Modulation spectroscopy. Kinetics for the self-reactions of some α-aminoalkyl radicals in solution[1]

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The optical spectra and reaction kinetics of some α-aminoalkyl radicals, $R\dot{C}HN(CH_2R)_2$; R ≡ H, Me, Ph, were measured in solution using the technique of modulation spectroscopy. These radicals undergo diffusion controlled self-reaction with rate constants $\simeq 10^9\ M^{-1}\ s^{-1}$. When R ≡ Ph, the absorption spectrum has a well defined maximum at 346 nm; $\varepsilon = 3390\ M^{-1}\ cm^{-1}$, while the spectra when R ≡ H or Me were less intense (ε_{346} nm $\simeq 500\ M^{-1}\ cm^{-1}$) and tailed into the visible. These spectra are substantially red-shifted when compared with those of simple alkyl radicals, an effect which is thought to be due to the interaction between the unpaired electron and the lone pair of electrons on nitrogen.

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Faisant appel à la technique de spectroscopie modulée en solution, on a mesuré les spectres optiques et les cinétiques de réaction de quelques radicaux α-aminoalkyles, $R\dot{C}HN(CH_2R)_2$ où R ≡ H, Me, Ph. Ces radicaux subissent une auto-réaction, contrôlée par la diffusion, avec une constante de vitesse de $10^9\ M^{-1}\ s^{-1}$. Le spectre d'absorption, lorsque R = Ph, a un maximum bien défini à 346 nm; $\varepsilon = 3390\ M^{-1}\ cm^{-1}$. Cette absorption est moins intense quand R = H ou Me ($\varepsilon_{346\ nm}$ de $500\ M^{-1}\ cm^{-1}$) et s'étale dans le visible. Ces spectres glissent de façon marquée vers le rouge si on les compare à ceux des radicaux alkyles simples; c'est un effet que l'on attribue à l'interaction entre l'électron non apparié et le doublet libre de l'azote.

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Introduction

Modulation spectroscopy has been successfully applied to the study of transient intermediates in the gas phase (see for example refs. 1 and 2). The technique involves photolytic generation of a transient using modulated initiation coupled with phase sensitive detection of that transient. This combination allows spectroscopic detection of short lived intermediates with high signal-to-noise levels and also provides information on the kinetics of their reactions.

The most recent advance in the field of modulation spectroscopy has been made by Huggenberger *et al.* (3) who have constructed a spectrometer for the study of free radicals *in solution*. With this instrument, radicals are generated using sinusoidally modulated light and are detected optically. In this work, we have used such a spectrometer in a kinetic study of the self-reactions of some α-aminoalkyl radicals.

Experimental

Materials

All materials were commercially available. Iso-octane (Spectrograde) and trimethylamine were used as received. Di-*tert*-butyl peroxide was purified by chromatography through alumina which removes traces of the hydroperoxide impurity. Tribenzylamine was purified by recrystallization from ethanol. Triethylamine was purified by the standard procedure (4) and was distilled under nitrogen.

Apparatus

The modulation spectrometer used in this work follows closely on the design developed by Huggenberger and Fischer (3*b*). It is shown diagramatically in Fig. 1.

A fluorescence flow cell (Helma 178f-QS) was used as the sample chamber. Radicals were generated by irradiating solutions through the front window of the cell (10 mm × 10 mm) using light from a 1000 W, dc-powered mercury–xenon lamp (Hanovia 997B001; Oriel 6141 lamp housing). The irradiating light was modulated as a sine wave using a mechanical chopper (Brookdeal 9479) which was fitted with sine shaped irises.

