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CHEMICAL AND THERMODYNAMIC PROPERTIES OF *o*-, *m*- AND *p*-FLUOROTOLUENE

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ABSTRACT

The ideal gas thermodynamic constants of *o*-, *m*- and *p*-fluorotoluene, $C_{p,\mathrm{m}}^{\ominus}$, $S_{\mathrm{m}}^{\ominus}$ and $H_{\mathrm{m}}^{\ominus}(T) - H_{\mathrm{m}}^{\ominus}(0)$, were calculated in the temperature range 0–3000 K by a statistical mechanical method. The contribution to internal rotation from the presence of the CH_3 rotor was evaluated by the method of Pitzer and Gwinn (J. Chem. Phys., 10 (1942) 428).

INTRODUCTION

The valid comparison of the thermodynamic properties of positional isomers of an organic compound requires the determination of its thermal, spectroscopic and molecular properties as precisely as possible. In general, optimal precision is obtained when these constants are obtained by the same method.

In this context, data are provided by Green [1–3] on the assignment of vibrational frequencies to the three isomers of fluorotoluene. In addition, the values of potential energy barriers impeding methyl group rotation have been obtained by microwave spectrometry [4–6]. This is not the case for rotational constants, since they require the determination of geometric structures which, unfortunately, are not available for each of the isomers. In consequence, they are determined from molecular wave function calculations.

GENERAL POINTS

Under standard conditions (pressure, $P = 1$ bar) and using the most recent values of physical constants (h, k, N, c, etc.), expressions for thermo-

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dynamic functions were recalculated as follows

$$C^{\ominus}_{p,\mathrm{m}}(T) = R\left(4 + \sum_i \frac{x_i\,\mathrm{e}^{-x_i}}{(\mathrm{e}^{x_i}-1)^2}\right) + C_{p,\mathrm{m}}\ (\mathrm{int.\ rot.}) \tag{1}$$

$$H^{\ominus}_{\mathrm{m}}(T) - H^{\ominus}_{\mathrm{m}}(0) = RT\left(4 + \sum_i \frac{x_i}{\mathrm{e}^{x_i}-1}\right) + \left[H^{\ominus}_{\mathrm{m}}(T) - H^{\ominus}_{\mathrm{m}}(0)\right]\ (\mathrm{int.\ rot.}) \tag{2}$$

$$S^{\ominus}_{\mathrm{m}}(T) = R\left[\tfrac{3}{2}\ln M + 4\ln T + \sum_i\left(\frac{x_i}{\mathrm{e}^{x_i}-1} - \ln(1-\mathrm{e}^{-x_i})\right)\right.$$
$$\left. + \tfrac{1}{2}\ln \prod_i I_i 10^{117} - \ln\sigma - 1.1691\right] + S^{\ominus}_{\mathrm{m}}\ (\mathrm{int.\ rot.}) \tag{3}$$

The contribution to internal rotation by the CH_3 group was calculated by interpolating the values in the tables of Pitzer and Gwinn [7]. The partition function of free rotation of CH_3, Q_F, is given by

$$Q_F = 2.7929\frac{\left(I_r 10^{38} T\right)^{1/2}}{3}$$

where I_r is the reduced moment of inertia of the CH_3 group.

Determination of the geometric structures of the three isomers was effected from AM1 calculations. In all cases, the geometric structure adopted to carry out the calculation of rotational constants took account of symmetry constraints imposed on the overall molecular structure. It was nevertheless verified that the removal of this constraint did not significantly affect the result of the calculation, and that the sequence and difference evaluated in the determination of the products of the principal moments of inertia were retained.

The AM1 method was chosen because, among semi-empirical methods, it is one of those which best describe the potential energy surface near stable stationary points. The resulting geometric structures and vibrational frequencies may thus reasonably be adopted for calculation of the corresponding partition functions in the absence of precise experimental data. In addition, this method has the advantage of relatively correctly reflecting interactions between atoms not chemically bound, which could make it useful for justifying the observed sequence in the calculation of barriers to rotation.

The standard enthalpy of formation $\Delta_f H^{\ominus}_{\mathrm{m}}(T)$ and standard free enthalpy of formation $\Delta_f G^{\ominus}_{\mathrm{m}}(T)$ correspond to

$$7\mathrm{C(gr,\ s)} + \tfrac{7}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{F_2(g)} \rightleftharpoons \mathrm{C_7H_7F(g)}$$

Their calculation requires the determination of the functions $H^{\ominus}_{\mathrm{m}}(T) - H^{\ominus}_{\mathrm{m}}(0)$ and $[G^{\ominus}_{\mathrm{m}}(T) - G^{\ominus}_{\mathrm{m}}(0)]/T$ associated with the elements C(gr, s),

H_2(g) and F_2(g). These functions were taken from T.R.C. Hydrocarbon Project tables [8].

