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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

# Photochemical Investigations. IV. The Photochemical Decomposition of Deutero-ammonia[1]

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The photochemical decomposition of deutero-ammonia is of interest since it can be investigated at wave lengths which, although near one another in wave length, show different types of absorption. Both ammonia and deutero-ammonia show absorption beginning at about λ 2300 Å. and extending to shorter wave lengths.[2] In ammonia the bands are diffuse, but in the case of deutero-ammonia the principal band at λ 2136–39 Å. is discrete, while at about λ 2105–22 and λ 2065–80 Å. there are exclusively diffuse bands.[3] The latter $ND_3$ bands correspond to predissociation and the primary process should presumably be the same as in the similar ammonia bands, a dissociation into $ND_2$ and D. Absorption of light in the discrete band should result in the formation of an electronically excited molecule. The photochemical decomposition of deutero-ammonia in the bands at about λ 2136–39 and 2105–22 Å. might, therefore, proceed differently, although the energies involved are almost identical.

This paper presents the results of a study of the photolysis of deutero-ammonia by the zinc spark lines at λλ 2138 and 2100 Å., in the discrete and diffuse bands, respectively. In order to compare these results with those for ammonia, measurements of the quantum yield for the latter at λ 2100 Å. were also made in the same cell.

## Experimental Details

The light source and apparatus were the same as those used in previous investigations dealing with ammonia.[4] As the two earlier cells were not available, use was made of a third cylindrical cell, Cell 3, 25 mm. in diameter and 100 mm. long, with plane parallel windows fused on the ends. The materials used, with the exception of the deutero-ammonia, were prepared as before. The corrections for the energy loss at the rear cell window at the two wave lengths investigated were obtained from photolysis of hydrogen bromide under conditions identical with those prevailing in the ammonia or deutero-ammonia decompositions. The data for the hydrogen bromide decompositions have been omitted since they are similar to earlier data.[4]

## Results

The quantum efficiencies obtained in the decomposition of deutero-ammonia at λλ 2100 and 2138 Å. and of ammonia at λ 2100 Å. in Cell 3 at room temperatures (23–29°) are shown in Tables I, II and III, respectively. For purposes of comparison these data are plotted in Figs. 1 and 2. In the calculation of the quantum yields it was assumed that the products are $N_2 + 3D_2$ from analogy with the ammonia photodecomposition. The question of a change in composition of the gaseous products as their pressure is decreased has already been discussed.[4] In a number of preliminary experiments with deutero-ammonia good checks could not be obtained.

(1) The results of this investigation were presented at the Rochester, N. Y., Intersectional meeting of the American Chemical Society, June 16–18, 1936.

(2) Dixon, *Phys. Rev.*, **43**, 711 (1933); Duncan, *ibid.*, **47**, 822, 886 (1935); **50**, 700 (1936).

(3) The present experiments were undertaken at the suggestion of Professor Hugh S. Taylor of Princeton University. The author is greatly indebted to Professor Taylor and Dr. W. S. Benedict for communicating to him the results of their study of the absorption spectrum of deutero-ammonia and for supplying a sample of pure $ND_3$.

(4) Wiig, THIS JOURNAL, **57**, 1559 (1935); **59**, 827 (1937).

This effect was eliminated by the following procedure. Deutero-ammonia at high pressure (500 mm.) was admitted to the cell (previously heated and evacuated, and cooled), the pressure reduced to 410 mm. and the quantum yield, $\phi$, determined for λ 2100 and then λ 2138 Å. The pressure was again reduced to the next desired pressure, followed by a determination of $\phi$ for λ 2138 and then λ 2100 Å., and this procedure continued down to low pressures. Four samples of deutero-ammonia were used in this fashion in the experiments in Tables I and II. Exclusive of the preliminary runs, a total of 81 experiments, including checking the apparatus against hydrogen bromide, were performed. Of these only two have been omitted from the tables, both being rejected because of experimental difficulties.

TABLE I

PHOTOLYSIS OF DEUTERO-AMMONIA IN CELL 3

λ 2100 Å. Volume, 228 cc.

