Radiolysis of Inorganic Molecular Ions in Crystalline Solids. Raman Spectroscopic Measurements of the Decomposition of ^{18}O- and ^{15}N-Enriched Polycrystalline Potassium Nitrate and Potassium Nitrite by Cobalt-60 γ-Rays[1]

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Abstract: Laser-excited Raman spectroscopy was employed in the quantitative measurements of the changes produced in the relative abundances of the isotopic nitrate and nitrite ions in oxygen-18- and nitrogen-15-enriched polycrystalline KNO_3 and KNO_2 when these solids were irradiated at room temperature under vacuum and in air with ^{60}Co γ-rays. Strong support for an oxygen-atom mechanism for the radiation-induced decomposition of nitrate ion was given by the observed random substitution of ^{18}O in this ion and in the nitrite ion formed in the KNO_3 by prolonged irradiation under vacuum. The radiolytic oxygen gas possessed the same enrichment as the nitrate from which it was formed and ^{18}O also was randomly substituted, suggesting that a radiation-induced dissociation of O_2 must occur. Irradiations of solid solutions of ^{15}N-enriched KNO_2 in KNO_3 yielded $K^{15}NO_3$ and $K^{14}NO_2$, consistent with the view that oxygen-atom transfer occurred and with the fact that a random substitution of ^{18}O occurred in the enriched KNO_2 (and in its nitrate impurity) when it was irradiated under vacuum. Irradiations in air caused extensive ^{16}O exchange with ^{18}O-enriched KNO_3 and KNO_2, but no exchange of ^{14}N from air with the respective ^{15}N-enriched salts was detected.

Researches on the decomposition of nitrate ion in crystalline alkali-metal and alkaline-earth nitrates by energetic ionizing radiations have led to a general agreement[3,4] that the stoichiometry of the reaction at room temperature is given by

$$\mathrm{MNO_3} \rightsquigarrow \mathrm{MNO_2} + {}^{1}/_{2}\mathrm{O_2(g)}$$

There is less than a general consensus, however, as to the mechanism whereby nitrite and oxygen are formed. Oxygen atoms have been assumed to play an important role[5,6] in the production of nitrite, and it has been suggested that $O_2(g)$ may be formed by an atomic and/or a molecular mechanism but not by direct recombination

$$\mathrm{O} + \mathrm{O} \longrightarrow \mathrm{O_2}$$

because its 100 eV yield appears to be independent of the dose rate.[7]

Oxygen-18- and nitrogen-15-enriched KNO_3 have been employed in several attempts to clarify the mechanism for the radiation-induced decomposition of nitrate ion by ^{60}Co γ-rays, and a surprisingly large ^{18}O kinetic isotope effect (KIE) appears to be reasonably well established for small decompositions. Cunningham[8] first showed that $^{14}N^{16}O_3^-$ ion decomposed 12 ± 2% more easily than $^{14}N^{18}O_3^-$ when KNO_3 was irradiated *in air*, but that in contrast the decomposition of 99.6% ^{15}N-enriched KNO_3 was the same as with KNO_3 of normal nitrogen isotope abundance. The greater decomposition rate of the ^{16}O-substituted ion was confirmed by Ladov and Johnson[9] who have reported a 19 ± 3% difference when ^{18}O-enriched KNO_3 was irradiated. Measurements of the Raman spectrum of a heavily irradiated sample of this $KN^{18}O_3$ by Melveger, Johnson, and Ladov[10] showed that its ^{18}O enrichment diminished from 70.5 to 57%. The relative abundance of the $^{14}N^{18}O_3^-$ was decreased by 65% while that of $^{14}N^{16}O_3^-$ increased over fourfold indicating that an extensive exchange of ^{16}O from air with NO_3^- ions occurs in the presence of ionizing radiation. Significantly, a 13% greater decomposition rate of $^{14}N^{16}O_3^-$ than of $^{14}N^{18}O_3^-$ also has been observed[11] for irradiations of 84% ^{18}O-enriched KNO_3 under vacuum.

A radiolysis mechanism consisting at least of several steps appears necessary to explain a 12 ± 2% KIE in solid KNO_3. A difference of only 3–4% for the breaking of a N–O bond is predicted by theory, and because $(18/16)^{1/2} = 1.06$, an additional 6% effect can be assumed if diffusion of the oxygen atom in the crystal occurs. The requisite total KIE can be attained if a further 3–4% effect is contributed by the breaking of a N–O bond in the reaction of O atoms with nitrate to give oxygen gas. If, however, part of the O_2 is formed directly from a single nitrate ion a smaller KIE should be observed. Pogge and Jones,[11] in fact, have argued for contributions by such a mechanism based on their mass spectrometric measurements of the isotopic composition of the gas formed assuming a 6% KIE for each of the two N–O bonds broken and assuming that their initial ^{18}O-labeled nitrate was stepwise rather than randomly substituted with ^{18}O.

