687. *The Thermodynamic Functions of Methyl Nitrite and the Potential Barrier to Free Rotation.*

By PETER GRAY and M. W. T. PRATT.

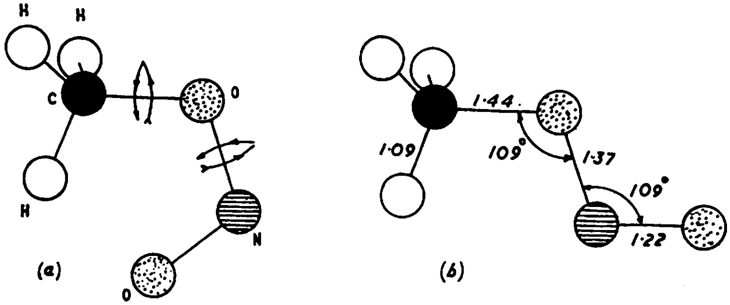
Methyl nitrite is an equilibrium mixture of the *cis-* and the *trans-*isomer, interconvertible by rotation about the O–N bond. At any specified temperature and pressure, their relative abundance is determined by the differences in their thermodynamic functions while their rate of interconversion is determined by the height of the potential-energy barriers which hinder the internal rotations of the molecule.

Equilibrium and thermochemical data are used to derive thermodynamic functions for the (gaseous) equilibrium mixture at 25° C and 1 atm. They are: $\Delta H_f^\circ = -14{,}930 \pm 260$ cal. mole^{-1}; $\Delta G_f^\circ = -450$ cal. mole^{-1} and $\Delta S_f^\circ = -48{\cdot}6$ cal. deg.$^{-1}$ mole^{-1}. The standard entropy relative to the crystal at absolute zero, S_{298}°, is thus $71{\cdot}5 \pm 0{\cdot}9$ cal. deg.$^{-1}$ mole^{-1}. Theoretical calculations of S_{298}°, based on the geometry of the isomers and their vibrational frequencies, lead to $S_{298}^\circ + S_b = 74{\cdot}1 \pm 0{\cdot}14$ cal. deg.$^{-1}$ mole^{-1}, *i.e.*, to $S_b = 2{\cdot}6 \pm 0{\cdot}9$ cal. deg.$^{-1}$ mole^{-1}, where S_b is the entropy "deficit" due to the hindrance imposed on rotation by the potential-energy barriers.

If the methyl group rotates freely about the C–O axis, the barrier hindering free rotation of the N=O group is about 8000 cal. mole^{-1}.

SPECTROSCOPY has recently demonstrated that rotational isomerism is a general property of alkyl nitrites. Tarte [1] studied the infrared and ultraviolet absorption spectra of fifteen nitrites. He found that the characteristic absorption bands of the O–N=O group were doublets in all cases and that the relative intensity of the constituents of the doublets changed with temperature. This is readily explained by the presence of two rotational isomers, having slightly different vibrational frequencies, whose relative abundance varies with temperature. Haszeldine and his co-workers interpret their spectroscopic work [2] on the nitrite esters by the same postulate of rotational isomerism.

Structures of cis- *and* trans-*methyl nitrite* (*a and b respectively*), *showing bond lengths* (Å) *and angles, and internal rotation.*



The infrared spectrum of methyl nitrite has been investigated further by Tarte,[3] and Wagner [4] has studied its Raman spectrum. It exists in two isomeric forms, in both of which the carbon, oxygen, and nitrogen atoms lie in the same plane. These are a *cis*-form (Figure *a*) and a *trans*-form (Figure *b*).

Since two rotational isomers of methyl nitrite can be distinguished, rotation about

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[1] Tarte, *J. Chem. Phys.*, 1952, **20**, 1570; *Bull. Soc. chim. belges*, 1951, **60**, 227, 240.

[2] Haszeldine and Jander, *J.*, 1954, 691; Haszeldine and Mattinson, *J.*, 1955, 4172.

[3] Tarte, *Bull. Soc. chim. belges*, 1953, **62**, 401.

[4] Wagner, *Acta Physica Austriaca*, 1953, **8**, 175.

the $CH_3{\cdot}O{-}NO$ single bond is not free but is opposed by a potential-energy barrier. The existence of this barrier must be reflected in the thermodynamic functions of methyl nitrite, for the entropy of a molecule having restricted rotation is less than that of the same molecule rotating freely. The entropy deficit depends directly upon the size of the barrier. The size of the barrier also determines the rate of *cis* $\rightleftharpoons$ *trans* interconversion but not the equilibrium proportions of the two species, which are decided by the *difference* between the potential-energy minima on either side of the barrier. In fact, as will be shown later, although the barrier to interconversion is large, the actual energy difference between the isomers is probably small, and may be only 100—200 cal. mole^{-1}.