| $P_{ND_3}$, mm. | Exposure, sec. | Quanta absorbed × $10^{-14}$ | $P_{N_2+D_2}$, microns | Quantum yield |
|---|---|---|---|---|
| 2 | 1800 | 219 | 0.34 | 0.059 |
| 5 | 1440 | 294 | .49 | .063 |
| 20 | 1200 | 516 | 2.00 | .147 |
| 30 | 1500 | 886 | 4.12 | .176 |
| 34 | 1200 | 826 | 4.79 | .221 |
| 35 | 1440 | 929 | 5.19 | .216 |
| 50 | 900 | 620 | 3.17 | .193 |
| 65 | 1260 | 716 | 4.12 | .209 |
| 82 | 900 | 620 | 3.47 | .213 |
| 92 | 900 | 862 | 4.83 | .213 |
| 100 | 960 | 766 | 4.12 | .204 |
| 120 | 1020 | 844 | 4.53 | .204 |
| 145 | 1380 | 1026 | 5.27 | .196 |
| 146 | 900 | 786 | 4.49 | .217 |
| 180 | 1440 | 1439 | 7.49 | .199 |
| 201 | 900 | 877 | 4.20 | .182 |
| 253 | 1200 | 1521 | 6.75 | .168 |
| 300 | 900 | 840 | 3.64 | .164 |
| 340 | 1260 | 1740 | 7.34 | .160 |
| 375 | 900 | 747 | 2.84 | .144 |
| 410 | 1200 | 1992 | 7.44 | .142 |
| 430 | 1320 | 1194 | 4.49 | .141 |

TABLE II

PHOTOLYSIS OF DEUTERO-AMMONIA IN CELL 3

λ 2137 Å. Volume, 228 cc.

| $P_{ND_3}$, mm. | Exposure, sec. | Quanta absorbed × $10^{-14}$ | $P_{N_2+D_2}$, microns | Quantum yield |
|---|---|---|---|---|
| 2 | 2040 | 54 | 0.13 | 0.109 |
| 5 | 1740 | 78 | .19 | .114 |
| 20 | 1560 | 224 | 1.12 | .190 |
| 30 | 1740 | 328 | 1.64 | .191 |
| 35 | 1560 | 434 | 2.76 | .239 |
| 50 | 1560 | 247 | 1.53 | .230 |
| 64 | 1500 | 471 | 3.34 | .271 |
| 82 | 1680 | 326 | 2.23 | .258 |
| 92 | 1500 | 337 | 2.37 | .266 |
| 100 | 1500 | 277 | 1.80 | .245 |
| 120 | 1320 | 338 | 2.50 | .281 |
| 146 | 1800 | 447 | 3.12 | .264 |
| 180 | 1800 | 571 | 3.44 | .230 |
| 200 | 1200 | 318 | 1.53 | .183 |
| 200 | 1260 | 301 | 1.75 | .223 |
| 200 | 1200 | 291 | 1.71 | .225 |
| 253 | 1680 | 517 | 2.84 | .209 |
| 253 | 2040 | 308 | 2.00 | .247 |
| 255 | 1260 | 439 | 2.61 | .225 |
| 300 | 1200 | 385 | 2.23 | .222 |
| 345 | 1260 | 478 | 2.72 | .216 |
| 370 | 1200 | 294 | 1.75 | .226 |
| 413 | 1200 | 460 | 2.15 | .177 |
| 430 | 1200 | 405 | 2.10 | .196 |

TABLE III

PHOTOLYSIS OF AMMONIA IN CELL 3

λ 2100 Å. Volume, 228 cc.

| $P_{NH_3}$, mm. | Exposure, sec. | Quanta absorbed × $10^{-14}$ | $P_{N_2+H_2}$, microns | Quantum yield |
|---|---|---|---|---|
| 1 | 1800 | 194 | 0.38 | 0.074 |
| 8 | 1200 | 736 | 1.51 | .078 |
| 21 | 1200 | 879 | 4.49 | .194 |
| 29 | 2040 | 1610 | 8.49 | .199 |
| 41 | 4860 | 3750 | 22.48 | .247 |
| 41 | 1800 | 787 | 4.78 | .252 |
| 45 | 1260 | 1050 | 7.78 | .280 |
| 60 | 900 | 929 | 7.06 | .291 |
| 60 | 900 | 661 | 4.87 | .279 |
| 81 | 960 | 777 | 6.55 | .319 |
| 83 | 900 | 944 | 7.49 | .303 |
| 98 | 960 | 997 | 7.11 | .272 |
| 106 | 900 | 894 | 7.11 | .302 |
| 117 | 960 | 843 | 5.89 | .266 |
| 149 | 900 | 826 | 5.43 | .247 |
| 193 | 900 | 762 | 4.87 | .242 |
| 232 | 900 | 838 | 5.03 | .227 |
| 235 | 1020 | 964 | 6.51 | .259 |
| 267 | 900 | 838 | 4.79 | .216 |
| 320 | 960 | 947 | 5.19 | .207 |
| 335 | 960 | 930 | 5.15 | .209 |
| 417 | 900 | 832 | 4.72 | .214 |
| 442 | 900 | 730 | 3.70 | .192 |

