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Thermodynamic Functions for Methyl Thiocyanate

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Thermodynamic functions of heat capacity, entropy, Gibbs energy function, and enthalpy function have been calculated at selected temperatures between 273.15° and 1000° K. for methyl thiocyanate in the ideal gas state at 1 atm. pressure.

THE recent availability of vapor state far infrared spectroscopic data and the barrier to internal rotation of the methyl group have allowed the calculation of ideal gas thermodynamic functions for methyl thiocyanate. The vapor state frequencies for the low frequency vibrations are necessary, because there is usually a thermodynamically significant liquid-vapor frequency shift for the vibrations below about 250 cm.^{-1}. For example, the liquid state wavenumber for the lowest bending fundamental of methyl thiocyanate is 190.6 cm.^{-1} (*1*), and the vapor state wavenumber is 170 cm.^{-1} (*2*).

Rotational constants and the potential barrier hindering internal rotation for methyl thiocyanate have been determined recently by Nakagawa *et al.* (*3*). The principal moments of inertia used in calculating the contribution of over-all rotation are $I_a = 5.314 \times 10^{-39}$, $I_b = 20.20 \times 10^{-39}$, and $I_c = 25.03 \times 10^{-39}$ gram sq. cm. Nakagawa's value of 1592 cal. per mole for the barrier height was used in calculating the contribution of restricted internal rotation. The reduced moment of inertia for internal rotation of the methyl group was calculated by the method of Pitzer and Gwinn (*4*) to be 5.089×10^{-40} gram sq. cm.

Thermodynamic functions for methyl thiocyanate in the ideal gas state at 1 atm. pressure were calculated at selected temperatures (Table I). The contributions of translation, over-all rotation, and vibration were made with standard formulas of statistical thermodynamics (*5*). These calculations were based on the rigid rotator-harmonic oscillator model. For methyl thiocyanate, the moments of inertia for over-all rotation are independent of internal rotational coordinates, so the treatment of Pitzer and Gwinn (*4*) applies. The contributions of restricted internal rotation were taken from their tables. Vibrational contributions were calculated with the following wavenumbers for the fundamental vibrations: 170, 389, 460, 674, 705, 968, 989, 1328,

Table I. Molal Thermodynamic Properties of Methyl Thiocyanate in the Ideal Gas State

Temp., °K.	$-(G - H_0^\circ)/T$, Cal./Deg.	$(H^\circ - H_0^\circ)/T$, Cal./Deg.	$H^\circ - H_0^\circ$ Kcal.	S° Cal./Deg.	C_p°, Cal./Deg.
273.15	57.88	12.24	3.344	70.12	16.70
298.15	58.97	12.64	3.770	71.61	17.37
300	59.05	12.67	3.802	71.72	17.42
400	62.90	14.17	5.669	77.07	19.85
500	66.22	15.51	7.758	81.73	21.92
600	69.15	16.73	10.04	85.88	23.69
700	71.82	17.83	12.48	89.65	25.22
800	74.26	18.85	15.08	93.11	26.54
900	76.54	19.77	17.79	96.31	27.70
1000	78.66	20.62	20.62	99.28	28.70

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1437, 2174, 2951, and 3031 cm.$^{-1}$. The values 1437 and 3031 cm.$^{-1}$ were used twice, for a total of 14 wavenumbers. The first three values in this list (below 600 cm.$^{-1}$) were taken from Crowder (*2*), and the remaining values were taken from Moritz (*6*). The methyl thiocyanate molecule has seven atoms and therefore has 15 fundamental vibrational frequencies. Vapor state infrared frequencies are available for all 15 except for the methyl torsion, for which no experimental value is available, and the symmetric C—S—C stretch, for which the liquid state value is available. However, the methyl torsional frequency is not needed for calculation of the thermodynamic functions because the barrier to internal rotation has been determined from the microwave spectrum. Also, it is unlikely that the vapor state frequency for the C—S—C stretch would differ enough from the liquid state value of 674 cm.$^{-1}$ to affect the calculated thermodynamic properties appreciably, especially at the lower temperatures.

