GAS-PHASE NITRATION OF THIOPHENE AND N-METHYLPYRROLE BY PROTONATED ALKYL NITRATES

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Gas-phase nitration of thiophene (1) and N-methylpyrrole (2) was studied by radiolytic techniques, supported by chemical ionization mass spectrometry. The substrate and positional selectivities of protonated alkyl nitrates ($CH_3NO_3H^+$, $CF_3CH_2NO_3H^+$) were deduced from competitive reactions with benzene performed under different conditions. The apparent k_S/k_B ratios, which are independent of the pressure and unaffected by the presence of a strong base (NEt_3), depend on the nature of the electrophile, passing for 1 and 2 from 7·2 and 6·4, respectively, with $CH_3NO_3H^+$ to 1·1 and 1·0, respectively, with the more reactive fluorinated cation. Predominant (88%) α-substitution takes place in 1, whereas no appreciable positional discrimination is displayed by 2. The results suggest that the electrophilic attack can also occur at the heteroatom, and point to the same mechanism postulated for gas-phase nitration of aromatic substrates, the reactivity being essentially governed by electrostatic interactions within the 'encounter pair.'

INTRODUCTION

A combination of mass spectrometric (MS), radiolytic and computational techniques has recently allowed the study of aromatic nitration in the gas phase and the evaluation of the mechanistic features, in particular the selectivity of the attack by $(RNO_3)H^+$ cations, which appears to conform to solution chemistry trends.[1-6]

Extension of the study to heteroaromatic molecules is of interest, especially since examples of predominant β-substitution of the latter by gaseous alkylating cations have been reported,[7] which represents a noticeable departure from their behaviour in solution.

It should be noted that heteroaromatic nitration in condensed media is mechanistically complex, and strongly dependent on the reaction environment,[8,9] which emphasizes the interest of a corresponding study in the dilute gas state, free from complicating effects such as solvation and ion pairing.[10]

This study was aimed at evaluating the reactivities of three model heteroaromatic molecules, pyrrole, thiophene (1) and N-methylpyrrole (2), towards gaseous $(RNO_3)H^+$ nitrating cations.

Pyrrole yielded only intractable tars under the experimental conditions employed, which restricted investigation to 1 and 2. As a useful background, it can be mentioned that in solution these substrates are nitrated by mild reagents predominantly at the α-

position,[11-13] which has been rationalized by arguments based on π-electrons and total charge density for 1[14] and on electrostatic potentials and specific transition-state features for 2.[15-17]

EXPERIMENTAL

Materials. The gases, having a stated purity of 99·9 mol-%, were obtained from Matheson Gas Products. Fluka supplied benzene, thiophene and N-methylpyrrole, the last compound being freshly redistilled before use. The chemicals used as reference standards in the analyses were obtained from Fluka or prepared according to established procedures.

Radiolytic experiments. The gaseous samples were prepared by using a greaseless vacuum line, as described in detail elsewhere.[10] The irradiation were performed at 37·5 °C in a 220 Gammacell from Nuclear Canada, to a total dose of $1·2 \times 10^4$ Gy at a dose rate of 6×10^3 Gy h^{-1}.

The irradiated vessels were cooled to 77 K and a measured amount of a methanolic solution of the internal standard (p-nitrotoluene) was added. They were allowed to come to room temperature and their walls were carefully washed with the solution. The dilute solutions obtained were then used for gas chromatographic (GC) analyses, using a Sigma 1 gas chromatograph from

Perkin-Elmer and a HP 5980A instrument from Hewlett-Packard.

The identities of the products were established by comparison of their retention times with those of authentic samples, and verified by GC–MS using a Hewlett-Packard 5970B quadrupole instrument.

The following columns were used: (i) a 3·3 m × 3 mm i.d. stainless-steel column, packed with SP-2100 (20%, w/w) and Carbowax 1500 (1%) on 100–120 mesh Supelcoport, operated at 185 °C; (ii) a 10 m × 0·53 mm i.d. fused-silica column, coated with Carbowax 20M, operated from 60 to 120 °C; and (iii) a 12 m × 0.25 mm i.d. fused-silica column coated with methylsilicone, operated from 70 to 140 °C. The last column was used for the GC—MS analyses.

