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Oxidation of Heterocycles in the Atmosphere: Kinetic Study of Their Reactions with NO_3 Radical

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The fast-flow-discharge technique has been used to determine the absolute rate coefficients for the gas-phase reactions of the NO_3 radical with a series of five-membered heterocycles (furan, pyrrole, tetrahydrofuran, and tetrahydrothiophene). The experiments involved monitoring the NO_3 radical by laser-induced fluorescence. The influence of temperature was studied in the range 260−345 K for the reactions of NO_3 with furan, tetrahydrofuran, and tetrahydrothiophene, and the proposed Arrhenius expressions are respectively $k = (1.3 \pm 0.8) \times 10^{-13} \exp[(700 \pm 200)/T]$ (cm^3 molecule^{-1} s^{-1}), $k = (2 \pm 2) \times 10^{-9} \exp[-(3800 \pm 400)/T]$ (cm^3 molecule^{-1} s^{-1}), and $k = (1 \pm 1) \times 10^{-13} \exp[(1000 \pm 200)/T]$ (cm^3 molecule^{-1} s^{-1}). For the reaction of NO_3 with pyrrole, only an upper limit value ($<1.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) of the rate constant at 298 K is given due to decomposition processes observed in the flow tube. The rate coefficients obtained were compared with those from previous studies carried out using different techniques. The differences in the rate constants and the activation energies suggest different reaction mechanisms for the studied reactions. Mean atmospheric lifetimes for these compounds have been calculated in relation to their reactions with NO_3 and OH radicals.

1. Introduction

In the 1970s, a study of the hydrocarbon content of the ambient air in large cities provided evidence of the presence of aromatic heterocycles such as thiophene, furan, and substituted furans.[1] Oxygen heterocycles such as furan are emitted as primary anthropogenic pollutants from biomass burning[2,3] and from processes in which meat is boiled, fried, and conserved.[4] These systems are also secondary pollutants produced in the photooxidation of some conjugated dienes, such as 1,3-butadiene,[5−7] *cis*-1,3-pentadiene[5] and isoprene,[8,9] and aromatic compounds, such as toluene and *o*-xylene.[10] The N-heterocycles (like pyrrole) are products of incomplete combustion of nitrogen-containing substances and of other organics in the presence of NO. These N-heterocycles are also found along with PAHs (polyaromatic hydrocarbons) in respirable particulate matter from ambient air, diesel and spark-ignition engines, and wood smoke.[11]

In relation to sulfur-containing heterocycles, these compounds are mainly released into the atmosphere by anthropogenic sources (fossil fuel combustion, in waste or biomass burning and in fuel conversion[12−15]) and to a lesser extent by biogenic sources.[1,16,17] Additionally, qualitative and quantitative analysis of thiophenes in gasoline reveals that more than 20 kinds of thiophenes including thiophene and tetrahydrothiophene were present in fluid catalytic cracking (FCC) and residue fluid catalytic cracking (RFCC) gasoline.[18]

Once in the atmosphere, the behavior of heterocyclic compounds is not well understood, and very few monitoring data are available. In this sense, heterocyclic compounds could be chemically removed from the troposphere by photolytic processes and by reaction with the OH radical during the daytime or with NO_3 radical at night. To a lesser extent, the reaction of heterocycles with O_3 could provide another sink for these compounds. In this sense, the reactions of heterocycles with OH and O_3 have been the subject of different studies,[19−25] but research about their reactivity with NO_3 radical is scarce. Thus, furan and substituted furans with NO_3 have been the most widely investigated and gas-phase relative rate constants and products have been determined in several works.[26−31] In contrast, the reaction of thiophene with NO_3 has been less investigated,[29,30,32,33] with only the Cabañas et al.[33] study being an absolute rate study. Finally, there are only single studies of the pyrrole[29] and tetrahydrofuran (THF)[30] reactions with NO_3, both using the relative rate technique.

In this context, we have undertaken a systematic investigation, using an absolute technique, of the reactions of the NO_3 radical with certain heterocycles. Results concerning the reaction of the NO_3 radical with thiophene were published in a previous paper.[33] As a continuation of this research, we have developed the first absolute, temperature-dependent study of the reaction of NO_3 with tetrahydrothiophene (THT), furan, tetrahydrofuran, and pyrrole. Kinetic data for these NO_3 reactions are needed to gain a better understanding of the role of heterocyclic compounds in atmospheric chemistry and to develop a reliable structure−reactivity relationship for these compounds.

