U. S. NAVY
OFFICE OF NAVAL RESEARCH
Research Contract N7onr-32912
Project NR 096 162

STUDIES ON HYDRAZINE

Status Report

15 December 1953

by

Harry E. Gunning and Mary L. Kilpatrick

with

C. Luner, C. C. McDonald and R. Pertel

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Department of Chemistry
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A. THE THERMAL DECOMPOSITION OF HYDRAZINE ON VARIOUS SURFACES

Under the direction of Dr. M. L. Kilpatrick, an investigation has been carried out in this laboratory on the thermal decomposition of hydrazine using various surface coatings in the reaction vessel in an attempt to eliminate the heterogeneous component in the reaction.

The apparatus used was developed by Kilpatrick and Hillenbrand in their study of the thermal decomposition of nitromethane.[1] In Technical Report No. 2,[2] a complete description will be given of the experimental techniques and results on the hydrazine decomposition. Discussion here will be limited to a brief account of the status of the investigation.

The thermal decomposition of hydrazine was studied under flow conditions in the temperature range from 300° to 500°C. Carefully purified nitrogen was used as the carrier gas, and the hydrazine was introduced into the carrier gas stream by means of a calibrated motor-driven syringe. In all, four surfaces were investigated: (a) Pyrex, (b) CdS, (c) CaO, and (d) ZnO-KOH-waterglass mixture. For (a) and (c), the surface-to-volume ratio was varied by packing the reaction vessel with Pyrex glass beads having the same coating as the reaction tube.

The results of the investigation showed that the CdS and CaO coatings brought about a large increase in the rate of decomposition of hydrazine over that observed for Pyrex surfaces. These results are not regarded as evidence of a catalytic effect of these surfaces on the reaction rate, since a more logical explanation would be that the enhancement of rate arose from the increased surface-to-volume ratio over Pyrex, owing to the microcrystallinity of the coated surfaces. A comparison of rates for the packed and the unpacked vessels for the CaO coating revealed the interesting fact that the packed vessel caused a considerably smaller increase in rate than was found for the Pyrex surfaces. These results would suggest that the heterogeneous reaction reaches a maximum value at a sufficiently high surface-to-volume ratio.

The ZnO-KOH-waterglass surface gave lower rates than any of the other coatings. In fact, the rates were comparable to those obtained for the uncoated surfaces. The appearance of the coating suggests the reason for such behavior. Thus while the other surfaces were powdery in character,

the waterglass surface had a glass-like appearance indicating a surface-to-volume ratio comparable to the Pyrex surface.

As originally indicated, the homogeneous thermal decomposition would have made an important kinetic study if a suitable coating could have been found. The continued search for a coating becomes the "Edisonian" type of research which is not suitable for graduate students. Consequently, Mr. Pertel was permitted to choose another problem, which does not happen to be in the field of this contract.

Since Mrs. Kilpatrick's return from Denmark, where she was a Fulbright research scholar, she has devoted part of her time to a study of the results of Mr. Pertel's work; and these results are given in Technical Report No. 2.[2] As her own work on the thermal decomposition of nitromethane is now published in the literature,[1] the subsequent work by the Aerojet Corporation, under Contract No. NOa(s)10365, as well as other homogeneous thermal decompositions are being examined critically.

The flow apparatus is now available for further work on thermal decompositions and if the ONR has any considerable interest in a fundamental study of the kinetics of homogeneous gas reactions, Mrs. Kilpatrick would be interested in submitting a proposal, for a three-year study, under the general title, "Kinetics of Homogeneous Reactions in the Gas Phase." If not, she will terminate her connection with this contract and turn attention to other studies in kinetics.

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(1) L. J. Hillenbrand, Jr. and Mary L. Kilpatrick, J. Chem. Phys., 21, 525-535 (1953)

(2) M. L. Kilpatrick, R. Pertel and H. E. Gunning, "The Thermal Decomposition of Hydrazine on Various Surfaces," Technical Report No. 2, Contract N7onr-32912, November 1953

B. THE PHOTOCHEMICAL SYNTHESIS OF HYDRAZINE FROM AMMONIA

During the past four years, fundamental studies have been in progress in this laboratory on the photochemical synthesis of hydrazine from gaseous ammonia. The work has now reached a stage at which the mechanism of the synthesis is sufficiently well understood to enable a reasonable prognosis of the commercial feasibility of the method to be made.

