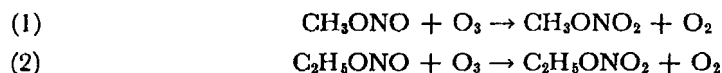


The Reactions of Ozone with Methyl and Ethyl Nitrites

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Abstract

The reactions of O₃ with CH₃ONO and C₂H₅ONO were studied using infrared absorption spectroscopy in a static reactor at temperatures between 298 and 352K. Both reactions followed simple second-order kinetics forming the corresponding nitrate:



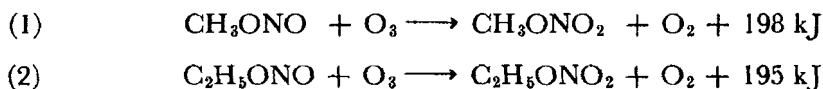
The rate coefficients are given by

$$\begin{aligned} \log_{10} k_1(\text{cm}^3/\text{molec}\cdot\text{sec}) &= (-12.17 \pm 0.23) - \left(\frac{5315 \pm 172}{2.303 T} \right) \\ \log_{10} k_2(\text{cm}^3/\text{molec}\cdot\text{sec}) &= (-15.50 \pm 0.16) - \left(\frac{2351 \pm 116}{2.303 T} \right) \end{aligned}$$

Introduction

The methoxy radical CH₃O is produced in the atmosphere as an intermediate in the photochemical oxidation of hydrocarbons and from the photolysis and oxidation of methane [1-3]. In the presence of nitrogen oxides NO_x, CH₃O may be converted into the corresponding nitrite and nitrate, CH₃ONO and CH₃ONO₂ [3-5]. In spite of the potential atmospheric importance of methyl nitrite, few quantitative studies of its chemistry have been published although the photolysis [3], pyrolysis [6], and bond dissociation [7] processes have been investigated.

We report here measurements of the rate coefficients k_1 and k_2 for the reactions of methyl and ethyl nitrites with ozone at several temperatures in the range of 298-352K.



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The reactions have been carried out in a static gas reactor using continuous monitoring of infrared absorptions due to reacting species.

Experimental

Methyl nitrite was prepared by the dropwise addition of 33% H_2SO_4 to a saturated solution of sodium nitrite in a 50% methanol-water mixture. The methyl nitrite vapor was swept by a stream of nitrogen through columns of CaCl_2 and soda asbestos into a cold trap at 195K and purified by trap-to-trap distillation immediately prior to use. Ethyl nitrite was prepared similarly using ethanol. Methyl nitrate was prepared by the method described in [8].

Ozone from a Welsbach ozonator was trapped onto silica gel at 195K and the residual oxygen pumped off. Before the commencement of each experiment the required amount of ozone was distilled directly off the silica gel into a 7.5-cm long black-painted reaction cell. Two sodium chloride windows on the cell allowed the transmission of infrared radiation between 2000 and 600 cm^{-1} supplied by an infrared Perkin Elmer model 421 dual-beam spectrophotometer.

In a typical experiment, nitrite vapor ($\sim 2-3$ torr) was mixed with argon (~ 350 torr) in an isolated sidearm of the reaction cell while ozone was added directly into the main cell. The experiment began with the opening of the tap between the sidearm and the reaction cell and the large pressure difference ensured rapid mixing. Most results were obtained with ozone present in excess over the nitrite by at least a factor of 10 for ease of analysis of the kinetic data.

At temperatures other than room temperature, water from a thermostatically controlled water bath was pumped through water jackets surrounding the sidearm and the reaction cell to ensure thermal equilibrium of the gases before mixing. Reactant pressures were measured with a Texas Instruments model 144 quartz spiral gauge.

