

(16). (a) *Via Enynic Ester*.—In the foregoing manner was prepared the crude liquid ester *trans*-3,5-dimethoxycinnamyl propiolate (8): nmr (CDCl₃) δ 2.92 (s, C \equiv CH), 3.76 (s, 2 MeO), 4.80 (d, J = 6 Hz, CH₂), 6.2–6.7 (m, aromatic and vinylic H). Refluxing this ester in Ac₂O gave lactone 16, mp 201–210° (5% overall). Sublimation at 0.5 mm raised the melting point to 212.5–214°.

(b) *Via Diynic Ester*.—Likewise was obtained the crude liquid ester 3,5-dimethoxyphenylpropargyl propiolate (5): ir (CCl₄) 3320 (≡CH), 2130 (C \equiv C), 1720 cm⁻¹ (ester C=O); nmr (CCl₄) δ 2.91 (s, C \equiv CH), 3.77 (s, 2 MeO), 4.25 (s, CH₂), 6.2–6.6 (m, aromatic H). Cyclization was effected in 10% yield to give lactone 16: mp 201.5–204.5°, raised to 212.5–214° on recrystallization from benzene–petroleum ether plus sublimation at 0.5 mm; ir (CHCl₃) 1760 cm⁻¹ (γ -lactone); nmr (CDCl₃, HA-100) δ 3.96 and 4.01 (2 s, 3 each, 2 MeO), 5.41 (s, 2, CH₂), 6.54 and 6.77 (2 d, 1 each, J_m = 2.5 Hz, H-5 and H-7), 7.64 (slightly split s, 1, H-4), 8.81 (s, 1, H-1); identical with product from method a as based on mixture melting point, as well as ir and nmr spectra.

Anal. Calcd for C₁₄H₁₂O₄: C, 68.84; H, 4.95. Found: C, 69.06; H, 5.18.

Registry No.—1b, 4711-50-6; 3, 29577-27-3; 4, 29577-28-4; 5, 29577-29-5; 6, 29584-68-7; 7, 29584-61-0; 8, 29584-62-1; 9, 29577-30-8; 10, 29577-31-9; 11, 29577-32-0; 12, 29577-33-1; 13, 29584-63-2; 14, 29577-34-2; 15, 5656-51-9; 16, 29577-36-4; 17, 29577-37-5; 18, 29577-38-6; phenylpropargyl chloride, 3355-31-5; ethyl *trans*-3,5-dimethoxycinnamate, 29584-64-3; methyl *trans*-3,5-dimethoxycinnamate, 29584-65-4; *trans*-3,5-dimethoxycinnamyl alcohol, 29584-66-5; 3-(3,5-dimethoxyphenyl)-1-propanol, 1080-05-3; ethyl *trans*-2-bromo-3,5-dimethoxycinnamate, 29641-89-2; *trans*-2-bromo-3,5-dimethoxycinnamic acid, 29584-67-6; 3,5-dimethoxyphenylpropargyl alcohol 29577-41-1.

Electrolyte and Micellar Effects on Meisenheimer Complex Equilibria^{1,2}

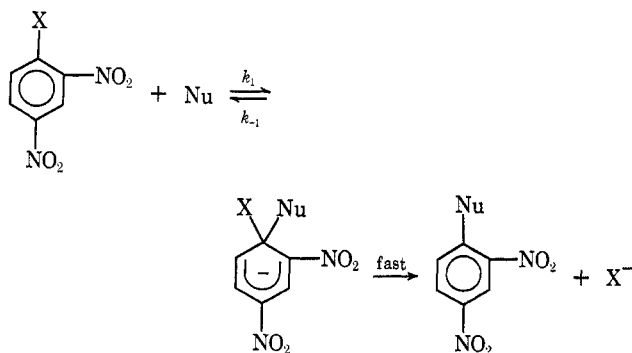
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Electrolytes, with the exception of lithium salts, decrease the rate constant for the decomposition of sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide (1) in aqueous solutions. Cationic micellar CTAB and nonionic micellar Igepal CO-730 also decrease the decomposition rate of 1 by factors of 12 and 3.7, respectively, and anionic NaLS does not affect it. Both enthalpy and entropy factors are involved. The magnitude of micellar rate retardation is smaller for 1,1-dimethoxy-2,4-dinitro- (2) and 1,1-dimethoxy-2,4,5-trinitronaphthalene (3) complexes but is significantly greater for the spiro Meisenheimer complex of 1-(β -hydroxyethoxy)-2,4-dinitronaphthalene (5) than for 1. The electrolyte and micellar effects originate from less destabilization of the initial state than of the transition state. CTAB enhances the equilibrium constants for the formation of the spiro complex of 1-(β -hydroxyethoxy)-2,4,6-trinitrobenzene and 5 by factors of 4750 and 250, respectively, while NaLS or Igepal have no appreciable effects. These results are compared critically to those obtained for other nucleophilic aromatic substitutions.

