

A study of the enolization of some alkyl ketones in lyomesophases formed by alkylammonium surfactants

By GIAN PIERO SPADA, GIOVANNI LESA and GIOVANNI GOTTARELLI

Dipartimento di Chimica Organica, Università di Bologna, via S. Donato, 15,
I-40127 Bologna, Italy

PAOLO DE MARIA

Istituto di Chimica Organica, Università di Palermo, via Archirafi, 20,
I-90123 Palermo, Italy

and PAOLO MARIANI

Centre de Génétique Moléculaire, CNRS, F-91190 Gif-sur-Yvette, France

(Received 25 November 1987; accepted 30 January 1988)

The kinetics of enolization of acetone, 3-pentanone, and 6-undecanone have been studied in lyotropic systems in the isotropic, nematic, and lamellar phases. The data, analysed in terms of spontaneous and acid-catalyzed rate constants, do not show any relevant influence of the physical nature of the phase. Effects are instead observed in relation to the length of the alkyl chains of the ketones and the type of the amphiphilic molecule. 6-undecanone has a surprising effect in stabilizing ordered mesophases.

1. Introduction

There is continuing interest in chemical reactivity in ordered systems [1, 2]. In the literature many papers deal with reactivity in thermotropic liquid crystals [3-5], however there are very few on lyotropic systems. The earliest studies [6] investigated mainly the effects of the transition between a liquid crystalline and the isotropic phase. Ramesh and Labes [7] have also studied the influence of modifications in shape (and size) of micellar aggregates and found small but significant effects in the rate of two bimolecular reactions: the bromination of *trans*-stilbene in sodium decylsulphate aggregates and the *o*-iodosobenzoic acid catalyzed ester hydrolysis of *p*-nitrophenyl laurate in myristyltrimethylammonium bromide micelles. In addition the unimolecular isomerisation of a photochromic merocyanine has recently been reported to be phase sensitive [8].

Enolization of simple carbonyl compounds is one of the best documented processes in organic chemistry [9] and has played a central role in the development of the mechanism of acid-base catalysis [10]. Under favourable conditions, enolization rates can be accurately measured by studying the halogenation of the ketone. In these reactions, the halogen acts as a scavenger by reacting with the enol (or enolate) formed by proton-transfer from the CH group adjacent to the carbonyl group. In this work we describe the study of the enolization of some ketones in different lyomesophases. The kinetic constants are discussed in terms of the length of the alkyl chains of the ketone, of the type of the cationic surfactant, and of the changes in the micellar organization. The influence of the solute on the stability of the phase is also discussed.

In aqueous solution and under appropriate concentration and temperature conditions, amphiphilic molecules, with or without addition of cosurfactants and electrolytes, may form several kinds of phases [11]: an isotropic micellar solution, nematic aggregates, and a lamellar or a hexagonal smectic phase. Just above the critical micellar concentration, the aggregates are roughly spherical in shape [11(b)]. By increasing the surfactant concentration the micelles are first forced to adopt an anisometric shape [11(b), 12] and then their interaction may stabilize a nematic phase with orientational order [13]. These phases are classified [11, 14–18] on the basis of the structural unit shape, as discotic nematic, N_D , formed by disk-shaped micelles, or calamitic nematic, N_C , formed by rod-shaped micelles. Also biaxial nematic phases are reported [11(b), 17]. These nematics align in a magnetic field and so they can also be classified as type I or type II according to whether they possess positive or negative diamagnetic anisotropies respectively. On decreasing temperature or on increasing amphiphile concentration, a transition to a smectic phase may occur [11]. Discotic nematics usually evolve to a lamellar phase (neat soap, L_α), constituted by an alternating arrangement of soap bilayers and water, while calamitic nematics evolve to a hexagonal phase (middle soap, H_α), formed by a hexagonal array of cylindrical micelles.

2. Results

The lyomesophases used as a solvent in our work are composed of the ternary system decylammonium chloride (DACl), ammonium chloride and water [14, 19], or by the quaternary system myristyltrimethylammonium bromide (MTAB), decanol (DOH), ammonium bromide and water [16]. Both systems are known to form lamellar phases (L_α), discotic nematics with negative diamagnetic anisotropy (type II, N_D) and isotropic micellar solutions (I), depending on the relative concentration of the components at a fixed temperature.

