# Chemical Periodicity on the μs Time-scale of an Intermediate Following ns Flash Photolysis of Benzilic Acid Sensitised by Oxidising Metal Ions

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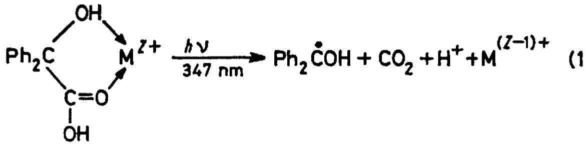
*Summary* The 347 nm ns flash photolysis of acetone solutions of benzilic acid containing sensitising metal ions ($Ag^+$, $Cu^{2+}$, $Fe^{3+}$ and, less markedly, $HgCl_2$) above certain photo-oxidant concentrations produces a structured, transient absorption spectrum spanning the entire visible spectrum which displays complex, but reproducible oscillatory behaviour.

RATHER few well differentiated examples of chemical systems operating under homogeneous, solution conditions and exhibiting periodicity have been reported.[1] Whilst the criteria for producing continuous oscillations are very rigid (the existence of at least two autocatalytic steps), as in the Belousov–Zhabotinskii reaction[2] and the $H_2O_2$–$IO_3^-$–$I^-$–$I_2$ system,[3] those for damped oscillations are less so[4] in requiring only one autocatalytic step, as in the decomposition of aqueous dithionite ion.[5] Nesmeyanov and his colleagues[6] have recently reported on damped oscillatory behaviour during continuous photochemical irradiation of either octamethylferrocene or octamethylferricinium ion in ethanol (giving no mechanism).



(1)

We report here that both the nature and the kinetic behaviour of the organic intermediate produced during laser flash photolysis (347 nm, *ca.* 25 ns pulse) of acetone solutions of benzilic acid (0·21 mol dm$^{-3}$) containing various oxidising metal ions ($Ag^+$, $Cu^{2+}$, $Fe^{3+}$, and $HgCl_2$) depend critically upon the metal ion concentration. At low concentrations ($10^{-4}$ mol dm$^{-3}$ for $Ag^+$, $10^{-3}$ for $Fe^{3+}$ and $Cu^{2+}$, and 0·1 for $HgCl_2$), the expected oxidative decarboxylation takes place [equation (1)] as previously reported,[7] and the spectrum of $Ph_2\dot{C}OH$ ($\lambda_{max}$ 542 nm)[8] is observed which decays with pseudo-first-order kinetics in the presence of the oxidant to yield second-order rate constants for the reaction of $Ph_2\dot{C}OH$ with $M^{z+}$ as follows: $Cu^{2+}$, $(1{\cdot}83 \pm 0{\cdot}05) \times 10^6$; $Fe^{3+}$, $(4{\cdot}91 \pm 0{\cdot}26) \times 10^7$; $Ag^+$, $(3{\cdot}71 \pm 0{\cdot}37) \times 10^6$; and $HgCl_2$, $(6{\cdot}50 \pm 0{\cdot}50) \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$. At slightly higher [$M^{z+}$] the smooth decay of $Ph_2\dot{C}OH$ at 542 nm is replaced by one exhibiting two or three ripples, while when [$Cu^{2+}$] or [$Fe^{3+}$] $> 5 \times 10^{-2}$ [when $\tau(Ph_2\dot{C}OH)$ is only *ca.* 10 and 1 μs, respectively] or when [$Ag^+$] $> 2 \times 10^{-3}$ mol dm$^{-3}$, the decay character is replaced by one of initially very strong irregular fluctuations in concentration, giving way to smaller, more regular oscillations (Figure 1). When complete point-to-point spectra were taken of the transient giving rise to the oscillations, it was found that although it absorbs strongly at 550 nm and at shorter wavelengths