The experiments were performed in a fast-flow system using laser-induced fluorescence (LIF) detection for NO_3 monitoring. The absolute rate constants at different temperatures were measured, and the activation energies were calculated. Only the rate constant at 298 K was determined for the reaction of NO_3

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radicals with pyrrole due to decomposition processes observed in the flow tube.

2. Experimental Section

All the absolute kinetic experiments were conducted using a discharge flow tube reactor equipped with LIF detection for the nitrate radical. The arrangement of the apparatus and experimental procedures were previously described in detail,[34,35] and only a brief description is given here.

Helium was used as the carrier gas. NO_3 was generated in a sidearm tube by reaction of anhydrous gaseous HNO_3 with fluorine atoms and was detected by monitoring the fluorescence emitted by excitation at $\lambda = 662$ nm with radiation from a dye laser. Fluorine atoms were obtained by passing F_2/He mixtures through a microwave discharge. Anhydrous gaseous HNO_3 in helium carrier was prepared by bubbling He through a mixture of H_2SO_4/HNO_3. In all the experiments, the HNO_3 concentration was in a sufficiently large excess over the F atom concentration to prevent secondary reactions. Initial nitrate radical concentrations were in the range of $(3-15) \times 10^{12}$ molecule cm^{-3}, and they were determined either before or after each kinetic run by chemical titration with a known amount of tetramethylethene (TME).[36]

The reactants were added to the flow through a sliding injector, whose position could be varied up to 70 cm from the center of the observation region, thus obtaining contact times between the NO_3 radical and the reactant of $t = (0.01-0.6) \times 10^{-2}$ s for THT, $t = (0.1-12.5) \times 10^{-2}$ s for THF, and $t = (0.1-6) \times 10^{-2}$ s for furan. Flow rates were in the range from 4.6 to 10 m s^{-1}. The concentrations of heterocyclic compounds were varied between $(2-8) \times 10^{13}$ molecule cm^{-3} for furan, $(3-4) \times 10^{12}$ molecule cm^{-3} for pyrrole, $(3-32) \times 10^{14}$ molecule cm^{-3} for tetrahydrofuran, and $(8-22) \times 10^{13}$ molecule cm^{-3} for tetrahydrothiophene.

The experiments were conducted at a total pressure of (1.1−1.5)(±0.1) Torr and at temperatures ranging from 260 to 345 K (±1 K). In the case of THF, we observed significant heterogeneous reactions at temperatures lower than 287 K, so the limited temperature range for this compound has been 287−340 K. The flow tube was cooled and heated at the desired temperature by circulating liquid silicone through an external jacket connected by Viton tubes to a thermostatic bath, where the temperature was controlled.

Rate Constant Measurement. The experiments for the reaction of THF were performed under pseudo-first-order conditions, with a large excess of reactant over NO_3 ([THF]/[NO_3] was between 23 and 437). The integrated rate expression used to analyze the experimental data in this case was

$$\ln\left(\frac{[NO_3]_0}{[NO_3]_t}\right) = (k[\mathrm{THF}]t) = k't \qquad (1)$$

where k' is the pseudo-first-order rate constant and k is the second-order rate constant. Plotting $\ln([NO_3]_0/[NO_3]_t)$ vs time gives k' as the slope of the straight lines in accordance with eq 1. This rate constant should be corrected considering the possible axial diffusion of the reactant because this effect could be important at high flow rates. However, under our experimental conditions, the rate correction would be between 0.1% and 3%, and therefore, the effect of the axial diffusion can be avoided.

The obtained first-order rate constants, k', at different concentrations (at one given temperature) are plotted against the reactant concentrations. In this way, the second-order rate coefficient k is obtained as the slope of the least-squares fit of these data.

In the case of furan, it was not possible to perform the experiments with a large excess of reactant over NO_3 due to its lower volatility and to the limited sensitivity of our detection system. The ratio [furan]/[NO_3] was varied between 3 and 5, so the data for the reaction of NO_3 with this compound were analyzed using the second-order integrated rate expression[37] assuming 1:1 stoichiometry:

$$\ln\frac{(M - X_a)}{[M(1 - X_a)]} = (B_0 - A_0)kt \qquad (2)$$

where $M = [\mathrm{furan}]_0/[NO_3]_0$, $B_0 = [\mathrm{furan}]_0$, $A_0 = [NO_3]_0$, and

$$X_a = \frac{[NO_3]_0 - [NO_3]_t}{[NO_3]_0} \qquad (3)$$

A second-order rate constant may be obtained from the slope of plots of $1/(B_0 - A_0) \ln[(M - X_a)/M(1 - X_a)]$ vs time.

