TABLE I

PROPERTIES OF NITROSYL AZIDE OBSERVED IN VARIOUS PROCEDURES

Chemical reaction → Property measured	$NOCl + NaN_3$ (anhydrous)	$NOCl + NaN_3$ (trace of water)	$HNO_3(70\%) + NaN_3$	$HNO_3/H_2SO_4(1:1) + NaN_3$	HNO_3 wh. fum. $+ NaN_3$	$NOSO_2OH + NaN_3$	$NOSO_2OH + HN_3$
Vapor pressure, mm. (°C.) $\log p = 7.306 - 1215.6/T$	200(−32) 60(−58)	20(−68) 30(−66)	30(−61) 31(−67) 70(−50)	40(−61) 37(−62)	35(−60) 37(−60)	70(−51) 30(−62) 42(−60) 205(−30)	37(−62) 60(−50) 37(−61)
M.p. (°C.)	−66 to −59	−60 to −58	−58 to −56	−59 to −55	−60 to −57	−60 to −58	−59 to −57
Nitrogen anal.: calcd. for N_4O; 77.79	76.41	75.09	75.93	75.12	75.93		
Mol. wt.: calcd. for N_4O; 72.04	71.0	71.9		71.8	71.5	70.7	71.5
Yield (%)	1	5	4	5	1	6	5
Other gaseous products Note: N_2O and N_2 common to all preparations			NO_2, N_2O_3 HN_3	NO_2, HN_3	NO_2, HN_3	NO_2, HN_3	NO_2, HN_3

by $\log p = 7.306 - 1215.6/T$ where p is in mm. and T is in degrees Kelvin. The extrapolated boiling point is 1.5°; the heat of vaporization is 5.6 kcal./mole; the Trouton constant is 20.2. The extrapolated boiling point was in good agreement with that which one might expect. Nitrosyl chloride and nitrosyl bromide boil at −6.5°[15] and −2°,[16] respectively. The melting point −60° to −57° falls between those for the corresponding chloride, −64.5°[12] and bromide, −55.5°.[13]

Discussion

Nitrosyl azide is a yellow compound of marked instability. It was possible to prepare this compound by several procedures; however, the amounts obtained were small. The low yields are attributed to its instability and to the slow and incomplete reactions by which it was prepared. Yields based on sodium azide did not exceed about 6%. The yields of the various reactions decreased in the order: $NOHSO_4 + NaN_3 > NOCl + NaN_3$ (moist) $> H_2SO_4/HNO_3(1:1) + NaN_3 > HNO_3(70\%) + NaN_3 > HN_3 + NOHSO_4 > NOCl$(anhyd.) $+ NaN_3$. Although low, yields from $NaN_3 + NOCl$ were increased almost threefold by adding water to the extent of about 60 mg./ml. of NOCl. Excessive quantities of water resulted in reactions which were difficult to control and primarily involved the hydrolysis of nitrosyl chloride. Improvement in the yield could also be obtained by using molar excesses of sodium azide with nitrosyl chloride and in all procedures by operating at the lowest practicable temperature. No significant difference in yield of nitrosyl azide was observed between the preparations in the vacuum system and those at atmospheric pressure; however, vacuum line experiments were simpler from a manipulative standpoint.

The characterization of nitrosyl azide was based on conventional analytical data as well as a study of its decomposition into nitrous oxide and nitrogen and infrared studies. The observation that the compound quantitatively decomposes into equimolar quantities of nitrous oxide and nitrogen not only assisted in identifying nitrosyl azide but also corroborated the results of previous speculations.[5-7]

CLEVELAND, OHIO

[15] L. Beckhan, W. Fessler and M. Kise, *Chem. Revs.*, **48**, 321 (1951).

[16] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. I, Longmans, Green Co., New York, N. Y., 1940, pp. 619–620.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STEVENS INSTITUTE OF TECHNOLOGY]

Radiation Induced Decomposition of Lead Nitrate[1]

BY EVERETT R. JOHNSON

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Lead nitrate decomposes under γ-radiation to yield nitrite ion and oxygen in the stoichiometric ratio 1:1. As the radiation proceeds the yield of oxygen appears to fall off to a steady-state ratio of 2:1. The yield of nitrite ion is decreased by heating at 60° but not the oxygen yield.

