Oxidation of Nylon Model Systems

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The effect of light intensity, photosensitiser concentration, oxygen pressure, and temperature on the rate of the photochemical oxidation of a series of *N*-alkylamides R·CONR′R″ where R and R″ are alkyl groups and R′ is an alkyl group or hydrogen, has been studied. Sodium anthraquinone-2-sulphonate was a powerful photosensitiser. Rates of oxidation and apparent energies of activation are recorded for several amides. A stepwise variation in the rate of oxidation with *N*-alkyl substituent through the *N*-methyl, -ethyl, -propyl, and -butyl derivatives of acetamide and propionamide is found. A mechanism is advanced for the formation of hydrogen peroxide, acyl amides (R·CONH·COR), formylamides (R·CONH·CHO), and unsubstituted amide ($R·CONH_2$) among the oxidation products.

THERMAL and photochemically induced oxidation of polyamides and amide model systems has been studied; Sharkey and Mochel [1] showed that the photo-oxidation of *N*-alkylamides yields acids, aldehydes, and unsubstituted amide. The pentanal and pentanoic acid formed in the oxidation of *N*-pentylhexanamide were proved to come from the amine part of the molecules by using amide labelled with ^{14}C. The products were explained by a chain mechanism involving the formation and decomposition of hydroperoxides. It was also shown that substitution of the hydrogens on the methylene group adjacent to the nitrogen afforded complete protection to oxidation in their experimental conditions. Flett [2] compared the rate of reaction and apparent energy of activation of the photosensitised oxidation of acetamide and *N*-methyl- and *N*-t-butylacetamide. Acetamide and butylacetamide were found to be the most resistant. The photosensitised oxidation of *N*-alkylamides was studied by Lock and Sagar [3] who found *N*-acylamide, formylamide, and unsubstituted amide among the oxidation products. Mikolajewski, Swallow, and Webb [4] conclude from studies on the wet oxidation of Nylon and simple amides that degradation proceeds principally by rupture of the bond between the nitrogen of the amide and the carbon of its α-methylene group. Work by Kroes *et al.*[5] on the photo-oxidation of Nylon 6 and 66, has shown that the mechanism suggested by Sharkey and Mochel holds for polyamides to some extent.

The detection of small quantities of oxygenated groups attached to long polymer chains, as may occur in a polymer which has degraded under normal weathering, is extremely difficult. For this reason and for experimental convenience we have studied the photosensitised oxidation of simple *N*-alkylamides which can be considered as models for polyamides. The compounds studied were mostly liquids or low-melting solids which

[1] W. H. Sharkey and W. E. Mochel, *J. Amer. Chem. Soc.*, 1959, **81**, 3000.
[2] A. C. Flett, Ph.D. Thesis Aberdeen, 1958.
[3] M. V. Lock and F. B. Sagar, *Proc. Chem. Soc.*, 1960, 358.
[4] E. Milolajewski, J. Swallow, and M. Webb, *J. Appl. Polymer Sci.*, 1964, **8**, 2067.
[5] G. H. Kroes, *Rec. Trav. chim.*, 1963, **82**, 979; 1962, **81**, 624.

enabled oxidation to be studied on the pure materials without solvents. The oxidations were photosensitised by sodium anthraquinone-2-sulphonate, a compound similar to certain vat dyes, which functions by an extremely efficient cyclic mechanism investigated by Bolland and Cooper [6] and by Wells,[7] involving abstraction of a hydrogen atom by the activated quinone to give a semiquinone radical which regenerates the original quinone on reaction with oxygen:

$$A + h\nu \longrightarrow A^*$$
$$A^* + RH \longrightarrow AH\cdot$$
$$AH\cdot + O_2 \longrightarrow A + HO_2$$

We used *N*-methyl, *N*-ethyl, *N*-propyl, *N*-isopropyl, *N*-n-butyl, *N*-t-butyl, *N*-n-heptyl, *N*-benzyl, and *N*-diethyl-acetamide, *N*-methyl, *N*-ethyl, *N*-n-propyl, and *N*-n-butyl-propionamide, and *N*-n-propyl, *N*-n-butyl, and *N*-isobutyl-butyramide.