Finally, in relation to THT, the preliminary results showed the possible contribution of secondary chemistry in this reaction when working with a small excess of reactant over NO_3. Indeed, the data analysis indicated that only when [THT]/[NO_3] is higher than 40, the rate coefficients are independent of this ratio. The vapor pressure of THT was a limiting factor in the concentration range. Subsequently, the THT concentration could not be varied in a significant range, and therefore, eq 1 was rearranged as shown in the study of Wayne et al.,[38] varying in this case the product $(1/[\mathrm{THT}]) \ln([NO_3]_0/[NO_3]_t)$ vs time and obtaining directly the bimolecular coefficient k, according to eq 4:

$$\frac{1}{[\mathrm{THT}]} \ln\left(\frac{[NO_3]_0}{[NO_3]_t}\right) = kt \qquad (4)$$

Chemicals. The source of the organic reactants and their purity levels were as follows: furan (99+%) and pyrrole (99%) were from ACROS Organics, and tetrahydrofuran (99+%), stabilized with 250 ppm of BHT (2,6-diter-butyl-4-methylphenol) and tetrahydrothiophene (99%) were from Aldrich Chemical Co. These reagents were purified by freeze−pump−thaw cycles prior to use. The use of THF stabilized with BHT was necessary because in the case of using the unstabilized reagent, the rate coefficients obtained were irreproducible.

Helium (Carburos Metalicos, C50) was used as a carrier gas, and its quality was improved using an Oxisorb (Messer Griesheim) trap and a molecular-sieve trap at room temperature.

H_2SO_4 and HNO_3 were supplied by Panreac and were of AR quality.

Molecular fluorine was supplied by Praxair as a mixture with helium (5% F_2, 95% He).

3. Results

The absolute experiments for tetrahydrofuran, as mentioned above, were performed under pseudo-first-order conditions with a large excess of reactant over NO_3. Some preliminary experiments were developed in order to check that heterogeneous losses of NO_3 were negligible. Figure 1 shows the pseudo-first-order loss of NO_3 vs time, for this reaction at 340 K for different concentrations of THF. The slope of this plot yields the pseudo-first-order coefficient k', according to eq 1. There is a small positive intercept in the first-order plots, which could be attributed to the initial consumption of NO_3 by a rapid reaction with impurities (i.e., THF stabilizer). So long as the impurities react rapidly, the plots will be linear, and their slopes will correctly represent the pseudo-first-order rate coefficients. Figure

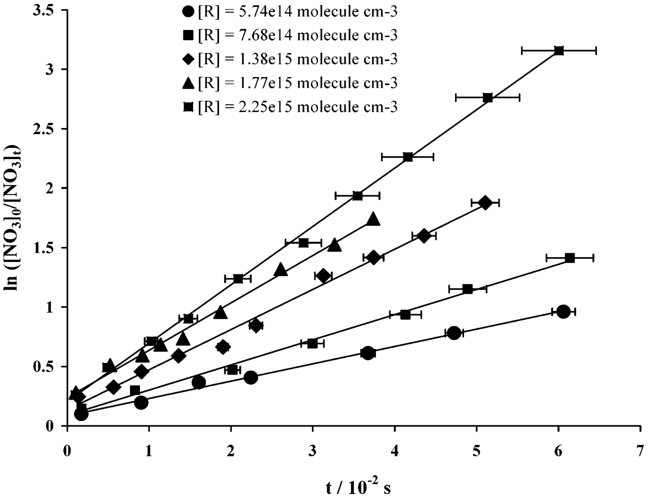


Figure 1. First-order plots for the reaction of NO_3 with tetrahydrofuran at 340 K.