GEOMETRIC STRUCTURES AND MOMENTS OF INERTIA

The AM1-optimized geometric structures of the three isomers furnished parameters whose values were very close. The values obtained for the aromatic ring (C=C varying from 1.39 Å to 1.41 Å depending on the bond; CH close to 1.10 Å; $\widehat{CCC}$ angles close to 120°) are in good agreement with the structure of *o*-fluorotoluene proposed by Susskind [4].

The C–F bond length is little affected by the position of the substituent, since it was calculated at 1.355 Å for the *m*- and *p*-isomers and at 1.356 Å for *o*-fluorotoluene, again confirming the value proposed by Susskind (1.35 Å). The geometric parameters most affected by substituent position are the length of the C–C(H_3) bond and the corresponding angle C–C–C(H_3), which vary from 1.480 Å to 1.482 Å and from 121.7° to 120.4° between *o*-fluorotoluene and the *m*- or *p*-compound, respectively.

It may also be noted that these geometric structures were modified only very slightly when the symmetry constraint was removed, causing notable modifications only on the structural parameters of the CH_3 group.

Based on the theoretical determination of geometric structures, the principal moments of inertia and the reduced moment of inertia I_r of CH_3 were calculated. Table 1 lists the I_r values and the product of the principal

TABLE 1

Molecular constants for *o*-, *m*- and *p*-fluorotoluene

	o-Fluorotoluene	*m*-Fluorotoluene	*p*-Fluorotoluene
Molecular weight, M (g)	110.1319	110.1319	110.1319
Point group and symmetry number, σ	C_s	C_s	C_{2v}
Product of the three principal moments of inertia, $\Pi_i I_i$ ($g^3\,cm^6$)	65.986×10^{-114}	78.075×10^{-114}	66.830×10^{-114}
Reduced moment of inertia, I_r ($g\,cm^2$)	5.480×10^{-40}	5.497×10^{-40}	5.480×10^{-40}
Vibrational wavenumber, ν_i (cm^{-1})	3067, 3067, 3045,...	3081, 3081, 3060,...	3068, 3068, 3040,...
Potential barrier height, V ($J\,mol^{-1}$)	2717	261	57
Enthalpy of formation at 298.15 K, $\Delta_f H_m^{\ominus}$ ($kJ\,mol^{-1}$)	−116.9	–	−147.5

moments of inertia for the three isomers. The values agree with the data of Susskind [4] for the *o*-isomer.

VIBRATIONAL FREQUENCIES

Vibrational frequencies of the three isomers were determined and assigned [1–3] by IR and Raman spectroscopy in the interval 3650–50 cm^{-1}. These experimental results were used in the calculation of the vibrational contribution to thermodynamic functions. In addition, it should be noted that these frequencies were subsequently confirmed in the region of asymmetric CH_3 stretching for the *o*- and *p*-isomers [9] and in the far IR for the *m*-isomer [10].

The vibrational frequencies obtained with the AM1 method are in relatively good agreement with experimental frequencies. The mean difference between the calculated spectra and those experimentally observed by Green [1–3] was not more than 7%.

INTERNAL ROTATION OF METHYL GROUP: POTENTIAL BARRIER HEIGHT

Among the different published potential barrier heights impeding methyl group rotation, we chose those obtained using a single technique: microwave spectrometry. This enables a direct comparison of the barrier values associated with each isomer and also furnishes results wholly adapted to the study of the isolated molecule.

Thus, the values listed in Table 1 are those of Susskind [4] for the *o*-isomer, those of Rudolph and Trinkaus [5] for *m*- and those of Rudolph and Seiler [6] for *p*-fluorotoluene. The reliability of these values is reinforced by the recent study of excitation fluorescence and dispersed fluorescence spectra published by Okuyama et al. [11]. The very weak barrier observed for *p*-fluorotoluene was also confirmed by Moss et al. [12].

The sequence observed (see Table 1) in the potential barrier heights is corroborated by barrier calculations carried out in AM1, even though the energy differences are not quantitatively comparable. Furthermore, this sequence can be correlated with the frequency of the torsion mode of the methyl group calculated at a higher wavenumber for the *o*-isomer than for the *m*- and *p*-derivatives.

It is appropriate to cite several published barrier values. Thus, for the *o*-isomer in the solid state, Ahmed and Eades [13] used magnetic relaxation to deduce a variable barrier with temperature (1.172 kJ mol^{-1} between 30 K and 45 K, 2.427 kJ mol^{-1} between 50 K and 97 K), confirming the values published by Haupt and Müller-Warmuth [14]. These authors [13,14] determined for the *m*-isomer the respective values 0.920 kJ mol^{-1} and 0.753 kJ mol^{-1} between 40 and 53 K and 2.761 kJ mol^{-1} and 1.799 kJ mol^{-1} between 53 and 95 K.

