Nitrogen Containing Phosphorus Oxy-Anions in Neutron Irradiated
Hypophosphites When Dissolved in Liquid Ammonia

CASA, 7-1-65

Sir:

H.C. 3.00; MA 65

The observation (1) that neutron irradiated ammonium hypophosphite showed

1. Anselmo, V. C., in press.

the presence of two activities identified as being nitrogen containing phosphorus oxy-anions, led to the further study of this salt in another solvent. Calcium hypophosphite was studied concurrently because the salt itself has no nitrogen atoms, so the presence of any nitrogen containing species after solution in liquid ammonia would reflect a reaction between a fragment in the solid and the solvent. Ammonium and calcium hypophosphites were irradiated with thermal neutrons in the Omega West Reactor at Los Alamos Scientific Laboratory; quenched and stored in liquid nitrogen; dissolved in the appropriate solvent, and separated. Separation was achieved by means of an anion exchange column after isothermal annealing for a predetermined time. The non-aqueous solvent chosen was liquid ammonia because of the presence of nitrogen atoms and its basicity.

If one considers that the recoiling atom generates a hot-zone during its thermalization, then a large number of fragments will be produced. These fragments are assumed to be found in the same ratio as the atomic ratio in the original salt. Once formed, the fragments will recombine randomly to form binary, tertiary, and even quaternary and higher fragments, with some restrictions, under the impetus of the thermal energy introduced during annealing. Solution of the sample results in a chemical reaction between the solvent and the fragments in their various degrees of association. This is the importance of the solvent reaction and by comparing results with different solvents a mechanism should evolve consistent with this "fragmentation" theory briefly outlined above. Quantitative isothermal annealing data are presented on ammonium hypophosphite dissolved in liquid ammonia. Calcium hypophosphite is virtually insoluble in liquid ammonia, so quantitative data are lacking. The mechanics of the separation and irradiation procedures are described elsewhere (see ref. 1).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

A sample was taken and separated without annealing for what is called a zero time. All other samples were annealed in an air oven at $61 \pm 3^\circ \text{C}$, or $120 \pm 3^\circ \text{C}$. Following annealing, the sample was dissolved in either the eluant (0.025 M NaCl) or in liquid ammonia. In the latter case after solution the solvent was evaporated off and then the residue dissolved in the eluant after which it was added to the column. An example of the quality of the separation is given in Figure 1 and a summary of the results in Table I. The identification of these peaks which are labeled is based on retention times compared to pure compounds. The one labeled P_x is a high molecular weight complex polyphosphate as has been shown (2). There were three additional activities observed in irradiated ammon-

(2) Anselmo, V. C., *Radiochim. Acta*, 4, 203 (1965).

ium hypophosphite when dissolved in liquid ammonia over the experiments in water. These are labeled la, lb, and lc in Figure 1. Peak ld is identical to the activity previously labeled peak 1 (ref. 1) and peak 5 is the same in both conditions. It is suggested that the activities represented in peaks la, lb, and lc are nitrogen containing phosphorus oxy-anions of unknown compositions that are formed by a reaction between a fragment in the solid and the liquid ammonia. Not enough is known of the chromatographic behavior of the amidophosphates or imidophosphates of various oxidation states, to permit exact identification. Figure 2 illustrates the behavior of calcium hypophosphite after reaction with liquid ammonia and treated as described above. Peaks la, lb, ld, and perhaps 5 appear. This is the most conclusive evidence for fragment reactions with the solvent. The first three peaks gave half-lives corresponding to P^{32} . There was no evidence for Ca^{45} in peak la and this is attributed to an experimental oddity that resulted in a precipitate when the residue was dissolved in the eluant after the ammonia had been evaporated from the original reaction mixture. This precipitate was attributed to the incomplete loss of ammonia resulting in a basic solution and hence the precipitation of the calcium as its hydroxide.

A separate experiment was performed to determine if the unique activities observed were real or the result of a chemical reaction between the bulk solute and the solvent. To test this, a sample was first dissolved in liquid ammonia

and then the regular separation procedure followed. The spectrum of activities was identical to that when the sample was dissolved only in the aqueous solvent with the exception that the activity as 1d in irradiated ammonium hypophosphite appeared in 1a.