In this paper, equilibrium and thermochemical data are used to derive " best " values of the standard thermodynamic functions of gaseous methyl nitrite (*cis–trans* equilibrium mixture) at 25° and 1 atm. and, from them, an "experimental" value of its standard entropy relative to absolute zero, $S_{298}°$. Next, a value of $S_{298}° + S_b$, where S_b is the entropy " deficit " due to restriction on free rotation, is calculated by the standard methods of statistical mechanics. In deriving this " calculated " value allowance is made for entropy of mixing and for deviations from ideal-gas behaviour. From the difference between the two values the sizes of the potential barriers to rotation are estimated.

Unless otherwise stated, all thermodynamic functions refer to the gaseous state at 25° and 1 atm.

EXPERIMENTAL VALUES FOR THE THERMODYNAMIC FUNCTIONS OF METHYL NITRITE

Independent values of the heat ($\Delta H_f°$) and standard free energy of formation ($\Delta G_f°$) of methyl nitrite can be derived from existing experimental data, and by their combination yield the standard entropy of formation ($\Delta S_f°$): $T\Delta S_f° = -(\Delta G_f° - \Delta H_f°)$.

Standard Heat of Formation.—Baldrey, Lotzgesell, and Style [5] have recently measured and compared the heats of hydrolysis of pure methyl nitrite and of pure sodium nitrite: the unstable nitrous acid liberated during the reaction was immediately oxidised *in situ* by ceric sulphate to nitric acid. The value of ΔH_f of liquid methyl nitrite thus found is $-20{,}330 \pm 253$ cal. mole^{-1}.

They also measured ΔH_v, the latent heat of vaporization of methyl nitrite, finding $\Delta H_v = 5400 \pm 40$ cal. mole^{-1}. Thus, the standard enthalpy of formation of gaseous methyl nitrite $\Delta H_f° = 14{,}930 \pm 255$ cal. mole^{-1}.

Standard Gibbs Free Energy of Formation.—A value for $\Delta G_f°$ of methyl nitrite can be obtained from the work of Leermakers and Ramsperger [6] on the gas-phase equilibrium

$$CH_3{\cdot}O{\cdot}NO(g) + HCl(g) \rightleftharpoons CH_3{\cdot}OH(g) + NOCl(g) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

They measured quantitatively the amount of NOCl present at equilibrium by means of its light absorption, using stoicheiometry to find the concentration of the other components. They derived the equilibrium constant, and hence the standard free-energy change, $\Delta G°$, of the reaction at 25° and 50°. Modern thermodynamic data [7] being used, their result for the Gibbs free energy of formation is corrected from $\Delta G_f° = -100$ cal. mole^{-1} to $\Delta G_f° = -450$ cal. mole^{-1}.

Entropy of Methyl Nitrite.—These values of $\Delta H_f°$ and $\Delta G_f°$ lead to the result * $\Delta S_f° = -48{\cdot}6 \pm 0{\cdot}9$ cal. deg.$^{-1}$ mole^{-1}. The entropy of gaseous methyl nitrite at 25°

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* By using the equation:

$$(\Delta S°/\boldsymbol{R}) = (T_1 \ln K_1 - T_2 \ln K_2)/(T_1 - T_2),$$

a value for the average entropy change $\Delta S°$ over the temperature range 25—50° for reaction (1) could be obtained from Leermakers and Ramsperger's data alone. However, the precision of $\Delta S°$ so found from two readings only is too low for this work; the error is large and the " best " value obtainable leads to an absurdly large entropy deficit.

[5] Baldrey, Lotzgesell, and Style, personal communication.

[6] Leermakers and Ramsperger, *J. Amer. Chem. Soc.*, 1932, **54**, 1837.

[7] Nat. Bur. Stand. Circular 500, " Selected Values of Chemical Thermodynamic Properties," U.S. Dept. of Commerce, Washington, D.C., 1952.

and 1 atm. relative to that at absolute zero, $S_{298}°$, is calculated from this standard entropy of formation by means of the modern values [7] for the standard " absolute " entropies of the elements: it is $S_{298}° = 71·5 \pm 0·9$ cal. deg.$^{-1}$ mole^{-1}.

CALCULATION OF THE ENTROPY OF METHYL NITRITE

Bond Lengths and Angles in Methyl Nitrite.—The only determination of the structure of methyl nitrite is that of Rogowski (Figure).[8] From the electron diffraction of the vapour he finds that the carbon, nitrogen, and both oxygen atoms lie in one plane, and that the molecule is " twice bent at the tetrahedral angle." * Rogowski's results are shown in Table 1 together with values of similar bond lengths and angles in other molecules.[10, 11, 12] Although 120° might be thought more likely on theoretical grounds for an RO–N=O interbond angle (because of the likelihood of trigonal hybridization of the electrons of the nitrogen atom), in fact it makes little difference whether it or the tetrahedral angle is accepted. The value supported by experiment is chosen here. The values for methyl nitrite agree fairly well with those [10] for other compounds, and are accepted for this calculation. The length of the tetrahedral C–H bonds is taken as 1·09 Å.

