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# Thermodynamic Properties of Organic Compounds. 2. Combustion and Sublimation Enthalpies of 2,4,6-Trimethylbenzonitrile *N*-Oxide

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**Experimental vapor pressures and enthalpy of combustion are reported for 2,4,6-trimethylbenzonitrile *N*-oxide, along with the enthalpy of sublimation derived from the temperature dependence of the vapor pressure. Results of these measurements are used to compute standard enthalpies of formation in the crystalline and gaseous states, $\Delta_f H_m{}^\circ(\mathrm{cr}) = 49.25 \pm 3.54$ kJ·mol$^{-1}$ and $\Delta_f H_m{}^\circ(\mathrm{g}) = 137.0 \pm 4.0$ kJ·mol$^{-1}$, respectively.**

## Introduction

Nitrile *N*-oxides are highly reactive organic compounds prepared from oxidation of aldoximes and dehydration of nitro compounds. Reported half-lives of aliphatic nitrile *N*-oxides range from a few seconds to minutes before rearrangement to isocyanates or polymerization occurs. Aromatic nitrile *N*-oxides are considerably more stable, particularly 1,4-dicyanobenzene di-*N*-oxide (*1*, *2*), which can be stored for several months without noticeable degradation. Bulky substituents in the ortho positions of the benzene ring or on the α-carbon aliphatic derivatives enhance stability. Sterically hindered nitrile *N*-oxides such as 2,6-dimethylbenzonitrile *N*-oxide and di-*tert*-butylacetonitrile *N*-oxide are "permanently stable" at room temperature (*3*–*5*).

Chemical reactivity of the nitrile *N*-oxides undoubtedly arises because of the ionic nature of the N–O dative bond. Nuclear magnetic resonance $^{13}$C chemical shift data for 2,4,6-trimethylbenzonitrile *N*-oxide (*6*) suggest that the carbon atom carries substantial negative charge (i.e., the $\mathrm{R{-}C^{-}{=}N^{+}{=}O}$ resonance form) and are in accord with published X-ray crystallographic bond distances for 4-methoxy-2,6-dimethylbenzonitrile *N*-oxide (*7*). Surprisingly, very few precise thermochemical quantities are available in the chemical literature for nitrile *N*-oxides. Acree, Pilcher, and co-workers (*8*) previously reported the standard enthalpies of combustion and sublimation for 2,4,6-trimethylbenzonitrile *N*-oxide and 2,4,6-trimethoxybenzonitrile *N*-oxide as determined by static bomb calorimetric and "vacuum sublimation" drop microcalorimetric methods, respectively. Because of the scarcity of experimental data for this relatively novel class of compounds, we have undertaken a comprehensive thermodynamic study of 2,4,6-trimethylbenzonitrile *N*-oxide, which includes both heat capacity and vapor pressure measurements, as well as redetermination of the enthalpy of combustion. In this short communication we report results from the combustion and vapor pressure measurements. The heat capacity data will be presented at a later date.

## Experimental Methods

2,4,6-Trimethylbenzonitrile *N*-oxide was prepared by the procedures outlined by Grundmann and Dean (*5*) and Beltrame et al. (*9*). Hydroxylamine hydrochloride was added to a hot solution of 2,4,6-trimethylbenzaldehyde in methanol, and the resulting aldoxime was converted to the nitrile *N*-oxide with sodium hypobromite. The crude sample was further purified by three recrystallizations from a benzene–hexane mixture. Elemental analysis on the purified sample was in excellent agreement with calculated values. Anal. Found for $C_{10}H_{11}NO$ (mass %): C, 74.58; H, 6.94; N, 8.62. Calcd (mass %): C, 74.51; H, 6.88; N, 8.69. The sample was stored in a cool, dark place for several weeks and later shipped to the Soviet Union via airmail during a period of heightened airport security.

Experimental procedures and instrumentation are described in detail elsewhere (*10*–*13*). Briefly, combustion energies were measured in a calorimeter with an isothermal jacket whose temperature was controlled to within 0.0015 K. The calorimeter vessel temperature was measured with 100-Ω platinum resistance thermometers and recorded on a digital voltmeter. The calorimeter has been automated in order to facilitate transfer of information from the digital voltmeter to a microcomputer. An automation scheme enables one to vary the temperature intervals between measurements, warms the operator of the approaching ignition time, checks the success of ignition, and signals the end of measurements. The volume of the empty bomb was 0.3205 dm$^3$. The sample was ignited using a 10 000 μF capacity bank discharged through a 0.05-mm platinum wire (*14*, *15*). All experiments were performed at an initial bomb pressure of 3.0 MPa. Oxygen was prepurified from an organic admixture, carbon dioxide and water. The energy equivalent of the calorimeter 14 889.9 ± 6.4 J·K$^{-1}$ was determined for the standard benzoic acid K–I with a specific energy of combustion of 26 460.6 ± 4.6 J·g$^{-1}$.