A magnified image of the arc was brought to a focus at the sample cell which was positioned in a region of the image of fairly uniform light intensity. The quality of the sinusoidal modulation and the uniformity of light intensity were checked by manoeuvering a photomultiplier tube and housing with a small entrance slit (0.5 × 0.5 mm) throughout the region normally occupied by the sample chamber. The modulated sine wave generated by the irradiating light was compared on an

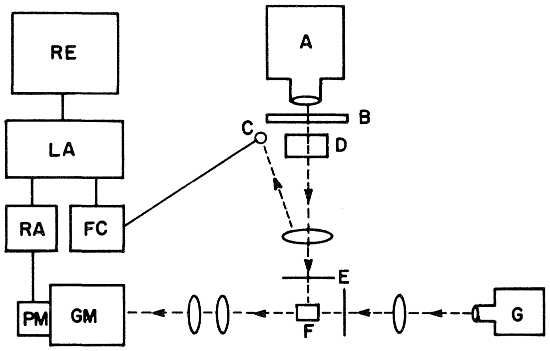

FIG. 1. Block diagram of modulation spectrometer. A, 1000 W mercury xenon lamp. B, light chopper. C, photocell. D, Co/Ni aqueous filter solution. E, cut-off filters. F, sample cell. FC, frequency counter. G, 100 W xenon lamp. GM, grating monochrometer. LA, lock-in amplifier. PM, photomultiplier tube. RA, ratiometer. RE, recorder.

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oscilloscope with one of the same amplitude and frequency produced by a sine wave generator and was indistinguishable from it. In addition, the maximum variation of light intensity across the sample cell was ± 8% of the mean.

The irradiating light was always passed through a water filter (10 cm path length) which removed much of the infrared radiation. The light could be further filtered using bandpass or cut-off filters.

Changes of optical density in the sample were followed using a monitoring beam arranged at right angles to the irradiating light path. A 100 W xenon lamp (Bausch and Lomb) provided the monitoring light which was passed through the side windows of the sample cell and then through a grating monochromator (Oriel 7240) fitted with photomultiplier tube (RCA 4840) and housing. In kinetic studies cut-off filters were always placed in the monitoring beam to prevent sample photolysis by the interrogating light.

Output from the photomultiplier tube was "terminated" by a suitable resistance. The signal at this point consisted of a large dc component and a very much smaller oscillating component which was due to the modulated absorption of starting materials, transient, and products. A ratiometer was used to divide ac by dc when recording spectra so as to correct for changes in signal intensity due to wavelength-dependent variations in the output of the monitoring light and in the sensitivity of the monochrometer/photomultiplier tube arrangement. In kinetic runs, which were carried out at fixed wavelength, the ratiometer was not used since its circuitry introduced an additional time constant into the system.

The modulated part of the signal was analysed using a lock-in amplifier (PAR 124A). The reference channel of the amplifier was driven by a photocell positioned so as to detect light from the irradiating beam. Finally, the output of the amplifier was displayed on a strip chart recorder.

Sample preparation and analysis

In a typical run an iso-octane solution of amine (5–10% v/v) and di-*tert*-butyl peroxide (5% v/v) was purged for ca. 20 min with a stream of nitrogen. The deoxygenated solution was taken up in a syringe and was then passed through the sample cell as ca. 1 mL/min by the use of a mechanical syringe drive.

Kinetic runs were carried out at fixed wavelength, with a 312 nm cut-off filter and an aqueous cobalt – nickel sulphate filter solution in the photolysis beam. This provides a window for photolysis of the peroxide between 312 and 340 nm. The concentration of reagents was adjusted so that > 90% of the incident light was transmitted in this wavelength range. In addition, the monitoring beam was always filtered with 316 nm or 325 nm cut-off filters. This procedure, combined with uniform irradiation at the front face of the cell, ensures a reasonably homogeneous distribution of transient which is necessary for the accurate analysis of second order kinetics. In addition, the sample flow rate was adjusted so that reagent depletion was < 1% and was further checked spectrophotometrically to ensure that the products did not absorb significantly at the photolysis wavelengths. The photolyzed mixture was analysed by vpc for *tert*-butyl alcohol using benzene as an internal standard (24 ft, 20% Carbowax 20 M).