Raman and infrared spectroscopy have been applied in this research to determine the details of the kinetic

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Table I. Radiolysis of ^{18}O-Enriched Polycrystalline KNO$_3$[a]

	Per cent of total nitrate				Total ^{18}O enrichment, %	Per cent of total nitrite			Total ^{18}O enrichment, %
	$N^{16}O_3^-$	$N^{16}O_2{}^{18}O^-$	$N^{16}O^{18}O_2^-$	$N^{18}O_3^-$		$N^{16}O_2^-$	$N^{16}O^{18}O^-$	$N^{18}O_2^-$	
Original NO$_3$ Sample (Not Irradiated)									
Observed	11.7	37.1	37.6	13.6	51.0 ± 0.3				
Calculated	11.8	36.7	38.2	13.3					
KNO$_3$ Irradiated under Vacuum (24×10^{21} eV g^{-1})									
Observed	11.9	36.7	38.0	13.4	51.0 ± 0.3	19.2	57.5	23.3	52.1 ± 0.2
Calculated	11.9	36.8	38.3	13.2		22.9	49.9	27.2	
KNO$_3$ Irradiated in Air (24×10^{21} eV g^{-1})									
Observed	14.7	37.5	35.7	12.2	48.4 ± 0.3	32.5	47.5	20.0	43.8 ± 2.0
Calculated	13.7	38.7	36.2	11.3		31.6	49.2	19.2	

[a] Comparisons between observed ^{18}O-enriched NO$_3^-$ and NO$_2^-$ species concentrations and calculated concentrations on the basis of random distribution.

Table II. Radiolysis of ^{18}O-Enriched Polycrystalline KNO$_3$[a]

	Per cent of total nitrite			Total O^{18} enrichment, %	Per cent of total nitrate				Total ^{18}O enrichment, %
	$N^{16}O_2^-$	$N^{16}O^{18}O^-$	$N^{18}O_2^-$		$N^{16}O_3^-$	$N^{16}O_2{}^{18}O^-$	$N^{16}O^{18}O_2^-$	$N^{18}O_3^-$	
Original KNO$_2$ Sample (Not Irradiated)									
Observed	3.5	31.8	64.7	80.6 ± 0.4	41.8	14.9	20.9	22.4	41.3 ± 1.0
Calculated	3.8	31.2	64.8		20.5	42.9	30.3	7.1	
KNO$_2$ Irradiated under Vacuum (*ca.* 16.3×10^{21} eV g^{-1})									
Observed	4.5	32.0	63.6	79.5 ± 0.4	0.7	13.2	42.1	44.6	77.0 ± 0.5
Calculated	4.2	32.5	63.1		1.2	12.2	40.9	45.6	
KNO$_2$ Irradiated in Air (*ca.* 16.3×10^{21} eV g^{-1})									
Observed	43.6	42.9	13.5	35.0 ± 0.4	8.3	22.6	40.3	28.9	63.3 ± 0.5
Calculated	42.3	45.5	12.3		4.9	25.6	44.1	25.7	

[a] Comparisons between observed ^{18}O-enriched NO$_3^-$ and NO$_2^-$ species concentrations and calculated concentrations on the basis of random distribution.

isotope effect if possible. The effects of radiation on ^{18}O-enriched polycrystalline KNO$_3$ and KNO$_2$ were measured, and ^{15}N-enriched KNO$_3$ and KNO$_2$ were examined to determine if there is a radiation-induced exchange of ^{14}N from air with these salts. Measurements of the relative intensities of laser-excited Raman or of infrared bands were employed in quantitative estimations of the redistribution of ^{18}O or ^{15}N effected by the radiation-induced decompositions. Quantitative, *in situ*, analyses for the concentration of NO$_2^-$ in KNO$_3$ and of NO$_3^-$ in KNO$_2$ were based on band intensities.

Experimental Section

Polycrystalline KNO$_3$ of nominal 41% ^{18}O content and KNO$_2$ of nominal 73% ^{18}O content were obtained from Isomet Corp., Palisades, N. J., and from Miles Laboratory, Elkhart, Ind., respectively. Potassium nitrate enriched to greater than 95% ^{15}N was prepared[12] by neutralizing H^{15}NO$_3$ with freshly prepared KOH. Nominal 82 and 99% ^{15}N-enriched K^{15}NO$_2$ were obtained from Isomet Corp.

Milligram quantities of the normally abundant and isotopically substituted salts were placed in Pyrex glass capillaries and irradiated in air and under vacuum in the center of a 10-kCi ^{60}Co γ-ray source at *ca.* 35°. The dose rate was 1.3×10^{18} eV g^{-1} min^{-1} in water as determined by a Fricke dosimeter with $G = 15.4$ molecules of Fe(II) oxidized per 100 eV absorbed. The doses absorbed by polycrystalline KNO$_3$ and KNO$_2$ were estimated from the dose rate, the duration of the irradiations, and the ratio of electrons per gram of compound to electrons per gram of water (*i.e.*, 0.890 and 0.888, respectively). Raman spectra were measured with a Jarrell-Ash Model 25-300 recording spectrophotometer (Jarrell-Ash Co., Waltham, Mass.). An argon ion laser source of 4880-Å radiation (Spectra-Physics, Mountain View, Calif.) was used to excite the spectra, and a narrow band pass interference filter served to remove Ar$^+$ ion emission lines when required. Frequency calibrations for the Raman spectra were based on these lines. Infrared absorption spectra were measured at liquid nitrogen temperature with a Perkin-Elmer Model 621 spectrophotometer over the frequency interval 250–2000 cm^{-1}, using KBr pellet sampling techniques. Frequency calibration was performed with polystyrene film.