TABLE 1. *Bond lengths* (Å) *and angles in methyl nitrite compared with similar values in other molecules.*

Bond length			*Interbond angle*		
Bond	In methyl nitrite	In other molecules	Bond	In methyl nitrite	In other molecules
C–O	1·44 ± 0·02	Of 22 compounds, mean 1·437 (range 1·40—1·46)	C–O–N	109° 28′	111° ± 3°, *O*-methylhydroxylamine
O–N	1·37 ± 0·02	1·36, pentaerythritol tetranitrate 1·37, *O*-methylhydroxylamine 1·41, nitric acid	O–N=O	109° 28′	114° ± 2°, *cis*-nitrous acid 118° ± 2°, *trans*-nitrous acid
N=O	1·22 ± 0·02	1·22, nitric acid 1·22, methyl nitrate 1·27, pentaerythritol tetranitrate			

Term-by-term Calculation of the Entropy.—The molar entropy of *cis*-methyl nitrite, S_{cis}, is the sum of translational, rotational, and vibrational contributions:

$$S_{cis} = (S_{transl} + S_{rot} + S_{vib})_{cis}$$

S_{rot} is the sum of contributions made by rotation of the whole molecule in three dimensions, S_p, and the internal rotations S_{int}:

$$(S_{rot} = S_p + S_{int})_{cis}$$

If S_f is the entropy contribution which would be made by the internal rotations of the molecule if they were completely unhindered, and S_b is the reduction in entropy caused by the existence of a potential-energy barrier to free rotation, which is assumed to be the same for both the *cis*- and the *trans*-form:

$$(S_{int})_{cis} = (S_f)_{cis} - S_b$$

Thus $$S_{cis} = (S_{transl} + S_{vib} + S_p + S_f)_{cis} - S_b$$

Similarly $$S_{trans} = (S_{transl} + S_{vib} + S_p + S_f)_{trans} - S_b$$

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* It is erroneously reported by Allen and Sutton in their review [9] that Rogowski found the methyl nitrite molecule to be linear. This unfortunate error has found its way into the literature; see, *e.g.*, W. Klyne, " Progress in Stereochemistry," Butterworths, London, 1952.

[8] Rogowski, *Ber.*, 1942, *B*, **75**, 244.

[9] Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

[10] Cox and Jeffrey, *Proc. Roy. Soc.*, 1951, *A*, **207**, 110.

[11] D'Or and Tarte, *Bull. Soc. roy. Sci. Liège*, 1951, Nos. 8–9–10, 478; Jones, Badger, and Moore, *J. Chem. Phys.*, 1951, **19**, 1599; Palm, *J. Chem. Phys.*, 1957, **26**, 855.

[12] Cohn, Ingold, and Poole, *J.*, 1952, 4272.

After allowances for the entropy of mixing the two isomers in the correct proportions at 298° K and corrections for gas imperfection have been made, an expression is found for the entropy relative to that at absolute zero of the real equilibrium mixture, $S_0°$, in which all quantities except S_b are known. The separate contributions are discussed individually below and the calculated entropy functions are in Table 2.

Contribution due to the translation and rotation of the molecule as a whole. Calculations of the contribution of translation to the entropy are conventional and the result is entered in Table 2. The error in S_{transl} is negligible. The expression for the rotational partition function involves the product of the three principal moments of inertia, A, B, and C, of the molecule.

TABLE 2. *Calculated entropy functions (cal. deg.$^{-1}$ mole^{-1}) of* cis- *and* trans-*methyl nitrite and of the equilibrium mixture.*

		cis	*trans*
Translation	S_{transl}	38·24 ± 0·00	38·24 ± 0·00
Rotation of the molecule as a whole	S_{rot}	23·29 ± 0·05	23·15 ± 0·05
Free internal rotations	S_f (N=O)	5·80 ± 0·04	5·80 ± 0·04
	S_f (CH_3)	3·58 ± 0·07	3·55 ± 0·07
Vibration	S_{vib}	1·95 ± 0·10	2·06 ± 0·10
Totals for the isomers		72·86 ± 0·14	72·80 ± 0·14
Maximum entropy of mixing		1·41	
Entropy of equilibrium mixture (ideal gas)		74·21 ± 0·14	
Correction for gas imperfection		−0·07	
Total for equilibrium mixture at 1 atm., 25° C	$S_{298}°$	74·1 ± 0·14	

When allowance is made for the probable error in Rogowski's structural measurements,[8] it is calculated that for *cis*-methyl nitrite $ABC = (5{\cdot}92 \pm 0{\cdot}30) \times 10^{-115}$ g.^{3} cm.^{6} and for *trans*-methyl nitrite $ABC = (5{\cdot}15 \pm 0{\cdot}26) \times 10^{-115}$ g.^{3} cm.^{6}. From this $(S_{rot})_{cis} = 23{\cdot}29 \pm 0{\cdot}05$ and $(S_{rot})_{trans} = 23{\cdot}15 \pm 0{\cdot}05$ cal. deg.$^{-1}$ mole^{-1}.

