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Mechanism of thermal decomposition of metal azides

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Abstract

The mechanism of dissociative evaporation was used for a quantitative interpretation of the kinetics and mechanism of thermal decomposition of the azides of Na, K, Pb, Ag, Tl, Ba, Sr and Ca. Decomposition is assumed to proceed by way of gasification of all primary products, including free metals, with nitrogen evolving partially as free atoms and, in the case of lead azide, in the form of neutral N_3 molecules as well. The actual decomposition pathways were chosen based on the best fit between the calculated and experimental values of the absolute decomposition rates and the activation energies. An analysis of published mass spectrometric studies into the thermal decomposition of NaN_3 and TlN_3 has confirmed partial evolution of nitrogen in the form of free atoms. The mechanism and specific features of the UV-chemiluminescence and chemi-electron emission accompanying the decomposition of azides has been interpreted in terms of this approach. © 1997 Elsevier Science B.V.

Keywords: Decomposition mechanism; Dissociative evaporation; Metal azides; N-to-N_2 over equilibrium ratio; UV-emission

1. Introduction

Investigation of the kinetics and mechanism of thermal decomposition of azides has been dealt with extensively, and referenced to in several reviews and monographs [1–4]. Interest in these compounds originates not only from their application in technologies making use of their explosive properties but also from the possibility of using them as comparatively simple, both chemically and structurally, model systems to study solid-state reactions [4].

Despite a certain progress achieved in the interpretation of the mechanisms involved in decomposition of the azides of some metals [2,3], it has not culminated in the development of a general theory capable of describing on a quantitative basis the kinetics of thermal decomposition of various azides, as well as the generation of the fairly unusual phenomena involved, in particular, the generation of intense UV-radiation in the course of decomposition. Thus, for instance, the correlation between the activation energies for azide decomposition and the position of the first exciton level, which is predicted by the well-known theory of formation of neutral azide radicals [2], is observed to be valid, at best, only for about one half of the azides studied [3]. Besides, this theory does not account for the azide decomposition rate being proportional to the sample surface area. This relationship was established by Walker et al. [5] from experiments on several samples of NaN_3 and TlN_3 differing in specific surface area of crystal particles by a factor of 10^3.

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The present work is an attempt at interpreting the mechanism and kinetics of azide thermal decomposition based on the mechanism of dissociative evaporation of solids, which is in full agreement with the observations of Walker et al. [5]. This approach has been developed and used successfully in a number of our studies in the interpretation of the mechanism of thermal decomposition of metal nitrates in vacuum [6–8], of metal oxides and hydroxides in an argon atmosphere [9], as well as of some compounds (salts, nitrides, etc.) in vacuum [10].

This approach consists essentially in comparing the kinetic parameters of the process, namely, of the activation energies E_a and pre-exponential factors A in the Arrhenius equation, or of the absolute fluxes J of the gaseous products, with the values of these parameters calculated for possible pathways of this process. The experimental data used in these studies [6–10] were obtained by quadrupole mass spectrometry [6–8], electrothermal atomic absorption spectrometry [9], and classical methods of thermal analysis, primarily by thermogravimetry [10]. The selection among the possible pathways was guided by the assumption that, according to the gasification mechanism, thermal decomposition of a solid compound involves congruent gasification of all reaction products, irrespective of their saturated vapor pressures, with subsequent condensation of the molecules of the non-volatile components as they collide with one another or with any surface. It was also assumed that nitrogen, oxygen, sulfur and selenium can evolve as free atoms, rather than in the form of diatomic molecules which are thermodynamically stable at the decomposition temperatures.

It appears appropriate to use the same assumptions in the case of thermal decomposition of azides as well. The experimental kinetic parameters of a process are taken from available results of thermal analysis. The above assumptions will be validated by the data from mass spectrometric and optical studies available in the literature.

2. Theoretical

The flux J of a gaseous product under the conditions of monatomic evaporation is given by the well-known Hertz–Knudsen–Langmuir equation:

$$J = \frac{N_A P}{(2\pi MRT)^{1/2}} \tag{1}$$

where N_A is the Avogadro number, P the partial pressure of the gaseous product corresponding to a hypothetical equilibrium for the evaporation process, M the molar mass of the gaseous particles, R the gas constant, and T the temperature.