The regions of the ν_1 band of nitrate ion at *ca.* 1050 cm^{-1} and the ν_2 band of nitrite ion at *ca.* 800 cm^{-1} in the Raman spectrum were chosen for the measurements. For the infrared studies, the ν_2 region of nitrate (*ca.* 840 cm^{-1}) and the ν_3 region of nitrite (*ca.* 1275 cm^{-1}) were used. Raman bands from the symmetric vibrational modes were selected because of their large molar scattering coefficients and small half-widths and because they show the largest frequency shifts on ^{18}O substitution.

The four intense Raman bands associated with the totally symmetric stretching vibration of ^{18}O-substituted NO$_3^-$ ion appear to have identical molar scattering coefficients, and, therefore, their relative intensities can be used to estimate isotopic constitution. The intensities of the ν_2 bands of nitrite ion also were taken as linearly proportional to the concentrations of their respective isotopically substituted species. The per cent of ^{18}O enrichment in the initial and radiolyzed KNO$_3$ and KNO$_2$ was estimated by determining the areas under the bands for each isotopic species with a polar planimeter, summing, and computing the percentage of ^{18}O. The uncertainty in the determination of the areas was a major contributor to the error in deriving the relative concentrations of the different isotopic species. This uncertainty was largely governed by the signal-to-noise ratio (S/N) with nonlinearity in phototube response and changes in optical alignment being minor factors. Band areas could be measured to *ca.* 1% when the S/N ratio was large, as in the ν_1 region of NO$_3^-$ ion in the ^{18}O-enriched KNO$_3$. The S/N ratio in the ν_2 region for NO$_2^-$ ion, however, was quite small, and errors in the estimates of the concentrations of the isotopic forms of this ion produced in KNO$_3$ were sometimes as great as 15%. In the measurements of NO$_2^-$ and NO$_3^-$ ions in ^{18}O-enriched KNO$_2$, the S/N ratio was such that the areas of the bands of the isotopically different species possessed errors of between 2 and 5%. The uncertainty in the calculated total ^{18}O enrichments (Tables I and II) is less than that for the isotopic ion concentrations because of the cancellation of errors.

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(12) G. M. Begun, J. S. Drury, and E. F. Joseph, *Ind. Eng. Chem.*, **51**, 1035 (1959).

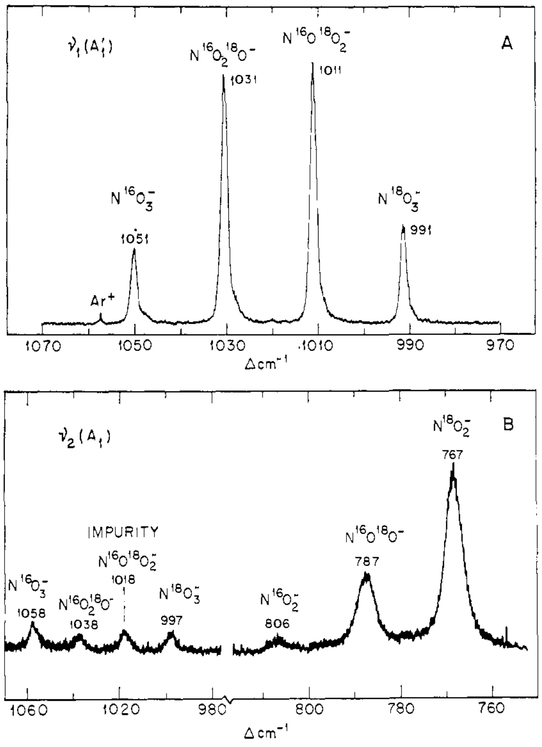

Figure 1. (A) A Raman spectrum of the ν_1 region of unirradiated 51.0% ^{18}O-enriched KNO_3 (1.0 cm⁻¹ slit, 5 × 10³ cps, 0.5 sec period; a weak Ar⁺ ion plasma line appears at 1057.3 cm⁻¹). (B) A Raman spectrum of the ν_2 region of unirradiated 80.6% ^{18}O-enriched KNO_2 (3.0 cm⁻¹ slit, 5 × 10³ cps, 1 sec period, 10 cm⁻¹ min⁻¹ scan speed).

The relative abundances for randomly substituted nitrite ions were computed from the total ^{18}O enrichment of the KNO_2, f_{18}, by the expressions: $F_{16,16} = (1 - f_{18})^2$, $F_{16,18} = 2(1 - f_{18})f_{18}$, and $F_{18,18} = f_{18}{}^2$, respectively. Corresponding expressions for the nitrate ions were: $F_{16,16,16} = (1 - f_{18})^3$, $F_{16,16,18} = 3(1 - f_{18})^2 f_{18}$, $F_{16,18,18} = 3(1 - f_{18})f_{18}{}^2$, and $F_{18,18,18} = f_{18}{}^3$, respectively. These formulas may be derived by statistical methods.[13]

The concentrations of radiolytically produced nitrite in KNO_3 and of nitrate ion in KNO_2 were determined from Raman band intensities following established procedures.[14] Neither the sensitivity nor the accuracy of the Raman method for the measurement of nitrite concentration in nitrate is as great as for the microchemical method.[15] However, the Raman method is more convenient, the total concentration of NO_2^- in the solid is measured directly, and the concentration of each of the isotopically different species can be determined. The sensitivity of detection of nitrate in nitrite, or *vice versa*, is limited to about 0.1 mol % with present instruments. The accuracy of the nitrite or nitrate determinations in KNO_3 or KNO_2, respectively, was about ±5%.