Results and Discussion

Reaction Product Identification

The rates of disappearance of methyl and ethyl nitrites were determined by monitoring the absorption arising from the RO—NO stretching vibration at either 805 cm^{-1} for methyl nitrite or 798 cm^{-1} for ethyl nitrite [9]. At these frequencies there was negligible interference from absorption bands due to other reactants and products. Methyl nitrate was identified as the product of reaction (1) from a comparison of the reaction product spectrum with that of an infrared spectrum of a sample of pure methyl nitrate. The most important distinguishing feature between the absorption spectra of methyl nitrite and methyl nitrate is that methyl nitrate shows an absorption in the region of 1270–1300 cm^{-1} due to an NO_2 symmetric stretch [10], whereas methyl nitrite does not. Also, two peaks in the absorption spectrum of the nitrite between 1600 and 1700 cm^{-1} , which arise because of the presence of both the *cis* and *trans* configurations [9], merge into a single absorption between 1640 and 1680 cm^{-1} when the nitrite is converted

to nitrate. As both the merging of these two peaks and the appearance of an absorption around 1300 cm^{-1} were also observed during the course of reaction (2), we conclude that ethyl nitrate is produced from the ozonolysis of ethyl nitrite.

Reaction Stoichiometry

No change in total pressure was observed during the course of either reactions (1) or (2), or when pure ozone, in the absence of added reactant, was present in the reaction cell. Also, the absorbance of the nitrate at reaction completion was the same per mole of nitrite (with ozone in excess) and per mole of ozone (with nitrite in excess). This indicates that the stoichiometry of the reaction is 1 mole of nitrite reacting with 1 mole of ozone as written in eqs. (1) and (2), and that ozone is stable with respect to decomposition within a typical reaction duration.

Rate Coefficients

In most kinetic experiments rate coefficients were determined under pseudo first-order conditions with ozone present in greater than ten fold excess. The disappearance of the nitrite or appearance of nitrate were the quantities measured directly, and the reaction rate coefficients were then calculated from the disappearance or appearance data using the Guggenheim method [11]. When excess nitrite was present, absorption bands from the reactant nitrite overlapped with those of the product nitrate, and generally it was not possible to monitor the rate of nitrate appearance accurately under these conditions. One experiment with methyl nitrite was carried out using a much lower excess of ozone (approximately four fold) and the rate coefficient for this experiment calculated using the full integrated second-order rate equation. The results of individual experimental determinations of k_1 and k_2 at different temperatures are shown in Tables I and II for reactions (1) and (2), respectively. It should be noted that the value obtained for k_1 using the low ozone excess and second-order rate law analysis lies within the spread of values obtained under pseudo first-order conditions at the same temperature. This is further evidence of the assumed reaction stoichiometry and indicates that the reaction is kinetically simple. Activation energies were found from a least squares analysis of the Arrhenius plot, $\log_{10} k$ versus $1/T$ (Fig. 1) obtained from the Arrhenius equation in the form

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303 RT}$$

Over the limited temperature range studied (298–352K) the slope and intercept of these plots gave the following results for the above equation:

$$\log_{10} k_1(\text{cm}^3/\text{molec} \cdot \text{sec}) = (-12.17 \pm 0.23) - \left(\frac{5315 \pm 172}{2.303 T} \right)$$

$$\log_{10} k_2(\text{cm}^3/\text{molec} \cdot \text{sec}) = (-15.50 \pm 0.16) - \left(\frac{2351 \pm 116}{2.303 T} \right)$$

TABLE I. Reaction (1): CH₃ONO + O₃

Temp K	P ^o CH ₃ ONO Torr	P ^o O ₃ Torr	(pseudo first-order rate constant) × 10 ³ s ⁻¹	k ₁ × 10 ²⁰ cm ³ molecule ⁻¹ s ⁻¹
298	0.879	14.76	6.78	1.42
298	1.451	18.65	7.45	1.24
298	0.925	18.23	7.68	1.31
298	1.237	18.06	7.68	1.31
298 ^a	1.169	16.09	6.46	1.24
298	0.748	14.26	6.02	1.30
298 ^b	4.574	19.75		1.25
316	1.10	12.60	9.12	2.36
316	1.06	13.11	15.4	3.83
316	1.05	14.33	13.7	3.13
316	0.56	9.72	8.62	2.90
338	0.56	11.52	28.0	8.40
338	0.54	9.63	29.6	10.8
338	0.89	12.07	44.2	12.8
352	0.69	11.25	59.7	19.3
352	0.82	10.53	56.9	19.7
352	0.82	12.16	60.0	18.0
352	0.86	11.83	70.0	21.7

^aReaction followed by the appearance of methyl nitrate.