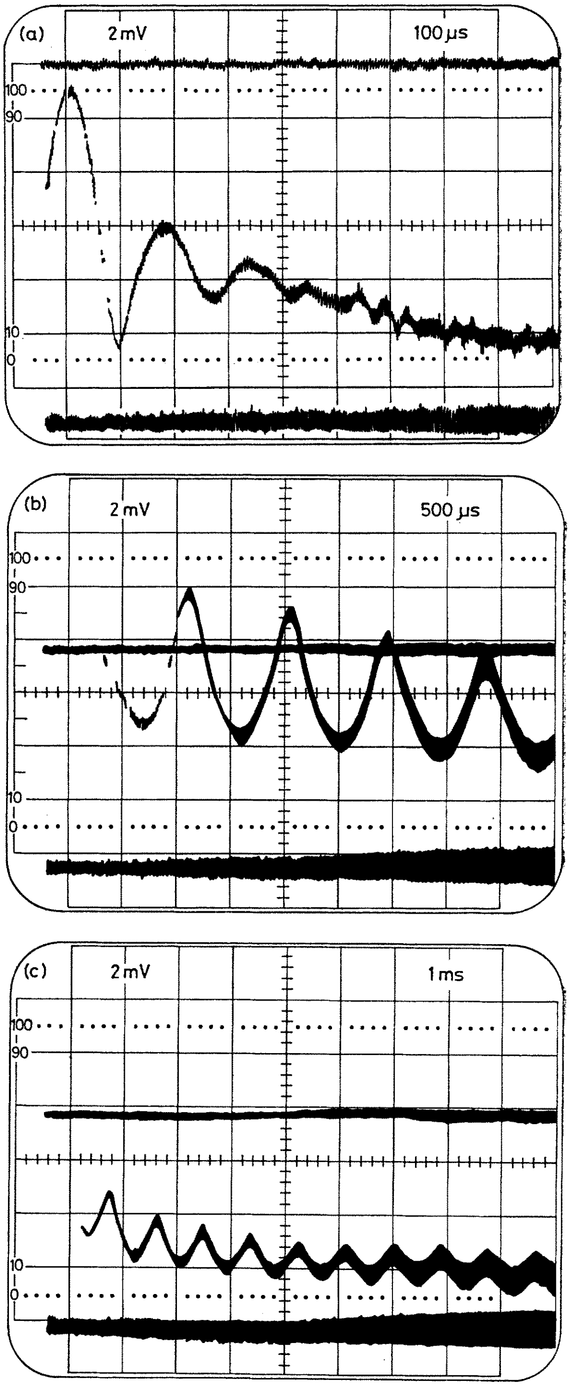


FIGURE 1. Examples of oscillograms produced at $\lambda = 548$ nm during the ns flash photolysis of an acetone solution of benzilic acid (0·214 mol dm$^{-3}$) containing $Fe^{3+}$ ion (0·023 mol dm$^{-3}$). (a): 6 mV offset of 0% light transmission level; (b) and (c): 12 mV offset of 0% light transmission level.

(appearing rather like $Ph_2\dot{C}OH$), it also absorbs strongly throughout the region 600—900 nm (Figure 2) where $Ph_2\dot{C}OH$ has zero absorption. Neither this spectrum nor (within a factor of two) the period of the oscillation is sensitive to the nature of $M^{z+}$, indicating that the transient is not an organometallic ion and that the oxidation of the transient by $M^{z+}$ is not kinetically critical. No precipitation was found in the case of $Fe^{3+}$ oxidation, and precipitation was observable with the other oxidants only after several laser pulses. Reduction of the intensity of the analysing light (Xe arc) tenfold (by inserting a neutral density filter) failed to influence the oscillatory behaviour, indicating that it is not due to post-pulse photolysis; systematic detuning of the doubling crystal (to reduce the laser pulse intensity by a factor of ten) also failed to suppress the oscillations, although the transient absorbance was reduced in proportion. The oscillations were also present when acetone as solvent was replaced either by methanol or by MeCN (in the case of $Fe^{3+}$–benzilic acid) and even when benzilic acid was replaced by the same concentration of benzhydrol. Neither oscillations nor the new transient are obtained from benzilic acid–$[UO_2]^{2+}$ solutions, although a strong $Ph_2\dot{C}OH$ spectrum was obtained, nor when nitroaromatic compounds are used as oxidants for $Ph_2\dot{C}OH$.

