8. *A Study of the Photolysis of Organic Nitrogen Compounds. Part III. Methyl* iso*Cyanate.*

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The absorption spectra, and the mercury-sensitised and the direct photolysis of gaseous methyl *iso*cyanate in the near ultra-violet have been studied. The products of decomposition can be accounted for in both cases by the simultaneous occurrence of two primary acts, producing NCO and CH_3N radicals severally. The relative importance of these processes depends on the temperature. The mechanism of sensitisation is briefly discussed. By irradiation in the presence of nitric oxide it is shown that both the above radicals enter into simple and nearly quantitative reactions with this gas.

Continuing the study of the formation and reactions of free radicals containing nitrogen, we have investigated the photodecomposition of methyl *iso*cyanate. The absorption spectrum of this substance (slightly contaminated with sulphur dioxide) was studied by Woo and Liu (*J. Chem. Physics*, 1935, **3**, 544; 1937, **5**, 499), who recorded the absence of structure in the spectrum, and, using the pure ester, we confirm their results. Hence, the primary act in the photolysis is most probably a dissociation into radicals. The results now described are consistent with the view that this dissociation is twofold:

$$\mathrm{CH_3{\cdot}NCO} + h\nu \begin{array}{l} \nearrow \mathrm{CH_3 + NCO} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1) \\ \searrow \mathrm{CH_3N + CO} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2) \end{array}$$

The mercury-sensitised decomposition has been studied in detail. The NCO radicals under these conditions appear to interact to form nitrogen and carbon monoxide, whereas the CH_3N radicals react with methyl *iso*cyanate in the cold to form a white cloud. At higher temperatures no cloud is formed, but instead a viscous oil appears, which may be a polymer of CH_3N. The direct photolysis is similar, except for the fact that practically all the NCO radicals seem to be hydrogenated to HCNO. An explanation of this is suggested later. Both the NCO and the CH_3N enter into simple reactions with nitric oxide, and these may be used both as a check upon the mechanism of photolysis suggested, and as a test for the presence of these radicals in other reactions.

EXPERIMENTAL.

1. *Preparation of Materials.*—Methyl *iso*cyanate, prepared from methyl sulphate and potassium cyanate (Slotta and Lorenz, *Ber.*, 1925, **58**, 1320), was fractionated, and the product of b. p. 44° was further fractionated in a vacuum. A few units % of sulphur dioxide always remained after this treatment, but this could be removed completely by passing the vapour over anhydrous sodium carbonate, followed by a further fractionation at − 80° to remove the carbon dioxide formed. The absorption spectrum of the final product showed no trace of the characteristic sulphur dioxide bands. It was necessary to keep the substance at − 80° to prevent polymerisation.

2. *Apparatus.*—A Hilger E3 spectrograph was used for photographing the absorption spectrum. The source of light was a hydrogen lamp, and a quartz absorption tube 1 m. long was employed. This could be heated electrically to any desired temperature.

The apparatus used for the photolysis was similar to that already described (Bamford, *Trans. Faraday Soc.*, 1939, **35**, 568). The quartz reaction vessel was, however, arranged inside a furnace so that photolysis could be carried out at elevated temperatures. The gaseous products were removed for analysis in two fractions at − 190° and − 80° severally. For studying the sensitised reaction, a mercury lamp with water-cooled electrodes consuming 200 watts and emitting 90% resonance radiation was used. The direct photolysis was carried out by means of a 250-watt mercury arc running hot.

3. *Results.*—The absorption spectrum appears to be completely continuous. At 15° the highest pressure used was 50 mm. and the long-wave limit of the absorption band was approximately 2350 A. No appreciable change occurred when the temperature was raised to 140°. With a pressure of 70 mm. at this temperature the long-wave limit of the band was 2400 A. The absorption extends to the short-wave limit of the plate. The effective wave-lengths in the experiments described below, in which the hot arc was used, thus lay between 2400 and 2100 A., since the lamp gave only very feeble lines below 2100 A. Similarly, with the cold arc the reaction was sensitised at least to the extent of 90%.

The gaseous products for the sensitised reaction are shown in Table I. The results are scaled to $N_2 = 100$ to facilitate comparison. The figure in parentheses for N_2 is the volume of nitrogen (in c.c. at N.T.P.) obtained in the experiment. No special precautions were taken to ensure the same intensity in each experiment.

TABLE I.

