# Photochemistry of C-Nitroso-compounds. Part 6.[1] Quantum Yields for the Solution-phase Photolysis of Some Geminal Chloro-nitroso-compounds

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The quantum yields for photolysis at 580—680 nm of the geminal chloro-nitroso-compounds (1)—(4) have been determined and were found to depend on the structure of the substrate, the viscosity and type of solvent, and the presence of oxygen but to be wavelength independent. The effects observed are explained with an efficient initial C—NO bond homolysis producing α-chloroalkyl radicals and nitric oxide in the primary step. The variation of the relative extent of competing recombination and radical scavenging reactions is found to be the major factor dominating the observed overall quantum yields.

FROM our previous work [1-5] it is apparent that aliphatic and alicyclic C-nitroso-compounds can undergo photolysis at ca. 600 nm by cleavage of the carbon–nitrogen bond with the production of free radicals due to the unique combination that these molecules have weak C–N bond dissociation energies [6] and absorb light of wavelength ca. 600 nm. Our previous study of geminal chloro-nitroso-compounds in particular indicated that other suggestions for the primary process such as C–Cl cleavage,[7] the elimination of HNO [8] or HCl,[9] and reactions of electronically excited molecules with hydrogen-containing solvents [10] or with oxygen [11] are unable to account for the important features of the photochemistry.

The nitroso-compound will usually scavenge the organic radical with the production of a nitroxide (1). The isolated products are formed from this and other intermediates in extensive dark reactions including solvolytic reactions in hydroxylic solvents.[1,3-5]

$$R\cdot + R\text{-}NO \longrightarrow R_2NO\cdot \qquad (1)$$
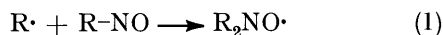
The present study was initiated in order to obtain information about the efficiency of the photodissociation.

The following four compounds were chosen as substrates: 2-chloro-2-nitrosopropane (1), 2-chloro-2-nitrosobutane (2), 1-chloro-1-nitrosocyclohexane (3), and 2,2-

(1)   (2)   (3)   (4)
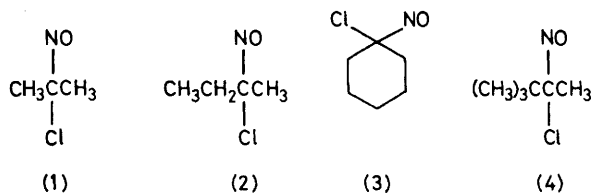
dimethyl-3-chloro-3-nitrosobutane (4). Inspection of Table 1 shows that previous quantum yield measure-

ments show wide variations with solvent, oxygen, and wavelength and suggest that a clarification is desirable.

TABLE 1

Previous measurements of quantum yield for compounds used in this investigation

Compound	λ/nm	Solvent	φ (absence of O_2)	φ (presence of O_2)	Ref.
(2)	632.8	C_6H_6	0.2	0.6	7
(2)	632.8	MeOH	0.6	1.3	7
(2)	632.8	$CHCl_3$	0.2	0.6	7
(2)	632.8	$[CH_2]_4O$	1.0	2.0	7
(2)	650	MeOH	1.2		9
(3)	a	C_6H_6		0.81	12
(3)	a	MeOH		2.42	12
(3)	a	EtOH		2.17	12
(3)	654	MeOH	0.96		13
(4)	a	C_6H_6		0.91	12
(4)	a	$CHCl_3$		0.93	12
(4)	a	MeOH		1.75	12
(4)	a	EtOH		1.56	12
(4)	670	MeOH	0.62		13
(4)	614	MeOH	0.93		13

a Unfiltered light.

RESULTS

Electronic Absorption Spectra of Compounds (1)—(4).— All the geminal chloro-nitroso-compounds studied exhibited two regions of absorption, a weak separate band from 500 to 750 nm (ε ca. 20) and a strong continuous absorption (ε ca. 10^3) extending from ca. 260 nm towards the vacuum–u.v. region, which is preceded by a very weak shoulder at 320—260 nm (ε ca. 10) partially hidden by the strong u.v. band (see Figure). The absorption in the u.v. region appears to be a complex composite band and an assignment is difficult. The absorption band in the visible region (Table 2), however, can be confidently assigned to an $S_1 \longleftarrow S_0$ electronic transition with n_-,π^*-character † and is characteris-

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† We adopt the nomenclature employed by Ha and Wild [14] for the electronic transitions of nitroso-compounds.

