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Thermochemical Studies on 3- and 4-Nitroanilines and Their *N,N*-Dimethyl Derivatives[†]

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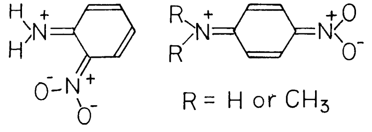
Standard enthalpies of combustion and of sublimation at 298.15 K were determined and standard enthalpies of formation in crystalline and gaseous states were derived for *N,N*-dimethyl-3- and *N,N*-dimethyl-4-nitroanilines by calorimetric measurements. Stabilization energies due to the intramolecular interaction between substituents were evaluated and discussed for these compounds and 3- and 4-nitroanilines.

For most of disubstituted benzenes, dipole moment in benzene solution may be approximated by the vector sum of the dipole moments of the appropriate monosubstituted benzenes.[1)] However, there are a group of exceptional compounds, 2- and 4-nitroanilines and *N,N*-dimethyl derivative of the latter being examples of such compounds. Observed dipole moments in benzene solution are by 16 and 20 per cent higher than the calculated values for 2- and 4-nitroanilines, respectively, whereas that of 3-nitroaniline is only 3 per cent higher than the calculated value.[1)] The corresponding deviations are 23 and 4 per cent for *N,N*-dimethyl-4- and *N,N*-dimethyl-3-nitroanilines, respectively.[1)]

The unusual dipole moments were attributed to the enhanced contribution of the following polar ortho- and para-quinonoid resonance structures to the ground state configurations of these molecules:[2)]



These resonance structures are characterized by the intramolecular charge transfer interaction between (dimethyl) amino and nitro substituents through the benzene ring. In this sense, the resonance has been called "interaction resonance" or "through resonance" between "push" (electron-donating) and "pull" (electron-accepting) substituents. For 3-nitroaniline and its *N,N*-dimethyl derivative, meta-quinonoid structures are available, but their contributions to the ground state configurations were considered to be small owing to the presence of a transannular bond. The normal dipole moments of 3-nitroaniline and its *N,N*-dimethyl derivative were explained along this line.

In a previous paper,[3)] standard enthalpies of formation at 298.15 K were reported for 3- and 4-nitroanilines (**1** and **2**, respectively) in gaseous state by the present authors. In this paper, standard enthalpies of combustion and sublimation are reported and standard enthalpies of formation in crystalline and gaseous states are derived for *N,N*-dimethyl-3- and *N,N*-dimethyl-4-nitroanilines (**3** and **4**, respectively). Stabilization energies have been evaluated and discussed for these molecules.

Experimental

Materials. Commercial **3** (Tokyo Kasei, G.R.) was purified by recrystallization from ethanol solution, preliminary sublimation *in vacuo*, zone melting, and fractional sublimation *in vacuo*. Commercial **4** (Tokyo Kasei, G.R.) was purified by recrystallization from ethanol, ethyl acetate, and benzene solutions, and fractional sublimation *in vacuo*. The purified sample of **4** is highly pure as revealed by the results of CO_2 determination to be shown later. That of **3** is slightly less pure as compared with the former, judging from DSC curves in the melting region.

Combustion Calorimetry. A constant temperature jacket type rotating bomb calorimeter with a platinum-lined bomb, described elsewhere,[4)] was used without rotating the bomb. The calorimeter was calibrated by burning thermochemical standard benzoic acid (N. B. S. SRM 39i) under certificate conditions. Mean and standard deviation of mean of observed energy equivalents for the empty calorimeter were (15161.76±0.90) J K^{-1} (8 experiments) and (15162.9±1.3) J K^{-1}(4 experiments) for 3 and 4, respectively. In contrast to **1** and **2**,[3)] **3**, and **4** in pellet form could be burnt completely without using a promoter, in most cases, in an ordinary open crucible at 3 MPa of oxygen pressure. Carbon monoxide was barely detected for **3** and **4**. Nitric acid was determined by titration with aqueous sodium hydroxide. For **4**, carbon dioxide recovery was determined by the method described elsewhere.[4b)]

Sublimation Calorimetry. A sublimation calorimetric system incorporating a Calvet microcalorimeter, described elsewhere,[5)] was employed. Apparatus Mark II with sample containers Mark B and apparatus Mark I with sample containers Mark A were used for **3** and **4**, respectively.

