

Effect of Heterophase Additives on the Gamma-Radiolysis of some Nitrates, Eutectic Mixture and Sr²⁺ Doped Eutectic Mixture of NaNO₃-KNO₃.

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ABSTRACT

Studies of gamma-radiolysis of eutectic NaNO₃-KNO₃, pure Cu(NO₃)₂·3H₂O and Sr²⁺ doped eutectic NaNO₃-KNO₃ and in presence of additives like oxides (Co₃O₄, As₂O₃, MgO, Bi₂O₃, Tl₂O₃, PbO, PbO₂, Pb₂O₃) or metal powders (Zn and Cd powders) reveals that, these additives accelerate the rate of radiolysis.

Gamma rays interact with matter mainly by four processes namely photoelectric effect, Compton effect, pair production and photonuclear reactions.

During radiation decomposition of these nitrates, the nitrite (NO₂⁻) formed as a function of dose absorbed in these systems is estimated as G(NO₂⁻) using the modified Shinn's method of di-azo complex. These results are explained on the basis of energy transfer processes occurring at the surfaces of the constituents and also in terms of electron donor-accepter properties of oxides and metal powders.

KEY WORDS: Gamma radiolysis, Heterophase additives, NaNO₃-KNO₃ eutectic mixture..

I. INTRODUCTION

Though the radiolysis of oxy-compounds has been the subject of extensive field of research for many years, a limited work⁽¹⁻⁷⁾ seems have been done on the radiolysis of eutectic mixtures of nitrates, doped eutectic mixtures and the influence of Heterophase additives on nitrate systems.

The present work deals with

- i) the study of gamma radiation decomposition of eutectic of NaNO₃-KNO₃, pure Cu(NO₃)₂·3H₂O crystals.
- ii) the study of effect of dopant (Sr²⁺) on the radiolysis of eutectic of NaNO₃-KNO₃.
- iii) the study of the influence of Heterophase additives, oxides as Co₃O₄, As₂O₃, MgO, Bi₂O₃, Tl₂O₃, PbO, PbO₂, Pb₂O₃ as well as metal powders as Zn and Cd powders on the rate of radiolysis of nitrates, eutectic mixtures and doped (Sr²⁺) eutectic mixture of NaNO₃-KNO₃.

The yield of nitrite in presence of various additives (oxides and metal powders) are determined in given systems of nitrates in order to understand the energy transfer processes taking place at the interface between additive and the nitrate during irradiation.

II. Experimental:

Commercially available AR grade salts and oxides or metal powders required were dried, ground and sieved to a uniform mesh size. The eutectic of NaNO₃-KNO₃ was prepared by mixing NaNO₃ (45%) and KNO₃ (55%), fused at 225^o C and cooled naturally. The Sr²⁺ doped eutectic mixture of NaNO₃-KNO₃ was prepared by adding 5 mole % Sr(NO₃)₂ and then fusing at 225^o C followed by natural cooling. The homogeneity of the doped sample were tested by X-ray diffraction patterns. No appreciable difference in the X-ray patterns of doped and pure nitrate was observed.

The mechanical mixtures containing appropriate quantities of the additives and nitrate were prepared and mixed thoroughly before exposure to gamma radiation. The heterophase additives used are oxides such as Co₃O₄, As₂O₃, MgO, Bi₂O₃, Ti₂O₃, PbO, PbO₂, Pb₂O₃ and metal powders are Zn and Cd powders.

The samples were irradiated in ⁶⁰Co – gamma source with a dose rate of 3.5 KGy. h⁻¹ measured by Fricke dosimeter.

The nitrite (NO₂⁻) formed in irradiated mixture, after dissolution and removal of the insoluble oxide or metal powder, was estimated spectrophotometrically using the modified Shinn's method⁽⁸⁾ of diazo complex.

The formation of nitrite (NO₂⁻) during radiation decomposition of nitrate systems as a function of dose absorbed are plotted. The G(NO₂⁻) values have been computed from the slopes of latter portion of the curve showing linear nature. These G(NO₂⁻) values are tabulated for various systems of nitrates.

III. Results and Discussion:

A) Gamma-radiolysis of some nitrates and eutectic mixture of nitrates.

The results of radiolytic decomposition of eutectic mixture of NaNO₃-KNO₃ and of pure Cu(NO₃)₂.3H₂O crystals are discussed. Further, the effect of heterophase additives on the radiolysis of these nitrate systems are studied.

The formation of nitrite (NO₂⁻) as a function of radiation-dose absorbed in the range of 0 to 10 × 10²⁰ eV.g⁻¹. The examination of the curve, molecules of NO₂⁻ formed against radiation dose, in case of eutectic mixture of NaNO₃-KNO₃ shows two regions, having different slopes through the initial small region is not very distinct. Hence the G-value of this region could not be calculated. The G-values therefore have been computed from the latter portion of the curve showing linear nature.