			Products,					
Temp.	Time of irradn. (mins.).	Initl. press. of $CH_3\cdot NCO$ (mm.).	CO.	N_2.	CH_4.	C_2H_6.	H_2.	Ratio of primary acts (2)/(1)
20°	50	150	350	100 (1·64)	30	83	0	0·75
20	20	106	350	100 (0·46)	28	82	19	0·66
20	52	46	355	100 (0·60)	39	80	3	0·76
139	26	129	394	100 (0·18)	65	65	9	0·93
160	25	120	477	100 (0·18)	67	66	37	1·20
234	14½	148	547	100 (0·17)	100	48	61·5	1·43
247	25	131	565	100 (0·20)	165·5	19	55	1·55
307	9	159	670	100 (0·14)	220	0	60	2·05
307	20	166	635	100 (0·28)	227	0	40	1·98
307	50	162	715	100 (0·40)	220	0	120	1·98
347	12	140·5	811	100 (0·13)	222	0	122	2·45

The results indicate that the methane and ethane originate from methyl radicals. At the lower temperatures the majority of these form ethane, but as the temperature is raised an increasingly large proportion becomes hydrogented to methane. The yield of methane with respect to ethane increases rapidly between 230° and 260°; above the latter temperature no ethane is formed. Over the whole range of temperature the total methyl is practically equivalent to the nitrogen, *i.e.*, $CH_4 + 2C_2H_6 = 2N_2$. This would be the case if the primary act was the dissociation (1) followed by the reaction

$$2NCO \longrightarrow N_2 + 2CO \quad . \; . \; . \; . \; . \; . \; . \; . \; . \tag{3}$$

The yield of carbon monoxide is considerably greater than can be accounted for by these reactions. This is best explained by the occurrence of the second primary act (2).

It will be noticed that considerable amounts of hydrogen can be produced, especially at the higher temperatures. The yields of hydrogen vary markedly with the period of irradiation and also the rate of reaction, and it therefore seems clear that the hydrogen arises from a secondary photolysis. From the experimental results, especially those at 307°, it is seen that the production of hydrogen is accompanied by the formation of a roughly equivalent volume of carbon monoxide. This suggests that the source of these compounds is formaldehyde. To test this, a short irradiation was carried out at 307°, and the reaction vessel was removed after being allowed to cool. On shaking the contents with water and applying Schryver's test a strong positive result was obtained. A blank test, carried out under similar conditions but without irradiation, was negative.

After a prolonged irradiation at high temperatures during which most of the *iso*cyanate was decomposed, hydrogen cyanide in considerable quantities could be detected among the products. At ordinary temperatures this forms a solid addition compound with the ester and so may escape detection. At high temperatures the compound dissociates (cf. Slotta and Tschesche, *Ber.*, 1927, **60**, 1022), but in order to detect the hydrogen cyanide sufficient methyl *iso*cyanate must be decomposed to give an excess of the former over any undecomposed ester. The presence of formaldehyde and hydrogen cyanide makes it difficult to observe directly the amount of the ester decomposed, since they cannot readily be separated from the unchanged ester.

In order to obtain additional evidence for the two primary acts (1) and (2), the sensitised decomposition was carried out in the presence of nitric oxide. This was done at two temperatures, the results being given in Table II.

TABLE II.

Temp.	Initl. $CH_3 \cdot NCO$ (c.c.).	Initl. NO (c.c.).	Products (c.c.). CO.	N_2.	CO_2.	N_2O.	NO used (c.c.).	Ratio of primary acts (2)/(1).
20°	11·5	6·2	1·5	1·2	1·1	1·4	5·5	0·79
307	5·1	3·1	1·26	0·56	0·5	1·1	3·0	2·2

The mercury-sensitised decomposition of nitric oxide has been shown by Noyes (*J. Amer. Chem. Soc.*, 1931, **53**, 514) to be very slow. To confirm this in the present conditions, 63 mm. of nitric oxide were irradiated for one hour. Less than 0·1 c.c. of nitrogen was produced, and it may be concluded therefore that the substances given in Table II are produced almost completely by interaction of nitric oxide and the products of photolysis of the *iso*cyanate. The results are accounted for by the reactions :

$$NCO + NO \longrightarrow N_2 + CO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \tag{4}$$

$$CH_3N + NO \longrightarrow CH_3 + N_2O \quad . \; . \; . \; . \; . \; . \; . \tag{5}$$

It will be noticed that at both temperatures the nitrogen and carbon dioxide are approximately equivalent. The methyl radicals formed in (5) and in the primary act (1) also interact with nitric oxide, mainly according to the equation :

$$CH_3 + NO \longrightarrow H_2O + HCN \quad . \; . \; . \; . \; . \; . \; . \; . \tag{6}$$