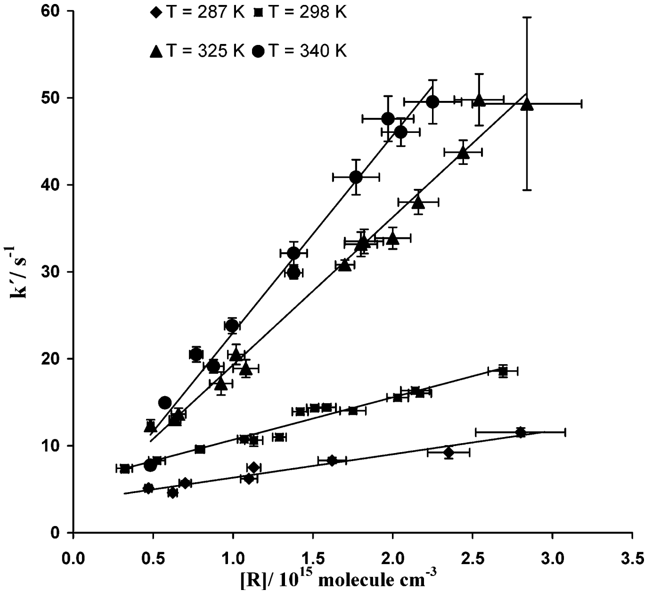


Figure 2. Plots of the pseudo-first-order rate coefficients k' vs concentration of tetrahydrofuran at different temperatures.

2 shows plots of the values of k' vs [THF] for this reaction at different temperatures. The second-order rate coefficient, k, at each temperature was obtained as the slope of these straight lines in accordance with eq 1. The positive intercepts observed at low temperatures in Figure 2 can be attributed to heterogeneous processes since the reaction could not be studied at temperatures lower than 287 K due to the curvature observed in the second-order plots at $T < 287$ K (the curvature is much more pronounced at lower temperatures). However, for temperatures higher than 287 K these plots did not present curvature and it can be concluded that heterogeneous processes do not influence the second-order slopes, which are reasonable straight lines in the temperature range tested. It can also be observed that the rate constant for the wall losses is more intense as the temperature diminishes.

As indicated previously, the reactions of NO_3 with furan were performed without a large excess of reactant over NO_3. In this case, according to eq 2, plots of $Y = 1/(B_0 - A_0) \ln[(M - X_a)/M(1 - X_a)]$ vs time yield the bimolecular rate constant. Figure 3 shows such a plot for this reaction at different temperatures. In relation to THT, plots of (1/[THT]) $\ln([NO_3]_0/[NO_3]_t)$ vs time yield directly the bimolecular coefficient, k, according to eq 4.

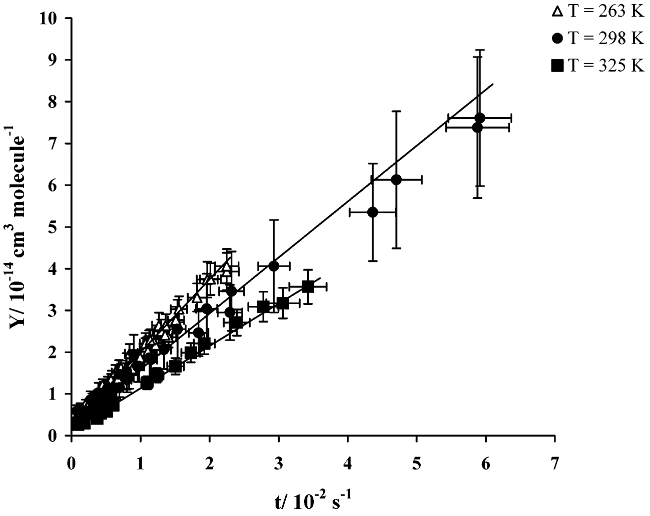


Figure 3. Plots of Y ($Y = (1/(B_0 - A_0)) \ln[(M - X_a)/M(1 - X_a)]$) vs time for the reaction of the nitrate radical with furan at different temperatures.

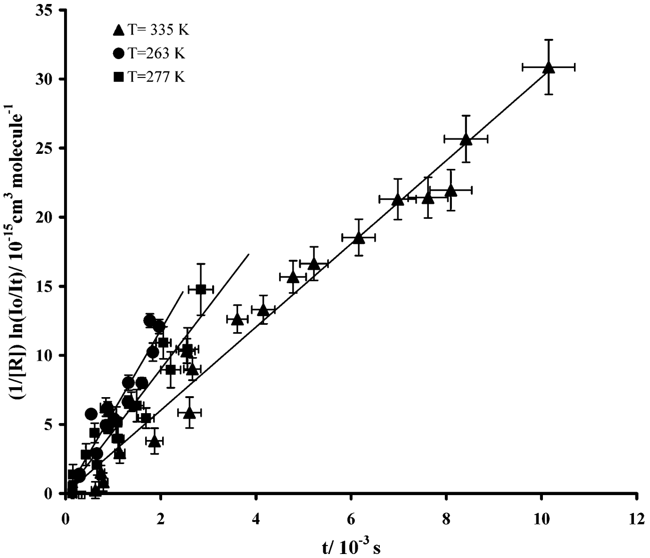


Figure 4. Plots of (1/[THT]) $\ln([NO_3]_0/[NO_3]_t)$ versus t for the reaction of NO_3 radical with tetrahydrothiophene at different temperatures.

