Pulse Radiolysis of Dimethyl Sulphoxide

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Summary Three absorptions associated with the electron (925 nm), the positive ion (625 nm), and an unidentified species (300 nm) have been observed on pulse radiolysis of dimethyl sulphoxide.

THE physical properties of dimethyl sulphoxide raise the question of the solvation of electrons in this medium and of their subsequent reactions. If the electrons are not solvated they may either form the ion Me_2SO^- or lead to dissociative electron attachment. Pulse-radiolysis studies of aqueous solutions of Me_2SO indicate that its reaction with the hydrated electron is slow ($k \simeq 1\cdot7 \times 10^6 M^{-1}s^{-1}$)[1] and mass-spectrometric studies[2] show that the ion Me_2SO^- does not appear among the several negative ions formed.
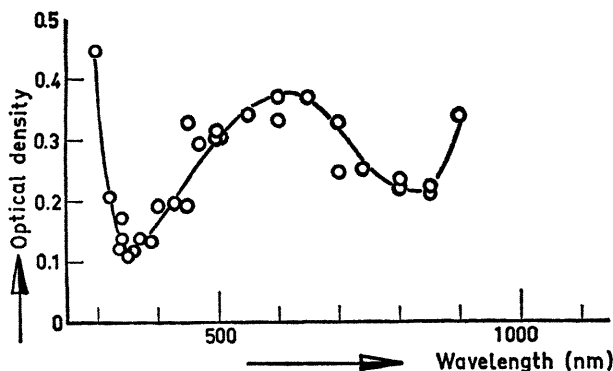

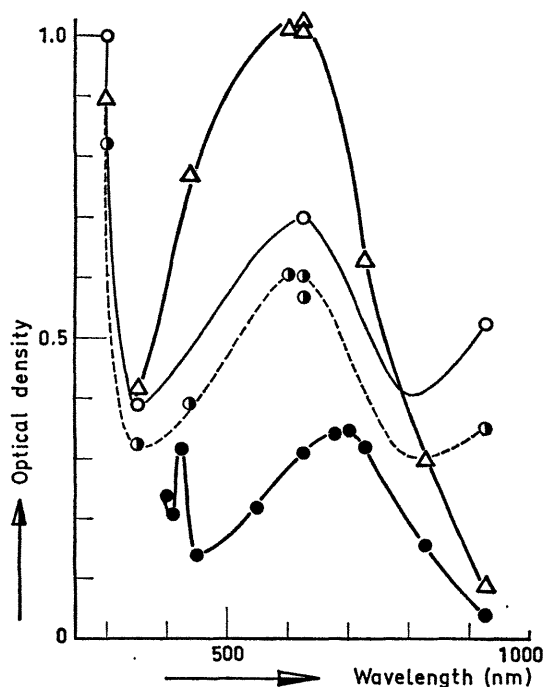FIGURE 1. *Optical density of transients measured immediately after the end of the pulse as a function of wavelength.*

FIGURE 2. *Influence of solvated-electron scavengers on the optical density of the transients formed from* Me_2SO: O *Ar saturated*; ◑ O_2-*saturated*; △ $0\cdot1M$ H_2SO_4; ● 5×10^{-3} M-*anthracene (path length of analysing light reduced by* 3·5).
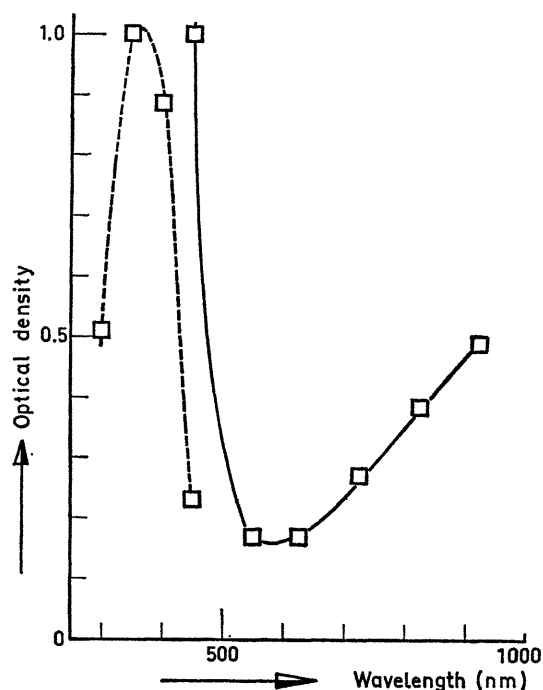

FIGURE 3. *Optical density versus wavelength for* $10^{-1}M$-KBr (-------- *path length of analysing light reduced by* 3·5).