EXPERIMENTAL

N-Alkylamides.—All except methylacetamide and *N*-methyltrimethylacetamide were synthesised from the amines and acid chlorides, as exemplified for *N*-n-propylpropionamide. n-Propionylchloride (0·5 mole in 100 ml. of dry benzene) was added during 1 hr. to n-propylamine (0·5 mole) and pyridine (1 mole) in 250 ml. of dry benzene. The mixture was stirred and kept cool to prevent volatilisation. The product was filtered free from pyridine hydrochloride and separated by fractional distillation. Similarly prepared were *N*-ethylacetamide, b. p. 204—205°/758 mm. (Found: C, 55·0; H, 10·3; N, 15·8. Calc. for C_4H_9NO: C, 55·2; H, 10·4; N, 16·1%), *N*-n-propylacetamide, b. p. 110—112°/10 mm., 222—225°/760 mm. (Found: C, 59·6; H, 11·1; N, 13·4. Calc. for $C_5H_{11}NO$: C, 59·5; H, 10·9; N, 13·9%), *N*-isopropylacetamide, b. p. 74—75°/1·5 mm., 118°/15 mm. (not analysed); *N*-n-butylacetamide, b. p. 228—230°/760 mm., 92°/1·5 mm. (Found: C, 62·3; H, 11·4; N, 11·6. Calc. for $C_6H_{13}NO$: C, 62·6; H, 11·3; N, 12·2%), *N*-n-heptylacetamide, b. p. 123°/1 mm., 155°/13 mm. (Found: C, 68·6; H, 12·0; N, 8·8. Calc. for $C_9H_{19}NO$: C, 68·7; H, 12·1; N, 8·9%), *N*-methylpropionamide, b. p. 63—64°/0·3 mm. (Found: C, 55·0; H, 10·3; N, 16·3. Calc. for C_4H_9NO: C, 55·2; H, 10·4; N, 16·1%), *N*-ethylpropionamide, b. p. 100°/10 mm. (Found: C, 59·4; H, 10·3; N, 13·1. Calc. for $C_5H_{11}NO$: C, 59·5; H, 10·9; N, 13·9%), *N*-n-propylpropionamide, b. p. 84°/1 mm. (Found: C, 61·8; H, 11·3; N, 10·1. Calc. for $C_6H_{13}NO$: C, 62·6; H, 11·3; N, 12·2%), *N*-n-butylpropionamide, b. p. 243°/760 mm., 100°/5 mm. (Found: C, 65·1; H, 11·7; N, 10·9. Calc. for $C_7H_{15}NO$: C, 65·0; H, 11·7; N, 10·9%), *N*-n-propyl-n-butylamide, b. p. 93°/0·7 mm. (Found: C, 65·8; H, 11·7; N, 10·9. Calc. for $C_7H_{15}NO$: 65·0; H, 11·7; N, 10·9%), *N*-n-butylisobutylamide, b. p. 94°/1 mm. (Found: C, 67·0; H, 12·1; N, 9·6. Calc. for $C_8H_{17}NO$: C, 67·0; H, 11·9; N, 9·8%), benzylacetamide, m. p. 61° (not analysed), *NN*-dimethylacetamide, b. p. 165—167°/760 mm. (Found: C, 54·7; H, 10·3; N, 15·8. Calc. for C_4H_9NO: C, 55·2; H, 10·3; N, 16·1%), and *NN*-diethylacetamide, b. p. 182—185°/760 mm. (Found: C, 62·0; H, 11·3; N, 11·5. Calc. for $C_6H_{13}NO$: C, 62·6; H, 11·3; N, 12·2%).

N-Acylamides.—Except for the formylamides, these were prepared by the method of Polyn and Spotswood.[8]

N-Formylamides.—*N-Formylpropionamide.* A solution of 2 g. of barium hydroxide in 22 c.c.s. of 37% formaldehyde solution was added to 20 g. of propionamide and the mixture heated for 2 min. to effect solution. After several hours CO_2 was passed to precipitate barium carbonate and the filtrate evaporated to dryness under vacuum and the *N*-methylolpropionamide [9] recrystallised from ethyl acetate. The methylol derivative was oxidised at room temperature in light petroleum solution by shaking for 5 hours with MnO_2 prepared by the method of Mancera *et al.*[10] The solution was filtered and the solvent removed under vacuum leaving pure *N*-formylpropionamide, m. p. 65°.

