## Structure and Reactivity of Lithium and Sodium Aryloxides in Dimethylformamide. Ions, Ion Pairs, and Ion Triplets

## Manuela Crescenzi, Carlo Galli,\* and Luigi Mandolini\*

Centro CNR di Studio sui Meccanismi di Reazione, and Dipartimento di Chimica, Università 'La Sapienza,' 00185 Roma, Italy

Reactivity and u.v. spectra of aryloxide ions in dimethylformamide are affected by the addition of either Li<sup>+</sup> and Na<sup>+</sup> ions in a way that suggests the occurrence of ion triplets M<sup>+</sup>A<sup>-</sup>M<sup>+</sup> in addition to free ions and ion pairs.

Quantitative treatments of rates of reaction of an anionic reactant A<sup>-</sup> with a neutral electrophile RX under conditions where cation association is important are usually performed in terms of separate contributions from free ions and ion pairs<sup>1</sup> whose relative proportions are ruled by the mass-law effect exerted by the counter-ion M<sup>+</sup> [Scheme 1, reactions (a)—(c)]. As a continuation of our quantitative studies of the consequences of ion association on reactivity of alkali metal aryloxides,<sup>2,3</sup> we have now obtained evidence that, besides free ions and ion pairs, ion triplets M<sup>+</sup>A<sup>-</sup>M<sup>+</sup> (M<sup>+</sup> = Li<sup>+</sup> or Na<sup>+</sup>) play a definite role in dimethylformamide (DMF) solution. Therefore, for quantitative treatments or even for qualitative discussions, equations (a)—(c) have to be expanded by the inclusion of (d) and (e).

Indications of the significant formation of ion triplets first came from kinetic experiments in which  $[Li^+]$  or  $[Na^+]$  was varied over a wide range by adding increasing amounts of the perchlorate salts, which behave as strong electrolytes in

$$A^- + RX \xrightarrow{k_i} Product$$
 (b)

$$A^-M^+ + RX \xrightarrow{\kappa_{ip}} Product$$
 (c)

$$M^+A^-M^+ + RX \xrightarrow{\kappa_{it}} Product$$
 (e)

DMF,<sup>4</sup> to a very dilute solution of (1) in DMF at 25.0 °C.<sup>+</sup> The spectrophotometrically determined specific rate constant  $k_{obs.}$  for closure of (1) to (2) significantly decreases upon increasing [M<sup>+</sup>] (Figure 1) in a way that is clearly suggestive of extensive



<sup>&</sup>lt;sup>†</sup> Anion (1) was generated *in situ* by neutralizing a  $1 \times 10^{-4}$  mol dm<sup>-3</sup> solution of the parent phenol in DMF with either potassium hexamethyldisilazane ( $8 \times 10^{-3}$  mol dm<sup>-3</sup>) in toluene or Bu<sub>4</sub>NOH ( $5 \times 10^{-2}$  mol dm<sup>-3</sup>) in benzene-methanol (4:1). The rate of cyclisation of (1) in the absence of added salts was unaffected by the nature of the counter-ion, showing the unimportance of ion association phenomena under the given conditions ( $k_{obs.} = k_i = 26.7 \pm 1.1 \text{ s}^{-1}$ ).



**Figure 1.** Log { $[M^+]/mol dm^{-3}$ }-rate profiles for the reaction of (1) to give (2) in the presence of added LiClO<sub>4</sub> and NaClO<sub>4</sub> in DMF at 25 °C. The horizontal line represents log  $k_i$ . The points are experimental ( $k_{obs}/s^{-1}$ ) and curves (A) and (B) are calculated from equations (1) and (2), respectively.

$$k_{\rm obs.} = \frac{k_{\rm i}}{1 + K_{\rm ip} \gamma_{\pm}^2 [{\rm M}^+]}$$
(1)

ion association. However, there is observed a much stronger dependence upon  $[M^+]$  than predicted by equation (1)‡ which is a direct consequence of equations (a)—(c) and applies when contributions from the ion pair path are negligible over the whole concentration range. Equation (1) was found to fit closely analogous rate data in Me<sub>2</sub>SO solution.<sup>2</sup> In contrast, in the present cases downwards drifts from plots of equation (1)[curves (A) in Figure 1] are apparent for runs where [M<sup>+</sup>]  $>10^{-2}$ . The rate depressing effects exerted by Li<sup>+</sup> and Na<sup>+</sup> ions are well accounted for quantitatively by expanding equations (a)—(c) to include triple-ion formation, equations (d) and (e), of the type  $M^+A^-M^+$ . This leads to equation (2), which holds when both ion pairs and ion triplets are unreactive.3 A non-linear least squares treatment of the data5 gave the following values for the adjustable parameters (units dm<sup>3</sup> mol<sup>-1</sup>): Li<sup>+</sup>,  $K_{ip} 2.0 \times 10^4$ ,  $K_{it} 20$ ; Na<sup>+</sup>,  $K_{ip} 1.38 \times 10^3$ ,  $K_{\rm it}$  20. How closely equation (2) fits the experimental data is shown by curves (B) in Figure 1.

$$k_{\rm obs.} = \frac{k_{\rm i}}{1 + K_{\rm ip} \gamma_{\pm}^2 [{\rm M}^+] + K_{\rm ip} K_{\rm it} \gamma_{\pm}^2 [{\rm M}^+]^2}$$
(2)



Figure 2. Effect of LiClO<sub>4</sub> ( $\bullet$ ) and NaClO<sub>4</sub> ( $\bigcirc$ ) on the u.v. spectrum of the anion (3) (4 × 10<sup>-4</sup> mol dm<sup>-3</sup>). The free anion has  $\lambda_{max}$ . 310 nm,  $A_{max}$ . 2.53.



