

Pulse Radiolysis of Hexamethylphosphoric Triamide

By A. M. KOULKES-PUJO, L. GILLES, B. LESIGNE, and J. SUTTON

(Centre National de la Recherche Scientifique et Département de Recherche et Analyse, Cen. Saclay, B.P. No. 2, Gif-sur-Yvette 91190)

and J. Y. GAL

(Université de Limoges)

Summary The pulse radiolysis of pure or an NaBr solution of hexamethylphosphoric triamide (HMPT) (saturated either with Ar or N₂O) suggests that the transient with a maximum absorption at 600 nm is due to a bromine atom charge-transfer complex giving an ionization potential for HMPT of 8.1 eV and also that the u.v. absorption is associated with an excited state of HMPT.

SEVERAL authors¹ have shown that the reaction of alkali metals with hexamethylphosphoric triamide (HMPT) gives a blue species having a lifetime of several minutes considered to be the solvated electron e_s⁻.² E. Mal'tsev and his co-workers³ detected an entity with a similar absorption between 700 and 1600 nm during pulse radiolysis of HMPT, a result confirmed by H. Nauta and his co-workers⁴.

On the basis of the results obtained by pulse radiolysis of dimethyl sulphoxide (DMSO),⁵ and taking into account the similarity of DMSO and HMPT as solvents and the relatively long lifetime of e_s⁻ in HMPT we have searched for the formation of other species in this latter solvent.

In the case of DMSO an absorption band associated with the positive ion or with some derivative species has already been observed^{5,6} and, in HMPT, a supplementary band obtained in the presence of chloride or bromide has been attributed to the complex [M⁺ ··· e_s⁻].³ This assignment now seems open to question; the band could also be due to a transient chlorine or bromine atom charge-transfer complex, similar to that recently identified in the pulse radiolysis of bromobenzene.⁷ However, the existing data do not enable a clear-cut decision to be made. We have recently carried out pulse-radiolysis experiments on carefully purified,⁸ deaerated HMPT using 6 ns pulses of 1.8 MeV electrons delivered by a modified Febetron 707.⁹ Doses up to 20 krad/pulse were employed. Dosimetry measurements with 10⁻¹M ferrocyanide solutions saturated with N₂O were used to calibrate a Faraday cup¹⁰ which gave a direct voltage signal proportional to the dose per pulse. In the results all optical densities are given in arbitrary units normalised to a fixed unit of dose.

The absorption spectrum of the transient species present in argon-saturated HMPT 15 ns after the pulse and its variation with time confirm the existence, previously reported, of the visible absorption^{3,4} but the relative intensity of the u.v. band is much greater in our case than in the earlier work.⁴ Moreover the latter absorption does not decrease during our observation time whereas the red absorption decreases with a first half-life of 50 ns. Addition of 10⁻¹M NaBr to argon-saturated HMPT induced the formation of another absorption band around 600–650 nm, although its maximum could not be accurately determined because of the simultaneous presence of e_s⁻. The disappearance of the 600–650 nm band and the formation of a new one with a maximum centred at 360 nm are in agreement with previous results.³

The Figure shows the absorption spectrum and its variation with time of a pulsed N₂O-saturated 10⁻¹M NaBr solution in HMPT. Whereas the absorption band due to the solvated electron does not appear, a peak around 600 nm is observed and its disappearance coincides with the formation of the 360 nm band (the rate constant of formation of Br₂ is 2 × 10⁸ M⁻¹ s⁻¹ and that of disappearance at 600 nm is 2.5 × 10⁸ M⁻¹ s⁻¹, both reactions being pseudo-first-order.