Figure 4 displays this plot for the reaction of NO_3 with THT at different temperatures. Some deviation from the straight lines was obtained, indicating a good mixing of the reactants in the flow tube even for such small times used in these experiments, due to the high rate constant. In the figure, it can also be seen that the intercepts are insignificant.

The studies of the temperature dependence of the reaction of NO_3 with the compounds under investigation were carried out in the flow tube over the temperature range 263−335 K, apart from the reaction of NO_3 with tetrahydrofuran as explained previously. In this last case, the temperature range was 287−340 K. The results allowed the activation energy, E_a, to be calculate using the Arrhenius equation. Figure 5 shows Arrhenius plots, where ln k has been plotted vs $1/T$, for the reactions of NO_3 with tetrahydrothiophene, furan, and tetrahydrofuran.

Error bars in the figures have been determined by propagation of errors taking into account the errors in all the initial parameters. There are no error bars for $\ln[NO_3]_0/[NO_3]_t$ (Figure 1) since they are negligible (estimated at 1%).

The results obtained for the reaction of NO_3 with pyrrole suffer from a level of uncertainty, possibly due to the influence of secondary chemistry and decomposition processes in the flow

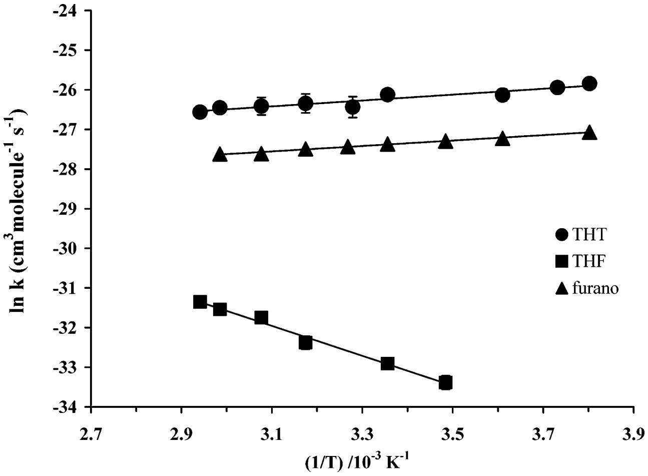


Figure 5. Arrhenius plots for the reactions of NO_3 with tetrahydrothiophene, furan, and tetrahydrofuran.

tube (evidence for the reaction of pyrrole with HNO_3 was found). Therefore, only an upper limit value for the kinetic constant at room temperature is given here, and a more complete kinetic study is required for this particular reaction.

A summary of rate coefficients, k, at different temperatures for the reactions of NO_3 with the heterocyclic compounds under investigation is given in Table 1 along with their activation energies E_a.

According to these experimental results, the proposed Arrhenius expressions are as follows:

Furan:

$$k = (1.3 \pm 0.8) \times 10^{-13} \exp[(700 \pm 200)/T] \quad (\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) \quad (5)$$

Tetrahydrofuran:

$$k = (2 \pm 2) \times 10^{-9} \exp[-(3800 \pm 400)/T] \quad (\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) \quad (6)$$

Tetrahydrothiophene:

$$k = (1 \pm 1) \times 10^{-13} \exp[(1000 \pm 200)/T] \quad (\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) \quad (7)$$

These expressions can be used to predict the rate coefficients of the reactions of the compounds in question with NO_3 in the range of temperatures cited above (errors are calculated as $t\sigma$ where t is the t-Student for 95% confidence degree).

4. Discussion

Rate constants for the reactions between NO_3 and the heterocycles under investigation, with the exception of THT, have previously been determined by a relative technique, but to the best of our knowledge, this is the first absolute study concerning such reactions. The rate coefficients determined here at 298 K are compared with available literature data in Table 2. Moreover, the rate coefficient corresponding to the reaction of NO_3 with thiophene[33] has also been included in the table for the sake of comparison with the heterocycles studied here.

