

Catalysis of the ethanolysis of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide by alkali metal ions

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Dedicated issue to Professors Rita H. Rossi, Julio C. Podestá, Manuel González Sierra and Oscar S. Giordano to recognize their achievements in organic chemistry

DOI: <http://dx.doi.org/10.3998/ark.5550190.0012.723>

Abstract

The goal of this study was to report on the catalytic effects by alkali-metal ions in the ethanolysis of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS). We confirmed that the nucleophilic attack at the sulfur center was the only reaction pathway. The reactions of MNTS with metal ethoxides (MOEt) were discussed on basis of a kinetic scheme considering simultaneous reaction of free ethoxide and ion-paired ethoxide with the substrate. The trend for ion-paired ethoxide reactivity was clear and showed an increase on increasing the size of the ion ($\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$). For evaluate the free ethoxide reactivity we performed additional experiments in the presence of the complexing agents 18-crown-6 ether (18-C-6) and 2,5,8,11,14-pentaoxapentadecane (glyme). The results obtained were discussed in terms of the interaction of the metal ions with the ground state and the transition state.

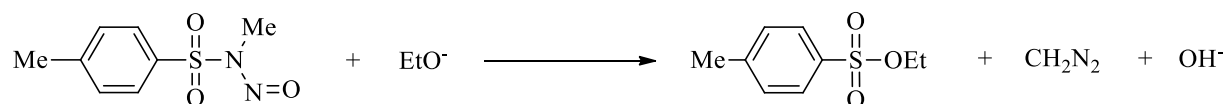
Keywords: Ethanolysis, sulfonamide, metal ethoxide, crown ether, glyme

Introduction

Nitroso compounds have attracted considerable attention mainly due to their cancer chemotherapeutic potential.¹ The basic hydrolysis of *N*-methyl-*N*-nitrososulfonamides yields diazomethane, a powerful alkylating agent of DNA.² Diazomethane is valued for its reactivity and selectivity under mild conditions in a large number of reactions.³ The most important precursor of diazomethane is *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) which in addition to being a methylating agent can also be used for nitrosation reactions under mild conditions.⁴ The possible carcinogenic effect of these *N*-nitroso compounds can be even larger when considering the possibility that they may transfer the nitroso group to other nucleophilic

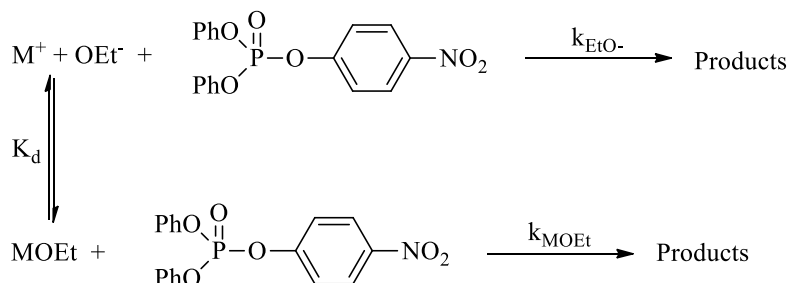
substrates by a transnitrosation process.⁵ MNTS is less hazardous than other *N*-nitroso compounds, even though still carcinogenic⁶ and sensitizing.⁷

The biochemical activity of MNTS becomes more complex due to the existence of two reactive centers: the nitrogen atom of the nitroso group and the sulfur atom of the sulfonyl group. Previous results obtained in our laboratory show that different types of nucleophiles react at either one or the other electrophilic center. Soft nucleophiles react exclusively at the nitroso group.⁸ Amines, carbanions and other nucleophiles such as: SCN^- , I^- , $\text{S}_2\text{O}_3^{2-}$ and SO_3^{2-} must be included in this category.⁹ Hard nucleophiles such as the hydroxyl ion or very basic alkoxides react through the sulfonyl group (Scheme 1).¹⁰