Measurements also were made on solid solutions of isotopically substituted KNO_2 with KNO_3. Thus, for example, an equimolar mixture of 82% ^{15}N-enriched KNO_2 with KNO_3 of naturally occurring nitrogen isotope abundance was prepared by mixing 0.1 *M* solutions of each salt and freeze drying to obtain a polycrystalline solid.

Results

Spectra of Unirradiated ^{18}O-Enriched Salts. The Raman spectrum of ^{18}O-enriched KNO_3 is shown in Figure 1A. The integrated intensities of the isotopic nitrate ion bands give a calculated enrichment of 51.0%, a value somewhat higher than the nominal enrichment of 41% quoted by the vendor (*vide supra*). The intensity ratios of the bands correspond to those expected if there were a random replacement in nitrate ion of ^{16}O by ^{18}O atoms (Table I). The frequency values for the bands were 1051 ± 1, 1031 ± 1, 1011 ± 1, and 991 ± 1 cm⁻¹, which are in agreement with a previous assignment[16] of the ν_1 modes of $N^{16}O_3^-$, $N^{16}O_2{}^{18}O^-$, $N^{16}O^{18}O_2^-$, and $N^{18}O_3^-$, respectively. A small splitting of the nondegenerate $\nu_1(A_1')$ vibration arising from correlation field effects[17] also can be seen in Figure 1A. No nitrite-ion impurity was detected in the ^{18}O-enriched KNO_3.

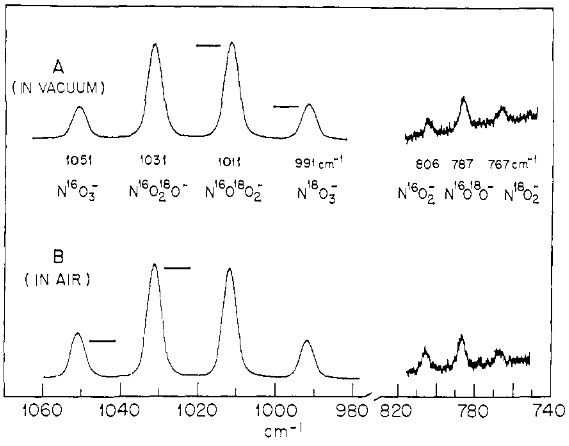

Figure 2. Portions of Raman spectra from ^{60}Co γ-irradiated ^{18}O-enriched KNO_3: (A) irradiated under vacuum; (B) irradiated open to the atmosphere. Both samples received an identical dose of *ca.* 24 × 10²¹ eV g⁻¹. Instrument conditions: (1) nitrite region-3.0 cm⁻¹ slit, 2 × 10³ cps, 5 sec period, 2 cm⁻¹ min⁻¹ scan speed; (2) nitrate region-3.0 cm⁻¹ slit, 1 × 10⁵ cps, 0.5 sec period, 10 cm⁻¹ min⁻¹ scan speed.

The spectrum of nitrite ion in ^{18}O-enriched KNO_2 is shown in Figure 1B. The calculated enrichment was 80.6%, which is slightly larger than the nominal value of 73%. The relative intensities of the three isotopic nitrite bands agree with the statistically predicted intensity distribution estimated with the calculated ^{18}O enrichment. The frequencies of the ν_2 bands for the $^{14}N^{16}O_2^-$, $^{14}N^{16}O^{18}O^-$, and $^{14}N^{18}O_2^-$, ions were 806 ± 1, 787 ± 1, and 767 ± 1 cm⁻¹, respectively.

Figure 1B also shows that nitrate ion was present as an impurity in the ^{18}O-enriched KNO_2. Measurements of the intensities of the ν_2 bands of NO_3^- ion led to an estimate of *ca.* 2 mol % KNO_3 in the KNO_2. Interestingly, the calculated ^{18}O enrichment of the nitrate-ion impurity was 41.3%, a value much less than for NO_2^- ion (80.6%). Moreover, the distribution of ^{18}O among the isotopic nitrate ions was not statistical (Table II).

Raman Spectra of Irradiated ^{18}O-Enriched KNO_3. A comparison of the Raman spectra of ^{18}O-enriched KNO_3 irradiated under vacuum and in air to a dose of 24 × 10²¹ eV g⁻¹ is afforded by Figure 2. Changes in the relative concentrations of the isotopic NO_3^- and NO_2^- ions are given in Table I. Several observations may be made. (a) Irradiation under vacuum produced no change in the ^{18}O enrichment of nitrate ion, but irradiation in air caused a decrease from 51.0 ± 0.3 to 48.4 ± 0.3%. (b) The distribution of ^{16}O and ^{18}O among the isotopic nitrates was changed by

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(13) N. Davidson, Ed., "Statistical Mechanics," McGraw-Hill, New York, N. Y., 1962, p 138ff.

(14) M. H. Brooker and D. E. Irish, *Can. J. Chem.*, 46, 229 (1968).

