Enthalpies of sublimation and vapor pressures of 2,2′-bis-1,3-dithiole (TTF), 7,7,8,8-tetracyanoquinodimethane (TCNQ), and TTF–TCNQ (1:1)

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Torsion and mass loss effusion techniques are applied simultaneously to measure the saturation vapor pressures as a function of temperature. The enthalpies of sublimation are derived from the temperature dependence of vapor pressure. Overall mean values for both techniques are: TTF, ΔH^0(344.91 K) = (95.3 ± 1) kJ mol^{-1}; TCNQ, ΔH^0(431.74 K) = (126.1 ± 1) kJ mol^{-1}; TTF–TCNQ(1:1), ΔH^0(410.65 K) = (130.0 ± 2) kJ mol^{-1}. The temperatures given are midrange values at which the saturation vapor pressure of each sample is 0.4 Pa. It is shown that the TTF–TCNQ sample evaporates stoichiometrically but not as a complex.

I. INTRODUCTION

There is growing interest in the study of molecular interaction in organic donor–acceptor crystals with high electrical conductivity.[1] To study the lattice energies and to assess the relative importance of the various types of molecular interaction via quantum mechanical or semiempirical methods one needs the experimental values of thermodynamic quantities, such as the enthalpies of sublimation and formation. A well-known example of highly conducting organic donor–acceptor crystals is TTF–TCNQ, discovered in 1973 by Ferraris et al.[2]

The aim of this investigation is to determine experimental enthalpies of sublimation derived from the temperature dependence of vapor pressure. In order to define the enthalpy of sublimation of the TTF–TCNQ (1:1) complex we have to know to what degree the complex is dissociated into molecular particles in the vapor phase. The fact that the molecular masses of TTF and TCNQ happen to be virtually the same (204.36 and 204.19) permits the vapor pressure data to be treated in the same way as the data for the lower carboxylic acids which form dimers in the vapor phase. This matter has already been treated exhaustively in Ref. 3. In short, the method is based on the following: from the torsion effusion experiment total vapor pressure is obtained while the mass loss effusion experiment provides a value for the weighted mean molecular mass of the vapor. If TTF–TCNQ exists in the vapor phase (partly) as a complex, then a weighted mean molecular mass between 204.3 and 2×204.3 will be found. A quadrupole analyzer was used to detect whether or not the sample evaporated stoichiometrically.

II. EXPERIMENTAL

A. Materials

TCNQ and TTF, which were both obtained from Aldrich (USA), were stated to be at least 98% and 97% pure, respectively. The samples were handled and stored under argon and kept in the dark. The melting point of TCNQ was found to be 290 °C (DSC II–Perkin Elmer). Chen[4] gives a value of 290–295 °C and Gemmer

et al.[12] 294–296 °C. The melting point of TTF was found to be 119 °C which is somewhat higher than the value given by Chen[4] (103 °C), but in accordance with the results of Gemmer et al.[12] (119.1–119.5 °C). Micro-crystalline samples of TTF–TCNQ (1:1) were grown from solutions containing equimolar quantities of both source materials. As solvent we used either acetone or acetic acid ethylester. Decomposition was observed at 219 °C, which is essentially the same temperature as that reported by Chen.[4]

B. Measuring methods

Use is made of simultaneously applied torsion and mass loss effusion techniques. Since the description[5] of the apparatus, we have introduced some improvements and automated the measurements. The given measuring method has not changed. The stainless steel effusion cell has a cylindrical shape: 12 mm diameter. The 1 mm orifices are drilled in platinum foil of 6 μm The distance of the orifices to the axis of rotation is 10 mm. In order to determine the relative concentration of TTF and TCNQ in the effusing vapor, we added a quadrupole gas analyzer (UTI 100 C) equipped with an electron multiplier. Part of the molecular gas stream leaving the oven surrounding the effusion vessel is directed into the ionizer of the gas analyzer. The distance between ionizer and oven slit is 20 cm. So after leaving the oven, the molecules reach the ionizer without additional collisions, and fractionization in the molecular gas stream is thereby avoided.

By comparing the mass spectra of pure TTF and pure TCNQ it was possible to select two different fragments which could be allocated unambiguously to the parent compounds: ion masses 140 and 146 for TCNQ and TTF respectively. Because TTF and TCNQ have equal molecular masses, the parent peaks and some fragment peaks could not be used. By recording the ion currents we determined the (relative) concentration of the parent compounds, when we evaporated the TTF–TCNQ (1:1) samples. The quadrupole gas analyzer was coupled to an HP-9825 desktop computer which controlled all settings and compiled the measuring values from an HP-3455 A digital voltmeter.