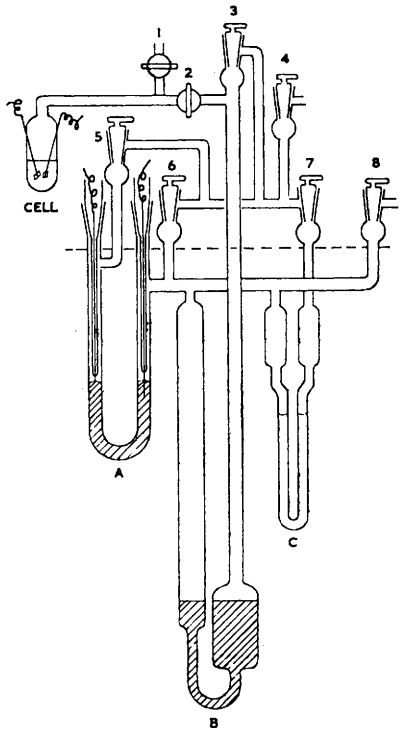


FIGURE 1 Manostat

N-Formylbutyramide and formylisobutyramide were prepared similarly; yields were poor and purity not high. All formyl derivatives were extremely deliquescent.

Unsubstituted Amides.—These were prepared from ammonia and the acid chloride.[11]

Gas Chromatography.—Products were analysed on a Pye argon gas chromatograph at 125°. The stationary phase was 5% polypropylene sebacate on Kieselguhr.

Apparatus and Technique.—The apparatus for measuring the rate of oxygen absorption at constant temperature and pressure (Figure 1) is basically that devised by Cooper and Melville.[12] The manostat was immersed up to the level indicated by the broken line in a thermostat regulated at 25° ± 0·05°. The Pyrex reaction cell had two parallel 3 cm.

[6] J. L. Bolland and H. R. Cooper, *Proc. Roy. Soc.*, 1954, *A*, **225**, 405.
[7] C. F. Wells, *Trans. Faraday Soc.*, 1961, **57**, 1703, 1719
[8] J. B. Polya and T. M. Spotswood, *Rec. Trav. chim.*, 1948, **67**, 927; 1952, **71***b*, 76.
[9] A. Einhorn and A. Hamburger, *Annalen*, 1908, **361**, 122.
[10] O. Mancera, G. Rozenkranz, and F. Sandheimer, *J. Chem. Soc.*, 1953, 2189.
[11] G. E. Philbrook, *J. Org. Chem.*, 1954, **19**, 623.
[12] H. R. Cooper and H. W. Melville, *J. Chem. Soc.*, 1951, 1984.

diameter faces 3 cm. apart. This, joined to the manostat through a glass coil attached to tap 8, was immersed in a water thermostat through which it was irradiated with a Metrovic 250w low-pressure mercury lamp. This system effectively filters out all radiation below 3000 Å. The reaction cell was vigorously shaken by clamping it to a beam actuated by an eccentric wheel driven by a motor at 640 rev./min. Preliminary experiments showed that the rate of oxidation was independent of shaking speed above 300 c./min.

The manostat consists of a control manometer *A*, calibrated mercury gas burette *B*, and a sensitive reference manometer *C*. With the reaction cell containing amide in position, taps 1 and 2 closed and taps 4, 5, 6, 7, and 8 open, the manostat was evacuated to less than 10^{-3} mm. Hg. The system was then filled with pure oxygen to the required pressure *via* tap 4 which was then closed. The electrolytic cell containing oxalic acid solution was then evacuated to the same pressure as the manostat *via* tap 1, and the apparatus brought into operation by closing taps 3, 4, 5, 6, and 7 and opening 2, thus connecting the electrolytic cell with the gas burette. Absorption of oxygen in the reaction cell slightly decreases pressure in the right-hand limb of the control manometer *A*, thus breaking a relay circuit and bringing the cell into operation. The gas generated by the cell causes a rise in the level of gas burette *B*, equivalent to the oxygen absorbed. At the same time the pressure in *A* is equalised, thus switching the cell off. Manometer *C* indicates any pressure difference in the system due to malfunction of the electrical circuit or gas leaks.

Procedure.—The amide, containing dissolved sodium anthraquinone-2-sulphonate, was weighed directly into the reaction cell which was connected to the manostat. The system was evacuated, filled with oxygen as described above, and exposed to an ultraviolet source while being agitated vigorously.

Rate measurements were made over the first few percent. of oxidation.