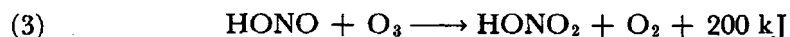
^bRate constant determination by second-order analysis.

(The error limits shown are least square standard deviations of the experimental data. Inclusion of systematic errors in individual measurements of k would increase the estimated uncertainty in activation energies to $\pm 8\%$.) Measured rate constant values for k_1 and k_2 are $1.30 (\pm 0.15) \times 10^{-20}$ and $1.17 (\pm 0.15) \times 10^{-19}$ cm³/molec · sec, respectively, at room temperature. No previous measurements of k_1 and k_2 have been reported.

TABLE II. Reaction (2): C₂H₅ONO + O₃

Temp	P ^o C ₂ H ₅ ONO	P ^o O ₃	(pseudo first-order rate constant) x 10 ²	k ₂ x 10 ¹⁹
K	Torr	Torr	s ⁻¹	cm ³ molecule ⁻¹ s ⁻¹
298	1.08	13.61	4.72	1.07
298	0.782	9.34	3.42	1.13
298	1.07	12.69	5.04	1.22
298	0.600	13.19	4.97	1.17
298	1.61	12.75	5.12	1.24
310	1.00	13.44	6.54	1.56
310	0.88	14.60	7.59	1.67
310	1.11	11.94	5.39	1.45
310	0.82	12.19	6.63	1.75
310	0.92	12.17	5.88	1.55
324	1.02	12.92	8.47	2.20
324	0.86	12.53	7.38	1.97
324	0.89	12.61	7.71	2.05
324	1.00	13.45	8.91	2.21
324	1.00	12.46	8.02	2.16
328	1.02	12.15	8.96	2.50
328	1.02	11.90	9.67	2.76
328	0.83	11.64	8.05	2.35
328	0.90	12.67	9.22	2.46

The very slow rate measured for k_1 shows that the oxidation of methyl nitrite by ozone is not likely to be an important process in polluted atmospheres. The analogous reaction of O₃ with HONO



has been suggested as having a potentially significant influence on stratospheric NO densities if $k_3 \geq 10^{-17} \text{ cm}^3/\text{molec} \cdot \text{sec}$ [12]. The trend in our results does no more than suggest that k_3 may be less than $10^{-17} \text{ cm}^3/\text{molec} \cdot \text{sec}$.

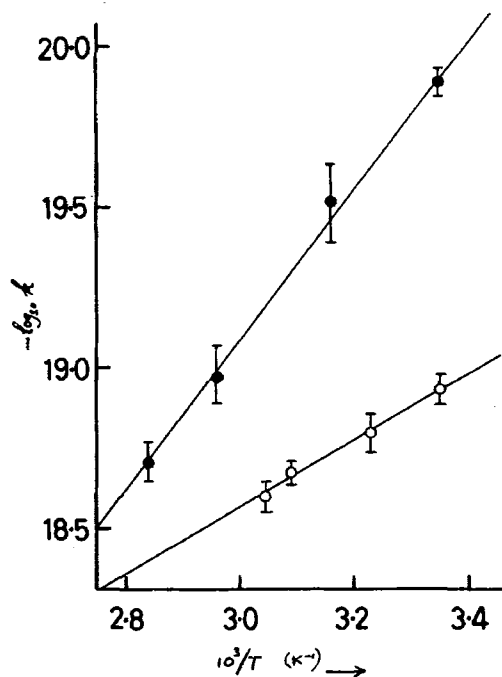


Figure 1. Arrhenius plots for k_1 (methyl nitrite, filled circles) and k_2 (ethyl nitrite, open circles). The points plotted represent the averaged values of k_1 and k_2 at each temperature from the data of Tables I and II. Error bars correspond to twice the standard deviation present in the averaged sets of k values.

Acknowledgment

The authors wish to thank Dr. A. Metcalfe for assistance with the infrared measurements. This work was supported by the New Zealand Universities Research Committee. D. R. H. acknowledges the award of a B. P. Postgraduate Scholarship.

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