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Condensation of Aromatic and Heterocyclic Aldehydes with Benzenediacetonitriles

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A number of benzylidene-*p*-benzenediacetonitriles were prepared by base-catalyzed condensation of aromatic aldehydes with *p*-benzenediacetonitrile. Four products, substituted in the 4,4′-positions of the benzylidene groups, formed liquid crystals (mesomorphism) on melting. All were high melting solids. *m*-Substitution on the benzylidene groups lowered melting points and increased solubilities. Benzylidene-*m*-benzenediacetonitriles were lower melting and more soluble than the corresponding *p*-substituted compounds. The thermal stability of distyrylbenzene was lower than for the diphenyl ether fluids. A difunctional derivative was converted to a polymer.

A STUDY of the properties of high melting and relatively heat stable materials led to an investigation of the condensation of aldehydes with aromatic acetonitriles. Of particular interest, because of relatively high molecular weight, were the distyrylbenzenes derived from the reaction of aromatic aldehydes with benzenediacetonitriles (Table I). The authors anticipated that potentially useful functional variants of α,α'-dibenzylidene-*p*-benzenediacetonitrile should be readily obtainable at moderate cost and that this structural system should have good thermal stability. For products with a given functionality, melting points and solubilities should be controlled by variation from the symmetrical *p*-benzenediacetonitriles to the less symmetrical *m*- and *o*-structures.

Several products related to those made in this study have been described previously. These are: the distyrylbenzene from *o*-benzenediacetonitrile and *o*-nitrobenzaldehyde (*16*) and the distyrylbenzenes from reaction of *p*-benzenediacetonitrile with *o*-chloro-, *p*-chloro-, 3,4-dichloro-, and 4-methoxybenzaldehydes (*5*). Also, a polymer has been prepared (*12*) by the condensation of terephthaldehyde and *p*-benzenediacetonitrile, which on heating to 550° C. lost less than 30% of its weight and formed a stable polymeric residue. Utility of this polymer appears to be limited by its insolubility and infusibility.

There is little doubt that the condensation products of aromatic aldehydes with *m*- and *p*-benzenediacetonitrile obtained in this study are of the trans, trans configuration with respect to the stilbene grouping. The trans and cis forms of α-phenylcinnamonitrile were prepared (*15*), and the nitrile group of the isomer in which the phenyl substituents are trans was almost completely resistant to acid hydrolysis, whereas the cis form was readily hydrolyzed. Further, a number of cases (*4*, *11*) have shown that the base-catalyzed condensation of aromatic aldehydes with phenylacetonitrile leads to trans products. Since the present materials were prepared by base-catalyzed condensations and since they were very resistant to acid hydrolysis, the trans structures seem assured.

The several α,α'-dibenzylidene -*p*- benzenediacetonitriles are high melting crystalline solids with limited solubilities in most common organic solvents. In the corresponding *m*-benzenediacetonitriles, the melting points are decreased 65° to 125° C., and the solubilities are increased greatly. The ease of preparation is reduced owing to the difficulties in isolation and owing to the fact that the driving force of having the product precipitate out, as in the case of the para compounds, is absent. A drop in melting point of 122° C. is shown between α,α'-dibenzylidene -*p*- benzenediacetonitrile (I), m.p. 255–6° C. and the *m*-isomer (II), m.p. 133–4° C. A striking difference in solubility is observed; in ethyl acetate at 25° C. the *p*-isomer is soluble to the extent of 0.06 gram per 100 ml., while the *m* - isomer is soluble to the extent of 2.3 grams per 100 ml. Similar increases in solubility were noted qualitatively for other solvents. Functionally varied *m*-benzenediacetonitriles showed similar changes in properties compared with the corresponding para compounds.