radical ion favor also the reverse reaction. Aromatic hydrocarbon of greater electron affinity forms a stronger $^-\alpha\alpha$–aromatic$^-$ bond as well as more stable aromatic$\cdot^-$ radical ion.

Conclusions

The electron-transfer processes involved in the oxidation of the dicarbanions, $^-DD^-$ and $^-\alpha\alpha^-$, by aromatic hydrocarbons are initiated by equilibria such as

$$^-DD^- + A \rightleftharpoons {}^-DD\cdot + A\cdot^- \text{ or } {}^-\alpha\alpha\cdot A^- \rightleftharpoons {}^-\alpha\alpha\cdot + A\cdot^-$$

These equilibria lie far to the left, because the electron affinity of $^-DD\cdot$ or $^-\alpha\alpha\cdot$ radicals are much higher than those of the investigated acceptors. Hence, only a minute concentration of $^-DD\cdot$ or $^-\alpha\alpha\cdot$ is maintained in the system, and the decomposition of these radicals, *viz.*

$$^-DD\cdot \longrightarrow D\cdot^- + D \text{ or } {}^-\alpha\alpha\cdot \longrightarrow \alpha\cdot^- + \alpha$$

provides a sink which drives the over-all reaction to the right.

The radical $^-DD\cdot$ is formed directly through electron-transfer process arising from a bimolecular collision between $^-DD^-$ and the acceptor. On the other hand, the investigated acceptors form an adduct, $^-\alpha\alpha$–aromatic$^-$ with $^-\alpha\alpha^-$, which in turn decomposes into $^-\alpha\alpha\cdot$. This indirect route is more favorable than a direct electron transfer. The reaction with Pe$\cdot^-$ is an exception. In this system $^-\alpha\alpha\cdot$ is formed directly in a bimolecular process.

Formation of adducts is not limited to the monoadduct. A diadduct, $^-$aromatic–$\alpha\alpha$–aromatic$^-$, is also formed, but the latter contributes only a little to the oxidation. Its formation accounts for the curious observation that the rate of $^-\alpha\alpha^-$ oxidation increases with the initial concentration of the acceptor, but eventually it reaches a maximum and declines when the acceptor concentration becomes sufficiently high.

Acknowledgment. The financial support of this study by the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

Kinetic Isotope Effect in the Radiation-Induced Decomposition of Crystalline Potassium Nitrate[1]

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Contribution from the Department of Chemical Engineering,
University of Maryland, College Park, Maryland. *Received May 27, 1969*

Abstract: A kinetic isotope effect in the radiolysis of crystalline $KN^{18}O_3$ has been observed which has a maximum of 19 ± 3% at an absorbed dose of 0.5×10^{21} eV/g. The isotope effect is explained by the simultaneous occurrence of two reaction paths which produce an additive isotope effect. One of these paths involves an exciton-induced reaction of randomly diffusing oxygen molecules at preferred lattice sites. The amount of decomposition occurring *via* this reaction path is a function of the concentration of these "preferred" sites which in the case of most inorganic solids is on the order of 10^{17}–10^{19} per cm^3. The other reaction path is that associated with direct decomposition of excited or ionized nitrate ions.

The radiation-induced decomposition of crystalline potassium nitrate by electrons and γ rays has been the subject of numerous investigations.[2–15] The stoichiometry of the room-temperature decomposition is generally accepted to be

$$KNO_3 \rightsquigarrow KNO_2 + {}^1\!/_2O_2 \quad (1)$$

The room-temperature decomposition was shown to exhibit an abnormally high isotopic effect in the oxygen fragment[7] (~13%); however, this effect was only observed in the initial stages of the decomposition (~0.8 mole %). The yield of product as a function of absorbed dose was linear and could be represented as two straight lines intersecting at an absorbed dose of about 7×10^{21} eV/g giving rise to an apparent "break" in the plot, the isotope effect being observed only in the region prior to the "break." A diffusion-controlled mechanism (2), where the oxygen fragment initially produced diffuses away from the NO_2^- simul-

$$KNO_3 \rightsquigarrow [KNO_2 + O] \quad (2)$$

taneously formed, was postulated and the isotope effect was explained by the Franck–Rabinowitch cage effect and the jump frequency of the oxygen fragment. The isotope effect was only evident in the oxygen,

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(1) Research conducted under the auspices of the U. S. Atomic Energy Commission Contract No. AT(40-1)-3660.