(15) M. Shinn, *Ind. Eng. Chem., Anal. Ed.*, 13, 33 (1941).

(16) R. Kato and J. Rolfe, *J. Chem. Phys.*, 47, 1901 (1967).

(17) M. H. Brooker, *J. Chem. Phys.*, 53, 2670 (1970).

the irradiation in air; there was a 13% decrease in the relative concentration of $N^{18}O_3^-$ (13.8 to 1.2%) and a 34% increase in $N^{16}O_3^-$ (11.0 to 14.7%). (c) The nitrite ion produced by irradiation under vacuum showed the same enrichment as the nitrate, and the ^{18}O substitution in the nitrite was random within the error in the intensity measurements mentioned earlier. (d) The nitrite produced by irradiation of KNO_3 *in air* showed a 19% decrease in enrichment from that under vacuum (*i. e.*, 52.1 to 43.8% ^{18}O) and an isotopic distribution close to that expected for a random replacement of ^{18}O by ^{16}O. There was a 69% increase in the relative amount of $N^{16}O_2^-$, while the amount of $N^{18}O_2^-$ and $N^{16}O^{18}O^-$ decreased by 15 and 21%, respectively (*cf.* Table I).

Infrared Spectra of Irradiated ^{18}O-Enriched KNO_3. Determinations were made of the infrared absorption spectra of 51% ^{18}O-enriched KNO_3 which had been irradiated under vacuum and in air to doses of 18.5 × 10^{21} and 35 × 10^{21} eV g^{-1}, respectively. The intensities of the ν_2 bands of the isotopic nitrates gave an ^{18}O enrichment of 52% for the vacuum irradiated salt and of 45% for the salt irradiated in air. The intensities of the ν_3 bands of the isotopic nitrites gave an ^{18}O enrichment of 52% for the vacuum irradiation and 41.9% for the irradiation in air. The close similarity of the Raman results (Table I) with those from the infrared determinations supports the view that the former measures the isotopic concentrations throughout the bulk of the KNO_3 sample. It follows that the exchange of ^{16}O from the air with nitrate and nitrite occurs to an appreciable depth below the crystal surface.

Raman Spectra of Irradiated ^{18}O-Enriched KNO_2. Comparisons of the spectra of ^{18}O-enriched KNO_2 irradiated under vacuum and in air to a dose of 16 × 10^{21} eV g^{-1} can be made with Figure 3. Changes in the relative abundances of the isotopic NO_2^- ions are given in Table II. For approximately equal doses, polycrystalline KNO_2 is much more susceptible to radiation-induced ^{16}O uptake from air than is KNO_3. The following detailed observations may be drawn. (a) Nitrate ion was created by irradiation both under vacuum and in air, but the amount formed in air was three times greater than under vacuum. (b) Irradiation of KNO_2 under vacuum produced a small decrease in the ^{18}O enrichment of nitrite ion; however, irradiation in air caused a decrease from 80.6 to 35.0%. (c) The ^{18}O enrichment of NO_3^- ion on irradiation of KNO_2 under vacuum *increased* from 41.3 to 77.0% and appeared to approach the ^{18}O enrichment of the KNO_2; the enrichment increased to only 63.3% for irradiation in air. (d) There were large increases in the concentrations of the $N^{16}O^{18}O_2^-$ and $N^{18}O_3^-$ ions under vacuum irradiation, and the substitution of ^{18}O approached the statistical values. (e) The lowering of the total enrichment of nitrite irradiated in air compared with that for vacuum irradiation was accompanied by a large increase in the concentration of $N^{16}O_2^-$ and a decrease in $N^{18}O_2^-$.

Raman Spectra of Irradiated ^{15}N-Enriched KNO_2 and KNO_3. Polycrystalline KNO_2 enriched to 82% and KNO_3 enriched to greater than 95% in ^{15}N were irradiated *in air* to a dose of *ca.* 16 × 10^{21} eV g^{-1}. The unirradiated enriched $K^{15}NO_2$ has ν_1 = 1301 cm^{-1} and ν_2 = 801 cm^{-1}, whereas $K^{14}NO_2$ has ν_1 = 1322 and ν_2 = 896 cm^{-1}, respectively. The Raman and infrared spectra of the irradiated $K^{15}NO_2$ were measured. The frequencies of the ν_1 (Raman) and ν_2 (infrared) band maxima were unchanged at 1301 and 801 cm^{-1}, respectively, and no $K^{14}NO_2$ was formed as shown by the absence of any increase in intensity at 1322 or 806 cm^{-1}. Unirradiated enriched $K^{15}NO_3$ has ν_2 = 811 cm^{-1} in the infrared, and for $K^{14}NO_3$ ν_2 = 827 cm^{-1}. No change in the relative intensity of these two bands was detected after the irradiation. Raman spectral measurements on $K^{15}NO_3$ gave no indication whatsoever for ν_3 bands of $^{14}NO_3^-$ ion at 1356 and 1361 cm^{-1}, respectively, either before or after irradiation in air. It was concluded that there was no reaction of atmospheric ^{14}N with $K^{15}NO_2$ or $K^{15}NO_3$ induced by ^{60}Co γ-rays in the doses employed.