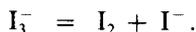
The rate of iodination was measured at $20.0 \pm 0.1^\circ\text{C}$ by observing the decrease in the triiodide absorption at 353 nm. For the iodination reactions, a zero-order loss of iodine was observed (over at least 90 per cent of the reaction), according to the rate law

$$-d[I_2^*]/dt = k_{\text{obs}}[\text{ketone}], \quad (1)$$

where $[I_2^*]$ refers to the total concentration of iodine ($[I_2] + [I_3^-]$). For $[I^-] < 0.01 \text{ M}$ and $[H^+] < 0.02 \text{ M}$ no evidence of reversibility was observed. This kinetic behaviour is expected when the enolization of the ketone is rate-determining. The *pseudo*-first order velocity constants, k_{obs} , were calculated from slopes S of the optical density versus time plots according to

$$k_{\text{obs}} = S/\varepsilon^*[\text{ketone}], \quad (2)$$

where ε^* is the effective molar absorbance of the triiodide ion at 353 nm, which allows for the slight dissociation [10(c)]



The observed rate constant, k_{obs} , was of the form

$$k_{\text{obs}} = k_0 + k_{H^+}[H^+], \quad (3)$$

where k_0 and k_{H^+} were determined as intercept and slope of k_{obs} versus $[H^+]$ plots, respectively. k_0 represents the so-called spontaneous rate constant and k_{H^+} the specific acid catalyzed rate constant.

Table 1. Rate constants of the acid-catalysed enolization of three ketones measured at 20.0°C in different lyomesophases.

Ketone	Amphiphile	Composition†	Phase	k_0 (std.dev.)/ 10^{-8} s^{-1}	k_{H^+} (std.dev.)/ $10^{-7} \text{ M}^{-1} \text{ s}^{-1}$
Acetone	DACl	<i>a</i>	N _D	4.34 (0.48)	1.8 (3.6)
		<i>b</i>	I	3.91 (0.39)	5.9 (2.9)
	MTAB	<i>c</i>	I	0.24 (0.10)	2.02 (0.70)
3-Pentanone	DACl	<i>d</i>	N _D	0.06 (0.11)	9.79 (0.81)
		<i>e</i>	I	0.34 (0.38)	8.4 (2.9)
		<i>f</i>	I'	0.06 (0.25)	17.2 (1.7)
	DACl	<i>g</i>	L	0.19 (0.12)	3.98 (0.95)
6-Undecanone	DACl	<i>h</i>	N _D	0.10 (0.12)	4.72 (0.94)
		<i>i</i>	I	0.192 (0.043)	3.03 (0.33)
		<i>j</i>	L	n.d.	3.12 (0.22)
		<i>k</i>	N _D	n.d.	3.40 (0.66)
	MTAB	<i>l</i>	I	n.d.	3.62 (0.11)

n.d. = not detectable

†Compositions: see the Experimental section

Individual values of k_0 and k_{H^+} for the three ketones under investigation are reported in table 1. It should be noted that values of k_0 are, in all cases but acetone, subject to considerable uncertainty because small changes in the slope (k_{H^+}) of the k_{obs} versus $[H^+]$ plots lead to a large variation of k_0 . For acetone, of course, the situation is reversed. Another cause of the relatively high standard deviations is the complexity of the anisotropic system investigated. From the inspection of the data one can notice the following points. For a given ketone and amphiphile the spontaneous rate constant k_0 , as well as the specific acid-catalyzed constant k_{H^+} , are not affected when the lyotropic phase is modified from L_x to N_D and to I. In all lyotropic phases, for all the ketones studied, the k_{H^+} s are not very different and are about two orders of magnitude smaller than that for acetone in water (at 25°C, $k_{H^+} = 2.85 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$) [10(b)]. In contrast the spontaneous rate constant k_0 has variable behaviour for the different lyophases (DACl and MTAB) with respect to the data obtained for acetone in water (at 25°C, $k_0 = 4.4 \times 10^{-1} \text{ s}^{-1}$) [10(b)]. There is a marked decrease in k_0 on passing from acetone to the other ketones with longer alkyl chain. On passing from the DACl alkylammonium system to the MTAB tetraalkylammonium system, a marked decrease in k_0 is evident.

3. Discussion

Within the limit of the accuracy of our experiments, the kinetics of the enolization reaction of ketones is not affected by changes of the phase from the isotropic micellar to nematic and lamellar. Even though studies on different reactions are necessary before general conclusions can be drawn, in our view this behaviour is likely to be the most common one.