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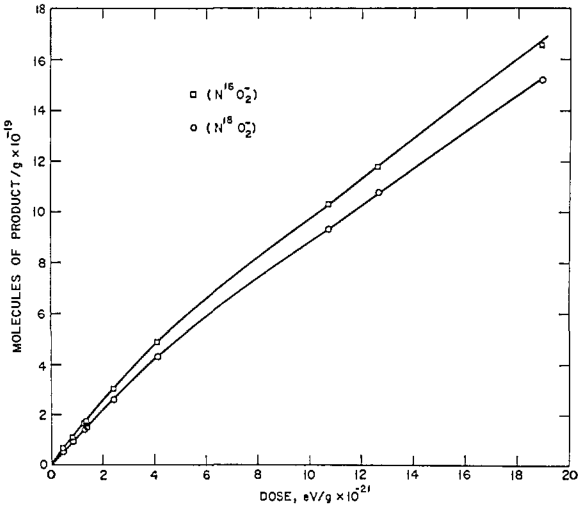

Figure 1. Nitrite yield *vs.* absorbed dose for the decomposition of normal and isotopically enriched (70.5%) KNO_3 at room temperature.

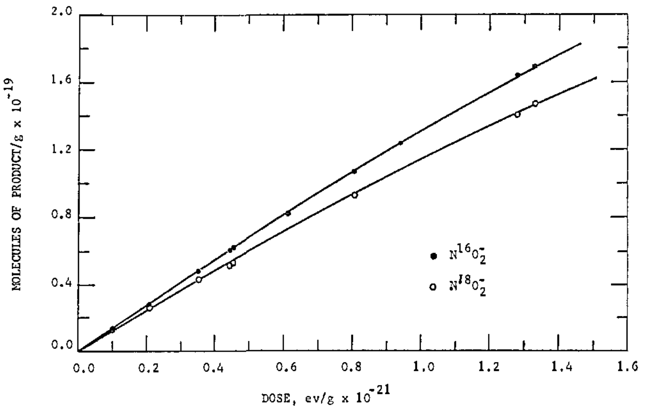

Figure 2. Initial yield *vs.* absorbed dose for the decomposition of normal and isotopically enriched (70.5%) KNO_3.

not the nitrogen; *i.e.*, no isotope effect was observed in $K^{15}NO_3$. The mechanism postulated could not, however, explain the lack of an isotope effect beyond an absorbed dose of about 7 × 10^{21} eV/g. The existence of a back reaction which gives nonlinear NO_2^- yield *vs.* dose curves[8a] and other information obtained in this laboratory and by others[13,14] led us to investigate further this unusually high isotope effect.

Experimental Section

The KNO_3 enriched in oxygen-18 was purchased from Miles Laboratory and was used without further purification. The enrichment, confirmed by Raman spectra, was about 70%. The normal KNO_3 was Fisher Scientific and was crystallized once and dried at about 100°.

Dosimetry was determined by ferrous sulfate oxidation. A G value of 15.45 molecules of ferrous ion oxidized per 100 eV absorbed was used in all calculations.

Nitrite ion was determined by the method of Shinn.[16] The molar extinction coefficient at 536 mμ was 52,000. Ferric ion was determined at 305 mμ, and the molar extinction used was 2201.

The radiation source was a cylinder of cobalt-60 which is described elsewhere.[17] Unless stated otherwise all irradiations were done using the center of the source. Reproducibility was assured by means of a sample holder of fixed position which was rotated at 30 rpm which permitted uniform irradiation of all samples.

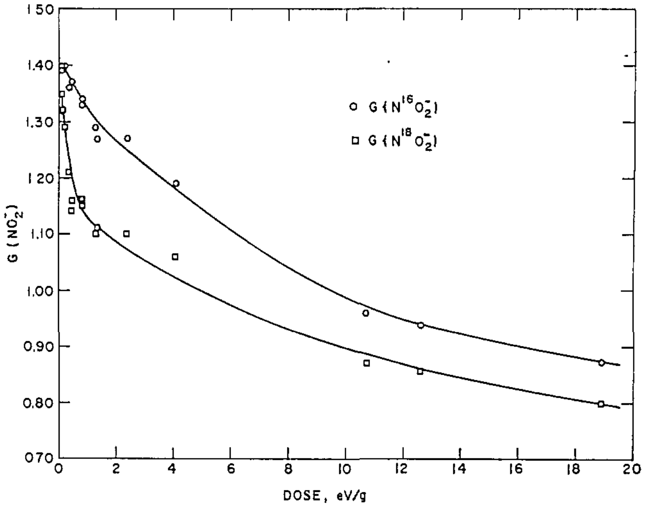

Figure 3. G values for the decomposition of $KN^{16}O_3$ and $KN^{18}O_3$ as a function of absorbed dose.

