TABLE I

EQUILIBRIUM CONSTANTS FOR FORMATION OF NEUTRALIZATION COMPOUNDS

Base Acid	H^+	Ag^+	Cu^+	Hg^{++}
CN^-	2.5×10^9	2.6×10^{18}	1×10^{16}	2.5×10^{41}
NH_3	1.8×10^9	1.7×10^7		
$SO_3^=$	1×10^7	3.3×10^8		
Cl^-	weak		3.4×10^5	9×10^{15}
Br^-	weaker		8.3×10^5	4.3×10^{21}
I^-	weakest		7.1×10^8	1.9×10^{30}

The constants for CN^- and $SO_3^=$ should decrease relative to that of NH_3 in changing from H^+ as reference acid to Ag^+ (which shows a higher coordination number) because of the unfavorable repulsion of the charged bases. However, we find that the change is in the opposite direction.

Another comparison may be made, using the bases Cl^-, Br^-, I^-, CN^- and the acids H^+, Cu^+, Hg^{++}. Here, using H^+ for our reference acid we find: $CN^- > Cl^- > Br^- > I^-$; using Cu^+: $CN^- > I^- > Br^- \sim Cl^-$; and using Hg^{++}: $CN^- > I^- > Br^- > Cl^-$.

In both sets of data considered, we see that there is a reversal of relative strength of some of the bases upon changing the reference acid. Therefore there can be no single monotonic order of base strengths which would be applicable to all cases.

Summary

1. A consideration of the forces involved in the neutralization of an acid and a base, as defined by Lewis, indicates that it is not possible to arrange acids or bases in a single monotonic order of strength.

2. A consideration of a series of equilibrium constants, taken from the literature, shows definitely that bases cannot be so arranged, and that, by changing the reference acid, a reversal of relative base strength can in some cases be observed.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Photochemistry of Acetamide in Water Solution

BY DAVID H. VOLMAN

Evidence has been presented by Gopala Rao and Dhar,[1,2] that the formation of ammonia in the soil from amino acids is mainly an oxidative de-amination, accelerated by sunlight. Thus it has been shown that aqueous solutions of amino acids photolyze in the presence of various photosensitizers. Likewise, it has been shown that amides are hydrolyzed in aqueous solution with the formation of the corresponding ammonium salt, when exposed to sunlight in the presence of photosensitizers.[3] Hence, it has been postulated that the process of ammonification of nitrogenous compounds in the soil may be mainly photochemical in tropical countries, taking place under the influence of sunlight.[3]

It was believed that a study of the photochemical reaction involved in the ultraviolet region of absorption would be of value in elucidating the mechanism for the photosensitized reaction.

The experiments reported herein on the ultraviolet photolysis of acetamide are found to give results which may be compared with those obtained by Rao and Pandalai[3] on the photosensitized reaction. Data on the variation of the quantum yield with temperature and concentration are given. In addition, analyses on the gaseous products obtained in the acetamide solution photolysis, and experiments with propionamide and butyramide, are reported.

Experimental Method

The solutions of amide in water were irradiated by a parallel ultraviolet light beam obtained from a mercury lamp (Hanovia Alpine) through a quartz lens of $f = 10$ cm. At a constant distance a quartz cell of 10-cm. length and 83-ml. volume was placed in the path of the light beam.

Quantum yields were obtained by comparing the reaction with the photodecomposition of monochloroacetic acid in the somewhat crude way described by Weizmann, Bergmann and Hirshberg.[4] A second cell containing a monochloroacetic acid solution was placed behind the first cell described above. The difference between the amount of monochloroacetic acid decomposed in the second cell when the first cell contained (a) water, and (b) the investigated solution could be used to calculate the number of quanta absorbed in the solution. The quantum yield of 0.32 for the monochloroacetic acid hydrolysis at 25° recently reported by Smith, Leighton and Leighton[5] was used.

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(1) Rao and Dhar, *J. Indian Chem. Soc.*, **10**, 699 (1933).

(2) Rao and Dhar, *ibid.*, **11**, 617 (1934).

(3) Rao and Pandalai, *ibid.*, **11**, 623 (1934).

(4) Weizmann, Bergmann and Hirshberg, THIS JOURNAL, **58**, 1675 (1936).

(5) Smith, Leighton and Leighton, *ibid.*, **61**, 2299 (1939).