The effects of electrolytes and micelles on the reactions between nucleophiles and 2,4-dinitrohalobenzenes have been determined in aqueous solutions.⁴ Such nucleophilic aromatic substitutions involve the rate-determining formation of an intermediate which decomposes rapidly to products. The relative effects



of electrolytes on the rate constants for the reaction of hydroxide ion with 2,4-dinitrochlorobenzene, for

example, are Me₄NCl > K₂SO₄ > Na₂SO₄ > KCl ~ H₂O > NaCl > NaBr ~ NaNO₃ > Li₂SO₄ > LiCl > LiBr > CH₃C₆H₄SO₃Na > LiClO₄.⁴ These electrolyte effects have been dissected into those on the activity coefficient of the aryl halide and those on the ratio of the activity coefficient of the hydroxide ion to that of the transition state. KCl, NaCl, NaBr, and LiBr increase f_{ArX} but decrease f_{OH^-}/f^\ddagger ; NaClO₄, on the other hand, decreases both f_{ArX} and f_{OH^-}/f^\ddagger .

Cationic micellar surfactants were found to enhance k_1 by factors of ca. 60–80, the magnitude of the rate decrease by anionic surfactants was somewhat more modest, and neutral micellar surfactants had no effect on k_1 .^{4,5}

In order to obtain information on the effects of electrolytes and micelles on nucleophilic aromatic substitutions in which the rate-determining step is governed by the decomposition of the complex, we have investigated these effects on the rates of decomposition of sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide (1). Since micellar catalysis involves specific substrate-micelle interactions, we have also examined the influence of micellar surfactants on the rates of decomposition of the methoxyl complexes of 1-methoxy-2,4-dinitronaphthalene (2) and 1-methoxy-2,4,5-trinitronaphthalene (3) and of the spiro Meisenheimer

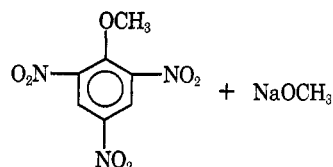
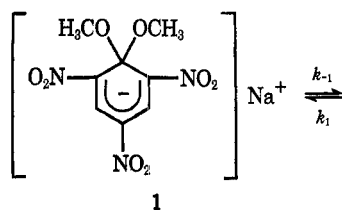
(1) Supported in part by the U. S. Atomic Energy Commission.

(2) Reported, in part, preliminarily by E. J. Fendler and J. H. Fendler, *Chem. Commun.*, 816 (1970).

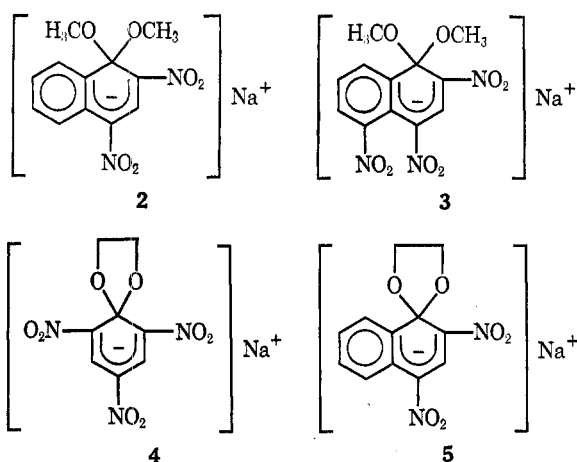
(3) (a) Texas A & M University; (b) Department of Chemistry, Franklin and Marshall College, Lancaster, Pa. 17604.