Results

To ensure good reproducibility the decomposition of normal KNO_3 as a function of dose was first determined. The average of a minimum of four samples at the absorbed doses indicated was used to determine the G value at that point. Subsequently the isotopically enriched salt was irradiated. However, these irradiations were always done simultaneously with additional samples of the normal salt. For example, two samples of $KN^{18}O_3$ were irradiated simultaneously with two samples (all samples of approximately identical weight) of normal KNO_3 in equivalent positions in the source, and the KNO_2 yield was determined. The results for the isotopically enriched and normal salt are summarized in Figures 1 and 2; Figure 2 is the low-dose region. Since the yield *vs.* dose curves are nonlinear, G values (number of molecules decomposed or product molecules formed per 100 eV) are a function of absorbed dose. G values for the normal and isotopically enriched salt are summarized in Table I. Figure 3 is a plot of $G(NO_2^-)$ *vs.* dose for the two salts.

Table I. Decomposition of Normal and Isotopically Enriched (70.5%) KNO_3[a]

Dose, eV/g × 10^{-21}	Molecules of product/g × 10^{-19} $N^{16}O_2^-$	$N^{18}O_2^-$	$G(N^{16}O_2^-)$	$G(N^{18}O_2^-)$	$G(N^{16}O_2^-)$/ $G(N^{18}O_2^-)$
0.101	0.141	0.136	1.40	1.35	1.04 ± 0.02
0.104	0.145	0.137	1.39	1.32	1.06 ± 0.02
0.207	0.289	0.267	1.40	1.29	1.08 ± 0.03
0.351	0.479	0.425	1.36	1.21	1.12 ± 0.03
0.445	0.608	0.509	1.37	1.14	1.19 ± 0.03
0.451[b]	0.619	0.523	1.37	1.16	1.18 ± 0.03
0.807	1.08	0.925	1.34	1.15	1.16 ± 0.03
0.807	1.07	0.936	1.33	1.16	1.15 ± 0.03
1.27	1.64	1.40	1.29	1.10	1.17 ± 0.03
1.33	1.69	1.47	1.27	1.11	1.14 ± 0.03
2.38	3.02	2.62	1.27	1.10	1.15 ± 0.03
4.07	4.87	4.33	1.20	1.06	1.12 ± 0.03
10.7	10.3	9.33	0.963	0.872	1.10 ± 0.03
12.6	11.8	10.8	0.937	0.857	1.09 ± 0.03
18.9	16.6	15.2	0.878	0.804	1.09 ± 0.03

[a] Irradiated at room temperature (20°). [b] Irradiated *in vacuo*.

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Table II. Isotopic Effect as a Function of Temperature

Expt no.	Temp, °K	Dose, eV/g × 10^{-21}	Decomposition, molecules of product/g × 10^{-19}		$G(N^{16}O_2^-)$/ $G(N^{18}O_2^-)$
			$N^{16}O_2^-$	$N^{18}O_2^-$	
			0.315	0.283	
			0.336	0.288	
2	77	0.268	0.326	0.286	1.14
			0.263	0.246	
			0.288	0.246	
3	77	0.230	0.275	0.246	1.12
			0.376	0.341	
			0.376	0.341	
5	343	0.252	0.376	0.341	1.10

For the normal salt the G value at an absorbed dose of 1.04 × 10^{20} eV/g is 1.39 ± 0.02 uncorrected for the differences in mass absorption coefficients for the Fricke solution and KNO_3. This value compares favorably with that of Chen and Johnson, who obtained a G value of 1.40 (uncorrected) for a similar absorbed dose[18] and with that of Hochanadel and Davis,[4] who obtained a value of 1.38 (uncorrected). A value of 1.30 was obtained by Cunningham,[7] 1.33 by Forten and Johnston,[5] and 1.94 by Cunningham and Heal.[3] The last value is probably in error since the authors used calorimetry, and accurate ferrous sulfate dosimetry in the LET region used by these authors was not available.