To ascertain the completeness of combustion, a gravimetric technique was used to determine the amount of $CO_2$(g), undissolved $NO_2$, and in some tests CO, with the sensitivity of indicator tubes being $1 \times 10^{-4}$ (volume percent). In the $CO_2$ tests, an $MnO_2$ tube was inserted into the absorption system to absorb nitrogen oxides that might interfere with the $CO_2$ measurements (*16*). To reduce the effect of nitrogen oxides, the gravimetric analysis was performed after the contents were stored in the bomb for 24 h (*17*). As the accuracy of weighing the trap system for gravimetric analysis was lower than that of the sample mass measurement, $\Delta_c U_m{}^\circ$ was calculated from the mass of the calorimetric sample. In a series of special experiments we established that nitric oxides formed in the combustion of 2,4,6-trimethylbenzonitrile *N*-oxide during the main period had time to turn in the bomb into $HNO_3$ solution;

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**Table I. Experimental Evaluation of the Enthalpy of Combustion of 2,4,6-Trimethylbenzonitrile *N*-Oxide**[a]

| run no. | $m_0$/g | $\alpha$ | $\Delta T$/K | $q_{\mathrm{ign}}$/J | $q_{\mathrm{HNO_3}}{}^{b}$/J | $\sum q$/J | $-\Delta_c U_m°/m_0$/(J·g$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 | 0.528 19 | 0.001 00 | 1.224 10 | 2.0 | 31.0 | 9.2 | 34 428.1 |
| 2 | 0.489 29 | 0.001 04 | 1.134 43 | 2.0 | 28.6 | 8.4 | 34 442.8 |
| 3 | 0.485 03 | 0.001 08 | 1.124 86 | 2.0 | 28.6 | 8.3 | 34 451.6 |
| 4 | 0.461 27 | 0.001 07 | 1.069 59 | 2.0 | 28.0 | 7.8 | 34 444.6 |
| | | | | | | | 34 441.8 ± 15.6 (av) |

[a] Density of the solid at 293.15 K is 1.1565 g·cm$^{-3}$. [b] Estimated uncertainty is ±0.1 J.

**Table II. Vapor Pressure Data for 2,4,6-Trimethylbenzonitrile *N*-Oxide at Various Temperatures**

| $T$/K | $p$/Pa | $10^6 m$/kg | $t$/s |
|---|---|---|---|
| Sample I: Original Sample as Received | | | |
| 300.33 | 0.0872 | 3.76 | 26 688 |
| 304.43 | 0.149 | 9.91 | 41 454 |
| 308.16 | 0.247 | 5.94 | 15 054 |
| 308.16 | 0.239 | 4.83 | 12 654 |
| 313.23 | 0.447 | 10.23 | 14 454 |
| 318.02 | 0.798 | 11.54 | 9 204 |
| 323.32 | 1.416 | 12.08 | 5 476 |
| 328.43 | 2.250 | 12.71 | 3 654 |
| 333.71 | 3.661 | 13.78 | 2 454 |
| 338.20 | 5.523 | 15.60 | 1 854 |
| 342.68 | 10.12 | 28.40 | 1 854 |
| Sample II: Purified by Vacuum Sublimation | | | |
| 299.95 | 0.153 | 5.87 | 23 679 |
| 304.33 | 0.216 | 6.33 | 18 220 |
| 308.16 | 0.364 | 6.72 | 11 573 |
| 312.40 | 0.542 | 8.19 | 9 535 |
| 316.78 | 0.845 | 9.98 | 7 504 |
| 321.25 | 1.355 | 16.26 | 7 676 |
| 325.11 | 2.084 | 12.14 | 3 749 |
| 329.32 | 3.093 | 11.72 | 2 454 |
| 333.46 | 4.507 | 22.57 | 3 264 |
| 338.38 | 7.250 | 20.43 | 1 850 |

that is why the correction for $HNO_3$ generation was determined by the titration results extrapolated to the end point of the main period. The extrapolated value of the volume of 0.01 mol·dm$^{-3}$ of alkali hydroxide used for titration was below 0.5 cm$^3$. The Washburn corrections were estimated using the technique suggested by Prosen (*18*) with regard to recommendations given in ref 19.