(4) C. A. Bunton and L. Robinson, *J. Amer. Chem. Soc.*, **90**, 5965, 5972 (1968); C. A. Bunton and L. Robinson, *J. Org. Chem.*, **34**, 780 (1969); C. A. Bunton and L. Robinson, *ibid.*, **35**, 733 (1970); C. A. Bunton and L. Robinson, *J. Amer. Chem. Soc.*, **92**, 356 (1970).

(5) For reviews of micellar effects on reaction rates, see E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 329 (1969), and E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).



complexes 4 and 5. Micellar effects on the equilibrium constants for the formation of complexes 4 and 5 from their parent glycol ethers, 1-(β -hydroxyethoxy)-



2,4,6-trinitrobenzene (6) and 1-(β -hydroxyethoxy)-2,4-dinitronaphthalene (7), have also been determined.

Experimental Section

The preparations of 1-(β -hydroxyethoxy)-2,4,6-trinitrobenzene (6),⁶ 1-(β -hydroxyethoxy)-2,4-dinitronaphthalene (7),⁶ their spiro Meisenheimer complexes 4⁶ and 5,⁶ and the methoxyl complexes of 2,4,6-trinitroanisole (1),⁷ 1-methoxy-2,4-dinitronaphthalene (2),⁸ and 1-methoxy-2,4,5-trinitronaphthalene (3)⁹ have been described. Reagent grade salts were dried *in vacuo* over phosphorus pentoxide immediately prior to their use in making up the electrolyte solutions. The sources of the surfactants and their purification have been described previously.¹⁰ The buffer, electrolyte, and surfactant solutions were prepared in deionized distilled water. The pH's of the solutions were adjusted using HCl or NaOH to the required value and were measured at 25.0° with an Orion-801 pH meter. Both in the case of the decomposition of complexes 1-3 and in the determinations of the equilibrium constants for the formation of complexes 4 and 5 in micellar solutions, the pH remained within ± 0.02 during the experiments.

Four solubility determinations were carried out for each solvent system; saturated solutions of 1, 2, and 5 containing undissolved solid were shaken at 25.00° and filtered, and the concentration of complex 1, 2, or 5 in the filtrate was determined spectrophotometrically. The error in the individual measurements is $\pm 10\%$. In some cases, the complex concentration in the saturated solutions was greater than 1.0 M and thus is not ideal.

(6) E. J. Fendler, J. H. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, **33**, 4144 (1968).

(7) J. H. Fendler, E. J. Fendler, and C. E. Griffin, *ibid.*, **34**, 689 (1969).

(8) J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *ibid.*, **33**, 977 (1968).

(9) J. H. Fendler and E. J. Fendler, *ibid.*, **35**, 3378 (1970).

(10) E. J. Fendler, R. R. Liechti, and J. H. Fendler, *ibid.*, **35**, 1658 (1970).

The required absorbance measurements were carried out at the appropriate wavelength⁸⁻⁹ in the thermostated cell compartment of a Beckman DU-2 spectrophotometer. The temperature was measured inside the cells and was maintained within $\pm 0.02^\circ$. The decomposition of the complexes obeyed good first-order kinetics.

Results

In aqueous solution, the decomposition of Meisenheimer complexes is pH independent in solutions more alkaline than pH 8.0.⁶⁻⁹ All of the present investigations, unless stated otherwise, have been carried out in the middle of the plateau of the pH-rate profile, *i.e.*, in the pH-independent region at pH 10.8.

Electrolytes have significant effects on the rate of decomposition of Meisenheimer complex 1 (Table I).

TABLE I
ELECTROLYTE EFFECTS ON THE DECOMPOSITION RATES OF
1,1-DIMETHOXY-2,4,6-TRINITROCYCLOHEXADIENYLIDE ION (1)
IN WATER AT 25.00°^a

Electrolyte	$10^4 k_{-1}, \text{sec}^{-1}$	
	1.0 M	2.0 M
None		5.08 ^b
LiClO ₄	6.51	7.43
LiCl	5.98	6.19
NaNO ₃	4.25	3.54
NaCl	4.16	3.33
NaBr	4.21	3.33
Me ₄ NCl	4.12	2.68
NaClO ₄	3.98	2.97
KCl	3.63	2.56
Na ₂ SO ₄	3.45	2.30
<i>p</i> -MeC ₆ H ₄ SO ₃ Na	2.64	1.18

^a At pH = 10.8. ^b Mean of six runs, each within $\pm 3\%$.