It can be seen from the results in Table 2 that, with the exception of pyrrole, there is a good agreement between our results and those of other authors. In the case of pyrrole, there is a significant difference between our values and the ones reported in the literature.[29,39] It is possible that our higher value could be due to an increase in the reactivity of pyrrole in an acidic medium,[40] which in our system is due to the HNO_3 used as a precursor for the NO_3 radical. For this reason, only an upper limit value is proposed in this work. In the case of tetrahydrothiophene, this is the first kinetic study undertaken to investigate the reaction of this heterocycle with NO_3 and, as such, literature data are not available.

TABLE 1: Summary of the Absolute Rate Coefficients and Activation Energies Measured for the Reactions of NO_3 with the Heterocycles Analyzed[a]

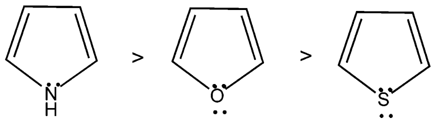
compound	T/K	k/cm^3 molecule^{-1} s^{-1}	E_a/kJ mol^{-1}
furan	263	$(1.75 \pm 0.08) \times 10^{-12}$	-6 ± 1
	277	$(1.5 \pm 0.1) \times 10^{-12}$	
	287	$(1.40 \pm 0.08) \times 10^{-12}$	
	298	$(1.3 \pm 0.2) \times 10^{-12}$	
	306	$(1.2 \pm 0.1) \times 10^{-12}$	
	315	$(1.1 \pm 0.1) \times 10^{-12}$	
	325	$(1.02 \pm 0.09) \times 10^{-12}$	
	335	$(1.01 \pm 0.07) \times 10^{-12}$	
THF	287	$(3.17 \pm 0.54) \times 10^{-15}$	32 ± 3
	298	$(5.1 \pm 0.2) \times 10^{-15}$	
	315	$(9 \pm 1) \times 10^{-15}$	
	325	$(16 \pm 1) \times 10^{-15}$	
	335	$(20 \pm 2) \times 10^{-15}$	
	340	$(24 \pm 2) \times 10^{-15}$	
THT	263	$(6.0 \pm 0.6) \times 10^{-12}$	-8 ± 2
	268	$(5.5 \pm 0.9) \times 10^{-12}$	
	277	$(4.5 \pm 0.7) \times 10^{-12}$	
	298	$(4.1 \pm 0.5) \times 10^{-12}$	
	305	$(3.3 \pm 0.7) \times 10^{-12}$	
	315	$(4 \pm 1) \times 10^{-12}$	
	325	$(3.4 \pm 0.7) \times 10^{-12}$	
	335	$(2.6 \pm 0.2) \times 10^{-12}$	
	340	$(2.7 \pm 0.5) \times 10^{-12}$	

[a] Errors are calculated as $t\sigma$ where t is the t-Student for 95% confidence degree.

TABLE 2: Rate Constant Determined in This Work for the Reactions of NO_3 with Heterocycles, Compared with Bibliographic References, at 298 K

compound	k_{NO_3}/cm^3 molecule^{-1} s^{-1}, this work (absolute technique)	k_{NO_3}/cm^3 molecule^{-1} s^{-1}, [reference] (relative techniques)
thiophene	$(3.2 \pm 0.2) \times 10^{-14}$	$(3.1 \pm 0.7) \times 10^{-14}$ [29]
		$(3.9 \pm 0.5) \times 10^{-14}$ [30]
THT	$(4.1 \pm 0.5) \times 10^{-12}$	
furan	$(1.3 \pm 0.2) \times 10^{-12}$	$(1.4 \pm 0.2) \times 10^{-12}$ [29]
		$(1.4 \pm 0.2) \times 10^{-12}$ [30]
		$(1.0 \pm 0.06) \times 10^{-12}$ [27]
THF	$(5.1 \pm 0.2) \times 10^{-15}$	$(4.9 \pm 0.3) \times 10^{-15}$ [30]
pyrrole	$<1.8 \times 10^{-10}$	$(4.6 \pm 0.1) \times 10^{-11}$ [29]

Comparison of the rate coefficients obtained at room temperature for the three base heterocycles shows the following trend in reactivity: pyrrole > furan > thiophene.