Two methods were studies in detail: (a) the flow photolysis of ammonia at 1849 Å, and (b) the mercury-6($^3P_1$)-photosensitized decomposition

of ammonia under flow conditions, using 2537 Å radiation. Method (a), while commercially uninviting from the outset owing to the high cost of producing 1849 Å radiation, served the dual purpose of providing information on the mechanism of the reaction under the simple conditions of direct photolysis, as well as establishing continuity with the large body of published literature on the photolytic reaction at other wavelengths in the absorption spectrum of ammonia. Our work on the photolytic reaction has been prepared for publication,[3] and this manuscript has already been reviewed by the Office of Naval Research. In addition, the work was presented at the "Symposium on Hydrazine and Its Applications" sponsored by the Committee on Fuels and Lubricants, Department of Defense, which was held at the Department of Chemistry, Illinois Institute of Technology, February 2-3, 1953. The manuscript has appeared in the confidential report of the aforementioned symposium,[4] and the essential material of the manuscript has been submitted to ONR as Technical Report No. 1.[5]

In Technical Report No. 3,[6] the doctoral thesis of Mr. C. C. McDonald of this laboratory, which is in preparation, a comprehensive discussion of our fundamental studies on both the photolytic and photosensitized reactions under both static and flow conditions will be given. From that report, pertinent data will be cited here. In addition, data have been obtained on a larger reactor by Dr. C. Luner of this laboratory. Our detailed findings will be included in a later technical report, and only the salient features will be brought out in the present report.

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(3) C. C. McDonald, A. Kahn and H. E. Gunning, J. Chem. Phys., (submitted for publication)

(4) Symposium on Hydrazine and Its Applications, Vol. 1 (1953) p. 36

(5) C. C. McDonald, A. Kahn and H. E. Gunning, "The Photolysis of Ammonia at 1849 Å in a Flow System," Technical Report No. 1, Contract N7onr-32912, February 1953

(6) C. C. McDonald and H. E. Gunning, "Chemical Effects of Resonance Radiation, including the Photodecomposition of Ammonia," Technical Report No. 3, Contract N7onr-32912, January 1954

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1. Current Status of the Investigation of the Mercury-6($^3P_1$)-Photosensitized Synthesis of Hydrazine from Gaseous Ammonia

Our fundamental study of the reaction, employing a small reactor with light intensities variable in the range from 0.4-1.2 x 10^{-4} einsteins (moles of quanta) per minute, has been completed. From these data a very clear understanding can be obtained concerning the conditions

most favorable for hydrazine formation. The essential features of our findings are summarized below:

(a) The products of the reaction under static conditions are exclusively nitrogen and hydrogen in 1:3 ratio.

(b) Hydrazine appears as a recoverable product of the reaction at linear flow rates of ammonia greater than approximately 5 cmm per second.

(c) The quantum yield of ammonia consumption, i.e., moles of ammonia decomposed per einstein of radiation absorbed, decreases slowly from 0.3 at 50 mm. to 0.1 at 700 mm. ammonia pressure.

(d) The quantum yield of ammonia consumption is independent of the linear flow rate of the ammonia molecules through the reaction zone.

(e) When corrections are made for incomplete quenching of the photo-excited atoms by the ammonia molecules, the results indicate that the quantum yield approaches unity at low pressures.

(f) The percentage of the decomposed ammonia which was recovered as hydrazine increased rapidly with increasing linear flow rate at a given ammonia pressure.

(g) For a given linear flow rate the percent hydrazine recovered increased with increasing ammonia pressure. It may be reasonably assumed that at linear flow rates greater than 120 cm. per second, at least 90% of the ammonia decomposed can be recovered as hydrazine for substrate pressures greater than 500 mm.

(h) It was found that the quantum yield of ammonia consumption increased linearly with increasing light intensity. However, the percentage of the ammonia decomposed which was recovered as hydrazine, ceteris paribus, decreased linearly with increasing light intensity.

(i) The addition of ethylene was shown to have a marked effect on the percentage of ammonia recovered as hydrazine, while preserving the quantum yield of ammonia consumption constant. Thus percentage hydrazine increased from 40% to 93% upon the addition of 8 mm. of ethylene to the ammonia stream which was flowing at 16 cm. per second at 360 mm. pressure.

In the large reactor, results which have been obtained to date are in excellent agreement with the quantitative findings on the smaller system. The lamp intensity is variable from approximately 1 to 5×10^{-3} einsteins per minute. The major difficulty encountered in this aspect of the work involves the achievement of sufficiently high linear flow rates for high hydrazine recovery. Owing to the large cross section of the reactor,

linear flow rates could not be achieved greater than 20 cm. sec. under laboratory conditions. The data on quantum yield of ammonia consumption and percentage hydrazine recovery were in consonance with the values obtained in the smaller reactor at the same flow rates and reaction pressures.