## Discussion

It will be seen from Fig. 1 that, at the same wave length (λ 2100 Å.) and for the same type of absorption, the decomposition proceeds about 1.3–1.5 times as rapidly with ammonia as with deutero-ammonia. This is apparently in disagreement with the results of Melville,[5] who reports $NH_3$ to $ND_3$ ratios of 2.6, 2.3 and 2.6 to 1. These ratios were obtained with 2.0 cm. length of ammonia and of deutero-ammonia, respectively, at pressures of 100 mm. exposed to a quartz mercury arc. The mercury lines around λ 2100 Å. were effective in these experiments,

(5) Melville, *Proc. Roy. Soc.* (London), **A152**, 325 (1935).

since absorption by $NH_3$ and $ND_3$ increases with decrease in wave length. Under his condition, Melville states, the absorption by $NH_3$ is about 96% for light around λ 2100 Å. and, presumably, absorption by $ND_3$ would differ only slightly from this. Calculations from actual measurements made in this Laboratory on 3.5 cm. of $NH_3$ at 100 mm. pressure indicate for a 2.0 cm. path 88% absorption with monochromatic light of λ 2100 Å., in fair agreement with the above 96%. But absorption by $ND_3$ of λ 2100 Å. is considerably weaker. From measurements on 10.0 cm. of $ND_3$ at 100 mm. pressure the absorption for a length of 2.0 cm. is calculated to be only 40% instead of the 88% obtained with $NH_3$. Thus Melville's ratios are much too high and the disagreement vanishes when allowance is made for the different absorptions.

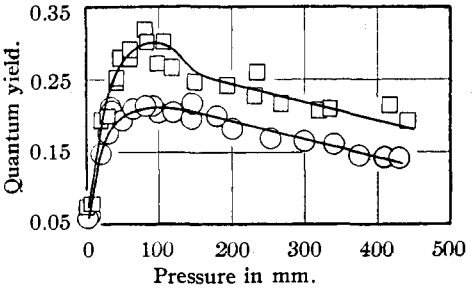


Fig. 1.—A comparison of the quantum yields for ammonia, □; and deutero-ammonia, ○, at λ 2100 Å.

The same sort of pressure dependence of the quantum yield as has previously been found[4] for ammonia is shown by deutero-ammonia (Fig. 1). This indicates that the mechanisms of the reactions following the primary process are similar. At λ 2100 Å. $ND_3$ and $NH_3$ show the same type of absorption,[3] so that the mechanism suggested for $NH_3$ should be applicable to $ND_3$. Melville[5] has shown that $NH_3$ and $ND_3$ are inhibited about equally by both hydrogen and deuterium atoms. It follows from the reactions suggested for the $NH_3$ decomposition[4] that the smaller yields with $ND_3$ are due to the reaction

$$ND_2 + ND_2 \longrightarrow N_2 + 2D_2$$

being slower than the corresponding one involving hydrogen. This suggestion has already been made by Melville and, as he points out, this is in keeping with previous experience in the kinetics of hydrogen and deuterium compounds.

The greater quantum yield for $ND_3$ with λ 2138 Å. as compared with λ 2100 Å. (Fig. 2) is rather puzzling. Offhand, most investigators would probably guess just the opposite, although a similar result has been found by West and Ginsburg[6] in the photolysis of gaseous ethyl iodide in the regions of continuous and banded absorption. In the photodecomposition of acetaldehyde Leighton and Blacet[7] found a higher yield in the region of fine structured bands as compared with the diffuse bands but they were able to show that the mercury line absorbed in the former region fell directly between two band maxima and the absorption was really due to the underlying continuum. In the case of deutero-ammonia there is no such underlying continuum, λ 2138 Å. falling in the discrete band at λ 2136–39 Å. The similarity in the pressure dependence of the yields at λλ 2138 and 2100 Å. indicates a

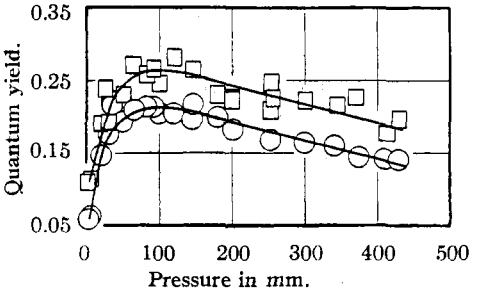


Fig. 2.—A comparison of the quantum yields for deutero-ammonia at λ 2138 Å., □; and λ 2100 Å., ○.

similarity in the mechanisms and suggests that at λ 2138 Å. we have

$$ND_3 + h\nu \longrightarrow ND_3' \quad (1)$$
$$ND_3' + ND_3 \longrightarrow ND_2 + D + ND_3 \quad (2)$$