Contribution due to internal rotation. There are two possible internal rotations in methyl nitrite as indicated in the Figure. These are rotation of the methyl group about the C–O bond and rotation of the N=O group about the O–N bond.

The contributions to the total entropy which these internal rotations make if they are perfectly free, S_f, may be calculated as follows. Let I_A be the moment of inertia of a molecular group about its axis of rotation and I_B be the moment about the axis of rotation of all the atoms except the group whose rotation is being considered. Then the reduced moment of inertia of the rotating group $I = I_A I_B/(I_A + I_B)$ and the formula quoted by Pitzer:[13]

$$S_f = \mathbf{R}(-0{\cdot}767 + \tfrac{1}{2}\ln T + \tfrac{1}{2}\ln I \times 10^{40} - \ln n)$$

enable the entropy contribution of the free internal rotation to be calculated. In this formula n, the number of potential energy minima of (approximately) equal depth passed through during one rotation, is taken as 3 for rotation of the CH_3 group, and 2 for rotation of the NO group. Errors due to assuming that the axes of rotation of the N=O and CH_3 groups coincide exactly with the O–N and C–O single bonds are negligible.

In Table 3 are shown the values of I and the entropy contributions, S_f, of the internal rotations of methyl nitrite. They are virtually identical for the two isomers.

Contribution due to vibration. A non-linear molecule of x atoms has $3x - 6$ vibrational modes and internal rotations. For methyl nitrite $x = 7$ and $3x - 6 = 15$. The two internal rotational modes have already been considered. Therefore, thirteen vibrational modes remain. The vibrational assignment is shown in Table 4. The sources used for this are principally the infrared spectral measurements by Tarte;[3] use is also made of

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[13] Pitzer, *J. Chem. Phys.*, 1937, **5**, 469; see also Kemp and Pitzer, *J. Chem. Phys.*, 1936, **4**, 749; *J. Amer. Chem. Soc.*, 1937, **59**, 276.

the Raman shifts quoted by Wagner[4] and Hibben;[14] and, for some of the frequencies of the methyl group, the values given by Brand and Cawthon[15] for methyl nitrate, which are assumed to be identical with the corresponding vibrations in methyl nitrite. (As none of these methyl group vibrations makes a large entropy contribution, the error involved is negligible).

TABLE 3. *Reduced moments of inertia and entropy contributions of freely rotating methyl and nitrosyl groups in methyl nitrite.*

Isomer	Rotating group	Reduced moment of inertia (g. cm.^{2})	Entropy contribution (cal. deg.$^{-1}$ mole^{-1})
cis	CH_3	$(5{\cdot}15 \pm 0{\cdot}20) \times 10^{-40}$	$3{\cdot}58 \pm 0{\cdot}07$
trans	CH_3	$(5{\cdot}00 \pm 0{\cdot}20) \times 10^{-40}$	$3{\cdot}55 \pm 0{\cdot}07$
cis and *trans*	N=O	$(21{\cdot}4 \pm 0{\cdot}8) \times 10^{-40}$	$5{\cdot}80 \pm 0{\cdot}04$

TABLE 4. *Vibrational assignment of* cis- *and* trans-*methyl nitrite.*

	cis		*trans*			
	Frequency ν (cm.$^{-1}$)	Contribution to $S/\boldsymbol{R}$	Frequency ν (cm.$^{-1}$)	Contribution to $S/\boldsymbol{R}$	Approximate description of vibration	Ref.
	364	0·556	364	0·556	C–O–N bending	4, 14
	617	0·212	565	0·263	O–N–O bending	3
	844	0·088	814	0·099	N–O stretching	3
	993	0·048	1045	0·039	C–O stretching	3
	1630	0·003	1680	0·003	N=O stretching	3
	1132	0·027	1132	0·027	CH_3 rocking	15
	1176	0·023	1176	0·023	CH_3 rocking	15
	1434	0·008	1434	0·008	CH_3 deformation	15
	1468	0·007	1468	0·007	CH_3 deformation	15
	1445	0·008	1370	0·010	CH_3 deformation	3
	2944	0·000	2944	0·000	C–H stretching	14
	3048	0·000	3048	0·000	C–H antisymm. stretch. (doubly degenerate)	14
Total contribution to $S/\boldsymbol{R}$		0·980		1·035		

If ν_i represents the frequency of the *i*th vibrational mode of the molecule, then:

$$S_{vib}/\boldsymbol{R} = \sum_{i=1}^{i=13} \{(\boldsymbol{h}\nu_i/\boldsymbol{k}T)[\exp(\boldsymbol{h}\nu_i/\boldsymbol{k}T) - 1] - \ln[1 - \exp(-\boldsymbol{h}\nu_i/\boldsymbol{k}T)]\}$$

Values of $S/\boldsymbol{R}$ for each of the thirteen vibrational modes and for the totals are shown in Table 4. The probable error in the totals is estimated to be less than $\pm 0{\cdot}1$ cal. deg.$^{-1}$ mole^{-1} and the values for the two isomers, $(S_{vib})_{cis} = 1{\cdot}95$ and $(S_{vib})_{trans} = 2{\cdot}06$ cal. deg.$^{-1}$ mole^{-1}, are not significantly different.