Scheme 1

Alkali metal ions are ubiquitous in biological systems and are implicated in a number of vital physiological roles.¹¹ However, the study of the kinetic effects of alkali metal ions has been few. Such studies were initiated by Bunce *et al.*, analyzing the influence of alkali metal ions on nucleophilic displacement reactions at carbon, phosphorus and sulfur centers.¹² Significantly, for the ethanolysis of phosphorus-based esters in anhydrous ethanol is catalyzed by alkali metal ions: 4-nitrophenyl diphenylphosphinate,¹³ 4-nitrophenyl dimethylphosphinate,¹⁴ 4-nitrophenyl diphenylphosphate¹⁵ and 4-nitrophenyl phenylphosphonate.¹⁶ A characteristic feature of the ethanolysis of these substrates is the upward curvature of plots of the observed first-order rate constant against metal ethoxide (MOEt) concentration, indicating concurrent reaction of free and ion-paired ethoxide with the substrate (Scheme 2).¹⁶ Analysis of kinetic results has provided, in each case, values of the second-order rate constants for the reactions of free ethoxide (k_{EtO^-}) and metal ethoxide ion-pair (k_{MOEt}). The relative magnitude of these rate constants ($k_{\text{MOEt}} > k_{\text{EtO}^-}$) points to a catalytic role for the alkali metal ions.¹⁷



Scheme 2

We report in this work data obtained from a kinetic study of the ethanolysis reactions of MNTS with LiOEt, NaOEt, KOEt and CsOEt in anhydrous ethanol. Upward curvature in the k_{obs}

vs. $[\text{MOEt}]_0$ plots is indicative of catalysis of the title reaction by the alkali metal ions Li^+ , Na^+ , K^+ and Cs^+ . This behavior leads us to propose a reaction scheme on the basis of the Bunce formalism (Scheme 2). The aim of this study is to obtain information on the effect of metal ion binding on TS structure.

Results and Discussion

The rates of the reaction of MNTS with MOEt were studied spectrophotometrically in anhydrous ethanol at 25 °C by monitoring the removal of MNTS under first-order conditions, with the nucleophilic reagent in significant excess relative to the substrate. In all cases, good first-order kinetics was obtained.

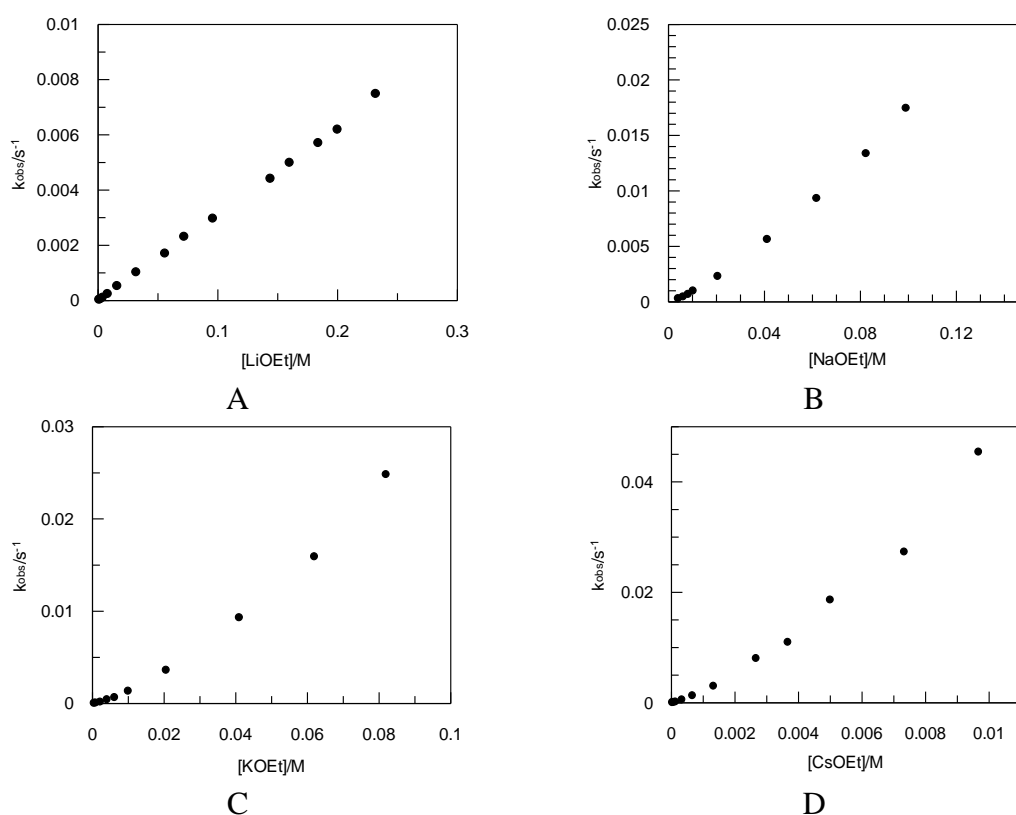


Figure 1. Plots of k_{obs} vs. $[\text{MOEt}]$ for the reaction, at 25 °C, of MNTS with LiOEt (A), NaOEt (B), KOEt (C) and CsOEt (D).