The radiation induced decomposition of lead nitrate has been studied by Cunningham and Heal,[2a] and Hochanadel and Davis.[2b] The specific purpose in both papers was to attempt to explain the difference in yields (*G*-values) found, when several nitrates are decomposed by ionizing radiation. Hochanadel and Davis assumed the radiation induced decomposition of lead nitrate to be as indicated in equation 1

$$Pb(NO_3)_2 \rightsquigarrow Pb(NO_2)_2 + O_2 \qquad (1)$$

No gas analysis was performed by these authors and since the yield of nitrite ion was proportional to dose they believed that the above reaction was occurring. It has been found, however, that the radiation induced reaction of lead nitrate is much more complex and cannot be expressed by the simple equation 1 above.

[1] Research supported by the AEC Contract No. AT(30-1)1824.

[2] (a) J. Cunningham and H. G. Heal, *Nature*, **179**, 1021 (1957); (b) C. J. Hochanadel and T. W, Davis, *J. Chem. Phys.*, **27**, 333 (1957).

Experimental

The radiation source was a cylinder of Co_{60} of about 300 curies. The source is so arranged that both the center and outside of the cylinder may be used.[3]

C.P. lead nitrate previously ground to a uniform mesh was placed in small medicinal vials with bakelite caps and irradiated at room temperature. Air was not excluded from the samples. After irradiation analyses were performed for both nitrite ion and oxygen.

Nitrite ion was determined by the color developed with dimethyl-α-naphthylamine-sulfanilic acid reagent. The molar extinction at 5300 Å. was 407.

Oxygen was determined by dissolving a thoroughly evacuated sample in deaerated water in a vacuum system, pumping the liberated gas at Dry Ice temperatures into an analysis system and analyzing by combustion with hydrogen.[4]

Dose was determined by ferrous sulfate dosimetry using a G-value (molecules converted per 100 e.v. absorbed) of 15.5 molecules of Fe^{++} oxidized per 100 e.v. absorbed. The calculated absorption of γ-rays by the lead nitrate was not done as accurately as that by Hochanadel and Davis,[2b] and the G-values reported here are estimated to be in error by about 5%.

Reflectance spectra were performed on powders using the reflectance spectra attachment supplied by the Beckman Instrument Co. for the Beckman DU Spectrophotometer.

Results and Discussion

In Fig. 1 a plot of the oxygen and nitrite ion yields *versus* dose is shown. As can be seen in the initial stages of the decomposition the yields of both products are identical, *i.e.*, the stoichiometric ratio of NO_2^-/O_2 is 1:1. As the radiation proceeds the oxygen yield falls off to what appears to be a steady value of approximately one half the nitrite ion yield, giving a stoichiometric ratio of nitrite ion to oxygen of 2:1. As a comparison and also as a check on the analysis, the radiation induced decomposition of potassium nitrate was done. Typical results are shown in Table I. In the same dose range the ratio of oxygen to NO_2^- for potassium nitrate decomposition is 2:1 in agreement with others.[5] The nitrite ion yields for $Pb(NO_3)_2$ and KNO_3 decompositions are linear at least to a dose in the case of $Pb(NO_3)_2$ of 2.6×10^{21} e.v./g. and for KNO_3 1.6×10^{21} e.v./g.

Equations 2 and 3 below could account for the observed stoichiometry in the initial decomposition, *viz.*, when the ratio of NO_2^-/O_2 1:1, and equation 4 could account for the change in the ratio of NO_2^-/O_2 with dose. The over-all stoichiometry may be represented by equation 5.

$$Pb(NO_3)_2 \rightsquigarrow Pb + 2NO_2 + O_2 \qquad (2)$$

$$2NO_2 + H_2O = 2H^+ + NO_2^- + NO_3^- \qquad (3)$$

$$Pb + {}^1/_2O_2 \rightsquigarrow PbO \qquad (4)$$

$$Pb(NO_3)_2^* + H_2O = PbO + NO_2^- + NO_3^- + {}^1/_2O_2 + 2H^+ \qquad (5)$$

($Pb(NO_3)_2^*$ = irradiated salt)

The above equations are the only ones consistent with the experimental results. No other products such as nitric oxide are present.

