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A CORRELATION BETWEEN THE ν_4 FREQUENCY OF VIBRATIONS OF METAL NITRATES AND THEIR TEMPERATURE OF THERMAL DECOMPOSITION

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ABSTRACT

The temperature T_m of thermal decomposition of nitrates, as found by thermal analysis by Belov et al. (Zh. Neorg. Khim., 30 (1985) 2520), is correlated with their ν_4 frequencies of vibration. The asymmetric deformation of the NO_3^- group corresponding to this frequency seems to be the only possible mode able to rupture the N–O bond and cause decomposition of the nitrates to MO_x and NO_x. Furthermore, T_m is also related to the electronegativity parameter ϕ^* of the metal, which corresponds to a modified work function of it, according to Miedema et al. (J. Phys. F, 3 (1973) 1558; J. Less-Common Met., 46 (1976) 271; Physica B, 100 (1980) 145). The meaning of this correlation in relation to the strength of the M–O bond is also discussed.

INTRODUCTION

In a recent article, Belov et al. [1] studied the decomposition of nitrate salts by thermal analysis. The results of this study give the apparent activation energy E of the decomposition and the pre-exponential factor k as well as the temperature T_m corresponding to the maximum of the thermal decomposition peak. The authors conclude that the activation energy E of the process correlates satisfactorily with the characteristic temperature T_m of the last endothermic peak, which is apparently due to nitrate decomposition. In contrast, E does not seem to be correlated with the atomic number N of the nitrate cation.

During nitrate decomposition, rupture of the N–O bond is inevitable, the oxygen atom remaining bound to the metal in an oxide form. The strength of the ruptured N–O bond is difficult to estimate but it is influenced by the metal atom bound to the oxygen and is reflected in the temperature necessary for decomposition. In this work, we shall discuss the main factors influencing the thermal stability of nitrate salts as expressed by the T_m values.

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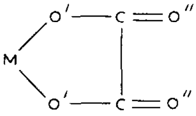
DISCUSSION

In the past, it has been shown [2] that the main factor which influences the enthalpy $(-\Delta H_{M-O})$ of the metal–oxygen bond in simple oxides is the difference $(\phi_O^\star - \phi_M^\star)$ between the electronegativity parameters $\phi^\star$ of oxygen and the metal. The quantity $\phi^\star$ corresponds to a modified work function of the electrons in the elements and was introduced by Miedema et al. [3–6] in a successful attempt to describe the heats of formation of alloys. According to ref. 2, metals with low $\phi^\star$ values have high values of $(-\Delta H_{M-O})$ and vice versa. Although extrapolation is not always reliable, a similar situation seems to apply in compounds where, unlike in the oxides, oxygen is bound by one of its valences to a metal and to a third element, such as nitrogen in this case, by the other. Thus a gradually decreasing $\phi_M^\star$ value should result in an incremental increase in $(\phi_O^\star - \phi_M^\star)$ and therefore $(-\Delta H_{M-O \cdots N})$ should increase. Such a situation may result in a weakening of the neighbouring bond between oxygen and nitrogen, for reasons related to the depletion of electrons from the bond. Consequently, the temperature necessary to break the bond should be smaller.

This hypothesis agrees with some previous suggestions in relation to the thermal decomposition of oxalates.



Fujita et al. [7] suggested that the extent to which the M–O′ bond is covalent depends on the electronegativity of the metal and as this bond becomes stronger, the O′–C bond is lengthened, and presumably weakened. Decomposition will occur when a temperature is reached at which rupture of the C–O′ bond is possible.

To test this hypothesis, as far as the nitrates are concerned, in Fig. 1 $\phi_M^\star$ is plotted against T_m from the data in Table 1 taken from the corresponding references. As can be seen, to a first approximation, a first-order relation is observed between them described by the equation

$$T_m = 1173 - 192\phi_M^\star \qquad (1)$$

with a correlation coefficient $R = 0.94$ which has a better than 99% significance level. Therefore, it seems that the above hypothesis is very close to reality. In other words, strengthening of the metal–oxygen bond in nitrates, which can be the result of low $\phi_M^\star$ values, results in a weakening of the adjacent oxygen–nitrogen bond, and as a result a lower temperature is necessary to break it. In eqn. (1), $T_m \rightarrow 0$ as $\phi_M^\star \rightarrow 6.1$ eV. It is interesting that the electronegativity parameter $\phi_O^\star$ of oxygen was estimated in ref. 2 to approximate to such a value. This may mean that substitution of the metal

