Thermochimica Acta, 121 (1987) 413–436
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL PROPERTIES, THERMOCHEMISTRY AND KINETICS OF THE THERMAL DISSOCIATION OF HYDROCHLORIDES OF AROMATIC MONO-AMINES *

JACEK ŁUBKOWSKI and JERZY BŁAŻEJOWSKI

Institute of Chemistry, University of Gdańsk, 80-952 Gdańsk (Poland)

(Received 8 December 1986; in final form 10 February 1987)

ABSTRACT

Thermal properties of hydrochlorides of several aromatic mono-amines were examined by thermoanalytical methods (TG, DTG and DTA). The majority of hydrochlorides studied undergo decomposition upon heating with the simultaneous release of HCl and amines to the gaseous phase. The thermal dissociation of these derivatives proceeds essentially in one step, in which up to 88% of the sample volatilizes, followed by a slow step, seen as a "tail" in TG curves, due to the decreased geometric surface area of the condensed phase. This thermal behaviour is also typical of hydrochlorides of other nitrogen organic bases and can be qualitatively accounted for by the Jacobs and Russell-Jones model for the kinetics of dissociative sublimation processes. Some of the compounds studied, however, decompose in two distinct stages. The first step corresponds to the release of HCl while the second one is the volatilization of free amine. The latter thermal decomposition pattern is characteristic of compounds exhibiting the complex structure of an amminium cation.

The thermodynamics and kinetics of thermal dissociation were examined using non-isothermal TG curves. The enthalpies of volatilization were evaluated from the Van't Hoff equation. These derived values, together with information from the literature, were used to estimate the enthalpy of formation and crystal lattice energy of some of the salts. The "thermochemical" radii for amminium ions were also evaluated from the Kapustinskii–Yatsimirskii equation. The Jacobs and Russell-Jones approach was applied to describe the kinetics of volatilization. However, standard phonomenological procedures do not seem to be appropriate for examining the kinetics of dissociative volatilization processes.

INTRODUCTION

Aromatic mono-amines can form salt-type derivatives with numerous acids due to the presence of the lone electron pair at the nitrogen atom. For

---

* This paper is dedicated to Professor W.W. Wendlandt on his 60th birthday. With his many contributions he drew the attention of scientists to the importance of thermoanalytical methods in chemistry. Through his work he has influenced many chemists including the authors of this article.

this reason aromatic amines behave similarly to aliphatic amines [1] or nitrogen aromatic bases [2]. However, while the presence of aliphatic substituents at the nitrogen atom increases the basicity (or proton affinity) of amines, the attached phenyl groups markedly decrease the electron density at the nitrogen atom, thus decreasing the capability of interaction with the proton [3–6]. Therefore, one might expect differences in the behaviour of salts derived from both of these groups of amines.

Hydrochlorides of amines are the simplest ionic derivatives of organic compounds. Some of the most important properties of these derivatives are their thermochemical and thermal characteristics which so far have only been examined thoroughly in this laboratory for several alkanaminium chlorides [1,7]. Information on the thermal behaviour of hydrochlorides of aromatic amines is scattered and fragmentary [8–14]. In continuation of our study on the thermal properties of simple salts of amines we extend the investigation to the hydrochlorides of aromatic amines. In such a study we expected to gather more information on the behaviour of highly unsymmetrical ions. Other aims of this work are to provide the basic thermochemical characteristics for solid amine hydrochlorides and to establish general regularities between the structure of an amine cation and the thermal properties of amine hydrochlorides. Moreover, this study should also help to elucidate general features governing the thermal dissociation of amminium salts.

EXPERIMENTAL

N-Methyl-*N*-phenyl-benzenamine (Eastman Kodak), benzenemethanamine (Fluka AG, Buchs SG), *N*-methyl-benzenemethanamine (Schuchard), *N*,*N*-dimethyl-benzenemethanamine (Aldrich), *N*-methyl-*N*-phenyl-benzenemethanamine (Schuchard), *N*-(phenylmethyl)-benzenemethanamine (Fluka AG, Buchs SG) and *N*,*N*-bis(phenylmethyl)-benzenemethanamine (Ubichem Ltd., U.K.) were used as received. Benzenamine (P.O.Ch., Poland), *N*-methyl-benzenamine (Fluka AG, Buchs SG) and *N*,*N*-dimethyl-benzenamine (P.O.Ch.) were purified following methods described in the literature [15,16]. *N*-Phenyl-benzenamine (P.O.Ch), *N*,*N*-diphenyl-benzenamine (Koch Light Lab.), *N*-phenyl-benzenemethanamine (P.O.Ch.) and *N*-phenyl-*N*-(phenylmethyl)-benzenemethanamine (Fluka AG, Buchs SG) were purified by repeated crystallization from various solvents (e.g. light petroleum, methanol and ethanol). *N*,*N*-Diphenyl-benzenemethanamine was synthesized and purified by a method described elsewhere [17]. All amines were checked for purity by GC (liquid samples) or elementary analysis (solid samples), and also by determination of their boiling or melting points. They always showed a purity of > 99%.

The hydrochlorides were prepared by passing a stream of dried HCl through a solution of the amine in anhydrous diethyl ether or benzene

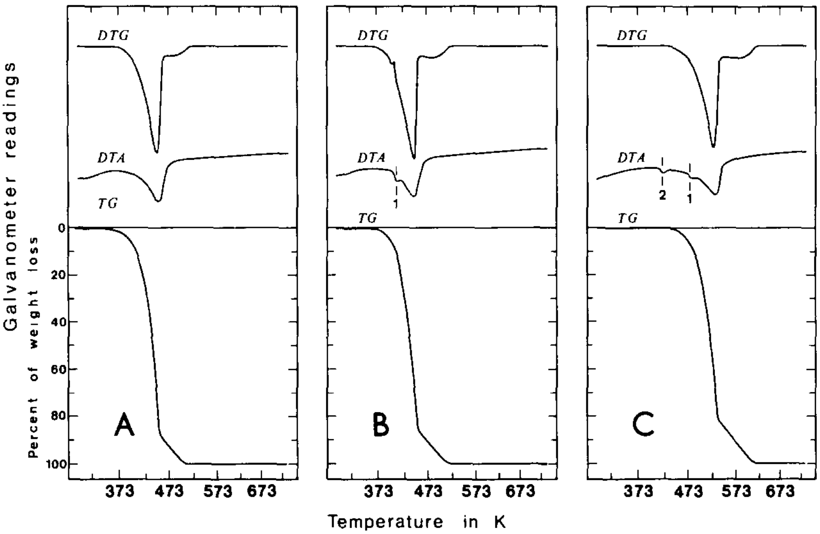

Fig. 1. Thermal analyses of hydrochlorides of benzenamine (A), *N*,*N*-dimethylbenzenamine (B) and benzenemethanamine (C). (1) in (B) = melting; (1) and (2) in (C) = phase transitions.

[18,19]. The resulting precipitates were filtered and thoroughly washed with ice-cold, dry solvents. The majority of compounds were recrystallized from methanol–diethyl ether mixtures and finally dried in a vacuum desiccator over P_2O_5. The purity of the hydrochlorides was checked by elementary analysis and by mercurometric determination of chloride ions. The compounds used in the thermoanalytical investigations were > 99% pure. All the hydrochlorides studied were ground in an agate mortar before analysis. Highly hygroscopic derivatives, e.g. *N*,*N*-dimethyl-benzenamine hydrochloride, were additionally dried by heating for 2 h in vacuo (in a vacuum pistol), prior to analysis, at temperatures just below the onset of decomposition.

