Reactions of Alkylamino-radicals. Part I. Photolysis of Dialkylamino-compounds

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Alkylamino-radicals may be produced by the photolysis of *N*-alkyl amides, ureas, and tetrazenes. Reactions of the radicals are unaffected by the presence of oxygen or nitric oxide and their stability in oxidation systems may partly explain the inhibiting action of aliphatic amines under certain conditions. Dialkylamino-radicals are shown to autodisproportionate to form hydrogen and an imine, in competition with the recombination to form hydrazines.

THE reactions of alkylamino-radicals may have great significance in the chemistry of alphatic amines. Previous studies of the photolysis of amines,[1] and of oxidative reactions in the presence of amines[2] have not fully considered the possible reactions of alkylamino-radicals, which may be formed[3] by direct photolysis, oxidation of alkyl groups attached to nitrogen, or by hydrogen abstraction in the case of primary and secondary amines. Considerable uncertainty about the completeness of the suggested mechanisms for some of the reactions must exist, particularly those involving tertiary amines.

There may be a significant contribution from alkylamino-radicals during the inhibition reactions of aliphatic amines under certain conditions.[4] One important feature of an accepted mechanism for inhibition of oxidation is the stability of the inhibitor radical which is formed as a result of chain termination through hydrogen abstraction from the inhibitor by a peroxy-radical [equations (1)—(4)]. This mechanism illustrates the dual role of an inhibitor, InH, since not

$$RH + O_2 \longrightarrow R^\bullet + HO_2^\bullet \quad (1)$$

$$R^\bullet + O_2 \longrightarrow RO^\bullet_2 \quad (2)$$

$$RO_2^\bullet + InH \longrightarrow In^\bullet + ROOH \quad (3)$$

$$RO_2^\bullet + RH \longrightarrow R^\bullet + ROOH \quad (4)$$

only are oxidation chains involving $RO_2^\bullet$ broken, but the suggested stability of $In^\bullet$ to oxidation, compared to $R^\bullet$, prevents the initiation of fresh chain reactions. Whilst a previous paper has shown that alkylamino-radicals appear to be resistant to oxidation,[4] kinetic studies[5] and the observation of significant isotope effects[5,6] have demonstrated that the free amine itself is unlikely to be responsible for inhibition of low temperature oxidation since Schiff's bases are preferentially formed from reaction with aldehydes. Nevertheless, since this reaction with aldehydes is an equilibrium,[7,8] a finite concentration of free amine will always be present, and thus inhibition by the free amine itself cannot be completely ruled out. At higher temperatures, however, during the inhibition of flames and explosions[9] and oxidation of hydrogen,[10] the free amine must become important, and thus amino-radicals are more likely to play an important role.

This paper presents new data on the chemistry of alkylamino-radicals. Two recent publications[11,12] have confirmed both the e.s.r. splitting constant for the dimethylamino-radical[4] (in preference to the slightly higher value previously reported[13]) and the stability of alkylamino-radicals,[4,8,14] which is of great importance to the inhibition mechanism discussed earlier.

EXPERIMENTAL

Apparatus.—The apparatus consisted of a static vacuum line of conventional design, with facilities for distillation at reduced pressure, gas sampling for chromatographic analysis, and removal of samples for direct mass spectral analysis. The apparatus was electrically heated in order to minimize condensation of the less volatile materials. The reaction vessel (290 ml) was a cylindrical quartz cell, and was suspended in an electrically heated air oven fitted with quartz windows. A Hanovia S-500 medium-pressure arc was used to provide illumination of the cell. Analyses for permanent gases were made on a Burell K7 chromatograph with a hot wire detector using a 1·5 m × 2 mm silica gel (100—120 mesh) column with helium carrier gas; the aliphatic nitrogen compounds were determined using an Aerograph Hi Fy 600B flame ionisation gas chromatograph using a 1·5 m × 2 mm Poropak Q (80—100 mesh) column treated with 20% polyethyleneimine, using nitrogen carrier gas. Mass spectral analyses were made using

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Hitashi–Perkin-Elmer RMU-6D and Consolidated Electrodynamics Corporation 21-130 mass spectrometers. ^1H N.m.r. spectra were recorded on a Varian A-56/60A spectrometer.

Materials.—Reagents used were the best grade commercially available and were dried with barium oxide or potassium hydroxide. The middle fraction from bulb-to-bulb distillation was collected for use in each case.

