Electrolyte and Micellar Effects on the Rate Constants for the Decomposition of Meisenheimer Complexes

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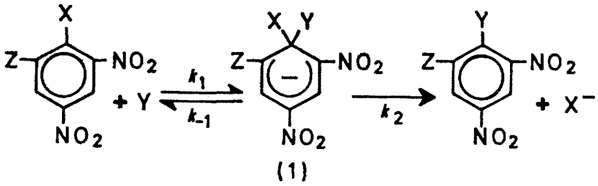
Summary The reactivity order for the decomposition of 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide ion in the presence of electrolytes ($LiClO_4 > LiCl > NaNO_3 > NaBr > NaCl > Me_4NCl > NaClO_4 > KCl > Na_2SO_4 >$ p-$MeC_6H_4SO_3Na$) arises from a smaller destabilization of the initial state than of the transition state; the significant rate retardation of micellar cationic and neutral surfactants and the absence of an effect by an anionic surfactant are discussed.

THE effects of electrolytes and micelles[1] on the rates of a number of nucleophilic aromatic substitutions have recently been examined quantitatively.[2] The overall salt effects have been separated into those on the activity coefficients of the initial state and of the transition state; cationic surfactants were generally found to increase and anionic ones to decrease the rates of these reactions while nonionic amphiphiles exerted little or no effect.[2] Bimolecular nucleophilic aromatic substitutions occur in two steps:



(1)

involving an intermediate, the Meisenheimer complex, whose formation or decomposition may be rate determining.[3] The nucleophilic aromatic substitution reactions for which electrolyte and micellar effects have been examined to date have been confined to the cases in which the *formation of the complex*, governed by k_1, is the rate-determining step, followed by a rapid elimination of the leaving group ($Z = H$; $X = Cl$ or F; $Y =$ a variety of anions and neutral nucleophiles).[2] In order to gain a more complete understanding of the nature of these processes, we have undertaken a systematic study of the effects of electrolytes and micelles on nucleophilic aromatic substitution reactions in which the *decomposition of the complex* is the rate-limiting step by investigating the kinetics and thermodynamics of the decomposition of 1,1-dimethoxy-2,4-6-trinitrocyclohexadienylide ion (**1**; $Z = NO_2$, $X = Y = OMe$) and other Meisenheimer complexes. The rate constant for the decomposition of (**1**), k_{-1}, is subject to large and specific salt effects. All the electrolytes examined with the exception of the lithium salts decrease the rate, the order of reactivity being:

$$LiClO_4 > LiCl > NaNO_3 > NaBr > NaCl > Me_4NCl > NaClO_4 > KCl > Na_2SO_4$$

(Table 1). Not unexpectedly the kinetic salt effects for the reaction of nucleophiles with 2,4-dinitrohalogeno-benzenes, exhibited essentially the reverse order.[2] Using the Brønsted–Bjerrum rate equation,

$$k^{s}_{-1} = k^{o}_{-1}\frac{f_1}{f^{\ddagger}}$$

where f_1 is the activity coefficient of (**1**) and $f^{\ddagger}$ is that of the transition state for its decomposition in the aqueous salt solutions, the experimentally obtained rate constants for decomposition of (**1**) in the presence and in the absence of electrolytes, k^s_{-1}, and k^o_{-1}, and the solubility measurements of (**1**) in the presence and absence of electrolytes allowed the separation of the electrolyte effects on f_1 from those on $f^‡$ relative to water (Table 1). All the electrolytes with the exception of 1·0 M-$LiClO_4$, increase f_1, *i.e.*, destabilize the initial state of the substrate. More significantly, all the electrolytes destabilize the transition state to a greater extent than the initial state. The effects of the bulky ions are striking. Debye–Hückel theory cannot be used, of course, to interpret these results, and the need for evaluation of all the terms in the Brønsted–Bjerrum rate equation is evident.

TABLE 1

Electrolyte effects on the rate constants and the activity coefficients for decomposition of (**1**) *in aqueous solutions at* 25·00°

Electrolyte	1·0 M-Electrolyte			2·0 M-Electrolyte		
	k^s_{-1}/k^o_{-1} [a]	f^s/f^o [b]	$f^{s‡}/f^{o‡}$ [c]	k^s_{-1}/k^o_{-1} [a]	f^s/f^o [b]	$f^{s‡}/f^{o‡}$ [c]
$LiClO_4$	1·28	0·81	0·633	1·46	1·06	0·726
LiCl	1·18	1·03	0·873	1·22	2·98	2·44
$NaNO_3$	0·837	6·18	7·38	0·697	10·5	15·0
NaCl	0·819	9·08	11·08	0·656	19·5	29·7
NaBr	0·829	8·95	10·79	0·656	13·7	20·88
Me_4NCl	0·810	13·0	16·04	0·528	27·8	52·65
$NaClO_4$	0·783	4·60	5·87	0·585	5·93	10·14
KCl	0·715	37·3	52·16	0·504	45·8	90·87
Na_2SO_4	0·679	20·6	30·33	0·452	74·1	165·2
p-$MeC_6H_4SO_3Na$ ..	0·520	3·04	5·84	0·232	1·74	7·49

[a] Determined by following the rates of decomposition of isolated crystalline (**1**) at pH 10·8 (see J. H. Fendler, E. J. Fendler, and C.E. Griffin, *J. Org. Chem.*, 1969, **34**, 689 and references cited therein); $k_0^{-1} = 5·8 \times 10^{-4}$ sec^{-1}.