The greater yield at λ 2138 Å. can then readily be accounted for by supposing that a small proportion of the collisions of electronically excited molecules, $ND_3'$, with normal molecules, reaction (2), results in

$$ND_3' + ND_3 \longrightarrow N_2 + 3D_2 \quad (3)$$

This would lead to a constant difference in the yields down to pressures where the reaction becomes heterogeneous,[4] in agreement with experiment. A somewhat similar suggestion has been made by West and Ginsburg and by Rollefson.[8] The homogeneous bimolecular decomposition of ammonia would probably require an activation energy greater than about 80 kcal.,[9] which is

(6) West and Ginsburg, THIS JOURNAL, **56**, 2626 (1934).
(7) Leighton and Blacet, *ibid.*, **55**, 1766 (1933).
(8) Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).
(9) Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, London, 1933, p. 365.

considerably less than the 135 kcal. supplied by one einstein at λ 2138 Å.


## Summary

The photodecomposition of ammonia is found to proceed about 1.3–1.5 times as rapidly as that of deutero-ammonia in the predissociation bands at λ 2100 Å. Approximately the same ratio holds for the rate of decomposition of deutero-ammonia at λ 2138 Å. in a discrete band to that at λ 2100 Å. in a diffuse band. These differences in rates are discussed and explanations to account for them suggested.


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# The Chemical Composition of the Active Principle of Tuberculin. XX. Comparative Study of the Yield, Potency, Specificity and Acid–Base-Combining Capacities of the Proteins from Five Human Tubercle Bacilli Culture Filtrates and other Acid-Fast Bacilli

BY FLORENCE B. SEIBERT[1]

During comparative studies of the chemistry of different strains of tubercle bacilli, the question has arisen whether as great differences might not occur on repeated examinations of the same strain. It is also a question whether constant differences can be established between tubercle bacilli and other members of the large group of acid fast bacteria, to which the tubercle bacillus belongs. In addition to the well-known method of differentiating the human, bovine and avian types of tubercle bacilli by means of their respective virulences for different animals, the distinctions made by Wilson[2] on the basis of agglutination and by Furth[3] on the basis of complement fixation and absorption experiments, it has recently been possible to differentiate them by means of the serological precipitin reaction,[4] using the purified proteins isolated from the bacillary culture filtrates as antigens. Furthermore, the proteins from these three types of tubercle bacilli, as well as from the acid-fast bacillus found on timothy grass, differed quantitatively in potency when equal doses were injected in the skin of tuberculous animals,[5] whereas no difference whatever could be distinguished between the potencies of proteins prepared from three different strains of the human type tubercle bacilli which differed widely in their virulence.

Chemical differences in the lipide contents of the different types of tubercle bacilli, human, bovine, avian, and the acid-fast timothy bacillus have been reported by Anderson[6] and his coworkers, and Chargaff and Dieryck.[7] Anderson noted especially the presence of an optically active liquid saturated fatty acid, phthioic acid, in the human H37 strain, whereas analogous acids from the other types of acid-fast organisms were optically inactive. He has made a further report[8] on the lipide contents of the bacilli of four different cultures of tubercle bacilli, recently isolated from human cases of tuberculosis, in comparison with results obtained on a freshly grown lot of the human type H37 bacillus.

The following paper is a comparative study of the proteins isolated from the culture filtrates of the same five batches of human tubercle bacilli used in Anderson's[8] studies. The results will be compared with similar studies on comparable proteins prepared from the bovine and avian tubercle bacilli and leprosy and timothy grass acid-fast organisms.

## Experimental

**History of Strains of Human Tubercle Bacilli Used.**—*Strain A10*—isolated May, 1932, on guinea pig passage from retroperitoneal lymph glands of patient (25435). Pathogenic for guinea pigs and only very slightly for rabbits. Recent test showed no pathogenicity for rabbits.

*Strain A12*—isolated November, 1932, from the sputum of patient (38135). Pathogenic for guinea pigs; nonpathogenic for rabbits.

*Strain A13*—isolated December, 1932, from the sputum of

(1) Aided by a grant from the Committee on Medical Research of the National Tuberculosis Association.

(2) G. S. Wilson, *J. Path. Bact.*, **28**, 1, 69 (1925).

(3) J. Furth, *J. Immunol.*, **12**, 273 (1926).

(4) F. B. Seibert, *Am. Rev. Tuberc.*, **21**, 370 (1930).

(5) F. B. Seibert and N. Morley, *J. Immunol.*, **24**, 149 (1933).

(6) R. J. Anderson, *Physiol. Rev.*, **12**, 166 (1932).

(7) E. Chargaff and J. Dieryck, *Biochem. Z.*, **255**, 319 (1932).

(8) J. A. Crowder, F. M. Stodola, M. C. Pangborn and R. J. Anderson, THIS JOURNAL, **58**, 636 (1936).