Amides.—The *NN*-dialkyl amides were prepared [15] from the corresponding acid chloride and secondary amine. The purity was shown to be at least 98% by gas chromatography, and the structures were confirmed by mass spectrometry.

Tetramethylhydrazine.—The fully substituted hydrazine was prepared by the successive methylation of *NN*-dimethylhydrazine by use of methyl formate,[16] and was obtained in only 94% purity, but this was sufficient for the calibration purposes for which it was prepared. The n.m.r. of the product showed an unresolved singlet at τ 7·78.

Tetramethyltetrazene.—This was prepared by the action of mercuric oxide upon *NN*-dimethylhydrazine.[17] The product was identified by mass spectral analysis (>98% pure), and the n.m.r. spectrum showed a singlet at τ 7·33. Contrary to early reports,[18] the material did not prove hazardous to handle and it was accidentally shown not to be explosive at its normal b.p. as reported.

RESULTS AND DISCUSSION

Preliminary investigations of the reactions of alkylamino-radicals involved the photolysis of *NNN'N'*-tetramethylurea (TMU) and *NN*-dimethylacetamide (DMA). The initial rates of formation of products were obtained by analyses of independent photolyses having varying durations up to 2% decomposition and extrapolation of the data to zero time. All plots of formation of products with time were linear up to the extent of decomposition considered; however, tetramethylhydrazine showed some fall-off, but this was only above *ca.* 5% decomposition. The results are in Table 1 in which the carbon balance is based on yield of CO.

TABLE 1

Products from the photolysis of tetramethylurea (50 mmHg) and *NN*-dimethylacetamide (50 mmHg) at 150 °C

	Tetramethyl-urea		*NN*-Dimethyl-acetamide	
Product	(%)	Carbon balance (%)	(%)	Carbon balance (%)
CO	26·9	100	61·0	100
H_2	5·9		1·04	
CH_4	9·6	9·5	11·7	19·0
C_2H_6	1·2	2·4	8·4	27·3
Me_2NH	15·9	31·4	0·51	1·7
Me_3N	3·0	9·1	5·4	26·1
$Me_2N{\cdot}NMe_2$	4·0	15·7	1·47	8·6
CO_2 (from polymer)	33·0	32·4	10·7	17·4

The extent of formation of polymeric material on the surface of the reaction vessel was determined by oxidation with molecular oxygen, above 600 °C, following the routine analysis and evacuation of the vessel. The carbon dioxide formed was measured, and hence the extent of polymer formation was calculated.

Photolysis of the urea can yield two dimethylamino-radicals, whilst the amide can give only one. The products, which showed relatively higher yields in the former case, are hydrogen, methane (with respect to ethane), dimethylamine (with respect to trimethylamine), tetramethylhydrazine, and the polymer. Although the yield of methyl radicals [calculated from $(CH_4 + 2C_2H_6 + Me_3N)$] from DMA, is more than twice that from TMU, the considerable increase in the relative yield of methane from TMU may be due to easy hydrogen abstraction, possibly from the polymer. Although the yield of dimethylamine from TMU is surprisingly large, this may again be due to increased ease of hydrogen abstraction. A mechanism has recently been suggested for the formation of dimethylamine and ' a polymeric material ' from dimethylamino-radicals [19] [equation (5)]. However, since the ratios of dimethylamine to polymer differ by an order of magnitude in the two systems cited here, we suggest that this mechanism is not of major importance in this study.

$$2Me_2N^{\bullet} \longrightarrow Me_2NH + \begin{array}[t]{c}[CH_2{=}NMe]\\ \big\downarrow \\ \text{polymer}\end{array} \qquad (5)$$

It is shown later by kinetic and isotopic studies that the important competitive reactions of dimethylamino-radicals are autodisproportionation and dimerization, to form *N*-methylenemethylamine and hydrogen, and tetramethylhydrazine, respectively [equations (6) and (7)]. None of these products were observed by previous workers, although the imine was suggested [19] as an intermediate in the formation of the polymer. No attempt was made to remove polymer from the reaction vessel between experiments and this could explain the poor material balance in earlier results. The formation of the trimer, perhydro-1,3,5-trimethyl-1,3,5-triazine, from the *N*-methylenemethylamine has been studied,[20] and although this has been observed in the products from the decomposition of trimethylamine at high temperatures,[21] it was probably formed during the low temperature analysis. Pyrolysis of the trimer [20]

$$2Me_2N^{\bullet} \longrightarrow 2CH_2{=}NMe + H_2 \qquad (6)$$

$$2Me_2N^{\bullet} \longrightarrow Me_2N{\cdot}NMe_2 \qquad (7)$$

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was used to produce monomer in the amine decomposition, but the trimer was not found to be a product in our case. However, the yield of hydrogen relative to total methyl from DMA is very similar to that obtained in the thermal decomposition of trimethylamine at the higher temperatures[21] and thus consistent with the primary formation of $^\bullet$Me and $^\bullet NMe_2$ in both systems.