[1] Part 5, B. G. Gowenlock, G. Kresze, and J. Pfab, *Annalen,* 1975, 1903.

[2] J. R. Dickson and B. G. Gowenlock, *Annalen,* 1971, **745,** 152.

[3] B. G. Gowenlock, G. Kresze, and J. Pfab, *Tetrahedron Letters,* 1972, 593.

[4] B. G. Gowenlock, G. Kresze, and J. Pfab, *Tetrahedron,* 1973, **29,** 3587.

[5] B. G. Gowenlock, G. Kresze, and J. Pfab, *J.C.S. Perkin II,* 1974, 511.

[6] P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *J.C.S. Perkin II,* 1973, 1853.

[7] L. Creagh and I. Trachtenberg, *J. Org. Chem.,* 1969, **34,** 1307.

[8] K. D. Anderson, C. J. Crumpler, and D. L. Hammick, *J. Chem. Soc.,* 1935, 1679.

[9] S. Mitchell and J. Cameron, *J. Chem. Soc.,* 1938, 1964.

[10] H. A. Morrison in ' The Chemistry of the Nitro and Nitroso Groups,' ed. H. Feuer, Interscience, New York, 1969, p. 203.

[11] J. A. Maassen and Th. J. de Boer, *Rec. Trav. chim.,* 1972, **91,** 1329.

[12] D. L. Hammick and M. W. Lister, *J. Chem. Soc.,* 1937, 489.

[13] S. Mitchell, K. Schwarzwald, and G. K. Simpson, *J. Chem. Soc.,* 1941, 602.

tic of monomeric blue nitroso-compounds.[14-17] There is a slight hypsochromic shift of the $n_-–\pi^*$ maxima as expected and the absorption band is broadened with consequent loss of incipient fine structure and a decrease of $\varepsilon_{max.}$ values with increasing solvent polarity.
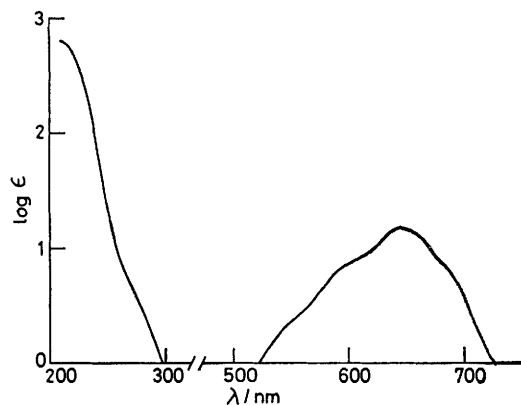
Electronic absorption spectrum of 2-chloro-2-nitrosopropane (1) in methanol

All of the following results were obtained by excitation of the S_1 (n_-,π^*) transition. We have not yet investigated the photochemistry of these compounds in the u.v. region. The values obtained for the quantum yields are accurate to ± 0.03.

Quantum Yields for Photolysis of Benzene Solutions.—The quantum efficiencies ϕ_λ^1 for the disappearance of (1)—(4) were determined by spectrophotometric analysis at the absorption maxima (Table 2) and are summarised in Table 3. The formation of light absorbing insoluble photolysis products [12] prevented a reliable measurement of ϕ for (3). A

TABLE 2

Absorption maxima $\lambda_{max.}$ and absorption coefficients ($\varepsilon_{max.}$) of nitroso-compounds (1)—(4) in the visible region

Compound	Solvent	$\lambda_{max.}$/nm	$\varepsilon_{max.}$/l mol^{-1} cm^{-1}
(1)	CH$_3$OH	647	14.2
(1)	C$_6$H$_6$	652	23.8
(2)	CH$_3$OH	651	15.1
(2)	C$_6$H$_6$	653	21.2
(2)	[CH$_2$]$_4$O	651	17.1
(2)	C$_2$H$_5$I	654	20.5
(3)	CH$_3$OH	650	18.1
(4)	CH$_3$OH	666	14.0
(4)	C$_6$H$_6$	668	18.8

