

982. *The Volatility of Nitrates and Nitrites of the Alkali Metals.*

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The nitrates of all the alkali metals, and the nitrites of sodium and potassium, have been distilled without significant decomposition (except for lithium nitrate trihydrate) from their melts at reduced pressure ($\sim 5 \times 10^{-3}$ mm. Hg) at 350–500°. The volatility of these salts is compared, on the one hand, with that of the covalent nitrate-complexes of various metals and, on the other, with that of the alkali-metal halides which are considered to exist as ion pairs in the vapour state. Possible practical applications of the distillation of these salts are discussed.

THE nitrates of sodium and potassium have long been known (Scheele, 1774) to evolve oxygen and form the nitrites when strongly heated. However, the nitrate ion has considerable stability towards thermal decomposition when it is associated with alkali-metal ions and its decomposition reactions are not simple. Sodium nitrate decomposes rapidly at $>800^\circ$ to give the oxide, but potassium nitrate must be heated to 1000° to obtain a comparable extent of decomposition (and is not completely decomposed at 1200°).¹ As the temperature is increased peroxides are also formed; they are detectable² at 750° with sodium and at 850° with potassium. Nitric oxide has also been detected³ in the thermal decomposition of potassium nitrate in an evacuated quartz tube at $>550^\circ$.

¹ Leschewski and Zulla, *Ber. Ges. Freunden tech. Hochschule, Berlin*, 1942, **1**, 168.

² Leschewski and Degenhard, *Ber.*, 1939, **72**, 1763.

³ Butkov and Chassoveny, *Acta Physicochim. U.R.S.S.*, 1936, **5**, 137.

Differential thermal analysis has been used to study⁴ in detail the decomposition of alkali-metal nitrates at atmospheric pressure.

It has seemed likely to us that at a given temperature above the melting point the nitrates of the alkali metals must exert an appreciable vapour pressure above the liquid phase in addition to the pressure exerted by the products of thermal decomposition, and that it should be possible to distil them under certain conditions. We now report that the nitrates of all the alkali metals and also the nitrites of sodium and potassium can be distilled without significant decomposition at $\sim 5 \times 10^{-3}$ mm. at temperatures in the range 350–500°.

EXPERIMENTAL AND RESULTS

The "AnalaR" nitrates and nitrites of the alkali metals (1–5 g.) were separately distilled in a Pyrex tube (with a swan-neck to prevent droplets of liquid "bumping" from the boiler) fitted with a water-cooled cold-finger in a two-way adaptor with Teflon-lined ground joints. The distillation tube was suspended in a silica beaker wound with a heating element controlled by a Variac. The temperature could be raised slowly to 600° and measured with a calibrated thermocouple. The tube was evacuated to about 5×10^{-3} mm. with a rotary pump and mercury diffusion pump, and the pressure was measured with a Pirani gauge between the tube and a liquid-nitrogen trap. The temperature was kept approximately constant at about 50–100° above that at which the vapour was first seen to condense on the cold finger. After a suitable amount of distillate had collected, the apparatus was cooled and dry helium was admitted before disconnection from the vacuum-line and transference to a dry-box for removal of the contents.

After a few experiments the Pyrex tube was replaced by a silica tube with a larger diameter and without a swan-neck, (a) to prevent contamination of the samples with sodium and potassium, etc., from the Pyrex, and embrittlement of the Pyrex by, for example, lithium ions, and (b) to allow the salt to be distilled more rapidly and at slightly lower temperature; the liquid surface was always quiescent and the expected "bumping" did not occur.

The trihydrate of lithium nitrate was dehydrated by slowly raising the temperature *in vacuo* until the m. p. of the anhydrous nitrate was reached. A constant vapour pressure of 0.08 mm. was observed at 60–100°, during which period most of the water was removed and a small amount of oxides of nitrogen was evolved and condensed in the liquid-nitrogen trap. The lithium nitrate boiled gently at $\sim 490^\circ/0.02$ mm. but this "boiling" may have been due to the evolution of small amounts of gaseous decomposition products rather than the vapour of the nitrate.

