3. *A Study of the Photolysis of Organic Nitrogen Compounds. Part I. Dimethyl- and Diethyl-nitrosoamines.*

By C. H. Bamford.

The photolysis of the vapours of dimethyl- and diethyl-nitrosoamines has been studied. Decomposition is produced by all wave-lengths lying in the absorption band, the quantum yield being low in all cases. The vapours do not exhibit any fluorescence. These observations are correlated with the absorption spectra of the nitrosoamines, and their bearing on the nature of the primary act is discussed. The latter results in the formation of dialkylamino-radicals and nitric oxide, by a rupture of the bond between the nitrogen atoms. The energy required for this change is estimated at 12 kg.-cals. Dialkylamino-radicals are shown to undergo a disproportionation reaction, with production of the corresponding secondary amine and a bivalent radical which subsequently polymerises. Prolonged irradiation produces considerable quantities of hydrogen, through photolysis of the secondary amine formed. Possible secondary reactions producing small quantities of nitrogen and olefin are discussed, and the primary act is contrasted with that occurring in the case of other nitroso-compounds.

Comparatively little work has been done upon the photolysis of simple organic nitrogen compounds. Anderson, Crumpler, and Hammick (J., 1935, 1679) found that the primary act in the photolysis of nitroso*iso*propylacetone and β-nitroso-βε-dimethylhexane consists in the elimination of an oximino-group, with formation of hyponitrous acid and its decomposition products and an olefinic substance. Similar modes of photodecomposition were recorded by Hirschlaff and Norrish (J., 1936, 1580) for nitromethane and nitroethane, by Hammick and Lister (J., 1937, 489) for some chloro- and nitro-nitroso-compounds, and by Thompson and Dainton (*Trans. Faraday Soc.*, 1937, **33**, 1546) for a number of alkyl nitrites. The last authors specify α-, β-, and γ-elimination of the oximino-group, according to whether the hydrogen atom which becomes associated with the nitroso-group is originally attached to the α-, β-, or γ-carbon atom. It appeared that a study of the photochemistry of the nitrosoamines might throw additional light on this tendency of nitroso-compounds to split off an oximino-radical on irradiation.

The absorption spectra of dimethyl- and diethyl-nitrosoamines have been studied by Purkis and Thompson (*Trans. Faraday Soc.*, 1936, **32**, 1465). The former shows a system of diffuse bands between 3900 and 3200 A., having no marked head, and giving place at shorter wave-lengths to a continuum which extends to longer wave-lengths as the pressure is increased; the most intense bands have centres at about 3768, 3645, 3522, and 3305 A. The spectrum of diethylnitrosoamine is similar, but the region between 4000 and 3200 A. has not been clearly resolved into bands. Experiments now described show that the vapours of the nitrosoamines exhibit no fluorescence, even when irradiated by wave-lengths lying near the long-wave limit of absorption. Further, decomposition is brought about by all wave-lengths which lie in the absorption band, but the quantum yield is always low—its value being 0·06 for wave-lengths in the continuum of dimethylnitrosoamine. The significance of these points is discussed later.

Although a process resembling β-elimination of the oximino-group is formally possible, yet in the photolysis of these two nitrosoamines a completely different mechanism participates, *viz.*, rupture of the molecule at the link between the nitrogen atoms, *e.g.*,

$$(CH_3)_2N{\cdot}NO + h\nu \longrightarrow (CH_3)_2N{\cdot} + NO \quad . \ . \ . \ . \ . \ (1)$$

The dialkylamino-radicals produced by (1) undergo a secondary reaction resulting in the formation of a secondary amine :

$$2(CH_3)_2N{\cdot} \longrightarrow (CH_3)_2NH + CH_3{\cdot}\dot{N}{\cdot}\dot{C}H_2 \quad . \ . \ . \ . \ . \ (2)$$

the free radical polymerising to form compounds with high boiling points. The volatile products are thus almost exclusively nitric oxide and secondary amine.

EXPERIMENTAL.

