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FORMATION OF HYDRAZINE FROM THE RADIOLYSIS OF
AMMONIA IN THE PRESENCE OF MINERAL SOLIDS *

Henry Kramer, Jacob Pruzansky, and Meyer Steinberg

Brookhaven National Laboratory

Upton, New York

February, 1962

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Abstract

The formation of hydrazine from the cobalt-60 gamma radiolysis of ammonia in the presence of mineral solids was investigated. Sorbed ammonia on Linde Molecular Sieve 13X powder, binder free, (sodium-alumino-silicate structure) indicated a maximum G value for hydrazine formation of 0.99 based on energy absorbed in ammonia alone. This is 12.4 times the value obtained by radiolysis of anhydrous liquid ammonia. However, the rate of hydrazine formation with sorbed ammonia on the Molecular Sieve is found to be only 1.2 - 3.3 times that in liquid ammonia, and is dose dependent. An energy transfer mechanism has been postulated.

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The radiolysis of anhydrous liquid ammonia has been studied in static systems using cobalt-60 gamma irradiation⁽¹⁾, and in a preliminary fashion with pile radiation combined with fission fragment energy^(2,3). The G value for hydrazine formation in a gamma field is in the range of 0.10 to 0.14, whereas the G value using fission fragment radiation is reported in the range of 1.1 to as high as 2.4. The radiolysis of liquid ammonia in the presence of mineral solids or ammonia sorbed on a mineral solid does not appear to have been investigated. Three questions prompted the investigation of the subject. First, would the presence of a large surface area increase the hydrazine G value? Second, in a heterogeneous system would there be a transfer of energy from one phase to another? Third, could hydrazine, once formed, be protected by occlusion in a solid material; that is, could primary recombination or secondary decomposition reactions be minimized?

To answer these questions a study was made using a variety of mineral substrates of relatively large surface area

with either liquid ammonia or ammonia occluded on a mineral solid. A maximum G value for hydrazine of 0.99 using the Linde Molecular Sieve, Type 13X, in the pure powder form, was obtained.

Experimental

The ammonia used was Matheson's pure grade, 99.95%. Infra red spectra indicated only trace quantities of water and organic material. The various solid powders are described in Table I. The uranium oxides were prepared by reduction or oxidation of UO_2 pellets containing a trace of nitrates. A fixed volume of about 16 cc of solid powder was weighed and transferred to a heavy walled pyrex irradiation vessel equipped with a break seal. This left a void space of about 8 cc in the irradiation vessel. The solids were preconditioned by evacuation and heating at 300°C in a vacuum rack for 18 hours. After evacuation to a pressure of $<10^{-5}$ mm, the radiation vessel was closed, cooled, immersed in an ice bath at 0°C , and equilibrated at 1 atmosphere NH_3 pressure, for ammonia sorption, or in a liquid nitrogen bath when little or no sorption of ammonia was observed. The quantity of gas sorbed or condensed into each vessel was determined manometrically. The irradiation vessel was then sealed under vacuum. The samples were irradiated with cobalt-60 γ rays at various

dose and total dose rates in a stainless steel canister in the BNL cobalt-60 facility. Dosimetry measurements were made with standard ferrous sulfate solutions. The amount of energy absorbed in the solutions calculated using $G(\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}) = 15.8$. After irradiation, each sample was cooled in a liquid nitrogen bath and the break seal opened under 50 ml of water. The ammonia was slowly absorbed by the water and the contents of the irradiation vessel were washed into the beaker. The mixture was stirred with a magnetic stirrer for five to ten minutes. The solution was then decanted into a 250 ml volumetric flask. The residue in the beaker was washed with an additional 50 ml of water and finally with dilute $\text{HCl}(10^{-4} \text{ M})$ in the same fashion. The solution was made to volume and a small quantity was filtered through a millipore filter to eliminate turbidity. A suitable aliquot was analyzed colorimetrically using p-dimethylaminobenzaldehyde, as described by Watt and Chrisp⁽⁴⁾. The 458 m band was scanned with a Beckmann DK-2 spectrophotometer. Reagent blanks were run on the un-irradiated mineral solids, and for the Linde Sieve, Type 13X, powder form, an irradiated blank was run when the material appeared to show an enhanced hydrazine yield. Qualitative tests for nitrate, ferric, and ferrous ions were made.

Results

Table I shows the hydrazine yield expressed first in terms of molecules formed per 100 electron volts of γ ray energy absorbed by the ammonia alone, and then by the entire contents of the vessel including the solid powder.