Auxiliary Quantities. Relative atomic masses were taken from the recommendation of IUPAC Commission on Atomic Weights (1977). Densities, specific heat capacities,

TABLE 1. AUXILIARY DATA FOR THE CALCULATION OF STANDARD ENERGIES OF COMBUSTION

Material	Formula	$\frac{\rho}{\mathrm{g\ cm^{-3}}}$	$\frac{c_p{}^{a)}}{\mathrm{J\ K^{-1}\ g^{-1}}}$	$\frac{(\partial U/\partial p)_T{}^{a)}}{\mathrm{J\ g^{-1}\ MPa^{-1}}}$
3	$C_8H_{10}O_2N_2$	1.313	(1.21)	(−0.0524)
4	$C_8H_{10}O_2N_2$	1.35	(1.21)	(−0.0519)
Cotton fuse	$CH_{1.86}O_{0.93}$	1.5	1.70	−0.0290

a) Parenthesized values are estimated ones.

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and $(\partial U/\partial P)_T$ values, which were used to reduce weights to masses in vacuum and to deduce standard energies of combustion from calorimetric data, are presented in Table 1. Other auxiliary quantities are as follows: T_h=298.15 K, V (bomb)=0.3469 dm^3, and $\Delta U_c^\circ/M$(fuse)=−16507 Jg^{-1}.

Results

Standard Energies of Combustion. Molar standard energies and enthalpies of combustion, given in this paper, refer to the following idealized combustion reactions at 298.15 K:

$$C_8H_{10}O_2N_2(c) + (19/2)O_2(g) = 8CO_2(g) + 5H_2O(l) + N_2(g).$$

Details of the combustion calorimetric results are presented in Table 2 and 3 for **3** and **4**, respectively. Most of the symbols in these tables are similar to those used by Hubbard *et al.*[6] Mean and standard deviation of the mean for the observed standard energies of combustion, ΔU_c°(c), were −(4555.91±0.66) and −(4540.63±0.22) kJ mol^{-1}, for **3** and **4**, respectively. Relative total carbon dioxide recovery, [m(CO$_2$, obsd)/m(CO$_2$, calcd)], where m(CO$_2$, obsd) and m(CO$_2$, calcd) are the observed and calculated total masses of recovered carbon dioxide, respectively, was (1.0000± 0.0002) for **4**, where uncertainty is the standard deviation of the mean.

Standard Enthalpies of Sublimation. Details of the sublimation calorimetric results are presented in Table 4 for both compounds. Observed enthalpies of sublimation for each substance were subjected to a regression analysis for linear relations between two variables.[7] Derived expressions are as follows:

TABLE 2. SUMMARY OF COMBUSTION CALORIMETRIC RESULTS ON *N*,*N*-DIMETHYL-3-NITROANILINE

Experiment	1	2	3	4	5
m'(compd)/g	1.01048	1.01128	1.01032	1.00732	1.00960
m'''(fuse)/g	0.00217	0.00227	0.00223	0.00226	0.00226
$m^i(H_2O)$/g	2.98	2.99	2.99	2.99	3.03
p^i(gas)/MPa	3.039	3.040	3.043	3.044	3.046
$(T_i/K)-273.15$	23.12877	23.12670	23.12545	23.12295	23.12771
$(T_f/K)-273.15$	24.98213	24.98114	24.97820	24.97007	24.98006
ΔT_{corr}/K	0.02157	0.02139	0.02157	0.02149	0.02181
$n^f(HNO_3)$/mmol	1.014	0.982	0.975	0.999	0.997
ΔU_{ign}/J	7.5	4.0	7.8	4.7	7.4
ΔU_Σ/J	17.9	17.9	17.9	17.8	18.0
$\Delta U_d(HNO_3)$/J	59.7	57.8	57.4	58.7	58.7
ε^i(cont)/J K^{-1}	25.4	25.5	25.5	25.5	25.7
ε^f(cont)/J K^{-1}	26.8	26.8	26.9	26.8	27.0
$-\Delta U_{IBP}$/J	27812.2	27835.1	27825.5	27721.6	27793.7
$-\{\Delta U_c^\circ/M(\text{compd})\}$/kJ g^{-1}	27.4115	27.4127	27.4303	27.4071	27.4116
$-\Delta U_c^\circ$(compd)/kJ mol^{-1}	4555.22	4555.41	4558.35	4554.49	4556.06