Table-1 : G(NO₂⁻) values observed in different nitrate systems

System	G(NO ₂ ⁻) values at dose region / 10 ²⁰ eV.g ⁻¹	
	0 to 0.70	0.70 to 10
Pure NaNO ₃ ⁽⁶⁾	-----	0.20

Pure KNO ₃ ⁽⁶⁾	----	0.97
Eutectic of NaNO ₃ -KNO ₃	1.20	0.58
pure Cu(NO ₃) ₂ .3H ₂ O	-----	0.15

It is seen that pure KNO₃ shows highest G-value, while pure Cu(NO₃)₂.3H₂O gives the least one.

The G(NO₂⁻) value in eutectic mixture of NaNO₃- KNO₃ is found to be double in the initial small dose region. Oxy-anionic compounds such as bromates, nitrates, sulphates etc. all undergo decomposition when irradiated by ionizing radiations.

The difference in the rate of radiolysis observed in the two dose regions of eutectic mixture of NaNO₃- KNO₃ is observed due to occurrence of back reactions.

B) Effect of heterophase additives on the gamma-radiolysis of different nitrate systems:

Table- 2 : The G(NO₂⁻) values of nitrate systems in presence of different oxides.

System	G(NO ₂ ⁻) values
Eutectic of NaNO ₃ - KNO ₃	0.58
Eutectic of NaNO ₃ - KNO ₃ +10 mole% MnO ₂	0.57
Eutectic of NaNO ₃ - KNO ₃ +10 mole% Co ₃ O ₄	0.63
Eutectic of NaNO ₃ - KNO ₃ +10 mole% As ₂ O ₃	0.66
Eutectic of NaNO ₃ - KNO ₃ +10 mole% MgO	0.69
Eutectic of NaNO ₃ - KNO ₃ +10 mole% Bi ₂ O ₃	0.76
Eutectic of NaNO ₃ - KNO ₃ +10 mole% Ti ₂ O ₃	0.88
Eutectic of NaNO ₃ - KNO ₃ +10 mole% PbO	0.61
Eutectic of NaNO ₃ - KNO ₃ +10 mole% PbO ₂	0.63
Eutectic of NaNO ₃ - KNO ₃ +10 mole% Pb ₃ O ₄	0.70
pure Cu(NO ₃) ₂ .3H ₂ O	0.15
pure Cu(NO ₃) ₂ .3H ₂ O +10 mole% MnO ₂	0.13
pure Cu(NO ₃) ₂ .3H ₂ O +10 mole% Pb ₃ O ₄	0.21

Table- 3 : The G(NO₂⁻) values of nitrate systems in presence of different metal powders.

System	G(NO ₂ ⁻) values
Eutectic of NaNO ₃ - KNO ₃	0.58

Eutectic of NaNO ₃ - KNO ₃ + 10 mole% Zn metal powder	0.66
Eutectic of NaNO ₃ - KNO ₃ + 10 mole% Cd metal powder	0.70
pure Cu(NO ₃) ₂ .3H ₂ O	0.15
pure Cu(NO ₃) ₂ .3H ₂ O + 10 mole% Zn metal powder	0.16
pure Cu(NO ₃) ₂ .3H ₂ O + 10 mole% Cd metal powder	0.19

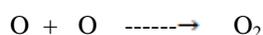
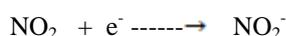
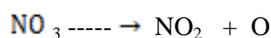
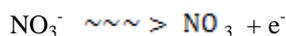
A critical examination of the $G(\text{NO}_2^-)$ values of eutectic mixture of NaNO₃-KNO₃ and of pure Cu(NO₃)₂.3H₂O systems and the effect of heterophase additives (oxides and metal powders) leads to following observations

- 1) The rate of gamma-radiolysis of eutectic mixture of NaNO₃-KNO₃ and of pure Cu(NO₃)₂.3H₂O are affected by the presence of oxides and of metal powders.
- 2) Some oxides enhance the rate of radiolysis of eutectic mixture of NaNO₃-KNO₃ and of pure Cu(NO₃)₂.3H₂O systems while other oxides retard the $G(\text{NO}_2^-)$ values of nitrates.
- 3) Rate of decomposition of eutectic mixture of NaNO₃-KNO₃ as well as of pure Cu(NO₃)₂.3H₂O systems increases in the presence of metal powder to a great extent.

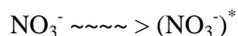
The influence of various oxides on the yield of nitrite(NO_2^-) in different nitrate systems can be explained by considering the energy transfer or electron transfer processes taking place at the interface of the two entities i. e. the oxide and nitrate⁽⁹⁻¹³⁾.

Cunningham⁽²⁾ proposed two mechanisms initiated by excitation and ionization processes for the decomposition of nitrates.

Ionization process:



Excitation process:



Both ionization and excitation processes involve the reactions which include electrons. During gamma-radiolysis of nitrates, these reactions take place generally in the Compton scattering region.

When the admixture containing oxide and nitrate is exposed to gamma rays, excitation as well as ionization processes occur in both the phases of the mixtures. The exchange of energy or electrons takes place between the two components of the mixtures affecting the rate of radiolysis. However, these processes occur only during irradiation.