Figure 4 shows a plot of the ratio of $G(KN^{16}O_2)/G(KN^{18}O_2)$ as a function of adsorbed dose. As can be seen, the ratio rises from a low initial value of 1.04–1.06 to a maximum at an absorbed dose of about 0.45 × 10^{21} eV/g. Beyond an absorbed dose of 6 × 10^{21} eV/g, however, the ratio appears to be constant. The isotope effect is about 19 ± 3% at the maximum and 9 ± 3% at the steady state. Cunningham observed a constant G value ratio for the normal/isotopically enriched (84%) salt of about 1.12 up to an absorbed dose of about 7 × 10^{21} eV/g. Beyond this observed dose he observed a ratio of 1.02 ± 0.07. The results therefore are in rough qualitative agreement; *i.e.*, up to an absorbed dose of about 6 × 10^{21} eV/g the isotope effect is substantially greater than beyond this absorbed dose.

Effect of Temperature. Four samples each of normal KNO_3 and the isotopically enriched salt were irradiated at liquid nitrogen temperatures. The irradiations were done in duplicate; *i.e.*, two samples of $KN^{18}O_2$ and two samples of $KN^{16}O_3$ were irradiated for a total absorbed dose of 0.230 × 10^{21} eV/g and the nitrite yield and the G value ratio $G(N^{16}O_2^-)/G(N^{18}O_2^-)$ determined. The experiment was then repeated. The results for the experiments were 1.14 and 1.12. These results are contrary to those of Cunningham, who found no isotope effect at −110°. Two samples each of the normal and isotopically enriched salt were irradiated at 70° for a total absorbed dose of 0.252 × 10^{21} eV/g. The G values were 1.49 and 1.36, respectively, for the normal and isotopically enriched salt and the ratio was 1.10. These results are summarized in Table II.

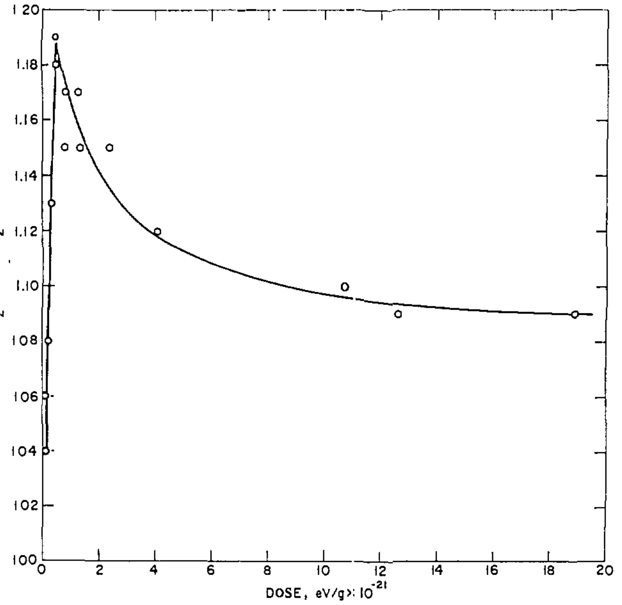

Figure 4. Ratio $G(N^{16}O_2^-)/G(N^{18}O_2^-)$ as a function of absorbed dose.

Annealing Experiments. Two samples each of normal and isotopically enriched KNO_3 were irradiated for 4 hr. One each of the samples was then annealed at 100° for 51.42 hr. All four samples were then reirradiated for an additional 4 hr. No difference in the ratio of G values for the annealed and unannealed samples was observed.

