39. Photochemical Studies of Some Organic Nitrogen Derivatives.

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An investigation has been made of the products of decomposition of solutions of some organic nitrogen derivatives in the full light, and in filtered light from a hot mercury arc. Particular attention has been given to gaseous decomposition products and to the development of unsaturation in paraffinoid solvents accompanying the decomposition.

It has been demonstrated that aliphatic primary and secondary amines, and ammonia itself, give products arising mainly from a primary photochemical act which involves the rupture of a nitrogen–hydrogen bond to give free radicals.

Experiments on aliphatic amides show that, in general, two main types of primary photochemical process occur. Both of these are of a molecular rather than of a free-radical nature. A close analogy is drawn between these reactions and the behaviour of the aldehydes and ketones under similar conditions.

Some extension of the work to the examination of the photolysis of proteins has been attempted.

It was observed by L. Farkas (*Z. physikal. Chem.*, 1933, *B*, **23**, 89) that, when a solution of ammonia in hexane is irradiated by the light from a mercury arc, the only gaseous product obtained is hydrogen. He ascribed this to a photodecomposition of the hexane, sensitised by the ammonia. The wave-length of the light required to bring about this reaction corresponds with the pre-dissociation region of ammonia. As the effect of light of this wave-length almost certainly involves the breaking of a N–H bond in the ammonia molecule, it was considered by Bamford and Norrish (*J.*, 1938, 1531), in the light of their investigation of the photolysis of aldehydes and ketones in the gas phase and in paraffinoid solution, that the ammonia reaction is not a true photosensitisation, but rather the result of reactions based on a primary photochemical act represented by:

$$NH_3 + h\nu \longrightarrow NH_2 + H$$

Subsequent work by Bamford (*J.*, 1939, 17) on the photodecomposition of aliphatic amines in the gas phase has added weight to this view. Here the primary act has been found to be:

$$R{\cdot}NH_2 + h\nu \longrightarrow R{\cdot}NH + H$$

This has been supported more recently by Wetmore and Taylor (*J. Chem. Physics*, 1944, **12**, 61) and Johnson and Taylor (*ibid.*, 1951, **19**, 613).

In the first part of the present work, the aim has been to substantiate this idea by an examination of the photochemical reactions undergone by both ammonia and the amines in hydrocarbon solution. Later, the work was extended to the investigation of similar reactions of amides, of which very little has hitherto been recorded. These compounds have been studied in hexane and in dioxan solution.

The power of the method lies in the great simplification of the dark reactions undergone by the entities produced by the primary photochemical act. In particular, a free radical produced in a hydrocarbon solution is most readily hydrogenated at the expense of the solvent, thereby giving a simple hydrocarbon radical, the ultimate fate of which may be easier to envisage.

The general conclusions drawn are that we have a series of reactions remarkably similar to those undergone by aldehydes and ketones. Evidence is cited for two main types of primary reaction.

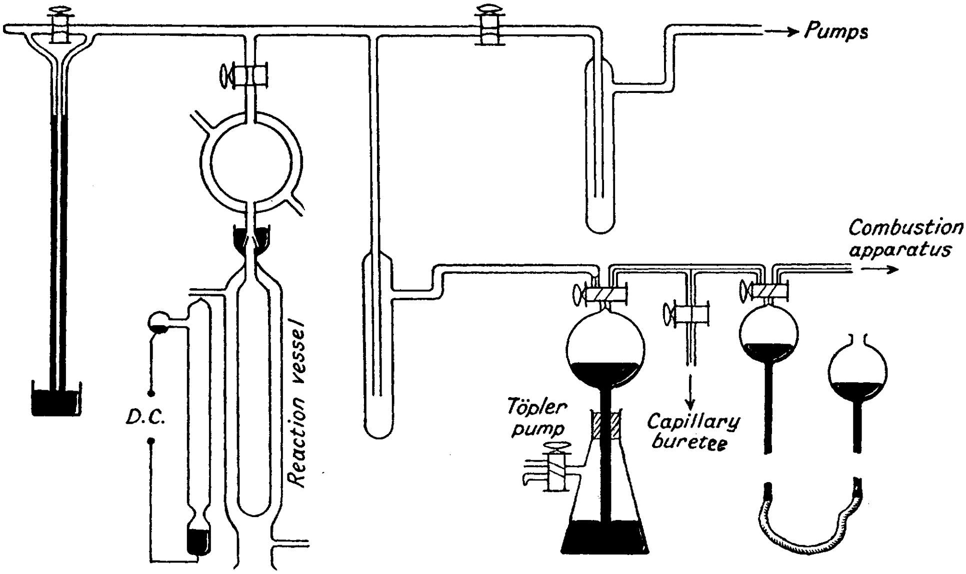
Some attempt has also been made to extend the method and general ideas to the investigation of the behaviour of proteins under ultra-violet radiation. Owing to the complexity of the starting materials, however, only very general inferences may be drawn from the results obtained.