Electron paramagnetic resonance experiments

A limited number of epr experiments were carried out on the amine systems using procedures which have been previously described (5).

Results and discussion

α-Aminoalkyl radicals are formed extremely efficiently in solution by the reaction of *tert*-butoxyl radicals with amines, eq. [1] and [2]. Rate constants for these reactions are among the largest measured for H abstractions by *tert*-butoxyl with $k_2 \simeq 10^8\ M^{-1}\ s^{-1}$ (5). Only abstractions at molecules such as 1,4-cyclohexadiene, which give rise to highly stabilized radicals, proceed with rate constants of this magnitude (6). Moreover, abstractions at amines show a pronounced stereoelectronic effect. That is, H abstraction is most rapid when the C—H bond being broken is eclipsed with the axis of the lone pair orbital on nitrogen (5).

[1] $t\text{-BuO-OBu-}t \xrightarrow{\hbar\nu} 2t\text{-BuO}\cdot$

[2] $t\text{-BuO}\cdot + (\mathrm{RCH_2})_3\mathrm{N} \rightarrow t\text{-BuOH} + \underset{\mathbf{1}}{\mathrm{R\dot{C}HN(CH_2R)_2}}$

[3] $\mathbf{1} + \mathbf{1} \rightarrow$ nonradical products

1*a* R = H; **1***b* R = Me; **1***c* R = Ph

While α-aminoalkyls can be efficiently generated they are nevertheless extremely difficult to detect in solution by using epr spectroscopy (5, 7, 8). Only the spectrum of $\mathrm{Me_2N\dot{C}H_2}$ is easily detected and this is probably because the spectral linewidth is small, ca. 0.1 G. In all other cases, spectra are barely detectable, presumably because of the large number of hyperfine interactions and greater linewidths. This means, of course, that α-aminoalkyls cannot be studied generally using the techniques of kinetic epr spectroscopy. To overcome this problem, we have used modulation spectroscopy to characterize the uv–visible spectra of α-aminoalkyl radicals and to determine the kinetics of their self-reactions.

Spectra

In modulation spectroscopy the concentration of a transient species is made to oscillate at a predetermined frequency, e.g. by generating the transient using modulated photolysis. The sample is monitored optically and phase sensitive detection is used to find the signals which oscillate at the modulation frequency. These signals can be due to the disappearance of starting material, the formation of a transient intermediate, or the appearance of products. However, these three components can be differentiated by measuring the phase of the signal detected with respect to the phase of the modulated photolyzing light. The phase relationships between the signals have been previously derived (3) and are shown in Fig. 2.

In this work, we have modulated the photolyzing light as a sine wave which considerably simplifies kinetic analysis of the data. Under this condition, the rate of transient generation can be expressed as

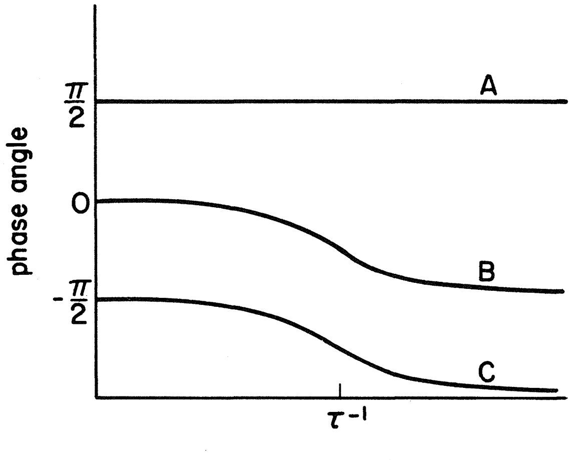

FIG. 2. Frequency dependencies of phases. A, reactant. B, radical. C, product.

a cosine function of the modulation frequency, which leads to simple solutions of the differential equations that describe the reaction kinetics (1, 3, 5, 9). By contrast, square wave or "on–off" modulation (2) requires that the rate of transient generation be expressed as a Fourier series which has obvious disadvantages.