It is well known that during radiolysis, electron-hole pairs are formed and they combine radiatively or non-radiatively at the defect sites or at the surface of the crystal. Therefore, there is every possibility that the energy is liberated due to recombination of electron-hole pair at the defect site, at the surface of one component to the other component, which in turn may further undergo decomposition reaction. It appears that in admixtures containing one component as oxide such as Co_3O_4 , As_2O_3 , MgO , Bi_2O_3 , Ti_2O_3 , PbO , PbO_2 , Pb_2O_3 and other component nitrate mixtures, the energy absorbed by these oxides during irradiation is effectively transferred to the nitrate leading to the enhancement in the decomposition of nitrate.

In case of additive MnO_2 in eutectic mixture of nitrate, the net transfer of energy during irradiation take place from nitrate lattice to the oxide, leading to the decrease in $G(\text{NO}_2^-)$ value as observed.

Alternatively, the results can also be explained by taking in to account electron donor-accepter properties of oxides added. When an oxide and nitrate is exposed to gamma radiation, electrons are released mainly due to Compton scattering. The electrons possessing sufficient energy due to Compton scattering may cross the surface of the particle of one constituent and even penetrate the surface of other constituent.

If the oxide in the mixture acts as a donor then, there is a net transfer of electrons from oxide phase to nitrate phase. The transferred electrons may then initiate the reactions like excitation and ionization, leading to the enhancement in $G(\text{NO}_2^-)$ values i. e. the decomposition of nitrates. Conversely in case of MnO_2 , it acts as acceptor of electrons, in each cases, there is an effective transfer of electrons from the nitrate to the oxide phase, which is suppressing the process of decomposition.

In metals, the flow of electrons from metal phase to the nitrate is most likely as metals have large number of free electrons available for Compton scattering. Thus flow of electrons seems to be from metal to nitrate which leads to the enhancement in the radiation decomposition of the nitrates as observed in the present studies.

C) Radiolysis of Sr^{2+} doped eutectic mixture of $\text{NaNO}_3\text{-KNO}_3$ and the effect of heterophase additives:

In order to examine the effect of doping on the yield of nitrite $G(\text{NO}_2^-)$, the eutectic mixture of $\text{NaNO}_3\text{-KNO}_3$ doped with 5 mole % Sr^{2+} ions was chosen for the radiolysis. Further, the effect of Heterophase impurity (

oxides and metal powders) on the radiolysis of Sr^{2+} doped eutectic mixture of $\text{NaNO}_3\text{-KNO}_3$ was also examined. The $G(\text{NO}_2^-)$ values are computed from the linear portion of yield verses dose curves.

Table-4: Variation of $G(\text{NO}_2^-)$ values in presence of different heterophase additives in Sr^{2+} doped eutectic $\text{NaNO}_3\text{-KNO}_3$

Sr No.	System	$G(\text{NO}_2^-)$ values , [Dose region 0.70 to 10 X 10^{20} eV g^{-1}
1	Pure $\text{Sr}(\text{NO}_3)_2$ ⁽⁵⁾	0.49
2	Eutectic of $\text{NaNO}_3\text{-KNO}_3$	0.58
3	Sr^{2+} doped Eutectic of $\text{NaNO}_3\text{-KNO}_3$	0.50
4	Sr^{2+} doped Eutectic of $\text{NaNO}_3\text{-KNO}_3$ + 10 mole% Pb_3O_4	0.64
5	Sr^{2+} doped Eutectic of $\text{NaNO}_3\text{-KNO}_3$ + 10 mole% Bi_2O_3	0.71
6	Sr^{2+} doped Eutectic of $\text{NaNO}_3\text{-KNO}_3$ + 10 mole% Zn metal powder	0.63
7	Sr^{2+} doped Eutectic of $\text{NaNO}_3\text{-KNO}_3$ + 10 mole% Cd metal powder	0.71

The $G(\text{NO}_2^-)$ value of $\text{Sr}(\text{NO}_3)_2$ is reported to be lower (0.49) than observed in Eutectic of $\text{NaNO}_3\text{-KNO}_3$ (0.58). The effective $G(\text{NO}_2^-)$ value of Sr^{2+} doped eutectic is lower (0.50) than pure eutectic of $\text{NaNO}_3\text{-KNO}_3$.

Observations in Table-4, further reveals that there is increase in the $G(\text{NO}_2^-)$ value in presence of Heterophase impurities (oxides or metal powders) in Sr^{2+} doped Eutectic of $\text{NaNO}_3\text{-KNO}_3$. For example, the $G(\text{NO}_2^-)$ value for Sr^{2+} doped eutectic containing 10 mole% Bi_2O_3 is found to be 42 % higher than the value observed in pure system. The same percentage increase in $G(\text{NO}_2^-)$ value is also observed in Sr^{2+} doped Eutectic of $\text{NaNO}_3\text{-KNO}_3$ containing 10 mole% Cd metal powder.

These observed results of doped eutectic can be accounted on the basis of same explanation offered in earlier discussion.

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