The Cu(I),Fe(III)/Cu(II),Fe(II) *Equilibrium and Its Influence on the Ferric Chloride Photosensitized, Cupric Chloride Inhibited Polymerization of Acrylonitrile in* N,N-*Dimethylformamide*

R. G. JONES

The Cu(I),Fe(III)/Cu(II),Fe(II) *equilibrium in dimethylformamide solution has been found to favour the ferric/cuprous states. Cupric chloride has been used to inhibit the ferric chloride-photosensitized polymerization of acrylonitrile in dimethylformamide. The kinetics of the reaction are discussed in terms of termination by both ferric and cupric chlorides, and the reduction of cupric chloride by ferrous chloride. The value* $1{\cdot}75\times10^5$ M^{-1} *sec*$^{-1}$ *has been obtained for the rate constant for the scavenging of polyacrylonitrile radicals by cupric chloride.*

THE equilibrium (1) in aqueous solution favours the ferrous/cupric states, however spectrophotometric evidence has been obtained indicating that the ferric/cuprous states are favoured in dimethylformamide (DMF) solution and that the equilibrium is rapidly attained.

$$\text{Cu (I)} + \text{Fe (III)} \rightleftharpoons \text{Cu (II)} + \text{Fe (II)} \qquad (1)$$

$$E^0\ \text{(aq.)} = 0{\cdot}60\ \text{V at } 25^\circ\text{C}$$

A $4{\cdot}35\times10^{-4}$ M solution of ferrous chloride in DMF was prepared *in vacuo* by photolysing (at 4 358 Å) a solution of ferric chloride[1]. Analytical reagent grade cupric chloride (sufficient to make the solution 10^{-3} M in $CuCl_2$) was then admitted via a break-seal-entry, mixing and measurement of the optical density of the solution at 3 620 Å being effected in about ten seconds. The spectrum of the solution is shown in *Figure 1* together with the spectrum of the pre-photolysed solution, the expected spectrum of the solution on the assumption that equilibrium (1) lies to the right, and the expected spectrum based on the converse assumption.

Figure 1 exhibits all of the characteristics normally associated with a spectrum of a ferric chloride solution in DMF[2]. As well as the total absence of the characteristic absorption peak of cupric chloride at 4 350 Å, the spectrum corresponds most closely in this region to that of a 0·435 mM solution of ferric chloride with enhanced peaks at 3 620 Å and 3 170 Å (characteristic of the $FeCl_4^-$ ion[1]). These features further suggest the consumption of the excess of cupric chloride by equilibrium (2) and the reaction of HCl molecules formed in the photolytic process, with ferric chloride according to equilibrium (3).

$$CuCl_2 + FeCl_3 \rightleftharpoons CuCl^+ + FeCl_4^- \qquad (2)$$

$$HCl + FeCl_3 \rightleftharpoons H^+ + FeCl_4^- \qquad (3)$$

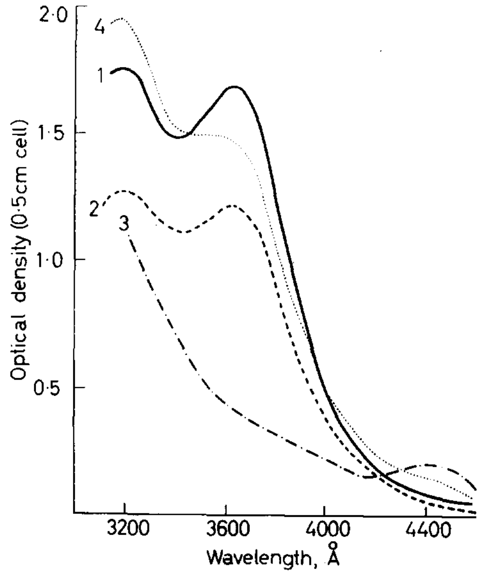

Figure 1—Spectrum of solution of ferrous chloride (0·435 mM) and cupric chloride (1 mM) in DMF. Curve 1: Actual spectrum; Curve 2: Spectrum of $FeCl_3$ (0·435 mM); Curve 3: Spectrum of $CuCl_2$ (1 mM); Curve 4: Spectrum of $CuCl_2$ (0·565 mM) and $FeCl_3$ (0·435 mM)

The position of equilibrium (1) is of consequence in the ferric chloride photosensitized cupric chloride inhibited polymerization of acrylonitrile in DMF. The rate of polymerization has been obtained dilatometrically at a variety of cupric and ferric chloride concentrations at a constant rate of initiation. In all cases the polymerization was preceded by an inhibition period, the duration of which was obtained by extrapolation to zero concentration of the linear portions of the concentration/time curves