Examination of Oxidation Products.—Analytical methods. No significant difference was obvious in the infrared spectra of oxidised and unoxidised materials. Traces of aldehydes were detected as their phenylhydrazones by the method of Roberts and Green,[13] but were not quantitatively estimated. The presence of amines and acids among the products could not be confirmed.

Peroxides were estimated by Sully's iodometric technique [14] with modifications. In one case organic peroxide was estimated by decomposing the hydrogen peroxide present with the enzyme catalase. Other oxidation products were detected on a Pye argon chromatograph.

RESULTS

The overall rate of oxygen uptake may be due to several factors, *viz.*, thermal oxidation or photochemical processes depending on the initial photolytic scission of the molecule or on the abstraction of hydrogen by activated sensitiser molecules.

Thermal Oxidation.—Preliminary experiments showed that thermal oxidation of *N*-alkylamides at the temperatures used is too slow to be detected by the apparatus and can be neglected. Several compounds can even be distilled in air at atmospheric pressure.

Photochemical Processes.—The sensitised and unsensitised rate of oxidation of *N*-methylacetamide and *N*-n-butylpropionamide was studied. Table 1 illustrates the efficiency of the sensitiser, and Figure 2 typical absorption plots. These results show that the uptake of oxygen may be assumed due only to the photosensitised reaction. The variation of rate with sensitiser concentration (Figure 3) is similar to that observed by Bolland and Cooper [6] and

TABLE 1

Rate of oxidation of amides (moles O_2/mole amide/min.) at 30°

	Rate (1)	Rate (2)
N-Methylacetamide	$8{\cdot}3 \times 10^{-7}$	$5{\cdot}97 \times 10^{-4}$
N-*n*-Butylpropionamide	$6{\cdot}6 \times 10^{-7}$	$7{\cdot}72 \times 10^{-4}$

(1) Unsensitised at 200 mm. (2) Sensitiser concn. $2{\cdot}54 \times 10^{-3}$ mole (mole amide)$^{-1}$ at 250 mm.

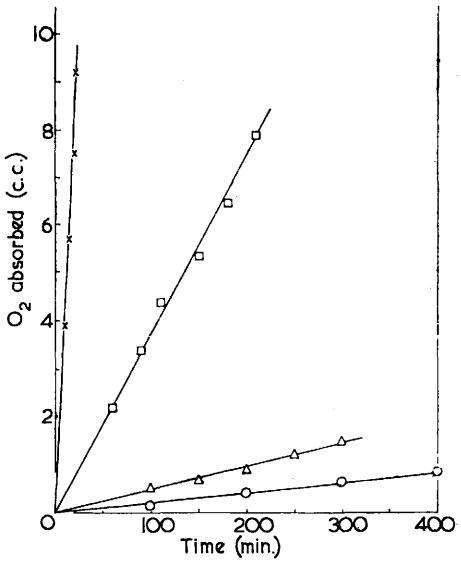


FIGURE 2 Typical absorption plots

○ Butylacetamide, 30° } No sensitiser
△ Methylacetamide, 30° }
□ Acetamide, 86° } Sensitised $2{\cdot}54 \times 10^{-3}$ moles/mole amide
× Methylacetamide, 30° }

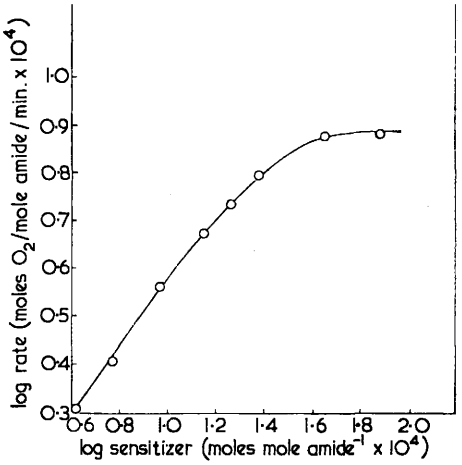


FIGURE 3 Dependence of rate on sensitiser concentration

[13] J. D. Roberts and C. Green, *Ind. Eng. Chem. Anal.*, 1946, **18**, 335.
[14] B. D. Sully, *Analyst*, 1954, **79**, 86.

Wells [7] for oxidation of alcohols and be attributed to the change in optical density of the system, the rate becoming independent of sensitiser when light absorption is complete.

Variation of Rate with Light Intensity.—Table 2 shows the direct dependence of rate on the first power of light intensity for three amides. Intensity was varied by placing a perforated screen between source and cell. The results confirm Flett's observations.