TABLE 3. SUMMARY OF COMBUSTION CALORIMETRIC EXPERIMENTS ON *N*,*N*-DIMETHYL-4-NITROANILINE

Experiment	1	2	3	4	5	6	7
m'(compd)/g	0.97711	0.99630	1.00090	1.00228	1.00831	1.00644	1.00778
m'''(fuse)/g	0.00227	0.00218	0.00224	0.00216	0.00226	0.00227	0.00221
$m^i(H_2O)$/g	3.37	2.89	2.99	3.01	2.96	2.96	3.01
p^i(gas)/MPa	3.041	3.040	3.045	3.040	3.043	3.040	3.048
$(T_i/K)-273.15$	23.12454	23.12655	23.12796	23.12511	23.12655	23.12440	23.12761
$(T_f/K)-273.15$	24.91463	24.94944	24.95898	24.95885	24.97036	24.96512	24.97065
ΔT_{corr}/K	0.02444	0.02248	0.02249	0.02273	0.02192	0.02190	0.02172
$n^f(HNO_3)$/mmol	1.014	1.020	1.067	1.039	1.079	1.043	1.063
ΔU_{ign}/J	7.2	2.7	3.3	7.4	7.6	7.6	7.5
ΔU_Σ/J	17.8	17.5	17.7	17.7	17.8	17.7	17.9
$\Delta U_d(HNO_3)$/J	59.7	60.1	62.8	61.2	63.5	61.4	62.6
ε^i(cont)/J K^{-1}	27.0	25.1	25.5	25.5	25.4	25.4	25.6
ε^f(cont)/J K^{-1}	28.3	26.4	26.8	26.9	26.7	26.7	26.9
$-\Delta U_{IBP}$/J	26812.7	27341.9	27465.2	27499.0	27663.6	27617.0	27655.4
$-\{\Delta U_c^\circ/\text{M}(\text{compd})\}$/kJ g^{-1}	27.3231	27.3295	27.3231	27.3221	27.3180	27.3244	27.3259
$-\Delta U_c^\circ$(compd)/kJ mol^{-1}	4540.53	4541.58	4540.52	4540.36	4539.67	4540.74	4540.99
$\left\{\frac{m(CO_2,\ \text{obs})}{m(CO_2,\ \text{calc})}\right\}$	0.9997	0.9996	1.0003	—	0.9998	1.0009	0.9998

$$\Delta H^\circ_{\rm sub}(T)/{\rm kJ\ mol^{-1}} = -(0.046\pm0.010)(T/{\rm K}) + (106.4\pm3.1), \qquad (1)$$

and

$$\Delta H^\circ_{\rm sub}(T)/{\rm kJ\ mol^{-1}} = -(0.031\pm0.012)(T/{\rm K}) + (111.9\pm4.5), \qquad (2)$$

for **3** and **4**, respectively, where associated uncertainties are those at the 95 per cent confidence level. Estimated standard deviation from the fit, s_f, was 0.04 kJ mol^{-1} and 0.22 kJ mol^{-1}, for **3** and **4**, respectively. $\Delta H^\circ_{\rm sub}$ (298.15 K) values, obtained by extrapolation of the fits given above to 298.15 K, were (92.72±0.27) kJ mol^{-1} and (102.7±1.0) kJ mol^{-1} for **3** and **4**, respectively.[8]

Standard Thermodynamic Quantities. Derived thermodynamic quantities are presented in Table 5. Uncertainties for ΔU°_c(c) and ΔH°_c(c) are the uncertainty intervals, defined by Rossini.[9] CODATA key values for thermodynamics[10] were used to calculate ΔH°_f(c). Uncertainties for ΔH°_f(c) and ΔH°_f(g) were calculated by using the equation of error propagation.

TABLE 4. SUMMARY OF SUBLIMATION CALORIMETRIC RESULTS ON *N*,*N*-DIMETHYL-3-NITROANILINE(**3**) AND *N*,*N*-DIMETHYL-4-NITROANILINE(**4**)

T/K	t/ks	m/mg	$E_{\rm calib}$/J	S_T/S_B	$\Delta H^\circ_{\rm sub}(T)$/kJ mol^{-1}
			(**3**)[a]		
320.9	79.00	87.86	3.6478	13.283	91.64
320.9	89.80	100.44	6.9432	7.9823	91.70
325.5	42.20	79.87	3.9675	11.220	91.46
325.8	31.00	61.93	16.436	2.0745	91.50
325.8	50.90	100.28	6.4565	8.5465	91.44
330.7	32.40	109.97	8.8955	6.7825	91.17
330.7	69.60	239.22	10.576	12.423	91.28
330.7	15.20	53.08	5.2880	5.5097	91.21
			(**4**)[b]		
350.3	39.60	39.04	2.406	9.791	101.10
350.4	50.40	48.88	1.946	15.439	101.12
372.7	19.44	65.47	6.954	5.683	100.30
372.7	22.32	77.48	10.393	4.509	100.51
402.6	29.76	87.49	11.255	4.641	99.22
402.0	29.52	86.81	8.340	6.252	99.82

a) Both the diameter and the depth of the orifice were 1.0 mm. b) The diameter and the depth of the orifice were 2.0 and 0.1 mm, respectively, for experiments at 350 and 373 K, and 2.0 and 0.1 mm, respectively, for experiments at 402 K.

