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The UV-enhanced decomposition of aqueous ammonium nitrite

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Abstract

As the decomposition of NH_4NO_2 to N_2 and H_2O is a potential pathway for the loss of N_2 from the aquatic environment, the above reaction has been studied by volumetric gas analysis. Experiments performed with UV irradiation were approximately four times faster than the rate of the dark reaction. However, the increase in the rate of decomposition with light intensity was not strictly linear. The rate of gas evolution increased with $[NO_2^-]$ and, to a lesser extent, with $[NH_4^+]$. An optimum rate was observed at pH 8–9. A proposed mechanism involves the formation of NO and NO_2 from dark reactions of the excited NO_2^- ions. N_2O_3, formed from NO and NO_2, is thought to react with NH_3, derived from NH_4^+, to produce an intermediate which dissociates to the products in fast steps. The decline in the rate of gas evolution at pH values greater than 9 is ascribed to the hydrolysis of N_2O_3, giving NO_2^- ions. An estimated activation energy was 26 kJ mol^{-1}. In the presence of anatase or colloidal $Fe(OH)_3$, the rate of gas evolution dropped as the concentration of the semiconductor increased. Quantum yields, estimated using uranyl oxalate actinometry, were $\phi_{240-248} = 0.058$, $\phi_{254} = 0.041$, $\phi_{257-300} = 0.047$ and $\phi_{300-400} = 0.016$.

Keywords: UV Decomposition of aqueous NH_4NO_2; N_2 Quantum yields; Activation energy; Semiconductor effect

1. Introduction

The thermal decomposition of aqueous NH_4NO_2 is relevant to the observed nitrogen losses from aquatic environments and soils. Hence the thermal reaction has been extensively studied, unlike the light-enhanced decomposition which has been scarcely investigated [1–3]. However, the intimate mechanisms of both these types of reaction have not been adequately discussed [4]. A recent re-examination of the kinetics of the thermal reaction indicated that the rate-determining step involves the nitrosation of NH_3, derived from NH_4^+ ions, by N_2O_3 [5], which is in equilibrium with HNO_2. Both NH_3 and HNO_2 are the products of hydrolysis of NH_4NO_2.

Early studies of the photo-enhanced decomposition of NH_4NO_2 in soils or in aqueous suspensions of the salt exposed to sunlight showed greater nitrogen losses under irradiation compared with experiments carried out in the dark [1–3]. However, these studies did not examine the relevant parameters which are likely to influence the photo-reaction, such as light intensity and wavelength. No quantum yields were measured and no photo-reaction mechanisms were proposed. In the present investigation the effects of the concentration of the reactants, the pH of the solution, temperature, light intensity and its wavelength are reported. In addition, the effects of isotopic substitution and the presence of two semiconductors have been investigated. Quantum yields for various wavelength ranges have also been measured. All these measurements elucidate the possible mechanism of the UV-enhanced decomposition of aqueous NH_4NO_2.

2. Experimental details

The spectra of aqueous solutions of NH_4NO_2, $NaNO_2$ and NH_4Cl were measured over the wavelength range 190–380 nm using a Perkin–Elmer Coleman 55 spectrophotometer and 2.0 mm matched quartz cells. The rate of decomposition of $NaNO_2$ and NH_4Cl solutions was generally followed volumetrically by measuring at intervals the volume of gas collected in a gas burette. This was connected to the cylindrical reaction vessel surrounding the mercury lamp. The temperature of the solution was normally maintained at 30 ± 1 °C by circulating water from a Grant thermostat through the annular space between the inner and outer thimbles of the lamp. The solution was pipetted into the reaction vessel to a constant level just above the position of the mercury arc and

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the thickness of the irradiated layer was accurately measured. The rate of gas evolution for 30 min prior to irradiation, due to the dark reaction, was subtracted from the rate after illumination to give the net rate of the photochemical reaction. Generally the irradiated solution, which was kept stirred at 700 rev min^{-1} with a Variomag electronic stirrer, was 0.50 mol dm^{-3} in NH_4Cl and in $NaNO_2$ and its pH was 6.5.

When the evolved gas was bubbled through acidified $KMnO_4$ solution and an aliquot was titrated with standard oxalate solutions, the titres before and after irradiation were identical within experimental error, indicating that no measurable amounts of nitrogen oxides were formed during irradiation. However, the evolved gas was also passed through Draeger scale tubes, from which the concentration of NO or NO_2 was determined [4].