THERMODYNAMIC FUNCTIONS

The thermodynamic functions $C^{\ominus}_{p,\mathrm{m}}$, $S^{\ominus}_{\mathrm{m}}$ and $H^{\ominus}_{\mathrm{m}}(T) - H^{\ominus}_{\mathrm{m}}(0)$ were calculated in the interval 0–3000 K using relationships (1), (2) and (3) and the data in Table 1. Their values are listed in Tables 2 (*ortho* isomer), 3 (*meta* isomer) and 4 (*para* isomer). Tables 2 and 4 also include the enthalpies and the standard free enthalpies of formation of the *o*- and *p*-compounds, for which the values of $\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m},T=298.15\mathrm{K}}$ are either known [15] (*p*-isomer) or calculated (*o*-isomer). The latter calculation was made from the standard enthalpy of formation of the *o*-isomer in the liquid state [16] and its enthalpy of vaporization [17]. It should nevertheless be mentioned, as

TABLE 2

Ideal gas thermodynamic properties of *o*-fluorotoluene

T (K)	$C^{\ominus}_{p,\mathrm{m}}$ (J mol^{-1} K^{-1})	$S^{\ominus}_{\mathrm{m}}$ (J mol^{-1} K^{-1})	$H^{\ominus}_{\mathrm{m}}(T) - H^{\ominus}_{\mathrm{m}}(0)$ (J mol^{-1})	$\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m}}$ (kJ mol^{-1})	$\Delta_{\mathrm{f}}G^{\ominus}_{\mathrm{m}}$ (kJ mol^{-1})
0	0	0	0	−95.9	−95.9
100	52.6	259.9	4100	−104.8	−85.9
150	66.0	283.7	7055	−107.6	−75.7
200	81.7	304.8	10737	−110.7	−64.8
273.15	107.4	333.9	17649	−115.4	−47.2
298.15	116.6	343.8	20442	−116.9	−41.0
300	117.3	344.5	20659	−117.0	−40.5
400	152.2	383.3	34168	−122.5	−14.1
500	182.2	420.4	50930	−127.0	13.6
600	206.7	455.9	70430	−130.5	42.0
700	226.7	489.3	92131	−133.3	71.1
800	243.1	520.7	115648	−135.4	100.8
900	256.9	550.1	140658	−136.9	129.9
1000	268.5	577.9	166956	−137.8	159.7
1100	278.4	603.9	194309	−138.2	189.2
1200	286.7	628.5	222553	−138.3	219.2
1300	293.9	651.7	251591	−138.2	249.0
1400	300.1	673.7	281279	−137.9	278.8
1500	305.4	694.6	311582	−137.4	309.8
1750	315.9	742.5	389368	−135.6	382.6
2000	323.5	785.2	469308	−133.5	456.4
2250	329.0	823.7	550932	−131.3	530.3
2500	333.2	858.5	633811	−128.9	603.4
2750	336.4	890.4	717477	−125.6	676.1
3000	339.0	919.9	801918	−122.0	752.4

TABLE 3

Ideal gas thermodynamic properties of *m*-fluorotoluene

T (K)	$C^{\ominus}_{p,\mathrm{m}}$ (J mol^{-1} K^{-1})	$S^{\ominus}_{\mathrm{m}}$ (J mol^{-1} K^{-1})	$H^{\ominus}_{\mathrm{m}}(T) - H^{\ominus}_{\mathrm{m}}(0)$ (J mol^{-1})
0	0	0	0
100	48.9	263.3	4046
150	63.4	285.8	6842
200	79.9	306.2	10421
273.15	106.4	335.0	17228
298.15	115.7	344.8	20005
300	116.4	345.4	20220
400	151.7	383.9	33662
500	181.8	421.0	50391
600	206.4	456.4	69835
700	226.4	489.8	91508
800	242.9	521.1	115007
900	256.7	550.6	140001
1000	268.3	578.2	166273
1100	278.2	604.3	193615
1200	286.6	628.9	221867
1300	293.8	652.1	250871
1400	300.0	674.1	280566
1500	305.3	694.9	310838
1750	315.8	742.8	388557
2000	323.4	785.5	468511
2250	329.0	824.0	550036
2500	333.2	858.8	632818
2750	336.4	890.7	716522
3000	338.9	920.1	800942