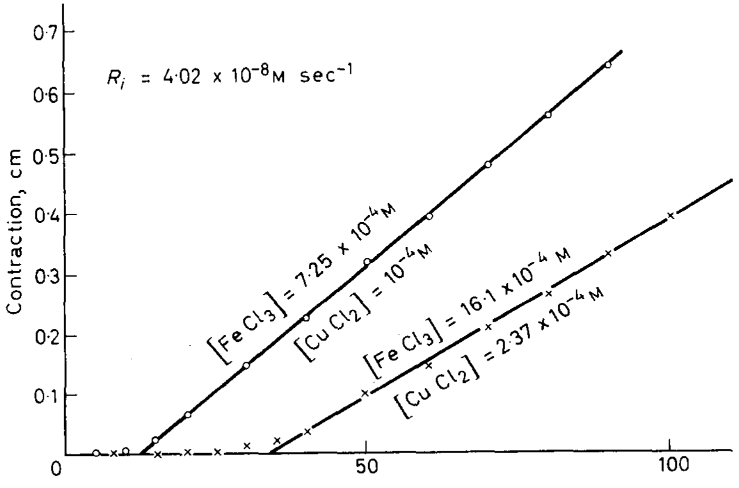

Figure 2—Typical contraction/time curves for the ferric chloride photosensitized, cupric chloride inhibited polymerization of acrylonitrile (1·37 M) in DMF; $R_i = 4{\cdot}02 \times 10^{-8}$ M sec^{-1}

(*Figure 2*). The final steady rate of polymerization was found to correspond within experimental error to that of the equivalent solution with cupric chloride absent[1]. It was further observed that during the inhibition period the absorption at 3 620 Å did not change, though at the end of this period the rate of photolysis of ferric chloride also corresponded to that of an equivalent solution with cupric chloride absent. A plot of inhibition period duration versus [$CuCl_2$] is shown in *Figure 3*, the slope of which corresponds to $-\mathrm{d}\,[CuCl_2]/\mathrm{d}t = 1{\cdot}20 \times 10^{-7}$ M sec^{-1}. That this value is approximately three times greater than the rate of formation of radical centres (assuming $R_i = \Phi I_a = 4{\cdot}02 \times 10^{-8}$ M sec^{-1}, where Φ is the quantum yield for the removal of ferric chloride and I_a is the intensity of light absorbed) is partially

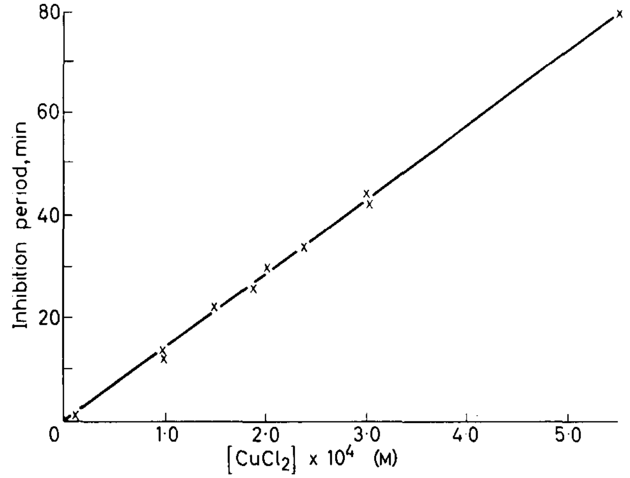

Figure 3—Variation of inhibition period duration with cupric chloride concentration. $R_i = \Phi I_a = 4{\cdot}02 \times 10^{-8}$ M sec^{-1}

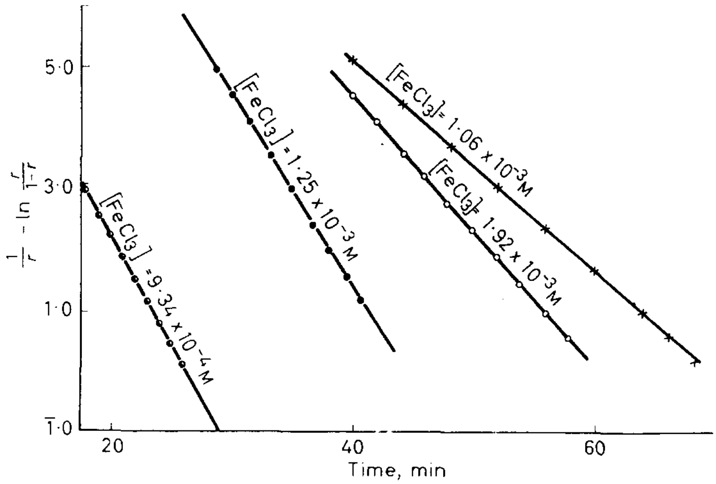

Figure 4—Plot of $1/r - \ln r/(1-r)$ versus time

explained by the consumption of two molecules of $CuCl_2$ for each molecule of $FeCl_3$ that is photolysed; one molecule being consumed by the inhibition process and the other by equilibrium (1). The apparent consumption of a third molecule of $CuCl_2$ can at present only be attributed to the variety of the equilibria involving transition metal species present in this system.