Back Reaction. There is considerable kinetic evidence that a radiation-induced back reaction occurs in the decomposition of KNO_3.

$$KNO_2 + {}^1/_2O_2 \rightsquigarrow KNO_3 \qquad (3)$$

However, this has never been substantiated by other techniques. The Raman spectra of a sample of the isotopically enriched salt before and after irradiation in air are shown in Figure 5. Curve A of Figure 5 shows the Raman spectrum prior to irradiation and curve B after irradiation to an absorbed dose of 1580 Mrads. The four peaks are due to the symmetric stretch of the NO_3^- and are due to $(N^{16}O_3^-)$ at 1052 cm^{-1}, $(NO^-{}_3)$ with one oxygen-18 atom at 1032 cm^{-1}, (NO_3^-) with two oxygen-18 atoms at 1012 cm^{-1}, and $(N^{18}O_3^-)$ at 992 cm^{-1}. As is apparent, the peaks associated with the ^{16}O-rich ion has increased substantially in the irradiated sample whereas those associated with the ^{18}O-rich ion have decreased. The nitrite yield in the decomposition of KNO_3 is not affected by the surrounding atmosphere; *i.e.*, samples irradiated *in vacuo* or in the presence of air or helium all give the same G value for the same absorbed dose. The reaction observed, therefore, is due to the slow diffusion of oxygen into the damaged lattice. Samples of the isotopically enriched salt irradiated to low doses do not show any changes in the relative peak heights because back reaction is primarily with the O_2 trapped in the lattice, and this O_2 has about the same isotopic composition as the salt. The lowest absorbed dose at which an effect was observed was 3.5 × 10^{21} eV/g. At this dose the peak associated with $(N^{16}O_3^-)$ had undergone a 30% increase and the $(N^{18}O^{16}O_2^-)$ peak about a 6% increase.

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(18) Chen and Johnson calculated the absorbed dose using an erroneous value for the mass absorption coefficient of the Fricke solution. The value used was 0.0256; the correct value is 0.308.

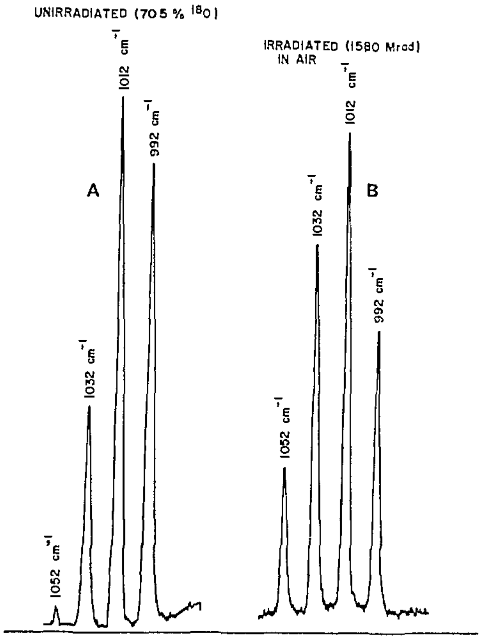

Figure 5. Raman spectra of $KN^{18}O_3$ (70.5% enriched) before and after irradiation to a total absorbed dose of 1580 Mrads.

Effect of Impurities. As indicated in the Experimental Section, the isotopically enriched salt was used as purchased. Analysis of the salt by atomic absorption spectroscopy indicated that the major impurities were $Ca^{2+} = 0.0065\%$ and $Na^{+} = 0.0165\%$. Sodium ion does not appear to have an effect on the decomposition; however, the effect of calcium is unknown. Samples of KNO_3 cocrystallized with $Ca(NO_3)_2$ and containing 0.027 and 0.74% of calcium ion were prepared. The samples were dried in the usual manner for different times. The effect of 0.027% Ca^{2+} on the decomposition on yield is 3% while that of 0.74% is about 9%. If, however, the yield of NO_2^- for KNO_3 is calculated on an electron-fraction basis, the effect of 0.74 %Ca^{2+} is only a few per cent.

The effect of anion impurities introduced during manufacture was also investigated. The $KN^{18}O_3$ is prepared by the exchange reaction of NO_3^- in $H_2{}^{18}O$. Concentrated HNO_3 is added to $H_2{}^{18}O$ and after equilibration neutralized with KOH. The KNO_3 is then separated out and recrystallized. Accordingly, normal KNO_3 was prepared using the method of preparation described for the isotopically enriched salt. One sample was crystallized from an acid solution (pH <1) and another sample of KNO_3 crystallized from a basic solution (pH >10). Both samples were washed and then dried at 100° and then irradiated simultaneously with two samples of that purchased from Fisher Scientific; no effect of sample preparation was observed.