The absence of nitrite ion as reaction product, confirmed by the Shinn method, indicates that nucleophilic attack at the sulfur center was the only reaction pathway (Scheme 1).

First-order rate constants, k_{obs} , were monitored from linear plots of $\ln(A_\infty - A_t)$ vs. t . Plots of k_{obs} vs. total metal ethoxide concentration, $[\text{MOEt}]$ ($M = \text{Li}, \text{Na}, \text{K}, \text{Cs}$), show an upward curvature in all cases. Typical plots are shown in Figure 1. The upward curvature of the plots

indicates the greater reactivity of the alkali metal ethoxide ion pairs than of free ethoxide ions, contrary to the generally observed reactivity order in nucleophilic substitution processes. The relative order of reactivity, CsOEt > KOEt > NaOEt > LiOEt, is qualitatively evident in Figure 1.

The reactions of MNTS with MOEt are discussed in terms of the reaction sequence given in Scheme 2, which assigns kinetic activity to both free and ion-paired ethoxide according to eqn. (1), with $K_d (= 1/K_a)$ defined in Equation 2. The rate constants k_{EtO^-} and k_{MOEt} in Equation 1 concern to the processes involving free ethoxide ion (the uncatalyzed reaction) and the metal alkoxide ion pair (the catalyzed reaction), respectively. It is to be well-known that the metal ion effects in this study arise from ground state and transition state interactions involving metal alkoxide ion pairs.

$$k_{obs} = k_{EtO^-} [EtO^-]_{eq} + k_{MOEt} [MOEt]_{eq} \quad (1)$$



In order to obtain k_{MOEt} in Scheme 2, Equation 1 is rearranged to obtain Equation 3.

$$\frac{k_{obs}}{[EtO^-]_{eq}} = k_{EtO^-} + \frac{k_{MOEt}}{K_d} [EtO^-]_{eq} \quad (3)$$

With the aim of apply Equation 3, equilibrium concentrations of free ethoxide are calculated by Equation 4 from the known initial stoichiometric concentrations of the metal ethoxide, since Equation 5 applies.

$$[EtO^-]_{eq} = 0.5 \left\{ -K_d + \left(K_d^2 + 4K_d [MOEt]_{eq}^{\frac{1}{2}} \right) \right\} \quad (4)$$

$$[MOEt] = [EtO^-]_{eq} + [MOEt]_{eq} \quad (5)$$

It is the expectation from Equation 3 that a plot of $k_{obs}/[EtO^-]_{eq}$ vs. $[EtO^-]_{eq}$ should yield a straight line with slope = k_{MOEt}/K_d , from which k_{MOEt} can be evaluated, since K_d values at 25 °C are known from the literature.¹⁸ Moreover, from the intercept k_{EtO^-} can be determined, too.

In Figure 2 we show the good linear correlation for the four ethoxydes and in Table 1 we show the values for k_{MOEt} . The trend for k_{MOEt} shows an increase on increasing the size of the ion (Cs > K > Li ≈ Na). However, for k_{EtO^-} (data not showed) there is a not clear trend, probably because the error in the determination of the intercepts is greater than in the determination of the slopes. To solve this problem, additional experiments were carried out in the presence of a complexing agent.