TABLE 3

Quantum yields ϕ_λ^1 for the disappearance of (1)—(4) upon photolysis with light of wavelength λ in benzene

Compound	ϕ_{579}^1	ϕ_{618}^1	ϕ_{641}^1	ϕ_{670}^1
(1)	0.11	0.13	<0.24	0.14
(2)	0.08	0.11	0.15	0.13
(4)	0.15	0.13	0.14	0.12

value of 0.13 for ϕ_{618}^1 for (2) was found in ethyl iodide as solvent indicating the absence of a significant heavy atom effect on ϕ_λ^1 since the corresponding value for benzene as solvent (0.11) is not significantly different.

Quantum Yields for Photolysis in Methanol.—Yields bigger than 95% of hydrogen chloride are usually obtained by

photolysis of geminal chloro-nitroso-compounds in alcohols.[5] We determined both ϕ_λ^1 and the quantum yields for the formation of hydrogen chloride, ϕ_λ^2 (Table 4).

The apparent disagreement between the ϕ^1 and ϕ^2 values was found to be due to a slow and incomplete release of hydrogen chloride in a secondary dark reaction. In agreement with this conclusion some separate measurements indicated that the ϕ_λ^2 values increase slightly with temperature, photolytic conversion, and dark reaction time. These complications are due to the slow methanolysis of an intermediate α-chloro-nitrone as previously inferred from product studies [5] rather than due to the primary process since the quantum efficiencies ϕ_2^1 as measured by the disappearance of substrate were free from these complicating effects of dark reactions.

TABLE 4

Quantum yields for the disappearance of nitroso-compounds (ϕ_λ^1) and for the formation of hydrogen chloride (ϕ_λ^2) in methanol on photolysis with light of wavelength λ

Compound	ϕ_{579}^1	ϕ_{579}^2	ϕ_{618}^1	ϕ_{618}^2	ϕ_{641}^1	ϕ_{641}^2	ϕ_{670}^1	ϕ_{670}^2
(1)		0.37	0.44	0.39	0.43	0.36	0.34	
(2)		0.38	0.40	0.40	0.40	0.32	0.42	0.31
(3)	0.34	0.32	0.37	0.35	0.39	0.32	0.35	0.29
(4)		0.23	0.20	0.18	0.23	0.21	0.26	0.20

TABLE 5

Quantum yields ϕ_λ^1 and ϕ_λ^2 in the presence of O$_2$

Compound	Solvent	ϕ_{618}^1	ϕ_{618}^2	ϕ_{641}^1	ϕ_{641}^2	ϕ_{670}^1	ϕ_{670}^2
(3) *	CH$_3$OH	0.5	0.3	0.5	0.2	0.5	0.2
(2)	CH$_3$OH	0.6	0.3	0.5	0.3	0.5	0.3
(2)	C$_6$H$_6$	0.3	<0.05	0.4	<0.05	0.3	<0.05

* $\phi_{579}^1 = 0.5$.

Effect of Substrate Concentration, Viscosity, Matrix, and Dissolved Oxygen.—Our experiments to establish a concentration dependence for the photolysis of (3) and (4) in methanol indicated that ϕ_λ^1 did not change within experimental error in the concentration range 10^{-2}—10^{-1}M. The absence of significant concentration effects for the photolysis of (2) is known from previous studies,[7,9] but these measurements cannot exclude the possibility that this dependence becomes observable only at very low concentrations. Several measurements with (3) as substrate and the more viscous alcohols n-butanol and cyclohexanol as solvents showed that ϕ_λ^1 decreases with increasing viscosity, but further work is required to confirm this effect and to establish a more quantitative relationship between ϕ_λ^1 and the solvent viscosity.

