

A kinetic study of gas-phase reaction of thiophene with NO₃ by using absolute and relative methods

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Abstract

The gas-phase rate coefficient for the reaction of thiophene with nitrate radical, NO₃, has been determined, using relative (gas chromatography as analytical tool) and absolute methods at 298 K. The absolute experiments were carried out using a fast-flow-discharge technique, with detection of the NO₃ radical by Laser Induced Fluorescence (LIF). The proposed rate coefficient at 298 K is, $k = (3.16 \pm 0.27) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The temperature dependence was studied by the absolute technique in the range 260–433 K, observing that in the interval of 260–277 K the rate coefficient decreases as the temperature increases and from 298 K onwards the rate coefficient increases with temperature. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Nitrate, (NO₃) and hydroxyl (OH) radicals together with ozone (O₃) are important oxidant agents in the Earth's atmosphere [1–6]. Their reactions are the principal degradation routes for many organic compounds. The OH radical reaction is normally the main sink for numerous compounds during the daytime. However the NO₃ radical that undergoes photolysis by sunlight [7] is mainly involved in night-time atmospheric chemistry. Many kinetic and mechanistic studies of the oxidation of organics by OH, O₃ and NO₃ have been reported [4–6,8–14]. The reactions of some heterocycles with OH and O₃ have been the subject

of different studies [14–24]. However, the investigation about the reactivity of these compounds, with the NO₃ radical, is specially scarce, and more kinetic data for the NO₃ reaction with heterocycle compounds are needed to get a better understanding on its role in the atmospheric chemistry.

Thiophene is a five-member heterocycle ring that is emitted in processes of energy production such as coal gasification, fuel oil, natural gas and coal combustion and also it is detected over seaweed fields [25–28]. Thiophene is a sulphur-containing compound and the study of its chemistry is important to understand the whole role of the sulphur compounds in the atmospheric global sulphur cycle. The reaction of thiophene with OH and O₃ has been reported in different works [6,14,15,21], but the night-time reaction of the NO₃ radical with thiophene has been less investigated [4,5,29]. So far the available rate constant

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has been obtained from relative technique and no data on the temperature dependence have been reported.

In this work, we report the first absolute kinetic study of the reaction of NO₃ with thiophene in a fast flow system by using LIF detection of the NO₃ radical at different temperatures between 260 and 433 K, together with the relative study of this reaction at 298 K, using 1-butene as reference compound.

2. Experimental

2.1. Absolute rate experiments

All the kinetic measurements of absolute rate constants were carried out using a discharge-flow tube reactor with LIF detection for the nitrate radical. The experimental set-up has been described elsewhere [30] and only the relevant details are given here. All the experiments were carried out at low pressure (about 1 Torr). The temperature flow tube was set between 260 and 435(±1) K.

Nitrate radicals were generated by the reaction, $F + HNO_3 \rightarrow NO_3 + HF$, and they were admitted into the flow tube through a fixed port. Fluorine atoms were obtained by passing F₂–He mixtures through a microwave discharge. The initial NO₃ concentrations were in the range $0.6\text{--}10 \times 10^{12}$ molecule cm^{−3}.

Quantitative detection of NO₃ was carried out by monitoring the fluorescence emitted after the (0–0) 2E' ← 2A₂' transition of NO₃, pumping with λ = 662.0 nm radiation from a dye laser (Quantel, TDL90). Absolute concentrations of NO₃ were determined before or after each kinetic run by chemical titration with known amounts of tetramethylethane (TME) [31]. The detection limit for the NO₃ concentration in our LIF system is around 10¹¹ molecule cm^{−3}.

Thiophene was introduced through a sliding injector, whose position could be varied up to 70 cm from the centre of the observation region. The concentrations, ranging from 1×10^{13} to 5×10^{13} molecule cm^{−3}. Contact times between NO₃ and the reactant were in the range 0–80 ms.