Mass spectrometric measurements. Chemical ionization (CI) mass spectra were recorded using a Hewlett-Packard 5982A quadrupole instrument and CH_4–RNO_3 mixtures at a source temperature of 50 °C and a pressure up to 1 Torr, as measured by a Bourdon-type mechanical gauge.
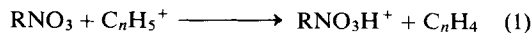
Caution. Alkyl nitrates are hazardous compounds, and should be handled with appropriate precautions, as indicated previously.[2]

RESULTS

Mass spectrometric evidence

The formation of protonated alkyl nitrates has been demonstrated by methane CI mass spectrometry[2,3]

according to the exothermic proton transfer

$$RNO_3 + C_nH_5^+ \longrightarrow RNO_3H^+ + C_nH_4 \quad (1)$$

where $R = CH_3$ or CF_3CH_2 and $n = 1$ or 2.

The CI mass spectra of mixtures containing CH_4 and CH_3NO_3 in the molar ratio 10^3 : 1 and a trace amount of thiophene display three major ions, corresponding to the protonated nitrate, the molecular ion of **1** and its protonated adduct (Figure 1). The ion most significant to the present study is that at m/z 130, corresponding to the nitrated adduct $[C_4H_4S \cdot NO_2]^+$ of unknown struc-
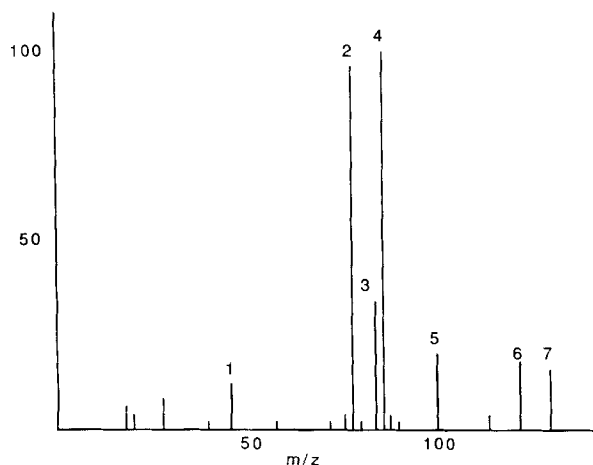
Figure 1. CH_4–CH_3NO_3 CI mass spectrum of thiophene: (1) NO_2^+; (2) $(CH_3NO_3 + H)^+$; (3) M^+; (4) $(M + H)^+$; (5) $(M + O)^+$; (6) $CH_3O(NO_2)_2H^+$; (7) $(M + NO_2)^+$

Table 1 Gas-phase radiolytic nitration of thiophene and N-methlypyrrole in competition with benzene by protonated methly nitrate in CH_4 at 750 Torr and 37.5 °C

Substrates (Torr)[a]			Isomeric distribution of nitroheteroaromatics (%)			
Benzene	Thiophene	N-Methylpyrrole	α	β	$G_{(+M)}$ total values	k_S/k_B
0·918	0·205		89	11	1·7	7·1
0·419	0·345		87	13	2·1	7·1
0·242	0·281		88	12	2·1	8·6
0·209	0·367		89	11	1·7	7·2
0·202	0·785		86	14	1·9	5·6
0·184	0·880		86	14	2·3	7·4
		Mean:	88 ± 2	12 ± 2	2·0 ± 0·2	7·2 ± 1·0
0·266		0·308	49	51	1·4	5·9
0·312		0·309	52	48	1·2	5·1
0·349		0·354	54	46	2·4	6·1
0·360		0·371	59	41	1·7	7·7
0·331		0·389	51	49	1·2	7·3
		Mean:	53 ± 4	47 ± 4	1·6 ± 0·5	6·4 ± 1·1

[a] All systems contained C_2H_4 (10 Torr), SF_6 (5 Torr) and CH_3NO_3 (16 Torr).

ture formed in the reaction

$$C_4H_4S + CH_3NO_3H^+ \longrightarrow [C_4H_4S \cdot NO_2]^+ \\ + CH_3OH \quad (2)$$
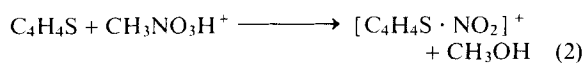
No similar adduct from thiophene is observed when CH_3NO_3 is replaced with $CF_3CH_2NO_3$, or from the reaction of N-methylpyrrole with either of the protonated nitrates. In both cases the spectra contain the protonated substrate and its molecular ion.

Despite the known difficulty of extrapolating CI results to the much higher pressures and lower temperatures prevailing in radiolytic experiments, the mass spectrometric observations are useful in the interpretation of the radiolytic data, in that they demonstrate the operation of an assuredly ionic nitration mechanism.