Thermal analyses were carried out on an OD-103 derivatograph (Monicon) with α-Al_2O_3 as reference, in a dynamic atmosphere of nitrogen. The

TABLE 1

α versus T dependence for the volatilization of benzenamine hydrochloride (A), *N*,*N*-dimethylbenzenamine hydrochloride (B) and benzenemethanamine hydrochloride (C) (cf. Fig. 1)

	T (K)								
	$\alpha = 0.10$	0.18	0.26	0.34	0.42	0.50	0.58	0.66	0.74
A	408.6	420.0	426.8	431.8	436.1	439.6	442.8	445.9	448.4
B	377.0	386.7	392.8	397.7	401.6	405.0	407.8	410.6	412.7
C	483.9	495.8	503.6	509.4	514.0	517.9	520.9	524.5	528.2

sample was placed on one platinum plate of a polyplate sample holder (ref. 20, Appendix 1, No. 4). Other operating conditions were: mass of sample = ~ 50 mg, heating rate = ~ 5 K min^{-1}, sensitivities of DTG, DTA and TG galvanometers = 1/10, 1/3 and 50 mg, respectively.

For the compounds showing a one-step thermal decomposition pattern (Fig. 1) the numerical values of temperature (T) corresponding to certain values of the extent of reaction (α) were derived as previously described [21]. For each such compound, a set of α–T data points was obtained as a mean from at least three replicate measurements. An example is given in Table 1.

RESULTS AND DISCUSSION

General characteristics of the thermal decomposition

Typical results of the thermoanalytical investigations are presented in Figs. 1 and 2. Table 2, on the other hand, gives essential parameters characterizing the thermal behaviour of all the compounds studied, derived from the thermal analysis curves, together with the available information from the literature. The majority of hydrochlorides studied show simple thermal decomposition patterns (Fig. 1 and Table 2 – "regular"). The thermoanalytical curves for these derivatives demonstrate that their dissociation proceeds in two stages. The first step, in which up to 88% of the sample

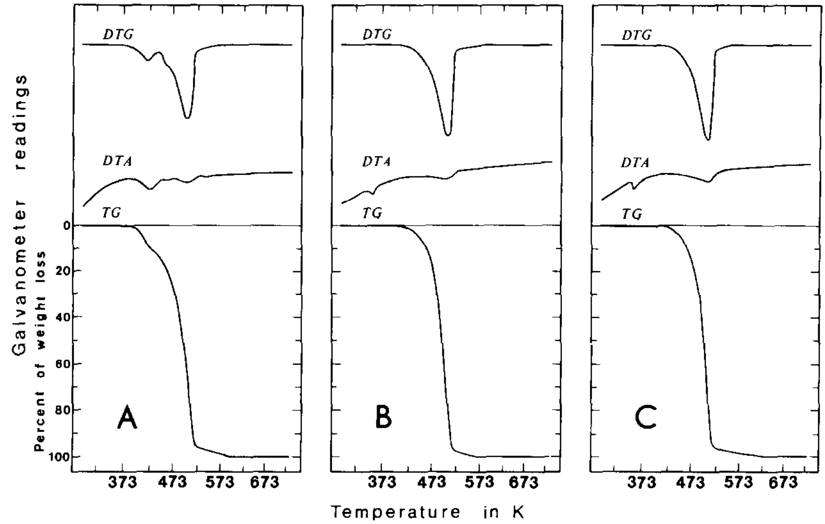

Fig. 2. Thermal analyses of N-phenyl-N-(phenylmethyl)-benzenemethanamine hydrochloride (A), the residue after heating the compound at 420 K for 1 h (B) and pure N-phenyl-N-(phenylmethyl)-benzenemethanamine (C).

volatilizes, is followed by a slow step, seen as a "tail", in which the remaining part of the sample disappears. Complementary investigations, analogous to those performed previously [1,2], revealed that the composition of the solid phase remained unchanged during both decomposition stages. Thus, the participation of side processes (e.g. destruction of organic fragments of molecules [98]), which could cause such an effect, must be excluded. It may, perhaps, be worthwhile to mention that noticeable decomposition of several amines (see e.g. refs. 9, 99–103) has been observed at temperatures much higher than those characteristic of the dissociation of appropriate hydrochlorides (Table 2) and under specific conditions. A possible explanation of the observed effect comes from the kinetic considerations which will be presented below.

Quite different thermal decomposition patterns are shown by compounds 4, 5 and 14 (Table 2 – "complex"). The thermoanalytical curves for these derivatives show that their dissociation is accomplished in two distinct steps (see, e.g., Fig. 2A). The weight loss in the first stage corresponds to the release of one molecule of HCl from one molecule of the salt. This means that the rate of HCl release is higher than the rate of amine evaporation and thus the second step should represent the volatilization of pure amine. Indeed, the thermogram of pure *N*-phenyl-*N*-(phenylmethyl)-benzenemethanamine (Fig. 2C) and that of a residue after heating of its hydrochloride at a temperature corresponding to the first step are identical (Fig. 2B), a fact which fully supports the above concept. Such a thermal decomposition pattern is characteristic of rather complex hydrochlorides of aromatic amines and has not been observed upon thermolysis of alkanaminium chlorides [1] or hydrochlorides of simple nitrogen aromatic bases [2].

Thorough examination of the thermal analysis curves reveals that additional endothermal effects are seen in DTA curves of compounds 2, 3, 7, 8 and 11 (Table 2). The appropriate effects for compounds 2, 3, 8 and 11 originate from fusion and the observed melting points correspond satisfactorily with those reported in the literature. Two additional effects observed before the onset of volatilization of benzenemethanamine hydrochloride were ascribed to the solid-phase transitions since they occur far below the literature m.p. values for the compound. Fusion processes have also been reported for several other amine hydrochlorides, i.e. compounds 1, 4, 7, 10, 13 and 15. Corresponding effects were not monitored in our experiments. Comparison of literature melting points with peak temperatures in DTG and DTA, and $T_{0.1}$ and $T_{0.74}$, reveals that the aforementioned derivatives melt when the volatilization process is far advanced. It may be that weak thermal effects originating from fusion are masked by much stronger thermal effects resulting from volatilization.

The temperatures of thermolysis, namely, T_p (from DTG and DTA), $T_{0.01}$, $T_{0.1}$, $T_{0.74}$ and ΔT_α, are the features characteristic of a given compound; nevertheless, some general trends can be revealed. Successive substitution at

TABLE 2

Thermal characteristics for hydrochlorides of aromatic mono-amines

Substance [a]			Peak temperatures [c] (K)					Temperature [c] (K)				Parameters of the onset of the second stage	
No.	Hydrochloride of (formula)	Thermal decomposition pattern [b]	DTG	DTA				$T_{0.01}$ [d]	$T_{0.1}$ [e]	$T_{0.74}$ [e]	ΔT_{α} [e]	α	T (K)
				T_{σ} (This work)	T_{m}		T_{p}						
					This work	From the literature							
1	$PhNH_2$	R	449			465 [23,24] 466–467 [25] 467 [23] 468 [26,27] 468–471 [28] 469–471 [29,30] 470 [31,32] 470.9 [33] 471 [23,34–36] 471.6 [37] 472.3–472.4 [8]	451	363	408.6	448.4	39.8	0.86	455
2	$PhNHCH_3$	R	440		405	394–395 [23] 395 [38] 395.6–396 [39] 396.8–397.3 [40] 398–399 [41]	442	363	400.3	436.7	36.4	0.85	440
3	$PhN(CH_3)_2$	R	416		367	358 [23] 358–368 [23,36]	418	344	377.0	412.7	35.7	0.88	419

4	Ph_2NH	C	403 437			389–390 [42]	405 440	357					
5	Ph_2NCH_3	C	402 438				401 445	352					
6	Ph_3N		does not form hydrochloride										
7	$PhCH_2NH_2$	R	526	422 478		511–516 [43] 513 [23] 514–519 [44] 515–518 [45] 516–517 [46] 519 [23] 521–522 [47] 521–523 [48] 521–525 [49] 522 [50] 525–528 [51] 526 [52] 526–527 [53,54] 528–529 [23] 528–531 [36] 528.6–531 [23] 529 [23] 531 [55,56] 533 [57] 534 [58]	527	438	483.9	528.2	44.3	0.82	534
8	$PhCH_2NHCH_3$	R	514		456	446–447 [59] 447–448 [23] 448–449 [60] 449–450.6 [61] 450–451 [62,63] 451 [64] 453.6 [65] 456–457 [66]	515	421	469.4	514.7	45.3	0.84	523