Pulse radiolysis of carefully purified deaerated Me_2SO was carried out using 30 ns pulses of 2 MeV electrons up to 90 krad/pulse. Dosimetry measurements were made with $10^{-1}M$-ferrocyanid solutions saturated with N_2O, at 440 nm, using $\epsilon_{\text{ferricyanide}} = 600M^{-1}cm^{-1}$ and $G(e_{aq}) + G(OH) = 6$.

Figure 1 shows the absorption spectrum of transient species present at the end of the pulse. Measurements in the red region were limited by decreasing detector sensitivity and it appears that the maximum of the first band is at higher wavelengths; the absorption below 300 nm was not completely resolved because of the absorption of the Me_2SO. The 925 nm absorption disappeared completely in 70 ns and the 625 and 300 nm absorptions diminished with half-lives of $0\cdot36$ and $1\cdot35 \mu s$, respectively, the former by a second-order reaction. After the disappearance of the 300 nm absorption, a residual absorption was observed in this region.

Addition of oxygen, anthracene, sulphuric acid, or nitrous oxide, all good solvated-electron acceptors, reduced or eliminated the 925 nm band. N_2O and O_2 do not appreciably reduce the other two absorptions, whereas

H_2SO_4 enhances the 625 nm band and anthracene gives two new bands at 690 and 425 nm (Figure 2). These results suggest that the 925 nm absorption should be attributed to the electron, partly or completely solvated, or to some species arising therefrom of which the yield will be designated G_{Red}.

Br⁻, which should be a good positive-ion scavenger, caused complete disappearance of the 625 nm band without affecting the 925 nm absorption, and gave a strong absorption at 365 nm which, on account of its similarity to the Br_2^- spectrum in water, was attributed to this species (Figure 3). The absorption of Br_2^- remains unchanged for $5 \times 10^{-3}M < |Br^-| < 1^{-1}M$ and also no increase in the 925 nm absorption occurs over this range. Thus it appears that Br⁻ does not react directly with Me_2SO^+ but rather with some oxidizing species formed from it, and the band at 625 nm should be associated with this last species. Assuming $\epsilon(Br_2^-) = 8200$ M⁻¹ cm⁻¹ as in water, we obtain $G(Br_2^-) = G_{ox} = 1\cdot9$ and $\epsilon_{625} = 2200$ M⁻¹ cm⁻¹. This value of G_{ox} is significantly lower than that found in the γ-radiolysis of $Me_2SO^3(G_{ox} = 3\cdot8)$ and one is led to suppose that at these high dose-rates the contribution of recombination reactions of ionic or radical solvent species is important.

In the presence of 5×10^{-3}M-anthracene, the strong anthracene anion band (A⁻) at 690 nm appeared and also the anthracene triplet (A^T) at 425 nm, in fair agreement with Hayon's results.[4] The value of the molar extinction coefficient for triplet anthracene in Me_2SO was determined by Lavalette[5] assuming a constant oscillator strength of 0·25 in all solvents. This gave $\epsilon_{425} = 53,000 \pm 3000$ M⁻¹ cm⁻¹, very similar to the value of $\epsilon(A^T)$ in tetrahydrofuran.[6] $G(A^T)$ is then equal to 0·25. The irradiation of a solution 10^{-1}M in Br⁻ and 5×10^{-3}M in anthracene gives $G(A^-) = G_{Red} = 0\cdot64$. Assuming $\epsilon(A^-) = 10^4$M⁻¹ cm⁻¹, this value leads to $\epsilon_{925} = 4700$ M⁻¹ cm⁻¹. These two G values are smaller than Hayon's[4] and no explanation for this difference can be suggested at this stage.

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