Radiolytic reaction

Irradiation of gaseous systems containing CH_4 (118–750 Torr), as the bulk component, together with RNO_3 (8–16 Torr) and the substrates 1 and 2 (0·2–0·9 Torr), gives nitrated heteroaromatic products in high yields.

Tables 1 and 2 illustrate the isomeric composition, the apparent k_S/k_B values (the k_S/k_B ratios were evaluated from the ratios of the yields of the products from the substrate S and from benzene, corrected for the relative concentrations of the competing species) and the yields of the products obtained from the reactions of 1 and 2 at high pressure, and Table 3 relates to low-pressure systems.

The composition of the irradiated systems deserves a brief comment. In addition to methane and alkyl nitrates, C_2H_4 and SF_6 were used as scavengers of radicals and thermal electrons, respectively. Very low concentrations of the substrates were used in order to minimize direct radiolysis.

The *absolute* yields of nitrated products, measured by the corresponding $G_{(+M)}$ values, which express the number of molecules formed per 100 eV absorbed by the gas, show that nitration is a major reaction route. In fact, the $G_{(+M)}$ values measured in CH_4–CH_3NO_3 systems cluster around 2, vs the 2·8 limit set by the

Table 2 Gas-phase nitration of thiophene and N-methlypyrrole by $CF_3CH_2NO_3H^+$ ions in CH_4 (750 Torr) at 37·5 °C

Substrates (Torr)[a]			Isomeric distribution of nitroheteroaromatics (%)		$G_{(+M)}$ total values	k_S/k_B
Benzene	Thiophene	N-Methylpyrrole	α	β		
0·193	0·290		87	13	1·3	1·0
0·338	0·354		90	10	1·5	1·1
0·377		0·398	50	50	1·7	1·2
0·321		0·274	49	51	0·93	0·80

[a] All systems contained C_2H_4 (10 Torr), SF_6 (5 Torr) and $CF_3CH_2NO_3$ (13 Torr).

Table 3 Gas-phase radiolytic nitration at low pressure and 37·5 °C

System composition (Torr)[a]				Isomeric distribution of nitroheteroaromatics (%)		$G_{(+M)}$ total values	k_S/k_B
Nitrate	Benzene	Thiophene	N-Methylpyrrole	α	β		
CH_3NO_3 10	0·369	0·374		88	12	1·1	7·2
	0·378	0·382		89	11	1·2	7·0
$CF_3CH_2NO_3$ 8	0·312	0·319		90	10	0·68	1·0
	0·266	0·392		91	9	0·83	0·90
CH_3NO_3 10	0·314		0·281	51	49	0·91	6·2
	0·220		0·203	57	43	1·3	6·7
	0·428		0·384	51	49	1·1	7·0
$CF_3CH_2NO_3$ 8	0·495		0·583	59	41	1·0	0·84

[a] All systems contained CH_4 (118 Torr), C_2H_4 (5 Torr) and SF_6 (3 Torr).

Table 4 $G_{(+M)}$ values of products from nitration of thiophene and N-methlypyrrole by RNO_3H^+ ions at 750 Torr in the presence of ET_3N

Nitrate	System composition (Torr)[a]				Isomeric distribution of Nitroheteroaromatics %		k_S/k_B	$G_{(+M)}$	
	Benzene	Thiophene	N-Methylpyrrole	Et_3N	α	β		$PhNO_2$	ring-NO$_2$
CH_3NO_3 16	0·448	0·369		0·538	90	10	6·4	0·13	0·68
	0·458	0·378		1·05	86	14	8·5	0·032	0·28
	0·613	0·505		1·70	91	9	7·6	0·024	0·15
	0·458	0·378		2·01	92	8	7·3	0·013	0·078
					Mean: 90 ± 3	10 ± 3	7·5 ± 0·86		
$CF_3CH_2NO_3$ 13	0·338	0·338		0·669	87	13	1·1	0·41	0·46
	0·541	0·562		2·00	91	9	1·0	0·13	0·13
CH_3NO_3 16	0·220		0·306	0·213	60	40	9·8	0·073	1·0
	0·235		0·278	0·504	62	38	6·3	0·078	0·58
	0·230		0·272	0·546	60	40	8·3	0·063	0·62
	0·257		0·300	1·08	64	36	7·0	0·034	0·28
	0·274		0·320	1·33	59	41	6·8	0·043	0·34
					Mean: 61 ± 2	39 ± 2	7·6 ± 1·4		
$CF_3CH_2NO_2$ 13	0·823		0·767	2·00[b]	58	42	1·3	0·083	0·10