When the reaction was followed by measuring the concentrations of the reactants, 1 dm^3 of 0.07 M solution in NH_4NO_2 at pH 8.5 was irradiated in a flask surrounding the lamp, which contained a thermometer. At hourly intervals 20.0 cm^3 aliquots were withdrawn and analysed for NH_4^+ spectrophotometrically [6] using Nessler's solution and reading $[NH_4^+]$ from a calibration plot [4]. NO_2^- and NO_3^- ions were determined by liquid chromatography in a Dionex 40001 instrument with suppressed conductivity detection, using carbonate/bicarbonate eluent. The peak area characteristic of each ion was compared with data in a calibration plot. A blank run, where $NaNO_2/NaCl$ solution was irradiated, indicated that no gas was evolved before or during irradiation, confirming an earlier report on the photolysis of nitrite solutions [7].

The lamps used in the present study were Hanovia 4 W low pressure and 100 W medium pressure mercury lamps whose spectral energy distributions were supplied by the manufacturer. The total output of each lamp was determined by uranyl oxalate actinometry [4,8]. For the latter lamp, determinations were carried out when either a quartz or Pyrex thimble was used. 150 cm^3 of 0.02 M solution of uranyl oxalate in 0.1 M oxalic acid was irradiated for 20–40 min. Aliquots of the solution were titrated, before and after irradiation, with 0.05 M permanganate standardized against masses of AR sodium oxalate. The absorption spectrum of the actinometric solution over the range 190–400 nm was obtained as described above and its quantum yields at the wavelengths of the mercury lamps were taken from the literature [8,9].

The effects of varying either $[NO_2^-]$ or $[NH_4^+]$ over the range 0.05–0.50 M, while keeping the other constant and temperature constant (at 30 °C), were also studied. By adjusting the pH, the photolysis was studied over the pH range 6–10 at constant $[NH_4NO_2]$ and temperature. Using ammonium-d_4 chloride and heavy water supplied by Aldrich, the effects of isotopic substitution at pD 6.4 and 8.0 were investigated. An ordinary combined glass electrode was used to measure pD [10], adjusting the value with 10% NaOD in heavy water. To attenuate the output of the medium pressure lamp, a 30 mesh or 80 mesh copper gauze was positioned next to the lamp's thimble. The lamp output in each case was determined by chemical actinometry as mentioned above. The rate of gas evolution from NH_4NO_2 solution was compared when either or none of the gauzes was used, keeping all other conditions constant. The rate of photolysis over a temperature range 20–50 °C was studied by adjusting the temperature of the Grant thermostat as mentioned above. $[NO_2^-]$ was determined at intervals by ion chromatography. Two semiconductors, titanium oxide anatase CLDD 1995/2 [11] and prepared iron(III) hydroxide colloid [12], were separately added to NH_4NO_2 solution prior to irradiation and the rate of gas evolution was followed as usual.

The quantum yield ϕ of nitrogen evolution at 254 nm was determined from the results of reaction using the low pressure lamp. The rate of gas production obtained with the medium pressure lamp with quartz or Pyrex thimbles represented the rates over the ranges 200–300 or 300–400 nm. Over the former range both NH_4NO_2 and actinometric solutions were completely absorbing under the photolysis conditions. As a first approximation an average ϕ was calculated using ϕ_{254} and assuming that $\phi_{240} = \phi_{248}$. Because these three lines are the ones strongly absorbed by the NH_4NO_2 solution, this approximation is permissible. From the value of $\phi_{240-248}$ obtained and the average ϕ an estimate of $\phi_{253-300}$ was computed. A similar weighted average $\phi_{300-400}$ was calculated [4]. However, over this wavelength range the fraction of light absorbed by the actinometric or test solution has to be taken into account in the calculation. A weighted average ϕ of the actinometer is obtained from the relation

$$\phi = \Sigma[(\text{fraction of lamp output at } \lambda) \times \phi_\lambda]$$