Analysis of Gaseous Product. The oxygen evolved from normal KNO_3 irradiated to at least 5% decomposition was analyzed mass spectrographically. The average of the results of seven separate determinations gave a value for the ratio of oxygen-18 in the gas to that of normal room air of 0.94, indicating that some fractionation of the heavy isotope has occurred. None of the samples revealed the presence of NO_2 or NO.

Mechanism of the Decomposition

As indicated earlier, Cunningham[7] observed the decomposition to be linear with absorbed dose, with an abrupt change in slope at about 7×10^{21} eV/g. To explain his results he proposed a diffusion-controlled mechanism, wherein the rate-determining process is the jump frequency of the oxygen fragment from an excited NO_3^- out of its sibling hole, and the Franck–Rabinowitch cage effect to account for the initial high isotope effect. There are, however, several serious arguments against such a mechanism, most important of which is the fact that the mechanism is not adequate to explain the decrease in isotope effect beyond an absorbed dose of $\sim 6 \times 10^{21}$ eV/g. Subsequent studies by Cunningham[12,19,20] and others[21–27] on esr and optical spectra and effect of pressure on the radiolysis[15] led Cunninhgam to postulate that there are three separable regions in the decomposition of KNO_3. The first of these is in the region $0–0.3 \times 10^{21}$ eV/g (region 0), the second 0.5–5 eV/g (region I), and the third >6 eV/g. The first region he postulated was that in which primary species NO, NO_2^{2-}, $NO_3{}^{2-}$, NO_2, O^-, O, and O_2^{2-} (identified by esr studies at 77°K) are formed. As the concentrations of these species build up they begin reacting with NO_3^- or each other, the reaction being diffusion controlled. This reaction occurs in region I. The last region is characterized by reactions which are no longer diffusion controlled (reactions 4–6 discussed below).

As to the primary species there does appear to be good agreement on the presence of NO_3^{2-} and NO_2 at 77°K in irradiated KNO_3.[22,23] The NO_2 is only observed, however, if NO_2^- is present in the lattice; *i.e.*, no NO_2 is observed in KNO_3 irradiated at 77°K. This species only appears if the irradiated salt is warmed to room temperature (NO_2^- then appears), cooled to 77°K, and then reirradiated, or if KNO_3 doped with NO_2^- is irradiated at 77°K.[22] The species NO_2^{2-}, O_2^{2-}, NO, and O^- have been reported by Cunningham,[20] but have not been confirmed by others.[22,23,25]

As for the radicals NO and NO_2, mass spectrographic analysis of the gas liberated from the decomposition of KNO_3 has not revealed any species other than O_2 and a trace of N_2 (from absorbed air). These analyses have been done on irradiated samples directly connected to the mass spectrometer,[1,2,15] on the gas collected over water[15] after dissolution of the irradiated salt, and by chemical means.[2,8a] The principal evidence advanced for the presence of NO by Cunningham is the fact that KNO_3 irradiated at 77°K and rapidly transferred to acid ceric sulfate solutions produces a reduction of ceric ion in excess of that due to the presence of nitrate ion. This effect is not observed

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when the experiment is repeated at room temperature. A similar effect has been observed in this laboratory when KI solutions are used instead of ceric sulfate. KNO_3 when irradiated at 77°K and rapidly transferred (to prevent warming) to 10^{-3} M KI solution shows an increase in I_3^- absorption in excess of that produced by nitrite ion. An explanation for the reduction of ceric ion and oxidation of iodide ion which does not require postulating any intermediary species is that trapped electrons and holes, produced by irradiation at 77°K, react in the aqueous media as

$$e^- + H_2O \longrightarrow H + OH^-$$

$$(+) + H_2O \longrightarrow H^+ + OH$$

The H atoms are free to reduce ceric ion, and the OH radicals in the absence of cerous ion could combine to form H_2O_2 which readily reduces ceric to cerous. In the case of iodide ion, the H atoms would combine to give H_2, and OH radicals oxidize I^- to iodine atoms which combine to form I_3^-. Reactions of electron-excess and -deficient centers with aqueous media have been well established.[28,29]

An explanation for the observed isotope effect consistent with experiment that does not require postulating the presence of reactive intermediates is that the decomposition of KNO_3 occurs *via* two different reaction paths which give an additive isotope effect, one reaction path occurring only in the initial stages of the decomposition while the other is constant (continuous). The two reaction paths are (1) decomposition *via* excited (or ionized) nitrate ions as has been postulated by several investigators[2-4,6,8a,30,31] (path I)