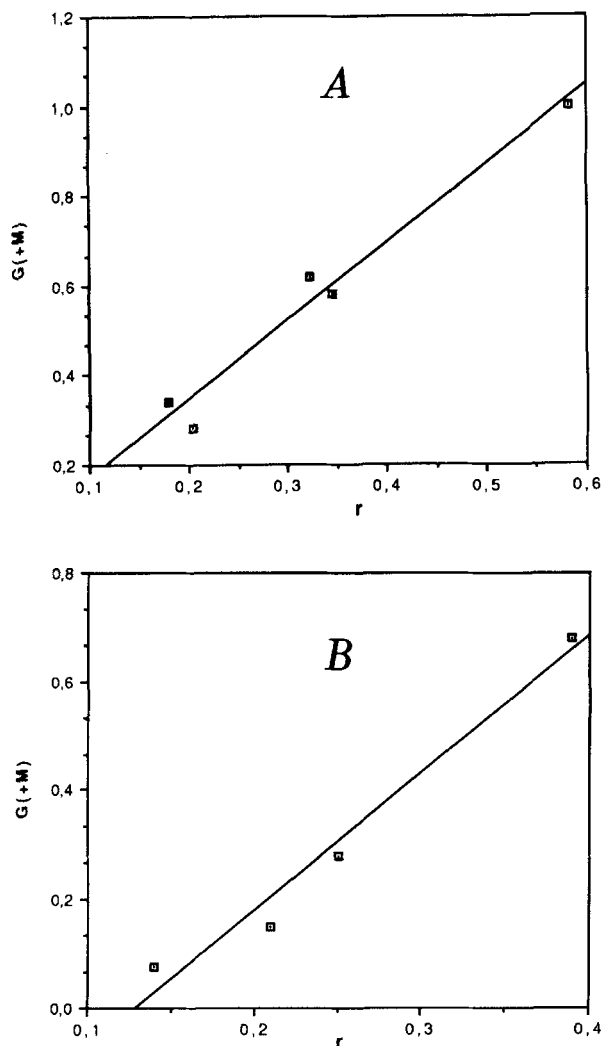[a] All systems contained C_2H_4 (10 Torr), SF_6 (5 Torr).
[b] Me_3N
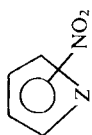
Figure 2. Absolute yields of the products from (A) N-methylpyrrole and (B) thiophene vs the r ratio (see text). The intercepts reflect the experimental uncertainties

$G_{(+M)}$ values of the primary ionic reactants, i.e. the $C_nH_5^+$ ($n = 1, 2$) cations from the ionization of methane.[18]

Effects of additives

The ionic character of the processes of interest was ensured by using in all systems an effective radical scavenger, e.g. C_2H_4, at concentrations appreciable higher than those of the substrates, and confirmed by the sharp decrease in the nitration yields when Et_3N was added to the systems (Table 4).

In fact, the gaseous strong base has been found to

depress gradually the yields of the ionic products G_0, measured in neat CH_4 by a factor r (Figure 2):

$$r = \frac{G}{G_0} = \frac{[MeNO_3][S]}{([MeNO_3] + [B])([S] + [B])}$$

The above relationship was deduced from a simple model based on the competition of the nucleophile (B) with the alkyl nitrate for the protonating cations, and with the substrate (S) for the protonated alkyl nitrate, by assuming that all processes occur at the ion–molecule collision frequency, i.e. at the' same specific rate.[19]

DISCUSSION

Ionic reagent

As discussed previously, RNO_3H^+ ions are electrophilic reagents of an efficient gas-phase nitration.[2,3] Both in CI mass spectrometry and in radiolytic experiments they are obtained by proton transfer from $C_nH_5^+$, produced in turn from the ionization of CH_4, to the alkyl nitrates, according to the exothermic reaction (1). [The reaction is estimated to be exothermic by 44 ($n = 1$) and 13 ($n = 2$) kcal mol^{-1} when R = CH$_3$, on the basis of a proton affinity (PA) of 176 of methyl nitrate. Passing to fluorinated alkyl nitrate, whose PA is unknown, the endothermic character of proton transfer from $C_2H_5^+$ to $CF_3CH_2NO_3$ would require the PA of the latter to be < 162·6 kcal mol^{-1}].