3. Results and discussion

Fig. 1 shows that the rate of photo-evolution of nitrogen from NH_4NO_2 solution did not vary linearly with the light intensity, suggesting that nitrogen was not produced in a primary act [13]. The variation in the rate of gas evolution with $[NO_2^-]$ at constant $[NH_4^+]$ and pH (6.4 and 8.0) is depicted in Fig. 2. The variation in the rate of nitrogen formation with $[NH_4^+]$ at the two pH values and constant $[NO_2^-]$ is shown in Fig. 3. Neither figure indicates an inte-

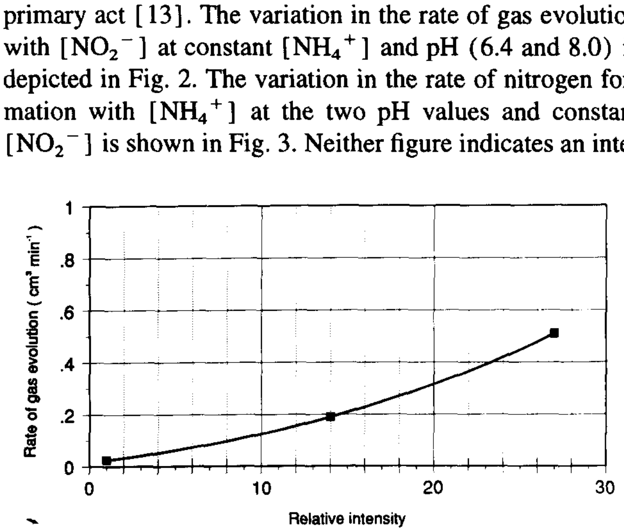

Fig. 1. Variation in rate of gas production with relative light intensity.

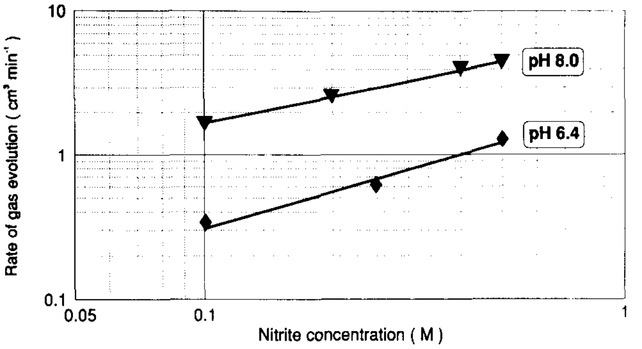

Fig. 2. Variation in rate of gas evolution with $[NO_2^-]$ at constant $[NH_4^+]$ and pH 8.0 (▼) and 6.4 (◆).

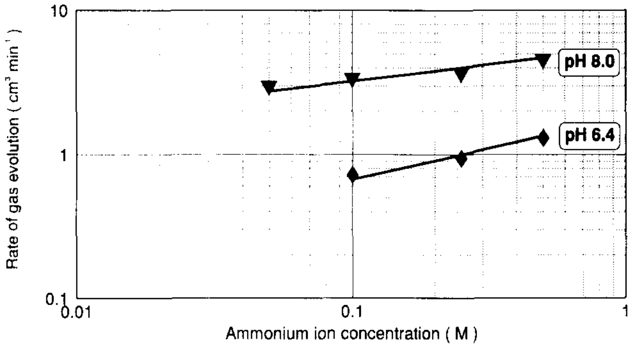

Fig. 3. Variation in rate of gas formation with $[NH_4^+]$ at constant $[NO_2^-]$ and pH 8.0 (▼) and 6.4 (◆).

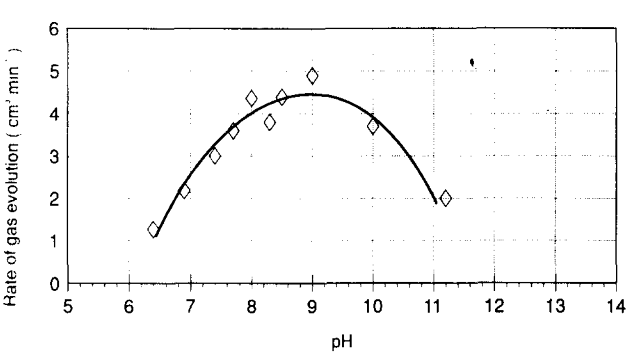

Fig. 4. Variation in rate of gas evolution from 0.5 M NH_4NO_2 at 303 K with pH.