When the photolyses were carried out in the presence of oxygen or nitric oxide, no methane, ethane, or trimethylamine was formed, owing to alternative preferential reaction of methyl radicals, whereas the remaining products were still formed in similar yields. Whilst previous low temperature e.s.r. experiments have demonstrated the stability to oxidation of the dimethylamino-radical relative to methyl,[4] the continued formation of hydrogen in the presence of oxygen or nitric oxide suggests that a hydrogen elimination reaction is probably occurring and that reactions involving hydrogen atoms are not of major importance.

Earlier work on the photolysis of trimethylamine[22] showed that in the presence of cyclopentane, the hydrogen yield was decreased. This also suggested that hydrogen atom reactions to yield hydrogen were unlikely, and it seems probable that the decrease in hydrogen was due to increased hydrogen abstraction by dimethylamino-radicals to form dimethylamine (which was not measured), although quenching of an excited state by the hydrocarbon cannot be ruled out on the evidence available. Furthermore, it may be shown that the ratio $(2[C_2H_6] + [CH_4])/[H_2]$ is approximately constant at a given temperature. Since the primary step is most probably equation (8)[22] the results are consistent

$$Me_3N \longrightarrow Me_2N^\bullet + {}^\bullet Me \qquad (8)$$

with the currently suggested mechanism for the formation of hydrogen by reaction (6). The present work has shown that *N*-methylenemethylamine is formed, further supporting the proposed disproportionation reaction (6). This product was confirmed by gas chromatography, comparison being made with the monomer generated from perhydro-1,3,5-trimethyl-1,3,5-triazine.[20] The mass spectrum of the product showed a parent peak at *m*/*e* 43, consistent with *N*-methylenemethylamine. Lower mass peaks were not distinct. In order to show the importance of the alkyl group attached to nitrogen in the dialkylamino-radicals, a series of compounds which would yield the radicals upon photolysis were examined; the initial rates of formation of hydrogen, relative to carbon monoxide, were measured in each case (Table 2).

When the alkyl group attached to the nitrogen atom of the amides is changed, there is an appreciable change in the relative hydrogen yield, whereas changing the alkyl group adjacent to the carbonyl group has a negligible effect. The ratio of hydrogen to hydrazine is shown to remain constant, within experimental error, and this is consistent with the suggested competitive reactions of alkylamino-radicals to form hydrazines or hydrogen and an imine. When the possible concentration of alkylamino-radicals which may be obtained by photolysis is significantly increased, as in the case of TMU and tetramethyltetrazene, the relative yield of hydrogen shows a considerable increase. Thus, whilst not proving the importance of dialkylamino-radicals themselves, these experiments nevertheless establish the importance of the dialkylamino-group in the formation of hydrogen from the parent compound.

TABLE 2

Photolysis of *NN*-dialkyl amides and tetramethylurea

	Yield rel. to CO Hydrogen	 Tetramethylhydrazine	Hydrogen/Tetramethylhydrazine
Me_2NAc	0·034	0·045	0·76
$Me_2N\cdot COEt$	0·032	0·048	0·67
$Me_2N\cdot COPr$	0·035	0·042	0·83
Et_2NAc	0·017		
Pr_2NAc	0·022		
$Me_2N\cdot NMe_2$	0·22	0·36	0·61

It is suggested that the possible reactions of dimethylamino-radicals include equations (6) and (7), by which hydrogen and tetramethylhydrazine may be formed.

$$2Me_2N^\bullet \longrightarrow H_2 + 2CH_2{=}NMe \qquad (6)$$

$$2Me_2N^\bullet \longrightarrow Me_2N\cdot NMe_2 \qquad (7)$$

$$RH \xrightarrow{h\nu} R^\bullet + H^\bullet \qquad (9a)$$

$$RH + H^\bullet \longrightarrow R^\bullet + H_2 \qquad (9b)$$

$$\frac{d[H_2]}{dt}\bigg/\frac{d[Me_2N\cdot NMe_2]}{dt} = \frac{k_6}{k_7} + \frac{k_9[RH]}{k_7[Me_2N^\bullet]^2} \qquad (10)$$

The concentration of amide [RH] is assumed to be effectively constant and k_9 is taken to be the observed rate constant for the formation of hydrogen by a free-radical mechanism.