With the exception of lithium perchlorate and lithium chloride, all the electrolytes decrease the rate constants for the decomposition of 1. Results of the solubility measurements, expressed as activity coefficients relative to water containing 10^{-3} M sodium hydroxide at 25.00°, show that all the electrolytes investigated substantially affect the activity coefficients of 1 (Table II).

TABLE II
ELECTROLYTE EFFECTS ON THE
RELATIVE ACTIVITY COEFFICIENTS OF SODIUM
1,1-DIMETHOXY-2,4,6-TRINITROCYCLOHEXADIENYLIDE (1)
AND ON ITS DECOMPOSITION TRANSITION STATE AT 25.00°

Electrolyte	~ 1.0 M Electrolyte		~ 2.0 M Electrolyte	
	f_1^s/f_1^o ^a	f_1^{*s}/f_1^{*o} ^b	f_1^s/f_1^o ^a	f_1^{*s}/f_1^{*o} ^b
LiClO ₄	0.81	0.633	1.06	0.726
LiCl	1.03	0.873	2.98	2.44
<i>p</i> -MeC ₆ H ₄ SO ₃ Na	3.04	5.84	1.74	7.49
NaClO ₄	4.60	5.87	5.93	10.1
NaNO ₃	6.18	7.33	10.5	15.0
NaBr	8.95	10.8	13.7	20.9
NaCl	9.08	11.1	19.5	29.7
Me ₄ NCl	13.0	16.0	27.8	52.7
Na ₂ SO ₄	20.6	30.3	74.1	165
KCl	37.3	52.2	45.8	90.9

^a Relative activity coefficients for 1. ^b Relative activity coefficient for the transition state for the formation of 2,4,6-trinitroanisole.

Cationic and neutral micellar surfactants decrease the rate constants for the pH-independent decom-

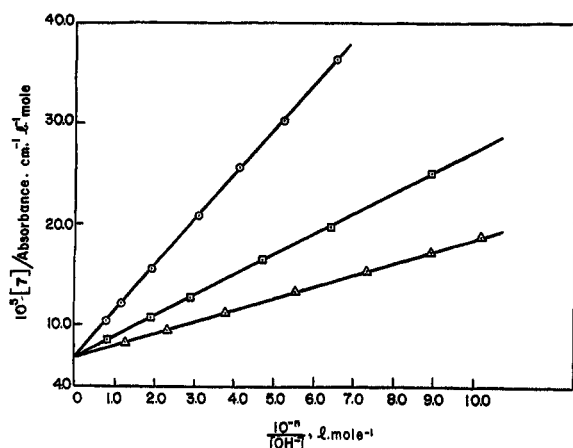


Figure 1.—Benesi-Hildebrand plots for the formation of **5** in water at 25.00°: ○ $1.0 \times 10^{-2} M$ CTAB, $n = 7$; □ $1.0 \times 10^{-2} M$ NaLS, $n = 4$; △ water, $n = 4$.

positions of complexes **1**, **2**, **3**, and **5**, but anionic NaLS has no effect on these rates (Table III). Table IV

TABLE III

MICELLAR EFFECTS ON THE DECOMPOSITION RATES OF MEISENHEIMER COMPLEXES IN WATER AT 25.00°^a

Complex	$10^5 k_{-1}$, sec ⁻¹ , in H ₂ O	$10^5 k_{-1}$, sec ⁻¹ , in CTAB	$10^5 k_{-1}$, sec ⁻¹ , in NaLS	$10^5 k_{-1}$, sec ⁻¹ , in Igepal
1	50.8	4.20 ^b 5.20 ^c	52.0 ^d	13.6 ^e 12.3 ^f 7.45 ^g
2	176	58.6 ^b	178 ^b	
3	16.0	8.32 ^b	17.0 ^d	
5	138	0.21 ^b	158 ^d	4.2 ^e

^a At pH 10.8. ^b $2.5 \times 10^{-2} M$ CTAB. ^c $2.0 \times 10^{-3} M$ CTAB. ^d $1.0 \times 10^{-1} M$ NaLS. ^e $1.0 \times 10^{-2} M$ Igepal CO-730. ^f $2.0 \times 10^{-2} M$ Igepal DM-730. ^g $2.5 \times 10^{-2} M$ Igepal CO-850. ^h $1.0 \times 10^{-2} M$ CTAB.