EXPERIMENTAL

The irradiation of the reaction systems was carried out in a double-walled cylindrical quartz vessel. The apparatus is shown diagrammatically in the figure. The space between the two walls of the reaction vessel was used for the circulation round the reaction mixture of water at controlled temperatures or of liquid colour filters. The inner compartment of the reaction vessel was connected to a conventional high-vacuum system and to a Töpler pump, by means of which gaseous reaction products could be removed for analysis.

Before irradiation, the reaction vessel and its contents were thoroughly " degassed," until nothing could be extracted by the Töpler pump, while the reaction vessel was immersed in liquid nitrogen.

The reaction mixture was illuminated by a hot mercury arc running at about 400 w. Only that part of the reaction vessel containing liquid phase was exposed, vapour above and (in some cases) solid below the liquid being carefully screened from the light.



After some hours' irradiation, the lamp was removed, the thermostat jacket drained, and a liquid-nitrogen bath placed round the reaction vessel. Gaseous reaction products were then removed for analysis through a liquid-nitrogen trap by means of the Töpler pump. This process was repeated after the system had been allowed to " degas " again. Whenever possible, further gaseous products were extracted, the reaction vessel being held at −80° in an acetone–carbon dioxide freezing mixture. These gases were examined separately from those removed at −196°.

Examination of Products.—(a) *Gases.* Unsaturated hydrocarbon gases (except ethylene) were determined by absorption in concentrated sulphuric acid. The method used was a capillary burette method based on that of Swearingen, Gerbes, and Ellis (*Ind. Eng. Chem., Anal.*, 1933, **5**, 369). Ethylene was determined similarly by absorption in fuming sulphuric acid.

Carbon monoxide, hydrogen, and methane were determined by combusion with oxygen on a heated platinum spiral in an apparatus similar to that used by Axford and Norrish (*Proc. Roy. Soc., A*, 1948, **192**, 518). From pressure changes in a known volume, as recorded by a sensitive Foord-type collapsed spoon gauge (*J. Sci. Inst.*, 1934, **11**, 126), the total change in pressure on combustion, the oxygen consumed, and the carbon dioxide produced could be computed. Hence, a three-component gaseous mixture could be fully analysed.

(b) *Liquid products.* Non-volatile products of reaction, and unchanged non-volatile reactants, were removed by distilling and collecting the volatile portion of the material, including the solvent, left in the reaction vessel. This distillation was done *in vacuo* into liquid nitrogen. For reactions in hydrocarbon solution, the distillate was washed with dilute acid and several lots of water. The washings were retained and examined separately. The washed hydrocarbon was examined for unsaturation by keeping it for some time with a known amount of standard bromine water and back-titrating the excess (*via* potassium iodide) with standard thiosulphate. The method was tested upon known solutions and found to be effective.

The washings from hydrocarbon solutions and the whole of residual dioxan solutions were examined qualitatively only for the presence or absence of various compounds, the formation of which might be inferred from a consideration of the gaseous products obtained.

Preparation and Purification of Reagents.—(a) *Hexane.* Commerical *n*-hexane (b. p. 67—69°) was used as starting material. This was shaken repeatedly with small portions of warm concentrated sulphuric acid (*d* 1·83) until the acid was no longer discoloured after contact with the hydrocarbon. This treatment serves to remove unsaturated constituents. To remove aromatic constituents, the hydrocarbon was allowed to run through a 1·5-ft. column of silica gel. The liquid, after being washed with dilute sodium hydroxide and water, was then dried ($CaCl_2$; Na) and redistilled, a large middle cut being collected. A small amount of residual unsaturation, not removed by repetition of the above process, was determined quantitatively and allowed for in subsequent measurements.

(b) *Dioxan.* Dioxan was refluxed for some hours with metallic sodium, then filtered and redistilled (b. p. 101°). The resultant liquid, which was stored over reduced copper to minimise peroxidation, was transparent to ultra-violet light down to 2350 Å.

(c) *Ammonia.* Gaseous ammonia was generated by gentle warming of the aqueous solution (*d* 0·880). The gas was passed successively through a vessel held at 0°, a quick-lime tower, and a trap at −10°. It was then either passed directly into a hexane saturator or collected in solid form in a liquid-nitrogen trap.

(d) n-*Hexylamine.* The amine was synthesised from *n*-hexyl bromide by the Hofmann method, the primary amine being separated. The final product, b. p. 130—132°/750 mm., gave a negligible reaction for secondary amine.

(e) *Ethylmethylamine.* A sample, b. p. 35°, was redistilled twice *in vacuo* into acetone–solid carbon dioxide traps, a middle cut being taken at each stage. The liquid gave no reaction for primary amines.

(f) *Amides.* A range of amides were recrystallised to constant m. p. from acetone–light petroleum. The final m. p.s were: acetamide, 81°; propionamide, 79°; *n*-butyramide, 115°; *n*-valeramide, 106°; *n*-hexanoamide, 100·5°; stearamide 108°.

RESULTS

Samples of the hexane and dioxan solvents were irradiated alone as blank experiments. After 10 hours' photolysis at 40°, a very small amount of gas (not enough to be measured) could be removed from the hexane. The amount of unsaturation developed in the hexane was likewise negligible, being equivalent to less than 1 drop of N/100-bromine. No gas was obtained from the dioxan.