The rate coefficient, *k*, is defined by:

$$\frac{d[NO_3]}{dt} = k[NO_3][\text{thiophene}]. \quad (\text{I})$$

As all the kinetic experiments were performed under pseudo-first-order conditions, with a large excess of reactants over NO₃ for the analysis of the experimental results of these reactions, the integrated rate expression [32] used:

$$\ln \frac{[NO_3]_0}{[NO_3]_t} = (k[\text{thiophene}])t = k't, \quad (\text{II})$$

where

$$k' = k[\text{thiophene}]. \quad (\text{III})$$

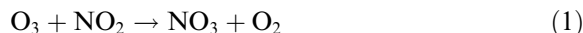
The pseudo-first-order rate coefficient, *k'*, is obtained as the slope of the straight line when $\ln([NO_3]_0/[NO_3]_t)$ is plotted vs. time. The second-order rate coefficient *k* is obtained as the slope of the plot of *k'* vs. [thiophene] according to Eq. (III).

2.2. Relative rate experiments

The relative rate experiments were carried out in a ca. 60 l collapsible Teflon bag (Alltech). The bag was housed in a dark cabinet, and operated at atmospheric pressure (720 ± 10 Torr) and 298 ± 1 K. Known quantities of each component of the reaction mixture were metered using a vacuum line and volume–pressure measurement. These components were introduced separately into the reactor in a stream of bath gas. Concentrations of thiophene, reference and internal-standard compounds contained in the bag were measured by sampling the bag to a gas chromatograph (SRI 8610C) equipped with flame ionisation detection (GC-FID) via a 5 cm³ sample loop. Separation of individual compounds in the sample was achieved using a stainless steel (SS) column packet Chromosorb 102 80–100 MT 250. The reference compound was 1-butene and the internal standard was ethane. Typical initial concentrations of the internal standard and reference compounds in the bag were $(3.4\text{--}3.7) \times 10^{15}$ and $(5.9\text{--}6.5) \times 10^{15}$ molecule cm^{−3}, respectively. The temperature for the column was programmed from 313 to 493 K.

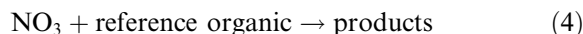
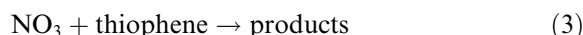
NO₃ radicals were generated by the thermal decomposition of N₂O₅, which was synthesized in

a separate set up by the reaction of O_3 excess with NO_2 according to reactions (1) and (2).



The relative rate technique is based on monitoring the relative decay rates of a series of organics, including at least one organic whose NO_3 radical reaction rate constant must be reliably known, in presence of NO_3 radicals.

The NO_3 radical reacts with thiophene, with an unknown rate coefficient k , and with a reference organic compound, in our case 1-butene with a known rate coefficient, $k_{1-butene} = (1.2 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [4]. The reactions are:



The rate coefficient, k , is defined by Eq. (I). Providing that thiophene and the reference organic only react with NO_3 radicals, the loss of organic compounds is given by

$$\ln \left(\frac{[\text{thiophene}]_0}{[\text{thiophene}]_t} \right) - D_t = k/k_{\text{reference}} \ln \left(\frac{[\text{reference}]_0}{[\text{reference}]_t} \right) - D_t, \quad (\text{IV})$$

where subscripts 0 and t refer to time 0 and t , respectively, of an experiment for the thiophene and the reference organic compound and D_t is the dilution factor at time t , due to the small amounts of dilution occurring from the incremental additions of N_2O_5 to the reactant mixtures. Plots of $\ln([\text{thiophene}]_0/[\text{thiophene}]_t) - D_t$ vs. $(\ln([\text{reference}]_0/[\text{reference}]_t) - D_t)$ should yield straight lines with slope $k/k_{\text{reference}}$.

With this experimental technique, the initial concentration of thiophene was $3.2 \times 10^{15} \text{ molecule cm}^{-3}$. Typical incremental amounts of N_2O_5 , in the range of $0.6\text{--}1.8 \times 10^{15} \text{ molecule cm}^{-3}$ per addition, were added to the reactor during the experiment.

To verify that there were no reaction products that would interfere with the chromatographic analysis, separate experiments were carried out on the following reactions: NO_3 radical and reference,

NO_2 and reference, NO_3 radical and substrate, NO_2 and substrate, NO_3 radical and internal standard, and NO_2 and internal standard. Some experiments were carried out in order to examine if any possible nitrogen oxide compounds, i.e. NO_2 , N_2O_5 , NO_3 , would react with the gas chromatographic column packing to produce 'ghost' peaks.