TABLE I

ULTRAVIOLET PHOTOLYSIS OF AMIDE SOLUTIONS

Expt.	Molar concn.	Temp., °C.	Exptl. time, min.	Quanta abs.	Moles excess acid	Total moles NH_3 formed	Moles NH_3 formed in dark react.	Molecules NH_3 formed in light react.	Φ
1	0.500	25	1060	1.0×10^{21}	0.0	0.0	0.0	0.0	0.0 (<0.005)
2	.500	58	1560	1.5×10^{21}	6.1×10^{-5}	5.92×10^{-5}	0.04×10^{-5}	3.51×10^{19}	.023
3	.500	70	1290	1.2×10^{21}	8.6×10^{-5}	8.37×10^{-5}	$.13 \times 10^{-5}$	4.99×10^{19}	.040
4	.500	79	1230	1.2×10^{21}	1.1×10^{-4}	1.08×10^{-4}	$.34 \times 10^{-5}$	6.36×10^{19}	.054
5	.500	92	470	4.5×10^{20}	8.0×10^{-5}	7.20×10^{-5}	$.39 \times 10^{-5}$	4.12×10^{19}	.091
6	.250	92	752	6.0×10^{20}	5.3×10^{-5}	5.03×10^{-5}	$.77 \times 10^{-5}$	2.58×10^{19}	.043
7	.750	92	462	4.3×10^{20}	1.3×10^{-4}	1.08×10^{-4}	$.15 \times 10^{-4}$	5.62×10^{19}	.130
8	1.000	92	440	4.3×10^{20}	1.6×10^{-4}	1.40×10^{-4}	$.28 \times 10^{-4}$	6.79×10^{19}	.159
9	0.500	92	467	4.4×10^{20}		1.67×10^{-5}		1.01×10^{19}	.023
10	.500	92	465	5.0×10^{20}		2.19×10^{-5}		1.44×10^{19}	.029

TABLE II

GASEOUS PRODUCTS OF ACETAMIDE PHOTOLYSIS

Expt.	Molar concn.	Temp., °C.	Exposure time, min.	Cmm. gas	CO_2, %	CO, %	CH_4, %	N_2, %	Relative rate of CH_4 formation
13	1.00	92	120	1470	2.2	10.8	71.8	15.2	0.164
14	0.50	92	240	1650	2.5	10.2	71.2	16.1	.091
15	.50	58	480	880	1.7	1.6	77.7	19.0	.026

After irradiation for definite periods, an aliquot was withdrawn from the amide solution. The solutions after illumination were found to be acid, and the excess acid was neutralized by titration with a standard alkali solution. The ammonia formed was then determined by the method of Ronchese.[6] An excess of neutral formaldehyde solution was added, and the resulting acid was titrated with alkali.

In some experiments the gaseous products formed were collected by means of a Toepler pump and analyzed by micro methods. The experimental methods used were the same as those described before by Blacet and Volman[7] for the non-condensable photolysis products of acetaldehyde.

Experimental Results

Numerical results are given in Tables I and II. Since the solutions were found to increase in acid strength as illumination progressed, and since hydrolysis occurs in the dark in presence of acid, it was found necessary to correct for the dark reaction. This was accomplished by following the rate of ammonia production in the dark immediately after irradiation. Φ is based on the number of molecules of ammonia formed in the light. Experiments 9 and 10 were on propionamide and butyramide solutions, respectively; all others were on acetamide solutions. The gaseous products represented in Table II were obtained in separate experiments under identical conditions of illumination as for the experiments reported in Table I.

Discussion

Although there is no direct evidence that the primary photochemical process is the formation of free radicals, the fact that the amide molecule absorbs only below 2537 Å., where the energy of a quantum is ample to bring about rupture of the C–N bond, indicates that the reaction

$$CH_3CONH_2 + h\nu \longrightarrow CH_3CO + NH_2 \qquad (1)$$

is probable. In order to explain the dependency of quantum yield upon concentration, it is assumed that there exists a competition between recombination

$$CH_3CO + NH_2 \longrightarrow CH_3CONH_2 \qquad (2)$$

and reactions between free radicals and amide molecules, and free radicals and solvent molecules. Presumably the latter reactions yield acetic acid and ammonia.

The dependency of quantum yield upon temperature may be explained on the same basis. The non-recombination reactions would be expected to have considerable activation energy, while the recombination reaction would have zero activation energy. Thus there should be an increase in quantum yield with increasing temperature.