TABLE IV

MICELLAR EFFECTS ON THE RELATIVE ACTIVITY COEFFICIENTS OF COMPLEXES **1**, **2**, AND **5** AND ON THEIR DECOMPOSITION TRANSITION STATES

Complex	$2.5 \times 10^{-2} M$ CTAB		$1.0 \times 10^{-1} M$ NaLS	
	f_m^m/f^o ^a	$f_m^\ddagger/f^o^\ddagger$ ^a	f_m^m/f^o ^a	$f_m^\ddagger/f^o^\ddagger$ ^a
1	0.65	7.9	0.65	0.63
2	1.01	3.1	1.01	0.99
5	1.04	665	0.97	0.85

^a f_m^m , f^o , f_m^\ddagger , and f^o^\ddagger are the activity coefficients of complexes **1**, **2**, and **5** in micellar surfactant solutions, in water, and that of their decomposition transition states in the presence of micelles and in water, respectively.

gives the relative solubilities, and hence the activity coefficients, of complexes **1**, **2**, and **5** in micellar CTAB and NaLS solutions. We have examined the effects of micelles on the acid-catalyzed decomposition of complex **3**. The second-order rate constants for the acid-catalyzed decomposition of **3** at 25.00° in water, $2.0 \times 10^{-2} M$ NaLS, and $1.0 \times 10^{-2} M$ CTAB in the pH range 4.0–6.4 ($5.0 \times 10^{-3} M$ KH₂PO₄ and CH₃CO₂Na buffers) are 1380, 2833 and 41 l. mol⁻¹ sec⁻¹, respectively.

The effects of micelles on the energies and entropies of activation for the pH-independent decomposition of complex **1** are given in Table V.

TABLE V

ARRHENIUS PARAMETERS FOR THE DECOMPOSITION OF 1,1-DIMETHOXY-2,4,6-TRINITROCYCLOHEXADIENYLIDE ION (**1**) IN MICELLAR SOLUTIONS^a

Media	E_{-1} , kcal/mol ^b	ΔS_{-1}^\ddagger , eu, ^b at 25.00°
Water	17.6 ± 0.8	-16.5 ± 2.0
$2.5 \times 10^{-2} M$ CTAB	24.9 ± 0.8	$+3.1 \pm 2.0$
$1.0 \times 10^{-2} M$ Igepal CO-730	20.5 ± 0.8	-9.6 ± 2.0

^a pH 10.8. ^b Calculated from linear Arrhenius plots obtained from runs at 25.00°, 30.25°, and 35.00°.

Although complexes **4** and **5** are formed from **6** and **7** in aqueous alkaline solutions,^{4,11} the rate of their equilibrium attainment is immeasurably fast by our technique.⁷ Using the Benesi-Hildebrand equation¹²

$$\frac{[6] \text{ or } [7]}{A} = \frac{1}{\epsilon} + \frac{1}{K\epsilon} \left(\frac{1}{[\text{OH}^-]} \right)$$

where A is the absorbance in a 1.0-cm cell, ϵ is the molar extinction coefficient, and K is the equilibrium constant for the formation of complex **4** or **5**, good linear relationships were obtained on plotting $[6]/A$ or $[7]/A$ vs. $1/[\text{OH}^-]$ (Figure 1) indicating that simple equilibria prevail. Since the intercept of the Benesi-Hildebrand plot (*i.e.*, $1/\epsilon$) is susceptible to large errors, previously obtained⁶ values of ϵ have been used to determine the K values. The determined values for the equilibrium constants for the formation of **4** and **5** in water and in micellar surfactant solutions at 25.00° are given in Table VI.

TABLE VI

MICELLAR EFFECTS ON THE EQUILIBRIUM CONSTANTS FOR THE FORMATION OF MEISENHEIMER COMPLEXES AT 25.00°^a

Complex	K , l. mol ⁻¹ , in H ₂ O	K , l. mol ⁻¹ , in CTAB	K , l. mol ⁻¹ , in NaLS	K , l. mol ⁻¹ , in Igepal
4	2.1×10^7	1.0×10^{11} ^b		
5	5.82×10^4	1.47×10^7 ^b	3.20×10^4 ^c	6.8×10^4 ^d

^a Determined from linear Benesi-Hildebrand plots (see Figure 1 for typical plots). ^b $1.0 \times 10^{-2} M$ CTAB. ^c $1.0 \times 10^{-2} M$ NaLS. ^d $1.0 \times 10^{-2} M$ Igepal CO-730.

