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Preparation, Vapor Pressure, and Infrared Spectrum of Methyl Nitrite

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A convenient preparation of ordinary and deuterated methyl nitrite has been described, their high-resolution infrared spectra have been recorded, and the vapor-pressure curve of CH_3ONO has been measured in the region $154 \leq T(K) \leq 225$: $\log P(\text{torr}) = -1365/T + 8.102$.

Introduction

In the course of some laser chemistry studies on methyl nitrite (CH_3ONO), it was found necessary to devise a convenient preparation and purification procedure for this molecule. Although methyl nitrite has been studied before, preparations were not very efficient and purification procedures were even less so (*1-3*). Further, no vapor-pressure data have been reported at temperatures below 210 K (*3*). This work reports a convenient preparation and purification procedure for both ordinary and perdeuterated methyl nitrite, their infrared spectra, and the vapor pressure of CH_3ONO in the range $154 \leq T(K) \leq 225$.

Experimental Section

***Methyl Nitrite*.** A 500-mL round-bottom flask is charged with 100 mL of H_2O and 25 mL of reagent-grade methanol. This solution is purged with helium for 15 min, followed by slow, dropwise addition of a mixture of 25 mL of concentrated H_2SO_4 and 25 mL of nitrosyl sulphuric acid with stirring. The reaction is carried out at room temperature. The product vapors are carried by slow helium flow to a trap cooled to 77 K. After completion of reaction, the crude product trap is attached to a vacuum line and pumped for 30 min at 77 K. The crude product is distilled from trap to trap in a closed vacuum system from 203 to 77 K. Three more distillations are carried out, distilling, again, from 203 to 77 K accompanied each time, however, with slow pumping to facilitate the removal of noncondensible gases from the methyl nitrite. About 3 mL of methyl nitrite is obtained following the above procedure. The product is a glassy, light green solid at 77 K. A gas-phase infrared spectrum was examined, and all of the spectral features could be associated with vibrational modes of CH_3ONO.

***Deuterated Methyl Nitrite*.** The above scheme is carried out in the same manner using methanol-d_4, D_2O, and D_2SO_4 as labeled starting materials. The nitrosyl sulphuric acid used is the ordinary.

***Vapor Pressure*.** Measurements were made by using two differential capacitance manometer heads (MKS-Baratron) with ranges from 0 to 10 torr and from 0 to 1000 torr, for which the manufacturer specifies 0.1% absolute accuracy when calibrated electronically in accord with their procedure (1 torr = 133.3 N/m^2). The heads were attached to a glass vacuum system (500-cm^3 volume) equipped with Teflon stopcocks; the evacuated base pressure was 2×10^{-6} torr. Samples of methyl nitrite were stored in liquid N_2, and, before pressures were measured, samples were pumped on for 30 min at 77 K. Melting-point temperature baths were prepared by using pure solvents. The methyl nitrite sample was allowed to equilibrate in the temperature baths for 30 min prior to recording the vapor-pressure measurements. All points were measured 3 times, and each time, once from below the final pressure and once from above the final pressure. Temperatures were measured by using a solvent thermometer having a range of $73 \leq T(K) \leq 303$, calibrated with LN_2, ice slush, and compared at room temperature with a previously calibrated thermometer. All temperatures were precise to with ±1.5 K. The accuracy was within this range of precision with the exception of the dry ice/ethanol temperature bath, which was about 4 K higher than the known temperature for sublimation of CO_2.

Table I. Values for Vapor Pressure of CH_3ONO from This Work[a]

T, K	*P*, torr	*T*, K	*P*, torr
154 ± 1.5	0.152 ± 0.025	200 ± 1.5	19.8 ± 0.060
180 ± 1.5	4.073 ± 0.013	225 ± 1.5	95.2 ± 0.058

[a] Three data points were measured for each temperature.

Table II. Observed Infrared Absorptions (in cm^{-1}) of CH_3ONO and CD_3ONO in the Gas Phase[a]

	CH_3ONO		
3336 m	1699 s, P	1225 m	838 vs
3319 m	1634 s, R	1143 s	834 s
3226 m	1623 vs, Q	1130 m	820 s, R
3212 m	1620 vs, Q	1115 w	812 vs, Q
3046 m, R	1611 s, R	1055 m, R	803 s, P
3037 s, Q	1470 m	1046 s, Q	636 s
3013 m, P, R	1463 s	1038 m, P	628 vs
2991 s, Q	1458 s	1004 vs	624 s
2963 m, P, R	1444 s	998 s	621 vs
2951 s, Q	1420 m	995 s	616 vs
2942 m, P	1380 m	991 vs	611 vs
1668 s, R	1361 w	985 s	604 s
1680 vs, Q	1250 m	851 s	574 vs
1677 vs, Q	1239 m	841 vs	564 s
	CD_3ONO		
3333 m	1686 s, R	1093 s, Q	811 m, R
3314 m	1678 vs, Q	1080 m, P	801 vs, Q
3241 m	1676 vs, Q	1052 w	787 m, P, R
3220 m	1668 s, P	1048 w	779 s, Q
3204 m	1633 s, R	1038 s	771 m, P
2289 m, R	1625 vs, Q	1030 w	606 m
2281 s, Q	1623 vs, Q	1028 s	598 vs
2265 m, P, R	1619 vs, Q	1025 s	595 s
2247 vs, Q	1612 s, P	1022 w	593 vs
2233 m, P	1353 m	1013 w	588 vs
2209 w	1332 m	957 m	586 s
2189 m	1323 m	951 w	583 s
2135 m	1220 w	937 w	559 m
2095 m, R	1185 w	926 m, R	550 s
2085 s, Q	1127 w	915 vs, Q	545 m
2079 m, P	1104 m, R	904 m, P	542 m