No measurable photodecomposition in the 540—760 nm range was found if chloro-nitroso-compounds were incorporated in low temperature glasses or host crystals or irradiated in the solid form. The effect of oxygen in the solution phase photolysis was appreciable resulting in a marked increase of the overall quantum yields but a decrease in the efficiency of hydrogen chloride formation. The values collected in Table 5 scatter appreciably and ought to be considered as lower limits since the solutions were not kept saturated with oxygen throughout the photolysis.

Hydrogen chloride is not formed in the aprotic solvent resulting in negligible ϕ^2 values. For methanol solutions the comparison with the corresponding values in the absence of

[14] T.-K. Ha and U. P. Wild, *Chem. Phys.*, 1974, **4**, 300.
[15] K. L. McEwen, *J. Chem. Phys.*, 1961, **34**, 547.
[16] J. Mason, *J. Chem. Soc.*, 1957, 3904.

[17] E. Müller, H. Metzger, and D. Fries, *Chem. Ber.*, 1954, **87**, 1449.
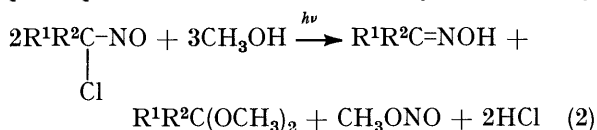
oxygen shows that the hydrogen chloride yields have dropped in spite of the increase of the overall quantum yields ϕ_λ^1.
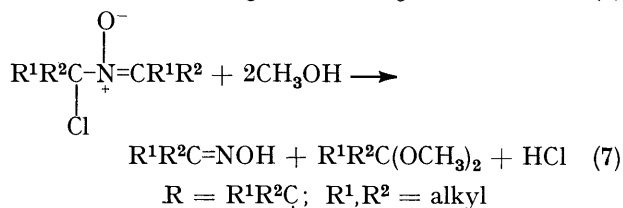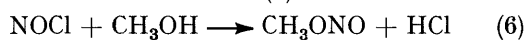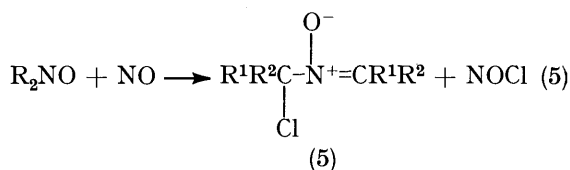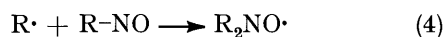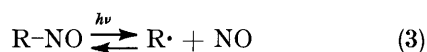
DISCUSSION

In the previous studies available for comparison quantum yields ϕ^1 up to 2 have been obtained. Our own results indicate that these overall quantum yields for the disappearance of all the compounds studied are considerably lower and only exceed a value of 0.5 if the photolyses are carried out in the presence of O_2. We believe that the discrepancy between our values and the published values for compounds (2)—(4) is predominantly due to the different methods employed for the measurement of the light intensity. It is generally accepted that chemical actinometry is the simplest of the available methods and least prone to gross errors provided that some simple precautions are met and a reliable actinometer and reasonably monochromatic light is used. Although the thermopile and photometric methods used in the previous studies may be capable of higher precision, our values [for (1)] and redetermined values [for (2)—(4)] are more reliable since they are based on a well proven and accurate chemical actinometer.[18] These results will now be discussed in conjunction with the mechanistic scheme deduced from our earlier work.[3-5]

Photolysis in Methanol.—Our previous product studies [5] have shown that the photolysis proceeds with solvent participation and the stoichiometry indicated by (2).

$$2R^1R^2\overset{|}{\underset{Cl}{C}}-NO + 3CH_3OH \xrightarrow{h\nu} R^1R^2C=NOH +$$

$$R^1R^2C(OCH_3)_2 + CH_3ONO + 2HCl \quad (2)$$

The initial photodissociation of the C–N bond is followed by formation of nitroxide radicals and NO which can undergo combination or disproportionation reactions. The observed products are formed by rapid nitrosation of the solvent and slow methanolysis of the solvolytically unstable α-chloro-nitrone (5) (Scheme).[5]

$$R-NO \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} R\cdot + NO \quad (3)$$