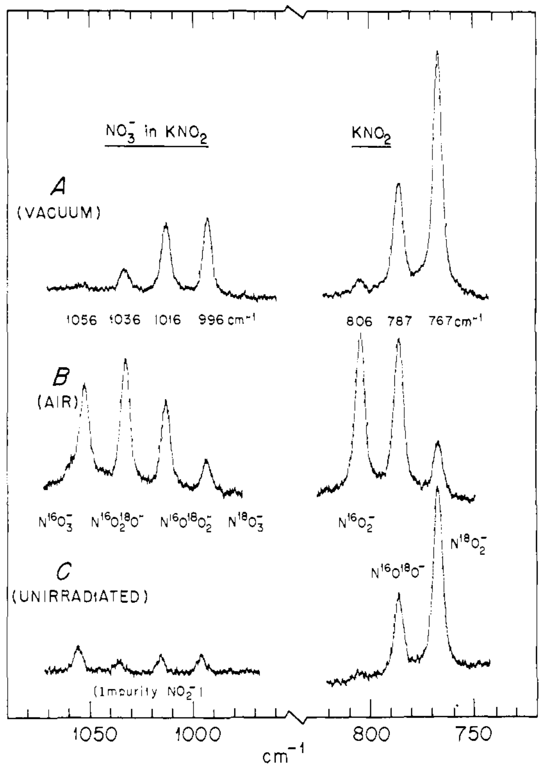

Figure 3. Portions of Raman spectra from ^{60}Co γ-irradiated ^{18}O-enriched KNO_2: (A) irradiated under vacuum; (B) irradiated open to the atmosphere; (C) unirradiated sample. Samples A and B received an identical dose of *ca.* 16 × 10^{21} eV g^{-1}. Instrument conditions: 3.0 cm^{-1} slit, 5 × 10^3 cps, 2 sec period, 10 cm^{-1} min^{-1} scan speed.

Raman Spectra of Equimolar Mixtures of $K^{15}NO_2$ with $K^{14}NO_3$. The changes produced in a solid solution of 82% ^{15}N-enriched KNO_2 with KNO_3 irradiated under vacuum to a dose of 24.8 × 10^{21} eV g^{-1} are shown in Figure 4B. The ν_1 bands for nitrite ion in Figure 4A are for unirradiated $K^{14}N^{16}O_2$ (lower) and unirradiated 82% ^{15}N-enriched KNO_2 (upper), respectively, while the ν_3 bands of nitrate ion in Figure 4C are for unirradiated $K^{14}N^{16}O_3$ (lower) and unirradiated 99% ^{15}N-enriched KNO_3 (upper), respectively. The lower section of Figure 4B shows that a vacuum irradiation of the equimolar mixture of $K^{15}NO_2$ and $K^{14}NO_3$ produced a *decrease* in the intensities of the ν_1 and ν_3 bands of $^{15}N^{16}O_2^-$ and $^{14}N^{16}O_3^-$. The intensity in the frequency region between 1300 and 1330 cm^{-1} is *increased* consistent with the growth of the ν_1 and ν_3

Table III. Radiolysis of ^{18}O-Enriched Polycrystalline KNO_3[a]

	Per cent of total nitrate				Total ^{18}O enrichment, %	Per cent of total oxygen			Total ^{18}O enrichment, %
	$N^{16}O_3^-$	$N^{16}O_2{}^{18}O^-$	$N^{16}O^{18}O_2^-$	$N^{18}O_3^-$		$^{32}O_2^-$	$^{34}O_2$	$^{36}O_2$	
Original ^{18}O-Enriched KNO_3 Sample (Not Irradiated)									
Nonrandom[a]	0.0	0.0	90.0	10.0	70.0				
Calculated random	2.7	18.9	44.1	34.3					
KNO_3 Irradiated under Vacuum (50–50 Mixture)									
Initial isotopic comp[b]	50.0	0.0	18.0	2.0					
Initial isotopic comp calcd[c]	51.4	9.4	22.1	17.1	35.0	45.8[d]	40.2[d]	14.1[d]	34.2
Calcd Random	27.5	44.4	23.9	4.3		43.3	45.0	11.7	
KNO_3 Irradiated under Vacuum (80–20 Mixture)									
Initial isotopic comp[b]	80.0	0.0	18.0	2.0					
Initial isotopic comp calcd[c]	80.5	3.8	8.8	6.9	14.0	76.6[d]	19.8[d]	3.8[d]	13.7
Calcd random	63.6	31.1	5.1	0.27		74.4	23.7	1.9	

[a] Comparisons between observed ^{18}O-enriched oxygen molecule concentrations and calculated concentrations on the basis of random distribution. [b] Incorrectly assumed in ref 14. [c] Assuming ^{18}O randomly substituted in ^{18}O-enriched KNO_3. [d] Observed in ref 14.