It may be seen from Tables I and II that there is no simple stoichiometrical relationship between the products of the reaction. Moreover, the ratio of carbon atoms to nitrogen atoms in the products is somewhat greater than for acetamide itself. This suggests that reactions producing condensable products other than acetic acid and ammonia take place. The products formed in these reactions must be richer in nitrogen than acetamide.

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[6] Ronchese, *Bull. soc. chim.*, [4] **1**, 900 (1908).

[7] Blacet and Volman, THIS JOURNAL, **60**, 1243 (1938).

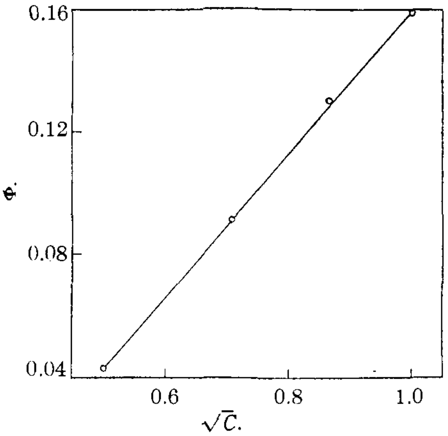

Fig. 1.—Dependence of quantum yield upon acetamide concentration at 92°.

The small quantity of carbon dioxide may be attributed to photolysis of acetic acid molecules. According to Farkas and Wansbrough-Jones,[8] the photolysis products from acetic acid in solution are equal volumes of methane and carbon dioxide. Since the photolysis of acetate ion yields hydrogen,[8] the decomposition of this ion must be negligible.

Carbon monoxide may be accounted for by the decomposition of acetyl radicals. That the reaction

$$\mathrm{CH_3CO} + \mathrm{M} \longrightarrow \mathrm{CH_3} + \mathrm{CO} \qquad (3)$$

can occur at elevated temperatures has been demonstrated.[9] Since this reaction has considerable activation energy, it should be favored by increasing temperature as Table II indicates.

The rate of production of methane, the main gaseous product, closely follows that of ammonia as may be seen by a comparison of the rates of formation of methane, Table II, and the quantum yield of ammonia production, Table I. This suggests that the reactions producing gaseous products are not independent of those producing acetic acid and ammonia in solution.

Plots of quantum yield against the square root of the concentration, Fig. 1, and log of quantum yield against the reciprocal of the absolute temperature, Fig. 2, yield straight lines. This indicates that the quantum yield may be expressed by an equation of the form

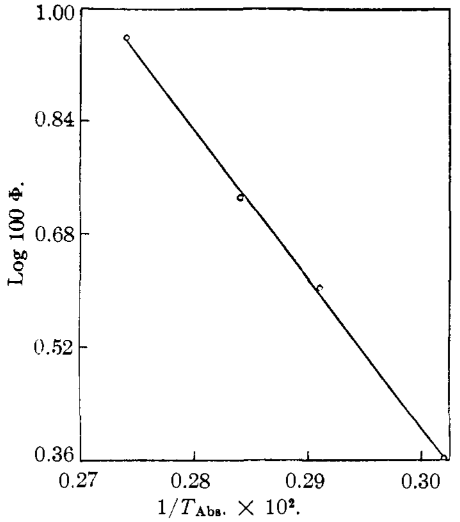

Fig. 2.—Dependence of quantum yield upon temperature for 0.50 *M* acetamide.

$$\Phi = ke^{-E/RT}[\mathrm{CH_3CONH_2}]^{1/2} \text{ for constant } I_{\mathrm{abs}}.$$

The implications of these observations on the ultraviolet photolysis are that the assumption of Rao and Pandalai[3] that, in the presence of photosensitizers, amides are hydrolyzed with the formation of the corresponding ammonium salt is too simple a picture. Investigations of the acid to ammonia ratio and possible gaseous products of the photosensitized reaction are intended.

Summary

1. A study of the photolysis of acetamide in water solution has been made.

2. The quantum yield of ammonia production was found to increase with increasing concentration and temperature.

3. Acetic acid, ammonia, carbon dioxide, carbon monoxide, methane and nitrogen were found in the reaction products.

4. The comparative rates of photolysis of acetamide, propionamide and butyramide were found to be in the ratio 1:0.25:0.31.

DAVIS, CALIF.

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[8] Farkas and Wansbrough-Jones, *Z. physik. Chem.*, **18**, 124 (1932).

[9] Spence and Wild, *J. Chem. Soc.*, 352 (1937).