Ammonia.—The photolysis of ammonia was studied in hexane solution only. The system was made up in two ways as follows:

(a) *Low concentration of ammonia.* The ammonia, prepared as above, was allowed to bubble in a slow stream through hexane held at 0° for about an hour. 50 Ml. of the solution were measured into the reaction vessel and degassed as described, the liquid-nitrogen bath holding back the ammonia in the hydrocarbon. The final pressure of ammonia over the solution was 20 mm. Hg. The solution was irradiated at 20°, the results being given in Table 1. The unsaturation developed in the solvent is expressed as ml. of gaseous olefin, on the assumption that the olefin behaves as an ideal gas.

TABLE 1.

Temp. = 20°.

Time of irradiation (hours)	H_2 obtained (ml. at N.T.P.)	Olefin in hydrocarbon (ml. at N.T.P.)
6	0·98	0·95
7	1·03	0·92
6	0·62	0·62
10	0·66	0·68

(b) *High concentration of ammonia.* 50 Ml. of hexane were thoroughly degassed in the reaction vessel, and excess of solid ammonia sublimed in. The whole system was allowed to warm to room temperature, the excess of ammonia escaping from the foot of a mercury manometer. The whole system was then refrozen in liquid nitrogen to give intimate mixing of the two constituents. After the mixture had been allowed to warm a second time, the final total pressure in the reaction system was adjusted to something under atmospheric by drawing off a little vapour with the pumps. The procedure was then as before. Table 2 presents the results.

TABLE 2.

Temp. = 20°.

Total pressure over solution (mm. Hg)	Time of irradiation (hours)	H_2 (ml.)	Unsaturation (ml.)
480	6	0·98	0·99
740	6	0·42	0·49
740	20	0·80	0·78
740	18	0·68	0·67

(c) A run, taken in a similar manner to those in (b) above, but in which the vapour phase only was irradiated, the liquid being shielded from the light, gave the following results :

Temp. = 20°. Time of photolysis = 12 hours.
H_2 obtained = 0·12 ml. Unsaturation in liquid at end = 0·14 ml.

Amines.—(a) n-*Hexylamine in hexane*. Results for this system were obtained under three different sets of conditions, namely : (i) Amine concentration varying; temperature and time of photolysis constant. (ii) Temperature varying; concentration and time constant. (iii) Time of photolysis varying; concentration and temperature constant.

The results are given in Tables 3, 4, and 5 respectively. During these runs, great care was taken to place the lamp as nearly as possible in the same position with respect to the reaction vessel. Even so, owing to variation in the mains supply to the lamp, constant intensity cannot be claimed.

TABLE 3.

Temp. = 20°. Time of photolysis = 10 hours.

Concn. of amine (mole/l.)	H_2 (ml.)	Unsatn. (ml.)	Ratio, unsatn./H_2
0·760	7·38	2·79	0·38
0·302	5·36	2·36	0·44
0·151	3·53	2·15	0·61
0·076	2·39	2·27	0·95
0·038	1·60	1·61	1·00
0·015	0·11	0·11	1·00

TABLE 4.

Amine concn. = 0·038 mole/l. Time of photolysis = 10 hours.

Temp.	H_2 (ml.)	Unsatn. (ml.)	Ratio, unsatn./H_2
40°	4·62	2·14	0·46
40	3·93	1·88	0·48
40	4·60	2·23	0·48
30	3·97	2·24	0·56
30	5·00	3·19	0·56
30°	3·92	1·95	0·50
20	3·38	2·30	0·68
20	3·06	2·09	0·68
13	1·60	1·6	1·00
2	1·47	1·47	1·00

TABLE 5.

Amine concn. = 0·038 mole/l. Temp. = 30°.

Time of photolysis (hours)	H_2 (ml.)	Unsatn. (ml.)	Ratio, unsatn./H_2
10	5·00	3·19	0·56
7·5	2·55	1·48	0·58
5	0·91	0·61	0·67
3·75	0·67	0·53	0·79
2·5	0·52	0·49	0·94

The variation of the ratio, liquid unsaturation : hydrogen, with concentration, temperature, and time is indicated in the final columns of these tables. It was observed in these experiments that, when the value of this ratio was less than unity, a yellow coloration appeared in the liquid during the course of the run. On extraction of the amine from the hydrocarbon with dilute acid, at the end of the run and before measurement of unsaturation, a brown scum collected at the interface between the organic and the aqueous layer. When hydrogen and unsaturation balanced, no such phenomenon was observed. This brown material, once having collected at the interface, could not be got back into solution either in hydrocarbon or in water. An examination of this " sludge " disclosed a positive reaction in the Lassaigne test for nitrogen.

The material always consumed bromine from bromine water, but the consumption was never sufficiently reproducible to allow quantitative assessment.