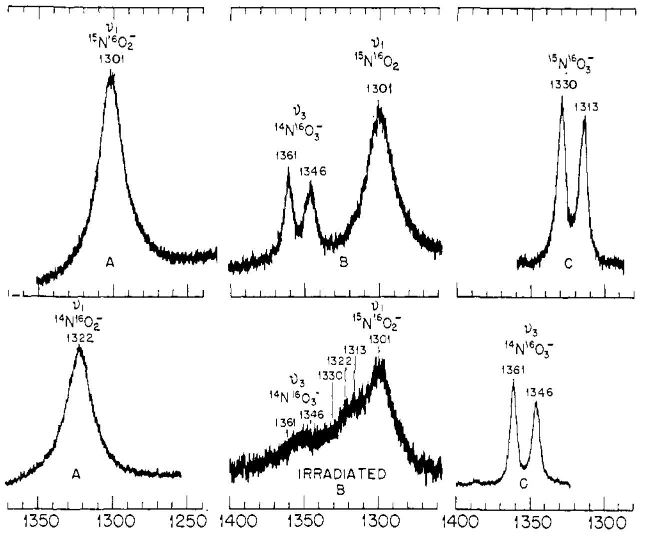

Figure 4. Portions of Raman spectra taken on nonirradiated (upper B) and on ^{60}Co γ-irradiated equimolar mixtures (lower B) of nonenriched KNO_3 (lower C) with ^{15}N-enriched KNO_2 (upper A: 99% $K^{15}N^{16}O_3$).

bands of $^{14}NO_2^-$ and $^{15}NO_3^-$ ions, respectively. Five bands occur in the frequency interval between 1300 and 1370 cm^{-1}, and these are largely unresolved in Figure 4B. It was concluded that a radiation-induced ^{15}N exchange occurred in the solid solution.

$$^{15}NO_2^- + {}^{14}NO_3^- \rightsquigarrow {}^{15}NO_3^- + {}^{14}NO_2^-$$

Production of Nitrite and Nitrate Ions in the Radiolysis of KNO_3 and KNO_2. The concentrations of nitrite ion in polycrystalline KNO_3 and of nitrate in KNO_2 at 25° were measured by the Raman band intensity method. Irradiations of KNO_3 of normal ^{15}O abundance and >95% ^{15}N-enriched KNO_3 to doses of 14.5 and 16.3 × 10^{21} eV g^{-1}, respectively, gave (uncorrected) 100 eV yields of nitrite ion, $G(NO_2^-) = 0.75$ and 0.84, respectively, which are in satisfactory agreement with Ladov and Johnson.[9] Identical values of $G(NO_2^-)$ were obtained for a constant dose irrespective of whether or not the $KN^{16}O_3$ or $K^{15}NO_3$ was irradiated under vacuum or in air.

Significant concentrations of nitrate were produced in the radiolysis of KNO_2 both under vacuum and in air. Thus, $G(NO_3^-) = 1.0 \pm 0.2$ for a dose under vacuum of 16.3 × 10^{21} eV g^{-1} to 81% ^{18}-enriched KNO_2, while with 82% ^{15}N-enriched KNO_2, $G(NO_3^-) = 1.3 \pm 0.2$. Irradiations in air to the same dose as under vacuum gave more than twice the concentration of nitrate in both compounds: with $KN^{18}O_2$, there was an increase from 2.0 to 9.6 mol % nitrate, whereas with $K^{15}NO_2$, the increase was from 1.7 to 8.7 mol %. Oxidation of nitrite to nitrate occurs in air at 25° in the presence of γ radiation.

Discussion

Mechanism for the Radiation-Induced Decomposition of KNO_3. Reactions I–III, in which oxygen atoms are assumed, form the basis for a mechanism which is capable

$$NO_3^- \rightsquigarrow NO_2^- + O \qquad (I)$$

$$O + NO_2^- \longrightarrow NO_3^- \qquad (II)$$

$$O + NO_3^- \longrightarrow NO_2^- + O_2 \qquad (III)$$

of describing many of the details of the radiation-induced decomposition of the alkali-metal nitrates.[5,6] Strong support for this scheme which postulates a back reaction, (II), and an abstraction reaction, (III), for oxygen gas formation is given by the observation (Table I) that prolonged irradiation of KNO_3 under vacuum produced a random substitution of ^{18}O in nitrate and in nitrite ion. Further, the radiolytic nitrite possessed the same total enrichment as the nitrate from which it was formed as expected from (I–III), but not if it had been formed irreversibly and thus was depleted in ^{16}O because of a kinetic isotope effect.

The oxygen gas, if formed irreversibly under vacuum irradiation, should have a lower ^{18}O enrichment than the nitrate from which it was formed. The calculated enrichment in Table III, based on the mass spectrometric analyses of Pogge and Jones,[11] shows only a very slight decrease, and, further, there appears to be a nearly random substitution of ^{18}O in the gas consistent with a radiation-induced dissociation

$$O_2 \rightsquigarrow O + O \qquad (IV)$$

and participation in reactions I–III. The foregoing authors have suggested, however, that their results indicate that a molecular decomposition

$$NO_3^- \rightsquigarrow NO^- + O_2 \qquad \text{(V)}$$

is responsible for about one-third of the gas formed. This interpretation rests on their assumption that the substitution of ^{18}O in the original, unirradiated KNO_3 was nonrandom. The Raman spectra demonstrate, however, that this is incorrect. The relative abundances of the isotopic nitrate ions in the unirradiated KNO_3 in this research were statistical (Table I), and this was also the case for the 70.5% ^{18}O-enriched salt examined by Melveger, Johnson, and Ladov,[10] although these authors do not mention this fact. Other measurements by us with a 91% ^{18}O-enriched $NaNO_3$ gave relative abundances of 75.2, 22.6, 2.2, and <0.1% for fully, doubly, singly, and unsubstituted NO_3^- ion, respectively, which are nearly identical with the corresponding statistical values of 75.4, 22.3, 2.2, and <0.1%. The enriched KNO_3 used by Pogge and Jones (and by Cunningham[9]) was procured from the same sources as the above preparations. We conclude that because of reactions I–IV the enrichment of the radiolytic nitrite and oxygen gas will not reflect the kinetic isotope effect known to occur, and, further, that the relative abundances of the isotopic NO_2^- ions and O_2 molecules should be close to the statistically expected values (*cf.* Tables I and III).