Vapor pressures were measured between ca. 300 and 340 K by an integral Knudsen effusion method (*12*, *13*). The diameter of the effusion hole in the nickel membrane was 0.82543 ± 0.0035 mm and the Knudsen constant, KS, was 50.4406 × 10$^{-8}$ m$^2$. Calculated vapor pressures are based upon the assumption that the true molecular mass of the gaseous species is that of the monomer, 161.203 g·mol$^{-1}$, which should be valid under these experimental conditions. Any polymerization product that could conceivably be formed from thermal/photochemical degradation of 2,4,6-trimethylbenzonitrile *N*-oxide is expected to have a much higher molecular mass and thus would be extremely nonvolatile.

## Results and Discussion

Combustion results are listed in Table I; $m_0$ is the mass of 2,4,6-trimethylbenzonitrile *N*-oxide determined in vacuum, $\Delta T$ is the corrected temeprature rise; $\alpha$ is the cooling constant of the calorimeter; $\sum q$ denotes the sum of the Washburn corrections; $q_{\mathrm{ign}}$ is the ignition contribution to the observed; and $g_{\mathrm{HNO_3}}$ refers to the correction for production of nitric acid, which was subtracted from the observed heat. Errors in $\Delta_c U_m°$ were computed as a product of standard deviation and Student coefficient for four independent determinations at the 95% confidence limit. Measurements on a smaller sample purified by vacuum sublimation gave essentially an identical $\Delta_c U_m°$ value but is not included in the statistical treatment. Standard molar enthalpies of combustion and formation in the crystalline state are $\Delta_c H_m°(\mathrm{cr}) = -(5\,556.45 \pm 2.51)$ kJ·mol$^{-1}$ and $\Delta_f H_m°(\mathrm{cr}) = 49.25 \pm 3.54$ kJ·mol$^{-1}$, respectively. To derive this latter quantity, the standard molar enthalpies of formation for $H_2O(l)$, $-(285.83 \pm 0.04)$ kJ·mol$^{-1}$, and for $CO_2(g)$, $-(393.51 \pm 0.13)$ kJ·mol$^{-1}$, were used. The calculated enthalpy of formation differs only slightly from the published value of 55.9 ± 1.5 kJ·mol$^{-1}$ determined by Acree et al. (*8*).

Vapor pressures for 2,4,6-trimethylbenzonitrile *N*-oxide at temperatures between 300 and 345 K are tabulated in Table II for the sample as received via airmail (sample I) and after subsequent purification by vacuum sublimation (sample II). Experimental values can be described by the following mathematical expressions

sample I

$$\ln(p/\mathrm{Pa}) = (35.9005 \pm 0.9952) - (11239 \pm 317)/(T/\mathrm{K}) \tag{1}$$

sample II

$$\ln(p/\mathrm{Pa}) = (33.0469 \pm 0.6803) - (10513 \pm 218)/(T/\mathrm{K}) \tag{2}$$

which upon the appropriate differentiation yield enthalpies of sublimation of $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m°(321.5\ \mathrm{K}) = 93.44 \pm 2.64$ kJ·mol$^{-1}$ and $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m°(319.2\ \mathrm{K}) = 87.41 \pm 1.81$ kJ·mol$^{-1}$ for samples I and II. Sublimation enthalpies at the mean temperature can be corrected to 298.15 K assuming $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_p° = -R$ (*20*). For the purified sample, the computed sublimation enthalpy is $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m° = 87.76 \pm 1.81$ kJ·mol$^{-1}$.

Not too much significance is placed on the first set of vapor pressure measurements because the sample became discolored at the elevated temperatures. To remove small impurities which may have resulted from prolonged shelf storage and/or X-ray inspections at airport security checkpoints, the original sample was purified by vacuum sublimation at 333 K, as noted above. Vapor pressure measurements on sample II are believed to be reliable. The sublimed sample retained its white color over the entire temperature range examined. Combustion measurements were identical for both samples, at least within experimental uncertainty, and thus suggest that the degradation product was likely 2,4,6-trimethylbenzene isocyanate rather than a polymerization product. Our experimental enthalpy of sublimation is approximately 10 kJ·mol$^{-1}$ more than the reported literature value of $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m° = 77.5 \pm 3.7$ kJ·mol$^{-1}$ (*8*) on the basis of vacuum sublimation drop microcalorimetry; however standard enthalpies of formation in the gaseous state are equivalent, $\Delta_f H_m°(\mathrm{g}) = 137.0 \pm 4.0$ kJ·mol$^{-1}$ versus $\Delta_f H_m°(\mathrm{g}) = 133.4 \pm 4.0$ kJ·mol$^{-1}$ (*8*). Agreement between experimental values is considered excellent, particularly in light of the thermal/photochemical instability of 2,4,6-trimethylbenzonitrile *N*-oxide. Replicate, independent experimental determinations are a necessity whenever reactive compounds such as nitrile *N*-oxides are studied. Finally, our studies indicate that aromatic nitrile *N*-oxides do not necessarily exhibit the reported stability on shelf storage, and extreme care should be exercized in transporting/receiving samples for thermochemical measurements.