At the present stage of the work, we can only conclude that the transient (Figure 2) responsible for the oscillations is an adduct of $Ph_2\dot{C}OH$ with, possibly, a photoproduct of the reaction, and that this adduct can rapidly revert to its components to provide the necessary 'pool' of intermediates which is a feature of these processes. The damped character of the oscillations suggests a classical Lotka-type mechanism.[9]

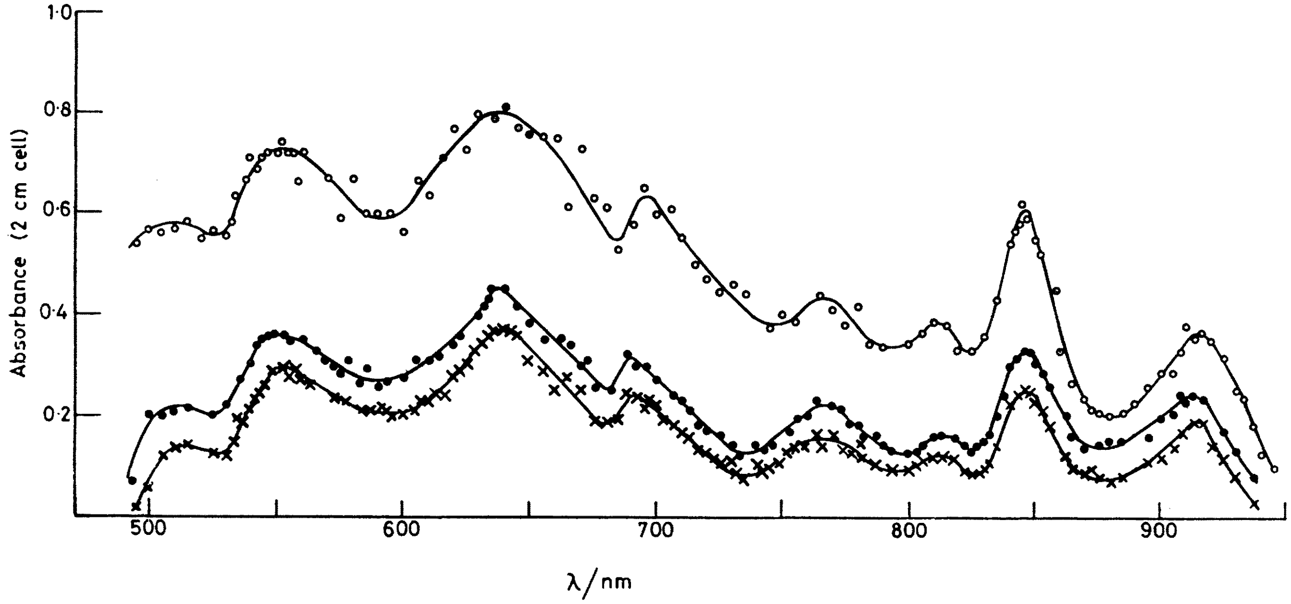


FIGURE 2. Spectrum of the transient responsible for oscillations during the ns flash photolysis of an acetone solution of benzilic acid containing $Fe^{3+}$ ion (concentrations as for Figure 1). Spectra were recorded 60 μs (○), 1·30 ms (●), and 3·1 ms (×) after the pulse.

We thank INVOTAN (Lisbon), the British Council, and the Instituto Politécnico da Covilhã, Portugal, for support of L. J. A. M.

(*Received*, 21*st September* 1978; *Com.* 1022.)

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