Path I

$$NO_3^- \rightleftharpoons NO_2^- + O \tag{4}$$

$$O + NO_3^- \longrightarrow NO_2^- + O_2 \tag{5}$$

$${}^1/{}_2O_2 + NO_2^- \rightsquigarrow NO_3^- \tag{6}$$

and (2) reaction of oxygen with nitrate ion at certain preferred locations (cation vacancies, dislocation sites or other) as a result of energy transfer *via*

Path II

$$[NO_3^-] + O_2 \xrightarrow{h\nu} NO_2^- + O_2 + O$$

$$NO_3^- + O \longrightarrow NO_2^- + O_2$$

or

$$O_2 + \text{trapped } e^- + NO_3 \longrightarrow NO_2^- + O_2 + O$$

Reaction path II occurs only as long as these sites are available and only as long as energy transfer can occur. A more detailed discussion of the energy-transfer process will be given in what follows.

Energy Transfer. Energy transfer in inorganic solids is a general phenomenon for which there is substantial evidence.

When KBr plus KNO_3 (about 0.05 wt %) are ground together, formed into a pellet, and then irradiated, $G(NO_2^-)$ is >100 when the absorbed dose is calculated on the basis of the electron fraction of the KNO_3 in the pellet.[32,33]

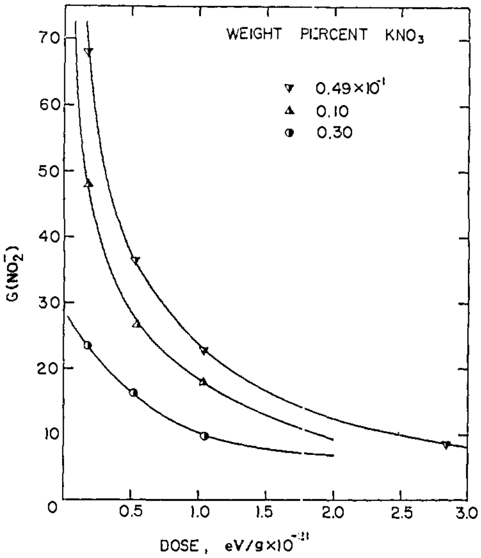

Figure 6. Decomposition of KNO_3 dispersed in KBr matrix (from M. Khare and E. R. Johnson, submitted for publication).

However, the yield of NO_2^- in these systems decreases rapidly with absorbed dose (Figure 6). The explanation for the enhancement in yield is based on energy transfer from the KBr matrix to the KNO_3. The decrease in yield of KNO_2 with absorbed dose in these systems is explained by the buildup of trapping (defect) sites in the KBr lattice which prevent further energy transfer. There is abundant evidence of this phenomenon in the literature on heterogeneous systems[34] which indicates that many inorganic solids are capable of transferring energy, and the ability to do so decreases with total absorbed dose. This effect is explained on the basis that energy is transferred by the substrate to the absorbate. The ability of the substrate to transfer energy decreases rapidly with absorbed dose and goes to zero at an absorbed dose of $\sim 0.5 \times 10^{21}$ eV/g. As with the KBr matrix studies, the fall-off in the ability of the system to transfer energy is attributed to the buildup of trapping sites which prevent energy transfer. Rabe, Rabe, and Allen,[29] in their studies on the radiation-induced decomposition of azoethane absorbed on silica gel, obtained a direct relation between the decrease in decomposition of azoethane and buildup of F center concentration (as determined by chemical analysis) as a function of absorbed dose.

The interesting phenomenon is that the critical absorbed dose in these studies on heterogeneous and alkali matrix systems appears to be about 0.5×10^{21} eV/g; *i.e.*, at about this absorbed dose sufficient trapping sites have been created so that energy transfer can no longer occur.

A plot of the difference in G values of the normal and isotopically enriched KNO_3 as a function of absorbed dose gives a curve identical in form with that of Figure 4. The difference reaches a maximum at an absorbed dose of 0.5×10^{21} eV/g.

The increase in the difference between the G values is due to the occurrence of decomposition *via* reaction path II which reaches a maximum at an absorbed dose of about 0.5×10^{21} eV/g. This is about the absorbed

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[33] M. Khare and E. R. Johnson, submitted for publication.