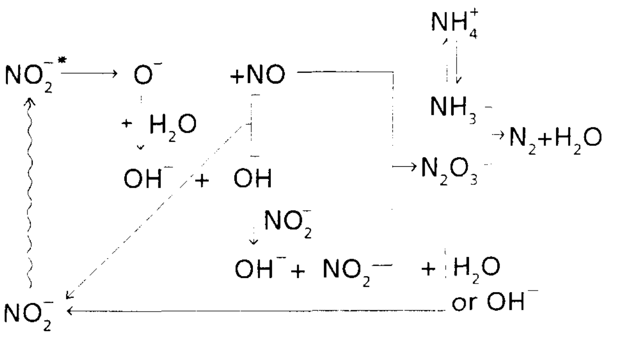

Fig. 5. Suggested reaction scheme for photo-enhanced decomposition of aqueous NH_4NO_2.

gral kinetic order. The more pronounced effect of $[NO_2^-]$ compared with $[NH_4^+]$ is evident from a comparison of Figs. 2 and 3 and is similar to their influence in the dark reaction. The higher rate of gas production in either case with pH is also evident from the figures. A wider range of pH values is depicted in Fig. 4, where a broad maximum of the range of gas evolution is seen.

A feasible reaction mechanism, represented in Fig. 5, partly resembles the mechanism suggested by Strehlow and Wagner [7] to explain the negligible quantum yield they reported when irradiating nitrite solutions. However, Fig. 5 includes the reaction of N_2O_3 with NH_3, derived from NH_4^+ ions, leading eventually to nitrogen formation [4,5]. On the other hand, Fig. 5 excludes the dimerization of NO_2 and other reactions of NO_2 or its dimer, since these reactions eventually regenerate NO_2^- ions [7].

The optimum pH range, exhibited in Fig. 4, can be accounted for as follows. As the pH increases from 6 towards the maximum, more NO_2^- ions are formed at the expense of HNO_2 according to

$$NO_2^- + H^+ \rightleftharpoons HNO_2$$

These nitrite ions, when photo-excited, produce more N_2. In addition, as the pH increases, the equilibrium

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

shifts to the right, producing more NH_3 which reacts with N_2O_3, via an intermediate, $[H_3N\cdots NO]^+$ [4,7], which rapidly breaks down, liberating N_2. The marked decrease in the rate of photolysis as the pH increases above the optimum range can be explained by the hydrolysis of N_2O_3, whose rate has been studied [7] and is plotted in Fig. 6 as a function of pH, superimposed on the data from Fig. 4.

The quantum yields over the wavelength ranges investigated are depicted in Fig. 7 together with the absorption spectrum of aqueous NH_4NO_2 and the spectral energy data of the medium pressure lamp. The spectrum is in good agreement with the reported spectrum of aqueous nitrite [14]. The three absorption bands had been assigned earlier [15], but this was questioned by Strickler and Kasha, who assigned bands I, II and III (in Fig. 7) to $n_o \rightarrow \pi^*$, $n_o \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively [14]. The last of these is believed to represent

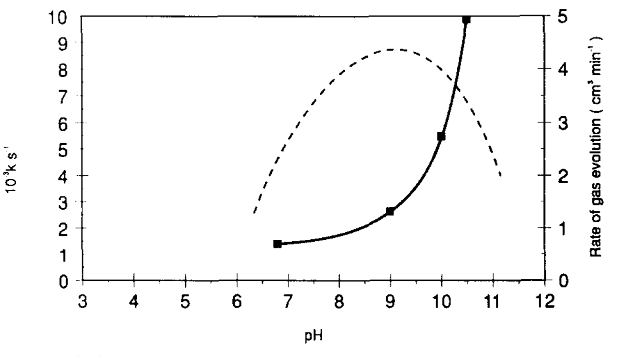

Fig. 6. Variation in rate of hydrolysis, k, of N_2O_3 with pH (——) and variation in rate of nitrogen formation with pH (----).