The polymerization results have been interpreted on the assumption that at the ferric chloride concentrations used, the sole mode of chain termination at the end of the inhibition period is first order termination by $FeCl_3$, i.e. mutual chain termination and chain transfer phenomena have been neglected in order to simplify the kinetics. At concentrations of $FeCl_3$ greater than 10^{-3} M (the lower limit of concentration used in the present kinetic investigation) this is justified[1].

The kinetic scheme for the polymerization may be summarized as follows:

		Rate
(*a*) Production of free radicals		
	$FeCl_3 \xrightarrow{h\nu} FeCl_2 + Cl^{\bullet}$	ΦI_Q
(*b*) Initiation		
	$Cl^{\bullet} + M \longrightarrow m_1^{\bullet}$	R_i
(*c*) Propagation		
	$m_j^{\bullet} + M \longrightarrow m_{j+1}^{\bullet}$	$k_p [m_j^{\bullet}] [M]$
(*d*) Termination		
	$m_j^{\bullet} + FeCl_3 \longrightarrow \text{products} + FeCl_2$	$k_f [m_j^{\bullet}] [FeCl_3]$
	$m_j^{\bullet} + CuCl_2 \longrightarrow \text{products} + CuCl$	$k_c [m_j^{\bullet}] [CuCl_2]$
(*e*) Equilibrium		
	$CuCl_2 + FeCl_2 \rightleftharpoons CuCl + FeCl_3$	(rapid)

Two expressions relating the variables and the rate constants can be

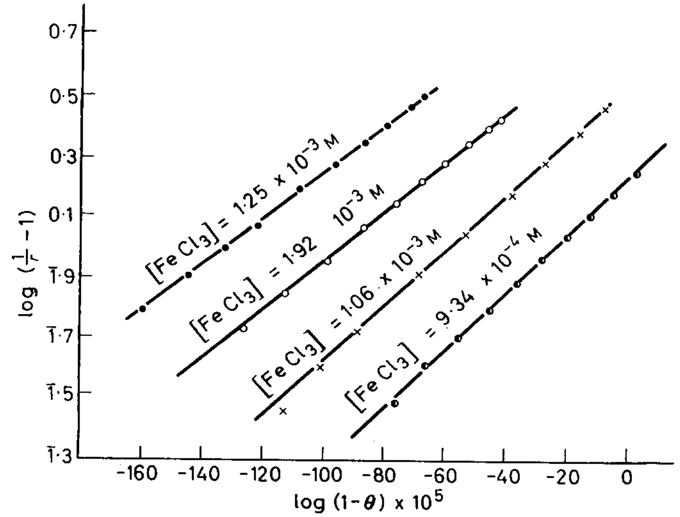

Figure 5—Plot of $\log(1/r-1)$ versus $\log(1-\theta)$

obtained by assuming instantaneous stationary state conditions during the inhibition and acceleration periods.

I. By a modification of the method of Bamford *et al.*[3]

$$\ln\{r/(1-r)\}-1/r=\frac{2k_c(R_p)_s t}{k_p[\mathrm{M}]}+\alpha$$

where $r=(R_p)_t/(R_p)_s$ = reduced rate of polymerization, when $(R_p)_t$ and $(R_p)_s$ are the rates of polymerization at time t and at the steady state respectively, and α is a constant of integration.

II. By a modification of the method of Bengough and Fairservice[4],

$$\log k_c=\log(k_f[\mathrm{FeCl_3}]/C_0)+\log(r^{-1}-1)$$
$$-(2k_c/k_p)\log(1-\theta)$$

where C_0 is the initial cupric chloride concentration and θ is the fractional conversion of monomer to polymer.

Both equations are applicable to the acceleration period and plots of $1/r-\ln\{r/(1-r)\}$ versus t and $\log(r^{-1}-1)$ versus $\log(1-\theta)$ are shown in *Figures 4 and 5* respectively. The value $k_c=(1\cdot75\pm0\cdot2)\times10^5\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$ has been obtained[1,5] from the slopes using the values $k_f=9\cdot8\times10^2\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$ and $k_p=3\cdot82\times10^2\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$.

Department of Chemistry and Metallurgy,
Lanchester College of Technology,
Coventry

(*Received February 1968*)

REFERENCES

[1] DAINTON, F. S. and JONES, R. G. *Trans. Faraday Soc.* 1967, **63,** 1512

[2] COLEBOURNE, N., COLLINSON, E. and DAINTON, F. S. *Trans. Faraday Soc.* 1963, **59,** 886

[3] BAMFORD, C. H., JENKINS, A. D. and JOHNSTON, R. *Proc. Roy. Soc. A,* 1957, **239,** 214

[4] BENGOUGH, W. I. and FAIRSERVICE, W. H. *Trans. Faraday Soc.* 1965, **61,** 1206

[5] COLEBOURNE, N., COLLINSON, E., CURRIE, D. J. and DAINTON, F. S. *Trans. Faraday Soc.* 1963, **59,** 1357