Nessler reagent tests for ammonia in the acid extract from the hydrocarbon were not conclusive, owing to interference by the amine which gives a copious white precipitate. However, some inference may be drawn from the fact that, when 5 ml. of the extract were contaminated with 1 ml. of solution containing 3·01 × 10^{-4} mole of NH_3 per l., the red-brown ammonia colour with Nessler reagent became apparent at once. A run on the hexylamine–hexane system at 40° at an amine concentration of 1·52 mole/l. gave in 6 hours 2·53 ml. of hydrogen. After removal of this gas, the residual solution, which now contained a visible amount of the brown by-product was set aside in the dark at 40° for a further 7 hours. An additional 0·12 ml. of hydrogen was then obtained. A Nessler reagent test on the dilute acid extract from the remaining mixture in the reaction vessel gave negative results for ammonia.

(b) *Ethylmethylamine in hexane.* Experiments on this system were conducted as for hexylamine, with an examination of the concentration effect only. The results are presented in the following table.

Temp. = 20°. Time of photolysis = 14 hours.

Concn. of amine (mole/l.)	H_2 (ml.)	CH_4 (ml.)	Unsatn. (ml.)	Ratio $\frac{\text{unsatn.}}{\text{total gas}}$
0·234	8·07	0·64	3·31	0·38
0·117	5·55	0·30	2·50	0·43
0·058	4·74	0·07	2·64	0·55
0·029	2·18	0·07	1·83	0·81
0·015	1·23	—	1·22	0·99

In no case could ethane be withdrawn from the reaction mixture, even at −80°.

A run on this amine in the gas phase at 20° in the presence of hexane vapour gave, in 5 hours, 1·92 ml. of hydrogen and 0·01 ml. of methane.

Brown insoluble material separated in all these runs in the same circumstances as with hexylamine. In the gas-phase reaction, the " sludge " was deposited as a thin film on the walls of the reaction vessel.

Amides.—(a) *With dioxan as solvent.* Owing to the very low solublity of the amides in hydrocarbons, it was decided to use dioxan as a solvent, in order to have a solution giving a large absorption and hence probably an increased yield of products. This substance, transparent to ultra-violet light down to 2350 Å, has the further advantage of being rich in hydrogen for the hydrogenation of free radicals.

(i) n-*Hexanoamide in dioxan.* A series of experiments with solutions of *n*-hexanoamide of varying concentration in dioxan at 40° gave the results presented in the annexed table.

Temp. = 40°.

Concn. of amide (mole/l.)	Time of photolysis (hours)	CO		H_2	
		(ml.)	(%)	(ml.)	(%)
0·337	17	0·810	79	0·210	21
0·241	19	1·060	69	0·470	31
0·172	10·5	0·320	69	0·145	31
0·172	11·5	0·375	66	0·190	34
0·139	12	0·630	66	0·325	34
0·138	13	0·380	53	0·340	47
0·104	14·5	0·755	65	0·415	35
0·046	17	0·530	65	0·285	35
0·037	16	0·750	63	0·445	37
0·017	10	0·505	62	0·310	38
0·003	24	1·735	69	0·760	31

The residual solution, on being tested with Nessler reagent, gave a yellow colour indicative of the presence of amines, in addition to the large white precipitate due to unchanged amide. The Schiff's reagent test for aldehydes and the *o*-phenylenediamine test for α-diketones both gave negative results.

(ii) n-*Butyramide in dioxan.* Some results for this system, obtained in the same way as above, are given in the following table.

Temp. = 40°.

Concn. of amide (mole/l.)	Time of photolysis (hours)	CO		H_2	
		(ml.)	(%)	(ml.)	(%)
0·090	11	0·665	74	0·230	26
0·043	14	0·355	54·5	0·295	45·5
0·007	10	0·360	59	0·250	41

(iii) *Propionamide in dioxan.* A concentrated solution of propionamide was irradiated at 40° for 8½ hours. No gas could be pumped away at liquid-nitrogen temperatures, but at $-80°$ 0·505 ml. of gas was obtained, which analysed as ethylene.

(iv) *Acetamide in dioxan.* Some results for strong solutions of acetamide at 40° are shown in the following table. A point to be noted here is that no methane at all was obtained.

	CO		H_2	
Time of photolysis (hours)	(ml.)	(%)	(ml.)	(%)
12	0·630	71·5	0·250	23·5
16	0·905	75	0·300	25

(b) *Experiments in hexane solution.* A knowledge of the gaseous decomposition products of the amides now having been obtained, examination of hydrocarbon solutions was undertaken. A rough measurement of the solubility of *n*-hexanoamide in hexane gave a value of about 0·34 g./l. at 40°. Solutions saturated at the working temperature were used in the ensuing experiments. Excess of solid amide was kept in the bottom of the reaction vessel, so as to keep up the concentration as reaction proceeded, and was screened from the light.

(i) n-*Hexanoamide in hexane.* Results at two temperatures are given in the annexed table. In all cases, the unsaturation developed in the hexane was in excess of that required for balance with the hydrogen evolved. A column is therefore included under the heading of " unsaturation minus hydrogen." The gases analysed were all drawn off at $-196°$.