TABLE 2 (continued)

Substance [a]			Peak temperatures [c] (K)					Temperature [c] (K)				Parameters of the onset of the second stage	
No.	Hydrochloride of (formula)	Thermal decomposition pattern [b]	DTG	DTA				$T_{0.01}$ [d]	$T_{0.1}$ [e]	$T_{0.74}$ [e]	ΔT_α [e]	α	T (K)
				T_σ (This work)	T_m		T_p						
					This work	From the literature							
9	$PhCH_2N(CH_3)_2$	R	487		453	445–449 [67] 446–447 [68] 446.6 [69] 448 [70,71]	487	404	443.3	488.0	44.7	0.81	494
10	$PhCH_2NHPh$	R	465			470 [72,73] 473–478 [74] 478–479 [67] 480–481 [45] 483–485 [75,76] 485 [77] 485–488 [78] 486.6–488 [79] 487–488 [80,81] 487–489 [23,82]	463	395	428.3	467.8	39.5	0.81	473
11	$PhCH_2NCH_3Ph$	R	525		466		527	446	481.5	524.2	42.7	0.84	532
12	$PhCH_2NPh_2$		does not form hydrochloride										

13	$(PhCH_2)_2NH$	R	518	525–526 [45] 528–529 [62,68,83,84] 528.6 [23] 529 [23,85] 529–531 [86,87] 530–531 [51] 531 [88,89] 531–532 [90] 533–534 [91] 536 [92] 537 [53] 539–540 [93,94]	520	426	476.0	520.8	44.8	0.82	527
14	$(PhCH_2)_2NPh$	C	417 502		419 500	394					
15	$(PhCH_2)_3N$	R	504	481 [23] 494 [95] 499–500 [96] 500 [97] 500–501 [23]	489	425	464.9	505.2	40.3	0.83	511

---

[a] 1 = Benzenamine (aniline); 2 = *N*-methyl-benzenamine (*N*-methylaniline); 3 = *N*,*N*-dimethyl-benzenamine (*N*,*N*-dimethylaniline); 4 = *N*-phenyl-benzenamine (diphenylamine); 5 = *N*-methyl-*N*-phenyl-benzenamine (*N*-methyldiphenylamine); 6 = *N*,*N*-diphenyl-benzenamine (triphenylamine); 7 = benzenemethanamine (benzylamine); 8 = *N*-methyl-benzenemethanamine (*N*-methylbenzylamine); 9 = *N*,*N*-dimethyl-benzenemethanamine (*N*,*N*-dimethylbenzylamine); 10 = *N*-phenyl-benzenemethanamine (*N*-phenylbenzylamine); 11 = *N*-methyl-*N*-phenyl-benzenemethanamine (*N*-methyl-*N*-phenylbenzylamine); 12 = *N*,*N*-diphenyl-benzenemethanamine (*N*,*N*-diphenylbenzylamine); 13 = *N*-(phenylmethyl)-benzenemethanamine (dibenzylamine); 14 = *N*-phenyl-*N*-(phenylmethyl)-benzenemethanamine (*N*-phenyldibenzylamine); 15 = *N*,*N*-bis(phenylmethyl)-benzenemethanamine (tribenzylamine).

[b] R = regular (see Fig. 1), C = complex (see Fig. 2A).

[c] The symbols were taken from ref. 22. T_p = temperature of the peak, T_σ = temperature of the solid-state phase transition, T_m = temperature of melting, T_α = temperature at which the degree of conversion is equal to α (i.e. $T_{0.1} = T_{\alpha=0.1}$), and $\Delta T_\alpha = T_{0.74} - T_{0.1}$.

[d] Temperature of the onset of the decomposition refers to the whole volatilization process.

[e] Temperatures corresponding to the fast step of the volatilization of compounds showing a regular decomposition pattern (cf. Fig. 1).

the nitrogen atom by the methyl group in the series of benzenamines causes a gradual decrease of all the characteristic temperatures of thermal dissociation of the appropriate hydrochlorides. Introduction of the phenyl group instead of hydrogen in the same series of derivatives, results in a further decrease of their thermal stability. It is worth mentioning that fully phenyl-substituted amine, i.e. *N,N*-diphenyl-benzenamine, does not form a hydrochloride under ordinary conditions [104]. For benzenemethanamine hydrochlorides all characteristic effects generally occur at higher temperatures than those for benzenamine hydrochlorides. However, trends in the characteristic thermolysis temperatures and thus in the thermal stability with substitution at the nitrogen atom by the methyl or phenyl groups are similar to those discussed above for the latter group of compounds. Moreover, successive substitution at the nitrogen atom by the $PhCH_2$ group leads to a decrease in characteristic thermolysis temperatures and consequently in thermal stability. An exception is *N*-methyl-*N*-phenyl-benzenemethanamine hydrochloride which does not follow the above trends. We have also made several attempts in order to synthesize *N,N*-diphenyl-benzenemethanamine hydrochloride. Unfortunately, our efforts did not succeed.

Nature of the volatilization process

Numerous experimental facts indicate that hydrochlorides of aromatic amines behave in condensed phases as typical ionic substances [19,105,106]. These derivatives show similar thermal properties to those characteristic of hydrochlorides of aliphatic amines or aromatic bases [1,2,7]. These and other similarities in the behaviour of various amine hydrochlorides demonstrate that the mechanism of the volatilization process is essentially the same for various amine hydrochlorides [1,2,7] and that the overall process can be summarized by the equation

$$\mathrm{Am}\cdot\mathrm{HCl}_{(c)} \rightarrow \mathrm{Am}_{(g)} + \mathrm{HCl}_{(g)} \qquad (1)$$

Since the vapour pressure of HCl at the decomposition temperatures is very high, it is transferred instantaneously to the gaseous phase. The amines released are characterized by fairly high boiling points [36]. Thus, less stable derivatives volatilize at higher temperatures as demonstrated by the two-step thermal decomposition pattern (cf. Table 2, compounds 4, 5 and 14). The remaining compounds studied decompose essentially in one step with the simultaneous release of both products to the gaseous phase. The question remains, however, whether gaseous products behave as kinetically free fragments or whether they interact with others forming aggregates. Weak interactions between compounds may be expected on the basis of both theoretical considerations [6,107–109] and certain experimental evidence [110] for simple model systems. Also the behaviour of some aromatic amines in non-polar solvents tends to confirm the existence of such interactions [111–113].

Enthalpy of volatilization

In several recent reports we demonstrated that dynamic thermogravimetric data can be used for the determination of the enthalpy of thermal dissociation of hydrochlorides of amines [1,7] or mono-nitrogen aromatic bases [2]. For this purpose the following equation was used:

$$\ln \alpha = -\frac{\Delta H_v}{2RT} + \text{constant} \qquad (2)$$

where ΔH_v is the enthalpy of the thermal process and R is the gas constant. The main premise of this approach is that the system attains equilibrium at a given temperature, T, and that dissociation fragments form an ideal gas mixture. This implies that the only energy barrier existing for the process is the thermochemical one, i.e. ΔH_v. Then the fraction reacted, α, is equal to $\frac{1}{2}P/P_0$, where P is the equilibrium vapour pressure at a given T value and P_0 is the atmospheric pressure. It is worth mentioning that eqn. (2) results directly from the application of the Van't Hoff rule to reaction (1).