Photolysis of an iso-octane solution of trimethylamine (5% v/v) and di-*tert*-butyl peroxide in the modulation spectrometer gave rise to a spectrum similar to that shown in Fig. 3. In the absence of trimethylamine, only very weak transient absorptions were detected. At the modulation frequencies used in these experiments (10–200 Hz), the phase of the signal lagged behind that of the modulated photolyzing light but did not reach −90° (see Fig. 2). Moreover, the shape of the spectrum was independent of the modulation frequency at which it was recorded. This behaviour implies that the signal is due to a single transient species, which we assign to radical **1***a*.

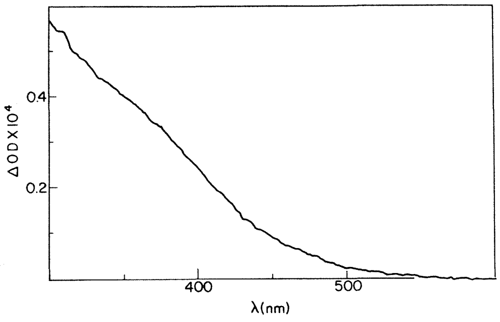

FIG. 3. Optical spectrum of radical **1***b* recorded at a modulation frequency of 43 Hz.

Photolysis of the above solution in the cavity of an epr machine gave rise to an intense spectrum of **1***a* (5), which supports the assignment of the optical spectrum. The signal intensity observed by epr was proportional to the square root of the incident light intensity when the latter was varied by a factor of 100, indicating that the radical decays with second order kinetics. In addition, prolonged photolysis of the sample gave *tert*-butyl alcohol and tetramethylethylenediamine as the major products identified by vpc analysis. Both the epr and modulation results are entirely consistent with the formation and decay of radical **1***a* according to reactions [1]–[3].

A similar optical spectrum was obtained when triethylamine was used in place of trimethylamine in the modulation spectrometer (Fig. 3). However, when tribenzylamine was used, a far more intense spectrum was obtained (Fig. 4) which had a well defined maximum at 346 nm. These spectra showed the properties associated with single transient species and we assign them to radicals **1***b* and **1***c* respectively. Similar spectra have also been obtained in laser flash photolysis experiments[2] and by gas phase modulation spectroscopy.[3]

Kinetics

Rate constants, k_3, for self-reactions of **1***a*–*c* were determined at a fixed wavelength. Using the lock-in amplifier, the signals due to the radicals were resolved into components which were out-of-phase and in-phase with the photolyzing light. The ratio of these components is tan ϕ, where ϕ is the *phase angle*, and the vector sum of these components is directly proportional (3) to ΔOD which is the modulated part of the optical density of the transient.

A plot of $-\tan \phi$ versus the modulation frequency, ω, gave the lifetime, τ, of the radicals, eq. [4]. The relationship between τ and the rate constant for self-reaction of the radicals, k_3, is given in eq. [5], where I_0 is the maximum rate of radical generation during the modulation cycle. An example of such a plot is given in Fig. 5.

[4] $-\tan \phi = \omega\tau$

[5] $\tau^{-2} = 4k_3I_0$

An alternative method of analysing the data yields the extinction coefficient for the radical, ε. In this approach, a plot of $(\Delta OD)^{-2}$ versus ω^2 gave a straight line of slope *a* and intercept *b* which are related (3) to τ, ε, I_0, and *l*, where *l* is the pathlength of the cell in the monitoring direction, eqs. [6] and

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[2] J. C. Scaiano, private communication.

[3] H. Hunziker, private communication.