[b] Determined from solubility measurements on (**1**); $S^o_1/S^s_1 = f^s_1/f^o_1$. Four solubility determinations were carried out for each solvent system by shaking saturated solutions of (**1**) at 25·00° and the concentration of filtered solutions were determined spectrophotometrically. The error in the individual measurements is ± 10%. The concentration of the saturated solutions in some cases is greater than 1·0 M and thus is not ideal.

[c] Activity coefficient ratios for the transition state for the decomposition of (**1**).

Cationic micellar hexadecyltrimethylammonium bromide, CTAB, decreases k_{-1} for (**1**) by a factor of 12, but anionic micellar sodium dodecylsulphate, NaLS, has no effect on the rate (Table 2). The effects of these ionic surfactants can be interpreted in terms of simple electrostatic considerations;[1] however, the rate retardation caused by nonionic surfactants indicates the importance of hydrophobic interactions between the substrate and the micelles. The rate retardation is, as has been observed in other cases of micellar catalysis,[1] a result of both enthalpy and entropy effects (Table 2). Very significantly, ionic micelles have been found, on the other hand, to exhibit opposing effects on the rate of substitution, k_1, for the cases in which the formation of (**1**) is rate-determining, *e.g.* cationic micelles markedly increased the rates of reaction of nucleophiles with 2,4-dinitrohalogenobenzenes while anionic micelles decreased them.[2]

The magnitude of the rate retardation by CTAB is dependent to a considerable extent on the nature of the substrate, *e.g.* k_{-1}(water)/k_{-1}(CTAB) is 12 for the decomposition of (**1**), 3·0 for that of the methoxy-complex of 1-methoxy-2,4-dinitronaphthalene, and 2·0 for that of the methoxy-complex of 1-methoxy-2,4,5-trinitronaphthalene. Specific substrate–micelle interactions in the decomposition of Meisenheimer complexes are under investigation in our laboratories.

TABLE 2

Micellar effects on the decomposition of (**1**) *in aqueous solutions at* pH 10·8[a]

Surfactant	10^5k_{-1}, sec^{-1} at 25·00°	E_{-1}[b] kcal/mole	$\Delta S^‡_{-1}$, e.u.[b] at 25·00°
Water	50·8	17·6 ± 0·8	−16·5 ± 2·0
2·5 × 10^{-2} M-CTAB	4·20	24·9 ± 0·8	+3·1 ± 2·0
2·0 × 10^{-3} M-CTAB	5·20		
2·5 × 10^{-4} M-CTAB	9·04		
1·0 × 10^{-1} M-NaLS	52·0		
2·0 × 10^{-2} M-Igepal CO-730	13·6	20·5 ± 0·8	−9·6 ± 2·0
2·0 × 10^{-2} M-Igepal DM-730	12·3		
2·5 × 10^{-2} M-Igepal CO-850	7·45		

[a] CTAB = $Me[CH_2]_{15}\cdot Me_3N^+Br^-$; NaLS = $Me[CH_2]_{11}SO_4^-$-Na^+; Igepal CO-730 = $C_9H_{19}\cdot C_6H_4O[CH_2\cdot CH_2O]_{14}CH_2\cdot OH$; Igepal CO-850 = $C_9H_{19}\cdot C_6H_4O[CH_2\cdot CH_2O]_{19}\cdot CH_2\cdot CH_2OH$; Igepal DM-730 = $[C_9H_{19}]_2\cdot C_6H_3O[CH_2\cdot CH_2O]_{23}\cdot CH_2\cdot CH_2OH$.

[b] Calculated from linear Arrhenius plots obtained from runs at 25·00°, 30·35°, and 35·00°.

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[1] For a comprehensive review on the effects of micelles on organic reactions, see E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, 1970, **8**, 271.

[2] C. A. Bunton and L. Robinson, *J. Amer. Chem. Soc.*, 1968, **90**, 5965, 5972; C. A. Bunton and L. Robinson, *J. Org. Chem.*, 1969, **34**, 780; 1970, **35**, 733; *J. Amer. Chem. Soc.*, 1970, **92**, 356.

[3] For recent reviews see: J. Miller, "Aromatic Nucleophilic Substitutions," Elsevier, Amsterdam, 1968; M. R. Crampton, *Adv. Phys. Org. Chem.*, 1969, **7**, 211.