An example of a fit of eqn. (2) to the experimental α vs. T data points for benzenamine hydrochloride (Table 1) is shown in Fig. 3A, whereas the values of ΔH_v evaluated for all the compounds studied are summarized in Table 3. The value of the heat of dissociation of benzenamine hydrochloride from this work correlates fairly well with that estimated by Konstantinov et al. [11] on the basis of measurements of the dissociation pressure. This value is, however, markedly lower in comparison with that derived from the calorimetric measurements [11]. Values of ΔH_v determined in this work for benzenamine hydrochloride and N,N-dimethyl-benzenamine hydrochloride

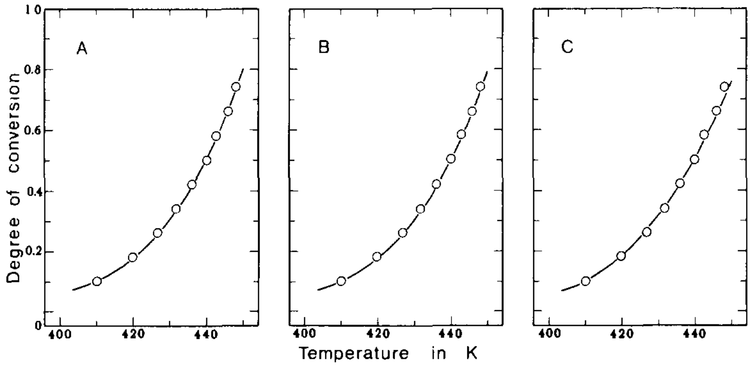

Fig. 3. Experimental α vs. T data points for the volatilization of benzenamine hydrochloride (Table 1) together with curves calculated from the relationships: (A) $\alpha = \exp[-\Delta H_v/(2RT) + \text{constant}]$ (obtained after rearrangement of eqn. (2), values of ΔH_v and the constant from Table 3); (B) eqn. (5) (values of X_1, X_2 and E from Table 4, $\Phi = 5$ K min^{-1}); (C) $\alpha = 1 - \{1 - TZ/\Phi \exp[-E^*/(RT)]\}^2$ (obtained after rearrangement of an equation for the contracting surface area model, values of Z and E^* from Table 4).

TABLE 3

Thermochemistry of the volatilization of hydrochlorides of aromatic mono-amines

Substance No. (Table 2)	Constant [a]	ΔH_v^0 (kJ mol^{-1})		
		This work [a]	From the literature [b]	Calculated from the standard enthalpies of formation at 298 K [c]
1	20.5	155	158.2 (380–480) [11] 165.5 [11]	173.0
2	22.0	162		
3	20.8	145		175.4
7	21.9	195		
8	20.6	179		
9	19.5	161		
10	21.7	171		
11	22.3	197		
13	21.5	189		
15	23.1	196		

[a] Values of ΔH_v and the constant were calculated from eqn. (2) within a range of α from 0.1 to 0.74. The linear correlation coefficient $|r|$ was always better than 0.999.

[b] The temperature range (K) is given in parentheses.

[c] Values used in the calculations are (kJ mol^{-1}): $\Delta H^0_{f,g}[HCl] = -92.3$ [36,114]; $\Delta H^0_{f,g}[PhNH_2] = 87.1$ [6,115]; $\Delta H^0_{f,g}[PhN(CH_3)_2] = 100.5$ [6,116]; $\Delta H^0_{f,c}[PhNH_2 \cdot HCl] = -178.2$ [115]; $\Delta H^0_{f,c}[PhN(CH_3)_2 \cdot HCl] = -167.2$ [115].

show rather poor agreement with those calculated on the basis of the standard enthalpies of formation. One possible explanation for such a discrepancy might be that the values used in the latter estimation were taken from various sources and that some of them might not be adequate. Other reasons will be discussed below.

Kinetics of volatilization

The volatilization of amine hydrochlorides cannot be considered as a simple physical process since it involves a chemical reaction. This category of processes is often called dissociative volatilization processes to distinguish them from chemical processes on one side and from typical physical processes on the other. So far, several models have been proposed to describe the kinetics of such processes. In this work we invoked the phenomenological theory outlined by Jacobs and Russell-Jones [117]. The main premise of this approach is that the migration of molecules over the surface of a condensed phase, followed by their diffusion through the gas phase, determines the kinetics of the whole process. A detailed discussion of this method and its adaptation to non-isothermal conditions have been presented elsewhere [7,117]. The final form of the integral equation, adequate for linearly increasing temperature conditions, is given below.

$$(X_2T - \Delta/a_0)\left[1-(1-\alpha)^{1/3}\right] + \tfrac{1}{2}\left[1-(1-\alpha)^{2/3}\right]$$
$$-\left(\frac{\Delta}{a_0}\right)^2 \ln\left[\frac{(1-\alpha)^{1/3}+(\Delta/a_0)}{1+(\Delta/a_0)}\right] = \frac{1}{3}\left(\frac{X_1}{\Phi}\right)T^{3/2}\exp[-E/(2RT)] \quad (3)$$

where X_1, X_2 and E are constants and E can be identified with the apparent activation barrier for the process, Φ is the heating rate, a_0 represents the initial radius of particles from which the volatilization process occurs, and Δ denotes the distance between collisions (i.e. the distance which a molecule travels after leaving the condensed phase, before a collision occurs). Δ can be identified using the mean free path of volatilizing molecules in the gaseous phase. The values of this quantity are of the order of 10^{-6} to 10^{-8} m, at atmospheric pressure. Therefore, for a great extent of the volatilization process the term Δ/a_0 is negligible since the initial dimensions of drops or crystals are a few orders of magnitude higher than Δ. Then, eqn. (3) can be simplified to the form

$$X_2T\left[1-(1-\alpha)^{1/3}\right] + \tfrac{1}{2}\left[1-(1-\alpha)^{2/3}\right] = \frac{1}{3}\left(\frac{X_1}{\Phi}\right)T^{3/2}\exp[-E/(2RT)] \quad (4)$$

which may be considered as an equation describing the kinetics of the first step of the volatilization of amine hydrochlorides showing a "regular" decomposition pattern (Table 2).

The situation changes at the end of the process, however, when the partial pressure of the volatilizing species drops markedly. Then the mean free path for the molecule increases in comparison with the dimensions of drops or particles, and Δ approaches a_0 in magnitude. This leads to a gradual decrease of the rate of the process since both terms involving Δ/a_0 in eqn. (3) are negative. The above effect is seen in TG curves of all amine hydrochlorides showing a "regular" thermal decomposition pattern (Table 2) and has also been observed upon non-isothermal volatilization of hydrochlorides of alkanamines [1,7] and nitrogen aromatic bases [2]. Therefore, this phenomenon, i.e. the decrease in the rate of volatilization with the geometric surface area of a condensed phase, appears to be characteristic for the volatilization of hydrochlorides of nitrogen organic bases. It is worth mentioning that this effect has been predicted earlier by several authors [117–119]. However, except in our studies, it has not yet been reported in non-isothermal investigations.

We would like to comment on the latter statement since a referee of one of our previous works argued that the effect might result from the experimental conditions. Thus, we performed thermal analyses of the same substance placed on a platinum plate using various masses and heating rates. A slow step was always observed in the TG curves, although it usually occurred at somewhat different extents of reaction. We then used different sample holders with the sample mass and heating rate kept constant. We noticed that the effect was much weaker if the sample was placed in crucibles (platinum or ceramic) instead of on a platinum plate. Therefore, it seems that the effect is strong only when the substance is placed in a thin layer on a relatively large surface. Presumably the use of a platinum plate as a sample holder increases the probability of formation of a large number of small drops or particles through which the volatilization process is restrained. More details regarding this effect will be presented in a separate communication.