Discussion

Effects of Electrolytes.—Lithium perchlorate and lithium chloride enhance whereas all the other electrolytes investigated retard the rate of decomposition of the methoxyl complex of 2,4,6-trinitroanisole (**1**). Simple electrostatic theory¹³ clearly fails to account for both the direction and the magnitude of these effects. The order of the electrolyte effects on k_{-1} , LiClO₄ > LiCl > H₂O > NaNO₃ > NaCl > NaBr > Me₄NCl > NaClO₄ > KCl > Na₂SO₄ > *p*-MeC₆H₄SO₃Na (Table I), is essentially the reverse of that found for the interaction of hydroxide ion with 2,4-dinitrochlorobenzene.⁴

These electrolytes also have substantial effects on the mean ion activity coefficient ratios of sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienyliide (**1**). With

(11) J. Murto, *Suom. Kemistilehti, B*, **38**, 255 (1965).

(12) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed., Cornell University Press, Ithaca, N. Y., 1969.

the exception of lithium perchlorate, all the salts increase the mean ion activity coefficient of **1** (Table II). In the 0–2.0 *M* electrolyte concentration range, the logarithms of the mean ion activity coefficient ratios do not vary linearly as a function of concentration; *i.e.*, the Setschenow equation is not obeyed. Since the extent of the changes in the activity coefficients of the single anion, 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylidene ion, and its sodium counterion are not known, this behavior is not unexpected. The observed order of the activity coefficient ratios for **1**, $\text{LiClO}_4 < \text{LiCl} < p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Na} < \text{NaClO}_4 < \text{NaNO}_3 < \text{NaBr} < \text{NaCl} < \text{Me}_4\text{NCl} < \text{Na}_2\text{SO}_4 < \text{KCl}$, does not follow any particular trend. It is worth noting, however, that the effects of electrolytes on the mean ion activity coefficients of **1** are significantly greater than those on the activity coefficients of 2,4-dinitrochlorobenzene.⁴ Furthermore, electrolytes with the exception of NaCl, LiCl, and Na_2SO_4 stabilize, *i.e.*, decrease the activity coefficient of 2,4-dinitrochlorobenzene, whereas they primarily destabilize complex **1**. The observed rate constant changes in the presence of electrolytes are therefore due partially to initial state effects. The magnitude of the electrolyte effects on the transition state can be determined by means of the Brønsted–Bjerrum rate equation

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

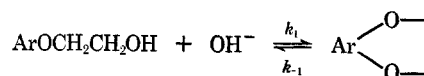
where k_{-1}^s and k_{-1}^o are the rate constants for the decomposition of **1** in the presence and absence of electrolytes and f_1 and f^\ddagger are relative mean ion activity coefficients for **1** and for its decomposition transition state. Since electrolyte effects have been obtained both on k_{-1} and on the mean ion activity coefficient ratios of **1**, substitution into the Brønsted–Bjerrum rate equation allows the determination of the effects of electrolytes on the transition state for the decomposition of **1** (see Table II). Electrolytes, with the exception of lithium salts, destabilize both **1** and its decomposition transition state. More significantly, their effects are considerably more pronounced on the transition state than on the initial state. The results of the present study clearly illustrate the inherent complications of kinetic salt effects even on relatively simple reactions.

Micellar Effects.—Cationic and nonionic micelles retard the pH-independent decomposition of Meisenheimer complexes, while anionic NaLS has no appreciable effect on the rate (Table III). As in the case of the electrolyte effects, the direction of the micellar effects on the rate of decomposition of the complexes is opposite to that found for the interaction of nucleophiles with dinitro-substituted halobenzenes,⁴ in which case the rate-determining step is the formation rather than the decomposition of the σ complex. Since the rate constants for the decomposition of **1** are decreased only by a factor of *ca.* 2 in the presence of 1.0–2.0 *M* trimethylammonium chloride and sodium *p*-toluenesulfonate while the addition of 10^{-2} *M* CTAB results in a 12-fold rate retardation, the latter effects are clearly not electrolytic but micellar in origin.