TABLE 2

Dependence of rate on light intensity

	Rate (ml. O_2/min.) Direct illumination (R_1)	Screened illumination (R_2)	n
N-n-Butylpropionamide ...	0·185	0·091	1·03
N-n-Butylacetamide	0·550	0·280	0·99
N-Methylacetamide	0·750	0·363	1·06

$n = [\log R_1/R_2]/[\log I_1/I_2]$ and $\log (I_1/I_2) = 0{\cdot}297$.

Variation of Rate with Oxygen Pressure.—In both cases (Table 3) studied the rates are independent of oxygen pressure between 200 and 600 mm. Slightly lower rates were recorded at lower pressures but then amides tend to distil and the efficiency of the sensitiser regeneration process is reduced, leading to slower rates.

TABLE 3

Influence of oxygen pressure on rate of amide oxidation (moles O_2/mole amide/min.) at 30°

Sensitiser concentration (1) $2{\cdot}43 \times 10^{-3}$. (2) $4{\cdot}28 \times 10^{-3}$ mole (mole amide)$^{-1}$.

N-Methylacetamide		*N*-n-Butylpropionamide	
O_2 pressure	10^4 Rate	O_2 pressure	10^4 Rate
50	5·64	50	9·51
60	5·76	250	9·80
100	5·72	300	9·74
200	6·03	400	9·90
313	6·07	500	9·80
356	5·94	600	9·81
490	5·93		
604	6·07		

TABLE 4

Apparent energy of activation and rate of oxidation of *N*-alkylamides at 30°

Amide	Rate (mole O_2/mole amide/min.) × 10^4	E (kcal. mole^{-1})
N-Methylacetamide.....	5·97	2·13
N-Ethylacetamide	8·60	4·0
N-n-Diethylacetamide	15·2	2·73
N-n-Propylacetamide	6·77	4·33
N-Isopropylacetamide	6·87	1·62
N-n-Butylacetamide	8·50	4·0
N-Methylpropionamide	5·77	
N-Ethylpropionamide.....	9·64	
N-n-Propylpropionamide ...	7·0	
N-n-Butylpropionamide.....	7·72	4·66
N-n-Propylbutyramide	6·10	
N-n-Butylbutyramide.....		4·87
N-n-Butyl iso-butyramide	4·40	4·16
N-Benzylacetamide.....	1·94 at 64°	
N-Methyltrimethylacetamide	5·4 at 88°	
Acetamide.....	$1{\cdot}23 \times 10^{-5}$ at 86°	

Comparison of Rates of Reaction with Structure of the Amide.—Samples of each *N*-substituted amide were tested under the same conditions (Table 4). Rates for *N*-benzylacetamide, *N*-methyltrimethylacetamide, and acetamide are included for comparison. One unexpected result is the alternation in rates of oxidation going through the methyl, ethyl, propyl, and butyl derivatives of acetamide and propionamide (Figure 4). Amides with an odd number of

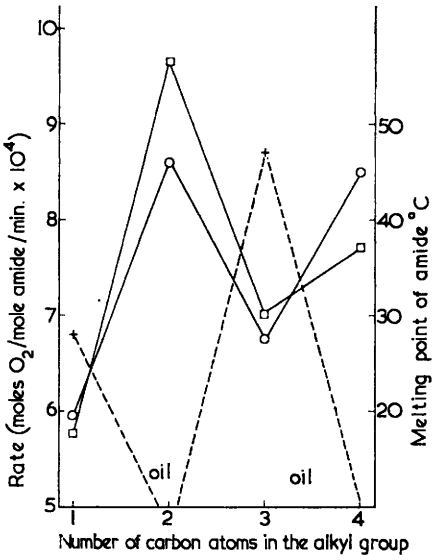


FIGURE 4 Dependence of rate on alkyl substituent variation of melting point with alkyl substituent

carbons in the *N*-alkyl substituent oxidise more slowly than those with an even number. This is similar to the step effect in the melting points in several homologous series such as carboxylic acids and derivatives and in some polyamides.[15] It appears that the lower-melting amides oxidise most rapidly (the m. p.s of *N*-ethyl- and *N*-n-butylacetamides and the *N*-alkylpropionamides are not available but they are generally oils at room temperature).