Since the ratio Δ/a_0 changes during the course of the process, eqn. (3) is not suitable for fitting the experimental data points. Moreover, this equation presents an entangled form of a mathematical relationship and, thus, it is difficult to apply statistical optimization procedures. Therefore, we attempted to fit the experimental α vs. T data with the equation in a simplified form, i.e. eqn. (4). Substituting $1-\alpha=y$ this equation can be rearranged to the standard quadratic equation for which only one square root, i.e. that given by eqn. (5), is physically significant.

$$\alpha = 1 - \left\{ -X_2T + \sqrt{(X_2T)^2 - 2/3(X_1/\Phi)T^{3/2}\exp[-E/(2RT)] + 2X_2T + 1} \right\}^3 \qquad (5)$$

Using the experimental α vs. T dependencies and applying the DFP optimization procedure [120,121], we derived values of X_1, X_2 and E which are listed in Table 4. The fit of eqn. (5) to the experimental α vs. T data for the volatilization of benzenamine hydrochloride (Table 1) is shown in Fig. 3B. Equations (4) and (5) are the simplified forms of eqn. (3); therefore, the derived constants may not be fully representative for the kinetics of the volatilization process. Nevertheless, some idea of the significance of thus derived parameters may be indicated. Equations (3)–(5) are most sensitive to changes in E since this parameter occurs in the exponential term. Thus, one can identify this parameter with the activation barrier for the process. As may be seen in Table 4 values of E are usually somewhat lower in comparison with the appropriate values of the enthalpy of volatilization. This might indicate that the process does not require the activation barrier to be overcome above that resulting from thermochemical requirements. It is more difficult to ascribe a physical significance to X_1 and X_2. Both constants should be positive. This is only observed in the case of X_1; The majority of derived values of X_2 are negative. This discrepancy may result from the simplifications introduced in eqn. (3) in order to obtain a simple, non-entangled form of the kinetic equation. Thus, values of X_1 and X_2

TABLE 4

Kinetic constants for the volatilization of hydrochlorides of aromatic mono-amines

Substance No. (Table 2)	From the Jacobs and Russell-Jones model: eqns. (4) and (5) [a]			From the contracting surface area equation [b]: $1-(1-\alpha)^{1/2} = T(Z/\Phi)\exp[-E^*/(RT)]$	
	E (kJ mol^{-1})	X_1 ($K^{-1/2}$ s^{-1})	$X_2 \times 10^4$ (K^{-1})	E^* (kJ mol^{-1})	Z (s^{-1})
1	146	1470	−7.4	83.2	4.3×10^5
2	140	1020	−8.6	87.2	2.3×10^6
3	132	1160	−8.5	77.9	6.6×10^5
7	169	651	−8.3	105.0	2.0×10^6
8	169	1610	−5.0	96.3	4.6×10^5
9	161	722	9.2	86.3	1.4×10^5
10	152	1540	−5.4	92.3	1.7×10^6
11	174	1330	−8.0	106.0	2.8×10^6
13	152	1540	−5.4	102.0	1.1×10^6
15	171	2210	−8.1	106.0	7.5×10^6

[a] Numerical values of E, X_1 and X_2 were derived using the DFP optimization procedure [120,121].

[b] Values of E^* and Z were evaluated from the logarithmic form of the equation shown in the Table, i.e. $\ln\{[1-(1-\alpha)^{1/2}]/T\} = \ln(Z/\Phi)-(E^*/R)(1/T)$ and using standard least-squares procedure.

should be considered rather as purely mathematical constants without any true physical significance.

From the formal point of view the classical methods can be used to describe the kinetics of volatilization of amine hydrochlorides. According to this approach, the kinetics of the process should follow the integral equation [122]:

$$g(1-\alpha) = T\left(\frac{Z}{\Phi}\right)\exp[-E^*/(RT)] \qquad (6)$$

where $g(1-\alpha)$ denotes a mathematical function describing the physical kinetic model for the process (see ref. 21, Table 1), E^* and Z are constants and E^* can be identified with the apparent activation energy for the process. Using the experimental α vs. T data points and applying the standard least-squares procedure, the numerical values of E^* and Z were derived for various $g(1-\alpha)$ functions [123]. As an example, the values of both constants for the contracting surface area model (R2) are shown in Table 4, whereas Fig. 3C gives the fit of eqn. (6) to the experimental data for benzenamine hydrochloride. We chose these data for the presentation since the R2 model has been proposed to describe the kinetics of volatilization of some ammonium salts [117,124].

Reviewing all the results of the calculations we noticed that E^* values show the same trend as appropriate ΔH_v values. Moreover, we found that $E^*/\Delta H_v$ ratios are almost identical for a given kinetic model (Table 5). It is, however, worth noting that values of E^* are usually much lower compared with the appropriate values of the enthalpy change for the process. Only for diffusion reaction models is E^* comparable to ΔH_v. The questions are how to choose the classical methods for describing the kinetics of dissociative volatilization processes and what physical meaning can be ascribed to thus derived values of the constants E^* and Z. To answer these questions, let us remember the basic assumptions of this approach. The use of an Arrhenius equation to describe kinetic phenomena requires that just one step determines the kinetics of the whole process (i.e. "bottleneck"). The derived values of E^* then refer to the energy barrier for the process. It is not known a priori whether a process actually involves one slow step and such information cannot be obtained from simple kinetic considerations. The widely used approach based on the "goodness of fit" of kinetic equations to the experimental α vs. T data points, using various statistical methods in order to discern different kinetic models, usually fails, since several kinetic functions often fit the experimental data equally well. Nor can it be ignored that the dissociative volatilization processes may proceed through several steps and that more advanced kinetic analysis would be required. All these facts imply that both kinetic constants, especially Z, should be considered as mathematical parameters without true phasical significance. On the other hand, on performing any kinetic analysis for simple chemical systems information is expected on the microscopic mechanism of the process, particularly the energy barrier for the process. Otherwise, there is not much reason for such an analysis. As mentioned above the classical approach does not seem to provide such information; it would indicate that only diffusion kinetic models are probable mechanisms for the dissociative volatilization of hydrochlorides of nitrogen aromatic bases. For other reaction models E^* is much lower in comparison with ΔH_v. Therefore, it is unlikely that the molecule can reach a high energy level as a result of the thermodynamic requirements if the rate-determining step has such a low activation barrier.

Thermochemical characteristics

The relations between various thermochemical quantities are convenient to consider on the basis of the thermochemical cycle. The cycle, in an appropriate form, is presented in Fig. 4. From the thermochemical cycle the following relationships can be evaluated:

$$\Delta H^0_{f,c}[\mathrm{Am \cdot HCl}] = \Delta H^0_{f,g}[\mathrm{Am}] + \Delta H^0_{f,g}[\mathrm{HCl}] - \Delta H^0_v \qquad (7)$$

$$\Delta H^0_{f,g}[\mathrm{AmH^+}] = \Delta H^0_{f,g}[\mathrm{Am}] + \Delta H^0_{f,g}[H^+] - PA[\mathrm{Am}] \qquad (8)$$

TABLE 5

$E^*/\Delta H_v$ ratio for various reaction models

Mechanism of the process [a]	R1	R2	R3	P1	P2	P3	P4	F1	A2	A3	D1	D2	D3	D4
$E^*/\Delta H_v$	0.48	0.54	0.56	0.35	0.31	0.23	0.10	0.61	0.29	0.19	0.98	1.06	1.15	1.08

[a] For details see ref. 21, Table 1.

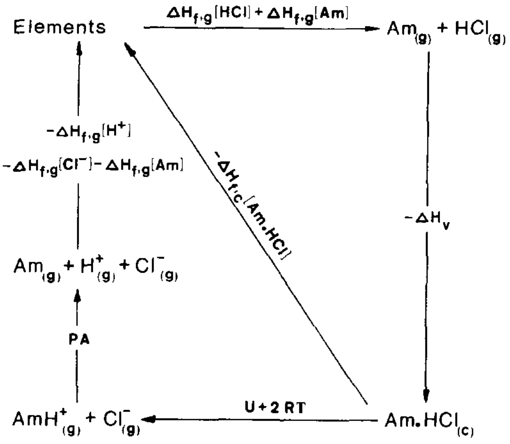

Fig. 4. The thermochemical cycle. All quantities refer to 298 K and 1 atm. Am is the aromatic amine; ΔH_f is the enthalpy of formation of a given substance; $U+2RT$ is the lattice enthalpy; U is the lattice energy; PA is the proton affinity of an organic base; and ΔH_v is the enthalpy of volatilization.

$$U^0[\mathrm{Am\cdot HCl}] = \Delta H^0_{\mathrm{f,g}}[\mathrm{AmH^+}] + \Delta H^0_{\mathrm{f,g}}[\mathrm{Cl^-}] - \Delta H^0_{\mathrm{f,c}}[\mathrm{Am\cdot HCl}] - 2RT \tag{9}$$

The values of ΔH_v derived from eqn. (2) do not refer to 298 K. Therefore, they should be corrected according to the equation:

$$\Delta H^0_{\mathrm{v},298} = \Delta H_\mathrm{v} + \Delta H^0_{\mathrm{fn}} + \Sigma\Delta H^0_\sigma - \int_{298}^{T} \Delta C^0_\mathrm{p}\,\mathrm{d}T \tag{10}$$

where ΔH^0_{fn} represents the enthalpy of fusion, the term $\Sigma\Delta H^0_\sigma$ arises from any polymorphic transitions which these compounds may undergo between 298 K and the onset of the fusion or volatilization process, and the term $\int_{298}^{T}\Delta C^0_\mathrm{p}\,\mathrm{d}T$ results from the heat capacity changes of the reactants.