The magnitude of the micellar effects is markedly dependent upon the nature of the substrate. CTAB retards the decomposition of **1**, **2**, **3**, and **5** by factors of 12, 3, 2, and 660, respectively. This substrate

specificity and the catalytic behavior in micellar solutions must result from differences in initial state or in transition state stabilities, *i.e.*, activities, or, indeed, from a combination of both, relative to those in water. In order to distinguish between these alternatives, we have calculated the activity coefficient ratios for complexes **1**, **2**, and **5** in CTAB and NaLS relative to water from solubility measurements (Table IV). Unlike the electrolytes (Table II), the micelles generally have only small or insignificant effects on the activity coefficients of these complexes. Complex **1** is solubilized to some extent by CTAB and NaLS, whereas the initial state activities of complexes **2** and **5** are not affected by these micelles. The micellar effects of CTAB and NaLS on both the rate of decomposition, k_{-1} , and the initial state stability of complex **1** parallel that found in water–DMSO solutions as a function of increasing concentration of the dipolar aprotic component.¹⁴ Combination of the rate constant data with the relative activity coefficients of complexes **1**, **2**, and **5** in the micellar surfactant solutions affords an estimation of the effects of CTAB and NaLS on the activity coefficients for the decomposition of these complexes (Table IV). It is apparent that the retardation of the rates of decomposition of the complexes in the presence of micellar CTAB is primarily the consequence of destabilization of the transition state, whereas the absence of catalysis by NaLS results from compensation of initial and transition state effects in the case of complex **1** and from insignificant differences for complexes **2** and **5**. The retardation of the rate of decomposition of **1** is, as has been observed in many other micellar catalyses,⁵ a composite of both enthalpy and entropy effects (Table V). These results suggest that the transition state for complex decomposition is further along the reaction coordinate in water than in micellar CTAB.

The equilibrium constants for the formation of spiro Meisenheimer complexes in methanol are considerably greater than those of their 1,1-dialkoxy analogs.⁶ Indeed, the dialkoxy Meisenheimer complexes have not been observed in water, whereas the spiro complexes **4** and **5** are quite stable (Table VI). The mechanism for the formation of complexes **4** and **5** can be described in terms of an initial rapid proton abstraction from the glycol ether, **6** or **7**, by hydroxide ion followed by rate-determining internal cyclization of the resulting glycolate ion. The rigidity of the cyclic substituent perpendicular to the benzene ring is responsible for the enhanced stabilities of these complexes.⁶ The dramatic 660-fold decrease in the rate of decomposition of the spiro complex **5** as compared to the threefold rate retardation for the 1,1-dialkoxy analog **2** by micellar CTAB is explicable exclusively in terms of transition state effects (Table IV). The rate retardation by nonionic Igepal CO-730 is also significant, whereas sodium dodecyl sulfate has no discernable effect on the rate of decomposition of **5** (Table III). The equilibrium constants ($K = k_1/k_{-1}$) for the formation of spiro σ complexes (as illustrated below) in the



presence and in the absence of micellar surfactants have also been determined (Table VI). Cationic micellar CTAB enhances the equilibrium constant for the formation of **4** and **5** by factors of 4750 and 252, respectively, while NaLS and Igepal do not affect it. Since the rate constants for the formation of spiro complexes, k_1 , are dependent on the hydroxide ion concentration, the observed micellar effects are composites of those on the parent glycol ethers **6** and **7** and those on the hydroxide ion. The effective hydrogen ion concentration at the micellar surface, however, may differ appreciably from that in the bulk phase.⁵ The considerably more pronounced micellar effect on the rate of the acid-catalyzed decomposition of **1** than that on its neutral decomposition substantiate this observation. The interpretation of this and similar results in buffered solutions is complicated by the uncertainties in the pH of these solutions.⁵ Combination of the values for k_{-1} and K for the spiro complex **5** in the absence and presence of CTAB (Tables III and VI) allows the calculation of the rate constants for the formation of **5** ($k_1^{\text{H}_2\text{O}} = 80 \text{ l. mol}^{-1} \text{ sec}^{-1}$, $k_1^{\text{CTAB}} = 31 \text{ l. mol}^{-1} \text{ sec}^{-1}$). Micellar CTAB thus decreases the rate constant for the formation of **5** by a factor of 2.6, whereas it catalyzes the hydroxydehalogenations of dinitrosubstituted arenes by factors of ca. 60–80.⁴ These micellar effects are not unexpected based on electrostatic considerations since the rate of the former reaction, which involves the internal cyclization of the naphthyl glycolate anion, would predictably be retarded in the presence of cationic micelles due to