Molecular association, which is expected to be greater in the odd series owing to the proximity of the experimental temperature and melting points, could influence the rate of reaction. The oxidation of *N*-n-propylacetamide was in fact carried out at several degrees below the recorded melting point, but it did not solidify in the presence of photosensitiser at 30°.

Influence of Temperature on Rate of Reaction.—The rate of oxidation of acetamide depended markedly on temperature ($8{\cdot}93 \times 10^{-6}$ at 84° and $1{\cdot}46 \times 10^{-5}$ at 87°). Arrhenius plots gave an apparent activation energy of 40·6 kcal. mole^{-1}. The effect of temperature on the oxidation of *N*-alkylamides is far less marked. Where an increase of 4° almost doubles the rate of oxidation of acetamide, an increase of 30—40° has the same effect with *N*-alkylamides. Wells [7] has shown that the abstraction of hydrogen from alcohols by activated sensitiser molecules is independent of temperature. We found that in the case of *N*-alkylamides the reaction has an apparent activation energy of 4—5 kcal. mole^{-1} (see Table 4 and Figure 5). Exceptions are *N*-methylacetamide, *NN*-diethylacetamide, and *N*-isopropylacetamide. As will be shown later, *N*-isopropylacetamide must oxidise by a slightly different mechanism.

[15] A. Bell, J. C. Smith, and C. J. Kibler, *J. Polymer Sci.*, 1965, **3**, 19.

Miscellaneous Reactions.—Variation of the surface to volume ratio of the reaction vessel by the addition of finely powdered glass was without effect on reaction rate. Cupric stearate which is a powerful catalyst for the autoxidation of olefins also had no effect on reaction rate. The rate of

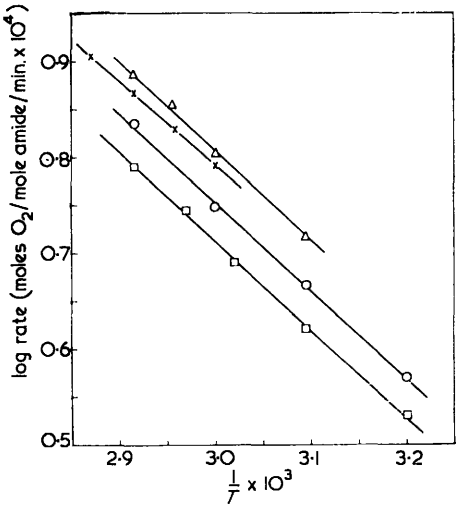


FIGURE 5 Typical Arrhenius plots

○ Ethylacetamide × Butylisobutyramide
□ Propylacetamide △ Butylpropionamide

oxidation of *N*-methylacetamide containing 2% cumene hydroperoxide in the presence of ultraviolet illumination at 30° was approximately $1{\cdot}3 \times 10^{-6}$ moles 0_2 mole amide^{-1} min.$^{-1}$.

Analysis of Products.—The results of peroxide analysis immediately after oxidation to approximately the same extent are in Table 5. Gas chromatography showed that

TABLE 5

Peroxide yields

Amide	Moles/mole O_2 absorbed
N-n-Propylacetamide	60·0
N-Methylpropionamide	61·6
N-Ethylpropionamide	60·7
N-n-Propylpropionamide	64·2
N-n-Butylpropionamide	63·1 *
N-n-Butylbutyramide	61·0
N-Isopropylacetamide	96·5

* After treatment with catalase to decompose hydrogen peroxide this value fell to *ca.* 40%.

(1) two oxidation products of *N*-methylacetamide occurred in all alkylacetamides examined; (2) the main oxidation product of *N*-n-propylacetamide occurred in oxidised *N*-ethylpropionamide; (3) the main oxidation products of *N*-n-butylpropionamide and *N*-propylbutyramide were identical; (4) the same products occurred in oxidised *N*-ethyl- and *N*-isopropylacetamide.