The type of solute added to the surfactant might certainly influence the phase observed (the case of 6-undecanone reported later is a clear example). On the other hand, variation of the type of phase does not seem to influence significantly the order of the surfactant chains [20]. Furthermore, the order of solutes of limited molecular dimensions, located in the hydrophobic part, does not seem to change with the shape

of the aggregates forming the nematic phases [21, 22]. The environment of a reactant dissolved in a micelle is not likely to change with the variations in shape and with the reciprocal ordering of the individual micelles. Hence, the changes in the reactivity expected are not great and should be smaller than those observed in thermotropic systems on passing from isotropic to liquid-crystalline phases [3–5]. An extensive discussion on the variations of the kinetic constants reported in table 1 is beyond the scope of our investigation. However, two points can explain most of the data:

- (i) In DACI micelles there is certainly a contribution to reactivity from the ammonium groups of the surfactant *via* the formation of Schiff bases [24]. Ammonium chloride is not involved in this process (see the data in MTAB) as it is probably too far from the Stern layer and from the ketones.
- (ii) The decrease in k_o observed with the increase of the length of the ketone alkyl chains is related to the partition of the ketone between the hydrocarbon core and the Stern layer or the aqueous part. A keto-group located deep in the hydrophobic core is effectively shielded. In table 2 we report spectroscopic data supporting this view, based on the well documented shift of λ_{\max} of the $n-\pi^*$ carbonyl transition with the polarity of the solvent [25]. The data show that acetone, which is more reactive, is located in a polar region of the DACI micelles, while the less reactive undecanone is in the hydrophobic core.

Table 2. Wavelength of the absorption maximum due to the $n-\pi^*$ transition of acetone and 6-undecanone in several solvents.

Acetone		6-undecanone	
Solvent	λ_{\max}/nm	Solvent	λ_{\max}/nm
Water	264	Water/methanol 2:1	276
DACI (isotropic)	266	Methanol	279
Methanol	270	DAC (isotropic)	281
Hexane	279	Hexane	284

Phase stabilization operated by 6-undecanone

An unexpected effect, which constitutes an indirect indication of the intercalation of undecanone between the amphiphilic molecules, is derived from the following observation. Starting from the DACI or MTAB nematic phases and increasing the undecanone concentration, without modifying the other components of the lyomesophase, a transition to a biphasic system and then to a lamellar phase is observed. From the structural point of view, some preliminary results obtained by X-ray diffraction technique are the following. In the DACI nematic phase of composition m (see the Experimental section), the bilayer dimension obtained from the position of the small angle broad peak is about 48 Å. Starting from this nematic phase, an increase of the bilayer repetition distance is observed as the 6-undecanone concentration increases. When the concentration is 3 per cent w/w, a two phase coexistent region, in agreement with microscopic observation, was detected: the nematic one with bilayer dimension of about 60 Å and an L_x phase with bilayer dimension of 47 Å. At higher undecanone concentrations only narrow peaks (first and very weak second order) corresponding to the L_x phase were observed. The bilayer dimension was 47 Å.

Different effects were observed after addition of equivalent amounts of different ketones to the DACI nematic phase of composition n (see the Experimental section).

3-Pentanone and acetone induce a transition to isotropic micelles, whereas 6-undecanone preserves the nematic phase. In particular, the bilayer repetition distance of the nematic phase in the presence of 6-undecanone is again greater than for the undoped lyotropic mesophase; this dimension changes from about 51 Å to about 55 Å after addition of 1.5 per cent w/w of 6-undecanone. The effect of 6-undecanone is similar to the effect reported for the addition of cholesterol to the DACl lyotropic system [26]. In this case, a decrease of flexibility of the hydrocarbon chains and then an increase in the amount of the all-*trans*-conformer was observed. This was explained as being caused by solute location deep in the hydrophobic region. For undecanone, the interpretation could be analogous. On the basis of the X-ray investigation alone, the interaction of the keto-group with the polar region cannot be excluded; however, together with the kinetic and absorption data, this observation indicates that the keto-group is more likely to be in the hydrophobic region.