In the case of compound S, decomposing into gaseous products A, B, C, etc.,

$$\mathrm{S(s/l)} \rightarrow a\mathrm{A(g)} + b\mathrm{B(g)} + c\mathrm{C(g)} + \ldots \tag{2}$$

the flux of product A can be expressed in terms of the partial pressure P_A of this product corresponding to the hypothetical equilibrium of reaction (2) in the following form [9,10]:

$$J_\mathrm{A} = \frac{N_\mathrm{A} P_\mathrm{A}}{(2\pi \overline{M}RT)^{1/2}} = \frac{a\gamma N_\mathrm{A}}{F^{1/\nu}(2\pi \overline{M}RT)^{1/2}} \times \exp\frac{\Delta S_T^0}{\nu R} \exp\left[-\frac{\Delta H_T^0}{\nu RT}\right] \tag{3}$$

where

$$F \equiv a^a \times b^b \times c^c \times \ldots \tag{4}$$

$$\nu \equiv a + b + c + \ldots \tag{5}$$

$$\overline{M} \equiv M_\mathrm{A}^{a/\nu} \times M_\mathrm{B}^{b/\nu} \times M_\mathrm{C}^{c/\nu} \times \ldots \tag{6}$$

Here ΔS_T^0 and ΔH_T^0 are the changes in entropy and enthalpy for reaction (2), and $\gamma = 1.01325 \times 10^5$ is the coefficient of conversion from atmospheres used to calculate partial pressures in chemical thermodynamics to Pascals. When calculating the combined pressure of several products, the coefficient a in Eq. (3) should be replaced with the sum of the corresponding stoichiometric coefficients and, in the case of the total pressure P_t, with the coefficient ν.

In accordance with Eq. (3), the activation energy for dissociative evaporation of a compound can be written as follows:

$$E_a = \Delta H_T^0/\nu \tag{7}$$

Table 1 presents the thermodynamic functions needed for calculation of the thermal decomposition kinetics (parameters J and E_a) for a group of eight of the most extensively studied azides of Na, K, Ag, Tl, Pb, Ca, Sr and Ba. The values of the enthalpy for all

Table 1
Thermodynamic functions [11,12] used in the calculations of kinetics of azide decomposition

Species	State of aggregation	ΔH^0_{298} kJ mol^{-1}	S^0_{298} J mol^{-1} K^{-1}
Ag	g	284.9	172.9
AgN_3	s	310.6	115.5
Ba	g	179.0	170.1
$Ba(N_3)_2$	s	−22.2	165.2
Ca	g	177.8	154.3
$Ca(N_3)_2$	s	46.0	145.3
K	g	89.0	160.2
KN_3	s	−1.3	120.4
N	g	472.7	153.2
N_2	g	0	191.5
N_3	g	436.0	223.0
Na	g	107.5	153.6
NaN_3	s	21.3	96.9
Pb	g	195.1	175.3
$Pb(N_3)_2$	s	483.5	175.3
Sr	g	160.5	164.5
$Sr(N_3)_2$	s	7.1	159.0
Tl	g	180.8	180.9
TlN_3	s	233.6	125.9

azides are taken from [11]. The entropies S^0_{298} for the Na, K, and Tl azides are found in [12]. There are no reference data on the entropies for the other azides. Based on the similarity of the entropies for the azides and iodides of Na, K and Tl, instead of the azides of the remaining metals (Ag, Pb, Ca, Sr and Ba), we used the tabulated values of S^0_{298} for the corresponding iodides [12]. The error involved in such evaluation of S^0_{298} does not exceed 10 J mol^{-1} K^{-1}. Judging from the discrepancies between the available data on ΔH^0_{298} [11,12], the error in the determination of the enthalpies of azides may be as large as 15 kJ mol^{-1}.

3. Results and discussion

3.1. Interpretation of kinetics

Our calculations of the kinetics of azide thermal decomposition were made under the following assumptions:

1. The azides decompose through gasification of all primary reaction products, including the free metals formed. The assumption rests on the a priori considerations underlying the analysis of the kinetics of decomposition of the other solid compounds [6–8,10].
2. The decomposition of the azide groups involves partial or total evolution of one of the three nitrogen atoms in the free form, i.e. by the following pathway:

$$MN_3(s/l) \rightarrow M(g) + (1-i)N + (1+0.5i)N_2 \qquad (8)$$

where the interaction parameter i varies from 0 to 1, depending on the extent to which the nitrogen atoms in the nearest azide groups interact with one another at the instant of decomposition. Considering that the separation between nitrogen atoms of the nearest-neighbor azide groups in the azide crystal lattice (for example, in the case of NaN_3 [11]) is three times the internuclear N–N distance (1.07 Å) in the nitrogen molecule, this assumption appears reasonable enough.

3. In cases where the nitrogen atom separation in azide group is less than the N–N internuclear distance in the N_3 molecule (1.181 Å), nitrogen can evolve in the form of neutral N_3 molecules.