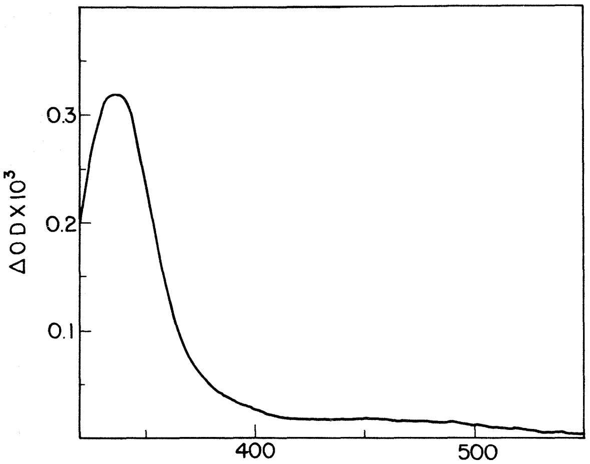

FIG. 4. Optical spectrum of radical **1***c* recorded at a modulation frequency of 43 Hz.

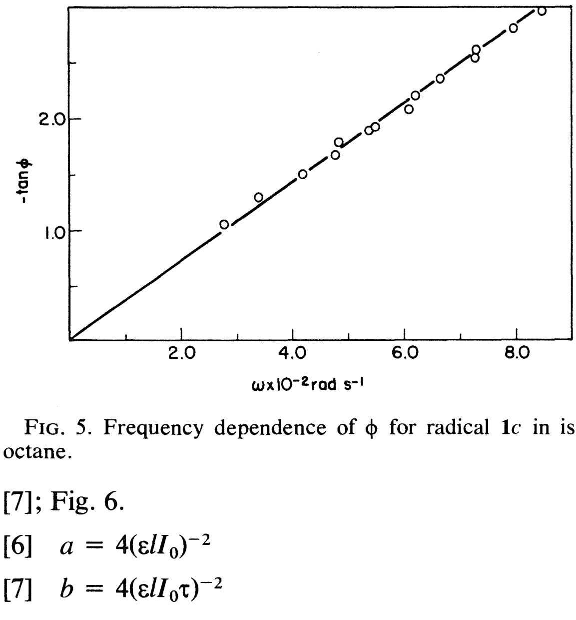

FIG. 5. Frequency dependence of φ for radical **1***c* in iso-octane.

[7]; Fig. 6.

$$[6] \quad a = 4(\varepsilon l I_0)^{-2}$$

$$[7] \quad b = 4(\varepsilon l I_0 \tau)^{-2}$$

In these experiments the mean rate of radical generation $I_0/2$ was determined by analysing the photolyzed reaction mixtures for *tert*-butanol. Values of τ obtained by the two graphical procedures were identical within experimental error. Moreover, τ was proportional to $I_0^{-\frac{1}{2}}$ when the light intensity was reduced using neutral density filters, which indicates that in all cases the radicals decay by bimolecular reactions. The data are summarized in Table 1. The experimental errors on rate constants and extinction coefficients were ca. ± 30%.

When amines were omitted from the reaction mixture the yield of *tert*-butanol obtained by photolyzing the solution under the conditions of the kinetic experiments was the same within experimental error as was obtained in the presence of trimethyl or triethylamine. This indicates that the α-aminoalkyl radicals do not induce decomposition of the peroxide under these experimental conditions. The slight reduction in $I_0/2$ observed when tribenzylamine was used as substrate was presumably due to slight light absorption by the amine in the region where the di-*tert*-butyl peroxide was being photolyzed.

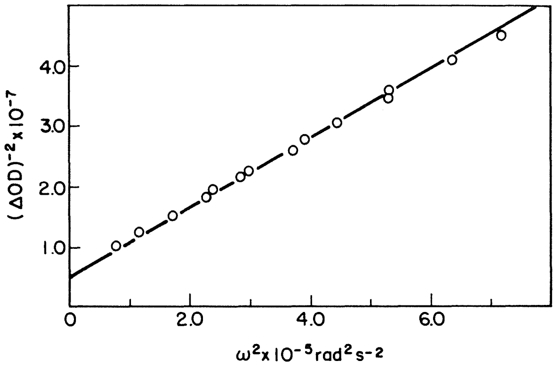

FIG. 6. Frequency dependence of ΔOD for radical **1***c* in iso-octane.

