Biphasic Photochemistry: Use of the Barton Reaction to Determine Micelle Microviscosity

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Summary The Barton reaction—the photolysis of alkyl nitrites—has been used to determine the microviscosity of a micelle core using a reciprocal relationship found between the ratio of hydroxy-ketone to ketone formed and the macroviscosities of solvents in homogeneous solution.

Amongst the techniques used for micelle[1] structure investigation photophysical tools have assumed some importance.[2] They have been used to ascertain micelle

Irradiation (>300 nm) of aqueous potassium 6-nitritododecanoate (A) (0·002 M) in potassium dodecanoate (B) as host micelle (0·04 M: CMC ca. 0·024 M†) (Scheme) gave, after acid treatment and esterification, methyl 6-hydroxy-9-oxo- (E), methyl 6-oxo- (F), and methyl 6-hydroxy-dodecanoate (G) in 5·4, 39, and 16% yields, respectively. When the free acid was irradiated in hexane the yields were 40, 4·8, and 12%. The impressive difference in the amount of Barton product, the hydroxyketone (E), cannot be attributed to the difference in polarity of the media,
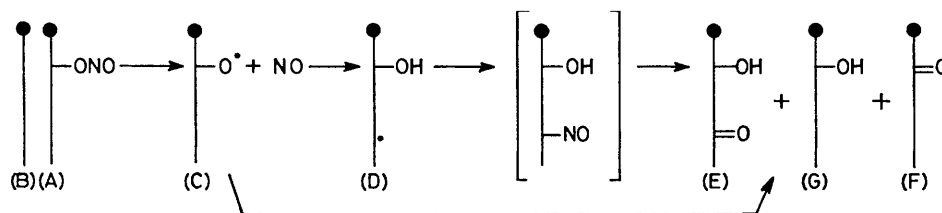
Scheme. ●— = dodecanoate chain. This scheme is not intended to convey any mechanistic implications.

microviscosity and other aspects of micelle structure by such methods as fluorescence depolarisation, fluorescence excimer emission, and fluorescence quenching. There has been virtually no application of photochemical methods[3] as a micelle structure probe. We report the successful use of the Barton reaction—alkyl nitrite photolysis[4]—for this purpose.

the micelle core and hexane, because alkyl nitrites have been irradiated in a variety of solvents, polar and non-polar, without dramatic change.[5] Further, even should water molecules penetrate the core of the micelle to the site of the reaction the expected intermediate alkoxyl radical (C) has been shown to undergo δ-hydrogen abstraction in an aqueous medium.[6] The property of the media presumed

† The critical micelle concentration (CMC) was essentially unchanged by the presence of the guest nitrite molecules. The nitrite ester was stable in the dark under these conditions. There were statistically 2·5 nitrite molecules per micelle, but with a Poisson distribution.

responsible for the different product distributions is the viscosity: it has been shown separately that the nitric oxide concentration after the initial *ca.* 5% conversion is irrelevant.[7]
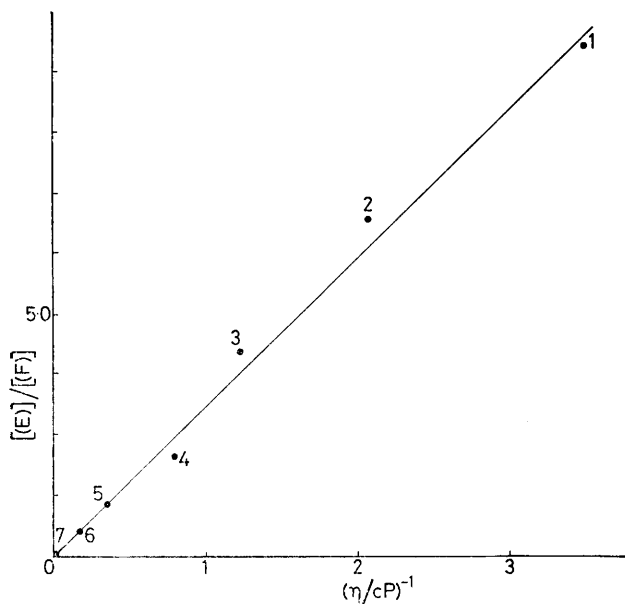

FIGURE. Ratio of Barton product to ketone, (E)/(F), from 6-nitritododecanoic acid photolysis in various solvents (viscosity at 27 °C in parentheses, in cP) 1, n-hexane (0·29); 2, n-octane (0·48); 3, n-decane (0·81); 4, cycloheptane (1·25); 5, hexadecane (2·85); 6, mineral oil–n-hexane, (2:3, v/v) (5·79); 7, mineral oil (127).