Of all the kinetic parameters characterizing thermal decomposition of azides available in the literature, namely, the activation energies (E_a) and, in some cases, the absolute decomposition rates (J), the latter is the most informative and reliable. Firstly, as follows from a comparison of Eqs. (3) and (7), it takes into account not only the enthalpy of the decomposition process but its entropy as well. Secondly, determination of the absolute rates, which requires carrying out additional measurements of the sample surface area and of the reaction vessel volume as well as calibration of manometer readings in absolute pressure units, turns out eventually to be more reliable from the standpoint of the precision and accuracy of the results obtained. Therefore, we chose agreement between the calculated and experimental values of the absolute decomposition rate as the main criterion in selecting the appropriate scheme of the process. The agreement between the activation energies served as a complementary criterion of correctness of that choice.

Table 2 presents the calculated and experimental absolute decomposition rates for azides of Na, Pb, K and Ba in the order of decreasing decomposition temperatures. We are not aware of any data on the

Table 2
Absolute rates for the thermal decomposition of azides

Implied reaction	T/K	Absolute decomposition rate (J/molecules m^{-2} s^{-1})	
		experiment	calculation
$NaN_3(s) \rightarrow Na(g) + 0.9N + 1.05N_2$	603	8.1×10^{19} [13]	5.8×10^{19}
	573	1.1×10^{19} [13]	9.6×10^{18}
$Pb(N_3)_2(s) \rightarrow Pb(g) + N + N_2 + N_3$	543	5.3×10^{19} [14]	1.6×10^{20}
	500	4.0×10^{18} [15]	8.9×10^{18}
$KN_3(s) \rightarrow K(g) + 0.72N + 1.14N_2$	524	1.7×10^{19} [14]	2.7×10^{19}
$Ba(N_3)_2(s) \rightarrow Ba(g) + 0.6N + 2.7N_2$	388	3.1×10^{19} [14]	6.5×10^{19}

absolute decompositions rates for the other metal azides. In view of possible errors in the measurement and calculation of the values of J, our choice of an appropriate decomposition pathway was guided by the requirement that the experimental and calculated values agree within a factor of three. As seen from the schemes given in Table 2, assumptions (1) and (2) lead to the gaseous metal and molecular or atomic nitrogen as the reaction products in all cases. The interaction parameter was found to be zero for $Pb(N_3)_2$, 0.1 for NaN_3, 0.28 for KN_3, and 0.7 for $Ba(N_3)_2$.

These two assumptions turned out to be insufficient for a theoretical description of the decomposition of $Pb(N_3)_2$. The calculated values of J for the reaction

$$Pb(N_3)_2(s) \rightarrow Pb(g) + 2N + 2N_2 \qquad (9)$$

were found to exceed by two orders of magnitude the experimental values of J obtained [14,15] at two different temperatures (543 and 500 K). Therefore, the two aforementioned assumptions were complemented by assumption (3) postulating partial evolution of nitrogen in the form of N_3 molecules. This approach has enabled us to propose the scheme

$$Pb(N_3)_2(s) \rightarrow Pb(g) + N + N_2 + N_3 \qquad (10)$$

with kinetic characteristics very close to the experimentally observed ones. In view of the lead azide crystal structure [11], the assumption of the nitrogen evolving in equal parts as N_3 and $(N+N_2)$ appears reasonable enough. The α modification of $Pb(N_3)_2$, which is the only form of this compound stable above 160°C, is actually a combination of four crystallographically distinct azide groups with different N–N distances (Table 3). A comparison of these distances with the N–N bond length (1.181 Å) in the neutral N_3 molecule shows that in the first two groups these spacings are smaller and, in the other two groups, larger than that in the free N_3 molecule. It may therefore be conjectured that one-half of the nitrogen released in the decomposition of $Pb(N_3)_2$ is in the form of N_3 molecules, and the other half as a sum of $N + N_2$. One cannot, however, exclude the possibility of the above correlation being purely accidental.

Table 4 presents experimental values (extracted from the publications available to us) and our calculations of the activation energies for the above four azides, as well as for the azides of Ag, Tl, Sr and Ca, arranged in the order of decreasing magnitude. We immediately note the remarkably large scatter among the experimental data, particularly for the azides of Na, K and Pb. Taking this into account, the agreement of the calculated values with experiment appears, on the whole, quite satisfactory. The decomposition for the azides of Ba, Sr and Ca differ from those for the other azides in a markedly smaller fraction of nitrogen evolving as free atoms.