stated by Stull et al. [18], that the value of $\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m}}$ (o-C_7H_7F, l) $= -155.2$ kJ mol^{-1} is old [19] and not very precise. Unfortunately no other thermodynamic data are presently available, and so the values of $\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m}}$ (T) and $\Delta_{\mathrm{f}}G^{\ominus}_{\mathrm{m}}$ for *o*-fluorotoluene should be treated with caution. This reservation is all the more justified because of the difference between the $\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m}}$ values of the *p*- and *o*-isomers is a priori too great. In the case of similar compounds, the values of these enthalpies (expressed as kJ mol^{-1}) are in fact quite comparable. Thus, for example, for difluorobenzenes [20] at 298.15 K, $\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m}}$(*ortho*, g) $= -283.0$, $\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m}}$(*meta*, g) $= -298.6$ and $\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m}}$(*para*, g) $= -295.8$. Similarly, for dimethylbenzenes [21] at the same temperature, we have $\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m}}$(*ortho*, g) $= 19.08$, $\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m}}$(*meta*, g) $= 17.32$ and $\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m}}$(*para*, g) $= 18.03$. This tendency for a similar enthalpy of formation of the three positional isomers is also reflected by the AM1 calculations.

TABLE 4

Ideal gas thermodynamic properties of *p*-fluorotoluene

T (K)	$C^{\ominus}_{p,\mathrm{m}}$ ($\mathrm{J\ mol^{-1}\ K^{-1}}$)	$S^{\ominus}_{\mathrm{m}}$ ($\mathrm{J\ mol^{-1}\ K^{-1}}$)	$H^{\ominus}_{\mathrm{m}}(T)-H^{\ominus}_{\mathrm{m}}(0)$ ($\mathrm{J\ mol^{-1}}$)	$\Delta_{\mathrm{f}}H^{\ominus}_{\mathrm{m}}$ ($\mathrm{kJ\ mol^{-1}}$)	$\Delta_{\mathrm{f}}G^{\ominus}_{\mathrm{m}}$ ($\mathrm{kJ\ mol^{-1}}$)
0	0	0	0	−126.1	−126.1
100	48.9	257.5	4072	−135.0	−115.9
150	63.4	280.0	6865	−138.0	−105.7
200	80.0	300.5	10441	−141.2	−94.5
273.15	106.4	329.2	17249	−146.0	−76.5
298.15	115.6	339.0	20022	−147.5	−70.2
300	116.3	339.7	20237	−147.6	−69.6
400	151.5	378.9	33659	−153.2	−43.0
500	181.6	415.2	50358	−157.7	−14.6
600	206.3	450.6	69793	−161.3	14.3
700	226.3	483.9	91454	−164.2	43.9
800	242.9	515.3	114938	−166.3	73.8
900	256.7	544.7	139936	−167.8	103.9
1000	268.3	572.3	166202	−168.7	134.1
1100	278.2	598.4	193541	−169.1	164.3
1200	286.6	623.0	221792	−169.3	194.8
1300	293.8	646.2	250822	−169.2	225.2
1400	300.0	668.2	280521	−168.8	255.8
1500	305.4	689.1	310796	−168.4	286.0
1750	315.9	736.9	388524	−166.7	361.4
2000	323.5	779.7	469537	−163.5	437.4
2250	329.0	818.1	550077	−162.3	511.9
2500	333.2	853.0	632874	−160.1	586.0
2750	336.4	884.9	716590	−156.7	660.3
3000	339.0	914.3	801018	−153.1	738.1

SUMMARY AND CONCLUSIONS

The thermodynamic functions of *p*-fluorotoluene have been previously calculated between 298 K and 1000 K and are listed in the tables of Stull et al. [16,18]. We have refined and extended these calculations to the temperature interval 0–3000 K. The comparison of the results leads to very satisfying agreement.

The parameters $C^{\ominus}_{p,\mathrm{m}}$, $S^{\ominus}_{\mathrm{m}}$, and $H^{\ominus}_{\mathrm{m}}(T) - H^{\ominus}_{\mathrm{m}}(0)$ for the three isomers are very similar, because of the very close geometric and vibrational structures. The molecular symmetry of *p*-fluorotoluene is the origin of its lower entropy, while below 1000 K the rotation barrier of the CH_3 group of the *o*-isomer contributes to the differences observed with the other two isomers.

The values of potential barriers impeding methyl group rotation are low for the *m*- and *p*-isomers. Their contribution to the calculation of the thermodynamic functions is insignificant throughout the temperature interval examined. In the case of the *o*-isomer, its contribution becomes significant below 1000 K; e.g., at 100 K it accounts for 14% of the molar heat capacity, for 1% of entropy and for 11% of the function $H_m^\ominus(T) - H_m^\ominus(0)$.

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