TABLE 5. DERIVED STANDARD THERMODYNAMIC QUANTITIES AT 298.15 K OF *N*,*N*-DIMETHYL-3-NITROANILINE(**3**) AND *N*,*N*-DIMETHYL-4-NITROANILINE(**4**)

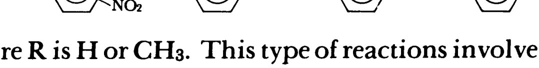
	3	**4**
$-\Delta U^\circ_c$(c)/kJ mol^{-1}	4555.9±1.5	4540.63±0.94
$-\Delta H^\circ_c$(c)/kJ mol^{-1}	4557.2±1.5	4541.87±0.94
$-\Delta H^\circ_f$(c)/kJ mol^{-1}	20.1±1.8	35.4±1.4
$\Delta H^\circ_{\rm sub}$/kJ mol^{-1}	92.72±0.27	102.7±1.0
ΔH°_f(g)/kJ mol^{-1}	72.6±1.8	67.3±1.7

Discussion

For **3** and **4**, neither ΔH°_f(c) nor ΔH°_f(g) has been reported. ΔH°_f(g) values reported in the previous paper[3] are (62.5±1.8) kJ mol^{-1} and (55.2±1.8) kJ mol^{-1} for **1** and **2**, respectively.

The difference in ΔH°_f (g) between **1** and **2** and between **3** and **4** are (7.3±2.5) kJ mol^{-1} and (4.7±2.5) kJ mol^{-1}, respectively. This shows that **2** and **4** are significantly more stable than **1** and **3**, respectively, in accordance with the resonance picture in terms of the quinonoid structures.

In this paper, stabilization energies $E_{\rm stb}$ of the disubstituted benzenes due to the intramolecular interaction between the substituents are defined as ΔH° $(=\Delta U^\circ)$ at 298.15 K of the following type of hypothetical gas-phase redistribution reaction:



where R is H or CH_3. This type of reactions involves the fission and formation of a $C_{\rm ar}$–NO_2 (or $C_{\rm ar}$–NR_2) bond and a $C_{\rm ar}$–H bond ,where $C_{\rm ar}$ denotes the aromatic ring carbon atom. The kind and number of the cleaved bonds are identical with those of the formed ones; the only change being the one from di- and un-substituted benzenes on the left-hand side to two mono-substituted benzenes on the right-hand side. In this sense, ΔH° of this type of reaction may be considered to be a reasonable measure of the degree of intramolecular interaction between the substituents through a benzene ring leading to the stabilization of the disubstituted benzene molecule with reference to benzene, aniline (or *N*,*N*-dimethylaniline), and nitrobenzene molecules.

Derived ($E_{\rm stb}$/kJ mol^{-1}) values are (9.3±2.2), (16.6±2.2), (12.6±3.0), and (17.9±3.5) for **1**, **2**, **3**, and **4**, respectively. The following [ΔH°_f(g)/kJ mol^{-1}] values were employed in this calculation: (67.6±1.0),[11] (87.8±0.8),[11] (100.5±2.9),[12] and (82.9±0.3)[11] for nitrobenzene, aniline, *N*,*N*-dimethylaniline, and benzene, respectively.

Parr and Wasylishen briefly reported the result of MINDO/3 calculation on **2**.[13] The reported value of ΔH°_f(g) was 26.51 kJ mol^{-1}, which is by 29 kJ mol^{-1} less positive than the value reported by the present authors.[3] Hehre *et al.*[14] calculated the interaction energy of **2**, which may be identified with ΔH° $(=\Delta U^\circ)$ at 0 K of the redistribution reaction described above, from calculated atomization energies of the relevant species based on *ab initio* MO theory, employing the STO-3G minimal set. They reported 9.2 and 12.6 kJ mol^{-1} for pyramidal and planar forms of the amino group, respectively. These values are comparable with the present result.

Comparison of $E_{\rm stb}$ between **1** and **3** and between **2** and **4** shows that the effect of *N*,*N*-dimethyl substitution on $E_{\rm stb}$ is not significant. It is to be noted that **1** and **3** as well as **2** and **4** have been shown to have positive stabilization energies by the present analysis. From the viewpoint of the resonance theory, the 1,3-isomers are expected to be barely stabilized with respect to benzene, aniline (or its *N*,*N*-dimethyl derivative), and nitrobenzene, since the contribution from the meta-quinonoid resonance structure would be small. The present result is not in accord with this expectation.

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8) Temperature dependence of vapor pressure has also been determined for **4** by using a DuPont Thermal Evolution Analyzer.[4b] Derived standard enthalpy of sublimation was 101.2 kJ mol^{-1} at the mid-range temperature of 376.1 K. The value calculated from equation (2) is (101.3±0.3) kJ mol^{-1}, with which the former value agrees well.

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