[34] For general reference see J. G. Rabe, B. Rabe, and A. O. Allen, *J. Phys. Chem.*, 70, 1098 (1966); E. A. Roja and R. R. Hentz, *ibid.*, 70, 2919 (1966).

dose that is observed in energy-transfer studies where energy transfer ceases to operate. What we believe is occuring is that O_2 formed *via* reaction path I undergoes a random diffusion. When it arrives at one of the "preferred" locations (sites), reaction occurs and that particular site is destroyed. This process continues until all these "preferred" sites are consumed. The exciton wave packet reacts only at certain lattice sites, and once decomposition has occurred at these sites the energy-transfer process is no longer operable there. These preferred sites are equivalent to the trapping sites found in the alkali halides; however, in the alkali halides these sites are stable at room temperature, whereas in the nitrates (chlorates, perchlorates, and bromates should also exhibit the same reaction) the sites are destroyed by the chemical reaction. Hence annealing will not rejuvenate the site, as is possible in the alkali halides. Indeed, samples of KNO_3 irradiated to an absorbed dose of 0.1×10^{21} eV/g, annealed at 100 and 25° for 50 hr, and then reirradiated to a total absorbed dose of 0.2×10^{21} eV/g all gave *G* values identical with a sample that has been irradiated without interruption for the same total dose.

We may also view the destruction of the energy-transfer process as occurring *via* interstitial oxygen, *i.e.*, the interstial oxygen acting in a manner to destroy or dissipate (scavenge) the exciton wave packet. The decomposition then would be a competition between diffusion of oxygen to preferred sites and buildup of oxygen (with increasing scavenging of excitons) in the lattice. If this is the situation that prevails, then annealing studies should show some effect. It is also possible that what we are observing is a combination of destruction of preferred sites by chemical reaction and scavenging of excitons by interstitial oxygen.

From the yield of NO_2^- (Table I) we estimate that the total number of these "preferred" sites in the KNO_3 lattice is about 0.5×10^{18} cm^{-3} which is the same order of magnitude as electron excess centers, as determined by chemical means, in the alkali halides.[28,29]

The oxygen that diffuses in reaction path II may be atoms. If so, their concentration would necessarily have to be quite low or their diffusion very rapid, since Hennig, Lees, and Matheson[2] found no net concentration of oxygen atoms by magnetic susceptibility measurements. As for oxygen molecules, they observed that these rapidly diffused into pockets which subsequently grow and coalesce on heating.

Energy transfer is common to all inorganic solids, and we predict that bromates, chlorates, and perchlorates will exhibit an isotope effect analogous to that shown here. In tightly bound lattices such as sodium nitrate which would restrict diffusion, the isotope effect would primarily be as a result of reaction path I.

The isotope effect beyond an absorbed dose of about 5×10^{21} eV/g (steady-state portion of Figure 4) is due to reaction path I and can be adequately explained on the basis of relative rates of the forward and back reactions. An isotope effect of 3–4% for the forward reaction (eq 1) is certainly reasonable[35] as is a similar isotope effect for the back reaction eq 3. This is the conclusion at least of theoretical calculations.[36] This would then, give an over-all isotope effect in this region of about 6–8%.

The isotope effect associated with reaction path II is due in part to diffusion of oxygen to preferred sites and in part to reaction at these sites, the diffusion process contributing about 6% and the chemical reaction about 3–4%. The isotope effect at the maximum, therefore, is the sum of reaction paths I and II which amounts to 19 ± 3%.

The experimental differences in *G* values obtained for the decomposition are for the normally enriched (0.204% ^{18}O) salt and a 70.5% enriched salt. If an extrapolation is made assuming the isotope effect to be linear with enrichment, then the true isotope effect would be about 12 ± 3% at the steady state.

We would expect the maximum observed in the isotope effect to be sensitive to the temperature of irradiation. At low temperatures we would expect the maximum to appear at some higher absorbed dose, whereas at high temperatures it should shift toward lower absorbed doses. At very low temperatures we would expect an isotope effect to occur but restricted to reaction path I only.

Acknowledgments. We wish to thank W. Dorko, National Bureau of Standards, for mass spectrographic analyses, Dr. Charles Dick, also of the National Bureau of Standards, for Van de Graaf irradiations, and Dr. A. Melveger of the University of Maryland Chemistry Department, for performing Raman and infrared spectra.

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