(1) *The Course of Photolysis.*—In order to determine the course of the photo-reactions, the vapours of the nitroso-compounds were irradiated in a vertical reaction vessel, constructed from quartz tubing 2 cm. in diameter and 25 cm. long. The lower end was sealed to a narrower tube which contained the liquid, and the upper end communicated with a reflux condenser by means of a ground joint. A series of liquid-air traps leading to a Toepler pump was connected to the condenser. The whole could be evacuated by a two-stage mercury-diffusion pump backed by a Hyvac pump. The liquid was refluxed gently in a vacuum by warming to about 70°, the portion of the reaction vessel exposed to the light being maintained at 100° by a quartz steam-jacket to prevent condensation of liquid on the walls. The liquid was protected from the light, and the progress of the reaction followed manometrically. A vertical quartz mercury arc, running hot, and consuming about 300 watts, was used in the majority of the experiments; in one case the mercury-sensitised decomposition was investigated by using a mercury lamp with cooled electrodes containing a few mm. of neon. At the conclusion of the irradiation the products were divided into three fractions according to their volatility. Fraction I was removed by the Toepler pump through two liquid-air traps. After the whole of the residual products had been condensed in one of the traps, this was maintained at −130° by alcohol–liquid nitrogen, and volatile substances were distilled into the second trap. When nothing further distilled over, the trap was isolated, allowed to warm, and the contents removed by the Toepler pump. This constituted Fraction II. The first two fractions were composed only of permanent gases, and were analysed in a Bone and Wheeler apparatus. Fraction III, distilled off at about 0°, was a volatile liquid, which was condensed into a small tube and weighed. The vapour density of the liquid was determined by measuring the pressure exerted by a sample in a bulb of known volume, then freezing out the substance in a tube and weighing it. The physical and chemical properties of Fraction III were also recorded.

Dimethyl- and diethyl-nitrosoamines were prepared from the corresponding secondary amines by the action of nitrous acid as described by Geuther (*Annalen*, 1863, **128**, 151) and Renouf (*Ber.*, 1880, **13**, 2170). The final products boiled sharply at 153·0° and 174·5°, respectively.

(a) *Dimethylnitrosoamine.* The results of a series of experiments are in Table I. The volumes of products are expressed in c.c. of vapour at *N.T.P.* In all cases photolysis was carried out at 100°.

Fraction I usually consisted of hydrogen, nitrogen, and methane, together with a little nitric oxide. Fraction II was practically pure nitric oxide, but generally contained a little ethylene. It contained no portion appreciably soluble in water or alcohol. Ammonia and nitrous oxide were therefore absent. Fraction III was a volatile liquid; it was purified by distillation in a vacuum at −50°, and then had b. p. 6·5°, and a molecular weight of 45. The liquid was soluble in water, had a strongly basic reaction, and a pungent ammoniacal smell. These properties characterise it as dimethylamine (b. p. 7·4°), and this was confirmed by preparation of the picrate, m. p. 158°, unchanged by an authentic specimen.

TABLE I.

Expt.	Light source.	Time of irradiation, hrs.	H_2.	N_2.	CH_4.	C_2H_4.	NO.	$NHMe_2$.
I	Full light of hot arc	7¾	12·8	8·6	1·5	2·1	37·3	Present, not estimated
II	,, ,, ,,	5½	9·7	4·2	1·0	0·5	43·3	
III	,, ,, ,,	5½	9·3	4·1	1·1	0·6	39·2	
IV	,, ,, ,,	1	0·6	0·4	0·2	0·1	10·2	4·8
V	,, ,, ,,	½	0·1	0·1	—	—	5·6	2·9
VI*	,, ,, ,,	1	0·4	0·9	0·1	0·1	10·0	Present, not estimated
VII	2536 A. lamp	4¼	4·8	1·4	0·6	0·2	26·8	
VIII	Hot arc, glass plate interposed	8¼	—	—	—	—	7·9	

* 40 Mm. of nitric oxide were introduced into the apparatus before beginning the irradiation in this experiment.

In the earlier experiments a considerable quantity of hydrogen was produced. Inspection of Table I shows, however, that the percentage of hydrogen falls off rapidly with diminishing periods of irradiation, being only 1·2% in Expt. V for a period of ½ hour. It is evident that the hydrogen arises from a secondary process. This appears to be the photolysis of some dimethylamine—a reaction which produces hydrogen together with a little methane as volatile products, the predominant primary act being

$$(CH_3)_2NH \longrightarrow (CH_3)_2N\cdot + H \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

This reaction is described in detail in the following paper. The small quantities of nitrogen, methane, and ethylene are also clearly secondary products, resulting from decomposition of some dimethylamine. In Expt. VIII the incident light consisted only of wave-lengths longer than 3400 A., shorter wave-lengths being filtered out by the glass plate. No permanent gas except nitric oxide was produced. Dimethylamine does not absorb appreciably above 2500 A., and so would not undergo any decomposition under these conditions.