I   II
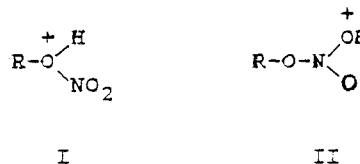
The most stable protonated adduct from CH_3NO_3 according to MINDO calculations is the isomer I, protonated at the ethereal oxygen,[20] but the stability difference between the isomeric structures I and II is calculated by ab initio methods to be very small (6.7 kcal mol^{-1}) and in the reverse order.[21] However, owing to the lack of selectivity of protonation by $C_nH_5^+$, the initial formation of I and II is very likely, and consequently both I and II can conceivably represent the kinetically relevant species in gas-phase nitration. In the radiolytic systems the charged electrophiles undergo a large number of unreactive collisions with the molecules of the bulk gas

$$(RNO_3H^+)_{exc} + CH_4 \longrightarrow RNO_3H^+ + (CH_4)_{exc}$$

before a reactive encounter with substrates can occur. Consequently, RNO_3H^+ ions are thoroughly thermalized before reacting with benzene and heteroaromatic compounds.

### Substrate and positional selectivity

The relative reactivity of **1** and **2** measured in CH_4–CH_3NO_3 systems, and characterized by apparent k_S/k_B ratios of 7·2 and 6·4, respectively, is largely independent of [S] and of the experimental conditions. Nitration by the more electron-deficient $CF_3CH_2NO_3H^+$ is less selective, being characterized by k_S/k_B values of 1·1 and 1·0, as would be expected from the lower binding energy of NO_2^+ to the ROH moiety.

By comparing these results with those obtained under the same conditions in aromatic nitration,[3–6] thiophene and N-methylpyrrole appear to react at the same rate as toluene with $CH_3NO_3H^+$. However, their reactivity towards $CF_3CH_2NO_3H^+$ is lower, from both a relative and an absolute standpoint. In fact, the k_S/k_B values drop to ca 1, while the absolute nitration yields from **1** and **2** decrease considerably (from ca 70 to ca 50%) on passing from $CH_3NO_3H^+$ to $CF_3CH_2NO_3H^+$.

This trend can be rationalized on the consideration that the electrophile can attack both the π- and the n-type nucleophilic centres of the multidentate substrate,[7a,22,23] yielding in the latter case adduct V, which cannot convert into a stable nitration product. The branching ratio between ring and Z attack depends on the nature of the electrophile, and could be rationalized by the HSAB theory,[24] already invoked to explain analogous trends in the gas-phase alkylation of anilines.[25]

Another factor that requires careful consideration is the ability of RNO_3H^+ ions to transfer a proton to the substrates [PA (N-methylpyrrole) = 220 kcal mol^{-1};[26] PA (thiophene) = 195·9 kcal mol^{-1};[27] PA (**1**) = 196·5,

PA (**2**) = 215, PA (C_6H_6) = 181·3 kcal mol^{-1};[28] PA (CH_3NO_3) = 176 kcal mol^{-1}.[2]] in competition with the nitration route:

$$S + RNO_3H^+ \longrightarrow
\begin{cases}
SH^+ + RNO_3 & (3) \\
SNO_2^+ + ROH & (4)
\end{cases}$$
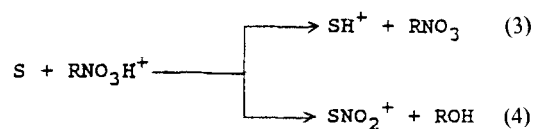
Proton transfer (3) from $CH_3NO_3H^+$ is exothermic by ca 20 kcal mol^{-1} with respect to thiophene and by 39 kcal mol^{-1} with respect to N-methylpyrrole. It has been shown to be the predominant reaction route to the latter substrate, and a major route to thiophene under CI conditions, although increasing the pressure in the ion source has been found to decrease the k_3/k_4 branching ratio, and nitration can be expected to predominate at the much higher pressures typical of radiolytic experiments. Probably, reaction (3) is more significant in the case of heteroaromatic than aromatic substrates, since proton transfer between n-type centres is known to be particularly fast in the gas phase. The greater protonating ability of $CF_3CH_2NO_3H^+$ compared with $CH_3NO_3H^+$ could represent an additional factor to explain the lower nitration yields from the fluorinated cation.

