# LETTERS TO THE EDITOR

## THERMODYNAMIC PROPERTIES OF METHANESELENOL

THE infrared spectrum of Methaneselenol was studied in the vapor phase by Harvey *et al.*[1] and all its fundamental frequencies were assigned on the basis of $C_s$ symmetry. Using this experimental spectroscopic data, the thermodynamic properties of methaneselenol are calculated and are reported here.

TABLE I

*Vibrational wavenumbers and rotations constants in* $cm^{-1}$

| Species | Wavenumbers |
|---|---|
| A | 3027, 2955, 2330, 1447, 1288, 980, 712, 584 |
| A″ | 3032, 1433, 921, 145 |
| A=3·070 | B=0·3069 C=0·2952 |

The calculations are all carried out over IBM–1130 Computer with a programme written by the authors in Fortran IV. The quantities calculated are the heat content, heat capacity, entropy and free energy at various temperatures from 100 to 2000 Kelvin, for the ideal gaseous state at 1 atmosphere pressure for a rigid rotor harmonic oscillator approximation[2]. The fundamental vibrational wavenumbers and rotational constants of the molecule used in these calculations are given in Table I, and the calculated thermodynamic quantities are given in Table II.

TABLE II

*Thermodynamic quantities of methaneselenol*

| Temp. | $(H_0-E_0^\circ)/T$ | $C_p^\circ$ | $S^\circ$ | $-(F^\circ-E_0^\circ)/T$ |
|---|---|---|---|---|
| 100 | 8·54 | 9·38 | 52·85 | 44·32 |
| 200 | 9·29 | 10·85 | 59·40 | 50·10 |
| 300 | 10·16 | 12·98 | 63·79 | 53·63 |
| 400 | 11·14 | 15·16 | 67·39 | 56·25 |
| 500 | 12·14 | 17·11 | 70·52 | 58·38 |
| 600 | 13·11 | 18·80 | 73·31 | 60·20 |
| 700 | 14·03 | 20·27 | 75·83 | 61·80 |
| 800 | 14·90 | 21·56 | 78·13 | 63·24 |
| 900 | 15·70 | 22·69 | 80·25 | 64·55 |
| 1000 | 16·45 | 23·69 | 82·21 | 65·76 |
| 1200 | 17·80 | 25·32 | 85·74 | 67·93 |
| 1400 | 18·97 | 26·56 | 88·83 | 69·86 |
| 1600 | 19·98 | 27·51 | 91·57 | 71·59 |
| 1800 | 20·86 | 28·23 | 94·02 | 73·16 |
| 2000 | 21·63 | 28·80 | 96·23 | 74·61 |

In Table II temperature is in degrees Kelvin and the other quantities are in cal $deg^{-1}$ $mole^{-1}$. $E_0^\circ$ is the energy of one mole of perfect gas at absolute zero temperature. The physical constants used in these calculations are taken from Ref. 3.

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## A NOTE ON THE ADVISABILITY OF RECORDING HIGHER DERIVATIVES OF N.M.R. ABSORPTION LINES

IN N.M.R., we usually modulate the absorption line with $h_m$ Sin $\theta$ (where $\theta = w_m t$) and we get the first derivative $g'(h)$ of the line shape function $g(h)$ after the phase-sensitive-detector (P.S.D.). But this is valid only when $h_m$, the amplitude of modulation, is very small.

When $h_m$ is not small, we have,

$$G(h) = a_0 g(h) + a_1 g'(h) + a_2 g''(h) + \ldots \tag{1}$$

Let us write,

$$\begin{aligned} a_0 &= b_0' \sin\theta + b_0'' \sin 2\theta + \ldots\ldots \\ a_1 &= b_1' \sin\theta + b_1'' \sin 2\theta + \\ a_n &= b_n' \sin\theta + b_n'' \sin 2\theta + \ldots\ldots \end{aligned} \tag{2}$$

If the P.S.D. is tuned to $w_m$, then its output $v_1$, will be

$$v_1 \propto b_0' g(h) + b_1' g'(h) + b_2' g''(h) + \ldots \tag{3}$$

[when $h_m$ is small we have $h_0{}^1 = 0$, $b_1' = h_m$, $b^{2\prime} = 0$, etc.]. Thus we see the experimentally recorded curve, when $h_m$ is not small, is a mixture of $g(h)$, $g'(h)$, $g''(h)$, etc., and the errors in assuming the curve to be only $g'(h)$ are proportional to $b_0'$ $b_2'\ldots)$ . $b_n'$.