In all cases, amines were detected in the acid extract from the volatile portion of the final liquid mixture, their presence being indicated by a pale yellow precipitate with Nessler reagent. Evaporation of the extract gave a very small crop of crystals of indefinite m. p., which gave positive reaction in the carbylamine test for primary amines. The Schiff and the *o*-phenylenediamine test both gave negative results.

Temp.	Time (hours)	CO (ml.)	H_2 (ml.)	Unsatn. (ml.)	Unsatn. $-$ H_2 (ml.)
40°	28·5	0·270	0·690	0·79	0·10
40	13	0·150	0·585	0·67	0·085
40	10·5	0·100	0·380	0·39	0·01
40	12	0·420	1·500	1·89	0·39
30	16	0·190	0·720	0·82	0·10
30	16	0·205	1·450	1·66	0·21
30	12	0·130	0·860	0·96	0·10

In some runs, the detailed results of which are not recorded, some unsaturated gas, completely soluble in concentrated sulphuric acid, was drawn off at $-80°$. The amount was, however, never sufficient to account for all the " extra " unsaturation. In the one case in which an amount enough for a combustion analysis was obtained, the gas burned as $CH_{2\cdot 2}$.

(ii) n-*Valeramide in hexane.* Results of experiments comparable to those above are given below. Gaseous product, withdrawn at $-80°$ and completely soluble in concentrated sulphuric acid, is entered as " gaseous unsaturation." Amines were again found in the acid extract.

Temp. = 40°.

Time of photolysis (hours)	CO (ml.)	H_2 (ml.)	Gaseous unsatn. (ml.)	Liquid unsatn. (ml.)
14	0·200	0·425	0·110	0·42
16	0·215	0·565	0·112	0·58

(iii) n-*Butyramide in hexane.* In this case, the extra gas obtained at $-80°$ was not soluble in concentrated sulphuric acid, but did dissolve in the fuming acid. It is entered in the table, with the other results, as ethylene.

Temp. = 40°.

Time of photolysis (hours)	CO (ml.)	H_2 (ml.)	C_2H_4 (ml.)	Liquid unsatn. (ml.)
11·5	0·115	0·425	0·056	0·43
14·5	0·335	0·460	0·151	0·46

(iv) *Propionamide in hexane.* A saturated solution was irradiated for 10 hours at 40°. The gas obtained at $-196°$ analysed as 0·065 ml. of carbon monoxide and 0·340 ml. of hydrogen. A further 0·120 ml. was obtained at $-80°$ and analysed as ethylene. After extraction of the hydrocarbon solvent, an unsaturation value of 0·34 ml. of olefin was found.

(v) *Acetamide in hexane.* Again in the case of acetamide, no extra gas was obtained at −80° and no methane was included among that withdrawn at −196°. The results were as follows :

Temp. = 40°.

Time of photolysis (hours)	CO (ml.)	H_2 (ml.)	Liquid unsatn. (ml.)
14·5	0·260	0·860	0·83
16	0·075	0·390	0·42
16	0·170	0·625	0·62

(vi) *Stearamide in hexane.* No gas condensable at −196° but volatile at −80° was obtained. The results were as follows :

Temp. = 40°.

Time of photolysis (hours)	CO (ml.)	H_2 (ml.)	Unsatn. (ml.)	Unsatn. − H_2 (ml.)
14	0·130	0·335	0·43	0·09
17	0·125	0·240	0·30	0·06

(vii) *Stearamide in medicinal paraffin.* A sample of medicinal paraffin was purified by Bamford and Norrish's method (*loc. cit.*), in order that some experiments might be conducted on solutions at 100°. It was found impracticable, however, for all amides except stearamide, owing to volatilisation. The solutions were all stripped of solute before sufficient photolysis had occurred, the amides collecting as crystals in the cooler and screened parts of the apparatus. Also, a slow progressive and irreproducible decomposition of the solvent itself occurred after about 8 hours' irradiation.

A solution of stearamide, however, gave, in 7 hours at 100°, 0·055 ml. of carbon monoxide and 0·230 ml. of hydrogen. Measurement of unsaturation was not possible, as the solvent and unchanged solute could not be separated.

Effect of Colour Filters on the Amide Reaction.—The hexanoamide–hexane system was studied at 40°, both in the full light of the arc and with a range of filters interposed between the lamp and the reaction vessel. These filters were all liquids with the exception of one of Pyrex glass. The results appear in the annexed table. The transmission limits of the filters were obtained by examination in a Beckman D.U. quartz spectrophotometer.