Table I shows that the yield per hour of nitric oxide falls off with increasing time of irradiation. This may, in part, be due to secondary reactions which remove nitric oxide. It is natural to associate these with the production of nitrogen. This is further brought out by a comparison of Expts. IV and VI. In the latter, additional nitric oxide was present, and the yield of nitrogen was increased. Only a very small amount of nitrogen could be formed by the direct photolysis of nitric oxide, however, since it was found that irradiation of 80 mm. of the gas by the hot arc, under similar conditions to those in the above experiments, gave a yield of nitrogen of only 0·13 c.c./hr. Possible secondary processes are reactions occurring between dimethylamino-radicals or hydrogen atoms, and nitric oxide. In the former case, a reaction such as (4) would account for the formation of small quantities of ethylene and nitrogen:

$$(CH_3)_2N\cdot + NO \longrightarrow C_2H_4 + H_2O + N_2 \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

and plausible reactions involving hydrogen atoms are

$$\left.\begin{array}{r} H + NO \longrightarrow HNO\cdot \\ (CH_3)_2NH + HNO\cdot \longrightarrow 2CH_3\cdot + N_2 + H_2O \end{array}\right\} \quad . \; . \; . \; . \; . \quad (5)$$

Reaction between dialkylamino-groups with production of nitrogen does not appear to occur, since in the photolysis of dimethylamine (which occurs through the formation of NMe_2 radicals) no nitrogen is formed. Further, the reactions (4) and (5) receive some support from the fact that irradiation of dimethylamine in the presence of nitric oxide produces nitrogen (see following paper, p. 21). The methyl groups liberated in (5) are mainly removed by reaction with nitric oxide (see, *e.g.*, Mitchell and Hinshelwood, *Proc. Roy. Soc.*, 1937, *A*, **159**, 32), a small percentage of them becoming hydrogenated to methane, however.

It is necessary to enquire what is the fate of the free radical produced in (2). It appeared possible that this might isomerise to ethyleneimine, and experiments were carried out with the object of identifying this compound. Ethyleneimine boils at 56°, and would be expected to distil off after the removal of the dimethylamine in the separation of the products. Fractions distilled off at room temperature from the residue remaining after the removal of fraction III were examined. On addition of alcoholic picric acid, no picrate was deposited, although ethyleneimine forms a well-defined crystalline picrate only very slightly soluble in alcohol. Since ethyleneimine forms a compound with bismuth tri-iodide which is very sparingly soluble in dilute acids (Gabriel, *Ber.*, 1888, **21**, 761), an attempt was made to prepare this compound from fraction IV, but the substance so obtained had the same solubility in hydrochloric acid as the addition compound formed from dimethylnitrosoamine, so ethyleneimine could only have been present in minute quantity if at all. It appears probable then that the $\cdot NMe\cdot CH_2\cdot$ radical polymerises rather than isomerises. Presumably the Schiff's base $NMe{:}CH_2$ is first formed, and then polymerises. A heavy polymer less volatile than dimethylnitrosoamine remained in the reaction vessel after distillation of the original nitrosoamine in a vacuum, and microanalysis [Found: C, 53; H, 10; N, 34; O, 3. Calc. for $(CH_2\cdot N\cdot CH_3)_n$: C, 55·9; H, 11·5; N, 32·6%] showed that the polymer was contaminated with a little nitrosoamine.

According to equations (1) and (2) the dimethylamine formed should be equivalent to half the nitric oxide, and these conditions are fulfilled satisfactorily in Expts. IV and V.

Expt. VII shows that the mercury-sensitised decomposition closely resembles the direct photolysis. From Expt. VIII we may conclude that wave-lengths lying in the banded region are effective in producing photodecomposition.

(b) *Diethylnitrosoamine.* The results obtained with diethylnitrosoamine at 100° are in Table II in the same form as for Table I. Fractions I and II contained the permanent gases.

TABLE II.

Expt.	Light source.	Time of irradiation, hrs.	H_2.	N_2.	CH_4.	C_2H_6.	Olefin.	NO.	$NHEt_2$.
I	Full light of hot arc	7½	0·5	2·8	0·9	1·5	0·9	15·8	Present, not estimated
II	,, ,, ,,	5¼	0·6	1·3	1·0	0·8	0·7	23·1	
III	,, ,, ,,	4	0·2	0·9	0·3	1·2	0·9	18·9	8·0
IV	,, ,, ,,	1	—	0·1	0·1	0·2	0·1	8·5	4·5
V*	,, ,, ,,	2	0·1	1·0	0·4	0·4	0·4	14·5	7·0
VI	Hot arc, glass plate interposed	11¾	—	—	—	—	—	6·8	3·3

* 28 Mm. of nitric oxide were introduced into the apparatus before irradiation in this experiment.