The evidence for the existence of PbO is largely indirect. Examination of the X-ray pattern of irradiated $Pb(NO_3)_2$ does give indications of the presence of PbO; however, because of the concentration and the nature of the pattern, positive identification is difficult. Outside of the observed stoichiometry, the best evidence for the existence of PbO is found in examining an aqueous solution of the irradiated salt. A solution of irradiated $Pb(NO_3)_2$ has a very definite amber color which is

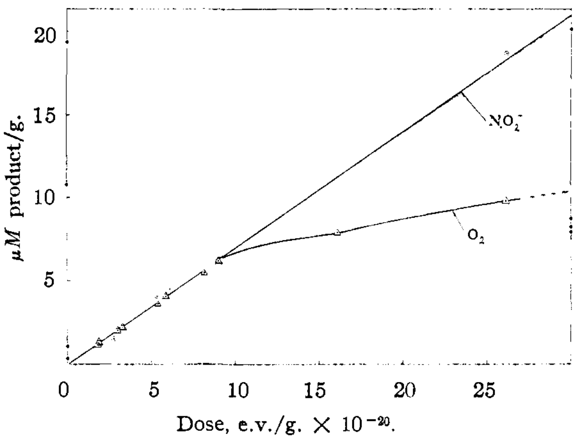

Fig. 1.—Yields of nitrite ion and oxygen as a function of dose.

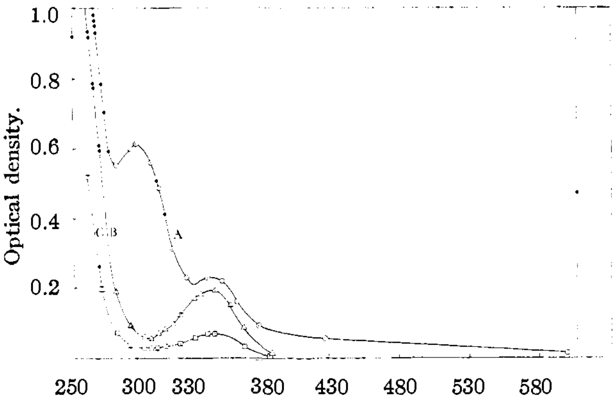

Fig. 2.—Absorption spectra of aqueous lead nitrate solutions: (A) solution of irradiated lead nitrate compared with water; (B) dilute solution of sodium nitrite in unirradiated lead nitrate; (C) irradiated lead nitrate solution compared with unirradiated lead nitrate.

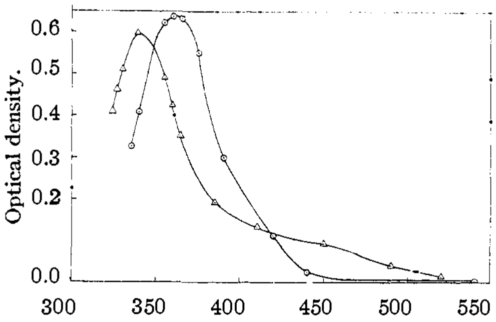

Fig. 3.—Δ, reflectance spectra of irradiated lead nitrate powder compared with the unirradiated salt; ⊙, reflectance spectra of irradiated potassium nitrate compared with the unirradiated salt.

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[3] E. R. Johnson, R. A. Bruce, R. Steinmann and V. Cagnati, *Nucleonics*, **14**, No. 11, 119 (1956).

[4] E. R. Johnson and A. O. Allen, THIS JOURNAL, **74**, 4147 (1952).

[5] G. Hennig, R. Lees and M. S. Matheson, *J. Chem. Phys.*, **21**, 664 (1953).

TABLE 1

COMPARISON OF YIELDS OF KNO_2 AND $Pb(NO_3)_2$

	Dose, e.v./g. × 18 × 10^{-19}	O_2, μmoles/g.	NO_2, μmoles/g.	G/O_2	G/NO_2^-
KNO_3	160	18.8	36.4	0.71	1.38
	65.5	7.5	13.5	.70	1.25
	55.5	6.5	12.5	.71	1.36
$PbNO_3$	90.2	6.3	6.2	.42	0.42
	59.1	4.07	4.08	.42	0.42
	261.0	9.78	18.65	.23	0.43
	161	7.96	...	.31	..

not removed by boiling. The absorption spectra of this solution (curve A,[6] Fig. 2) when compared to that of the non-irradiated salt, shows that NO_2^- is the only new chemical species. The only plausible explanation for the amber color is that it is due to a colloidal suspension and the only feasible substance to be in colloidal suspension is PbO.