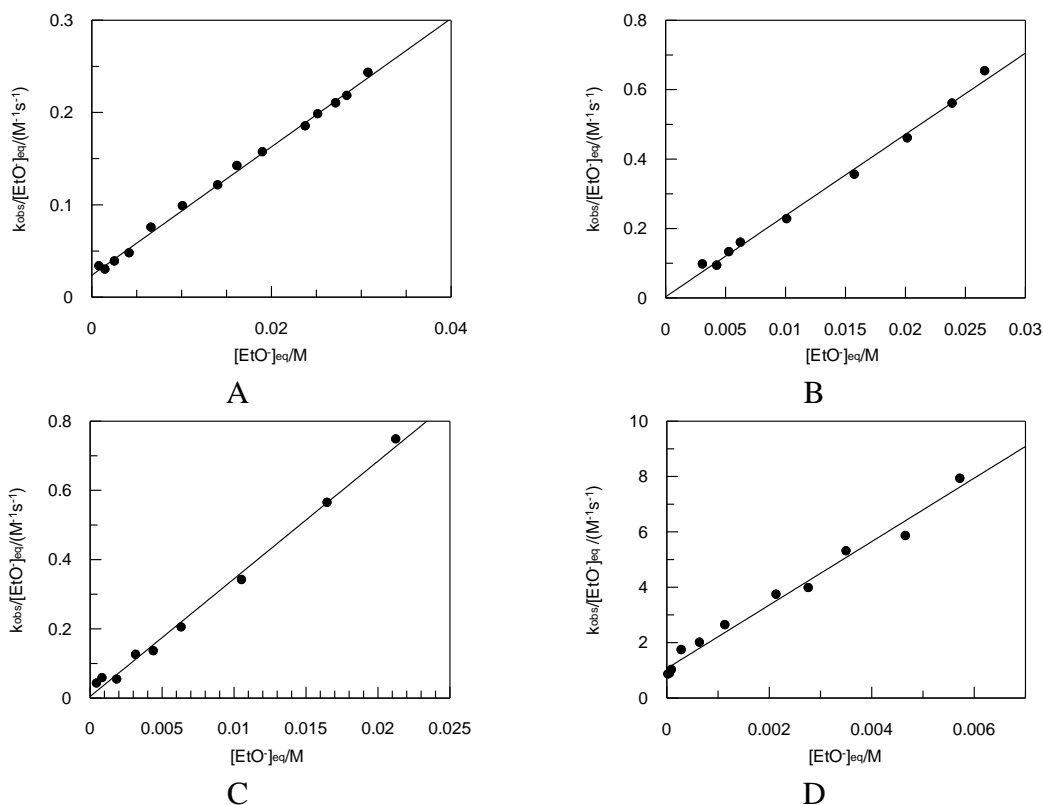
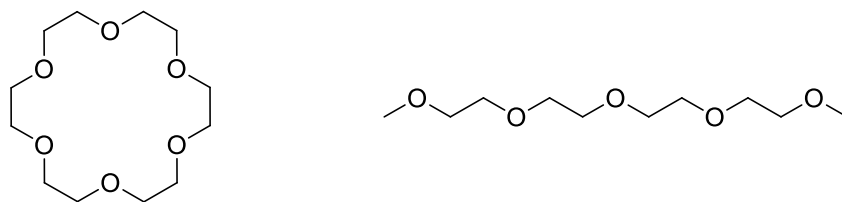


Figure 2. Plots of $k_{obs}/[EtO^-]_{eq}$ vs. $[EtO^-]_{eq}$ for the reaction of MNTS with LiOEt (A), NaOEt (B), KOEt (C) and CsOEt (D) at 25 °C according to the ion-pairing treatment of Equation 3.

Table 1. Calculated rate constants for the metal alkoxide ion pair in ethanolysis of MNTS at 25 °C

MOEt	LiOEt	NaOEt	KOEt	CsOEt
$k_{MOEt}/(M^{-1}s^{-1})$	$(3.3 \pm 0.1) \times 10^{-2}$	$(2.2 \pm 0.1) \times 10^{-2}$	$(3.3 \pm 0.3) \times 10^{-1}$	10.1 ± 0.7

In complementary experiments, the reactions of MNTS with MOEt were also investigated in the presence of excess of 18-crown-6 ether (18-C-6) and 2,5,8,11,14-pentaoxapentadecane (glyme). Scheme 3 shows the complexing agents 18-C-6 and glyme. The kinetic data obtained for reactions in the presence of the macrocycle are assembled in the supplementary information.



Scheme 3

Plots of k_{obs} vs. [complexing agent] at constant concentrations of MNTS and MOEt are shown in Figure 3. The reaction in the presence of the complexing agent involves free ions. With the exception of LiOEt, there is no effect, the rate constant decreases on increasing the [18-C-6] or [glyme] at constant [MOEt], until a limiting value of the rate constant is reached indicating that it corresponds to the EtO^- reaction. Further additions of the complexing agent beyond this point had no effect on k_{obs} . As we can see in Figure 3, 18-C-6 is a better complexing agent than glyme reaching the limit value at lower concentrations. Values of k_{EtO^-} for the reactions of MNTS with free ethoxide were obtained from plots of k_{obs} vs. [MOEt] using data collected in the presence of excess 18-C-6. Taking into account that $[MOEt]_{eq} = 0$ in the presence of excess of 18-C-6 Equation 1 can be simplified to:

$$k_{obs} = k_{EtO^-} [EtO^-]_{eq} \quad (6)$$

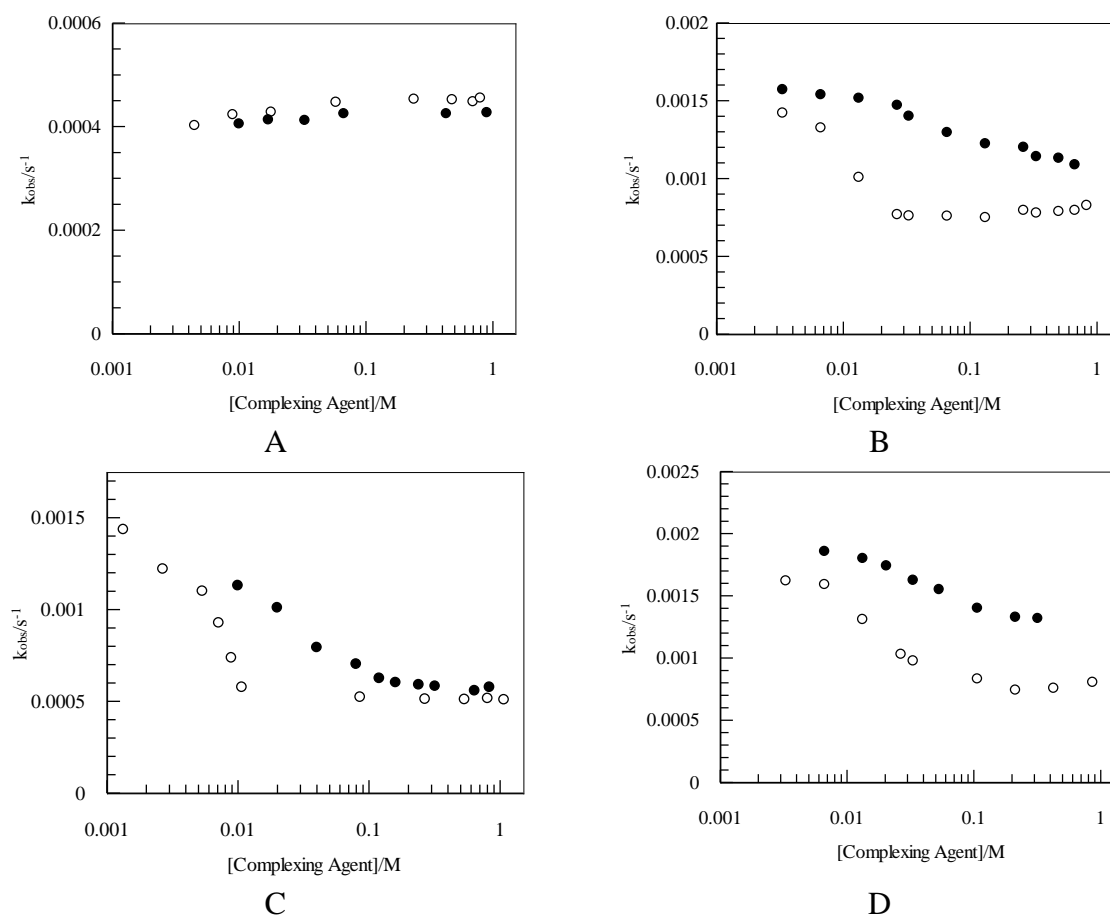


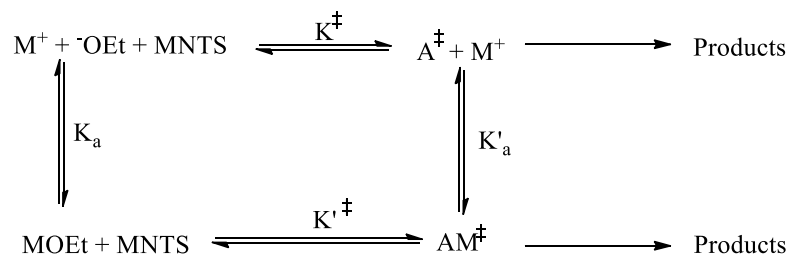
Figure 3. Plots of the kinetic data for the reaction of MNTS with MOEt [M = Li (A), Na (B), K (C) and Cs (D)] in the presence of increasing amounts of 18-C-6 (○) and glyme (●) in EtOH at 25 °C.