If sensitiser attack takes place on the methylene group, the following reactions are consistent with the observations.

$$CH_3{\cdot}CONH{\cdot}CH_3 \longrightarrow CH_3{\cdot}CONHCOH + CH_3{\cdot}CONH_2$$

$$\left.\begin{array}{l} CH_3{\cdot}CONH{\cdot}C_3H_7 \longrightarrow \\ C_2H_5{\cdot}CONH{\cdot}C_2H_5 \longrightarrow \end{array}\right\} CH_3{\cdot}CONH{\cdot}COC_2H_5 + \text{parent amides}$$

$$\left.\begin{array}{l} CH_3{\cdot}CONH{\cdot}C_2H_5 \longrightarrow \\ CH_3{\cdot}CONH{\cdot}CH(CH_3) \longrightarrow \end{array}\right\} \begin{array}{l} CH_3{\cdot}CONH{\cdot}COCH_3 + \\ CH_3{\cdot}CO{\cdot}NH{\cdot}CHO \\ + CH_3{\cdot}CONH_2 \end{array}$$

Some of the products are thermally labile. The chromatogram of oxidised *N*-n-butylpropionamide (Figure 6*A*) before and after heating for 15 min. at 150° shows that decomposition of the formyl derivative takes place with a corresponding increase in the concentration of propionamide. This instability makes quantitative interpretation of chromatograms difficult.

DISCUSSION

In *N*-substituted amides where the carbon adjacent to the nitrogen is primary or secondary, the initial reaction appears to be abstraction of hydrogen by an activated sensitiser molecule. It might be expected that an increase in chain length of the alkyl substituent would provide more sites for such attack, but rates and products indicate that attack is exclusively on the carbon atom. The high peroxide yield for *N*-isopropylacetamide oxidation is in keeping with the known ease

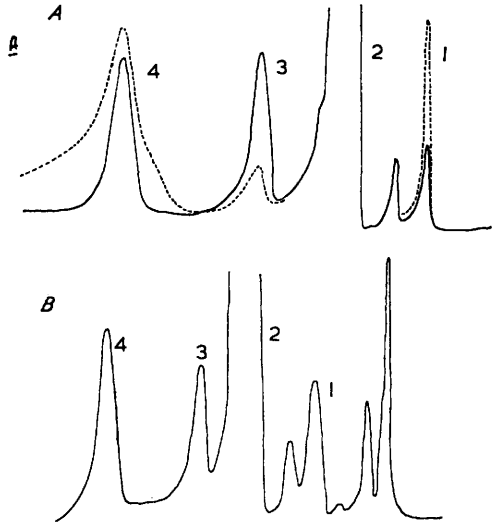


FIGURE 6 *A*, Chromatogram of oxidised n-butylpropionamide

—— Before heat treatment
– – – – Heated for 15 min. at 150°

1, Propionamide; 2, butylpropionamide; 3, formylpropionamide; 4, butyrylpropionamide

B, Chromatogram of oxidised n-butylacetamide

1, Acetamide; 2, butylacetamide; 3, formylacetamide; 4, butyrylacetamide

of oxidation of compounds containing the isopropyl group. The high rate of oxidation of *NN*-diethylacetamide is to be expected from the presence of two methylene groups. Organic peroxides and acylamides must be regarded as primary products arising directly from the amide. Hydrogen peroxide is formed predominantly by the cyclic sensitiser mechanism.

Representing the alkylamide by RH and the sensitiser by A, we write the following non-chain mechanism:

$$A + h\nu \longrightarrow A^* \quad (R_i)$$
$$1.\ A^* + RH \longrightarrow AH\cdot + R\cdot$$
$$2.\ R\cdot + O_2 \longrightarrow RO_2\cdot$$
$$3.\ AH\cdot + O_2 \longrightarrow A + HO_2\cdot$$
$$4.\ 2RO_2\cdot \longrightarrow \text{(i) } 2\text{Acylamide} + H_2O_2 \quad \text{(ii) } 2RO\cdot + O_2 + \text{products}$$
$$5.\ 2HO_2\cdot \longrightarrow H_2O_2 + O_2$$
$$6.\ RO_2\cdot + HO_2\cdot \longrightarrow \text{(i) Acylamide} + H_2O + O_2 \quad \text{(ii) } ROOH + O_2 + \text{products}$$
$$7.\ R\cdot + R\cdot$$
$$8.\ R\cdot + RO_2\cdot \quad \Big\} \text{ products}$$
$$9.\ R\cdot + HO_2\cdot$$