Although the ratio of $G(N_2H_4)$ values for ammonia sorbed to anhydrous liquid ammonia may show a marked effect, it is more useful to compare the reaction rates of the heterogeneous system, solid plus ammonia, to the homogeneous system, liquid ammonia.

An overall constant rate equation for a static system in a uniform gamma field, assuming a constant G-value, can be expressed as follows:

$$Q = 6.25 \times 10^{15} \frac{GIW}{V} = 6.25 \times 10^{15} GI\rho$$

where Q = rate of hydrazine formation per unit volume of reactant system expressed as molecules of N_2H_4 formed per hr/cc

G = molecules of N_2H_4 formed per 100 ev absorbed in reactant system

W = weight of reactants (NH_3 alone or NH_3 plus solid) in grams depending on definition of G value

ρ = bulk density for the heterogeneous system or the density of liquid ammonia for the homogeneous system.

The above assumes the mass absorption coefficients for the various substrate materials used are the same, which is approximately

true for the 1.13 Mev and 1.37 Mev cobalt-60 gamma photons.

The differences in energy absorption are probably within the accuracy of the dosimetric measurements.

The ratio of the rate of hydrazine formation in the heterogeneous system versus the homogeneous system at a constant dose rate is then

$$\frac{Q(\text{solid} + \text{NH}_3)}{Q(\text{liquid NH}_3)} = \frac{G(\text{solid} + \text{NH}_3) \times \rho(\text{solid} + \text{NH}_3)}{Q(\text{liquid NH}_3) \times \rho(\text{liquid NH}_3)}$$

From unpublished data⁽⁵⁾, the G values for hydrazine in anhydrous liquid ammonia were interpolated for each dose rate and total dose, and presented in Table I for comparison. In Table II the rate of formation of hydrazine for ammonia sorbed on the Linde Molecular Sieve 13X, washed powder, binder free, is compared to the rate of hydrazine formation in liquid ammonia. The results show a ratio of hydrazine formation G values ranging from 9.7 to 12.4 for ammonia sorbed to ammonia liquid in the absence of the sieve, while the rates of hydrazine formation vary from 1.2 to 3.3.

Discussion of Results

The results with the Linde Molecular Sieve, 13X pellets, given in Table I appear to be inconsistent. This is probably due to the clay binder incorporated in the material which contains a high percentage of exchangeable iron. In acid solutions

Most investigators have attributed the low hydrazine yields in static liquid ammonia to the primary recombination process. Reaction (2) cannot be excluded on energetic grounds, but it has been found that molecular hydrogen is not found experimentally in a photo-reaction. Reaction (1) postulating atomic hydrogen was determined by Farkas and Harteck⁽⁶⁾.

Unquestionably, ammonia is occluded in the zeolitic pore structure of the sieve. The pore sites are not completely saturated with NH_3 and can therefore also act as collector sites for the atomic hydrogen which subsequently forms molecular hydrogen. The molecular hydrogen then diffuses out of the pores and collects on other sieve sites thereby minimizing the recombination reaction (4). However, when the relative rate data are taken into consideration, it seems more reasonable to assume an energy transfer function of the sieve in the formation of hydrazine. The rate of hydrazine formation is 1.2 to 3.3 times faster in the presence of the sieve, as shown in Table II. This increase may be due to an increase in the reaction rate of intermediates formed in the adsorbed layer by simple increase of NH_3 concentration due to adsorption, or reactive intermediates from the bulk substrate may diffuse to the surface and there undergo catalyzed reactions.

The G value for hydrazine formation in the γ -radiolysis of anhydrous liquid NH_3 is found to be total dose dependent, and reaches a maximum of approximately 0.1 at a total dose of 1×10^6 Rads⁽⁵⁾. The intensity dependence is not as marked. At a total dose of 2×10^6 Rads, the $G(\text{N}_2\text{H}_4)$ value on the basis of sieve plus ammonia is 0.14 as against an interpolated value of 0.078 in liquid ammonia. Thus it is also possible that the sieve requires "activation" and the optimum total dose has not been reached for this system. Further study, including pre-radiolysis of the sieve and determination of optimum total dose, is required for a more thorough understanding of this system.

Conclusion

The data appear to indicate that sodium aluminosilicate structure is the most effective energy transfer medium among the solids studied for enhancing the yield of hydrazine from the cobalt-60 gamma radiolysis of ammonia.