4. Conclusions

The rate constants for spontaneous (k_o) and specific acid-catalysed (k_{H^+}) reactions of the ketones under investigation are not affected by the nature of the phase (isotropic, nematic and lamellar) of the micellar systems used as the solvent. Significant differences are observed instead between isotropic systems with high and low amphiphile concentration. In all cases the DACl solvent interacts chemically with the ketones. The effect of 6-undecanone on the structure of the micellar systems is surprisingly similar to that of cholesterol: the order of the phase is increased. In contrast acetone and 3-pentanone promote transitions to the less ordered isotropic phase.

5. Experimental

Materials. DACl was prepared by the Radley and Saupe method [14]; the other components of the lyosystems were all commercial products purchased from Aldrich and used without further purification. Acetone was purchased from Carlo Erba, and 3-pentanone and 6-undecanone from Aldrich.

Sample preparation. The samples were prepared by mixing and stirring together the appropriate quantities of all the components except iodine for 12 hours at room temperature. Iodine was then added. The concentration of the ketone was in the range 0.01–0.1 M and the initial concentration of iodine about 10^{-4} M. In all the reactions the iodide concentrations were close to 4×10^{-3} M. Under these conditions, the effective molar absorbance of iodine at 353 nm is $1.90 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. The hydrogenion concentrations investigated were in the range $6.2 \times 10^{-3} - 2 \times 10^{-2}$ M. At more acidic pHs, oxidation of iodide occurs



while at more alkaline ones, iodine reacts with the primary amine [12] (in the DACl system) and so a kinetic study is impossible. The average compositions of the lyosystems were:

DACl/ NH_4Cl /water per cent w: ((a) 35.7/3.8/60.5; (b) 29.3/3.8/66.9; (d) 36.7/4.0/59.3; (e) 30.9/3.9/65.2; (f) 2.5/0.8/96.7; (g) 37.1/4.0/58.9; (h) 33.2/3.9/62.9; (i) 26.0/4.0/70.0;

MTAB/DOH/ NH_4Br /water % w: (c) 35.0/2.2/3.0/59.8;

(j) 26.6/3.9/6.4/63.1; (k) 26.6/3.8/6.4/63.2; (l) 35.0/2.2/3.0/59.8.

The compositions of the samples used for the X-ray study were:

DACI/NH₄Cl/water per cent w: (*m*) 36.0/4.0/60.0; (*n*) 31.0/4.0/65.0.

Measurements. After preparation the samples were transferred into a 1 mm path cell and observed with a polarizing microscope in order to assign the type of phase. The lamellar phase was detected first by the microscopic technique, and then confirmed by X-ray diffraction with a small angle camera. The decrease in the triiodide absorption was measured at $20.0 \pm 0.1^\circ\text{C}$ with a Jasco UVIDEC spectrophotometer equipped with a thermostatted cell holder. U.V. spectra were recorded with the same instrument. X-ray diffraction studies were carried out at the same temperature as the kinetic measurements.

We thank Professor Bruno Samori for discussion and for providing the manuscript quoted in [21] prior to publication. Financial support from MPI and CNR (Rome) is gratefully acknowledged.

Note added in proof.—After this paper had been submitted for publication, an article by RAMESH, V., and LABES, M. M. (1988, *J. Am. chem. Soc.*, **110**, 738) was published. It reports the dramatic effect of the shape of the surfactant aggregates on the velocity of hydrolysis of two organophosphinate esters in lyotropic liquid crystals.