$$R\cdot + R-NO \longrightarrow R_2NO\cdot \quad (4)$$

$$R_2NO + NO \longrightarrow R^1R^2\overset{O^-}{\underset{\underset{Cl}{|}}{\overset{|}{C}-\overset{+}{N}}}=CR^1R^2 + NOCl \quad (5)$$

$$(5)$$

$$NOCl + CH_3OH \longrightarrow CH_3ONO + HCl \quad (6)$$

$$R^1R^2\overset{O^-}{\underset{\underset{Cl}{|}}{\overset{|}{C}-\overset{+}{N}}}=CR^1R^2 + 2CH_3OH \longrightarrow$$

$$R^1R^2C=NOH + R^1R^2C(OCH_3)_2 + HCl \quad (7)$$

$$R = R^1R^2\overset{|}{\underset{Cl}{C}}; \quad R^1,R^2 = \text{alkyl}$$

SCHEME

If every primary act (3) would result in a successful sequence of dark reactions (4)—(7), then a value of 2 would be expected for the overall quantum yield ϕ^1. The observed values are between 0.25 and 0.45 depending on the structure of the substrate indicating either an inefficient primary step, or the participation of an efficient recombination reaction. That this reduction in ϕ^1 is in fact predominantly due to the recombination is apparent from the marked increasing effect of added scavengers like oxygen and bromine [19,20] suggesting also that the primary step is efficient. The recombination can proceed by a cage reaction of geminal radical pairs and by random diffusive encounter. Both the effect of viscosity and the effect of scavengers suggest that the diffusive recombination is the more important process and that cage recombination may only become dominant at very high viscosities.

Photolysis in Aprotic Solvents.—From the previous studies it is known that an appreciable reduction of quantum yields occurs in aprotic solvents and our more detailed data (Table 3) agree with this observation. Both the evidence available from product studies [3,5] as well as considerations of the bond dissociation energies indicate clearly, however, that the interesting and unorthodox suggestion [7] of a change of the primary dissociative step from C–NO to C–Cl cleavage with the type of solvent is untenable. Our previously suggested scheme based on the homolytic cleavage of the weak C–NO bond [5] explains satisfactorily the reduction of quantum yields observable in solvolytically unreactive solvents. A significant solvent dependency of the quantum yield for the primary process (3) is as unlikely as an increase in the cage recombination efficiency. It follows that the decrease of ϕ^1 values in aprotic solvents appears to be largely due to an increase in the rate of diffusive recombination which in turn is best explained by larger stationary concentrations of nitric oxide in aprotic solvents compared with alcohols. We have previously argued [5] that the latter is caused by the predominance of (9) over (8) since the addition of NOCl has no significant

$$R\cdot + ClNO \longrightarrow R-NO + Cl\cdot \quad (8)$$

$$R\cdot + ClNO \longrightarrow R-Cl + NO \quad (9)$$
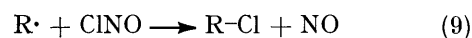
effect on the rate and consequently on the quantum yield for the photolysis of geminal chloro-nitroso-compounds in aprotic solvents.[7] Thus the apparent marked solvent dependency in the photochemistry of geminal chloro-nitroso-compounds is ultimately due to the insignificance of (9) in hydroxylic solvents where the removal of nitrosyl chloride by rapid solvolysis prevents the accumulation of nitric oxide *via* (9).

Dependence of Quantum Yields on Stereochemical Factors.—The results for ϕ^1 and ϕ^2 in Table 4 show an

[18] E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, 1966, **88**, 394.
[19] J. Pfab, *Tetrahedron Letters*, 1976, 943.
[20] J. Pfab, *J.C.S. Chem. Comm.*, 1976, 297 and unpublished results.

unusual and interesting decrease in quantum yields with increasing stereochemical bulk of substituents.

This steric effect suggests activation energy control and therefore a relatively slow reaction. It is suggested that the irreversible scavenging reaction (1) is the most likely bottle neck causing the observed pronounced steric control. Since both R and R–NO are removed in this kinetically controlling reaction the observed effect on the quantum yield becomes apparent. As R becomes bulkier in the series (1)—(4) the competition between scavenging reaction (1) and diffusive recombination favours the latter and therefore reduces both ϕ^1 and ϕ^2.