Alkali-metal Nitrates and Nitrites.—Table 1 gives the approximate temperatures of different events in our distillation experiments.

TABLE I.

Temperatures observed during distillation experiments.

Salt	M. p.	Condensation first observed on cold-finger	Steady condensation (ca. 0.1 g./hr.)	Salt	M. p.	Condensation first observed on cold-finger	Steady condensation (ca. 0.1 g./hr.)
LiNO ₃	250°	350°*	480°*	CsNO ₃	415°	450°	500°
NaNO ₃	310	350	450	NaNO ₂	272	350	450
KNO ₃	335	350	450	KNO ₂	445	470	490
RbNO ₃	315	390	450				

* In swan-neck tube.

The distillate from an experiment with potassium nitrate was analysed for nitrate; it contained 61.0% (by nitron nitrate; theor., 61.3%) and 0.1% of nitrite (by cerate titration). It was contaminated by sodium when distilled in a Pyrex tube, but not when distilled in a silica tube. No trace (<0.1%) of nitrite could be detected in the solid distillate of lithium nitrate, as would be expected since the nitrate normally decomposes to the oxide.

The infrared spectrum (2–15 μ) of the caesium nitrate distillate was examined to confirm the presence of nitrate ions; the mulls were prepared in Nujol and hexachlorobutadiene between

⁴ Gordon and Campbell, *Analyt. Chem.*, 1955, **27**, 1102.

silver chloride plates. Our spectra contained a very strong broad double peak at 1385, 1330 cm^{-1} and a medium-strength sharp single peak at 835 cm^{-1} for both the distillate and the "AnalaR" starting material. A double maximum (1386, 1345 cm^{-1}) has also been reported by Cuninghame and Heal,⁵ but Gatehouse⁶ reported a broad absorption peak at 1353 and a sharp peak at 835 cm^{-1} , and Vratny⁷ reported peaks at 1380 and 835 cm^{-1} .

The distillate from an experiment with potassium nitrite contained 54.5% nitrite (by cerate titration; theor. 54.1%).

Silver and Barium Nitrate.—We attempted to distil silver nitrate in view of the suggestion,³ based on spectrographic measurements in an evacuated quartz tube, that un-ionised molecules may be present. Slight volatility was observed at 450°/5 × 10⁻³ mm. but only a fraction of a milligram of white solid was obtained on the cold-finger after several hours, and extensive decomposition occurred in the liquid phase. The distillate gave positive tests for silver (as chloride) and nitrate (as nitron nitrate), but the amount was insufficient for quantitative analysis.

We also attempted to distil barium nitrate (selected as the most readily available anhydrous alkaline-earth nitrate) but observed only slight volatility; only a fraction of a milligram was condensed from a gram of starting material (m. p. 550°) in 5 hr. at 600°/5 × 10⁻³ mm. Evolution of small amounts of gas from molten barium nitrate is reported⁸ to occur at about 630° at atmospheric pressure. We found large amounts of nitrite and oxide in the residue and there may therefore have been nitrite in the distillate if the nitrite is volatile.

DISCUSSION

Relative Volatility of Metal Nitrates and Nitrate-complexes.—Volatile nitrate- and nitrate-oxide complexes which sublime or distil in a vacuum have been reported for a number of metals (Table 2). The dinitratocopper(II) complex has been shown⁶ to contain covalent nitrate-groups in the vapour state by infrared spectroscopy, and the complexes of several of the other metals have been shown to contain covalent nitrate-groups in the solid state. It is probable that all these complexes contain covalent nitrate-groups in the vapour state and they can be placed in one class (A, Table 2). Their volatility can be compared qualitatively with that of the covalent chlorides of the respective metals, but quantitative comparison is not possible because b. p.s or sublimation temperatures have not been measured under comparable conditions.