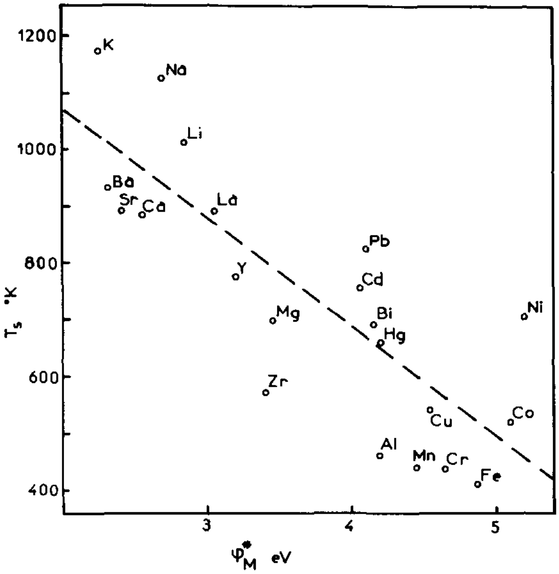


Fig. 1. Correlation between the characteristic temperature T_m of thermal decomposition of nitrates and the electronegativity parameter ϕ^*_M of the corresponding metal.

TABLE 1

Nitrate salts and their corresponding values of temperature of decomposition T_m [1], the electronegativity parameter ϕ^*_M [4–6] and the frequency of ν_4 vibration [8]

Cation	T_m (°C)	ϕ^*_M (eV)	ν_4 (cm^{-1})
Al	190	4.20	719
Ba	660	2.32	729
Bi	420	4.15	–
Ca	610	2.55	744
Cd	480	4.05	751
Co	250	5.10	762
Cr	170	4.65	–
Cu	270	4.55	770
Fe	140	4.93	–
Hg	390	4.20	750
K	900	2.25	–
La	620	3.05	–
Li	740	2.85	–
Mg	420	3.45	–
Mn	170	4.45	759
Na	850	2.70	–
Ni	430	5.20	758
Pb	550	4.10	726
Sr	620	2.40	741
Zr	300	3.40	–
Y	500	3.20	745

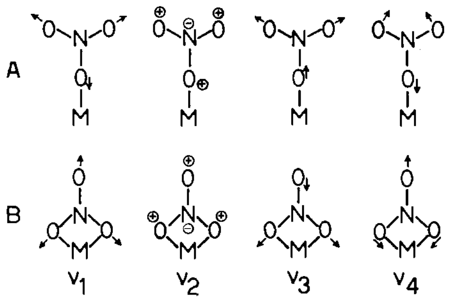


Fig. 2. The four possible modes of vibration of (A) mono- or (B) bi-dentate nitrates: ν_1, symmetric stretch (IR inactive); ν_2, out-of-plane symmetric deformation (800–830 cm^{-1}); ν_3, asymmetric stretch (1300–1500 cm^{-1}); and ν_4, asymmetric deformation (720–770 cm^{-1}).

atom in nitrates by oxygen, or by another atom having $\phi^\star$ values near to that of oxygen, results in a very low temperature of decomposition of the nitrate salt. Indeed the noble metals such as Pt, Pd and Ir which possess $\phi^\star_\text{M}$ values of around 5.5 eV are not able to form stable nitrates.

In order to determine the deeper reasons governing the nitrate decomposition, the influence of the oscillations of the nitro-group on the decomposition was investigated. To do so we examined the possible correlation between the different modes of vibration of the NO_3^- group, as found in the literature [8], with the temperature of decomposition T_m. It is well known that there are four such possible modes of vibration, namely ν_1, ν_2, ν_3 and ν_4, depicted in Fig. 2 for mono- and bi-dentates. Of these, it seems that only the asymmetric deformation ν_4 should favour the decomposition of the N–O bond of the nitrates to form oxides of metal and nitrogen. In contrast, the ν_1, ν_2 and ν_3 vibrations seem to have less influence on the N–O bond: ν_1 and ν_2 affect the three N–O bonds in a rather symmetrical manner, while ν_3 moves them towards the same direction. Only the ν_4 mode moves the two oxygen atoms away from the third one, thus assisting in their separation, with nitrogen remaining bonded to one fragment. An experimental verification of this comes from a comparison of the ν_4 values for different nitrates, taken from the literature [8], with the maximum temperature of decomposition [1], as shown in Fig. 3.