The pertinent data for ΔH^0_{fn} are not available for the compounds studied. Therefore, we estimated the numerical values of this magnitude using an empirical relationship relating to the entropy of fusion: $\Delta S^0_{\mathrm{fn}} = \Delta H^0_{\mathrm{fn}}/T_\mathrm{m}$ = constant. The value of ΔS^0_{fn} was assumed to be 13.6 J $\mathrm{mol^{-1}\,K^{-1}}$ [7] on the basis of the available literature data for mono-n-alkanaminium chlorides [125,126]. Taking this value and temperatures of melting from Table 2 we evaluated the enthalpies of fusion for compounds 2, 3, 8, 9 and 11. For the other compounds studied, the term ΔH^0_{fn} was ignored since they melt and decompose simultaneously and the process of fusion presumably does not affect the thermodynamics of their decomposition. For the heat of each polymorphic transition in benzenemethanamine hydrochloride, we arbitrarily assumed a value of 4 kJ $\mathrm{mol^{-1}}$ [1]. The magnitude and sign of the heat capacity term is also difficult to assess in the absence of appropriate C^0_p data for the majority of reactants. In our latest work, devoted to the

TABLE 6

Thermochemical characteristics for aromatic mono-amines, their cations and hydrochlorides at 298 K [a]

Substance (Am)	Am		Am·HCl			AmH$^+$	
	$\Delta H^0_{f,g}$	PA [b]	ΔH^0_v	$\Delta H^0_{f,c}$	U^0	$\Delta H^0_{f,g}$	r_K
$PhNH_2$	87.1 [6,115]	889 [6,131,132]	160	−165	661	734	0.165
$PhNHCH_3$	90.4 [127]	922 [6,131]	172	−174	641	705	0.177
$PhN(CH_3)_2$	100.5 [6,116]	945 [6,131,132]	153	−145	599	692	0.206
Ph_2NH	219.2 [128]						
Ph_2NCH_3							
Ph_3N	326.8 [128]	910 [132]				953	
$PhCH_2NH_2$	87.8 [129]	918 [6,133]	211	−216	684	706	0.152
$PhCH_2NHCH_3$			193				
$PhCH_2N(CH_3)_2$	84 [6]	961 [6]	173	−181	602	659	0.204
$PhCH_2NHPh$			176				
$PhCH_2NCH_3Ph$			212				
$PhCH_2NPh_2$							
$(PhCH_2)_2NH$			197				
$(PhCH_2)_2NPh$							
$(PhCH_2)_3N$			203				

[a] All ΔH, PA and U values in kJ mol^{-1}; r_K values in nm.

[b] Proton affinities were taken from references given in brackets (mean value) and were corrected relative to the PA value for ammonia of 860 kJ mol^{-1} [130].

thermochemistry of alkanaminium chlorides, we assumed that ΔC_p^0 can be approximated by the equation: $7.2 - 0.133T$ (J mol^{-1} K^{-1}) [1]. The same relationship can also be considered to hold for the compounds studied. The appropriate heat capacity terms were, thus, calculated in the temperature range 298 K–$T_{0.1}$. The modified values of the enthalpy of volatilization are listed in Table 6.

Other thermochemical quantities were evaluated from eqns. (7)–(9) using available literature values for $\Delta H_{f,g}^0$[Am] and PA[Am] (Table 6) and assuming $\Delta H_{f,g}^0$[HCl], $\Delta H_{f,g}^0$[H$^+$] and $\Delta H_{f,g}^0$[Cl$^-$] to be (kJ mol^{-1}): – 92.3 [36,114], 1536.2 [36,114] and – 233.1 [114], respectively.

The evaluation of all thermochemical characteristics was only possible for a few of the compounds studied due to the lack of pertinent data regarding proton affinities and enthalpies of formation of amines. Therefore, it is rather difficult to reveal general correlations between the thermochemistry of these derivatives and the structure of amminium cations. The enthalpies of formation of crystalline hydrochlorides present a feature characteristic for a given compound. Values of $\Delta H_{f,c}^0$[Am · HCl] for hydrochlorides of benzenamine and *N,N*-dimethyl-benzenamine (Table 6) are markedly lower than those reported in the literature (Table 3). These differences may be partially due to the fact that the method applied is actually a non-equilibrium technique and, thus, the experimental values of α (equal to $\frac{1}{2}P/P_0$) might be somewhat lower than those corresponding to the equilibrium conditions at a given temperature. However, analogous effect can also arise from the imperfect behaviour of dissociation fragments in the gaseous phase. We believe that the latter effect is primarily responsible for the observed discrepancies.

With respect to the crystal lattice energy problem, it would be appropriate to compare values derived from the thermochemical cycle with those evaluated independently from the crystal lattice parameters. Unfortunately, such data are not available for two reasons. Firstly, there are no methods to calculate the crystal lattice energy in the case of unsymmetrical ions. Secondly, a full structure of the crystal lattice has so far been established only for benzenamine hydrochloride [134]. To facilitate discussion regarding this quantity, we invoked an approximate method developed originally by Kapustinskii [135] and subsequently improved by Yatsimirskii [136]. The crystal lattice energy can be expressed with the equation [136]

$$U = 120.2\frac{[(\Sigma n)Z_K Z_A]}{(r_K + r_A)}\left[1 - \left(\frac{0.0345}{r_K + r_A}\right) + 0.087(r_K + r_A)\right](\text{kJ mol}^{-1}) \qquad (11)$$

where (Σn) is the total number of ions in the simplest formula unit of the molecule; Z_K and Z_A denote the numerical values of the charges of cation and anion, respectively; and r_K and r_A are the "thermochemical" ionic radii (nm). Assuming r_{Cl^-} is equal to 0.172 nm [137], we derived values of r_K (Table 6).

The values of *U* decrease with increasing size of the cation, i.e. in the series of hydrochlorides of benzenamine and benzenemethanamine, and their appropriate methyl-substituted derivatives. These trends remain in accord with the Kapustinskii–Yatsimirskii formulae. However, it is interesting that the value of *U* for the hydrochloride of benzenemethanamine is only somewhat lower than that for NH_4Cl [7]. On the other hand, the value of *U* for $PhNH_2 \cdot HCl$ exceeds the crystal lattice energy for methanamine hydrochloride [7]. It is also interesting that values of *U* for *N*,*N*-dimethylmethanamine [1], *N*,*N*-dimethyl-benzenamine and *N*,*N*-dimethyl-benzenemethanamine are almost identical. All these facts indicate that the presence of phenylmethyl or phenyl substituents at the nitrogen atom usually causes an increase in crystal lattice energy. Since this quantity is affected mostly by Coulombic interactions between centres of negative and positive charges, it may be that the presence of both Ph and $PhCH_2$ cause a decrease in the distance between charges. On the other hand, the separation of charges should be determined predominantly by the N–Cl distance. It has been found that the hydrogen bond $\geqslant \mathrm{N{-}H} \cdots \mathrm{Cl}$ plays an important role in the structure of amminium chlorides and that this distance is affected only insignificantly by attachment to nitrogen groups [134]. Consequently, the values of the crystal lattice energy for hydrochlorides of aliphatic and aromatic amines are almost constant.

Further progress in this area could be made by calculating the crystal lattice energy from lattice parameters or other parameters describing such systems. We are currently working on this problem.