TABLE I. Experimental results.

| | | $\frac{T_1}{K}$ | $\frac{T_2}{K}$ | Torsion effusion | | | | Weighing effusion | | |
				$\frac{\theta_t}{K}$	$\frac{\Delta G_t^0(\theta)}{J\,mol^{-1}}$	$\frac{\Delta H_t^0(\theta)}{kJ\,mol^{-1}}$	$\frac{\theta_w}{K}$	$\frac{\Delta G_w^0(\theta)}{J\,mol^{-1}}$	$\frac{\Delta H_w^0(\theta)}{kJ\,mol^{-1}}$	$p_w/p_t\,(\theta_t)$
TTF	290578	336	356	345.16	2630 ± 25	96.4 ± 2	344.81	2627 ± 15	95.7 ± 1	1.03
	040579	339	356	344.95	2628 ± 50	94.8 ± 2	344.68	2626 ± 10	94.2 ± 2	1.03
mean				345.06	2629 ± 25	95.6 ± 2	344.75	2626 ± 10	95.0 ± 1	1.03
TCNQ	280378	402	426	413.45	3150 ± 50	125.8 ± 1	413.51	3150 ± 50	123.3 ± 1.5	1.00
	240578	403	426	413.52	3150 ± 25	127.3 ± 1	413.73	3152 ± 20	126.1 ± 1	0.98
	060579	406	424	414.20	3155 ± 30	128.2 ± 1	414.03	3154 ± 30	125.9 ± 2	1.01
mean				413.72	3152 ± 30	127.1 ± 1	413.76	3152 ± 30	125.1 ± 2	1.00
TTF—TCNQ[a]	110579	401	428	410.51	3127 ± 200	128.7 ± 2	410.79	3129 ± 200	126.3 ± 2	0.98
	150579	401	425	411.03	3131 ± 200	133.0 ± 2	411.19	3133 ± 200	130.0 ± 2	0.98
	230779	402	423	410.16	3125 ± 200	132.0 ± 2	410.17	3125 ± 200	130.0 ± 1	1.00
mean				410.57	3128 ± 200	131.2 ± 2	410.72	3129 ± 200	128.8 ± 2	0.99

[a]1 mol TTF − TCNQ (1 : 1) is 204.3 g.

C. Treatment of results

From the measuring parameters we obtained values for p_t (torsion), p_w (weighing), and T (temperature). The value for p_w was found by inserting in the Knudsen equation, for the mass loss per second from an effusion cell, the molecular formula mass ($M_1 = 204.3$) of the solid. Then the following equation[6] was used to fit both p_t and p_w as a function of temperature,

$$R\ln(p/p^0) = -\Delta G^0(\theta)/\theta + \Delta H^0(\theta)(1/\theta - 1/T) \quad (1)$$

in which p^0 is a standard pressure (1 Pa) and θ a reference temperature such that the vapor pressure is 0.4 Pa. To calculate p_w one needs to know the weighted mean molecular mass M of the vapor. It can be shown that the ratio p_w/p_t is given by

$$p_w/p_t = (M/M_1)^{1/2} \quad . \quad (2)$$

So, when M is different from M_1, the ratio p_w/p_t will not be equal to 1. In general this will be observed when decomposition occurs[7] or when the vapor is more or less dimerized.[3] Also if the TTF—TCNQ sample evaporates as a complex, as suggested by Chen,[4] then a value greater than 1 will be found for p_w/p_t.

III. RESULTS AND DISCUSSION

In Table I we have given the experimental results expressed as θ, $\Delta G^0(\theta)$, and $\Delta H^0(\theta)$ of Eq. (1). Because there was an interval of over 1 yr between measurements, we decided to indicate this in the second column. In addition this permits a review of the reproducibility of the measurements, which is quite satisfactory and

well within the given error ranges. The mean values in Table I are the averages of the separate measurements which in turn are found from six or more runs. Each run contains about 100 (p_t, p_w, T) values, obtained by increasing the sample temperature from T_1 to T_2 in about 20 steps of 1 K in approximately 3 h.

The error ranges in $\Delta G^0(\theta)$ for the TTF—TCNQ sample are considerably larger as a result of a systematic drift of vapor pressure to lower values in successive runs. We ascribe this to a progressively bad heat contact between the very voluminous sample and the effusion cell. It was observed that the sample came loose from the wall of the cell. Furthermore, the covering of the sample with nonvolatile impurities could have reinforced the effect. Some residue was left when the sample was evaporated completely. The first two measurements in Table I were obtained with a sample grown from acetone. The use of acetic acid ethylester as a solvent (for preparing the last sample) did not change the results. So the $\Delta G^0(\theta)$ values for the TTF—TCNQ samples are the (extrapolated) values at the start of the measurements. The $\Delta H^0(\theta)$ values were essentially constant during all measurements.