3. Materials

3.1. Absolute experiments

Helium was used as carrier gas in the absolute experiments. Its purity (better than 99.999%, Carbueros Metálicos C50) was improved by means of an Oxisorb (Messer Griesheim) trap and a molecular-sieve trap at room temperature.

Nitric acid vapour was obtained by bubbling He through 2:1 concentrated sulphuric–nitric acid mixtures (P.A. quality, Panreac) at 252 K. Molecular fluorine was supplied by Praxair mixed with helium (5% F_2 , 95% He).

3.2. Gas chromatography

Nitrogen (C50) was supplied by Praxair, and hydrogen was generated by a Hydrogen Generator (Parker Chrom Gas, 9150).

3.3. N_2O_5 synthesis

NO_2 (Praxair + 99%) and O_2 (Carbueros Metálicos + 99%) were used as received.

3.4. Organics

Thiophene (96%) was purified by freeze-pump-throw cycles before use, ethane (99+%), and 1-butene (99+%) are from Aldrich.

4. Results and discussion

Obtained data from the absolute technique, are shown in Fig. 1, according to Eq. (I), where the pseudo-first-order loss of NO_3 is plotted vs. time, for the NO_3 –thiophene reaction at 298 K. The

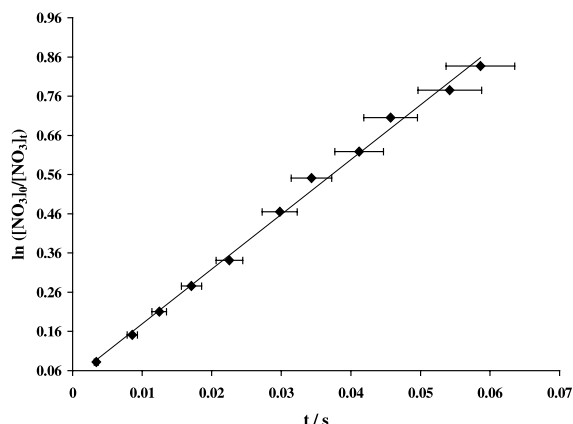


Fig. 1. First-order plot for the reaction of NO_3 with thiophene at 298 K.

slope of this plot yields the pseudo-first-order rate constant k' , based on Eq. (II). Fig. 2 shows the variation of k' vs. thiophene concentration at 260, 298 and 433 K. The second-order rate constants, k , are obtained from the slopes of such straight lines, according to Eq. (III).

By using the relative rate technique, the rate coefficient for the studied reaction was obtained from Eq. (IV). The data were fitted to a straight line by the linear least-squares procedure. The slope combined with the rate constant of the re-

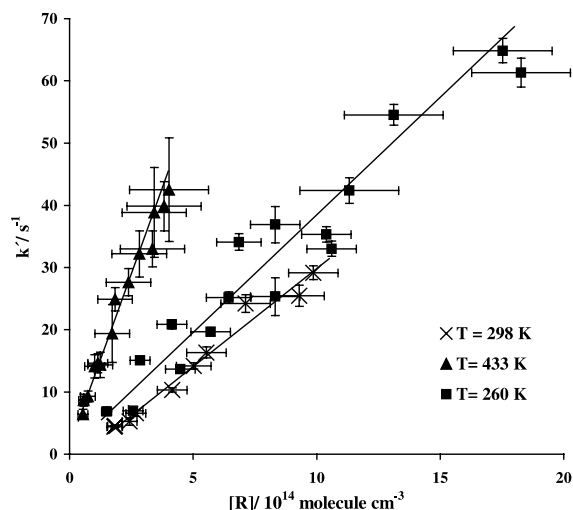


Fig. 2. Second-order plots for the reaction of NO_3 with thiophene at different temperatures. \mathbf{R} is thiophene.

action of reference, $k_{\text{reference}}$, gives the rate coefficient. Fig. 3 shows the data obtained for the reaction studied in the present work.

If we compare the results obtained for both relative ($k = 4.01 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and absolute ($k = 3.16 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) methods for the NO_3 –thiophene reaction, it can be seen that both methods lead to similar values, but the absolute rate coefficient is lower than the obtained by the relative method. This difference could be due to the uncertainty in the rate coefficient for the reference compound, or to a possible pressure dependence for such reaction. On the other hand, our absolute value agrees with the recommended one by Atkinson based on the relative method [4]. The concordance is an indicative of the absence of secondary chemistry at the conditions in which the absolute experiments were done in this work.