partial charge neutralization. The latter case, however, is a typical example of the effect of cationic micelles on a reaction between a solubilized neutral organic molecule and a small high-charge density anion.^{4,5} The unusually large increase in the equilibrium constant for the formation of **5** is, of course, the consequence of the micellar enhancement of the rate of formation, k_1 , and the micellar retardation of the rate of decomposition. Combining k_{-1} and K values for the influence of Igepal CO-730 on complex **5**, one estimates that this nonionic surfactant somewhat unexpectedly decreases the rate constant for the formation of the complex. Qualitatively, the effects of ionic micelles on the rates of Meisenheimer complex decomposition are explicable in terms of simple electrostatic interactions, however the rate retardation caused by nonionic surfactants cannot be accounted for solely in simple electrostatic terms, and environmental effects, such as hydrophobic and hydrogen bonding interactions, must be invoked to rationalize the observed effects.

Although specific steric effects clearly complicate the interpretation of the results for the spiro complexes **4** and **5**, it is evident that micelles affect both the initial and transition states for the formation and the decomposition of intermediates which are involved in nucleophilic aromatic substitution and that this dependence is very much influenced by the nature of the substrates and intermediates.

Registry No.—**1**, 12275-58-0; **2**, 29472-26-2; **3**, 29472-29-5; **4**, 1280-24-6; **5**, 29472-28-4.

Ionic vs. Free-Radical Additions with Opportunity for Phenyl Migration. Solvent Effects¹

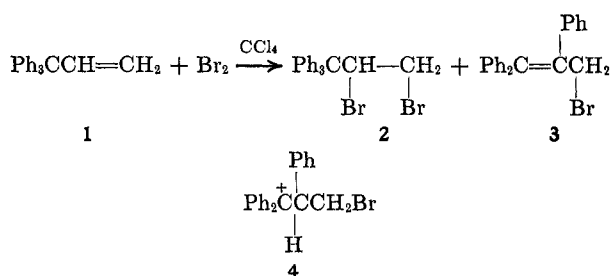
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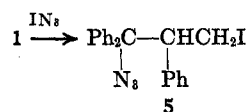
Addition of bromine azide to 3,3,3-triphenylpropene (**1**) proceeds with phenyl migration under ionic conditions (major product, **7**) but without phenyl migration under free-radical conditions (major product, **9**). The two products resulting from bromination of **1** were shown to derive from simultaneous ionic and free-radical addition processes. Addition of BrN_3 to 3,3-diphenylpropene (**10**) in polar solvents also proceeds with phenyl migration. The regiochemistry indicates steric control in the BrN_3 addition. Solvent effects of a different nature were observed during phenyl migration in the IN_3 addition to 3,3-diphenylpropene (**10**) and are interpreted in conjunction with three-membered-ring iodonium ion opening.

Recently Norman and coworkers² have shown that addition of bromine to 3,3,3-triphenylpropene (**1**) in carbon tetrachloride solution leads to a nonrearranged adduct **2** and an allyl bromide **3** in a ratio of 1:1.15. The unsaturated bromide **3** is a product of phenyl mi-



gration and probably arose from an intermediate of type **4** by loss of a proton. Norman, *et al.*, were in fact able to trap **4** by carrying out the bromination in methanol. 3-*p*-Anisyl-3,3-diphenylpropene, which reacts 25 times as fast as **1**, gave on bromination in CCl_4 only a rearranged allylic bromide and no unrearranged adduct, analogous to **2**, was detected.

It was postulated that both **2** and **3** result from an ionic addition of bromine. This interpretation seemed inconsistent with our recent findings³ that the pseudohalogens INCO and IN_3 reacted with **1** under ionic conditions to give exclusively rearranged adducts (*cf.* **5**).



(1) Stereochemistry. LXI. For paper LX, see A. Hassner, *Accounts Chem. Res.*, **4**, 9 (1971).

(2) R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. B*, 598 (1967).

(3) A. Hassner and J. S. Teeter, *J. Org. Chem.*, **35**, 3397 (1970).