(see, *e.g.*, Bamford, J., 1939, 17). The possibility of the production of carbon dioxide by reaction between water formed in (6) and methyl *iso*cyanate was also investigated. 15 Mm. of water vapour were mixed with 100 mm. of methyl *iso*cyanate in the reaction vessel and allowed to stand for one hour. There was no change in pressure at the end of this time and less than 0·1 c.c. of carbon dioxide had been formed. Reaction (4) is thus considered to be the only source of carbon dioxide. The absence of hydrocarbon products in these experiments is further evidence that these substances are produced from methyl radicals. The volume of nitric oxide used, observed experimentally, agrees well with that to be expected on the basis of equations (4), (5), and (6), as may be deduced from Table II.

From the ratios of the probabilities of the primary acts (1) and (2) in Table I, it will be noticed that (2) becomes increasingly important as the temperature is raised. The experiments with nitric oxide also enable the ratio to be estimated, and the results at the two temperatures employed agree well with those in Table I. This affords some confirmation for the suggested primary acts, and also for the reactions (4) and (5).

An approximate estimation of the quantum yield for the sensitised reaction at 307° was made by a comparison of the rate of photolysis with that of acetone vapour under similar conditions. It is necessary to assume that the rate of absorption of energy is the same in both cases. This is probably nearly true, since the mercury vapour present would absorb practically all the resonance light emitted. Further, it may be taken that the quantum yield of carbon monoxide in the sensitised decomposition of acetone vapour at 307° is not very different from that in the direct reaction, *i.e.*, unity (Leermakers, *J. Amer. Chem. Soc.*, 1934, **56**, 1899). Hence the absorption of resonance radiation by the acetone vapour will not invalidate the calculation. Pressures of 50 mm. of methyl *iso*cyanate and acetone vapour were used, and irradiation continued for 10 minutes. The mean volumes of carbon monoxide evolved (two experiments) were : from methyl *iso*cyanate, 0·92 c.c.; from acetone, 0·90 c.c. Hence the quantum yield of carbon monoxide from methyl *iso*cyanate is approximately unity at 307°. This is consistent with the mechanism of equations (1), (2), and (3), according to which the maximum value of the quantum yield is unity. The determination of the quantum yield at lower temperatures presents difficulties, since the formation of the cloud interferes with the estimation of the light absorption.

The results of a number of experiments with the hot arc are given in Table III. These results differ from those obtained with the sensitised reaction in two particulars : there is generally more hydrogen, and considerably less nitrogen, formed in the present experiments. The former can readily be accounted for, since formaldehyde absorbs strongly between 2500 and 3100 A., while methyl *iso*cyanate is practically transparent in this region. The hot arc emits a number of strong lines between these wave-lengths, and the formaldehyde would thus undergo considerable photolysis. In the case of the cold arc the decomposition would be mainly sensitised, and since the aldehyde would only be formed in low pressures for short periods of irradiation, the secondary decomposition would be considerably less.

TABLE III.

Temp.	Time, mins.	Initl. $CH_3{\cdot}NCO$ (mm.).	Products (c.c. × 10^2, N.T.P.).					Ratio of primary acts (2)/(1).
			CO.	N_2.	CH_4.	C_2H_6.	H_2.	
25°	123	*ca.* 95	90	4	22	37	10·5	0·82
150	60	,,	140	0·5	28·9	31·5	30	1·18
300	41	,,	155	3	57	0	31	2·1
310	30	,,	154	3	55	0	39	2·0
330	18	,,	150	7	47	0	37	2·2
370	30	,,	209	5	50	0	56	2·6
395	19	,,	174	0	39·5	0	63	2·8
420	18	,,	164	4	30	0	55	3·4
15	540	114	115	9	16	51	10	0·74

From the low yield of nitrogen it may be concluded that the NCO radicals in these circumstances enter into other reactions, rather than (3) : the most probable of these would seem to be hydrogenation at the expense of the methyl *iso*cyanate, with formation of cyanic acid, which would polymerise and escape photolysis. At the end of an experiment the cloud had settled as a deliquescent solid on the walls of the vessel, and on treatment with a little water it evolved ammonia. This behaviour suggests the presence of cyanic acid. No ammonia was evolved when the cloud produced in the sensitised reaction was treated similarly.

DISCUSSION.