In the last column of Table I a value for p_w/p_t is given. For the pure components this value is an indication of the mutual consistency of both techniques, assuming that no decomposition or dimerization occurs. For the TTF—TCNQ sample the value of p_w/p_t is 0.99. We, therefore, come to the conclusion that the effusing vapor consists only of species with a molecular mass of 204.3.

TABLE II. Mean values of the torsion and the weighing effusion experiment; literature values.

| | This work | | | Literature values | | | |
	$\frac{\theta}{K}$	$\frac{\Delta G^0(\theta)}{J\,mol^{-1}}$	$\frac{\Delta H^0(\theta)}{kJ\,mol^{-1}}$	$\frac{T_1}{K}$	$\frac{T_2}{K}$	$\frac{\Delta H^0}{kJ\,mol^{-1}}$	$\frac{P(\theta)}{Pa}$
TTF	344.91	2628 ± 25	95.3 ± 1	341	361	92.0 ± 6.3[a]	10
TCNQ	413.74	3152 ± 30	126.1 ± 1	433	499	104.8 ± 10[b]	$\cdots$
TTF—TCNQ[c]	410.65	3128 ± 200	130.0 ± 2				

[a]Reference 8.   [b]Reference 9.   [c]1 mol TTF − TCNQ (1 : 1) is 204.3 g.

TABLE III. Pressure—temperature table obtained by inserting mean values of Table II in Eq. (1).

p/Pa	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
					T/K					
TTF	331.10	337.86	341.95	344.91	347.24	349.17	350.82	352.26	353.54	354.69
TCNQ	398.66	406.06	410.52	413.74	416.27	418.37	420.15	421.71	423.10	424.35
TTF—TCNQ	396.22	403.31	407.57	410.65	413.07	415.07	416.77	418.26	419.58	420.77

This is in contrast with the suggestion of Chen[4] that the complex evaporates as a whole.

The two ion currents measured with the quadrupole analyzer were proportional to the measured vapor pressure but the ratio remained constant within 10% during the measurements. From this we conclude that the sample evaporates stoichiometrically. It will be obvious that the above facts must be considered when the TTF–TCNQ complex is prepared by means of vacuum sublimation. The combined conclusions also lead us to define the enthalpy of sublimation of the TTF–TCNQ (1:1) sample as the enthalpy difference per 204.3 g between vapor and crystalline phase in which the vapor phase consists of 0.5 mol TTF and 0.5 mol TCNQ. In Table II we have given overall mean values for both techniques and some literature values. Although the enthalpy of sublimation of TTF reported by Sandman et al.[8] is in agreement with our value, their vapor pressure data exceed ours by a factor of 25. The enthalpy of sublimation of TCNQ given by Boyd[9] deviates considerably from our value. He reported a midrange vapor pressure of 27 Pa at 465 K. When this is combined with our midrange values of 0.4 Pa at 413.94 K in the Clausius–Clapeyron equation, we calculate an enthalpy of sublimation of 131 kJ mol^{-1}, which supports our value.

As far as we know, no other direct experimental information is available on the enthalpy of sublimation of TTF–TCNQ. However, an indirect estimation of an experimental value can be obtained from the experimental values of the heats of formation of the complex and its components by Metzger[10] and the enthalpies of sublimation of pure TTF and TCNQ. Using the value of Boyd[9] for TCNQ one obtains an experimental heat of sublimation of TTF–TCNQ at 298.15 K of (123.8 ±13) kJ mol^{-1}, whereas our value for TCNQ leads to a value of (133.5 ± 9) kJ mol^{-1}. The latter is much more consistent with our direct experimental value of (130.0

± 2) kJ mol^{-1} at 410.65 K, particularly because specific heat capacities corrections will increase this value by several kJ mol^{-1}. For instance if ΔC_p is estimated, from an average for other organic compounds, as $\Delta C_p^0 = (63 \pm 40)$ J K^{-1} mol^{-1}, then this leads to ΔH (298.15 K) $= (137 \pm 5)$ kJ mol^{-1} for the complex. Calculations of the lattice energies of TTF, TCNQ, and TTF–TCNQ (1:1) with the help of the atom–atom approximation by Govers,[11] ΔH^0 (TTF, calc, 298.15 K) $= (95.8 \pm 4)$ kJ mol^{-1}, ΔH^0 (TCNQ, calc, 298.15 K) $= (110.9 \pm 5)$ kJ mol^{-1}, ΔH^0 (TTF–TCNQ, calc, 298.15 K) $= (134.3 \pm 5)$ kJ mol^{-1}, show a satisfactory agreement between calculated and experimental results presented in this investigation. In Table III we have given a pressure-temperature table, obtained by inserting the mean values of Table II in Eq. (1).

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