Interestingly, it may be inferred from the results in Table I that reaction II is relatively quite important. For a dose of 24×10^{21} eV g^{-1} approximately 5–6% of the nitrate ions undergo oxygen exchange, but only 2–3% of these ions are decomposed to nitrite.

Oxygen-16 Exchange Reactions Produced by Irradiation in Air. As shown in Table I and by the work of others,[10] irradiation of $KN^{18}O_3$ in air leads to a substantial decrease in its ^{18}O enrichment. Furthermore, the enrichment decrease in the radiolytically formed nitrite is larger than for the nitrate. The data of Table II also show a stronger reduction in ^{18}O enrichment of $KN^{18}O_2$ than of $KN^{18}O_3$ when both are irradiated in air. The substitution of ^{16}O for ^{18}O in both compounds appears to be random. The mechanism for the entry of atmospheric ^{16}O into these crystals would appear to involve reaction IV above, although (VI) cannot be rigorously excluded. Reaction IV may be assumed to occur at the gas–solid interface and to involve the transfer of energy to the surface from the bulk of the solid. The O atoms thus formed will participate in reactions II and III as they diffuse into the crystal. The diffusion of O_2 molecules through the KNO_3 crystal lattice will be much too slow[18] to account for the data.

$$NO_2^- + {}^1/_2O_2 \rightsquigarrow NO_3^- \qquad \text{(VI)}$$

In view of the apparent importance of O atoms in the radiolysis of KNO_3, it is perhaps surprising that identical values of $G(NO_2^-)$ are observed independently of whether or not the salt is irradiated in air or under vacuum. This result may suggest that a steady-state O atom concentration is established, and that reactions II and III compete effectively with one another. The assumption of a steady-state O atom concentration has been employed by Chen and Johnson[19] to give a quantitative description of the dose dependence of the radiation-induced decomposition of KNO_3.

The Absence of Nitrogen Isotope Effects in the Decomposition of KNO_3. No kinetic isotope effect for nitrogen has been observed in the radiation-induced decomposition of KNO_3,[8] nor could any radiation-induced exchange of ^{14}N with either NO_3^- or NO_2^- ions be detected in this work. The first of these observations is consistent with the atomic oxygen mechanism for the decomposition of KNO_3 and confirms the fact that the nitrite which is formed does not further decompose. The lack of any ^{14}N radiation-induced exchange in air may be a consequence of the much higher energy (9.76 eV) required to dissociate N_2 into nitrogen atoms than to produce oxygen atoms from O_2 (5.115 eV). Apparently, also there is no radiation-induced oxidation of nitrogen to give N_2O or NO.

The Radiation-Induced Decomposition of KNO_2. The effects of energetic ionizing radiation on polycrystalline KNO_2 appear to be significantly different from those on KNO_3. Paramagnetic NO_2[20,21] and $N_2O_4^-$[22] are formed and are stable in the solid at room temperature, but oxygen gas is not produced in the radiolysis of KNO_2[11,23] in contrast to KNO_3 indicating that the N–O bond in the nitrite ion is not broken. The radiolysis mechanism is then, at least in part

$$NO_2 \rightsquigarrow NO_2 + e^- \qquad \text{(VII)}$$

$$NO_2 + NO_2^- \longrightarrow N_2O_4^- \qquad \text{(VIII)}$$

The data of Table II, however, show that irradiation of KNO_2 under vacuum or in air produces a random substitution of ^{18}O throughout the solid. Oxygen atoms therefore must be formed, and a likely source of these under vacuum irradiations must be the NO_3^- ion impurity present in a *ca.* 2 mol % concentration. Oxygen-18 therefore can be transferred from enriched nitrite to nitrate, for example, by the reaction

$$N^{18}O_2^- + N^{16}O_3^- \rightleftharpoons N^{16}O^{18}O^- + N^{16}O_2{}^{18}O^- \qquad \text{(IX)}$$

producing a slight reduction in the nitrite enrichment and a substantial increase in the nitrate enrichment (see Figure 4 also). Reaction IX, in fact, appears (*cf.* Table II) to have almost reached equilibrium for a dose of 16×10^{21} eV g^{-1}. Energy transfer in KNO_2 to the nitrate ion impurity is strongly implicated by the observed changes in ^{18}O enrichment and in the relative abundances of the isotopically substituted ions which are close to the calculated values for random substitution.

The changes in enrichment and in relative abundances observed for the irradiations in air can be explained on the basis of reaction II, III, and IV above. The exceptionally rapid rate of ^{16}O substitution into KNO_2 compared with KNO_3 may be related to the fact that the former possesses a disordered crystal structure so that oxygen gas and/or atoms can migrate much more readily than in KNO_3 whose crystals are hard and dense.

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