Contribution due to mixing of the two isomers. The entropy S_{mix} of an ideal mixture of two isomers, having molar entropies S_{cis} and S_{trans} and present in the mole fractions y and $(1 - y)$ respectively, is given by:

$$S_{mix} = y\,S_{cis} + (1 - y)\,S_{trans} - \boldsymbol{R}\{y \ln y + (1 - y) \ln (1 - y)\}$$

The maximum value which this expression for S_{mix} can take occurs when $y = 1 - y$, *i.e.*, in an equimolar mixture, and is $S_{mix} = 74{\cdot}21 - S_b$. The exact value of the relative abundance of the isomers is discussed in the Appendix; but because S_{mix} is relatively insensitive to this ratio (S_{mix} differs only by 0·37 cal. deg.$^{-1}$ mole^{-1} from the maximum value for *cis* : *trans* ratios varying from 1 : 4 to 4 : 1) its exact value is unimportant in this calculation. In Table 2, the maximum value is entered. The point receives further discussion in the Appendix.

Effect of gas imperfection. The calculated entropy of methyl nitrite does not allow

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[14] Hibben, " The Raman Effect and its Chemical Applications," Reinhold, New York, 1939, p. 285.

[15] Brand and Cawthon *J. Amer. Chem. Soc.*, 1955, **77**, 319.

for the departure from ideality of methyl nitrite vapour, and a correction[16] is made for this by using the modified Berthelot equation:

$$(S_{ideal} - S_{real})/\boldsymbol{R} = (27/32)(T_c/T)^3(P/P_c)$$

For methyl nitrite, the critical temperature (T_c) is estimated as 380° K, and the critical pressure (P_c) as 50 atm. The correction is therefore 0·07 cal. deg.$^{-1}$ mole^{-1}. This is subtracted from the calculated entropy, so that both it and the experimentally derived entropy refer to the real vapour.

From the sum of all the above terms, listed in Table 2, the entropy at 25° C and 1 atm. of an equilibrium mixture of methyl nitrite is, relative to that at absolute zero, $S_{298}° + S_b = 74·1 \pm 0·14$ cal. deg.$^{-1}$ mole^{-1}.

The Magnitude of the Barriers to Free Rotation.—The calorimetric and equilibrium data give $S_{298}° = 71·5 \pm 0·9$ cal. deg.$^{-1}$ mole^{-1}, and the calculated terms above lead to $S_{298}° + S_b = 74·1 \pm 0·14$ cal. deg.$^{-1}$ mole^{-1}. Therefore the maximum value of the reduction in entropy below that of a freely rotating molecule caused by the potential barriers is $S_b = 2·6 \pm 0·9$ cal. deg.$^{-1}$ mole^{-1}.

The height of the potential-energy barrier hindering free rotation to which this entropy deficit corresponds can be derived from Pitzer's[13] tabulated results. The entropy reductions relative to free rotation (in parentheses, cal. deg.$^{-1}$ mole^{-1}) due to hindered rotation of the nitrosyl group about the O–N bond for various barrier-heights (cal. mole^{-1}) are: 1000 (0·3), 2000 (0·9), 3000 (1·4), 6000 (2·3), 9000 (2·7), 12,000 (3·1). Thus, to cause an entropy reduction of 2·6 cal. deg.$^{-1}$ mole^{-1}, rotation of the nitrosyl group must be opposed by a potential-energy barrier of 7800 cal. mole^{-1}.

DISCUSSION

Interpretation of the size and origin of the potential-energy barrier to free rotation in methyl nitrite is assisted by two comparisons. The first is of the place of methyl nitrite in relation to other nitrite esters and to nitrous acid; the second is the relation of the nitrite family to other, chemically similar, homologous series such as the nitrate esters and the nitrosamines. Since this work was done, both these aspects have been illuminated by the application of high resolution nuclear (proton) magnetic resonance spectroscopy.

We examine first the size of the potential energy barrier and next its origin. The problem of the relative stability and abundance of the two isomers, and its relevance to the entropy of mixing, is considered in the Appendix.