From Equation 6 we obtained k_{OEt^-} resulting in the selectivity order Cs > K > Na > Li (Table 2). This result leads us to propose that electrostatic interactions are not dominant over solvent rearrangement in the nucleophilic reactions of MNTS manifesting alkali metal ion catalysis.

Table 2. Calculated rate constants for the free ethoxide ion in ethanolysis of MNTS at 25 °C

	MOEt	LiOEt	NaOEt	KOEt	CsOEt
18-C-6	$k_{EtO^-}/(M^{-1}s^{-1})$	$(2.8 \pm 0.3) \times 10^{-2}$	$(5.5 \pm 0.4) \times 10^{-2}$	$(5.8 \pm 0.4) \times 10^{-2}$	$(7.7 \pm 0.2) \times 10^{-2}$
Glyme	$k_{EtO^-}/(M^{-1}s^{-1})$	$(2.6 \pm 0.1) \times 10^{-2}$	$(7.6 \pm 0.7) \times 10^{-2}$	$(5.8 \pm 0.2) \times 10^{-2}$	$(12 \pm 0.8) \times 10^{-2}$

Metal ion catalysis in these type of systems implies that participation by alkali metal ions decreases the free energy of activation of the reaction, which can result from the interaction of the metal ions with the ground state, the TS, or both (Scheme 4). We follow the earlier treatment of Buncl *et al.* of alkali metal ion catalysis,¹⁹ which assumes that the interaction between the metal ions and the substrates is negligible, *i.e.* M^+/EtO^- interaction, measured by K_a (or K_d^{-1}), is regarded as the dominant ground state interaction.



Scheme 4

Interactions between metal ions and the TS have been discussed in terms of Kurz's model²⁰ for the characterization of the transition states of catalyzed reactions. Different forms of this treatment have been applied by Mandolini and Tee.²¹

Association constants for interactions of alkali metals and ethoxides (K_a , in Scheme 4) are known (LiOEt, 212 M⁻¹; NaOEt, 102 M⁻¹; KOEt, 90 M⁻¹; CsOEt, 121 M⁻¹),²² and it is assumed that interaction between M^+ and MNTS in the ground-state can be neglected. Using the Scheme 3 we can then calculate a corresponding virtual association constant, K'_a , for the TS (Table 3). The K'_a can be obtained from kinetic data as:

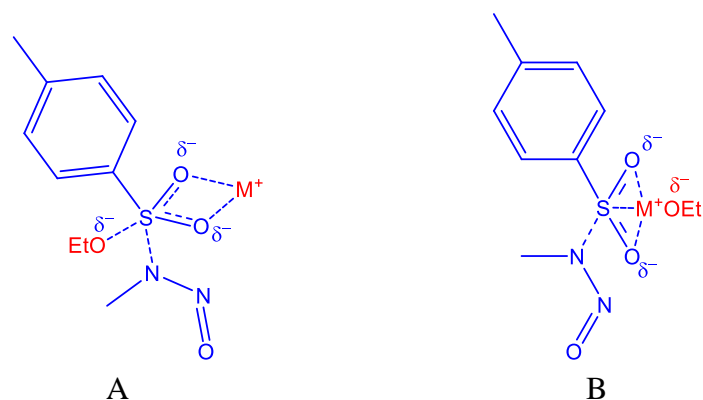
$$K'_a = \frac{k_{MOEt} K_a}{k_{EtO^-}} \quad (7)$$

Table 3. Calculated virtual association constant, K'_a , for the TS for the free ethoxide ion in ethanolysis of MNTS at 25 °C

