

Enhancement of Rates of Reaction using Neutral Water/Organic Microemulsions as Solvent Media

Michael J. Blandamer, John Burgess, and Barbara Clark

Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K.

Relative to the rate constants for reactions in aqueous solutions the rate constants for reactions involving (i) $\text{Fe}(\text{phen})_3^{2+}$ (phen = 1,10-phenanthroline), (ii) $\text{Fe}(\text{5-NO}_2\text{phen})_3^{2+}$, (iii) 2,4-dinitrochlorobenzene, and (iv) crystal violet with either hydroxide or cyanide ions are increased markedly when two water/organic microemulsions formed from liquid components are used as reaction media; a similar though less significant change is observed in the related rates of aquation (hydrolysis).

As part of a detailed study into the effects of solvent on the rates of both inorganic and organic reactions,¹ we have examined the kinetics of a range of reactions in water/organic (w/o)-microemulsions. In these systems, it is envisaged that small drops of water (*ca.* 10^{-8} m diameter) are distributed through the organic liquid system. We have observed that in microemulsions formed from non-ionic liquid components, the rates of many reactions are significantly higher than in more conventional aqueous solutions, the ratio of rate constants being in some cases 10^3 or more. Here we illustrate the point by reference to two microemulsions; A 60 mol % 2-butoxy-

ethanol, 20 mol % decane, and 20 mol % water;² B 45 mol % propan-2-ol, 40 mol % hexane, and 15 mol % water.³

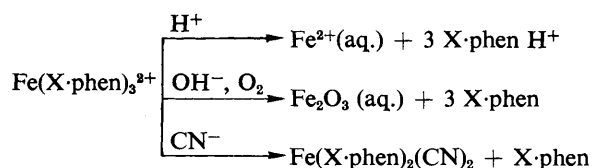
At 298 K, both microemulsions are, perhaps surprisingly, clear and transparent in the visible and near u.v. regions of the spectrum. Kinetic data for a series of reactions are summarised in Table 1, together with kinetic data for the corresponding reactions in aqueous solution. These reactions are given in Scheme 1.

The most dramatic effect is observed for reactions involving CN^- . Indeed, the rates were too fast for us to measure, being complete within a second or so of mixing. A similar trend was

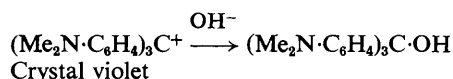
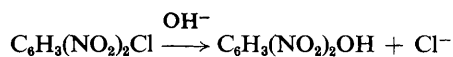
Table 1. Rates of reaction in two w/o-microemulsions at 298 K.

	Aquation (hydrolysis) k/s^{-1}	Hydroxide $k_2/dm^3 mol^{-1} s^{-1}$	Cyanide $k_2/dm^3 mol^{-1} s^{-1}$
Solvent: aqueous solution			
Fe(phen) $_3^{2+}$	7.33×10^{-5}	1.08×10^{-2}	2.4×10^{-2}
Fe(5-NO $_2$ phen) $_3^{2+}$	4.87×10^{-4}	9.3×10^{-2}	0.51 ^a
C $_6$ H $_3$ (NO $_2$) $_2$ Cl	— ^f	1.3×10^{-3}	— ^f
Crystal violet	1.1×10^{-5}	2×10^{-1}	6.1×10^{-2}
Solvent: microemulsion A			
Fe(phen) $_3^{2+}$	2.17×10^{-4}	44.9 ^b	>300
Fe(5-NO $_2$ phen) $_3^{2+}$	2.41×10^{-3}	>200 ^b	>300
C $_6$ H $_3$ (NO $_2$) $_2$ Cl	— ^f	1.37×10^{-1c}	— ^f
Crystal violet	—	>200 ^b	>300
Solvent: microemulsion B			
Fe(phen) $_3^{2+}$	2.3×10^{-4}	87.7 ^d	>200
Fe(5-NO $_2$ phen) $_3^{2+}$	5.2×10^{-3}	>200 ^d	>200
Crystal violet	—	333 ^e	—

^a $T = 305$ K. ^b $[OH]^- = 2 \times 10^{-3}$ mol dm $^{-3}$. ^c $[OH]^- = 1.49 \times 10^{-3}$ mol dm $^{-3}$. ^d $[OH]^- = 3 \times 10^{-3}$ mol dm $^{-3}$. ^e $[OH]^- = 1.5 \times 10^{-3}$ mol dm $^{-3}$. ^f No known reaction.



X = H or 5-NO $_2$

**Scheme 1**

observed for reactions between OH $^-$ and Fe(5-NO $_2$ phen) $_3^{2+}$ (phen = 1,10-phenanthroline). The reaction between OH $^-$ and Fe(phen) $_3^{2+}$ is slightly slower and we were able to calculate a second order rate constant (Table 1). On going from water to a w/o-microemulsion the rate constant increases by a factor of $>10^3$. This reaction is currently believed to involve attack at the ligand by OH $^-$ in a bimolecular process. Overall the process involves two ions of opposite charge. However, this is not the basis for an explanation of the rate enhancement as shown by the data for the reaction between OH $^-$ and the neutral molecule, 2,4-dinitrochlorobenzene⁴ (Table 1). Here the acceleration in rate is $>3 \times 10^3$. This reaction proceeds in a bimolecular displacement of Cl through a four-centre intermediate. The reaction between crystal violet and OH $^-$ was chosen because crystal violet is a soluble carbonium ion.⁵

Here again the acceleration in rate of reaction is dramatic (Table 1).

Kinetic data for the related aquation and hydrolysis reactions (Table 1) also show an increase in rate of reaction although here the effect is not so dramatic.

Microemulsions have been described as thermodynamically microstructured phases.⁶ However the precise structures and, as important, the persistence time for these structures are a matter for current speculation and research.⁷ Explanations of the kinetic results reported here can be offered in various terms. In one model, the rate enhancement can be understood in terms of phase-transfer catalysis coupled with extensive concentration fluctuations within the microemulsion.

We thank S.E.R.C. for a maintenance grant to B. C.

Received, 11th March 1983; Com. 324

References

- 1 M. J. Blandamer and J. Burgess, *Pure Appl. Chem.*, 1982, **54**, 2285.
- 2 J. E. Desnoyers, R. Beaudoin, G. Feron, and G. Roux, *Am. Chem. Soc. Symposium Series*, No. 90, ed. M. Tomlinson, 1979, 33.
- 3 B. A. Keiser, D. Varic, R. E. Barden, and S. L. Holt, *J. Phys. Chem.*, 1979, **83**, 1276.
- 4 M. J. Blandamer and D. Reid, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 2156.
- 5 K. Hillier, J. M. W. Scott, D. J. Barnes, and F. J. P. Steel, *Can. J. Chem.*, 1976, **54**, 3312.
- 6 E. W. Kaler and S. Prager, *J. Colloid Interface Sci.*, 1982, **86**, 359.
- 7 'Microemulsions,' ed. I. D. Robb, Plenum Press, London, 1982.