Filter	Short wave-length cut-off	H_2 (ml.)	CO (ml.)	Unsatn. (ml.)
—	<2500	1·500	0·420	1·89
1% Aq. $HgCl_2$	2600	0·440	0·360	0·86
4% Aq. $HgCl_2$	2700	0·105	0·125	0·23
Pyrex	2950	—	—	—
0·025% Aq. quinine HCl	3300	—	—	—
0·1% Aq. quinine HCl	3450	—	—	—
0·5% Aq. quinine HCl	3600	—	—	—

Experiments with Gelatin.—In view of the considerable similarities in general structure of the proteins to the amides, it was considered of interest to see whether any corresponding similarity existed in the manner of solution photolysis of the two types of compound. Gelatin was selected as a convenient material for examination. It is, unfortunately, completely insoluble both in hexane and in dioxan. Preliminary studies were made on a 1% aqueous solution. A disadvantage appears at once in that water is hardly a solvent suited to the ready hydrogenation of radicals. Furthermore, it is to be expected that the protein will undergo some hydrolytic decomposition in the course of a run, thereby complicating an already complex system. The possibility of assessing unsaturation, however or wherever it may arise, is also excluded, owing to a complex and irreproducible reaction between the protein and bromine.

Some figures for gas analysis of products drawn off at liquid-nitrogen temperature are given below in the table. It must be emphasised that some of the values given for hydrogen represent amounts tending towards the limit of accuracy of the analytical technique. It is believed, however, that they are significant.

Temp.	Time of photolysis (hours)	CO (ml.)	H_2 (ml.)
30°	18	0·645	0·060
30	17	0·215	0·020
40	14	0·685	0·090
40°	14	0·680	0·060
40	24	1·035	0·025

DISCUSSION

Ammonia and Amines.—The main points that emerge from the results and require discussion can be summarised as follows: (*a*) The only permanent gaseous product of photodecomposition in hydrocarbon solution is hydrogen, except for a small amount of methane from ethylmethylamine. (*b*) The amount of unsaturation developed in the hydrocarbon solvent is, in general, equivalent to the amount of hydrogen evolved, provided that the absorbing substrate is present in low concentration. (*c*) At higher concentrations, the amount of unsaturation falls off with respect to the hydrogen yield. (*d*) An insoluble nitrogenous material is found in association with this loss of unsaturation. (*e*) The extent of the imbalance of unsaturation and hydrogen is both temperature- and time-dependent for a given concentration of amine. (*f*) At no time does the unsaturation in the liquid significantly exceed the hydrogen produced.

Most of these points may be covered if we suppose that the primary step in the photochemical process involves the removal of a hydrogen atom from the $-NH_2$ group:

$$R{\cdot}NH_2 + h\nu \longrightarrow R{\cdot}NH + H$$

When the amine (or ammonia, for which R above is replaced by H) is present in low concentration, the following set of dark reactions can then proceed:

$$\begin{aligned} H + C_6H_{14} &\longrightarrow H_2 + C_6H_{13} \\ R{\cdot}NH + C_6H_{14} &\longrightarrow R{\cdot}NH_2 + C_6H_{13} \\ 2C_6H_{13} &\longrightarrow C_6H_{12} + C_6H_{14} \end{aligned}$$

and the amount of olefin, C_6H_{12}, produced corresponds with the amount of gaseous hydrogen formed. This primary step corresponds with that proposed by Bamford (*J.*, 1939, 17) for the photolysis of primary aliphatic amines in the gas phase.

An exactly similar scheme can be formulated for the secondary amine, ethylmethylamine, if we include a small contribution due to an initial step:

$$C_2H_5{\cdot}NH{\cdot}CH_3 \longrightarrow C_2H_5{\cdot}NH + CH_3$$

to account for the small amount of methane formed. No corresponding step is indicated in which an ethyl radical is split off since no ethane was detected in the products.

In the photodecomposition of methylamine and diethylamine in the gas phase, as reported by Bamford (*loc. cit.*) little methane was found, whereas Emeléus and Jolley (*J.*, 1935, 929) found large quantities of this gas in the thermal decomposition products. The small, but definite, amount of methane found in the present work suggests some slight overlap between the two types of decomposition.

The fact that the unsaturation never significantly exceeded the hydrogen precludes any possibility of reaction analogous to the Type II decomposition of the aldehydes and ketones of the form:

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2 \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 + CH_3{\cdot}NH_2$$

as this would clearly lead to an extra degree of unsaturation which, under the conditions of our experiments, would remain in the liquid.

As we increase the amine concentration, we introduce the probability of termination reaction in which the C_6H_{13} radicals, instead of undergoing hydrogen-exchange reactions with the solvent until two come together and disproportionate, may be hydrogenated at the expense of amine molecules. It has been shown by Trotman-Dickenson and Steacie (*J. Chem. Physics*, 1951, **19**, 329) that, for reactions of methyl radicals, the activation energies for hydrogen abstraction from paraffins and from amines differ extremely slightly. Hence at higher concentrations of amine, we may envisage reactions of the type:

$$C_6H_{13}{\cdot}NH_2 + C_6H_{13} \longrightarrow C_6H_{14} + C_6H_{13}{\cdot}NH$$

and

$$C_6H_{13}{\cdot}NH_2 + C_6H_{13} \longrightarrow C_6H_{14} + C_6H_{12}{\cdot}NH_2$$

It is clear that the former would not affect the issue, simply returning us to one stage in the simple scheme previously expounded. The second type, however, gives the likelihood of an ultimate compound of the type $C_6H_{11}\cdot NH_2$, in which the unsaturation has gone into the hydrocarbon chain of the amine. This unsaturation would be lost as far as determination by our experimental method is concerned, the unsaturated amine being removed in the acid wash.