The formation of the ketone (F) has been shown to be mainly attributable to the disproportionation of the alkoxyl radical formed by nitrite photolysis, and hence its rate of formation is controlled by diffusion rates.[7] The formation of the hydroxy-ketone (E) appears to depend on the viscosity for two reasons, since the nitric oxide must diffuse to the carbon-centred radical (D),‡ and segmental movement of the chain, in the attainment of the desired conformation for formation of (D) from (C), must be accomplished. The ratio of the hydroxy-ketone (E) to the ketone (F) might thus show an inverse relationship to the viscosity.§ The ratios (E)/(F) for the photolysis of 6-nitritododecanoic acid in a series of hydrocarbons of increasing viscosity were determined, and the result plotted against the reciprocal of the viscosity. A remarkably good linear relationship was found (Figure). On this basis, the value for the hydrocarbon core of the micelle nucleus corresponds to a viscosity of *ca.* 19 cP (1 cP $= 10^{-3}$ kg m^{-1} s^{-1}). Although this is less than that reported using an excimer fluorescence technique (150 cP)[8] it is in the range (17—50 cP) reported for several other micelles[9] and close to the value found for the ω-phenyldecanoate micelle (8·3 cP[10])¶ found by T_1 (^{13}C) relaxation methods.

In addition to the above observations there has been, as far as we are aware no previous report of such a dramatic change in a quasi-unimolecular process occurring over what is a 'normal' viscosity range (*ca.* 0·3—3·0 cP).

Added in proof. A recent report using the molecular motion of dipyrenylpropane as a probe has given, for sodium dodecyl sulphate, results similar to the above.[11]

‡ It has been shown that the nitric oxide in the Barton reaction is exchangeable with labelled material: M. Akhtar and M. M. Pechet, *J. Amer. Chem. Soc.*, 1964, **84**, 265; H. Suginome, T. Mizuguchi, and T. Masamune, *J.C.S. Perkin I*, 1976, 2365.

§ In a number of reactions the rate of formation of product in an intramolecular reaction has been shown to show an approximate empirical relationship with η^{-1}: see H. Shizuka, T. Ogiwara, and T. Morita, *Bull. Chem. Soc. Japan*, 1977, **50**, 2067; D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, 1968, **90**, 12.

¶ Microviscosities determined by different techniques need not be identical. The value for the rotation of a guest in the micelle host may be different from that for its linear translation or, as in the present case, the resistance to coiling. The exact location of the guest in the micelle may also produce differences.

[1] See, for example: J. H. Fendler and E. J. Fendler, 'Catalysis in Micellar and Macromolecular System,' Academic Press, New York, 1975.

[2] J. K. Thomas, *Accounts Chem. Res.*, 1977, **10**, 133.

[3] For examples of photochemical reactions in a micelle see: N. J. Turro, K. C. Liu, and M. F. Chow, *Photochem. Photobiol.*, 1977, **26**, 413; T. Miyata, A. Sakumoto, and M. Washino, *Bull. Chem. Soc. Japan*, 1977, **50**, 2950; Y. Nakamura, Y. Imakura, T. Kato, and Y. Morita, *J.C.S. Chem. Commun.*, 1977, 887.

[4] D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, *J. Amer. Chem. Soc.*, 1960, **82**, 2640.

[5] P. Kabasakalian and E. R. Townley, *J. Amer. Chem. Soc.*, 1962, **84**, 2711.

[6] B. C. Gilbert, R. G. G. Holmes, H. A. H. Laue, and R. O. C. Norman, *J.C.S. Perkin I*, 1976, 1047; B. C. Gilbert, R. G. G. Holmes and R. O. C. Norman, *J. Chem. Research*, 1977, (S), 1; (M) 0101.

[7] K. Y. Law, unpublished observations.

[8] H. J. Pownall and L. C. Smith, *J. Amer. Chem. Soc.*, 1973, **95**, 3136.

[9] M. Shinitzky, A. C. Dianoux, C. Gitler, and G. Weber, *Biochemistry*, 1971, **10**, 2106.

[10] F. M. Menger and J. M. Jerkunica, *J. Amer. Chem. Soc.*, 1978, **100**, 688.

[11] K. A. Zachariasse, *Chem. Phys. Letters*, 1978, **57**, 429.