The alkali-metal nitrates and ammonium nitrate can be placed in a separate class (B, Table 2) because they are ionic in the solid state (crystal structures,⁹ infrared spectra^{7,10}) and probably exist as ion-pairs in the vapour state. These metal nitrates can be compared with the slightly volatile ionic alkali-metal chlorides which are postulated to exist as ion-pairs in the vapour state from measurements of electron diffraction,¹¹ dipole moments, and photodissociation.¹²

The ease of decomposition of the anhydrous nitrates of many other metals may prevent appreciable volatilisation. Silver and barium are two such metals whose anhydrous nitrates only show slight evidence of volatilisation whilst undergoing extensive decomposition. Hydrated metal nitrates, on the other hand, usually decompose at relatively low temperatures to give basic nitrates and oxides,^{4,13} and only rarely give the anhydrous nitrates.

Volatility of Metal Nitrites and Other Salts.—The nitrites of sodium, potassium, and ammonium can be placed in the same class as the nitrates of the alkali metals (Table 2).

⁵ Cuninghame and Heal, *Trans. Faraday Soc.*, 1958, **55**, 1355.

⁶ Gatehouse, Ph.D. Thesis, London, 1958.

⁷ Vratny, *J. Appl. Spectroscopy*, 1959, **13**, 59.

⁸ Addison and Coldrey, *J.*, 1961, 468.

⁹ Landolt-Börnstein Tabellen, "Zahlenwert und Funktionen," 6th edn., Vol. I, Part 4, "Kristalle," p. 91 *et seq.*, Springer, Berlin, 1950.

¹⁰ Buijs and Schutte, *Spectrochim. Acta*, 1962, **18**, 307.

¹¹ Maxwell, Hendricks, and Mosley, *Phys. Rev.*, 1937, **52**, 968.

¹² Durrant and Durrant, "Advanced Inorganic Chemistry." Longmans, London, 1962.

¹³ Van der Wall, U.S.A.E.C. Report IDO-14597 (1962).

TABLE 2.

Volatile metal nitrates, nitrites, and nitrate-complexes.

(References in parentheses.)

Class	Complex	Volatility, °C/mm. Hg	I.r. spectra of solid indicates	B. p. of chloride
A Covalent nitrate- complexes	Cu(NO ₃) ₂ (a)	Subl. 150/vac. (a)	Covalent nitrate- groups (i); also in vapour (6)	CuCl ₂ decomp. to CuCl at 993°
	Hg(NO ₃) ₂ ? (b)	Subl. in vac. (b)	—	HgCl ₂ , 302°
	FeNO(NO ₃) ₄ (b)	Subl. 120/vac. (b)	Covalent nitrate- groups (h)	FeCl ₃ , 315°
	Ti(NO ₃) ₄ (c)	Subl. 20/0.02 (h)	Covalent nitrate- groups (h)	TiCl ₄ , 136°
Covalent nitrate-oxide complexes	Zr(NO ₃) ₄ (d)	Subl. 100/0.01 (d)	Covalent nitrate- groups (d)	ZrCl ₄ , subl. 300°
	Sn(NO ₃) ₄ (e)	Subl. in vac. (e)	—	SnCl ₄ , 114°
	Be ₄ O(NO ₃) ₆ (f)	Subl. 125/0.05 (h)	Covalent nitrate- groups (h)	BeCl ₂ , 520°
	CrO ₂ (NO ₃) ₂ (g)	B. p. 28/0.001 (g)	—	—
	VO(NO ₃) ₃ (g)	Boils 55—60/vac. (g)	—	VOCl ₃ , 127°
B Ionic nitrates	MNO ₃ (where M = Li, Na, K, Rb, Cs)	{ Distil at 350—500/ 0.005	Nitrate ions (7, j)	E.g., NaCl, 1413°
	NH ₄ NO ₃ (k)	Subl. 75/0.001 (h)	Nitrate ions (6)	—
Ionic nitrites	{ NaNO ₂ KNO ₂ NH ₄ NO ₂ (l)	{ Distil at 350—500/ 0.005 Subl. 32/vac.	Nitrite ion (5)	—