Given the above, the *overall* reactivity of **1** and **2** towards gaseous nitrating ions is comparable to that of activated aromatics. Therefore, the experimental measured k_S/k_B ratios are likely to represent only lower limits of the reactivity of **1** and **2**, being affected by Z

$(Z=S, NCH_3)$

III

IV

V
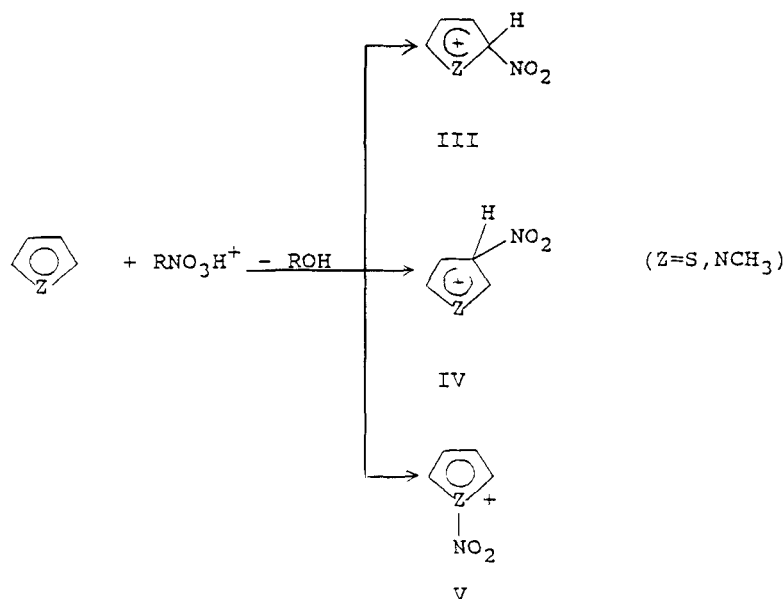
attack and competitive protonation [reaction (3)]. Since, however, the extent of the latter processes cannot be evaluated directly, no correction of the experimental values has been attempted.
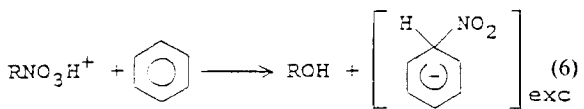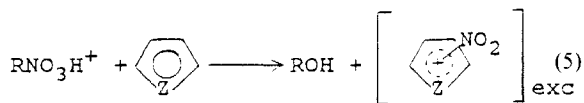
Concerning positional selectivity, thiophene is nitrated predominantly at the α-position, whereas no discrimination between the C_α and C_β sites of N-methylpyrrole is detected.

In principle, the high reactivity of the α-position of **1** and the β-position of **2** could be traced to the tendency of the heteroaromatic compounds to direct the electrophile towards the site characterized by the highest net negative charge. However, this interpretation fails to account for the enhanced reactivity of the α-position of **2** towards strong nitrating agents such as RNO_3H^+ ions.

In order to develop a unified picture that accounts for the experimental observations, one can invoke some kind of participation of the n-type centre. In fact, in addition to direct heteroatom attack, followed by isomerization to an α-substituted product, one can envisage an increased local concentration of the electrophile at the α-positions owing to the preliminary formation of a gaseous 'chelate', by analogy with the behaviour of other bidentate substrates.[25,29]

Nature of the nitration process

The thermalized RNO_3H^+ ions react with heteroaromatics **1** and **2** and benzene according to a process that can be regarded as a nucleophilic displacement of the corresponding alcohol:
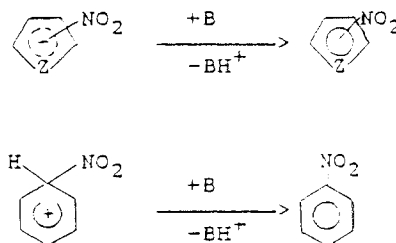
$$RNO_3H^+ + \langle \text{structure} \rangle \longrightarrow ROH + \left[\langle \text{structure} \rangle^{NO_2} \right]_{exc} \quad (5)$$

$$RNO_3H^+ + \langle \text{structure} \rangle \longrightarrow ROH + \left[\langle \text{structure} \rangle^{NO_2}_H \right]_{exc} \quad (6)$$

as suggested by a recent investigation concerning arylsilanes.[6] Nitration of C_6H_6 by protonated methyl nitrate via reaction (6) has been shown to be energetically allowed,[5] and the process is obviously more exothermic when the fluorinated cation is involved.[3] Lack of the necessary data prevents analogous calculations for process (5), which, however, can be reasonably regarded as exothermic. [On the basis of group additivity, reaction (5) of thiophene with $CH_3NO_3H^+$ ions should be exothermic if PA in the ipso position is >153 kcal mol^{-1}]. The nitrated adducts formed with excess of internal energy, before being

thermalized by unreactive collisions with the bath gas

$$(SNO_2^+)_{exc} \xrightarrow[-M_{exc}]{+M} SNO_2^+$$
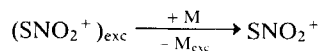
could conceivably isomerize into more stable structures. Isomerization seems unlikely, at least in the investigated pressure range, in view of the experimentally observed insensitivity of the isomeric composition of products to pressure changes.