Thus by choosing appropriately the contents of different forms of nitrogen (N, N_2 and N_3) in the

Table 3
N–N distances in different groups of α-$Pb(N_3)_2$ [11]

Azide group	Distances/Å	
	N_1–N_2	N_2–N_3
I	1.164	1.164
II	1.177	1.166
III	1.193	1.160
IV	1.213	1.147

Table 4
Activation engeries for the thermal decomposition of azides

Implied reaction	*i*-parameter	Activation energy/kJ mol^{-1}	
		calculation	experiment
$NaN_3(s) \rightarrow Na(g)+0.9N+1.05N_2$	0.10	173	144 [1] 154 [16] 193 [15] 172–197 [17]
$Pb(N_3)_2(s) \rightarrow Pb(g)+N+N_2+N_3$	0	155	125 [15] 152 [18] 159 [1]
$KN_3(s/l) \rightarrow K(g)+0.72N+1.14N_2$	0.28	152	130–135 [19] 151 [1] 160 [16] 205 [20]
$AgN_3(s) \rightarrow Ag(g)+N+N_2$	0	149	132 [21] 138 [22] 151 [23]
$TlN_3(s) \rightarrow Tl(g)+N+N_2$	0	140	149 [24]
$Ba(N_3)_2(s) \rightarrow Ba(g)+0.6N+2.7N_2$	0.70	113	98 [25] 102 [26] 109 [27]
$Sr(N_3)_2(s) \rightarrow Sr(g)+0.4N+2.8N_2$	0.80	82	84 [25]
$Ca(N_3)_2(s) \rightarrow Ca(g)+0.4N+2.8N_2$	0.80	76	75–79 [25] 79 [27]

products of decomposition, one can describe the kinetics of azide decomposition in terms of a common mechanism of dissociative evaporation.

3.2. Analysis of mass spectrometric studies

The most critical point in the proposed mechanism of thermal decomposition of azides is the assumption of partial release of nitrogen in the form of free atoms. It thus appears appropriate to analyze the available information on mass spectrometric investigation into the composition of the reaction products. The most valuable quadruple mass spectrometric measurements in our knowledge [3,5,13,15,19,24,28], are the studies of Walker et al. [5], Walker [13,24], and Fox and Walker [28]. These publications present the original mass spectra of the decomposition products for NaN_3 and TlN_3.

The difficulties involved in an analysis of the relative content of atoms and molecules in the primary decomposition products are due to the partial dissociation the molecules undergo in the mass spectrometer ionizer, the differences in the ionization cross sections of these particles, the superposition of background on account of the residual gases, as well as the differences in the solid angle collecting the particles at the entrance of the ionizer, if the particles of interest differ in their resistance in the process of collisions with the chamber walls.

Let us estimate the content of atomic and molecular nitrogen evolving in decomposition of NaN_3 based on the results of Walker [13], and taking into account the above factors. As seen from Figs. 12 and 16 of [13], the maximum ratio of the peak-height signals $I_{N^+}/I_{N_2^+}$, in the process of decomposition becomes as high as 0.20–0.25 whereas, in the absence of decomposition (Fig. 15 in [15]), it does not exceed 0.04. The latter ratio is in a good agreement with the value $I_{N^+}/I_{N_2^+} \cong 0.03$, quoted in the NBS Registry of Mass Spectral Data [29] for molecular nitrogen at conventional electron energies $\approx$ 70 eV. Taking into account this correction, as well as the superposition of the background due to residual nitrogen, we obtain the *pure* ratio, viz $I_{N^+}/I_{N_2^+} \geq 0.20$. Recalling the twofold difference between the ionization cross section of the N_2 molecules and N atoms [30], we obtain for the flux ratio of particles reaching the ionizer, the value

$$I_{N^+}/I_{N_2^+} > 0.40 \tag{11}$$

If we take into account the reflection of N_2 molecules and recombination of N atoms in collisions with the specimen holder surface and mass-spectrometer walls, this value further increases by a factor of two, which corresponds to a primary flux ratio of ≥ 0.80. We may recall that our scheme of NaN_3 decomposition yields $I_{N^+}/I_{N_2^+} = 0.86$ (see Table 2). Approximately the same primary signal ratio $I_{N^+}/I_{N_2^+}$ was observed by Fox and Walker (Fig. 3.1.4 in [28]) in the thermal decomposition of TlN_3. Thus, direct mass spectrometric measurements of the fluxes of N atoms and N_2 molecules evolving in thermal decomposition of NaN_3 and TlN_3 fully support the assumption of partial release of nitrogen as free atoms. (Remarkably, this essential fact has remained unnoticed for 30 years.)