A possible mechanism for the decomposition of $Pb(NO_3)_2$ and perhaps other inorganic salts containing both covalent and ionic bonds is that the electronic excitation energy received is rapidly transferred to lattice vibrational energy. This vibrational energy may be assumed to cause high local temperatures[7a,b] which are sufficient to thermally decompose the salt. The products then should be similar to those found in the thermal decomposition. A thermal mechanism is consistent with the observation of Cunningham and Heal[2a] that the yield (*G*-values) of the nitrates is proportional to the "Free Volume" as suggested by Hennig, Lees and Matheson.[5]

There is, of course, no positive evidence to support a thermal mechanism or a free radical mechanism.[2b] However, reflectance spectra of irradiated $Pb(NO_3)_2$ and KNO_3 (Fig. 3) show an absorption maximum at about 3500 Å. A similar peak at about 3600 Å. is found in the reflectance spectra of γ-ray irradiated sodium azide.[8] Heat treatment of unirradiated NaN_3 crystals also produces an absorption band at about 3600 Å. indicating that this band is connected with the decomposition of NaN_3 brought about either by irradiation or thermal treatment.

It is believed that the band at 3400 Å. found in irradiated $Pb(NO_3)_2$ is associated with the decomposition of the material; *i.e.*, it is possible that the band could be associated with metastable nitrate ions. Heating irradiated $Pb(NO_3)_2$ at 60° for several days results in a decrease in the intensity of the band at 3400 Å. with a corresponding decrease in the NO_2^- concentration, but no decrease in the oxygen concentration.

[6] This curve was extended to 1100 mμ not shown in Fig. 2.

[7] (a) F. Dessauer, *Z. Physik*, **38**, 12 (1923); (b) F. Seitz and J. S. Kohler, "Solid State Physics," Vol. II, Academic Press, New York, N. Y., pp. 351–448.

[8] H. Rosenwasser, R. W. Dreyfus and P. W. Levy, *J. Chem. Phys.*, **24**, 184 (1956).

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[CONTRIBUTION FROM THE SPRAGUE ELECTRIC COMPANY]

The Dissociation of Tetrachloroiodide Salts

BY DONALD M. SMYTH AND MARJORIE E. CUTLER

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The total dissociation vapor pressures of the tetrachloroiodide salts $KICl_4$, $RbICl_4$, NH_4ICl_4 and $N(CH_3)_4ICl_4$ have been measured over the temperature range 35–90°. Equilibrium pressures are obtained readily with increasing temperature but extremely slowly with decreasing temperature. Evidence is presented that the dissociation of $KICl_4$ proceeds through the dichloroiodide, $KICl_2$, as a solid intermediate rather than directly to KCl as previously reported.

Although the dissociation vapor pressures of polyhalide salts have been studied by many investigators,[1,2,3,4] the evidence does not indicate clearly whether the dissociation reactions proceed directly to the simple halide or through an intermediate, simpler polyhalide in cases where such an intermediate compound exists. The literature is particularly confusing concerning the mode of decomposition of the salts of the ICl_4^- anion.

Caglioti and Centola[4] have measured the equilibrium halogen pressure over potassium tetrachloroiodide using the technique of Ephraim. They concluded that $KICl_4$ dissociates directly to KCl and ICl_3, the latter undergoing further dissociation to ICl and Cl_2. This would indicate that the dissociation vapor is made up of equal partial pressures of Cl_2 and ICl since the ICl_3 should be completely dissociated under the experimental conditions used. This conclusion is not thermodynamically compatible, however, with the equilibrium pressure of ICl over $KICl_2$ as measured by Cornog and Bauer.[3] We also have measured the dissociation vapor pressure of $KICl_4$ and have made similar measurements on $RbICl_4$, $CsICl_4$, NH_4ICl_4 and $N(CH_3)_4ICl_4$. Our results differ somewhat from those of Caglioti and Centola, and in contrast to their conclusions we have direct evidence that $KICl_2$ is formed as a solid intermediate in the dissociation of $KICl_4$.

Results

The experimentally obtained dissociation vapor data for the several salts are shown in Fig. 1 as plots of log p_{mm} *versus* the reciprocal absolute temperature. The appropriate constants for expressing the pressures in terms of an equation of the type

$$\log p_{\text{mm}} = \frac{A}{T\,^\circ\text{K.}} + B \qquad (1)$$

are given in Table I.

[1] F. Ephraim, *Ber.*, **50**, 1069 (1917).

[2] H. W. Cremer and D. R. Duncan, *J. Chem. Soc.*, 2243 (1931).

[3] J. Cornog and E. E. Bauer, THIS JOURNAL, **64**, 2620 (1942).

[4] V. Caglioti and G. Centola, *Gazz. chim. ital.*, **63**, 907 (1933).