Ion Recombination and Delayed Emission in the Pulse Radiolysis of Liquid Isopentane Solutions at Low Temperature

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Summary Delayed emission (maximum at 380 nm) in the pulse radiolysis of biphenyl in liquid isopentane at 120 °C persists up to microseconds and is correlated in time with the rate of decay of biphenyl ions.

PULSE radiolysis of biphenyl in isopentane at 20 °C with a 5 ns electron pulse of *ca.* 0·4 krad gives immediate absorptions attributable to the anion, the cation, and the triplet state of biphenyl. About half of the ion absorption decays rapidly over *ca.* 50 ns by a process which is not dependent on dose and hence is probably a spur recombination process. The remainder decays over a few microseconds. The triplet half-life is *ca.* 30 μs in these conditions. Fluorescence is also produced, the spectrum being identical with the emission from the singlet excited state of biphenyl[1] but the decay half-life (19 ns) is somewhat longer than that from the u.v.-produced singlet (11 ns).

At −120 °C where isopentane is still liquid, the same absorptions are present. The spur recombination time now extends over some microseconds and the triplet half-life is *ca.* 100 μs. Immediately after the pulse the fluorescence spectrum is largely the same as at 20 °C except that there is now appreciable emission at 370 nm and higher. Most of the shorter wavelength emission now decays with a half-life of 24 ns and after 0·5 μs only *ca.* 0·5% remains. However, at 380 nm 10% of the original intensity is present after this time and there is still enough to measure easily after microseconds.

The spectrum of this delayed emission (Figure 1) indicates the presence of another emitting species, which from the CRO trace can be seen to grow and decay more slowly than the excited singlet state. This species could be either the excimer of biphenyl or a second excited singlet state. In previous work with liquid biphenyl at 100° C and above,[2] one emission above 400 nm was assigned to the former and another below 400 nm to the latter.

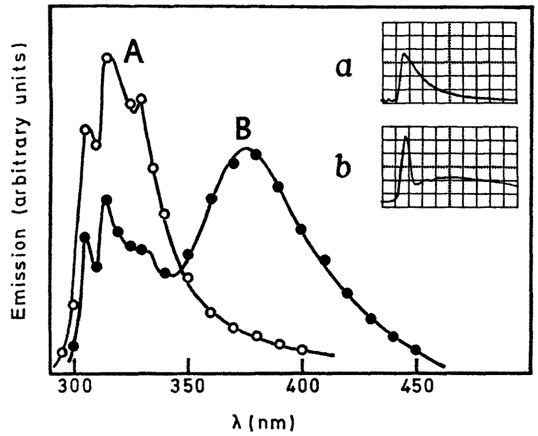

FIGURE 1. *Emission spectra (uncorrected for photomultiplier sensitivity) from* 2mM *biphenyl in isopentane at* −120 °C *after a* 5 ns 0·5 *krad electron pulse. Curve* A: 20 ns, *and curve* B: 0·4 μs *after end of pulse.* A *and* B *are at different relative sensitivities.*

Insets: *CRO traces of emission,* (*a*) *at* 315 nm, 20 ns cm^{-1}, (*b*) *at* 380 nm, 10 ns cm^{-1}, (*initial spike is Cerenkov radiation*).

The delayed emission cannot arise from the triplet (*e.g.* by triplet–triplet interaction) since the latter is too long-lived. There is a close correlation in time between the intensity of the emission and the decay of the ion absorption over a wide time range (see Figure 2). The rates of growth of the emission at 2mM and 1mM biphenyl are similar, although the intensity, as expected, is less at 1mM. This suggests that the simple anion and cation are involved and not, as in low temperature glasses,[3] the cation dimer. The more rapidly formed excited singlet state probably arises from cation recombination with the more mobile electron, but it may be formed from solvent cation–biphenyl anion recombination if the solvent cation has enhanced mobility due to charge transfer, as has been suggested[4] for 3-methylpentane.

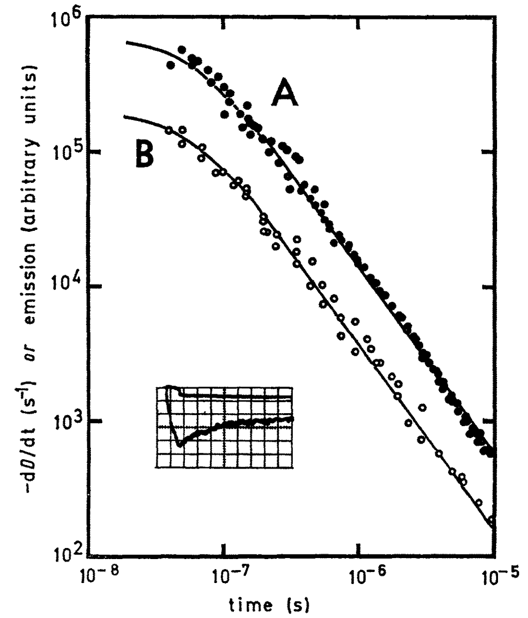

FIGURE 2. *Correlation of emission at* 380 nm (A) *with rate of decay of optical density* D *of ion at* 620 nm, (B) *from* 2 mM *biphenyl in isopentane at* −120 °C (50 ns *pulse*). *The full lines have constant vertical separation.*

Inset: *Ion decay at* 620 *nm,* 50 *ns cm.*$^{-1}$

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