References

- [1] RAMAMURTHY, V., 1986, *Tetrahedron*, **42**, 5753 (report No. 211).
- [2] SCHEFFER, J. (editor), 1987, *Organic Chemistry in Anisotropic media, Tetrahedron Symposia-in-print*, No. 29, *Tetrahedron* **43**.
- [3] NERBONNE, J. M., WEISS, R. G., 1978, *J. Am. chem. Soc.*, **100**, 2571. NACIRI, J., SPADA, G. P., GOTTARELLI, G., WEISS, R. G., 1987, *J. Am. chem. Soc.*, **109**, 4352; and references therein.
- [4] SAMORÌ, B., and FIOCCO, L., 1982, *J. Am. chem. Soc.*, **104**, 2634. SAMORÌ, B., DE MARIA, P., MARIANI, P., RUSTICHELLI, F., and ZANI, P., 1987, *Tetrahedron*, **40**, 1409, and references therein.
- [5] LEIGH, W. J., and JAKOBS, S. K., 1987, *Tetrahedron*, **43**, 1393, and references therein.
- [6] SWARBRICK, J., and CARLESS, J. E., 1964, *J. Pharm. Pharmac.*, **16**, 670. BARRY, B. W., and SHOTTON, E., 1967, *J. Pharm. Pharmac.*, **19**, 785. MURTHY, K. S., and RIPPPIE, E. G., 1978, *J. pharm. Sci.*, **59**, 459. AHMAD, S. I., and FRIBERG, S., 1972, *J. Am. chem. Soc.*, **95**, 5196. BACON, W. E., NEUBERT, M. E., WILDMAN, P. J. W., and OTT, D. W., 1983, *Molec. Crystals liq. Crystals*, **90**, 307, and references therein.
- [7] RAMESH, V., and LABES, M. M., 1986, *J. Am. chem. Soc.*, **108**, 4643. RAMESH, V., and LABES, M. M., 1986, *Proceedings of the 11th International Liquid Crystal Conference*, Berkeley, U.S.A., 30 June to 4 July.
- [8] RAMESH, V., and LABES, M. M., 1987, *J. Am. chem. Soc.*, **109**, 3228.
- [9] TOULLEC, J., 1982, *Adv. Phys. Org. Chem.*, **18**, 1.
- [10] (a) BELL, R. P., 1941, *Acid-Base Catalysis* (Oxford University Press). (b) BELL, R. P., 1973, *The Proton in Chemistry*, 2nd edition (Chapman & Hall). (c) COX, B. G., DE MARIA, P., and FINI, A., 1984, *J. chem. Soc. Perkin Trans. II*, p. 1647.
- [11] (a) FORREST, B. J., and REEVES, L. W., 1981, *Chem. Rev.*, **81**, 1; (b) SAUPE, A., 1984, *Nuovo Cim.*, **3**, 16.
- [12] HENDRIKX, Y., and CHARVOLIN, J., 1981, *J. Phys. (Orsay, Fr.)*, **42**, 1427. KUZMA, M. R., 1985, *J. phys. Chem.*, **89**, 4124.
- [13] LAWSON, K. D., and FLAUTT, T. J., 1967, *J. Am. chem. Soc.*, **89**, 5489.
- [14] RADLEY, K., and SAUPE, A., 1978, *Molec. Crystals liq. Crystals*, **44**, 227.
- [15] YU, L. J., and SAUPE, A., 1980, *J. Am. chem. Soc.*, **102**, 4879.
- [16] BODEN, N., RADLEY, K., and HOLMES, M. C., 1981, *Molec. Phys.*, **42**, 493.

- [17] YU, L. J., and SAUPE, A., 1980, *Phys. Rev. Lett.*, **45**, 1000. FIGUEREIDO NEO, A. M., GALERNE, Y., and LIEBERT, L., 1985, *J. phys. Chem.*, **89**, 3939.
- [18] RADLEY, K., REEVES, L. W., and TRACEY, A. S., 1976, *J. phys. Chem.*, **80**, 174.
- [19] HOLMES, M. C., and CHARVOLIN, J., 1984, *J. phys. Chem.*, **88**, 810.
- [20] CHARVOLIN, J., and HENDRIKX, Y., 1985, *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J. W. Emsley (Reidel), pp. 449–471.
- [21] LAURENT, M., and SAMORI, B., 1987, *J. Am. chem. Soc.*, **109**, 5109.
- [22] Order parameters are reported in [8] for a merocyanine dye in two N_L and N_C phases. In both cases the values observed in the N_L phases are about half those for the N_C phases. However, we believe that this is due mainly to the wall effect on the orientation of the N_D disk type phase. The disk-like aggregates tend with time to assume an orientation with the *quasi* flat surface of the disk parallel to the walls [15]. This configuration, which is compatible with the magnetic orientation, is not dichroic, hence the smaller order observed [21, 23].
- [23] SPADA, G. P., GOTTARELLI, G., SAMORI, B., BUSTAMANTE, C. J., and WELLS, K. S., 1988, *Liq. Crystals*, **3**, 101.
- [24] BENDER, M. L., and WILLIAMS, A., 1966, *J. Am. chem. Soc.*, **88**, 2504.
- [25] JAFFÉ, H. H., and ORCHIN, M., 1962, *Theory and Applications of Ultraviolet Spectroscopy* (Wiley), p. 186.
- [26] FUJIWARA, F. Y., and REEVES, L. W., 1976, *J. Am. chem. Soc.*, **98**, 6790.