At high oxygen pressures reactions 7, 8, and 9 become unimportant. From the usual stationary-state assumptions it can be shown that if 4 proceeds by route (i) and 6 by route (ii) and $k_4k_5 = k_6$ (see ref. 2): $[A^*] = R_i/k_1[RH]$; $[AH\cdot] = R_i/k_3[O_2]$; $[R\cdot] = R_i/k_2[O_2]$; $[RO_2\cdot] = (R_i/2k_4)^{\frac{1}{2}}$; $[HO_2\cdot] = (R_i/2k_5)^{\frac{1}{2}}$; $-d[O_2]/dt = k_2[R\cdot][O_2] + k_3[AH\cdot][O_2] - \frac{1}{2}k_5[HO_2\cdot]^2 - k_6[RO_2\cdot][HO_2\cdot]$ which on substitution of the derived radical concentrations gives: $-d(O_2)/dt = 5R_i/4$. Peroxide yield is given by $[d(\text{peroxide})/dt]/[-d(O_2)/dt]$

$$[d(\text{Peroxide})/dt] = \tfrac{1}{2}k_4(RO_2\cdot)^2 + \tfrac{1}{2}k_5(HO_2\cdot)^2 + k_6(RO_2\cdot)(HO_2\cdot) = R_i$$

$\therefore$ Peroxide yield = 80%

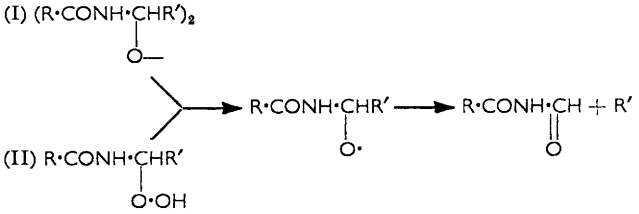
The acylamide yield = $[d(\text{acylamide})/dt]/[-d(O_2)/dt]$

$$[d(\text{acylamide})/dt] = \tfrac{1}{2}R_i$$

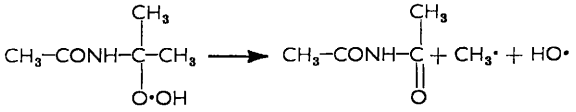
Therefore acylamide yield = 40%. One mole of oxygen produces two moles of acylamide.

Clearly the reaction is not completely represented by this scheme but it does produce a rate independent of oxygen pressure as found experimentally. The peroxide yields are about 15% lower than required by this mechanism. Complications probably arise from the competing reactions in 4 and 6. More rigorous analysis is required to solve this problem. Autoxidations have been extensively investigated recently; reactions involved in a radical-chain oxidation are hydrogen abstraction followed by oxygen addition. Our sequence for the photosensitised oxidation of *N*-alkylamides is widely different from the normal chain oxidation mechanism both in kinetic characteristics and in that the products are not exclusively peroxidic, yet the same two fundamental processes are involved. The differences can be traced to the inefficiency of the reaction $RO_2\cdot + RH \longrightarrow ROOH + R\cdot$. It is reasonable to suppose that reaction of AH· radicals with oxygen will predominate over other modes of removal, particularly at the oxygen pressures used.

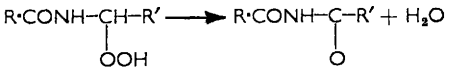
Peroxides decompose first at the O–O bond then at the weakest adjacent C–C bond.[16] In this manner *N*-formylamides could arise from an αβ C–C fission of the *N*-alkyl group of and oxyradical derived from a diperoxide (I) or hydroperoxide (II). The same mechanism



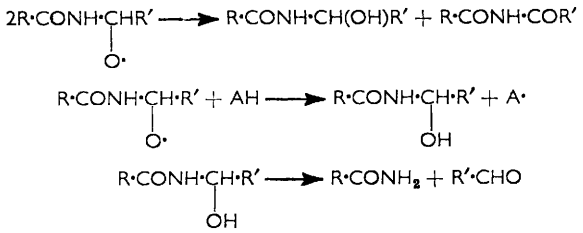
would account for the formation of acetylacetamide from *N*-isopropylacetamide. Primary and secondary



hydroperoxides can also dehydrate slowly to give carbonyl groups;[17] such a reaction would account for the formation of *N*-acylamide. This reaction, however, is



considered unlikely in our conditions. Unsubstituted amides could be formed by the decomposition of hydroxyalkylamides derived from the reaction between oxy- and semiquinone radicals:



The chromatogram in Figure 6*A* supports the view that unsubstituted amides result from the decomposition of *N*-formylamides.

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[16] P. George and A. D. Walsh, *Trans. Faraday Soc.*, 1946, **42**, 94.
[17] A. D. Walsh, *Trans. Faraday Soc.*, 1946, **42**, 269.