ACKNOWLEDGEMENTS

The authors would like to thank Professor J. Szychliński for valuable discussion, Mr. A. Liwo for help in performing calculations and Mrs. I. Nikel for experimental assistance. We are also greatly indebted to Professor F.W. Lampe of the Pennsylvania State University for providing amine samples.

REFERENCES

1 J. Błażejowski and E. Kowalewska, Thermochim. Acta, 105 (1986) 257.
2 J. Łubkowski and J. Błażejowski, J. Chem. Soc., Faraday Trans. 1, 82 (1986) 3069.
3 T.E. Mead, J. Phys. Chem., 66 (1962) 2149.
4 I. Dzidic, J. Am. Chem. Soc., 94 (1972) 8333.
5 R. Yamdagni and P. Kebarle, J. Am. Chem. Soc., 95 (1973) 3504.
6 S.G. Lias, J.F. Liebman and R.D. Levin, J. Phys. Chem. Ref. Data, 13 (1984) 695.
7 J. Błażejowski, Thermochim. Acta, 68 (1983) 233.
8 G.H. Leopold, Z. Phys. Chem., 71 (1910) 59.

9 E. Beckmann and E. Correns, Chem. Ber., 55 (1922) 852.
10 M. Zander and W.H. Franke, Justus Liebigs Ann. Chem., 741 (1970) 189.
11 I.I. Konstantinov, V.D. Selivanov and T.I. Melent'eva, Zh. Fiz. Khim., 49 (1975) 1058.
12 B.M. Tsigin, I.I. Konstantinov and Yu.M. Gusev, Zh. Prikl. Khim., 50 (1977) 499.
13 A.I. Korovin, N.A. Kiseleva, V.K. Promonenkov, B.P. Luzyanin and O.N. Vlasov, Zh. Fiz. Khim., 51 (1977) 1280.
14 Nippon Telegraph and Telephone Public Corp., Jpn. Kokai Tokyo Koho JP 82 83,527 (Cl. C08 G73/02), 25 May 1982, Appl. 80/158, 218, 12 Nov. 1980; Chem. Abstr., 97 (1982) 228575e.
15 B.S. Furniss, A.J. Hannaford, V. Rogers, P.W. Smith and A.R. Tatchell, Vogel's Textbook of Practical Organic Chemistry, Longman, London, 1978.
16 M. Struszynski, Qualitative Organic Analysis, PWN, Warsaw, 1960.
17 J. Forrest, D.A. Liddell and S.H. Tucker, J. Chem. Soc., (1946) 454.
18 S. Bruckenstein and I.M. Kolthoff, J. Am. Chem. Soc., 78 (1956) 2974.
19 A. Perrier-Datin, S. Julien-Laferriere, J.-M. Lebas and J. Belloc, J. Chim. Phys., 70 (1973) 1684.
20 G. Liptay (Ed.), Atlas of Thermoanalytical Curves, Akadémiai Kiadó, Budapest, 1973.
21 J. Błażejowski, J. Szychlinski and K. Windorpska, Thermochim. Acta, 46 (1981) 147.
22 R.C. Mackenzie, J. Therm. Anal., 21 (1981) 173.
23 Beilstein Handbuch der Organishen Chemie, Vierte Auflage (H), Verlag von Julius Springer, Berlin, 1918.
24 A. Ries, Z. Kristallogr., 58 (1923) 340.
25 S.A. Heininger, J. Org. Chem., 22 (1957) 704.
26 E.A. Braude, R.P. Linstead and K.R.H. Woolbridge, J. Chem. Soc., (1954) 3586.
27 R.P. Linstead and E.A. Braude, Br. Pat. 705,919, 24 Mar. 1954; Chem. Abstr., 50 (1956) 1079h.
28 W.T. Smith and G.G. King, J. Org. Chem., 24 (1959) 976.
29 A. Furst and R.E. Moore, J. Am. Chem. Soc., 79 (1957) 5492.
30 W. Heydkamp, E. Mueller and O. Bayer, Fr. Pat. 1,465,165 (Cl. C 07_c), 6 Jan. 1967; Ger. Appl. 22 Jan. 1965; Chem. Abstr., 67 (1967) 64019d.
31 L. Birkofer, Chem. Ber., 75 (1942) 429.
32 P.N. Rylander and E. Campaigne, J. Org. Chem., 15 (1950) 249.
33 C.D. Lewis, R.G. Krupp, H. Tieckelmann and H.W. Post, J. Org. Chem., 12 (1947) 303.
34 H.L. Klug and A.M. Pardee, Proc. S. Dakota Acad. Sci., 25 (1945) 48; Chem. Abstr., 40 (1946) 6951^2.
35 K. Starke, Can. J. Res., 28B (1950) 225.
36 Handbook of Chemistry and Physics, 66th edn., The Chemical Rubber Co., Boca Raton, FL, 1985/86.
37 M. Przyluska, J. Chim. Phys., 7 (1909) 511.
38 E.C. Jones and J. Kenner, J. Chem. Soc., (1932) 711.
39 S. Sugden and H. Wilkins, J. Chem. Soc., (1929) 1291.
40 W.H. Hunter and G.D. Byrkit, J. Am. Chem. Soc., 54 (1932) 1948.
41 A. Key and P.K. Dutt, J. Chem. Soc., (1928) 2035.
42 D. Peschanski, Ann. Chim. (Paris), 2 (1947) 599.
43 S. Umio, Yakugaku Zasshi, 79 (1959) 1133; Chem. Abstr., 54 (1960) 3376i.
44 S.C. Bunce and J.B. Cloke, J. Am. Chem. Soc., 76 (1954) 2244.
45 T. Sasa, J. Soc. Org. Synth. Chem., Jpn., 12 (1954) 211.
46 E. Slusarska and A. Zwierzak, Synthesis, (1981) 155.
47 F.E. Gould, G.S. Johnson and A.F. Ferris, J. Org. Chem., 25 (1960) 1658.
48 T. Sasa, J. Soc. Org. Synth. Chem., Jpn., 12 (1954) 105.
49 A.S. Radhakrishna, C.G. Rao, R.K. Varma, B.B. Singh and S.P. Bhatnagar, Synthesis, (1983) 538.

