations based on PM3 geometries for the *para*-substituted nitrosobenzenes $COCH_3$, H, $COOCH_3$, CH_3, CN, OCH_3 and NO_2 gave net charges at the nitroso nitrogens +0.0352, +0.0342, +0.0379, +0.0360, +0.0368, +0.0417 and +0.0433, respectively. It is apparent that as the net charges at the nitroso nitrogen increase the rate constant for oxidation of the nitroso compound by nitrogen dioxide falls.

The general correlation shown in Fig. 2 incorporating both k_2 and k_8 suggests that the mechanisms of the reactions (2) (nitrosoalkanes) and (8) (nitrosoarenes) are similar. The differences in the rate constants are reflected in the corresponding differences in the net charges at the nitroso N atoms between the two series of compounds. Some years ago[13] we observed that the reactions between nitrogen dioxide and both 2-chloro-2-nitrosopropane and 2-nitro-2-nitrosopropane were very slow. On the basis of the above correlation between the rate constant and the net charges at the nitroso N atoms it is to be expected that the corresponding net charges at the nitroso N atoms should be much larger than 0.045. The net charges calculated as before by TNDO/2 are 0.0522 (Cl) and 0.0675 (NO_2).

The absence of the water effect for reaction (2) may possibly be due to the fact that the faster direct oxidation step completely outweighs any contribution from reaction (7).

There is evidence[14] that the value for the spin trapping rate constant k_9 (299 K) is much greater (at least 60-fold) when R is phenyl than when it is *tert*-butyl, where R_1 is *tert*-butyl, and

$$RNO + R_1 \longrightarrow RR_1NO^{\bullet} \qquad (9)$$

also when R is 2,3,5,6-tetramethylphenyl than when it is *tert*-butyl and R_1 is either a primary, secondary or tertiary alkyl radical.[15] These results for the σ radicals contrast markedly with ours for the much less reactive nitrogen dioxide for which the reaction occurs *via* attack of an oxygen of the NO_2 on the nitroso nitrogen.

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