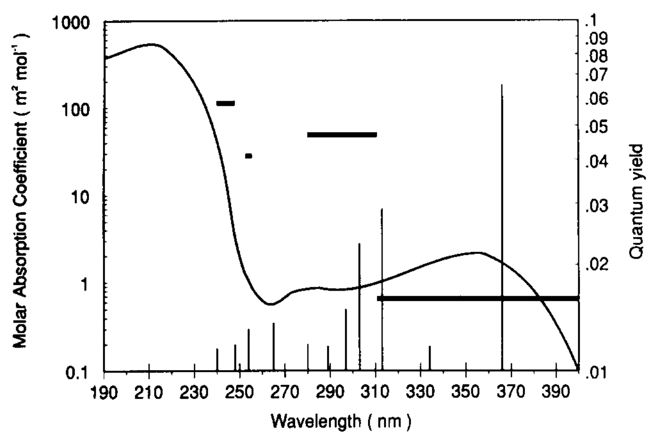

Fig. 7. Absorption spectrum of aqueous NH_4NO_2: molar absorption coefficient plotted against wavelength. Quantum yields (right-hand scale) over ranges of wavelengths studied. Spectral distribution of mercury lines of medium pressure lamp (vertical lines).

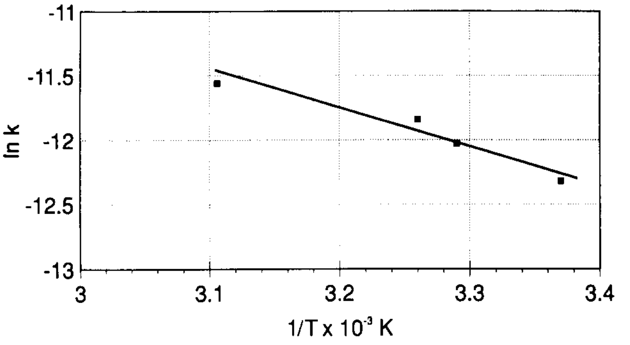

Fig. 8. Variation in logarithm of rate constant with reciprocal of absolute temperature.

an allowed transition, whereas bands I and II are due to forbidden transitions, of which the latter is said to be asymmetric. This difference is reflected in the relative magnitudes of $\phi_{300-400}$ and $\phi_{257-300}$ respectively.

The kinetic order with respect to NO_2^- ions at pH 8.5 approximates a half. Using the appropriate equation, kinetic plots at four temperatures were used to calculate the corresponding rate constants k [4]. Fig. 8, which shows a linear variation in ln k with the reciprocal of the absolute temperature, gave an activation energy of 26 kJ mol^{-1}. This magnitude of energy is sometimes found in photochemical reactions [16] and is associated with secondary reactions.

The deuterium kinetic isotope effect, i.e. the ratio of the rate of gas evolution from ND_4NO_2 in D_2O and to that from NH_4NO_2 in H_2O, was found to be 1.4 at pD(H) 6.4 and dropped to 0.9 at pD(H) 8.4. At the former pD(H) value, isotopic substitution affects acid–base equilibria [4,17], but at the higher pD(H) value, primary isotope effects prevail, e.g. in the reaction

$$O^- + H_2O \longrightarrow OH^- + OH$$

Fig. 9 depicts the variation in the rate of gas evolution with the semiconductor concentration used. The depression of the rate in the presence of either TiO_2 or colloidal iron(III) hydroxide suggests that the semiconductor photocatalyses a reaction such as

$$NO + OH \longrightarrow H^+ + NO_2^-$$

regenerating the reactant NO_2^- and depressing the photoenhanced decomposition.