One could also present other experimental evidences for the release of atomic nitrogen in thermal decomposition of azides. For example, Garner and

Reeves [25] point out the formation of NO_2 in thermal decomposition of AgN_3 in the presence of oxygen, a fact that can be easily explained as arising from a direct reaction

$$N + O_2 \rightarrow NO_2 \quad (12)$$

The release of atomic nitrogen also provides the simplest interpretation for the UV-radiation emitted in the Vegard–Kaplan bands during thermal decomposition of some azides, which is associated with the formation of highly excited N_2 molecules.

3.3. Mechanism of UV-emission

The emission of UV-radiation during thermal decomposition of azides was discovered by Audubert about 60 years ago [31,32]. For KN_3, NaN_3, AgN_3 and $Pb(N_3)_2$, the emission was found to be considerably higher than for $Ca(N_3)_2$ and $Ba(N_3)_2$. The spectrum with peaks at 198, 215, 230 and 240 nm was identified [33] as the Vegard–Kaplan band system originating from the $A^3 \sum_u^+ \rightarrow X^1 \sum_g$ (ground-state) transition in excited nitrogen molecules.

A larger number of studies deal with the emission of these bands in an electric discharge passed through molecular nitrogen or its mixtures with noble gases. When in the $A^3 \sum_u^+$ excited state, the N_2 molecules are known to have an energy of 6.17 eV and a lifetime of about 2.1 s. Summarizing the studies of many authors, Kondratiev and Nikitin [34] came to the conclusion that the main source of the UV-emission here is the recombination of ground-state nitrogen atoms.

It is natural to assume that the Vegard–Kaplan band emission during thermal decomposition of azides is likewise due to the recombination of free nitrogen atoms in the following reaction

$$N + N \rightarrow N_2^* \rightarrow N_2 + h\nu \quad (13)$$

Based on this assumption, we should expect the emission to increase proportionately with the square of the number of N atoms released in the azide decomposition, which would result in a doubled activation energy for the decomposition process. Indeed, the studies of Singer and Mueller [16] revealed activation energies, which characterize the change in the UV-emission with temperature, as high as 314 kJ mol^{-1}. However, the reproducibility and intensity of emission in this case were poorer and lower than those found under optimal measurement conditions, namely, in a weak flow of argon or another gas at pressure of about 0.05 atm. As for the activation energies for the UV-radiation emission measured for KN_3, NaN_3, RbN_3 and CsN_3 under optimal conditions, they turned out to be equal to those found for the decomposition process, which argues for a linear dependence of emission intensity on the nitrogen-atom concentration.

The most probable reason for this contradiction appears to be the radiation quenching as a result of collisions of excited nitrogen molecules with metal atoms and their ionization in the following reaction

$$N_2^* + M \rightarrow M^+ + N_2 + e \quad (14)$$

which also provides an explanation for the origin of the electron emission observed in the decomposition of azides. One should not exclude, here, the possibility of partial binding of free nitrogen atoms by an O_2 impurity in the gas environment to form NO_2 molecules. As a result of combined action of these factors, the temperature dependence of both processes (UV- and electron-emissions) occurring in the presence of a foreign gas turns out to be weaker than that expected and observed [16] in a high vacuum.

Finally, the connection of the UV-emission with the release of free nitrogen atoms during azide decomposition provides an explanation for the lower intensity of the UV-emission in the case of the azides of alkali-earth elements compared with those of other elements. Indeed, the fraction of nitrogen atoms in the total amount of nitrogen in the case of $Ba(N_3)_2$, $Sr(N_3)_2$, and $Ca(N_3)_2$ is three-to-four times smaller than that for the other azides (Table 4).

4. Conclusions

Taking into account the successful results of the foregoing analysis of kinetics and product composition for the azide thermal decomposition, as well as the sufficiently convincing interpretation of the phenomena accompanying the decomposition, the author believes that the mechanism of dissociative evaporation of azides may be of interest for further studies in this area. Direct arguments for, or against, this mechanism could be obtained in a mass spectrometric investigation of the primary products of decomposition, as this has been demonstrated in the case of the NaN_3 and TlN_3 azides. Of particular interest here would be a study of the decomposition of $Pb(N_3)_2$. Studies of the UV-chemiluminescence and chemi-electron emission in vacuum, as well as measurements of the absolute decomposition rates for the azides of various metals would likewise provide valuable information. Finally, revealing a possible relation of the crystal structure of azides with the composition and relative content of various forms of nitrogen in the primary products of decomposition would be of considerable interest.

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