50 F.E. Gould, U.S. 3,062,869 (Cl. 260–482), 6 Nov. 1962, Appl. 7 Nov. 1958; Chem. Abstr., 58 (1963) 5786b.
51 H. Lund, Acta Chem. Scand., 13 (1959) 249.
52 E.P. Frankland, J. Chem. Soc., 99 (1911) 1775.
53 M. Tomita and T. Sato, Yakugaku Zasshi, 77 (1957) 1024; Chem. Abstr., 52 (1958) 3719b.
54 J.A. Secrist and M.W. Logue, J. Org. Chem., 37 (1972) 335.
55 B. Reichert and W. Dornis, Arch. Pharm., 282 (1944) 100.
56 M. Olomucki, P. Hebrard, Fr. Pat. 1,579,561 (Cl. C 07_c), 29 Aug. 1969, Appl. 23 Apr. 1968; Chem. Abstr., 72 (1970) 100003h.
57 A.E. Martell and R.M. Herbst, J. Org. Chem., 6 (1941) 878.
58 O. Exner, Chem. Listy, 50 (1956) 779.
59 H. Boehme, A. Dick and G. Driesen, Chem. Ber., 94 (1961) 1879.
60 H. Takamatsu, J. Pharm. Soc. Jpn., 76 (1956) 1236, 1239.
61 E.M. Cherkasova and S.V. Bogatkov, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 5 (1962) 284.
62 K. Abe, Jpn. Pat. 1983, 14 Apr. 1954; Chem. Abstr., 49 (1955) 11700f.
63 K. Abe, J. Pharm. Soc. Jpn., 75 (1955) 159.
64 Z. Horii, T. Sakai and T. Inoi, J. Pharm. Soc. Jpn., 75 (1955) 1161.
65 A.L. Chen, E.H. Stuart and K.K. Chen, J. Am. Pharm. Assoc., 20 (1931) 339.
66 H. Boehme, R. Broese, A. Dick, F. Eiden and D. Schuenemann, Chem. Ber., 92 (1959) 1599.
67 E.C. Kornfeld, J. Org. Chem., 16 (1951) 131.
68 P.J. Stone, J.C. Craig and H.W. Thompson, J. Chem. Soc., (1958) 52.
69 L.I. Zakharkin and I.M. Khorlina, Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk, (1950) 550.
70 M. Tifeneau and K. Fuhrer, Bull. Soc. Chim. Fr., 15 (1914) 162.
71 J.O. Jilek and M. Protiva, Chem. Listy, 47 (1953) 1814.
72 H. Rupe and E. Hodel, Helv. Chim. Acta, 6 (1923) 865.
73 E. Bamberger, Chem. Ber., 57 (1924) 2085.
74 R. Jaunin, Helv. Chim. Acta, 39 (1956) 111.
75 W.S. Emerson, S.K. Reed and R.R. Merner, J. Am. Chem. Soc., 63 (1941) 751.
76 G.B. Bachman and M. Karickhoff, J. Org. Chem., 24 (1959) 1696.
77 W.P. Neumann and E. Heymann, Justus Liebigs Ann. Chem., 683 (1965) 24.
78 J.W. Schulenberg and S. Archer, J. Am. Chem. Soc., 82 (1960) 2035.
79 C.G. Overberger, J.G. Lombardino and R.G. Hisley, J. Am. Chem. Soc., 80 (1958) 3009.
80 E.R. Alexander and R.B. Wildman, J. Am. Chem. Soc., 70 (1948) 1187.
81 I. Hirao and M. Hayashi, J. Pharm. Soc. Jpn., 74 (1954) 853.
82 A. Roe and J.M. Montgomery, J. Am. Chem. Soc., 75 (1953) 910.
83 K. Kindler, G. Melamed and D. Matthies, Justus Liebigs Ann. Chem., 644 (1961) 23.
84 M. Chastrette, Ann. Chim. (Paris), 7 (1962) 643.
85 K. Kindler, W. Peschke and W. Dehn, Justus Liebigs Ann. Chem., 485 (1931) 113.
86 A. Skita and F. Keil, Chem. Ber., 61 (1928) 1682.
87 H. Thies, H. Schoenenberger and K.H. Bauer, Arch. Pharm., 291 (1958) 248.
88 J.V. Braun, M. Kuhn and O. Goll, Chem. Ber., 59 (1926) 2330.
89 L. Birkofer, Chem. Ber., 75 (1942) 429.
90 W. Theilacker and O.R. Leichtle, Justus Liebigs Ann. Chem., 572 (1951) 121.
91 A. Lambert, J.D. Rose and B.C.L. Weedon, J. Chem. Soc., (1949) 42.
92 L.W. Jones and R.T. Major, J. Am. Chem. Soc., 52 (1930) 669.
93 M. Borovicka, Z. Sedivy, J.O. Jilek and M. Protiva, Collect. Czech. Chem. Commun., 20 (1955) 437.
94 M. Borovicka, Z. Sedivy, J.O. Jilek and M. Protiva, Chem. Listy, 49 (1955) 231.

95 R. Wegler and W. Frank, Chem. Ber., 69 (1936) 2071.
96 M. Sekiya and M. Tomie, Chem. Pharm. Bull., 15 (1967) 238.
97 S.N. Danilov and O.P. Koz'mina, Z. Obshch. Khim., 19 (1949) 309.
98 H. Gutmann and A.S. Kertes, J. Inorg. Nucl. Chem., 31 (1969) 205.
99 S.S. Hirsch and M.R. Lilyquist, J. Appl. Polym. Sci., 11 (1967) 305.
100 D.M. Golden, R.K. Solly, N.A. Gac and S.W. Benson, J. Am. Chem. Soc., 94 (1972) 363.
101 M.Z.A. Bard and M.M. Aly, Can. J. Chem., 52 (1974) 293.
102 A.J. Colussi and S.W. Benson, Int. J. Chem. Kinet., 10 (1978) 1139.
103 M.Z.A. Bard, M.M. Aly and A.M. Fahmy, Can. J. Chem., 58 (1980) 1229.
104 N.V. Sidgwick, The Organic Chemistry of Nitrogen (revised by I.T. Millan and H.D. Springall), Clarendon Press, Oxford, 1966, p. 162.
105 S. Sugden and H. Wilkins, J. Chem. Soc., (1929) 1291.
106 A. Cabana and C. Sandorfy, Can. J. Chem., 40 (1962) 622.
107 A.V. Shtoff, Yu.Yu. Dmitriev and V.I. Temkin, Zh. Strukt. Khim., 20 (1979) 714.
108 Z. Latajka, S. Sakai, K. Morokuma and H. Ratajczak, Chem. Phys. Lett., 110 (1984) 464.
109 A. Brciz, A. Karpfen, H. Lischka and P. Schuster, Chem. Phys., 89 (1984) 337.
110 C.G. de Kruif, J. Chem. Phys., 77 (1982) 6247.
111 L. Abello and G. Pannetier, Bull. Soc. Chim. Fr., (1967) 3756.
112 P. Duterme, G. Debecker and P. Huyskens, Ann. Soc. Sci. Bruxelles, Ser. I, 82 (1968) 91.
113 H.R. Ellison and B.W. Meyer, J. Phys. Chem., 74 (1970) 3861.
114 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data, 11 (1982) Suppl. 2.
115 J.B. Pedley and J. Rylance, Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds, University of Sussex, 1977.
116 J. Furukawa, M. Sakiyama, S. Seki, Y. Saito and K. Kusano, Bull. Chem. Soc. Jpn., 55 (1982) 3329.
117 P.W.M. Jacobs and A. Russell-Jones, J. Phys. Chem., 72 (1968) 202.
118 N.A. Fuchs, Phys. Z. Sowjet, 6 (1934) 224.
119 R.S. Bradley, M.G. Evans and R.W. Whytlaw-Gray, Proc. R. Soc. (London), Ser. A, 186 (1946) 368.
120 R. Fletcher and M.J.D. Powell, Comput. J., 6 (1963) 163.
121 W.C. Davidon, Comput. J., 10 (1968) 406.
122 J. Blazejowski, Thermochim. Acta, 76 (1984) 359.
123 J. Blazejowski, J. Szychlinski and E. Kowalewska, Thermochim. Acta, 66 (1983) 197.
124 T.N. Naumova, L.S. Shevnina, V.A. Falin and B.D. Stepin, Zh. Fiz. Khim., 51 (1977) 3101.
125 J. Tsau and D.F.R. Gilson, J. Phys. Chem., 72 (1968) 4082.
126 V. Busico, A. Scopa and M. Vacatello, Z. Naturforsch., Teil A, 37 (1982) 1466.
127 B.I. Istomin and W.A. Palm, Reakt. Sposobnost. Org. Soedin., 10 (1973) 1011.
128 W.V. Steele, J. Chem. Thermodyn., 10 (1978) 441.
129 A.S. Carson, P.G. Laye and M. Yurekli, J. Chem. Thermodyn., 9 (1977) 827.
130 H.D.B. Jenkins and D.F.C. Morris, J. Chem. Soc., Faraday Trans. 2, 80 (1984) 1167.
131 R.G. Cavell and D.A. Allison, J. Am. Chem. Soc., 99 (1977) 4203.
132 S. Ikuta and P. Kebarle, Can. J. Chem., 61 (1983) 97.
133 M.R. Ellenberger, R.A. Eades, M.W. Thomsen, W.E. Farneth and D.A. Dixon, J. Am. Chem. Soc., 101 (1979) 7151.
134 C.J. Brown, Acta Crystallogr., 2 (1949) 228.
135 A.F. Kapustinskii, Q. Rev. Chem. Soc., 10 (1956) 283.
136 K.B. Yatsimirskii, Zh. Neorg. Khim., 6 (1961) 518.
137 H.D.B. Jenkins and K.P. Thakur, J. Chem. Educ., 56 (1979) 576.