Refs.: (a) Addison and Hathaway, *Proc. Chem. Soc.*, 1957, 19; *J.*, 1958, 3099. (b) Addison, Hathaway, and Logan, *Proc. Chem. Soc.*, 1958, 51. (c) Schmeisser, *Angew. Chem.*, 1955, 67, 493. (d) Field and Hardy, *Proc. Chem. Soc.*, 1961, 76. (e) Schmeisser and Brandle, *Angew. Chem.*, 1957, 69, 781. (f) Addison and Walker, *Proc. Chem. Soc.*, 1961, 242. (g) Schmeisser and Lutzow, *Angew. Chem.*, 1954, 66, 230. (h) Field and Hardy, 1962, unpublished work. (i) Addison and Gatehouse, *J.*, 1960, 613. (j) Buijs and Schutte, *Spectrochim. Acta*, 1962, 18, 307. (k) Ray and Jana, *J.*, 1913, 103, 1565; Shah, *J.*, 1932, 731. (l) Neogi and Adhichary, *J.*, 1911, 99, 116.

They are ionic in the solid state and probably exist as ion pairs in the vapour state. The only other nitrite which has been reported to be volatile is that of nickel(II).¹⁴ This was prepared by the gas-phase reaction of dinitrogen tetroxide with nickel carbonyl and was reported to show slight volatility. Infrared absorption bands were present in the solid state which could be ascribed not only to the nitrite ion but also to the covalent nitrito- and nitro-groups; it is not clear whether both ionic and covalent forms exist or whether all the molecules have some covalent character.

Volatility has been reported for a number of metal perchlorates [Cu(ClO₄)₂;¹⁵ CrO₂(ClO₄)₂, VO(ClO₄)₃, SnCl₂(ClO₄)₂;¹⁶], sulphates [CoSO₄, NiSO₄;¹⁷], and acetates [Be₄O(OAc)₆;¹⁸ Zn₄O(OAc)₆;¹⁹ Cu^IOAc²⁰], and it is reasonable to predict that other salts will be found to sublime or distil at reduced pressure and, in particular, some members of classes of oxy-salts which are unstable when heated at atmospheric pressure, e.g., carbonates, chlorates, and sulphites.

Possible Practical Applications.—The nitrates of sodium, potassium, rubidium, and caesium can easily be obtained anhydrous (as "AnalaR" reagents), but lithium nitrate is usually obtained as the trihydrate and is difficult to obtain in an anhydrous state. The method of dehydrating the trihydrate and distilling the anhydrous salt in a vacuum is

¹⁴ Addison, Johnson, Logan, and Wojcicki, *Proc. Chem. Soc.*, 1961, 306.

¹⁵ Hathaway, *Proc. Chem. Soc.*, 1958, 344.

¹⁶ Schmeisser, *Angew. Chem.*, 1955, 67, 493.

¹⁷ Klyachko-Gurvich, Bulgakova, and Gerasimov, *J. Gen. Chem. U.S.S.R.*, 1949, 18, 1580; Landolt-Börnstein Tabellen, 6th edn., Vol. II, Part 2, p. 49, Springer, Berlin, 1950.

¹⁸ Urbain and Lacombe, *Compt. rend.*, 1901, 133, 874.

¹⁹ Auger and Robin, *Compt. rend.*, 1924, 178, 1546.

²⁰ Angel and Harcourt, *J.*, 1902, 81, 1385.

simpler and less expensive than the slow reaction of dinitrogen tetroxide with lithium carbonate which has been recommended recently.²¹

Potassium nitrite is also difficult to obtain pure, and the commercially available material is usually slightly yellow and only about 96% pure. Distilled potassium nitrite is white and the microcrystals exhibit a brilliant iridescence; a study of their optical properties may be rewarding. It should be possible to obtain pure anhydrous nitrites of other alkali metals by this simple method.

Purification by distillation may be particularly useful where crystals or films of these salts are required to be of high purity with respect to heavy metals or non-volatile trace elements. The method will also enable thin films of large surface area to be prepared, and a study to be made of the crystal growth of nitrates and nitrites from the vapour phase on to a variety of substrates for comparison with orientated crystal growth from solution.

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²¹ Archambault, Sisler, and Ryschkewitsch, *J. Inorg. Nuclear Chem.*, 1961, **17**, 130.