Franck and Rabinowitch's principle (*Trans. Faraday Soc.*, 1934, **30**, 120) states that radicals produced by the fission of a chemical bond in solution are held together by a cage of solvent molecules and may make two or three collisons with each other before escaping. Under such conditions, primary recombination plays a large part in the ultimate fate of the radicals and the general low quantum yield of photochemical reactions in solution is explained. It seems quite probable, that, from this principle, an alternative to primary recombination will exist. To use the case of hexylamine as a specific example, hydrogenation of the hydrogen atom by the other fragment of the parent molecule, *i.e.*, the hexylamino-radical is to be expected. We would expect this to increase in probability as the temperature is raised.

Recent work in the gas-phase photolysis, by Johnson and Taylor (*loc. cit.*), suggests, as alternative to "lost" unsaturation, "extra" hydrogen arising from the thermal decomposition of the by-product polymer thus:

$$2CH_3\cdot NH_2 \longrightarrow H_2 + \frac{1}{n}(C_2H_8N_2)_n \text{ (over-all reaction)}$$

$$\frac{1}{n}(C_2H_8N_2)_n \longrightarrow H_2 + \frac{1}{n}(C_2H_6N_2)_n$$

$$\frac{1}{n}(C_2H_6N_2)_n \longrightarrow NH_3 + \frac{1}{n}(C_2H_3N)_n$$

They assume that the polymer of $C_2H_8N_2$ first arises by isomerisation of $CH_3\cdot NH$ radicals to $CH_2\cdot NH_2$ radicals, which then polymerise. We have indicated above how $C_6H_{12}\cdot NH_2$ radicals might arise directly without isomerisation. As no polymer was obtained at low initial amine concentration, this seems preferable to isomerisation.

We have been able to demonstrate a further evolution of hydrogen, after the lamp had been turned off, from a system favourable to the production of the polymer. No ammonia could be detected, however.

The observed fact that the fraction of "lost" unsaturation increases with time, under conditions of constant temperature and concentration, is in accord with the ideas of Johnson and Taylor (*loc. cit.*). It would seem that something formed in the course of the reaction is affecting its subsequent behaviour. Two types of compound are built up in the liquid phase during the reaction, namely olefin and the nitrogenous "sludge." It has been found that if we perform the irradiation in unpurified hexane solution, *i.e.*, hexane already containing an appreciable concentration of unsaturated constituents, the value of the ratio, unsaturation : hydrogen, after a given time, is the same as that obtained in the purified solvent. There is, of course, a reduction in the overall amount of decomposition owing to absorption of the active radiation by the solvent. The unsaturation loss (or hydrogen gain) therefore must be accounted for by some means such as that indicated above. A fuller knowledge of the precise nature of this polymeric material would be of very great value.

Amides.—The main points to be extracted from the results, on which a discussion may be formulated, are as follows: (*a*) Carbon monoxide and hydrogen are the gaseous products common to all the amides examined. (*b*) In all cases, primary amines are formed during the course of the reaction. (*c*) No methane is obtained from acetamide. (*d*) From propionamide, butyramide, valeramide, and hexanoamide we obtain some unsaturated hydrocarbon gas, this being established as ethylene from propionamide and butyramide and inferred as propylene and butylene from valeramide and hexanoamide. (*e*) Stearamide gives more liquid unsaturation than can be accounted for by the hydrogen yield. (*f*) Examination of end-products for the presence of aldehydes and αβ-diketones gives negative results. (*g*) When colour filters are introduced, it is found that the ratio of carbon monoxide to hydrogen increases with increase in wave-length.

We can account for these facts if we suppose that there are, in general, two different modes of decomposition for the amides, which are completely analogous respectively to the Type I decomposition of the aldehydes and Type II decomposition for the aldehydes and ketones as propounded by Bamford and Norrish (*loc. cit.*).

These processes may be represented by the following equations, butyramide being used as a typical example :

$$CH_3\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2 + h\nu \longrightarrow CH_3\cdot CH_2\cdot CH_2\cdot NH_2 + CO \quad \text{Type I}$$
$$CH_3\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2 + h\nu \longrightarrow CH_2{:}CH_2 + CH_3\cdot CO\cdot NH_2 \quad \text{Type II}$$

We then have the reactions :

$$CH_3\cdot CH_2\cdot CH_2\cdot NH_2 + h\nu \longrightarrow CH_3\cdot CH_2\cdot CH_2\cdot NH + H, \text{ etc., as for amines}$$
$$CH_3\cdot CO\cdot NH_2 + h\nu \longrightarrow CH_3\cdot NH_2 + CO \quad \text{Type I}$$
$$CH_3\cdot NH_2 + h\nu \longrightarrow CH_3\cdot NH + H, \text{ etc., as for amines}$$

On a scheme such as this, the hydrogen yield will equal the amount of unsaturation not accounted for by the Type II reaction. This is found in fact to be the case for butyramide and valeramide, where the ethylene and propylene respectively could be completely separated from solution in the hydrocarbon solvent.