If the P.S.D. is tuned to 2 $w_m$ (while modulating at $w_m$ itself) we see the output of the P.S.D. is,

$$v_2 \propto b_0'' g(h) + b_1'' g'(h) + b_2'' g''(h) + \ldots \tag{4}$$

In this case, if $h_m$ were small, we would have got only $g''(h)$ but when $h_m$ is not small the errors in assuming the line function to be only $g''(h)$ are proportional to $b_0''$, $b_1''$, $b_3''$, . . . . $b_n''$, In general, the errors in recording $g^n(h)$ and assuming it to be only $g^n(h)$ are proportional to $h_0^n$ $b_1^n$, ....$h^n_{n-1}$. It is quite reasonable to assume that the values of the $h$'s for various values of $n$ would be such that they would have the minimum value for a particular value of $n$ say N. If we record the N$^{th}$ derivative, *viz.*, $g^N(h)$, we can assume that the error, introduced when $h_m$ is not small, would be a minimum. So we should record $g(h)$, $g'(h)$, $g''(h)$....$g^n(h)$, etc., and convert all of them to $g(h)$ [*i.e.*, record $g'(h)$ and integrate it point by point to get $g(h)$, etc.], and then calculate the second moment for all of them and use the minimum value of the second moment in our calculation.

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## DIPOLE MOMENTS OF SOME ESTERS FROM THE MOLAR POLARISATION MEASUREMENTS

DIPOLE moments can be determined either from dilute solution measurement or from pure liquids. The dipole moments obtained from the pure liquid measurements when correlated with the dispersion data give some important information regarding the molecular structure.

The present communication reports the dipole moments of five esters, namely, diethyl phthalate, diethyl succinate, diethyl malonate, benzyl salicylate and benzyl butyrate from the molar polarisation measurements in pure liquids. The equation suggested by Hill[1] was employed for the determination of molar polarisation from the values of static dielectric constant and densities at different temperatures. The static dielectric constants are measured at 1 MHz by means of Franklin's oscillator in combination with G.R. precision condensers of 0·002 pf accuracy. The capacitance of the cell employed for these measurements is about 20 pf. Densities are measured with a specific gravity bottle. The substances are from Fluka Switzerland and were distilled before use.

The plot of molar polarisation *versus* 1/T is a straight line the slope of which is equal to B. The dipole moment $\mu$ is given by the relation

$$\mu = 0{\cdot}0128\sqrt{B}$$

Dipole moments were also calculated from the theoretical expressions proposed by Onsager[2], Kirkwood[3], and Syrkin[4], for these esters in pure liquids. They are given in Table I along with the values obtained from molar polarisation measurements and from dilute solution measurements. The dipole moments for benzyl salicylate and benzyl butyrate are reported here for the first time.

A comparison of different values of dipole moments lead to the following conclusions (1) the $\mu$ values obtained from Kirkwood and Syrkins equations are in close agreement in all the esters (2) the values obtained from Onsager's equation and molar polarisation measurements are somewhat lower than the values obtained from Kirkwood's and Syrkin's equations (3) there is a reasonable agreement between the $\mu$ values given by Kirkwood and Syrkin with that of dilute solution value. In these calculations the Kirkwood's 'g' factor is assumed to be unity, and the agreement of these values with the dilute solution values is a clear indication that the esters investigated are of non-associative type.

TABLE I

| Substance | Dipole moments in Debye Units | | | | |
|---|---|---|---|---|---|
| | Onsager | Kirkwood | Syrkin | Molar polarisation | Dilute solution |
| Diethyl phthalate .. | 2·12* | 2·56* | 2·60 | 2·23 | 2·70*–2·80* |
| Diethyl succinate .. | 2·23 | 2·20 | 2·30 | 2·10 | 2·03*–2·40* |
| Diethyl malonate .. | 2·48 | 2·54 | 2·55 | 2·24 | 2·10*–2·61* |
| Benzyl salicylate .. | 1·43 | 1·61 | 1·52 | 1·51 | 1·66 (Benzene) |
| Benzyl butyrate .. | 1·71 | 1·85 | 1·81 | 1·73 | 1·90 (Benzene) |

* Values taken from the Literature.

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