[a] w = weak, m = medium, s = strong (sharp), vs = very strong (sharp). P, Q, and R indicate band centers and branches.

***Infrared Spectra*.** Infrared Spectra were taken on a Nicolet FT-7199 Fourier transform infrared spectrometer. Resolution was set at 1 cm^{-1}, and 50 scans were taken for each sample. All IR data were obtained from gas-phase methyl nitrite at a

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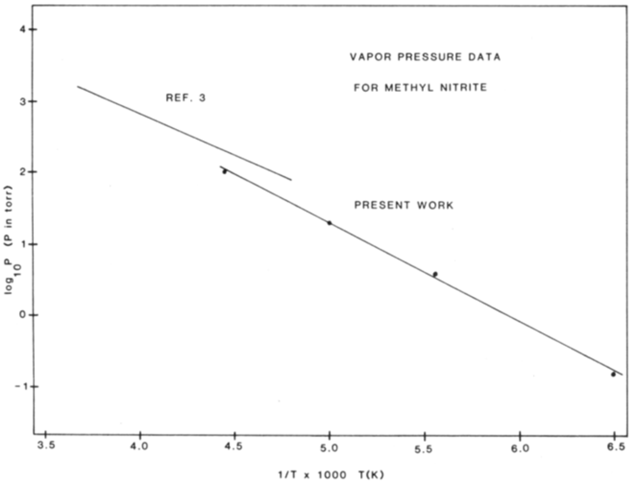

Figure 1. Vapor-pressure data from the present work compared to the previously reported curve (*3*).

pressure of 20 torr. Sample cells used had NaCl windows and a path length of 5 cm. Actual samples were referenced to an evacuated cell of the same specifications.

Results and Discussion

Figure 1 shows the vapor-pressure curve based on the present measurements and the previously reported curve (*3*) for methyl nitrite. Table I lists the measured values for this work.

The logarithm of the pressure shows a pronounced downward curvature vs. the reciprocal of the temperature; this is consistent with the expected negative ΔC_p of vaporization. The least-squares linear fit is

$$\log P(\text{torr}) = -1365/T + 8.102 \qquad (T = 154\text{–}225\ \text{K})$$

which yields

$$\Delta H_{\text{vap}} = 6.25 \pm 0.15\ \text{kcal/mol}$$

The boiling point = 261 K (calculated from the above equation).

The vapor-pressure equation of Thompson and Purkis (ref *3*) is also plotted in Figure 1; they do not tabulate their observations, although their slope is in fair agreement with the present work and the difference in slope is consistent with a negative ΔC_p of vaporization. Their observed pressures are significantly greater at a given temperature than those of the present work. It is subsequently believed that noncondensible impurities were lower in the present work.

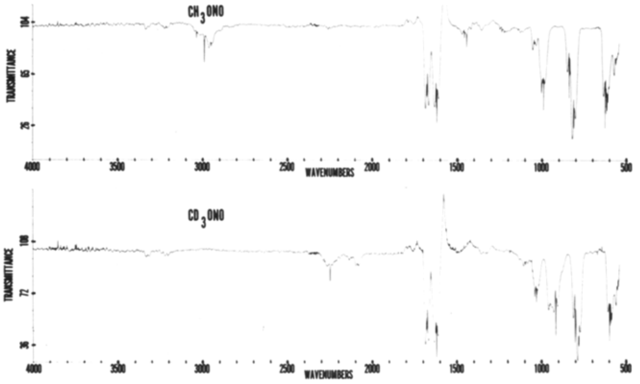

Figure 2. Gas-phase infrared spectra of methyl nitrite (ordinary and perdeuterated): path length, 5 cm; NaCl windows; pressure of 20 torr; T = 298 K; resolution = 1 cm^{-1}.

Figure 2 shows the gas-phase infrared spectra of ordinary and deuterated methyl nitrite. Previous IR spectral data for ordinary methyl nitrate were not as accurate insofar as values for band centers are concerned (*1*, *4*, *5*). The inaccuracy is probably due principly to the lower resolution of the previously used IR spectrometers. Further, no infrared spectrum has been reported for deuterated methyl nitrite. A detailed analysis of the spectral data will be given elsewhere (*6*). The sharp inverted band at ~1570 cm^{-1} is an artifact of the reference cell. Previous studies in this laboratory have indicated there to be no methyl nitrite bands in that region. Table II contains values for the observed vibrational frequencies for ordinary and deuterated methyl nitrite.

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