From photolyses of the amide and tetrazene, both alone and in the presence of oxygen and nitric oxide and determining the initial rates of formation of hydrogen and tetramethylhydrazine, the ratio $(d[H_2]/dt)/(d[Me_2N\cdot NMe_2]/dt)$ was calculated at three different intensities of incident light (Table 3).

TABLE 3

Determination of $(d[H_2]/dt)/(d[Me_2N\cdot NMe_2]/dt)$ during the photolysis of *NN*-dimethylacetamide and tetramethyltetrazene, with different filters and free-radical scavengers

	NN-Dimethylacetamide Scavenger			Tetramethyltetrazene Scavenger		
Filter	None	Oxygen	Nitric oxide	None	Oxygen	Nitric oxide
None	0·79	0·70	0·69	0·65	0·72	0·62
48%	2·6	0·75	0·63	3·1	0·81	0·77
26%	6·2	1·04	0·82	10·7	0·78	0·86

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In the absence of oxygen or nitric oxide, it would appear that some other hydrogen-forming reaction is occurring. If this additional reaction involved free radicals which were reactive towards oxygen and nitric oxide, it would be inhibited by the presence of such radical scavengers. However, if the mechanism involved molecular elimination of hydrogen from an excited state, it is also possible that the reaction could be suppressed through quenching by the additives.

As the light intensity is reduced, $[Me_2N^\bullet]$ is reduced, and thus k_9 will become more important, since it is suggested that this reaction is first-order in hydrogen atoms. Consequently, at low light intensities, the ratio would not be expected to remain constant, but to show the observed significant increase in the absence of oxygen or nitric oxide. Thus, in the presence of oxygen or nitric oxide, the reaction of the dimethylamino-radicals should reduce to the simple competition, since all other possible reactions (except hydrogen abstraction) will be prevented. In this case, the ratio $(d[H_2]/dt)/(d[Me_2N\cdot NMe_2]/dt)$ would be expected to remain constant, a finding which is borne out within experimental error. This would seem to indicate that the formation of hydrogen is not a primary process, as previously suggested in the case of trimethylamine.[22] The second-order dependence upon the dimethylamino-radical concentration again supports the autodisproportionation reaction (6).

Further evidence that the formation of hydrogen is second order in dimethylamino-radicals was obtained from isotopic labelling experiments with trimethylamine and $[^2H_9]$-trimethylamine. The primary process in this photolysis has been established [reaction (8)], and since no significant difference in quantum yield was observed upon separately photolysing the two amines, equimolar proportions of deuteriated and undeuteriated dimethylamino-radicals would be produced by the co-photolysis of an equimolar mixture of the corresponding trimethylamines. Thus, if there is no isotope effect in reaction (6), then the statistical distribution of isotopic hydrogens should be observed. Thus the ratio $H_2 : HD : D_2$ should be 1 : 2 : 1, because of cross-disproportionation reactions. In fact from the results obtained (Table 4) in the presence of oxygen or nitric oxide, it is apparent that there is an isotope effect of *ca.* 2 : 1 in the autodisproportionation reaction, allowing for which the isotopic ratios are almost 1 : 2 : 1. The apparently much smaller isotope effect when no additive is present, is presumably due to the existence of a concurrent free-radical reaction to form hydrogen, for which there is a negligible isotope effect. However, since the photolysis of amines leading to the breaking of C–H or C–D bonds to form free H or D atoms would be expected to show some isotope effect,[23] the mode of hydrogen formation could be some energetically favoured molecular elimination from an excited state which is quenched by the additives.

TABLE 4

Formation of H_2, HD, and D_2 from 1 h photolyses of equimolar mixtures of Me_3N and $(CD_3)_3N$, and the effect of adding O_2 and NO

Photolysis	Isotopic hydrogen ratios		
	H_2	HD	D_2
Alone	2·42	1·67	1·00
With 20% O_2	4·09	1·80	1·00
With 20% NO	4·05	2·62	1·00

The results of the isotope studies confirm the kinetic data and further support the proposed autodisproportionation reaction of dimethylamino-radicals.

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