The zero time value was the most difficult to reproduce and the one reported in Table I is the value farthest removed from the plateau value. The absolute error in all values is estimated at $\pm 2\%$. It should be noted that peak 1c was always less than about 1% of the total activity and was difficult to resolve from 1d. Therefore its activity was included with 1d. In Table II there is a comparison of the results when irradiated ammonium hypophosphite was dissolved in aqueous solvent and liquid ammonia after annealing. From Table II a generalization can be made concerning the behavior of a primary fragment, here defined as PH or PH_2 , from the observation that, among the simple anions, with aqueous solvent the species that increase are peaks 1d and parent (hypophosphite) while in liquid ammonia only parent increases. This definition of the primary fragment is based on a conclusion by Suess (3) that a recoiling fragment is likely

(3) Suess, H., Z. physik. Chem. B45, 312 (1940).

to retain an atom as small as hydrogen and also the absence of orthophosphate in irradiated orthophosphite and hypophosphite. Using this assumption on the nature of the primary recoiling species, then solution of the sample with no annealing results, in the case of aqueous solvent, in orthophosphite or hypophosphite being formed. Annealing increases the probability of the primary fragment reacting with other fragments, e. g., N, O, P, or H, resulting in increasing amounts of nitrogen containing species, oxygen containing ones of the same oxidation state, of the primary fragment, or species that are reduced by reaction with a hydrogen fragment. In the case of solution in liquid ammonia, no annealing should result in the formation of several different nitrogen containing activities while annealing should result in the reduction in the number of these because of reactions between the primary fragment with the other fragments. Specifically, the annealing reactions should manifest themselves in decreasing concentrations of the nitrogen containing activities and increasing concentration of the oxygen containing ones,

among others. This rationalization is adequate for the simple anions and agrees quantitatively with the results. Not enough information is available to be able to predict the difference in rates of formation of the several species because, first of all, the identity of these new activities must be ascertained, and also, not only the statistical probability of recombination of the primary fragments with the other fragments must be known but also the rate of recombination of the fragments to form other stable species, e. g., O_2 , N_2 , H_2 , H_2O , etc., must be calculated.

To summarize, the observation of new nitrogen containing activities in neutron irradiated ammonium hypophosphite dissolved in liquid ammonia, is beginning to shed new light on the reaction of primary fragment resulting from a recoiling P^{32} atom in the hot-zone it created. Further investigation will lead to finer definition of these reactions.

Vincent C. Anselmo (4)

Department of Chemistry

New Mexico Highlands University

Las Vegas, New Mexico

Ernest Sanchez

Radiochemistry Laboratory ✓

Eberline Instrument Company

Santa Fe, New Mexico

(4) The research was supported by Contract AT(11-1)-1618 with the United States Atomic Energy Commission. Acknowledgement is also made of the cooperation of the Los Alamos Scientific Laboratory at whose facilities the irradiations were performed.

LEGAL NOTICE

This report was prepared as an outcome of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission, makes any warranty or representation, expressed or implied with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights, or

B. Assume any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report

As used in the above "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor

TABLE I

Percent P^{32} in Neutron Irradiated $NH_4H_2PO_2$ After Reaction
With Liquid NH_3 at Zero Annealing Time and the Plateau Values

ACTIVITY	Annealing Temperature		
	61 $\pm$ 3 $^\circ$ C		120 $\pm$ 3 $^\circ$ C
	Zero Time	Plateau Value	Plateau Value
Peak 1a	17	5	2
1b	2	2	1
1c+1d	18	10	3
P^1	30	36	45
P^3	7	20	15
Peak 5	3	4	4
P^4 - P^4	3	5	2
P^5 -O- P^5	8	14	28
P^5 -O- P^5 -O- P^5	5	1	1
P_x	9	7	2

TABLE II

Comparison of Results (as Percent P^{32}) With Neutron Irradiated $NH_4H_2PO_2$
Dissolved in Aqueous Solution and Liquid Ammonia Before and After
Annealing at $120 \pm 30^\circ C$

ACTIVITY	Aqueous Solvent (a)		Liquid Ammonia	
	Zero Time	Plateau Value	Zero Time	Plateau Value
Peak 1a	0	0	17	2
1b	0	0	2	1
1c	0	0	} 18	} 3
1d	8	33		
P^1	17	30	30	45
P^3	23	8	7	15
Peak 5	2	3	3	4
$P^4 \cdot P^4$	17	3	3	2
$P^5 \cdot O \cdot P^5$	11	19	8	28
$P^5 \cdot O \cdot P^5 \cdot O \cdot P^5$	} 23	} 4	} 14	} 3
P_x

Fig. 1. Separation of Neutron Irradiated $\text{NH}_4\text{H}_2\text{PO}_2$ Dissolved in Liquid Ammonia Prior to Annealing.

Fig 2. Separation of Neutron Irradiated $\text{Ca}(\text{H}_2\text{PO}_2)_2$ Dissolved in Liquid Ammonia Prior to Annealing.