**Figure 3.** Log { $[M^+]$ /mol dm<sup>-3</sup>}- rate profile for the reaction of (4) to give (5) in DMF at 25 °C. The horizontal line represents  $k_i$ .

As the simple adherence of rate data to an equation with two adjustable parameters cannot be taken as a definitive demonstration of the existence of triple ions, additional evidence was sought. This first came from u.v. spectroscopy. Titration with  $LiClO_4$  and  $NaClO_4$  of a dilute solution (4 ×  $10^{-4}$  mol dm<sup>-3</sup>) of the model compound (3) in DMF shows the occurrence of significant hypsochromic and hypochromic shifts, which are indicative of cation associations of the contact type (Figure 2). On the basis of simple 1:1 associations with  $K_{ip} = 2.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$  for Li<sup>+</sup> and  $1.38 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ for Na<sup>+</sup>, one would predict saturation behaviour for the above spectral changes at concentrations higher than  $10^{-3}$  and  $10^{-2}$ mol dm<sup>-3</sup>, respectively. One observes, instead, the occurrence of inflexion points and subsequent spectral changes in the higher concentration region which are consistent with a further type of association which becomes significant when  $[M^+] > 10^{-2} \text{ mol } dm^{-3}$ 

A definite confirmation that the ion pairs gradually disappear on increasing cation concentration in the high concentra-

 $<sup>\</sup>ddagger$  The mean activity coefficient  $\gamma_{\pm}$  was calculated from the extended Debye–Hückel equation  $\log\gamma_{\pm}=1.594~\mu^{1/2}~(1+2.886~\mu^{1/2})^{-1}$ , which corresponds to a value of 36.7 for the dielectric constant of DMF and one of 6 Å for the adjustable parameter.

tion region is provided for the Na+ case by examining the effect of added NaClO<sub>4</sub> on the templated cyclisation of (4) to (5).<sup>3</sup> Unlike the reaction of (1) to give (2), here the ion pair is much more reactive than the free ion  $(k_{ip} > k_i)$ , which has been explained as resulting from a favourable interaction of the host-guest type for the transition state of the Na+-assisted reaction path.<sup>3</sup> On the other hand, the triple ion is easily predicted to be much less reactive than the ion pair  $(k_{it} < k_{ip})$ , and possibly even less than the free ion, as there is obviously no room for two Na<sup>+</sup> ions in the cavity of the ring shaped transition state leading to (5). Fully consistent with these predictions is the shape of the log [Na<sup>+</sup>]-rate profile shown in Figure 3. On increasing the concentration of Na<sup>+</sup>, the rate increases first, because the more reactive ion pair gradually replaces the less reactive free ion. Saturation kinetics are not observed, however, in the high concentration region, but, rather, a gradual reduction of the extent of catalysis which is diagnostic of the formation of an unreactive higher-order associated form at the expense of the ion pair.

When data from the present work are compared with analogous data previously obtained in Me<sub>2</sub>SO solution,<sup>2,3</sup> one notes that ion pairing is stronger in DMF than in Me<sub>2</sub>SO [ $K_{ip}$  (DMF)/ $K_{ip}$  (Me<sub>2</sub>SO) = 11 for Li<sup>+</sup> and 3.1 for Na<sup>+</sup>], which is consistent with the different values of the dielectric constants of the two solvents (Me<sub>2</sub>SO 46.7; DMF 36.7). No clear-cut evidence for the significant formation of ion triplets M<sup>+</sup>A<sup>-</sup>M<sup>+</sup> could be obtained in Me<sub>2</sub>SO. However, their intervention to a

very modest extent was suspected on the basis of downward drifts exhibited in the neighbourhood of  $[M^+] = 0.1 \text{ mol } dm^{-3}$  by the log  $[M^+]$ -rate profile related to the formation of benzo-18-crown-6.<sup>6</sup> If the above inferences were well-grounded, which seems likely in the light of present evidence, then the above ion triplets should be assigned  $K_{it}$  values significantly lower than 10, which are to be compared with  $K_{it}$  values of 20 in DMF. It appears therefore that the general behaviour of the alkali metal aryloxides is quite similar in the two given solvents, when allowance is made for a general weakening of ion associations in Me<sub>2</sub>SO relative to DMF.

Received, 19th December 1985; Com. 1789

## References

- 1 J. E. Gordon, 'The Organic Chemistry of Electrolyte Solution,' Wiley, New York, 1975, ch. 3, VIII.
- 2 G. Illuminati, L. Mandolini, and B. Masci, J. Am. Chem. Soc., 1983, 105, 555.
- 3 L. Mandolini and B. Masci, J. Am. Chem. Soc., 1984, 106, 168, see also Additions and Corrections, *ibid.*, p. 3706.
- 4 M. S. Grenberg and A. I. Popov, J. Solution Chem., 1976, 5, 653.
- 5 C. Galli and L. Mandolini, J. Chem. Soc., Perkin Trans. 2, 1984, 1435.
- 6 See Figure 3 and footnote 9 in ref. 2.