Fraction III was a volatile, strongly basic liquid with an ammoniacal smell (Found, by microcombustion: C, 64·9; H, 15·7; N, 19·8. Calc. for $C_4H_{11}N$: C, 65·7; H, 15·1; N, 19·2%). It was identified as diethylamine (b. p. 56·0°, f. p. − 50°) by its b. p. (55—56°), f. p. (− 52°), vapour pressures, and molecular weight (72—74). Its picrate did not separate readily from alcoholic solution, but the same difficulty was experienced with a sample of diethylamine.

Table II shows that, in its main features, the photolysis of diethylnitrosoamine proceeds similarly to that of its lower homologue. Nitrogen, hydrogen, ethane, and olefin are produced only in small quantity, which is negligible with short periods of irradiation (Expt. IV). They are completely absent when wave-lengths longer than 3400 A. are used (Expt. VI). Hence, these substances are probably formed by reactions analogous to those of equations (4) and (5). In agreement with this, addition of nitric oxide to the system increases the percentage yield of nitrogen and reduces that of ethane [by more complete removal of ethyl groups liberated by the reaction corresponding to (5)]. The source of the small quantities of methane is not clear. It may, however, be formed by the action of nitric oxide on ethyl radicals. No compound (*e.g.*, pyrrolidine) produced by the isomerisation of the $\cdot NEt\cdot C_2H_4\cdot$ radical formed by the process corresponding to (2) could be detected. This radical, like $\cdot NMe\cdot CH_2\cdot$, must mainly polymerise, probably through the intermediate formation of the Schiff's base.

As before, in the main reactions the secondary amine formed should be equivalent to half the nitric oxide, and this is approximately true in Expts. III, IV, V, and VI.

(2) *The Quantum Yield of Photolysis of Dimethylnitrosoamine.*—The apparatus and method employed for the determination of the quantum yields have been fully described by Bloch and Norrish (J., 1935, 1638). The vapour, at a pressure of about 100 mm., was irradiated in a quartz cell closed by a vacuum breaker, the whole being maintained at a constant temperature by an air thermostat. In order to eliminate any possibility of condensation occurring on the windows of the cell, the inlet for the hot air was arranged to deliver the latter directly on to the windows, which were consequently held at a slightly higher temperature than the rest of the

cell. Light intensities were measured by a Moll thermopile and a Broca galvanometer. The reflexion coefficients for the various quartz windows were estimated as described by Bloch and Norrish, *i.e.*, by taking intensity measurements with and without the windows in position. In the present experiments absorption of the active light was practically complete, and it was unnecessary to correct for light absorption from the beam reflected from the back windows of the cell and thermostat. The correction for light losses at the surfaces of the lens used to focus the beam on the thermopile was calculated to within a few units %.

Experiments were performed in two spectral regions. A filter of nickel chloride and gaseous chlorine in separate quartz cells served to isolate a region 2500—2800 A. from the light of the mercury arc (see Bowen, J., 1932, 2236). This filter transmitted also a certain amount of visible light which was not absorbed by the nitrosoamine. A separate determination of the ultra-violet intensity was made by interposing a glass plate. A filter of Corning glass 586, 5 mm. thick, was used to isolate the range of wave-lengths between 3500 and 3800 A. This filter transmitted practically no visible light, and the use of the glass plate to measure the ultra-violet was unnecessary. A quartz cell containing copper sulphate solution was used in conjunction with the Corning filter to absorb infra-red light.

At the conclusion of the irradiation, the vacuum breaker was broken, and permanent gases were removed by a Toepler pump and analysed. Since the volumes were rather small, they were measured by expanding the gas into a previously calibrated volume and measuring the pressure exerted.

Results.

Expt.	(i).	(ii).
Spectral region, A.	2500—2800	3500—3800
Temperature	107°	90°
Sensitivity of thermopile–galvanometer system, ergs/sec./cm.	365·5	3491
Intensity incident on vapour, galvo. deflexions, cm.	71·5	19·4
,, transmitted by vapour, galvo. deflexions, cm.	5·1	1·8
Time of irradiation, hrs.	8·0	8·0
Total energy absorbed $\times 10^{-7}$, ergs.	7·00	17·7
Number of quanta absorbed $\times 10^{-19}$	9·26	33·1
Vol. of NO obtained (c.c. at *N.T.P.*)	0·21	0·13
Quantum yield of nitric oxide	0·06	0·01

(3) *Absence of Fluorescence.*—In order to ascertain whether the nitrosoamines exhibit any fluorescence, a convergent beam of light of small cross-section was passed through a quartz bulb containing the vapour. The light source was a horizontal mercury lamp running hot and consuming 250 watts; the lamp had a plane window to give a strong horizontal beam, which was made to converge by a quartz lens. A side tube containing the liquid nitrosoamine was in communication with the bulb, and the pressure in the latter was adjusted to the desired value by maintaining the liquid at a suitable temperature. Observations were made at pressures from 0·1 mm. up to the vapour pressure at room temperature (*ca.* 5 mm.). At each pressure, the Corning 586 filter and the nickel chloride–chlorine filter were interposed in turn; the appearance was also noted when the vapour was irradiated by the full light of the arc. Neither nitrosoamine vapour gave any fluorescence under the conditions employed.