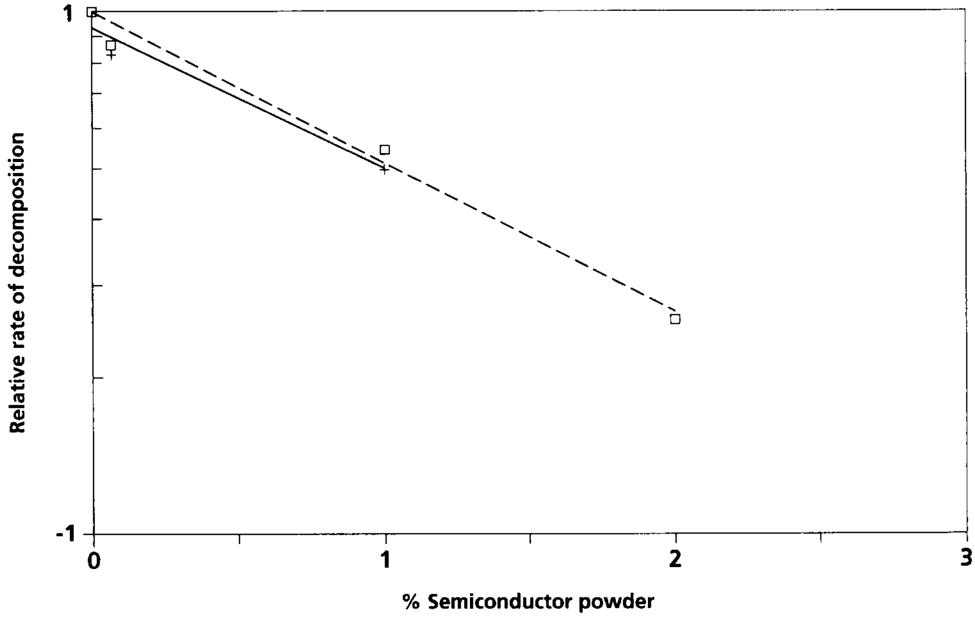

Fig. 9. Effect of amount of semiconductor, TiO_2 (+) or $Fe(OH)_3$ (□), on rate of photodecomposition of aqueous NH_4NO_2.

4. Conclusions

It can be concluded that when irradiating NH_4NO_2 solutions at wavelengths in the range 400–190 nm, i.e. where the salt absorbs, the rate of nitrogen evolution is greater than for the corresponding reaction in the dark. The excited nitrite ions give eventually, through secondary dark reactions, N_2O_3 in addition to that produced in the dark reaction. This extra N_2O_3, reacting with ammonia, leads to the formation of more nitrogen than in the dark reaction.

However, because of the small proportion of sunlight emitted in the above wavelength range, the photo-enhanced loss of nitrogen from NH_4NO_2 is not likely to be significant in aqueous environments. It is more likely that any extra N_2O_3 formed in the photo-reaction would react with organic amines present in solution rather than with ammonia, even at the highest expected $[NH_4{}^+]$.

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References

[1] N.R. Dhar, *Nature, 134* (1934) 572.

[2] N.R. Dhar and R.C. Kapoor, *Proc. Natl. Acad. Sci. India A, 201 (1951) 103.*

[3] A. Wahhab and F. Uddin, *Soil Sci., 80* (1955) 121.

[4] N.B. Smetham, *CNAA Ph.D. Thesis,* Mid-Kent College of Higher and Further Education, Chatham, 1990, and references cited therein.

[5] C.C. Harrison, M.A. Malati and N.B. Smetham, submitted.

[6] DOE Standing Committee of Analysts, *Analysis of Water and Associated Materials. Ammonia in Water,*HMSO, London, 1980.

[7] H. Strehlow and I. Wagner, *Z. Phys. Chem., 132* (1982) 151.

[8] G.S. Forbes and L.J. Heidt, *J. Am. Chem. Soc., 55* (1934) 2363; L.J. Heidt and E. Daniels, *J. Am. Chem. Soc., 54* (1932) 2384; W.C. Leighton and G.S. Forbes, *J. Am. Chem. Soc., 52* (1930) 3139.

[9] W.A. Noyes and W.S. Leighton, *Photochemistry of Gases,* Reinhold, New York, 1941.

[10] R.C. Bates, *Determination of pH. Theory and Practice,* Wiley, New York, 2nd edn., 1973.

[11] M.W. Rophael and M.A. Malati, *J. Photochem. Photobiol. A: Chem., 46* (1989) 367.

[12] A. Breeawsma and J. Lyklema, *Discuss. Faraday Soc., 52* (1971) 324.

[13] J.G. Calvert and J.N. Pitts, *Photochemistry,* Wiley, New York, 1967.

[14] S.K. Strickler and M. Kasha, *J. Am. Chem. Soc., 85* (1963) 2899.

[15] J.W. Sidman, *J. Am. Chem. Soc., 79* (1957) 2669.

[16] M.W. Rophael and M.A. Malati, *Photochem. Photobiol., 17* (1973) 377.

[17] F.A. Long and J. Bigeleisen, *Trans. Faraday Soc., 55* (1959) 2077.