Photolysis in the Presence of Oxygen.—Our results confirm earlier observations[7] of increases of quantum efficiencies in the presence of oxygen. The products of this reaction have been previously identified for the photolysis of (3) in CCl_4 as solvent.[5] Only 9% of the oxidation product 1-chloro-1-nitrocyclohexane is formed in this instance, the main products being cyclohexanone and 1,1-dichlorocyclohexane. Thus the previous interpretation, that the photoxidation of (2) proceeds by a rapid reaction of excited (2) with O_2 to form selectively the nitro-compound[7] is not substantiated by our results (Table 5) since up to 0.5 mole of HCl is formed per mole of photolysed nitroso-compound.

Conclusions.—The results of this study indicate that the photodissociation of geminal chloro-nitroso-compounds by light of wavelength *ca.* 600 nm is an efficient process, but that the observed overall quantum yields are reduced by diffusive and, to a lesser extent, by cage recombinations of photolytically generated α-chloro-alkyl radicals with accumulated nitric oxide. The simple reaction scheme proposed explains qualitatively the observed influence of solvent, stereochemistry of substrates and solvent viscosity on the quantum yields. The absence of wavelength and concentration effects suggests that geminal chloro-nitroso-compounds could be useful actinometers for the wavelength range 550—700 nm.

EXPERIMENTAL

Instruments and Apparatus.—The light source consisted of a water-cooled 400 W high pressure sodium lamp (Atlas Kolorson) which was mounted in a cylindrical aluminium housing and operated on stabilised mains voltage *via* the power supply recommended by the lamp manufacturer. The optical train used consisted of a shutter, quartz condenser lens, interference filter, and a 10 cm long cylindrical sample cell (2.5 cm diameter) supported by a black aluminium cell holder and screened from stray light by means of a removable cardboard mounting. The interference filters used provided maximum transmittances of 40—50% at half widths of 20—40 nm and were free of secondary windows between 200 and 800 nm.

Photometric measurements were carried out by means of a Unicam SP 1800 recording spectrophotometer. A Griffin pH meter was used to indicate the end point in titrations of hydrogen chloride.

Solvents and Materials.—Methanol was dried by reflux and distillation over magnesium turnings. Benzene was shaken with concentrated sulphuric acid and eluted through freshly activated alumina. The ethyl iodide used was purified by removal of free iodine, drying, and vacuum distillation. Tetrahydrofuran was refluxed over lithium aluminium hydride and distilled. n-Butanol was dried over 4Å molecular sieve whereas cyclohexanol was used as supplied.

The nitroso-compounds were obtained by the chlorination of oximes [21] and purified by repeated distillation or recrystallisation.

Actinometry.—The light intensities provided by the lamp at the different wavelengths chosen were determined by potassium reineckate actinometry [18] and were corrected for transmitted light. The free thiocyanate released by photoaquation of the actinometer was analysed by dual wavelength measurement of the iron(III) thiocyanate complex [22] and subtraction of the thiocyanate released thermally in blanks during the time of exposure.

Quantum Yield Determinations.—Solutions of the nitroso-compounds were prepared such that 99.9% of the incident light was absorbed, and degassed by purging with oxygen-free nitrogen for 1 h at 80 °C prior to preparation of the solution. After the lamp had been allowed to warm up for 30 min the sample was exposed for 4—6 h resulting in 2—7% photodecomposition. At 30 min intervals, the irradiations were interrupted when the cell was thoroughly shaken to avoid concentration gradients. The amount of photolysed nitroso-compound was determined spectrophotometrically at the absorption maxima (Table 1). Titration of the aqueous extract of the photolysis solution with standardised 10^{-3}M-sodium hydroxide solution allowed hydrogen chloride to be determined. Oxygen-saturated solutions were obtained by dissolving the nitroso-compounds in solvents which had previously been purged with dry oxygen.

[21] M. Kosinsky, *Lodz. Towarz. Nauk Acta Chim.*, 1964, **9**, 93.
[22] J. Para and L. S. Forster, *Trans. Faraday Soc.*, 1961, **57**, 87.