DISCUSSION.

As with other polyatomic molecules, it is very difficult to assess the precise significance of the diffuse bands in the spectra of the nitrosoamines. The difficulty arises partly on account of the fact that diffuseness may be due to the overcrowding of rotational structure in the spectrum. Alternatively, it may signify the occurrence of a predissociation reaction in which the life of the excited state is short compared to the period of one rotation. A third factor to be borne in mind is the broadening of rotational lines which must necessarily result from intermolecular collisions. It is to be expected that in the case of a large molecule such as dimethylnitrosoamine this effect would be considerable, owing to the possibility of a comparatively long life in the excited state, in accordance with the views of Franck, Spöner, and Teller (*Z. physikal. Chem.*, 1932, *B*, **18**, 88). In such circumstances the broadening may obscure the rotational structure completely.

The fact that decomposition occurs in the region of diffuse bands appears to be evidence of a predissociation process, but in view of what has been said above it is impossible to draw any definite conclusions with respect to the life of the excited state (except, of course, that in the banded region this is longer than the period of vibration). Whichever of the above possibilities be accepted, the low quantum yield and the absence of fluorescence show clearly that for all wave-lengths of the absorption band a large fraction of the absorbed energy is degraded into heat. If the process be a predissociation reaction involving a short-lived upper state, it appears necessary to account for the low quantum yield by recombination of primary products. On the whole it appears more acceptable to assume that the upper state has a longer life, and that the lack of structure is due to overcrowding or pressure broadening. The low quantum yield can then be ascribed to internal or external degradation of excitation energy to heat.

The analytical results show that the photolysis of the nitrosoamines is strikingly contrasted with that of the simple nitroso-compounds and alkyl nitrites. Whereas with the former nitrogen is produced only to a very small extent by secondary reactions, and nitrous oxide is absent, with the latter these two substances constitute the major portion of the gaseous products. Taken as a whole, the reactions of the nitrosoamines are much simpler. For these reasons it is considered that the primary act is the rupture of the molecule at the link between the nitrogen atoms, rather than the elimination of an oximino-group. A further point of difference is provided by the low quantum yield; the nitroso-compounds studied by Anderson, Crumpler, and Hammick (*loc. cit.*) and Hammick and Lister (*loc. cit.*) exhibit a quantum yield of approximately unity. The energy change involved in the primary act [equation (1)] may be calculated from thermal data as follows. It is necessary to estimate the energy liberated by a transition in the nitroso-group from the univalent state (in nitrosoamine) to the non-valent state (in nitric oxide). The heats of formation of nitrosyl chloride and nitric oxide are given in the following equations :

$$\tfrac{1}{2}Cl_2 + \tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \longrightarrow ClNO - 13\text{ kg.-cals.} \quad (a)$$

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \longrightarrow NO - 23\text{ kg.-cals.} \quad (b)$$

Taking the N–Cl and Cl–Cl links as 59 and 29 kg.-cals., respectively, we obtain equations (*c*) and (*d*) from (*a*) and (*b*) respectively :

$$\tfrac{1}{2}Cl_2 + \tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \longrightarrow Cl + \cdot NO - 72\text{ kg.-cals.} \quad (c)$$

$$\tfrac{1}{2}Cl_2 + \tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \longrightarrow Cl + NO - 52\text{ kg.-cals.} \quad (d)$$

whence we see that the transition $\cdot NO \rightarrow NO$ liberates 20 kg.-cals. Pauling (*J. Amer. Chem. Soc.*, 1932, **54**, 3570) has estimated the energy of the N•N bond as 32 kg.-cals. It follows that the primary act (1) is endothermic to the extent of about 12 kg.-cals. The minimum quantum corresponding to the long-wave limit of absorption is about 71 kg.-cals. Hence, when decomposition occurs about 83% of the absorbed energy is converted into heat.

The author is indebted to Trinity College for a Fellowship which made this work possible, and to the Chemical Society for a grant for liquid air. He also wishes to express his sincere thanks to Professor R. G. W. Norrish, F.R.S., for helpful advice and criticism.

University Chemical Laboratory, Cambridge. [*Received, November 14th, 1938.*]