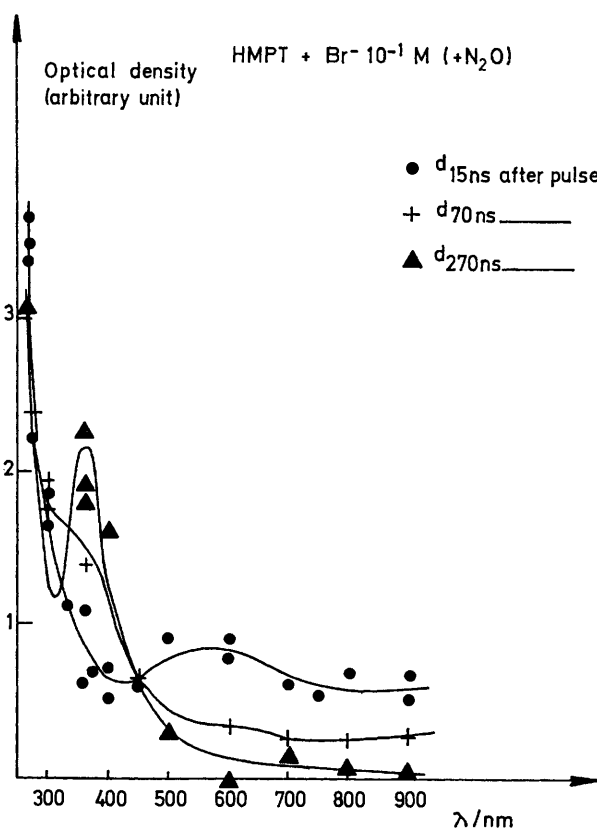
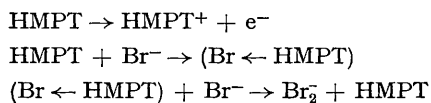


FIGURE. Absorption spectrum and its variation with time of a pulsed N₂O-saturated 10⁻¹M NaBr solution.

Under these different experimental conditions the u.v. absorption remains largely unchanged. After pulsing, pure HMPT saturated with N₂O shows no absorption down to 400 nm at which wavelength the u.v. band begins to appear as in the case of HMPT saturated with argon, with or without added NaBr.

Since the 600 nm band must be correlated with the presence of NaBr and seems unchanged by the presence of N₂O, we do not think it is due to a species (M⁺ ··· e_s⁻) but rather to a bromine atom charge-transfer complex which is



SCHEME

formed and disappears according to the Scheme. Such a complex has been suggested by Cooper and his co-workers⁶ in the case of DMSO. A test for charge-transfer complexes in different systems, in which the energy of the absorption maximum of the observed visible band is plotted against the ionization potential of the electron donor, was investigated by Bossy and his co-workers.⁷ Such a linear relation-

ship has already been discussed by Mulliken and his co-workers¹¹ and if the same correlation is assumed to hold in our case, this would give an ionization potential for HMPT equal to 8.1 eV.

No report of a direct measurement of this ionization potential exists in the literature but the present value appears reasonable since for DMSO the value is 8.85 eV.¹² Since the u.v. absorption does not disappear on addition of Br⁻ or N₂O it would to be associated, as in the case of DMSO⁵ with an excited state of HMPT.

(Received, 12th October 1973; Com. 1405.)

¹ T. Cuvigny, J. Normant, and H. Normant, *Compt. rend.*, 1964, C 258, 3503; M. Fontanille and P. Sigwalt, *Compt. rend.*, 1966, C 263, 316.

² J. M. Brooks and R. R. Dewald, *J. Phys. Chem.*, 1968, 72, 2655.

³ E. I. Mal'tsev, A. V. Vannikov, and N. A. Bach, *Rad. Effects*, 1971, 11, 79-84.

⁴ H. Nauta and C. van Huis, *J.C.S. Faraday I*, 1972, 68, 647.

⁵ A. M. Koulkes-Pujo, L. Gilles, B. Lesigne, and J. Sutton, *Chem. Comm.*, 1971, 749.

⁶ T. K. Cooper, D. C. Walker, H. A. Gillis, and N. V. Klassen, *Canad. J. Chem.*, 1973, 51, 2195.

⁷ J. M. Bossy and R. E. Bühler, *J. Amer. Chem. Soc.*, 1970, 92, 1099.

⁸ J. Y. Gal, Thèse Université de Limoges (1972).

⁹ B. Lesigne and R. Sauneuf, *Rapport CEA* (to be published).

¹⁰ B. Lesigne, L. Gilles, and R. J. Woods, *J. Phys. Chem.*, submitted for publication.

¹¹ R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, 1962, 13, 107.

¹² F. I. Vilesov and B. L. Kurbatov, *Doklady Akad. Nauk S.S.S.R.*, 1961, 140, 1364.