2. An Evaluation of the Mercury-Photosensitized Synthesis of Hydrazine

The quantum yield of hydrazine formation will be one-half of that for ammonia consumption, provided that the reaction proceeds according to the stoichiometry

$$2\ NH_3 \rightarrow N_2H_4 + H_2.$$

This stoichiometry is approached at linear flow rates greater than 140 cm. per second at light intensities of 10^{-4} einsteins per minute. At higher light intensities (see section (h) above), the quantum yield of hydrazine formation slowly decreases. However, the addition of an H-atom acceptor such as ethylene appears to negate the undesirable intensity effect on the quantum yield of hydrazine formation. Consequently, it would seem reasonable to assume that conditions can be so adjusted that the above stoichiometry is obeyed.

The use of the 2537 Å resonance lamp obviates the necessity of using quartz in its fabrication. Thus the lamp can be made of Vycor No. 7910 glass which is a 96% silica glass, costing approximately one-tenth the price of optical quartz. Such a lamp emits 30% of its input wattage as 2537 Å radiation. Lamps of this type are the most efficient monochromatic sources known.

In Table 1, power costs per pound of hydrazine produced are calculated as kilowatt hours per pound of hydrazine, for various values of the quantum yield of hydrazine formation.

TABLE 1. KILOWATT HOURS REQUIRED TO PRODUCE ONE POUND OF HYDRAZINE AS A FUNCTION OF THE QUANTUM YIELD OF HYDRAZINE FORMATION

Quantum Yield of Hydrazine Formation	KWH per pound of Hydrazine Produced
0.0	∞
0.05	124
0.10	62
0.20	31
0.3	21
0.4	15.5
0.5	12.4

Our data indicate that the quantum yield of ammonia consumption varies from 0.3 to 0.1, and hence the quantum yield of hydrazine consumption would lie in the range from 0.15 to 0.05, assuming no nitrogen formed. Hence the minimum power required for operation of the lamps would be approximately 45 KWH/lb. At 0.5 cents per KWH, this figure would yield a minimum value of 22.5 cents per pound of hydrazine. Such a figure would require that the reaction be run at 50 mm. ammonia pressure in stream, with linear flow rates greater than 140 cm. per second. This cost estimate, it should be emphasized, refers only to the power consumption in the operation of the lamps. The overall cost of producing hydrazine by this method would necessarily be increased by other operating costs associated with the process.

3. A Program for the Photochemical Synthesis of Endothermic Compounds

Over the past four years, during which time the photochemical hydrazine synthesis has been studied in this laboratory, a great deal of experience has been accumulated on the synthesis of such endothermic compounds as hydrazine. In addition, a well-equipped laboratory for photochemical investigations has been developed. There are two general attributes of the synthesis of endothermic compounds which deserve enunciation. These are that chain reactions are extremely unlikely to occur and that flow conditions will in general be required for high yields. The absence of chain reaction requires that the lamps used be of high efficiency. It was for this reason that mercury resonance lamps were employed in the hydrazine synthesis. Research has been in progress for some time on the development of more intense sources of mercury resonance radiation. Higher intensity sources would obviate the necessity of using bulky installation involving large quantities of expensive ultraviolet-transmitting glasses such as Vycor or quartz. On the present contract, the possibility of using salts of mercury in the resonance lamp is being studied as a means of increasing intensity.

Reference to Table 1 shows that at a quantum yield of 0.5, 12.4 KWH are required to produce 454/32 moles of product. This amounts to 0.87 KWH per mole. Higher efficiencies in radiation production and higher quantum yields would reduce this number still more. At an average molecular weight of 80, for the endothermic compound, about 8 KWH would be required per pound of product produced, which is equivalent to a power cost of roughly 4 cents on a 5 mill basis. The foregoing calculations indicate that the photochemical synthesis of endothermic compounds falls well within the range of economic feasibility.

It is therefore proposed that a general program be initiated in this laboratory on the study of photochemical reactions wherein the possibility of synthesizing endothermic compounds is the principal criterion of choice of the reaction to be studied.

Experience has shown that such programs are most fruitful when contractual arrangements can be made on a three-year basis, corresponding to the average residence time for the doctoral program. If it is assumed that the equipment now on hand which has been purchased with ONR funds can be retained in this laboratory, substantial economies will be reflected in the proposed budget. Thus a program embracing three graduate assistants could be satisfactorily operated for three years on a total budget of $60,000. A detailed proposal will be submitted on request.

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