This is the general trend for reactions between the aromatic heterocyclic compounds and electrophilic species, such as OH and ozone.[19−25] The decrease in reactivity could be related to the level of aromaticity (energy of resonance) exhibited by these compounds and to the electronegativity of the heteroatom present in each ring. Thus, thiophene is the least reactive since it has the greatest resonance energy. And, in the contrary, pyrrole is the most reactive one since, although it has a larger resonance energy than furan, nitrogen is more effective than oxygen at donating its nonbonding pair of electrons into the ring.

TABLE 3: Rate Constants, Activation Energies, and Calculated Mean Tropospheric Lifetimes of Selected Heterocycles with Respect to NO_3 and OH Radical Reactions[a]

compound	k_{NO_3}/cm^3 molecule^{-1} s^{-1} [b]	E_a/kJ mol^{-1}	k_{OH}/10^{-12} cm^3 molecule^{-1} s^{-1}	E_a/kJ mol^{-1}	τ_{NO_3}	τ_{OH}
thiophene	3.16×10^{-14} [c]	18.4 (260−277) K[c] −4.2 (298−433) K[c]	9.47[d]	−2.7[d] −4.9[e] −15[f]	12 h 11 min	12 h 42 min
furan	1.30×10^{-12}	−6	40.4[d]	−2.8[d]	17 min 46 s	3 h
THF	5.1×10^{-15}	32	17.8[g]		75 h 30 min	6 h 46 min
THT	4.14×10^{-12}	−8	19.7[d]	−1.4[d]	5 min 35 s	6 h 7 min
pyrrole	$<1.8 \times 10^{-10}$		105[e]	−3.4[e]	>8 s	1 h 9 min

[a] $[NO_3] = 5 \times 10^8$ molecule cm^{-3} (12 h average) from ref 44; $[OH] = 1.6 \times 10^6$ molecule cm^{-3} (12 h average) from ref 43. [b] Measured in this work. [c] From ref 33. [d] From ref 21. [e] From ref 24. [f] From ref 22. [g] From ref 45.

The reactivity of thiophene and furan can also be compared with that of their corresponding hydrogenated compounds, THT and THF, respectively. It can be seen from the results in Table 2 that the rate constant obtained for the reaction of the NO_3 radical with THT is approximately 2 orders of magnitude higher than that obtained for the reaction with thiophene. The reaction of THF with NO_3 has a rate constant that is around 3 orders of magnitude lower than that for the reaction between furan and NO_3. Moreover, the rate constant obtained for the reaction with THT is 3 orders of magnitude higher than the corresponding rate coefficient for the reaction with THF. These large differences in rate coefficients point to different reaction mechanisms for the reactions, and these will be discussed below.

In reference to the temperature dependence for the reactions between NO_3 and the heterocycles, as far as we know, this is the first determination of activation energies for the reactions of NO_3 with furan, tetrahydrothiophene, and tetrahydrofuran. A temperature study was not undertaken for pyrrole due to the decomposition process outlined above. The temperature-dependence behaviors of thiophene and furan are clearly different. The reactivity of NO_3 with thiophene shows an anomalous behavior, and this has been described previously.[33] At low temperatures (260−277 K), activation energy is negative, $E_a < 0$, and at high temperatures (298−433 K), $E_a > 0$. The rate constant appears to be essentially independent of temperature between 272 and 296 K. This result was explained in terms of two parallel mechanisms.[33] By contrast, the reaction of NO_3 with furan shows the usual Arrhenius behavior with negative activation energy. Furthermore, the reaction of THF with NO_3 shows a positive activation energy in the studied temperature range ($E_a = 32$ kJ/mol), in contrast to the reaction with THT which shows a slight negative activation energy ($E_a = -8$ kJ/mol) (see Table 1).

On considering these experimental results and in an attempt to draw some conclusions concerning the mechanisms of the reaction under investigation, a summary can be made of the reactivity of other organic compounds with the NO_3 radical.[39,41,42] On one hand, rate constants (in units of cm^3 molecule^{-1} s^{-1}) in the range of 10^{-17}−10^{-14} usually correspond to an H-abstraction mechanism and the reactions show positive activation energies. On the other hand, a double bond addition mechanism and negative activation energies are usually attributed to observed rate constants between 10^{-14} and 10^{-11} cm^3 molecule^{-1} s^{-1}. In addition, sulfur-containing organic compounds at room temperature show rate constants ranging from 10^{-12} to 10^{-13} cm^3 molecule^{-1} s^{-1} and the most probable mechanism proposed in these cases is an initial addition of NO_3 to the S atom. Moreover, for oxygen-containing compounds (ketones, alcohols, ethers, and aldehydes) the published rate constants in units of cm^3 molecule^{-1} s^{-1} range from 10^{-18} for ketones to 10^{-14} for aldehydes.