The Size of the Energy Barrier to Free Rotation.—The size of the barrier, $V_b = 7800$ cal. mole^{-1}, seems, at first sight, large. It was derived from the most probable value of the entropy deficit by assuming a cosine-form of the barrier profile; errors introduced by this assumption are unlikely to be large enough to alter V_b appreciably. Moreover, completely independent support for a large potential-energy barrier in methyl nitrite comes from recent nuclear magnetic resonance work by Piette, Ray, and Ogg.[17] These workers and, independently, Phillips, Looney, and Spaeth,[18] examined the spectra of a number of nitrite esters. Barrier heights V_b of *ca.* 10,000 cal. mole^{-1} are found[18] for *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, and *iso*pentyl nitrites by assuming the frequency of isomer interconversion to be adequately represented by a simple " absolute " rate equation $\nu = (\boldsymbol{k}T/\boldsymbol{h}) \exp(-V_b/\boldsymbol{R}T)$. The same interpretation of the data[17] for methyl and ethyl nitrites leads to a similar value of V_b. This simple approach is unlikely to be seriously in error.

In nitrous acid, the existence of a *cis*- and a *trans*-form has been deduced[11] from

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[16] Partington, " An Advanced Treatise on Physical Chemistry," Vol. I, page xli, Longmans, Green & Co., London, 1949.

[17] Piette, Ray, and Ogg, *J. Chem. Phys.*, 1957, **26**, 1341.

[18] Phillips, Looney, and Spaeth, *J. Molec. Spectroscopy*, 1957, **1**, 35.

infrared and ultraviolet spectroscopy; Jones, Badger, and Moore[11] infer that the *trans*-form is more stable than the *cis*- by 500 cal. mole^{-1} and that the barrier height is some 12 kcal. mole^{-1} above the lower minimum. A normal co-ordinate treatment by Palm,[11] with the assumption of a symmetrical two-fold potential function, also leads to barriers of between 10 and 14 kcal. mole^{-1}. In nitric acid there are identical pairs of potential maxima and minima; barrier heights between them of from 9 to 10 kcal. mole^{-1} have been deduced by Cohn, Ingold, and Poole[12] from spectroscopy and calorimetry.

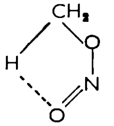
Methyl nitrate, $CH_3{\cdot}O{\cdot}NO_2$, offers an exception to this universal possession of potential barriers. The standard entropy of gaseous methyl nitrate relative to that at absolute zero can be calculated[15] from its structure and vibration frequencies. An experimental value is available from the calorimetric work of Gray and Smith[19] and recent latent heat data.[20] There is no entropy "deficit," and hence no appreciable barrier to free rotation.

No mention has yet been made of a barrier to free rotation of the methyl group. If such a barrier existed it would contribute to the entropy deficit and, as can be seen from the annexed table, if it were as high as 12 kcal. mole^{-1}, it would account for the whole deficit ($S_b = 2{\cdot}6$ cal. deg.$^{-1}$ mole^{-1}).

Postulated barrier (kcal. mole^{-1}) to free rotation of CH_3 about C–O bond	1	2	3	6	9	12
Entropy deficit (cal. deg.$^{-1}$ mole^{-1})	0·3	0·8	1·3	2·1	2·5	2·7

The reasons for its neglect are considered in the next section when the origin of the barrier to rotation is discussed. For the present it may suffice to remark that the barrier to N=O rotation derived here is not so high as to be unusual or to need supplementing by restricted CH_3 rotation.

The Origin of the Barrier to Free Rotation.—Rogowski,[8] who was the first to postulate the occurrence of methyl nitrite in *cis*- and *trans*-forms, concluded that at room temperature the *cis*-form predominated. Tarte,[1,3] and Wagner,[4] whose spectroscopic work confirmed the existence of isomers, also revealed the varying isomer ratio at different temperatures. Tarte and Wagner assumed that the form whose abundance diminished with increasing temperature was the *cis*-form. For all the primary nitrites (from ethyl upwards) this is confirmed by recent[17,18] work. Haszeldine and Mattinson[2] confirmed and extended Tarte's work. All these workers[1-4] agreed that the *cis*-forms of primary nitrites, and of methyl nitrite in particular, owed their stability to hydrogen bonding, *i.e.*, represented the *cis*- and the *trans*-isomer of methyl nitrite by (I) and (II). This explanation, although superficially attractive, leads to several difficulties. First, it offers no reason why a *trans*-form should be stable: if the only influence stabilizing the *cis*-form of a primary nitrite is the hydrogen bond, the *trans*-form should be much less stable. But nuclear magnetic resonance measurements on five primary nitrites (*n*-propyl, *n*- and *iso*-butyl, *n*- and *iso*-pentyl) show that the isomer ratios vary so little between −100° and +20° that the enthalpy increase for the isomerization *cis* ⟶ *trans* is very small; the average value is 130 cal. mole^{-1}. Secondly, hydrogen bonding implies strongly restricted rotation of the methyl group, which is not found. Thirdly, the nuclear magnetic resonance measurements on methyl and ethyl nitrites and on the five nitrites listed above fail to reveal any differentiation between the two hydrogen atoms of the sort which would arise if one of them took part in hydrogen-bond formation. For these general reasons, hydrogen-bonding is rejected as the principal factor in *cis-trans*-isomerism of all the primary nitrites.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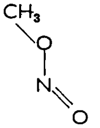
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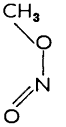
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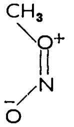
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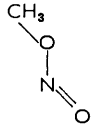
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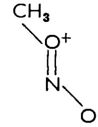
(VI)

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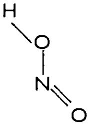
[19] Gray and Smith, *J.*, 1953, 2380.