**Registry No.** 2,4,6-Trimethylbenzonitrile *N*-oxide, 2904-57-6.

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# Vapor Pressure, Density, Refractive Index, Excess Enthalpy, and Heat Capacity of 2-Chloro-2-methylpropane or Chlorobenzene + 2,2,4-Trimethylpentane

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**Excess volumes of the binary liquid mixtures of 2-chloro-2-methylpropane (*tert*-butyl chloride) or chlorobenzene + 2,2,4-trimethylpentane (isooctane) have been determined at 293.15 and 313.15 K from density measurements at atmospheric pressure. The excess enthalpies, at 293.15 K, and the excess isobaric heat capacities, at 293.15 K and 313.15 K, have been measured using Picker calorimeters at atmospheric pressure. Also the excess Gibbs energy of chlorobenzene + 2,2,4-trimethylpentane has been calculated from isothermal vapor–liquid equilibrium data at 303.15 and 323.15 K, taken in a dynamic Cottrell type apparatus, the equilibrium compositions being determined refractometrically.**

## Introduction

The measurements of the excess properties of 2-chloro-2-methylpropane (*tert*-butyl chloride) or chlorobenzene + 2,2,4-trimethylpentane (isooctane) presented here are part of a study on liquid mixtures of polar components (with different dipole moments) with a common nonpolar component, 2,2,4-trimethylpentane. References to other parts of this investigation have been summarized recently (*1*, *2*).

2-Chloro-2-methylpropane and chlorobenzene are the least polar fluids in the series studied with dipole moments in the gas phase of 2.13 and 1.70 D, leading to reduced dipole moments of 0.695 and 0.494 (*2*), respectively.

## Experimental Section

***Materials.*** 2-Chloro-2-methylpropane (EGA-Chemie, p. a.) with a purity of 98.80 mol % and chlorobenzene (Fluka, puriss.) with a purity of 99.98 mol %, both checked by GLC, were dried by storage over calcium chloride and over potassium carbonate, respectively (J. T. Baker Chemicals, Analytical Reagent). 2,2,4-Trimethylpentane (Fluka, puriss., or Phillips, Research Grade) with GLC purities of 99.97 or 99.98 mol %, respectively, was stored over Na-Pb (Merck, p. a.). The substances were used without further purification. They were carefully degassed by several pump/thaw cycles prior to each measurement. The molar quantities were calculated using the relative atomic masses according to IUPAC (1987) (*3*).

In Table I, the experimental densities $\rho$, the molar isobaric heat capacities $C_p$ and, if measured, the vapor pressures $p$ and the refractive indices $n_D$ of the pure liquids are compared with literature data.

***Apparatus and Procedure.*** Molar excess volumes $V^E$ were calculated from precise density measurements of the liquids measured by means of a vibrating glass tube densimeter (Model DMA 02 D, Paar) at 293.15 and 313.15 K and atmospheric pressure. The precision in the densities is estimated as $3 \times 10^{-6}$ g cm$^{-3}$, the accuracies are $2 \times 10^{-5}$ g cm$^{-3}$, at 293.15 K, and $1 \times 10^{-4}$ g cm$^{-3}$, at 313.15 K. $V^E$ is accurate to 0.003 cm$^3$ mol$^{-1}$ at about equimolar composition. Mixtures were prepared from the degassed samples under vacuum by weighing them into airtight screw-capped tubes; the masses were corrected for the gas phase. This led to accuracies in the mole fraction $x_i$ of $3 \times 10^{-5}$. Details are given in ref 4.

The molar excess enthalpies $H^E$ (at 293.15 K) and the molar excess isobaric heat capacities $C_p{}^E$ (at 293.15 and 313.15 K) at atmospheric pressure were measured with a dynamic flow and a differential flow microcalorimeter, respectively, of Picker type (Setaram). At equimolar composition, $H^E$ could be measured with a relative error of less than 2.5%. The absolute molar $C_p$ values of 2,2,4-trimethylpentane were estimated to be accurate to 1.2 J mol$^{-1}$ K$^{-1}$; the errors for $C_p$ of 2-chloro-2-methylpropane and chlorobenzene were estimated to be 1%. In a stepwise procedure, only small differences of the volumetric heat capacities were measured from one concentration to another one over the entire range, for which uncertainties in the heat capacity of the pure compounds did not matter; from this $C_p{}^E$ could be determined with an accuracy of 0.02 J mol$^{-1}$

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