For acetamide, no Type II decomposition is possible and the reaction is simply of Type I. The complete absence of methane from all the reactions, but in particular from the acetamide system, indicates that the Type I reaction is of the aldehyde type, *i.e.* :

$$R\cdot CO\cdot NH_2 \longrightarrow R\cdot NH_2 + CO$$

and not of the ketone type :

$$R\cdot CO\cdot NH_2 \longrightarrow R + CO\cdot NH_2 \longrightarrow R + CO + NH_2$$

or

$$R\cdot CO\cdot NH_2 \longrightarrow R\cdot CO + NH_2 \longrightarrow R + CO + NH_2$$

since the latter would give subsequent reactions such as (for acetamide) :

$$CH_3 + C_6H_{14} \longrightarrow CH_4 + C_6H_{13}$$
$$CH_3\cdot CO + C_6H_{14} \longrightarrow CH_3\cdot CHO + C_6H_{13}$$
$$NH_2 + C_6H_{14} \longrightarrow NH_3 + C_6H_{13}, \text{ etc.}$$

and perhaps

$$2CH_3\cdot CO \longrightarrow CH_3\cdot CO\cdot CO\cdot CH_3$$

and we should expect materials in the final mixture which have been shown to be absent.

We are thus led to the conclusion that, in Type I reactions, we have decomposition into molecules rather than into free radicals, *i.e.*, an aldehyde Type I reaction.

Owing to the extremely low solubility of the amides in hydrocarbons, the subsequent amine concentration is also very low. Thus, the amine photolysis will be uncomplicated by the concentration effects observed for these compounds, and the observed balance between hydrogen yield and liquid unsaturation (apart from Type II) might be expected. The observed lack of coloration of the solvent and separation of polymeric material during the subsequent handling is in accord with these ideas.

The general indication from the treatment above is that it is either the C=O group or the complete CO·NH$_2$ group rather than the bare NH$_2$ group which controls the decomposition of amides. This is in accord with expectation from consideration of the absorption spectra of these substances. Bielecki and Henri (*Compt. rend.*, 1913, **156,** 1860), in measurements of the molar extinction coefficients in alcoholic solution, give values which may be compared thus :

	λ	ε		λ	ε
$CH_3\cdot NH_2$	2405	0·54	$CH_3\cdot CH_2\cdot NH_2$	2525	0·22
$CH_3\cdot CO\cdot NH_2$	2405	8·1	$CH_3\cdot CH_2\cdot CO\cdot NH_2$	2525	1·01

showing a large increase in absorption at a given wave-length by the introduction of the C=O group into the molecule. If the production of hydrogen arises from the photolysis of amines produced after Type I decomposition of the amide as we have suggested, then, by increasing the wave-length available for absorption, we should reduce the amount of hydrogen produced with respect to the carbon monoxide. An inspection of the table (p. 194) showing the effect of filters bears out this contention. We would expect no such reduction in the hydrogen yield, if, after absorption of a quantum of energy by the C=O group, the molecule were to decompose by a mechanism such as :

$$R{\cdot}CO{\cdot}NH_2 + h\nu \longrightarrow R{\cdot}CO{\cdot}NH_2^* \longrightarrow R{\cdot}CO{\cdot}NH + H$$

A comparison of the results on stearamide in hydrocarbon at 40° and 100° shows a marked increase in the hydrogen : carbon monoxide ratio at the higher temperature, and little change in the absolute amount of carbon monoxide. This is in accord with the idea that the carbon monoxide arises from a primary molecular photochemical step and that the hydrogen comes from a process requiring activation as has been postulated.

A difficulty appears in the case of propionamide. Here, Type II decomposition would give :

$$CH_3{\cdot}CH_2{\cdot}CO{\cdot}NH_2 \longrightarrow CH_2 + CH_3{\cdot}CO{\cdot}NH_2$$

and presumably the methylene would ultimately appear as methane. In practice we get ethylene. Bamford and Norrish (*loc. cit.*) found a similar phenomenon in the photolysis of ethyl methyl ketone which gave ethylene and acetaldehyde. They distinguished this reaction from the usual (Type II) reaction involving a fission of the bond between the α- and the β-carbon atoms by calling it Type III. In the case of propionamide, this would give :

$$CH_3{\cdot}CH_2{\cdot}CO{\cdot}NH_2 \longrightarrow CH_2{:}CH_2 + H{\cdot}CO{\cdot}NH_2$$

in addition to the general Type I reaction.

Protein.—The results on gelatin show that some at least of the photochemical degradation occurs in a manner similar to amide photolysis. It is quite clear that this is by no means the whole story, as is shown by the extensive work of Mandl and McLaren (*Nature*, 1949, **164,** 750; *J. Amer. Chem. Soc.*, 1951, **73**, 1826), and Roberts and Rideal (*Proc. Roy. Soc., A*, 1951, **205**, 391), who have demonstrated the occurrence of deamination and further condensation reactions.

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