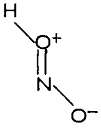
[20] Gray and Pratt, *J.*, 1957, 2163.

It is finally disposed of in the case of methyl nitrite by the recent nuclear magnetic resonance work. This reveals that, although in general at low temperatures the *cis*-form of the primary nitrites $R{\cdot}CH_2{\cdot}ONO$ is the more abundant, in methyl nitrite the *trans*-form predominates. At $-100°$ the *trans* : *cis* ratio is 3·4 : 1.

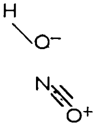
The most satisfactory interpretation [17,18] of the situation is in terms of partial double-bond character of the $CH_3{\cdot}O{-}NO$ link. Such an explanation has already been applied [18] to isomerism in the substituted amides and nitrosamines, and it may be made with equal validity here for the nitrite esters. Formulæ (III) and (IV) describe *cis*-methyl nitrite, and (V) and (VI) *trans*-. Such a description, by ascribing the resistance to rotation to double-bond character, permits isomers to have very little enthalpy difference and yet have a high potential barrier between them, a fact which the hydrogen-bond interpretation could not explain.* It is noteworthy that Jones, Badger, and Moore [11] reached the same conclusions about nitrous acid. They found that the *trans*-form predominated (*trans* : *cis* = 2·5 : 1 at 25°) and was more stable (ΔH) by 500 cal mole^{-1}. They wrote three canonical forms (VII—IX) for the *trans*-form, invoking (IX) to account for the superior stability of *trans*-nitrous acid.



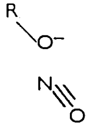
(VII)



(VIII)



(IX)



(X)

In view of the excellent nitrosating power of both nitrous acid and alkyl nitrites, "no-bond" ionic structures such as (IX) and (X) are less fanciful than is common among canonical forms.

APPENDIX

Relative Abundance of cis- *and* trans-*Isomers in the Alkyl Nitrites.*—Three methods have been used to make inferences about the abundance ratio: electron diffraction, nuclear magnetic resonance spectroscopy, and optical (infrared, ultraviolet, and Raman) spectroscopy.

The electron-diffraction data [8] refer only to methyl nitrite. They were obtained in 1941—2 before the introduction of rotating-sector methods and their precision leaves much to be desired. Nevertheless, historically they were the first results on this system and they revealed the presence of two isomers even if they gave an inaccurate ratio.

The most recent technique, high resolution nuclear magnetic resonance spectroscopy, is the most helpful so far.[17,18] At low temperatures, when the rate of *cis–trans*-isomerization is low, the nuclear magnetic resonance spectra show well-separated peaks attributable to the proton resonances of the two isomers: the relative abundances are in the ratio of the integrated intensities. At higher temperatures, when the peaks coalesce, the relative abundances can be determined from the position of the single, unresolved maximum by assuming the frequency shift corresponding to it to be the molar average of the separate constituents. Two sets of magnetic resonance data are available. One deals with methyl, ethyl, and *n*-propyl nitrites,[17] the other with *n*- and *iso*-propyl, *n*- and *iso*-butyl, and *iso*pentyl nitrites.[18] They are in excellent accord with one another and each requires only the correct assignment of the peaks to its own isomer. Assignment made on different bases by the two sets of workers agrees both internally and with the optical results [1-3] for ethyl and all higher primary nitrites: for methyl nitrite, nuclear magnetic resonance spectroscopy reveals that, in the liquid at low temperatures, it is the *trans*-isomer which predominates.

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* Ingold (personal communication) points out that this interpretation helps to explain why there is no effective barrier in methyl nitrate though there is one in nitric acid. Palm also concludes that partial double-bond character contributes to the high barrier.

Optical spectroscopy,[1-4] mainly infrared absorption, provides the third method. The vibration spectra are well enough resolved for pairs of bands ascribable to isomers to be distinguished and peak heights or, in favourable cases, integrated absorption bands can be compared. Two problems remain: not only must the bands be correctly assigned to *cis*- and *trans*-, but in order that relative abundances may be obtained from the optical densities the infrared absorption coefficients must be determined. It is, of course, unlikely that they will differ widely from *cis*- to *trans*- and a wide variation of optical density may be taken to imply a large abundance ratio.[1,3] In this way, the predominance of *trans*-forms of the secondary nitrites and the virtual absence of *cis*-forms in the tertiary nitrites has been inferred. When both optical density data and abundance ratios from nuclear magnetic

TABLE 5. *The relative stability and abundance of* cis- *and* trans-*alkyl nitrites.*

NMR = High resolution proton magnetic resonance spectroscopy; IR = Infrared (vibrational) absorption spectroscopy. L = liquid; G = gas.