The temperature dependence was investigated in the flow tube over the range of temperature 260–433 K. A calibration of the temperature along the flow tube was previously done as reported Canosa et al. [33] and Martinez et al. [34]. The calculated rate coefficients at different temperatures are shown in Table 1. Fig. 4 is an Arrhenius plot of the data. From this table and this figure it can be observed that the reaction between thiophene and NO_3 shows a complicated temperature dependence. For low temperatures (260–277 K),

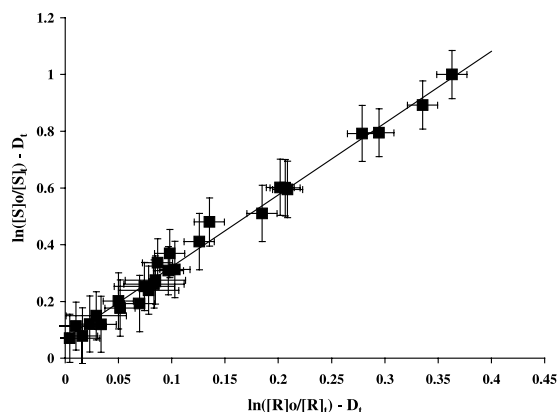


Fig. 3. Plots of Eq. (IV) for thiophene with 1-butene as the reference organic. Errors calculated by the method of Brauers et al. [35]. \mathbf{R} is thiophene and \mathbf{S} is 1-butene.

Table 1

Summary of the measured rate coefficients for the reactions of NO_3 with thiophene at different temperatures

T (K)	k ($10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
260	3.78 ± 0.20
263	3.39 ± 0.60
298	3.16 ± 0.27
321	2.40 ± 0.38
345	3.08 ± 1.17
367	3.53 ± 1.20
389	4.99 ± 1.70
433	11.0 ± 0.21

$[\text{NO}_3] = (0.6 - 3) \times 10^{12} \text{ molecule cm}^{-3}$, $P_{\text{T}} = 1$ to 1.2 Torr, $t = 0.006$ to 0.08 s , $v = 4$ to 9 m/s , error defined by student t -test.

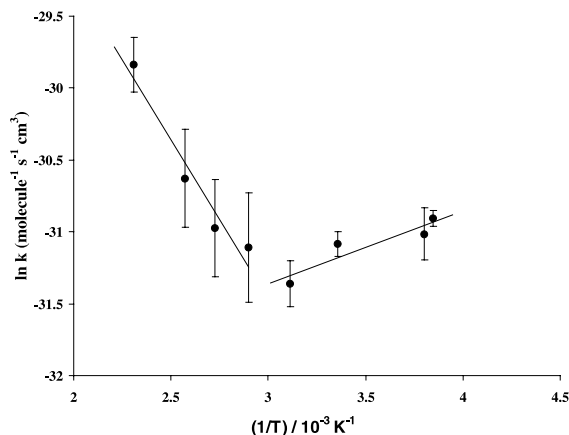


Fig. 4. Arrhenius plots for the reactions of NO_3 with thiophene.

we can see a slight decrease of the rate constant when the temperature increases and that the rate constant increases when the temperature changes from 298 to 433 K. A linear least-square analysis of the data in each zone yields to an activation energy, of 21 kJ/mol for the reaction at temperatures up 298 K (suggesting an H-abstraction mechanism), and a negative activation energy of -3 kJ/mol (may be due to an addition pathway) for lower temperatures. These observations agree with those of Atkinson group [4,5,29], who suggested that the rate constant appears to be essentially independent on temperatures between 272 and 296 K. This fact is also observed in our ex-

periments (see Table 1 and Fig. 4) where the rate constant at 277 and 298 K are quite similar and coincide at the inflexion zone in the figure. A similar behaviour has been observed in kinetic studies of OH radicals with aromatic compounds [15,22].

This result could be due to two parallel mechanisms. One of them predominant in the low temperature range, another one, more significant at higher temperatures. However, these suggestions have to be considered with caution due to the lack of data about these reactions. Therefore more kinetics and products information about the reactions of NO_3 radical with thiophene and other heterocycle compounds ought to be obtained to elucidate the reaction mechanism.

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