The preceding results have been shown to be in agreement with the view that photolysis of methyl *iso*cyanate results in the primary formation of two radicals containing nitrogen. The univalent NCO decomposes bimolecularly or hydrogenates, while the bivalent CH_3N appears to be less reactive and only enters into polymerisation reactions unless NO is present. This agrees with previous results, which have pointed to the tendency of other bivalent radicals, *e.g.*, $CH_3{\cdot}N{:}CH_2$, produced from nitrosoamines and amines, to polymerise, probably after rearrangement (Bamford, J., 1939, 12).

The primary act (1) is endothermic to the extent of about 49 kg.-cals. (taken from Pauling, "The Nature of the Chemical Bond," 1939), which is much smaller than the minimum quantum absorbed (*ca.* 112 kg.-cals. for the 2536 A. line). Woo and Liu (*loc. cit.*) have concluded that this is the only decomposition which is energetically possible. The latest value for the C—N link (94 kg.-cals.) suggests that this is not the case; also allowance must be made for the excitation energy of the carbonyl group, which is liberated in passing to the non-valent state (in carbon monoxide). If the latter energy is taken as 69 kg.-cals. (cf. Norrish, *Trans. Faraday Soc.*, 1934, **30**, 103),* the primary act (2) is seen to be about 25 kg.-cals. endothermic.

As mentioned previously, reaction (3) is much more important in the sensitised than in the direct photolysis. In order to account for this apparent inconsistency in the behaviour of the NCO radical it may be suggested that the process of sensitisation leading to the decomposition (1) is not merely the transfer of energy from the excited mercury atom to the methyl *iso*cyanate molecule, but rather the reaction

$$Hg^* + CH_3{\cdot}NCO \longrightarrow [HgNCO] + CH_3 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

It is conceivable that HgNCO, probably existing as a radical, would not hydrogenate so readily as NCO, but would react according to (3). In the direct reaction HgNCO is not formed and (3) is much less important, since most of the radicals are hydrogenated. It can be seen by comparing Tables I and II that this hydrogenation of the NCO radicals on methyl *iso*cyanate is not accompanied by the formation of carbon monoxide : also from Table I it is clear that no carbon monoxide results from the formation of methane by the reaction between methyl radicals and methyl *iso*cyanate (compare, *e.g.*, the results for 234° and 247°). The CH_2NCO residue from the *iso*cyanate presumably polymerises.

The secondary formation of hydrogen occurs more readily at the high temperatures (Table I), suggesting an increased formation of formaldehyde under these conditions, a plausible reaction being

$$CH_3N + CH_3{\cdot}NCO \longrightarrow (CH_3N{,}HCN) + H_2CO \quad . \quad . \quad . \quad . \quad (8)$$

The CH_3N may form an addition product with the HCN as represented above; alternatively it may undergo a reorganisation, *e.g.*, into CH_2NH, the excitation energy sufficing to dissociate the methyl *iso*cyanate into hydrogen cyanide and formaldehyde. Reaction (8) may well be favoured by higher temperatures, and in addition the relative production of CH_3N in the primary act also increases. Polymerisation of CH_2NH can account for the heavy oil produced on photolysis at high temperatures. At lower temperatures the CH_3N mainly polymerises, or adds on to methyl *iso*cyanate, thus forming the cloud. Further, since no hydrogen is formed on irradiation with nitric oxide, even at high temperatures, it is reasonable to suppose that no formaldehyde is produced in these circumstances. (The argument that formaldehyde is formed, but escapes notice on account of reactions with nitric oxide, either before or after photolysis, is unsatisfactory. In the first place the volumes of nitric oxide used, given in Table II, do not permit of such reactions, and secondly, hydrogen is formed in the molecular condition by photolysis of formaldehyde, and hence is unlikely to react with nitric oxide.) These facts are explained if the aldehyde is formed by a reaction involving CH_3N, as in (8), for when nitric oxide is present, (5) occurs to the exclusion of (8). It does not therefore appear that dissociation into formaldehyde and hydrogen cyanide occurs when methyl *iso*cyanate molecules collide with excited mercury atoms.

One of the authors (C. H. B.) expresses his thanks to Trinity College, Cambridge, for a Fellowship, which has made this work possible. Part of the work was carried out in the Physical Chemistry Department of the University of Sydney, N.S.W., and the authors have great pleasure in recording their gratitude to the Vice-Chancellor of the University and to Professor C. E. Fawsitt of the Chemistry Department for their many kindnesses.

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[*Received, November* 20*th*, 1940.]

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* Norrish's figure of 101 kg.-cals. becomes 69 kg.-cals. if recalculated on the basis of more recent energy values of the C–H and H–H links.