Nitrite	Temperature (°c) and state	*cis* : *trans* ratio	How obtained	Ref.
		Nitrous acid		
HO·NO	25 G	0·4	Calc. ΔS; meas. ΔH	11
		Methyl nitrite		
$\mathrm{CH_3}$·O·NO	−60 L	0·29	NMR integrated intensities	17
	21 L	~1	NMR mean frequency	17
	~20 G	~4	Electron diffraction	8
	23 G	(1·01)	IR optical density *	1
		Primary saturated nitrites		
$\mathrm{C_2H_5}$·O·NO	F. p. L	~2·8	NMR integrated intensities	17
	21 L	~1	NMR mean frequency	17
n-$\mathrm{C_3H_7}$·O·NO	F. p. L	~2	NMR integrated intensities	17
	−100 L	2·0	NMR integrated intensities	18
	20 L	1·8	NMR mean frequency	18
n-$\mathrm{C_4H_9}$·O·NO	−100 L	1·8	NMR integrated intensities	18
	20 L	1·7	NMR mean frequency	18
	23 G	(0·30)	IR optical density *	1
iso-$\mathrm{C_4H_9}$·O·NO	−100 L	2·3	NMR integrated intensities	18
	20 L	2·2	NMR mean frequency	18
	23 G	(0·29)	IR optical density *	1
iso-$\mathrm{C_5H_{11}}$·O·NO	−100 L	1·7	NMR integrated intensity	18
	20 L	1·3	NMR mean frequency	18
	23 G	(0·29)	IR optical density *	1
		Primary unsaturated nitrites		
$\mathrm{CH_2{=}CH{\cdot}CH_2}$·O·NO	23 G	(0·36)	IR optical density *	1
$\mathrm{C_6H_5{\cdot}CH_2}$·O·NO	23 G	(0·32)	IR optical density *	1
		Primary dinitrites		
ON·O·$\mathrm{[C_2H_4]_4}$·O·NO	−100 L	1·6	NMR integrated intensities	18
	20 L	1·2	NMR mean frequency	18
		Secondary nitrites		
iso-$\mathrm{C_3H_7}$·O·NO	−100 L	0·13	NMR integrated intensity	18
	20 L	~0·13	NMR mean frequency	18
	23 G	(0·17)	IR optical density *	1
sec.-$\mathrm{C_4H_9}$·O·NO	23 G	(0·14)	IR optical density *	1
sec.-$\mathrm{C_5H_{11}}$·O·NO	23 G	(0·1)	IR optical density *	1
cyclo-$\mathrm{C_5H_9}$·O·NO	23 G	(0·21)	IR optical density *	1
cyclo-$\mathrm{C_6H_{11}}$·O·NO	23 G	(0·11)	IR optical density *	1
		Tertiary nitrites		
tert.-$\mathrm{C_4H_9}$·O·NO	23 G	(~0·03)	IR optical density *	1
tert.-$\mathrm{C_5H_{11}}$·O·NO	23 G	(~0·02)	IR optical density *	1

* These figures in parentheses are optical density ratios, D_{cis}/D_{trans}, for the N=O stretching frequency. To convert them into abundance ratios it is necessary to divide by the infrared absorption coefficient ratio $r = k_{cis}/k_{trans}$. Approximate abundance ratios can be found by using a mean value of $\bar{r} \simeq 0{\cdot}4$.

resonance are known, ratios of infrared absorption coefficients can be determined. These ratios do not vary greatly. Thus it may be possible, without great error, to use a mean value of absorption-coefficient ratio in conjunction with optical density ratios of other nitrites to estimate the abundances of their isomers.

The three direct methods described here have been made to derive the entries in Table 5. The general results of all the methods agree.

Thus the tertiary nitrites are almost exclusively *trans*-isomer. The secondary nitrites are largely in the *trans*-form. The primary nitrites $R\cdot CH_2\cdot O\cdot NO$ contain appreciable amounts of both *cis*- and *trans*- with *cis*- predominating at low temperatures. The abundances do not change rapidly with temperature, and a mean value of ΔH for the isomerization *cis* ⟶ *trans* is only 130 cal. mole^{-1}. For methyl nitrite, in the liquid state, the *trans*-form predominates at low temperatures. In the liquid and probably in the gas at room temperature the ratio is nearer unity. Nitrous acid itself shows the same features: *trans*-nitrous acid predominates; it has an enthalpy of formation lower by 500 cal. than *cis*-nitrous acid. At room temperature the ratio is about 2·5 : 1.

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School of Chemistry, University of Leeds. [*Received, February* 27*th*, 1958.]