The values of $2k_3$ measured in this work indicate that radicals **1***a*–*c* undergo diffusion controlled self-reaction. Indeed, $2k_3$ decreases as the size of the radicals increases which is to be expected for a diffusion controlled process. The value of $2k_3$ obtained for **1***a* is in accord with the rate constant for self-reaction of *tert*-butyl (10), i.e. 7.4 × 10^9 M^{-1} s^{-1} (294°C; octane solvent) which is a radical of similar size monitored in a solvent of similar viscosity to the iso-octane used in this work. It should be noted that *tert*-butyl has been used as a model for the study of diffusion controlled processes and the kinetics of its self-reaction have been explored in considerable detail (3*b*, 10). Thus, α-aminoalkyl radicals behave kinetically as most other small unhindered alkyls and moreover they do not appear to induce the decomposition of di-*tert*-butyl peroxide at room temperature. We therefore conclude that the failure to detect members of this class of radicals other than **1***a* by epr, in

TABLE 1. Rate constants for the self-reactions of α-aminoalkyl radicals at 298 K

Radical	I_0 (M^{-1} s^{-1})	τ (s^{-1})	ε(340 nm) (M^{-1} cm^{-1})	$2k_3$ (M^{-1} s^{-1})
1*a*	1.66 × 10^{-4}	0.94 × 10^{-3}	493	3.4 × 10^9
1*b*	1.33 × 10^{-4}	1.41 × 10^{-3}	445	1.9 × 10^9
1*c*	7.76 × 10^{-4}	3.57 × 10^{-3}	3390[a]	5.1 × 10^8

[a] Measured at 346 nm.

solution, must be a consequence of the spectral characteristics of the radicals, e.g. linewidth and number of hyperfine interactions, rather than any intrinsic chemical property.

The uv–visible spectrum of radical **1***c* shows a strong absorption band at 346 nm; $\varepsilon = 3390\ M^{-1}\ \text{cm}^{-1}$. This band is typical of benzylic radicals which show strong absorption bands at ~ 316 nm with $\varepsilon_{\text{max}} \sim 9000\ M^{-1}\ \text{cm}^{-1}$ in hydrocarbon solvents.[4] By contrast, the absorption spectra of **1***a* and **1***b* show no well defined maximum in the accessible wavelength range but "tail" to ca. 500 nm. This "tail" is not generally observed in simple alkyl radicals which tend not to absorb significantly at wavelengths > 280 nm (3*c*) and must therefore be associated with the interaction of the unpaired electron with the lone pair of electrons on nitrogen.

The electronic interaction in α-aminoalkyl radicals between the unpaired electron and the nitrogen lone pair manifests itself in a number of ways. First, the epr spectra of α-aminoalkyls isolated in matrices (for matrix isolation studies see ref. 8) indicate that there is substantial delocalization of the unpaired electron between the α-carbon and the adjacent nitrogen atom. In addition, the interaction gives rise to a stereoelectronic effect in hydrogen abstractions from amines (5) and to low ionization potentials and high stabilization energies for the radicals themselves (11). The interaction between the unpaired electron and the nitrogen lone pair can be rationalized in terms of the model of the three-electron bond (see, for example, ref. 12). In this picture, two of these three electrons reside on a bonding orbital, while the third lies in the related antibonding orbital. Electronic transitions between these orbitals in α-aminoalkyl radicals presumably give rise to the absorptions observed in the visible region.

Summary

α-Aminoalkyl radicals undergo diffusion controlled self-reaction at 298°C in iso-octane solvent. Their optical absorption spectra are substantially different to those of simple alkyl radicals in that they absorb significantly up to 500 nm. This property is thought to be a consequence of the interaction between the unpaired electron and the lone pair of electrons on the nitrogen atom.

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[4] For a review of the literature data, see ref. 3*b*.