In addition to this, and since the kinetic and mechanistic behaviors of the reactions between organic compounds and OH and NO_3 radicals are very similar, more information can be obtained by comparing our results with literature results for OH reactions[19−25] (see Table 3). The reactions of OH with thiophene, furan, and pyrrole show negative activation energies, and an addition mechanism to the double bonds is proposed for these reactions. In the case of thiophene, an addition process to the sulfur atom is also possible, and in the case of pyrrole, an hydrogen abstraction of the −NH hydrogen could also be possible. The reaction of THT with OH also shows negative activation energy,[21] and H-abstraction and addition to the sulfur atom are proposed as possible reaction mechanisms in this case. Comparison of our results with literature values shows that the temperature dependence is similar for the reactions of OH and NO_3 with furan and tetrahydrothiophene but not for thiophene which, as explained above, has an anomalous dependence in the reaction with NO_3. Finally, hydrogen abstraction seems to be the only plausible route for the reaction of THF with OH. In this sense, and comparing the hydrogenated compounds, we could suppose the same reaction mechanism for both compounds (THF and THT): i.e., an H-abstraction at the α position. As the radical formed after abstraction is most stable for the THT, due to the lower electronegativity of the S atom, its reaction with the NO_3 radical is faster than the corresponding THF reaction. This fact can explain the difference observed in the reactivity of these compounds with the OH radical.[21] However, the increase observed for NO_3 reactions on comparing THT with THF is higher than expected and only a different reaction mechanism can explain this observation.

All the results presented here, as well as those from our review of the literature, allow certain conclusions to be drawn, and these can be summarized in the mechanism proposed for each of the studied reactions: In the case of the reaction of NO_3 with furan and thiophene, the results suggest that the reaction could proceed by initial NO_3 addition to the $>C{=}C<$ bonds, but for thiophene reaction an S-addition of the NO_3 to the S atom is also possible. In contrast, NO_3 + THF proceeds by H-atom abstraction. For the THT reaction, an addition mechanism to the sulfur atom could be the most probable path. Finally, in the case of pyrrole, a clear conclusion could not be drawn from our experimental results, although this reaction probably involves an initial addition of NO_3 to the double bonds or an abstraction of the hydrogen from the −NH bond, by analogy to the behavior of OH.

The proposed mechanisms could be confirmed by characterizing the products generated in the processes. In this sense, information on the products formed in the reactions of NO_3 with heterocycles is only available in the case of furan and its derivatives.[31] Both 3*H*-furan-2-one and *cis*-butenedial have been detected as products from the reaction of furan with the NO_3 radical. According to these results, Berndt et al.[31] conclude that the reaction mechanism involves initial addition of NO_3 to the double bond to give a resonance-stabilized radical. Subsequent rearrangement and loss of NO_2 generates *cis*-butenedial or 3*H*-

furan-2-one (the product from the intramolecular rearrangement of *cis*-butenedial). Therefore, analysis of these products confirms the mechanism for this reaction deduced from the kinetic data presented in this work. No product study has been developed for the other reactions described here, and the mechanism cannot be confirmed in this way. Product determination is necessary before the pathways of the reactions studied in this work can be completely elucidated.

Finally, the importance of the presence of these heterocycles in the atmosphere can be assessed by calculating their mean atmospheric lifetimes. This can be performed using the rate constants at room temperature for the gas-phase reactions of the series of heterocycles with OH and NO_3 radicals in combination with estimated ambient tropospheric concentrations of these reactive species [R].[43,44]

The rate constant measured in the present work has been used for the reactions of these heterocycles with NO_3, and the rate constants corresponding to the OH reactions were obtained from the literature. The results are shown in Table 3, and it can be clearly seen that the nighttime reaction of furan, tetrahydrothiophene, and probably of pyrrole with the NO_3 radical is the dominant loss process of these compounds in the atmosphere. In contrast, the nighttime reaction with NO_3 and the daytime OH radical reaction have a similar importance in the case of thiophene. Last, daytime reaction with OH is undoubtedly the main loss process for tetrahydrofuran since the OH radical reaction leads to significantly shorter mean lifetimes than the corresponding NO_3 radical reactions. In summary, it can be concluded that nighttime reactions with the NO_3 radical are an important, if not dominant, loss process for heterocycles in the atmosphere.

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