Eventually, the charged intermediates evolve into the detectable neutral products by proton transfer to any base present in the systems, including the same substrates:

$$\langle \text{structure} \rangle^{NO_2} \xrightarrow[-BH^+]{+B} \langle \text{structure} \rangle^{NO_2}$$

$$\langle \text{structure} \rangle^{NO_2}_H \xrightarrow[-BH^+]{+B} \langle \text{structure} \rangle^{NO_2}$$

The k_S/k_B ratios and the isomeric composition of products are largely unaffected by the presence of a strong base, such as Et_3N; these results show that the deprotonation step is not rate determining, and confirm that isomerization of the heteroarenium ions is not significant even in the absence of added bases. Hence the isomeric distribution of nitrated products reflects the kinetic attack of the nitrating agents on the heteroaromatics.

It should be observed that the relative reactivity data from this work refer exclusively to the C-nitration channel, rather to the overall nucleophilicity of **1** and **2**. Nevertheless, even taking into account the electrophilic attack to heteroatoms, as previously discussed, the substrate selectivity displayed by the RNO_3H^+ cation is exceedingly low by the reactivity standards of heteroaromatic nitration in solution.[11,30]

In contrast to the low substrate selectivity, a significant positional discrimination is observed in thiophene nitration, suggesting that the 'rate-determining' and the 'product-controlling' steps are kinetically distinct, as in gas-phase aromatic nitration.[4] This idea is consistent with the observation that on passing from $CH_3NO_3H^+$ to $CF_3CH_2NO_3H^+$ ions the k_S/k_B ratios decrease in the reaction of both substrates, but no change of the isomeric distribution of the products is measured.

Such a behaviour therefore represents the counterpart of the 'encounter rate' nitration occurring in solution:[8a] the reactants are trapped in a sort of 'electrostatic cage' (Formation of the early complex can be traced to the intense electrostatic forces between the free nitrating cation and the aromatic or heteroaromatic molecule, the stabilization energy of ion–molecule electrostatic

complexes being of the order of 10 kcal mol^{-1}),[31] kinetically, if not physically, equivalent to the solvent cage envisaged in solution, and the nitration rate of the heteroaromatics componds is limited by the encounter rate of RNO_3H^+ ions with the substrates.

On the other hand, the positional selectivity depends on the activation barriers for the formation of the σ-isomeric complexes, and the results are in agreement with the current ion–polar molecule interaction theories.[32] However, this study confirms, in accord with previous conclusions obtained for gas-phase alkylations,[22,33] that other factors, related to the structural and electronic features of the substrate and of the electrophile, appreciably modify the selectivity based on purely electrostatic arguments.

CONCLUSION

Nitration of thiophene and N-methylpyrrole by gaseous RNO_3H^+ ions occurs at a limiting rate, confirming that in the gas phase sufficiently activated compounds react at the 'encounter rate' with strongly charged electrophiles.

Heteroaromatic nitration displays an intriguing analogy with aromatic nitration. The rate appears to be first order with respect to the heteroaromatics, as well as to benzene, e.g. k_I/k_B is largely unaffected by a 21-fold change in the [1]/[B] ratio.

In conclusion, the mechanism is the same as that for aromatic compounds, as already envisaged from related reactions occuring in condensed media.[8a,12]

In the dilute gaseous state, the intrinsic reactivity of the free RNO_3H^+ ions towards heteroaromatics appears to be governed by factors strictly correlated with the interactions between the negatively charged sites of the substrate and the ionic reagent, as observed in gas-phase alkylations carried out under analogous conditions.