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Table I											
Hydrazine Yield in the Radiolysis of Ammonia on Mineral Solids											
Experiment No.	Supplier and Trade Name	Approximate Chemical Composition and Particle Size	NH ₃ Condition	Wt NH ₃ Grams	Wt Solid Grams	Dose Rate Megarads/hr	Total Dose Megarads	Wt N ₂ H ₄ Mg	Hydrazine on Mineral Solids		
									G(N ₂ H ₄) NH ₃ Alone	G(N ₂ H ₄) NH ₃ + Solid	G(N ₂ H ₄) * Liquid NH ₃
1	Merck Ignited Aluminum Oxide	Al ₂ O ₃ 74-100μ	Sorbed	0.046	16.0	0.426	40	0.00069	0.011	0.000032	0.0049
2	Harshaw γ - Aluminum Oxide	Al ₂ O ₃	Condensed	3.59	18.5	1.3	1.0	0.050	0.42	0.068	(0.10)
3	Merck Coconut Charcoal	C 74-300μ	Sorbed	0.89	8.0	0.426	40	Nil	Nil	Nil	0.0049
4	Merck Sodium Metasilicate Pentahydrate	Na ₂ SiO ₃ · 5H ₂ O	Condensed	2.29	21.3	1.3	1.0	0.0016	0.021	0.0020	(0.10)
5	Anakron A B S	Diatomaceous earth high in SiO ₂ 137-149μ	Condensed	2.78	17.0	0.285	1.0	0.013	0.14	0.020	0.10
6	Union Carbide Linde Molecular Sieve Pellets, 5A	0.75 CaO, 0.25 Na ₂ O 1.00 Al ₂ O ₃ , 2.00 SiO ₂ · x H ₂ O + Binder, 1/16" pellets	Sorbed	2.30	14.5	0.426	40	0.084	0.027	0.0038	0.0049
7	Union Carbide Linde Molecular Sieve Pellets, 13X	0.83 Na ₂ O, 1.0 Al ₂ O ₃ 2.48 SiO ₂ · x H ₂ O + Binder, 1/16" pellets	Sorbed	2.27	16.0	1.3	1.0	0.033	0.44	0.054	(0.10)
8	As 7	As 7	Condensed	4.18	15.0	1.3	1.0	0.0083	0.060	0.013	(0.10)
9	As 7	As 7	Sorbed	2.45	16.0	4.5	1.0	0.066	0.81	0.11	0.110
10	Union Carbide Linde Molecular Sieve Powder, 13X	0.83 Na ₂ O, 1.0 Al ₂ O ₃ , 2.48 SiO ₂ · x H ₂ O No Binder, 0.8-1.2μ	Sorbed	2.06	13.6	2.2	0.5	0.021	0.61	0.081	(0.053)
11	As 10	As 10	Sorbed	2.75	15.6	1.3	2.0	0.177	0.37	0.14	(0.078)
12	As 10	As 10	Sorbed	1.66	14.6	1.3	1.3	0.066	0.32	0.094	(0.095)
13	As 10	As 10	Sorbed	1.15	14.6	0.285	1.0	0.038	0.99	0.072	0.10
14	Westinghouse Uranium Dioxide	UO ₂	Condensed	4.19	21.0	1.3	1.3	0.012	0.066	0.011	(0.095)
15	Uranium Oxide	U ₃ O ₈	Condensed	4.11	36.9	1.3	1.3	0.0043	0.024	0.0024	(0.095)
16	Uranyl Oxide	UO ₃	Condensed	4.19	16.7	1.3	1.3	0.0086	0.043	0.0098	(0.095)

*The G(N₂H₄) values for anhydrous liquid NH₃ alone indicate interpolated values. (5)

Table II

Ratio of $G(N_2H_4)$ Values and Relative Rates of Hydrazine Formation for
Linde Molecular Sieve Powder, 13X

Exp. No.	Ratio of $G(N_2H_4)$ Values		Dose Rate Megarads/hr	Total Dose Megarads	Density Ratio	
	$\frac{G(N_2H_4, NH_3 + Sieve)}{G(N_2H_4, NH_3, Liquid)}$				$\frac{\rho(NH_3 + Sieve)}{\rho(NH_3, Liquid)}$	Ratio N_2H_4 Rates $\frac{Q(NH_3 + Sieve)}{Q(NH_3, Liquid)}$
10	11.5		2.2	0.50	1.58	2.4
11	12.4		1.3	2.0	1.85	3.3
12	9.70		1.3	1.3	1.64	1.6
13	9.90		0.285	1.0	1.59	1.2

END