The two variables in this figure are correlated via a first-order relation

$$T_\text{m} = 8183.725 - 9.968\nu_4 \qquad (2)$$

with a correlation coefficient of 0.83 which is better than 99% significance level. In calculating eqn. (2), the point corresponding to $Al(NO_3)_3$ has been ignored as its thermal decomposition occurs simultaneously with dehydration [9] and, as a result, it appears abnormally low. Equation (2) can easily be written as

$$E_{T_\text{m}} = 1.129 \times 10^{-19} - 6.878E_{\nu_4}(\text{Joules}) \qquad (3)$$

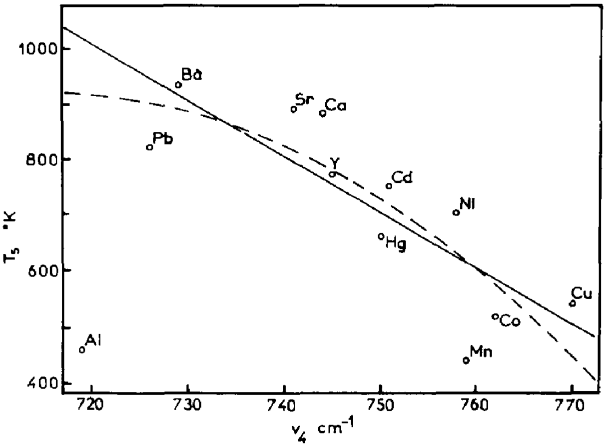


Fig. 3. Correlation between the characteristic temperature T_m (K) of thermal decomposition of nitrates and the characteristic ν_4 vibration.

where $E_T = kT_m$ and $E_\nu = h\nu_4 c$ representing the thermal and vibrational energy content of the molecule respectively (k = Boltzmann constant, h = Planck constant, c = velocity of light).

The last equation implies that decomposition occurs when the thermal energy exceeds the vibrational (due to the ν_4 mode) energy of a particular nitrate salt by a value of about 7. To put it in another way, decomposition happens when $\exp(h\nu c/kT) = \exp(1/6.878) = 1.154$. However, the meaning of the arithmetic values is rather obscure.

A second-order relationship between the same quantities depicted in Fig. 3 yields

$$T_m = -80850 + 228.4\nu_4 - 0.1595\nu_4^2 \qquad (4)$$

with a slightly better, as compared to the first-order, correlation coefficient of 0.85. This relation can again be written as

$$E_{T_m} = -1.116 \times 10^{-18} + 158.5E_{\nu_4} - 5.564 \times 10^{21}E_{\nu_4}^2 \text{ (Joules)} \qquad (5)$$

It is well known that $E_\nu = (h/2\pi)(k/\mu)^{0.5}$ where k is the force constant of the vibrating bond and μ is the reduced mass of the system. Then eqn. (5) can be used to calculate the term (k/μ). Thus for YNO_3 whose $T_m = 773$ K, eqn. (5), after substitution of the constants, yields

$$\left(\frac{k}{\mu}\right)_1 = 1.990 \times 10^{28} \text{ and/or } \left(\frac{k}{\mu}\right)_2 = 1.662 \times 10^{28} \qquad (6)$$

Assuming that the bond splitting separates the two fractions YO and NO_2, calculation of the reduced mass of the system results in $\mu_{YO-NO_2} = 5.312 \times 10^{-23}$ g. This value in combination with eqn. (6) results in a force constant value k of the system $YO \cdots NO_2$ equal to 10.57×10^5 or 8.83×10^5 dynes cm^{-1}. Such a result is very close to the force constants of similar bonds.

Thus, for $N \cdots O$, $k = 15.95 \times 10^5$ dynes cm^{-1}, which suggests that these results are valid.

Therefore, a combination of thermogravimetric and IR data can perhaps be used to approximate the force constants of the broken bond during the decomposition of nitrate salts. To what extent such a method can be applied to other similar systems can only be assessed by future work.

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