MOEt	LiOEt	NaOEt	KOEt	CsOEt
K'_a/M^{-1}	250	410	510	15700

In a recent work Buncel *et al.*²³ examined the selectivity among alkali-metal ions of their effect on the ethanolysis of ethyl and methyl paraoxon and ethyl and methyl parathion. They identified three types of reactivity and selectivity patterns: (1) For the P=O compounds, LiOEt > NaOEt > KOEt > EtO⁻; (2) for the P=S compound, KOEt > EtO⁻ > NaOEt > LiOEt; (3) for P=S, 18-C-6-crown-complexed KOEt > KOEt > EtO⁻ > NaOEt > LiOEt. These selectivity patterns are characteristic of both catalysis and inhibition by alkali-metal cations depending on the nature of the electrophilic center, P=O *vs.* P=S, and the metal cation. The explanation of this behavior is the ground-state (GS) *vs.* transition-state (TS) stabilization energies. An approach that explained the contrasting selectivity patterns toward alkali-metal cations in the P=O and P=S series is based on Eisenman's theory of ion exchange selectivity patterns being determined by competition between electrostatic factors and solvational energies.²⁴ The strength of the interaction between a cation and a fixed anionic group is determined by two competing factors: (i) electrostatic interactions resulting from the approach of ions of opposite charge and (ii) the difference in the solvation energies of the ions, accounted for by the energy required to rearrange the solvent molecules around the ions so that close contact can occur. From this approach it can be predicted that for high electric field strength an anionic group with localized charge, P=O, the electrostatic term would dominate over the solvation energy term, allowing ions with opposite charge to come into direct contact. This means that for such situations, smaller ions will bind more strongly, and vice versa, resulting in the selectivity order Li⁺>Na⁺> K⁺. On the other hand, when the counter-ion has a low electric field strength, as in the sulfonate system²⁵ where the incoming negative charge is delocalized over two oxygens in the TS, it can be predicted that the solvation energy term would dominate over the term for electrostatic interaction. Under these conditions, the resulting selectivity sequence (K⁺ > Na⁺ > Li⁺) is opposite to that observed in the phosphorus esters.

The affinity sequence for ethanolysis of MNTS is Cs⁺>K⁺>Na⁺>Li⁺. The sulfonyl group of MNTS, analogously to the sulfonate group (RSOC), is believed to have low electric field strength, and in fact, many different types of ion-exchange resins containing sulfonate groups have displayed the affinity sequence described above.²⁶ The results obtained for ethanolysis of MNTS both the selectivity order and the fact that $K'_a > K_a$ allows us to conclude that the transition state is stabilized by cations. The solvation energy term would dominate over the term for electrostatic interaction. The cations remain solvated, leaving the ions with the smaller solvated radii to be bound most strongly (Scheme 5).²⁷



Scheme 5

Conclusions

The kinetic study of the MNTS ethanolysis in ethanol showed that the nucleophilic attack takes place exclusively at the sulfur center of the nitrososulfonamide. The kinetic results have showed that the ethanolysis reaction proceeds by reaction of both free and ion-paired ethoxide. The ion-paired ethoxide catalytic pathway shows an increase on reactivity on increasing the size of the ion. The kinetic study in the presence of complexing agents allows us to obtain the association constant for the transition state showing an increase on increasing the size of the ion. The reaction of the ethanolysis of MNTS takes places by a mechanism where the solvation energy term is more important than the term for electrostatic interaction and the transition state being stabilized by cations.

Experimental Section

General. MNTS and 2,5,8,11,14-pentaoxapentadecane were from Aldrich, of the highest purity commercially available and used without further purification. The solutions of MOEt were prepared by dissolving the respective alkali metal in anhydrous ethanol under N_2 and stored in the refrigerator. The concentrations of MOEt were determined by titration with standard HCl solution. 18-Crown-6- ether was recrystallized from acetonitrile and dried over P_2O_5 *in vacuo*. The anhydrous ethanol used was further dried over magnesium and distilled under N_2 .

Nitrite ion was determined using a modification of Shinn's method.²⁸ The reaction mixture was brought to $pH \approx 1$ and mixed with sulfanilamide and naphthylethylenediamine. Absorbance at 550 nm of the dye formed was measured, and nitrite ion was quantified. Kinetic experiments were performed with a large excess of MOEt over MNTS, $[MNTS] = 1 \times 10^{-4}$ M. The ethanolysis reactions were followed by monitoring the UV-Vis absorbance of substrate solutions using a Cary 500 scan UV-vis-NIR spectrophotometer fitted with thermostatted cell holders. The

wavelengths used for the kinetic studies fell in the range of 240-260 nm. The integrated first-order rate expression was fitted to the absorbance-time data by linear regression ($r > 0.999$) in all cases. The observed rate constants, k_{obs} , could be reproduced with an error margin of 5%. All experiments were carried out at 25.0 ± 0.1 °C.

Acknowledgements

This work was supported by Ministerio de Ciencia y Tecnología (Project CTQ2008-04420/BQU) and Xunta de Galicia (PGIDIT07-PXIB209041PR, PGIDIT10-PXIB209113PR and 2007/085).

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