REFERENCES

1. M. Attiná and F. Cacace, J. Am. Chem. Soc. 108, 318 (1986).
2. M. Attiná, F. Cacace and M. Yañez, J. Am. Chem. Soc. 109, 5092 (1987).
3. M. Attiná, F. Cacace and A. Ricci, Tetrahedron 44, 2015 (1988).
4. M. Attiná, F. Cacace and G. de Petris, Angew. Chem. 26, 1177 (1987).
5. M. Attiná and F. Cacace, Gazz. Chim. Ital. 118, 241 (1988).
6. M. Attiná, F. Cacace and A. Ricci, Gazz. Chim. Ital. 119, 217 (1989).
7. (a) M. Speranza, J. Chem. Soc., Chem. Commun. 1177 (1981); (b) G. Angelini, C. Sparapani and M. Speranza, J. Am. Chem. Soc. 104, 7084 (1982).
8. (a) R. G. Coombes, R. B. Moodie and K. Schofield, J. Chem. Soc. B 800 (1968); (b) J. G. Hoggett, R. B. Moodie and K. Schofield, J. Chem. Soc., Chem. Commun. 605 (1969).
9. G. Marino, Adv. Heterocycl. Chem. 13, 235 (1971).
10. F. Cacace, Radiat. Phys. Chem. 20, 99 (1982); F. Cacace, Acc. Chem. Res. 21, 215 (1988).
11. B. Ostman, Ark. Kemi 19, 499 (1962).
12. A. R. Butler and J. B. Hendry, J. Chem. Soc. B 102 (1971).
13. G. Doddi, P. Mencarelli, A. Razzini and F. Stegel, J. Org. Chem. 44, 2321 (1979).
14. V. Gelius, B. Roos and P. Siegbahn, Theor. Chim. Acta 27, 171 (1972); F. Bernardi, A. Bottom and A. Mangini, Gazz. Chim. Ital. 101, 55 (1977).
15. I. A. Abronin, L. I. Belenkii and Ya. L. Gold'farb, New Trends in Heterocyclic Chemistry. Elsevier North-Holland, Amsterdam (1979).
16. N. P. Epiotis, W. R. Cherry, F. Bernardi and W. J. Hehre, J. Am. Chem. Soc. 98, 4361 (1976); J. T. Gleghorn, J. Chem. Soc., Perkin Trans. 2 479 (1972).
17. P. Politzer and H. Weinstein, Tetrahedron 31, 915 (1975).
18. P. Ausloos, S. G. Lias and R. Gorden, Jr. J. Chem Phys. 39, 3341 (1963)
19. D. K. Bohme, G. I. McKay and H. I. Schiff, J. Chem. Phys. 73, 4976 (1980).
20. M. J. S. Dewar, M. Sanshal and S. D. Worley, J. Am. Chem. Soc. 91, 3590 (1969).
21. F. Bernardi, F. Cacace and F. Grandinetti, J. Chem. Soc., Perkin Trans. 2 413 (1989).
22. G. Laguzzi and M. Speranza, J. Chem. Soc., Perkin Trans. 2 857 (1957).
23. S. Gronowitz and K. Dahlgren, Ark. Kemi 21, 201 (1961); Chem. Abstr. 59, 12740e (1963); P. Cogolli, F. Maiolo, L. Testaferri, M. Tiecco and M. Tingoli, J. Heterocycl. Chem. 16, 1495 (1979).
24. R. G. Pearson, J. Am. Chem. Soc. 85, 3533 (1963).
25. M. Attinà and P. Giacomello, J. Am. Chem. Soc. 101, 6040 (1979); M. Attinà and F. Cacace, J. Am. Chem. Soc. 105, 1122 (1983); M. Attinà, F. Cacace and G. de Petris, J. Am. Chem. Soc. 107, 1556 (1985).
26. J. L. Devlin, III, J. F. Wolf, R. W. Taft, W. J. Hehre, R. T. McIver, Jr, J. A. Pople and P. V. R. Schleger, J. Am. Chem. Soc. 96, 7162 (1974); D. H. Aue, H. M. Webb and M. T. Bowers, J. Am. Chem. Soc. 94, 4762 (1972).
27. R. Houriet, H. Schwartz, W. Zummack, J. G. Andrade and P. V. R. Schleyer, Nouv. J. Chim. 5, 505 (1981).
28. S. G. Lias, J. F. Liebman and R. D. Levin, J. Phys. Chem. Ref. Data 13, 695 (1984).
29. P. Schuster, G. Zundel and C. Sandorfy, The Hydrogen Bond. North-Holland, Amsterdam (1976).
30. A. R. Cooksey, K. J. Morgan and D. P. Morrey, Tetrahedron 26, 5101 (1970).
31. D. K. Sen Sharma and P. Kebarle, J. Am. Chem. Soc. 104, 19 (1982); P. Politzer, K. Jaysauriya, P. Sjoberg and

P. R. Laurence, *J. Am. Chem. Soc.* **107**, 1174 (1985).

32. M. T. Bowers and T. Su, in *Interaction Between Ions and Molecules*, edited by P. Ausloos, Plenum, New York (1974); W. J. Chesnavich, T. Su and M. T. Bowers, in *Kinetics of Ion–Molecule Reactions*, edited by P. Ausloos. Plenum, New York (1979).

33. A. Margonelli and M. Speranza, *J. Chem. Soc., Perkin Trans. 2* 1491 (1983).